

Stability and reactivity of ferrocenyl(2,4,6-trimethoxyphenyl)carbenium salts[☆]

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Abstract

Ferrocenyl(phenyl)methanols, $\text{Fc-CH}\Phi\text{OH}$ [$\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)$, $\Phi^a = 2,4,6\text{-(MeO)}_3\text{C}_6\text{H}_2$ (**1a**); $\Phi^b = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$ (**1b**)], were prepared by the reactions of Fc-CHO with ΦLi . **1a** reacted with only a slight excess of perchloric acid or tetrafluoroboric acid even in methanol and in 1 M HCl acid to give dark violet crystals of the carbenium salts, $[\text{Fc-CH}\Phi^a]\text{X}$ [$\text{X} = \text{ClO}_4$ (**2a**), BF_4 (**2a'**)]. **1b** reacted with these acids in diethylether to give the carbenium salts, $[\text{Fc-CH}\Phi^b]\text{X}$ [$\text{X} = \text{ClO}_4$ (**2b**), BF_4 (**2b'**) (dark red–brown crystals)] in good yields. The $\text{p}K_{\text{R}^+}$ values could be measured in HCl acid for **1a** (3.0) and for **1b** (1.6). **2a** and **2b** were labile in hot 2-propanol to give the reduced compounds, $\text{Fc-CH}_2\Phi$. **1a** and **1b** reacted with 1,3,5-trimethoxybenzene, $\Phi^a\text{H}$, in 2-methyl-2-propanol containing only a slight excess of HCl acid to give diphenyl(ferrocenyl)methanes, $\text{Fc-CH}\Phi^a_2$ and $\text{Fc-CH}\Phi^a\Phi^b$, respectively. While **1a** decomposed in neat 1,3-dimethoxybenzene, $\Phi^b\text{H}$, in the presence of acid, **1b** reacted to give 2,4-dimethoxyphenyl(2,6-dimethoxyphenyl)ferrocenylmethane, $\text{Fc-CH}\Phi^b\Phi^d$ [$\Phi^d = 2,4\text{-(MeO)}_2\text{C}_6\text{H}_3$]. The $^1\text{H-NMR}$ spectrum of **2a** was temperature-dependent and indicated that the free rotations of both Fc and Φ^a groups in **2a** existed at r.t. but were frozen at -60°C . © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Iron; 2,4,6-Trimethoxyphenyl; 2,6-Dimethoxyphenyl; Ferrocenyl(phenyl) methanol; Ferrocenyl(phenyl)carbenium; Ferrocenyl(phenyl)methane

1. Introduction

The number of methoxy substituents on phenyl groups influences the stability and reactivity of di- and triphenylcarbenium salts. Thus, bis(2,4,6-trimethoxyphenyl)carbenium perchlorate, $[\Phi^a_2\text{CH}]\text{ClO}_4$ ($\Phi^a = 2,4,6\text{-(MeO)}_3\text{C}_6\text{H}_2$), is recrystallizable even from methanol, and triphenylmethanols bearing at least four *o*-methoxy groups, such as $\Phi^b_3\text{COH}$ and $\text{Ph}\Phi^b_2\text{COH}$ [$\Phi^b = 2,6\text{-(MeO)}_2\text{C}_6\text{H}_3$], were highly basic to form isolable triarylcarbenium salts, $[\text{Ar}\Phi^b_2\text{C}]\text{X}$, even in secondary alcohols and water [1–3]. The ferrocenyl group also has been known to stabilize the carbenium salts [4–8]. In this report, the influence of the number of methoxy substituents on the phenyl group in ferrocenyl(phenyl)

carbenium salts, $[\text{Fc-CH}\Phi]\text{X}$ [$\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)$; $\Phi = \Phi^a, \Phi^b, \text{Ph}$; $\text{X} = \text{ClO}_4, \text{BF}_4$], on the physical and chemical properties is examined. The reactions mentioned below are summarized in Scheme 1.

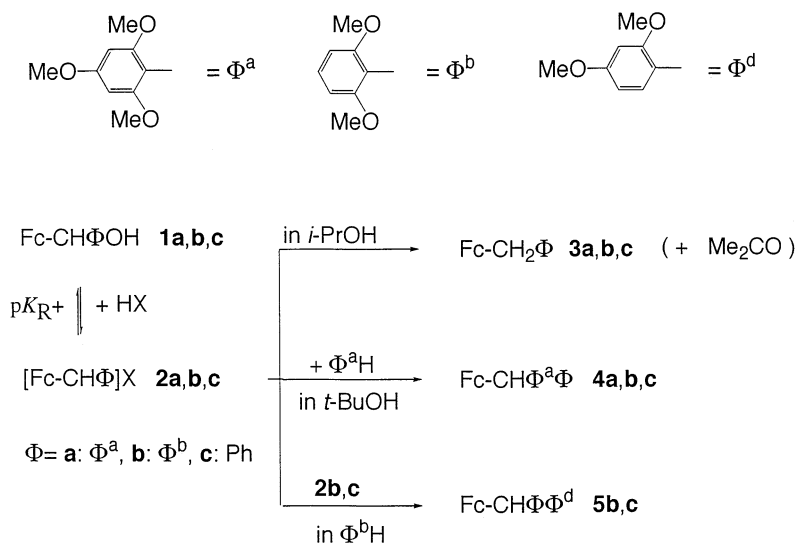
2. Results and discussion

2.1. Preparation of ferrocenyl(phenyl)carbenium salts

Ferrocenyl(phenyl)methanols, $\text{Fc-CH}\Phi\text{OH}$ [$\Phi = \Phi^a$ (**1a**), Φ^b (**1b**), Ph (**1c**)], were prepared as yellow crystals by the reactions of ferrocenylaldehyde with the corresponding phenyllithium. Compounds **1a–c** reacted with a slight excess of 60% aqueous perchloric acid in diethylether to give the carbenium salts, $[\text{Fc-CH}\Phi]\text{X}$ ($\text{X} = \text{ClO}_4$, **2a–c**) almost in quantitative yields even in the absence of a dehydration reagent, such as acetic anhydride as used by Allenmark et al. [7]. Using 42%

[☆] Dedicated to the memory of the late Professor Rokuro Okawara.

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tetrafluoroboric acid also gave analogous salts ($X = \text{BF}_4$, **2a'–c'**), although the yields decreased in the order of **2a'** > **2b'** > **2c'** due probably to the presence of larger amount of water. These salts are deeply colored in dark violet (**2a**, **2a'**), dark red–brown (**2b**, **2b'**) or dark brown (**2c**, **2c'**).

The electronic spectra (Table 1) of **1a–c** in 1,2-dichloroethane showed a band with λ_{max} at the analogous region (440–445 nm; $\log \varepsilon = 2.1$ –2.3) to those of ferrocene (440 nm) and phenylferrocene (446 nm) [9]. In contrast, the spectra of **2a–c** showed two bands in the region of 330–530 nm, of which the molar absorbances were much larger ($\log \varepsilon = 3.5$ –4.2). The bands shifted to lower wavelengths in the order **2a** > **2b** > **2c**. A carbenium salt, $[\Phi^a_2\text{CH}]\text{ClO}_4$, showed a strong band at 521 nm ($\log \varepsilon = 4.71$) [3]. Thus, the two bands of **2a–c** are tentatively assigned to charge transfers from the Φ^a group and ferrocenyl group to the cationic carbon, respectively.

The carbenium salt **2c** decomposed in methanol very fast to give the precipitates of methyl ether, Fc-CHPhOMe . In contrast, **2a** dissolved in methanol to give a violet solution, even at 4×10^{-4} M, and the color disappeared below 1×10^{-4} M. The high stability of **2a** in methanol is astonishing, and in fact, crystals of **2a** and **2a'** could be obtained in methanol by the reactions of **1a** with only a slight excess of 60% aqueous perchloric acid or 42% aqueous tetrafluoroboric acid at a concentration of 1×10^{-1} M. These salts could also be obtained in ethanol in analogous manners. Compound **2b** was less stable in methanol than **2a**, and the red–brown color disappeared at ca. 3×10^{-3} M.

The solubility of **2a** in 2-propanol was very poor. When it was heated at 50°C for 1 h at 1×10^{-1} M, it was reduced to give $\text{Fc-CH}_2\Phi^a$ (**3a**). Compounds **1b** and even **1c** were also reduced in hot 2-propanol con-

taining a slight excess of acid to give $\text{Fc-CH}_2\Phi^b$ (**3b**) and $\text{Fc-CH}_2\text{Ph}$ (**3c**), respectively, although the latter yield was poorer. Such a reduction by alcohols is one of the characteristic reactions observed for carbenium salts bearing Φ^a or Φ^b groups, and the aldehyde or ketone were detected as the by-product [1–3,10].

Fortunately, it was found that **1a** was soluble in concentrated hydrochloric acid (1 mmol/2 ml) to give a dark violet solution of **2a** ($X = \text{Cl}$). It could be diluted to 1 M hydrochloric acid solution without the loss of violet color. An addition of only a slight excess of aqueous tetrafluoroboric acid resulted to give the precipitates of **2a** in good yield. When the solution of **1a** in 1 M hydrochloric acid was neutralized by aqueous

Table 1
UV–vis spectral data of ferrocenyl(phenyl)methane derivatives^a

Compounds	λ (nm) ($\log \varepsilon$)
1a	440(2.30), 320(2.18, sh), 255(3.70, sh), 236(4.03)
1b	445(2.15), 320(2.18, sh), 260(3.65, sh), 233(3.95)
1c	444(2.18), 320(2.15, sh), 265(3.65, sh), 233(3.83)
2a	532(3.83), 397(4.24), 320(sh), 260(3.96, sh), 227(4.08)
2b	450(3.75) ^b , 362(4.09) ^b , 260(3.95, sh), 236(4.02)
2c	410(3.54) ^b , 336(4.12) ^b , 310(3.78, sh), 242(4.04)
3a	444(2.04), 325(2.08, sh), 255(3.70, sh), 235(4.02)
3b	450(2.04), 320(2.00, sh), 255(3.70, sh), 233(3.96)
3c	432(2.08), 320(2.18, sh), 255(3.60, sh), 233(3.74)
4a	427(2.15), 320(2.40, sh), 265(3.81, sh), 236(4.26)
4b	445(2.23), 325(2.48, sh), 270(3.79, sh), 233(4.23)
4c	445(2.11), 320(2.40, sh), 260(3.71, sh), 233(4.13)
5b	440(2.11), 320(2.00, sh), 273(3.73, sh), 233(4.19)
5c	442(2.08), 325(2.00, sh), 275(3.65, sh), 234(4.17)

^a In 1,2-dichloroethane.

^b In 1,2-dichloroethane containing CF_3COOH [0.1% (v/v)].

Table 2

¹H-NMR spectral data for ferrocenyl(phenyl)methane derivatives^a

	C ₅ H ₅	C ₅ H ₄	C _{central} -H	Others
1a	4.11 s ^b	4.42 m, 4.11 ^b , 3.99 m, 3.92 m	6.05 d (11)	6.16 s (2H, 3,5- <i>H</i>), 3.91 d (11) (1H, <i>OH</i>), 3.83 s (6H, 2,6- <i>MeO</i>), 3.82 s (3H, 4- <i>MeO</i>)
1b	4.11 s ^b	4.43 dt (2, 1), 4.11 ^b , 4.00 dt (2, 2), 3.96 m	6.13 d (11)	7.20 t (8) (1H, 4- <i>H</i>), 6.59 d (8) (2H, 3,5- <i>H</i>), 4.08 d (11) (1H, <i>OH</i>), 3.85 s (6H, 2,6- <i>MeO</i>)
1c	4.22 s	4.19 m (4H)	5.47 d (3)	7.40–7.25 m (5H, <i>Ph</i>), 2.45 d (3) (1H, <i>OH</i>)
2a	4.78 s	6.01 s (2H), 5.12 br (2H)	8.55 s	6.18 s (2H, 3,5- <i>H</i>), 4.01 s (9H, 2,4,6- <i>MeO</i>)
2a^c	4.76 s ^b	6.02 s, 5.93 s, 5.36 s, 4.76 ^b	8.45 s	6.15 s and 6.08 s (2H, 3,5- <i>H</i>), 4.07 s, 3.99 s and 3.89 s (9H, 2,4,6- <i>MeO</i>)
2b	4.98 s	6.31 s, 6.24 s, 5.37 s, 4.79 s	8.29 s	7.62 t (8) (1H, 4- <i>H</i>), 6.63 d (8) (2H, 3,5- <i>H</i>), 3.98 s (6H, 2,6- <i>MeO</i>)
2c	4.92 s	6.45 s, 6.29 s, 5.38 s, 4.99 s	8.40 s	7.84 d (7) (2H, 2,6- <i>H</i>), 7.65 t (7) (1H, 4- <i>H</i>) and 7.50 t (8) (2H, 3,5- <i>H</i>)
3a	4.10 s	4.14 t (2) (2H), 3.94 t (2) (2H)	3.59 s (2H)	6.11 s (2H, 3,5- <i>H</i>), 3.82 s (6H, 2,6- <i>MeO</i>), 3.78 s (3H, 4- <i>MeO</i>)
3b	4.10 s	4.17 t (2) (2H), 3.95 t (2) (2H)	3.67 s (2H)	7.10 t (8) (1H, 4- <i>H</i>), 6.51 d (8) (2H, 3,5- <i>H</i>), 3.83 s (6H, 2,6- <i>MeO</i>)
3c	4.11 s ^b	4.11 ^b , 4.08 br (2H)	3.69 s (2H)	7.28–7.16 m (5H, <i>Ph</i>)
4a	4.01 s	3.95 s (4H)	5.93 s	6.07 s (2H, 3,5- <i>H</i>), 3.77 s (6H, 4- <i>MeO</i>), 3.60 s (12H, 2,6- <i>MeO</i>)
4b	4.01 s	3.97 br (4H)	6.00 s	7.07 t (8) (1H, 4'- <i>H</i>), 6.48 d (8) (2H, 3',5'- <i>H</i>), 6.07 s (2H, 3,5- <i>H</i>), 3.77 s (3H, 4- <i>MeO</i>), 3.60 s (12H, 2,6- <i>MeO</i> and 2',6'- <i>MeO</i>)
4c	3.99 s	4.12–4.07 m (4H)	5.82 s	7.14–7.06 m (5H, <i>Ph</i>), 6.16 s (2H, 3,5- <i>H</i>), 3.82 s (3H, 4- <i>MeO</i>), 3.66 br (6H, 2,6- <i>MeO</i>)
5b	4.03 br	4.08 br (4H)	6.01 s	7.14 t (8) (1H, 4'- <i>H</i>), 7.03 d (9) (1H, 6- <i>H</i>), 6.56 d (8) (2H, 3',5'- <i>H</i>), 6.31 d (1H, 5- <i>H</i>) and 6.30 s (1H, 3- <i>H</i>) ^c , 3.73 s, 3.69 br and 3.64 s (12H, 2,4- <i>MeO</i> , 2',6'- <i>MeO</i>)
5c	4.01 s	4.12 br (2H), 4.03 br (1H), 3.92 br (1H)	5.50 s	7.26–7.10 m (5H, <i>Ph</i>), 6.89 d (8) (1H, 6- <i>H</i>), 6.42 d (2) (1H, 3- <i>H</i>), 6.38 dd (8, 2) (1H, 5- <i>H</i>), and 3.77 s (6H, 2,4- <i>MeO</i>)

^a In CDCl₃ (δ), 270 MHz; coupling constants (*J*_{HH} (Hz)) are given in parentheses; s, singlet; d, doublet; t, triplet; dd, double doublets; dt, double triplets; m, multiplet; br, broad.

^b Overlapped.

^c At –60°C.

sodium hydroxide, **1a** was recovered as precipitates almost in quantitative yield.

Compound **1b** also was soluble in concentrated HCl to give a red–brown solution, and it could be diluted to a 3 M HCl solution without the loss of the red–brown color.

Thus, the *pK*_{R+} value of **1a** and **1b** could be measured for the solutions in these aqueous HCl solutions by titration using aqueous sodium hydroxide to give values of +3.0 and +1.6, respectively. These values may be compared with those reported for **1c** (+0.49), Fc–CH(4-MeOC₆H₄)OH (+1.37) and Fc₂CHOH (+4.08) [6–8,11]. It is concluded that **1a** is slightly less basic than Fc₂CHOH.

2.2. Reactions of ferrocenyl(phenyl)carbenium salts with methoxybenzenes

The authors have reported that [Ar₂CH]⁺ salts (Ar = Φ^a, Φ^b) reacted with 1,3,5-trimethoxybenzene and 1,3-dimethoxybenzene to give the triphenylmethanes, such as Φ₃CH [3] or Φ₂Φ^dCH [Φ^d = 2,4-(MeO)₂C₆H₃] [10]. Ferrocenyl(phenyl)carbenium salts are also expected to react with these methoxybenzenes [12–14]. Unfortunately, **2a–c** and **2a'–c'** were only slightly soluble in 2-methyl-2-

propanol, and the reactions were performed for **1a–c** in the presence of HCl or trifluoroacetic acid. Thus, **1a** was treated with 1,3,5-trimethoxybenzene (Φ^aH) in 2-methyl-2-propanol containing only a slight excess of 1 M HCl, and yellow crystals of bis(2,4,6-trimethoxyphenyl)ferrocenylmethane, Fc–CHΦ₂^a (**4a**), were obtained in quantitative yield. Both **1b** and **1c** also reacted with Φ^aH in the presence of acid to give analogous compounds, Fc–CHΦ^aΦ^b (**4b**) and Fc–CHΦ^aPh (**4c**).

When **1a–c** were treated with 1,3-dimethoxybenzene in an analogous manners as above, however, complex mixtures containing a compound having two Fc–CHΦ moieties, possibly 1,3-dimethoxy-4,6-bis[ferrocenyl(phenyl)methyl]benzene, 1,3-(MeO)₂-4,6-(CHFcΦ)₂C₆H₂. When the reaction of **1a** was performed in neat 1,3-dimethoxybenzene, the GC–MS spectra showed the formation of Φ^aH and possibly Fc–CHΦ₂^d, of which pure isolation has not been achieved. When **1b** was treated in neat 1,3-dimethoxybenzene containing acid, yellow crystals of 2,4-dimethoxyphenyl(2,6-dimethoxyphenyl)ferrocenylmethane, Fc–CHΦ^bΦ^d (**5b**), were obtained in a good yield. Compound **1c** also reacted with 1,3-dimethoxybenzene in the presence of acid to give an analogous compound, Fc–CHPhΦ^d (**5c**), although the yield was less.

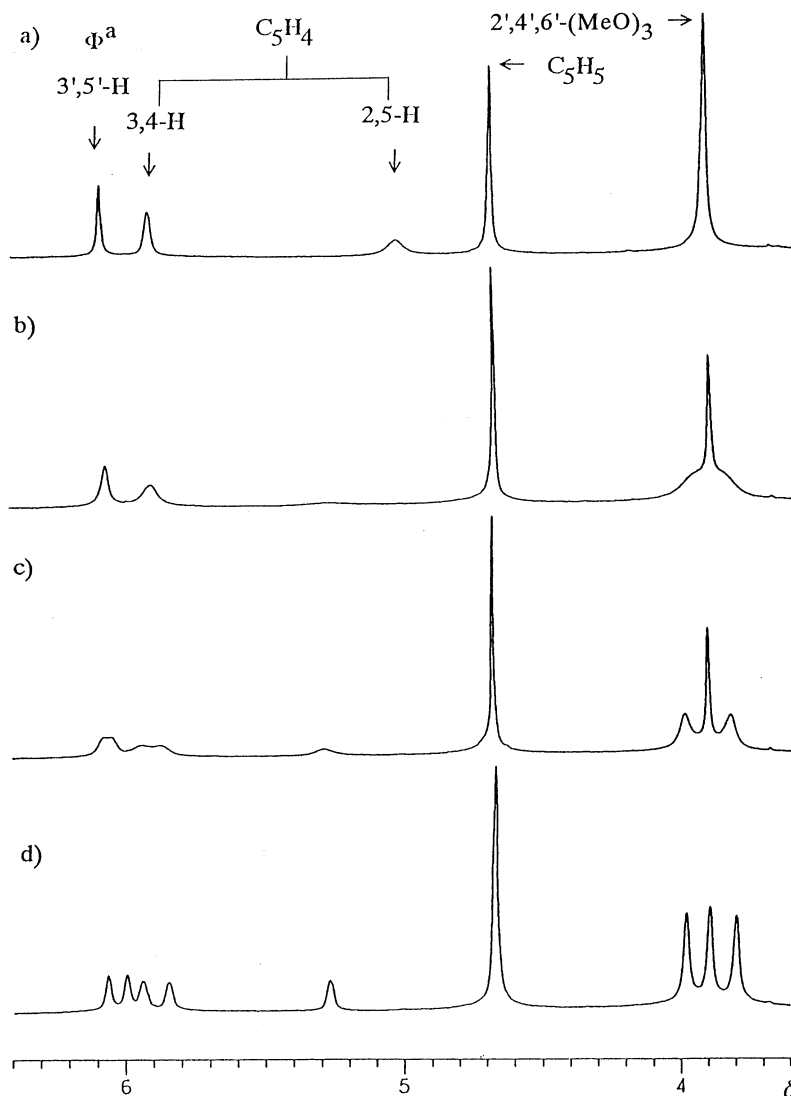


Fig. 1. ^1H -NMR spectra of **2a** in CDCl_3 at (a) 25°C , (b) -10°C , (c) -20°C , (d) -60°C .

2.3. NMR spectra

The ^1H -NMR spectrum of **1a** (Table 2) showed a 5H singlet attributable to C_5H_5 protons at 4.11, while that of **2a** showed a 5H singlet at much lower magnetic field (δ 4.78) reflecting the cationic character. Analogous low-field shifts were observed for **2b**, as well as for **2c**. The pattern of proton resonance of the C_5H_4 moiety depends largely on the type of compound. Those of **1a** and **1b** were observed as four multiplets, which reflect the lack of symmetry in these compounds. In contrast, the C_5H_4 proton resonances of **2a** were observed as two broad resonances, while four broad singlets were observed for **2b** and **2c**. The spectrum of **2c** has been explained by the lack of free rotation around the $\text{C}_5\text{H}_4\text{--C}$ bond [15], but the spectrum of **2a** seems to indicate the presence of free rotation (see below). The

proton resonances of the central C–H bond were observed in regions δ 6.2–5.5 for **1a–c** and δ 3.7–3.6 for **3a–c**, while those of **2a–c** were observed at a low magnetic field δ 8.6–8.2, also reflecting the cationic character of the latter compounds. The coupling constant of the central C–H with the hydroxide proton (J_{HH}) is significantly larger for **1a,b** (11 Hz) than for **1c** (3 Hz). There is evidence that the spectra of $\text{Fc-CH}\Phi\text{OH}$, where Φ is 2-methoxyphenyl or 2,5-dimethoxyphenyl, show a value of 5 Hz, indicating that the value is influenced by the number of methoxy groups at the 2,6-positions of the phenyl group (Φ). The methoxy proton resonances of **2a,b** were also observed at lower magnetic fields than those of **1a,b** and **3a,b**, respectively.

With a hope to confirm the presence of free rotation around the $\text{C}_5\text{H}_4\text{--C}$ bond in **2a** at r.t., the spectrum was

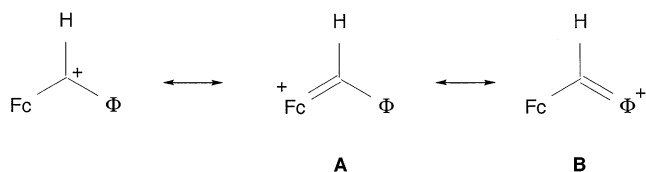
Table 3

¹³C-NMR spectral data for ferrocenyl(phenyl)methane derivatives^a

	C ₅ H ₅	C ₅ H ₄	C _{central}	Others
1a	69.3 (176)	92.7, 68.3, 68.2, 67.7, 67.6	66.4 (147)	161.0 (2,6-C), 158.9 (4-C), 113.0 (1-C), 91.7 (3,5-C), 56.2 and 56.0 (MeO)
1b	69.3 (174)	92.4, 68.2, 67.7, ^{-b}	66.6 (149)	158.2 (2,6-C), 129.2 (4-C), 120.2 (1-C), 105.1 (3,5-C), 56.3 (2,6-MeO)
1c	69.1 (174)	94.9, 72.8, 68.7, 68.1, 66.7	72.7 (145)	144.0 (1-C), 128.8 (3,5-C), 128.1 (2,6-C), 126.9 (4-C)
2a	78.8 (182)	94.9, 89.3, 80.0	138.3 (162)	170.8 (2,6-C), 164.0 (4-C), 108.5 (1-C), 93.0 (3,5-C), 57.43 and 57.37 (MeO)
2b	81.4 (182)	102.4, 93.8, 92.1, 83.0, 79.4	122.9 (164)	160.8 (2,6-C), 137.2 (4-C), 113.2 (1-C), 105.5 (3,5-C), 57.0 (2,6-MeO)
3a	69.1 (174)	89.9, 69.5, 67.4	22.9 (130)	160.1 (2,6-C), 159.2 (4-C), 112.0 (1-C), 91.2 (3,5-C), 56.2 and 56.0 (MeO)
3b	69.2 (176)	89.4, 69.6, 67.4	23.2 (129)	158.7 (2,6-C), 127.6 (4-C), 119.3 (1-C), 104.4 (3,5-C), 56.2 (2,6-MeO)
3c	69.3 (174)	88.7, 68.2, ^{-b}	36.8 (128)	142.3, 129.1, 128.9, 126.6
4a	69.6 (176)	94.9, 66.8, ^{-b}	32.5 (129)	160.1, 159.5, 115.2, 91.9, 56.3, 55.7
4b	68.9 (174)	93.7, 69.23, 69.17, 68.9, 66.4	32.9 (127)	160.0, 159.5, 129.6, 128.8, 127.1, 122.3, 114.8, 105.3, 91.7, 56.3, 56.2, 55.7
4c	69.2	91.3, 70.8, 69.7, 67.5, 67.4	40.1	160.3, 159.5, 146.7, 128.9, 127.7, 125.4, 115.7, 92.1, 56.1, 55.8
5b	69.2	91.8, 70.2, 70.0, 67.5, 67.1	36.6	159.4, 159.1, 158.2, 132.4, 127.8, 127.6, 122.2, 105.7, 104.0, 98.5, 56.3, 56.2, 55.8
5c	69.3	92.7, 69.9, 69.2, 68.3, 67.9	44.0	159.7, 157.8, 145.7, 130.6, 129.4, 128.3, 127.5, 126.3, 104.5, 99.0, 56.0, 55.9

^a In CDCl₃ (δ), 68 MHz; coupling constants (*J_H*/Hz) are given in parentheses.^b Not detected or overlapped.

measured at low temperatures. The spectrum observed at -60°C clearly showed three well-formed singlets at δ 6.02, 5.93 and 5.36 attributable to C₅H₄ protons (Fig. 1). The fourth singlet seemed to be overlapped with the strong peak of C₅H₅ protons at δ 4.76, as is expected from the spectra of **2b** and **2c**. Of special interest is the observation that the methoxy proton resonance at δ 4.01 split into three peaks with identical intensities at -60°C (Fig. 1). The 3,5-proton resonance of the Φ^{a} group also split into two peaks. These observations clearly indicate that the free rotations of both Fc and Φ^{a} groups in **2a** exist at r.t. but are frozen at -60°C , possibly with the C₅H₄ and Φ^{a} groups in almost the same plane. The coalescence temperature was -10°C for both Fc and Φ^{a} protons. The spectrum of **2b** is understood by the presence of free rotation of the Φ^{b} group and lack of free rotation of the C₅H₄ group around their bonds to the central carbon.



Scheme 2.

The ¹³C-NMR spectral resonances of **1a–c**, **2a,b**, **3a,b** and **4a,b** were assigned by measuring the coupling constants [*J_H*]. The spectrum of **1a** (Table 3) showed a resonance attributable to C₅H₅ carbons at δ 69.3 with a large magnetic coupling (*J_H* = 176 Hz). The spectrum of **2a** showed the resonance at a much lower magnetic field, δ 78.8 (*J_H* = 182 Hz) reflecting the cationic character. In accordance with the lack of symmetry, five resonances due to C₅H₄ carbons were observed for **1a**. The spectrum of **2a** showed only three resonances attributable to C₅H₄ carbons in agreement with the presence of a free rotation around the Fc–C bond at r.t., while that of **2b** showed five resonances. The spectra of **1a–c** showed the central carbon resonance at δ 66–73, with a magnetic coupling with the proton (*J_H* = 145–149 Hz), while those of **2a** and **2b** showed the resonance at a lower magnetic field δ 138.3 and 122.9, respectively, with a larger magnetic coupling (*J_H* = ca. 160 Hz) with the proton. The resonances for alkyl(ferrocenyl)carbenium salts, [Fc–CRR']X (R, R' = H or alkyl), have been observed in a wide range δ 87 (R, R' = H, H) to δ 161 (Me, Et) [16]. The spectrum of **2c** could not be measured precisely due to its lability, and no data has been reported in the literature [15,16].

Thus, the authors conclude that both resonances A and B in Scheme 2 contribute to the stabilization of **2a** in competition with each other, and that resonance A contributes more than B for the stabilization of **2b**.

2.4. GC–MS spectra

The GC–MS spectra of **1a–c** show that they decomposed during the measurement of GC at 300°C. For an example, the spectrum of an acetone solution of **1a** showed the formation of 6-(2,4,6-trimethoxyphenyl)fulvene in addition to at least three compounds, $\text{Fc-C}\Phi^{\text{a}}\text{O}$, **3a** and possibly $\text{Fc-CH}\Phi^{\text{a}}\text{-CH}_2\text{CMeO}$. No evidence of decomposition was observed by GC spectra of **3a–c**, **4a–c** and **5b,c**, of whose mass spectra showed very strong parent peaks, respectively.

3. Experimental

3.1. General

The NMR spectra were recorded for solutions in CDCl_3 using a JEOL model JNM-GX-270 spectrometer. IR spectra were recorded for Nujol® mulls using a Shimadzu FTIR-4200 spectrophotometer. GC–MS spectra were recorded using a Shimadzu QP-5000 mass spectrometer for acetone solutions. UV–vis spectra were recorded using a Shimadzu UV-160 spectrophotometer, and the spectral data are summarized in Table 1. The ^1H - and ^{13}C -NMR spectral data for compounds **1–5** are summarized in Tables 2 and 3, respectively.

3.2. Preparation of ferrocenyl(phenyl)methanols

To a 15% hexane solution of butyllithium (4.4 ml, 7 mmol), diethylether (10 ml), 1,3,5-trimethoxybenzene (1.34 g, 8 mmol), and *N,N,N',N'*-tetramethylethylenediamine (0.1 ml) were added at 0°C under argon. The mixture was stirred at 0°C for 2 h to give a white suspension of $\Phi^{\text{a}}\text{Li}$. To the suspension, a solution of ferrocenylaldehyde (1.07 g, 5 mmol) in diethylether (40 ml) was added, and the mixture was stirred at r.t. for 24 h to give a yellow suspension. Toluene (100 ml) was added, the mixture was washed with water (50 ml) and the organic layer was concentrated to ca. half volume. Hexane (30 ml) was added and the solution was cooled to -30°C to give yellow crystals of $\text{Fc-CH}\Phi^{\text{a}}\text{OH}$ (**1a**) in 79% yield. This compound is very soluble in chloroform, soluble in toluene, acetone, hot methanol, and hot 2-propanol, and poorly soluble in diethylether and hexane. The analytical sample was obtained by recrystallization from toluene.

In essentially the same way as above but using 1,3-dimethoxybenzene or bromobenzene, yellow crystals of $\text{Fc-CH}\Phi^{\text{b}}\text{OH}$ (**1b**) or Fc-CHPhOH (**1c**) were obtained in 89 and 81% yields, respectively.

1a: M.p. 159–161°C, IR 3580 cm^{-1} (OH). Anal. calc. for $\text{C}_{20}\text{H}_{22}\text{FeO}_4$. Found: C, 62.73; H, 5.79%. Calc.: C, 62.85; H, 5.80%.

1b: M.p. 139–140°C, IR 3540 cm^{-1} (OH). Anal.

calc. for $\text{C}_{19}\text{H}_{20}\text{FeO}_3$. Found: C, 64.53; H, 5.86%. Calc.: C, 64.79; H, 5.72%.

1c: M.p. 75–77°C (reported, 81–82°C [17], 78–80°C [18]).

3.3. Reactions of ferrocenyl(phenyl)methanols with acid (HClO_4 , HBF_4) to give ferrocenyl(phenyl)carbenium salts

To a yellow suspension of **1a** (0.382 g, 1 mmol) in diethylether (10 ml), 60% aqueous perchloric acid (0.12 ml, 1.1 mmol) was added. The resultant dark violet suspension was stirred at 0°C for 15 min to give dark violet crystals of $[\text{Fc-CH}\Phi^{\text{a}}]\text{ClO}_4$ (**2a**) in 94% yield.

In a similar way to above but using **1b** or **1c**, crystals of $[\text{Fc-CH}\Phi^{\text{b}}]\text{ClO}_4$ (**2b**) or $[\text{Fc-CHPh}]\text{ClO}_4$ (**2c**) were obtained in 97 and 86% yields, respectively.

In similar ways as well, but using 42% aqueous tetrafluoroboric acid (a slight excess), crystals of $[\text{Fc-CH}\Phi^{\text{a}}]\text{BF}_4$ (**2a'**), $[\text{Fc-CH}\Phi^{\text{b}}]\text{BF}_4$ (**2b'**) or $[\text{Fc-CHPh}]\text{BF}_4$ (**2c'**) were obtained in 96, 73 or 22% yields, respectively.

To suspensions of **1a** (1 mmol) in methanol (10 ml) or ethanol (10 ml), 60% aqueous perchloric acid (0.12 ml, 1.1 mmol) was added. The mixtures were stirred at 0°C for 15 min and were cooled to -30°C to give dark violet crystals of **2a** in 86 or 98% yields, respectively. When 42% aqueous tetrafluoroboric acid (a slight excess) was used in methanol or ethanol, **2a'** was obtained in 71 or 80% yields, respectively. The crystals obtained from ethanol were served for the elemental analysis without recrystallization.

Compound **1a** (1 mmol) dissolved in 12 M HCl (2 ml) to form a dark violet solution. It was immediately diluted with water (22 ml) to give a 1 M HCl solution, which kept the dark violet color for a prolonged period. To this solution, 42% aqueous tetrafluoroboric acid (1.1 mmol) was added to give **2a'** in 80% yield.

When an analogous solution of **1a** in 1 M HCl was neutralized by 5 M NaOH, yellow crystals of **1a** were recovered in 91% yield. The purity of each product obtained above was confirmed by ^1H -NMR and IR spectra.

2a: M.p. 130°C, decomposed, IR 1100 cm^{-1} (ClO_4^-).

2a': Dark violet crystals, m.p. 121°C, decomposed; IR 1055 cm^{-1} (BF_4^-). Found: C, 53.02; H, 4.48%. Calc. for $\text{C}_{20}\text{H}_{21}\text{BF}_4\text{FeO}_3$: C, 53.14; H, 4.68%.

2b: Dark red–brown crystals, m.p. 103°C, decomposed, IR 1100 cm^{-1} (ClO_4^-).

2b': Dark red–brown crystals, m.p. 73°C, decomposed, IR 1055 cm^{-1} (BF_4^-).

2c: Dark brown crystals, m.p. 120°C, decomposed, IR 1100 cm^{-1} (ClO_4^-).

2c': Dark brown crystals, m.p. 69–70°C; IR 1055 cm^{-1} (BF_4^-). This compound has been reported [5,7].

The solubilities were studied for 0.1 mmol of samples in solvents.

2a was very soluble in acetonitrile to give a violet solution, even at 10^{-3} M, while **2b** gave dark red–brown solution at 10^{-2} M and a light brown solution at 10^{-3} M.

2a dissolved in dimethyl sulfoxide to give dark brown solutions at 10^{-1} and 10^{-2} M, but gave a light brown solution at 10^{-3} M, while **2b** gave a light brown solution at 10^{-2} M.

2a dissolved in acetone to give dark violet solutions both at 10^{-1} and 10^{-2} M, but on standing for a few hours, the color changed to dark green (10^{-1} M) or orange (10^{-2} M). **2b** dissolved in acetone to give dark red–brown solutions at 10^{-1} and 10^{-2} M, but on standing for a few hours, the color changed to green.

In methanol, **2a** was partly soluble at 10^{-1} M and almost soluble at 10^{-2} M to give dark violet solutions. The violet color was observed even at 10^{-3} M but disappeared below 10^{-4} M. **2b** also was partly soluble at 10^{-1} M and soluble at 10^{-2} M to give light brown solutions. Analogous results were observed in ethanol.

When 10^{-1} M suspensions of **2a** in methanol or in ethanol were heated to 50–60°C for 1 h, they decomposed to give mixtures containing 1,3,5-trimethoxybenzene ($\Phi^a\text{H}$) and Fc-CHO ($^1\text{H-NMR}$ and GC–MS spectra). Both **2a** and **2b** were poorly soluble in 2-propanol at r.t. When 10^{-1} M suspensions of **2a** were heated at 50°C, it was reduced to give $\text{Fc-CH}_2\Phi^a$ (**3a**) (see Section 3.4).

2c (0.374 g, 1 mmol) decomposed in methanol (10 ml) during mixing to give Fc-CHPhOMe in 77% yield; m.p. 106–107°C (reported, 111–112°C [17]); $^1\text{H-NMR}$ (CDCl_3) δ 7.40–7.25 m (6H, Ph and CHCl_3), 5.00 s (1H, $\text{C}_{\text{central}}\text{-H}$), 4.26 s, 4.13 s, 4.04 s (C_5H_5) and 3.95 s (9H, C_5H_4) and 3.29 s (3H, OMe).

3.4. Reactions of ferrocenyl(phenyl)carbenium salts in 2-propanol to give ferrocenyl(phenyl)methanes

A suspension of **2a** (0.466 g, 1 mmol) in 2-propanol (10 ml) was heated at 50°C for 1 h to give a dark green suspension. Water (40 ml) was added, and the precipitates were dissolved in acetone (20 ml). The acetone solution was filtered through Florisil, and the filtrate was concentrated under reduced pressure to give yellow crystals of $\text{Fc-CH}_2\Phi^a$ (**3a**) in 83% yield. The analytical sample was obtained by recrystallization from diethylether.

To a suspension of **1b** (0.352 g, 1 mmol) in 2-propanol (10 ml) was added 60% perchloric acid (0.12 ml, 1.1 mmol) to give a dark suspension. It was heated at 50°C for 1 h to give a green suspension, which was treated as above to give yellow crystals of $\text{Fc-CH}_2\Phi^b$ (**3b**) in 89% yield. The analytical sample was obtained by recrystallization from diethylether. In an analogous manner but using **1c**, yellow crystals of $\text{Fc-CH}_2\text{Ph}$ (**3c**) were obtained in 36% yields.

3a: M.p. 137–140°C, MS m/z (relative intensity) 366 (100, M^+). Anal. calc. for $\text{C}_{20}\text{H}_{22}\text{FeO}_3$. Found: C, 65.42; H, 6.05%. Calc.: C, 65.59; H, 6.05%. This compound is very soluble in toluene, chloroform, acetone and methanol, soluble in hot 2-propanol and diethylether, and poorly soluble in hexane.

3b: M.p. 103–104°C, MS m/z (relative intensity) 336 (100, M^+). Anal. calc. for $\text{C}_{19}\text{H}_{20}\text{FeO}_2$. Found: C, 67.63; H, 6.00%. Calc.: C, 67.88; H, 6.00%.

3c: M.p. 71–73°C (reported, 70–74°C [17]), MS m/z (relative intensity) 276 (100, M^+).

3.5. Reactions of ferrocenyl(phenyl)carbenium salts with 1,3,5-trimethoxybenzene to give diphenyl(ferrocenyl)methanes

To a yellow suspension of **1a** (1 mmol) in 2-methyl-2-propanol (10 ml), 1,3,5-trimethoxybenzene (0.202 g, 1.2 mmol) and 12 M HCl (0.1 ml, 1.2 mmol) were added. The resulting dark brown suspension was stirred at r.t. for 2 h to give a yellow suspension. Hexane (6 ml) was added and the mixture was cooled to 5°C to give yellow crystals of $\text{Fc-CH}\Phi_2^a$ (**4a**) in 96% yield. The analytical sample was obtained by recrystallization from hexane.

In an analogous way as above but using **1b** or **1c**, yellow crystals of $\text{Fc-CH}\Phi^a\Phi^b$ (**4b**) or $\text{Fc-CH}\Phi^a\text{Ph}$ (**4c**) were obtained in 83 and 90% yields, respectively.

4a: M.p. 164–165°C, MS m/z (relative intensity) 532 (100, M^+).

4b: M.p. 189–191°C, MS m/z (relative intensity) 502 (100, M^+).

4c: M.p. 129–130°C, MS m/z (relative intensity) 442 (100, M^+).

3.6. Reactions of ferrocenyl(phenyl)carbenium salts with 1,3-dimethoxybenzene to give diphenyl(ferrocenyl)methanes

To a brown suspension of **1b** (1 mmol) in 1,3-dimethoxybenzene (5 ml), trifluoroacetic acid (0.08 ml, 1.1 mmol) was added at 0°C. The resulting dark brown suspension was stirred at 0°C for 1 h to give a dark green–brown solution. It was filtered through Florisil. To the filtrate, hexane (5 ml) was added and the mixture was cooled to -30°C to give yellow crystals of $\text{Fc-CH}\Phi^b\Phi^d$ (**5b**) in 90% yield. The analytical sample was obtained by recrystallization from hexane.

In an analogous way but using **1c**, yellow crystals of $\text{Fc-CHPh}\Phi^d$ (**5c**) were obtained in 52% yield.

5b: M.p. 163–164°C, MS m/z (relative intensity) 472 (84, M^+), 121 (100, Cp_2Fe^+). Anal. calc. for $\text{C}_{27}\text{H}_{28}\text{FeO}_4$. Found: C, 68.77; H, 6.02%. Calc.: C, 68.65; H, 5.97%.

5c: M.p. 121–122°C MS m/z (relative intensity) 412 (83, M^+), 121 (100, Cp_2Fe^+), 56 (93, Fe^+). Anal. calc. for $\text{C}_{25}\text{H}_{24}\text{FeO}_2$. Found: C, 72.94; H, 5.93%. Calc.: C, 72.83; H, 5.87%.

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