Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 691 (2006) 3285–3292

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Comparison of the bis(ferrocenylethynyl)phenylmethylium cation with bis(ferrocenylethenyl)methylium analogues

Christofer Arisandy [a], Elizabeth Fullam [a], Stephen Barlow [a,b,*]

[a] Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, UK
[b] School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, USA

Received 21 December 2005; received in revised form 3 April 2006; accepted 3 April 2006
Available online 15 April 2006

Abstract

Several new ferrocenylethynyl derivatives, $(FcCC)_2CHOH$, $(FcCC)_2CH_2$, $(FcCC)_2CPhOH$ have been synthesised from ethynylferrocene. Attempts to synthesise the corresponding bis(ferrocenylethynyl)-stabilised carbocations by hydroxyl or hydride abstraction from the bridging group was unsuccessful for $(FcCC)_2CHOH$ and $(FcCC)_2CH_2$, respectively. In the case of $(FcCC)_2CPhOH$, the $[(FcCC)_2CPh]^+$ cation could be observed by ^1H and ^{13}C NMR, and by UV–Vis–NIR spectroscopy, but was too unstable for isolation or prolonged study in solution. The UV–Vis–NIR spectrum of $[(FcCC)_2CPh]^+$ is compared to that of the considerably more stable cations, $[Fc(CHCH)_2CH]^+$ and $[(FcCHCH)_2CPh]^+$.

Keywords: Ferrocene; Polymethine; Alkyne

1. Introduction

Organic polymethines, or cyanines, are predicted to undergo localisation at sufficiently long chain lengths [1–3]; this has been demonstrated for a couple of all-organic examples [4,5], the first example being the species shown in Fig. 1 with $n = 6$ [4]. We have recently shown that the choice of the charge-stabilising end group in polymethines can affect the chain length at which localisation occurs; we have found that 1,3-bis(ruthenocenyl)allylium cation is localised, whereas its ferrocenyl analogue is a symmetrical species (Fig. 1) [6,7]. This result can be rationalised by analogy with mixed-valence chemistry [4,8]; the localisation in the ruthenium system can be attributed to the large reorganisation energy of the ruthenocene/(η^5-cyclopentadienyl-η^6-fulvene)ruthenium(II) cation system. We were interested in whether localisation could also be induced in relatively short polymethine-like species by reduction of coupling through the conjugated bridge.

Several studies of mixed-valence compounds have revealed weaker coupling in alkyne-bridged mixed-valence compounds than in the corresponding alkenes [9–15]. Hence, we identified species in which the pentamethine bridge is replaced with the $-C{\equiv}CCRC{\equiv}C-$ bridge (Fig. 2) as interesting targets and here we describe some synthetic studies aimed at obtaining cations of the form $[(FcCC)_2CR]^+$. Related $-C{\equiv}CCRC{\equiv}C-$bridged cations with the $Cp(PR_3)_2Ru-$ end group have been reported; these have been shown to be symmetrical in solution on the NMR timescale and, in one case, in the solid state by X-ray crystallography [16]. Several reactions of $(PhCC)_2CHOH$ under acid conditions, including conversion to $PhC{\equiv}CCH{=}C{=}CPhBr$ and $PhC{\equiv}CCH{=}CHC(O)Ph$, presumably involve $[(PhCC)_2CH]^+$ as an intermediate [17]. However, attempts to isolate cations such as $[(4\text{-}Me_2NC_6H_4CC)_2CR]^+$ (R = Ar, CCAr) from treatment of the corresponding alcohol with perchloric acid gave the cyclised pyrylium species [18].

---

[*] Corresponding author. Tel.: +1 404 385 6053; fax: +1 404 894 5909.
E-mail address: stephen.barlow@chemistry.gatech.edu (S. Barlow).

0022-328X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2006.04.002

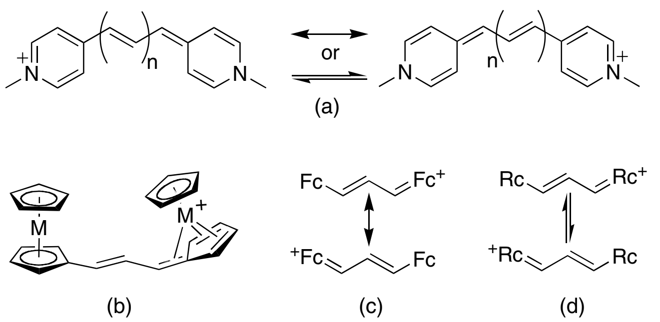


Fig. 1. (a) Polymethines studied by Tolbert and Zhao [4]; for $n = 4$ these two structures are related by the resonance arrow, whereas for $n = 6$ they are related by the equilibrium arrow. (b) Structure representing a termethine with group 8 metallocene end groups; (c) shows that this represents one of two resonance structures where M = Fe {Fc = ferrocenyl} whereas (d) shows that this represents one of two equilibrating structures where M = Ru {Rc = ruthenocenyl} [6,7].

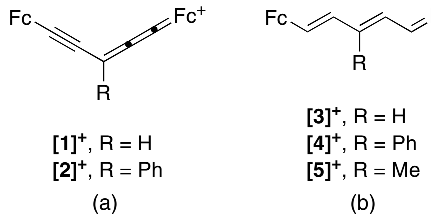


Fig. 2. (a) $[(\mathrm{FcCC})_2\mathrm{CR}]^+$ cations targeted in this work, with (b) their polymethine analogues, $[(\mathrm{FcCHCH})_2\mathrm{CR}]^+$, shown for comparison.

2. Experimental

2.1. General

Electrochemical data were acquired at 298 K using a BAS potentiostat, a glassy-carbon working electrode (circular, 3 mm diameter), a platinum-wire auxiliary electrode, and a silver wire (coated with AgCl by anodising in 1 M KCl solution) pseudo-reference electrode. Cyclic voltammetry (CV) data were acquired in deoxygenated dry dichloromethane solutions 0.1 M in $[^n\mathrm{Bu}_4\mathrm{N}]^+[\mathrm{PF}_6]^-$ and ca. 10^{-4}–10^{-3} M in analyte using a scan rate of ca. 50 mV s^{-1}. Potentials were referenced to ferrocenium/ferrocene by addition of 1,2,3,4,1′,2′,3′,4′-octamethylferrocene (the potential of which was measured as −445 mV vs. ferrocene [19]) to the cell; the error in the reported potentials is estimated from comparison of successive scans to be ca. ±10 mV. $\mathrm{FcC{\equiv}CH}$ [20], $\mathrm{FcC{\equiv}CCHO}$ [21] and $\mathrm{FcCH{=}CHBr}$ [7] were synthesised according to literature procedures (in our hands, the 0.5 M aqueous NaOH specified in the literature did not successfully effect the conversion of $\mathrm{FcCHCl{=}CHCHO}$ to $\mathrm{FcC{\equiv}CH}$, but we found 1.3 M aqueous NaOH to be effective).

2.2. $(\mathrm{FcCC})_2\mathrm{CHOH}$ (**I**)

n-Butyllithium (2.1 mL of a 2.5 M solution in hexane, 3.2 mmol) was added dropwise to a solution of $\mathrm{FcC{\equiv}CH}$ (1.00 g, 4.8 mmol) in THF (30 mL) at −78 °C. After 30 min a solution of $\mathrm{FcC{\equiv}CHCHO}$ (1.13 g, 4.8 mmol) in THF (60 mL) was added dropwise to the stirred solution. After 45 min at −78 °C the solution was allowed to warm to room temperature over 1 h and left to stir for a further 1 h, by which time the reaction appeared complete by TLC. The solution was then poured into an ice–water mixture (100 mL). THF was removed under reduced pressure, before extracting with diethyl ether (3 × 100 mL). The combined ether extracts were then washed with water (5 × 100 mL), washed with a saturated solution of NaCl (2 × 100 mL), dried over potassium carbonate, filtered, and evaporated under reduced pressure. The resulting brown-yellow oil was recrystallised from a hot dichloromethane/hexane to give a red-brown solid (1.51 g, 3.4 mmol, 71%). Anal. Calc. for $\mathrm{C_{25}H_{20}OFe_2}$: C, 67.01; H, 4.50; Fe, 24.92. Found: C, 66.70; H, 4.76; Fe, 24.16%. ^{1}H NMR (chloroform-*d*, 300 Mz) δ 5.35 (1H, d, $J = 7.3$ Hz, C*H*OH), 4.47 (4H, m, two overlapping $\mathrm{C_5H_4}$), 4.24 (10H, s, $\mathrm{C_5H_5}$), 4.21 (4H, m, $\mathrm{C_5H_4}$), 2.23 (1H, d, $J = 7.3$ Hz, OH). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ (chloroform-*d*, 75 MHz) δ 83.4 (alkyne), 83.0 (alkyne), 71.6 ($\mathrm{C_5H_4}C\mathrm{H}$), 71.5 ($\mathrm{C_5H_4}C\mathrm{H}$), 70.0 ($\mathrm{C_5H_4}C\mathrm{H}$), 68.9 ($\mathrm{C_5H_5}$), 63.7 ($\mathrm{C_5H_4}$ quat.), 53.5 (CHOH). EI MS *m*/*z* 448 (M^+). IR (KBr) ν 3408 (–O–H), 2292 (alkyne) cm^{-1}.

2.3. $(\mathrm{FcCC})_2\mathrm{CH}_2$ (**II**)

A solution of **I** (107 mg, 0.24 mmol) in diethyl ether (30 mL) was added dropwise to a mixture of $\mathrm{AlCl_3}$ (64 mg, 0.48 mmol) and $\mathrm{LiAlH_4}$ (18 mg, 0.47 mmol) in diethyl ether (50 mL). After stirring at room temperature for 2 h, the reaction was quenched by the dropwise addition of deoxygenated water (125 mL). The solution was extracted with diethyl ether (3 × 100 mL); the combined ether extracts were combined, dried over magnesium sulfate, filtered, and evaporated under reduced pressure. The resulting red/brown solid was recrystallised from a mixture of dichloromethane and pentane at −80 °C (80 mg, 2 mmol, 77%). Anal. Calc. for $\mathrm{C_{25}H_{20}Fe_2}$: C, 69.49; H, 4.66; Fe, 25.85. Found: C, 68.38; H, 4.92; Fe, 24.29%. ^{1}H NMR (chloroform-*d*, 300 MHz) δ 4.40 (4H, m, $\mathrm{C_5H_4}$), 4.21 (10H, s, $\mathrm{C_5H_5}$), 4.14 (4H, m, $\mathrm{C_5H_4}$), 3.29 (2H, s, $\mathrm{CH_2}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ (chloroform-*d*, 75 MHz) δ 80.1 (alkyne), 78.8 (alkyne), 70.0 ($\mathrm{C_5H_4}C\mathrm{H}$), 69.8 ($\mathrm{C_5H_5}$), 68.4 ($\mathrm{C_5H_4}C\mathrm{H}$), 65.4 ($\mathrm{C_5H_4}$ quat.), 11.5 ($\mathrm{CH_2}$). EI MS *m*/*z* 432 (M^+). IR (KBr) ν 2230 (alkyne) cm^{-1}.

2.4. $(\mathrm{FcCC})_2\mathrm{CPhOH}$ (**III**)

n-Butyllithium (3.56 mL of 2.5 M solution in hexane, 8.9 mmol) was added dropwise to a solution of $\mathrm{FcC{\equiv}CH}$ (1.74 g, 8.3 mmol) in THF (20 mL) at −78 °C. After 30 min, methyl benzoate (0.6 mL, 4.2 mmol, dried by distillation from $\mathrm{CaH_2}$) was added dropwise to the stirred solution. After 1 h at −78 °C, the solution was allowed to warm to room temperature over 1 h and then poured into ice–water (100 mL). THF was removed using a rotary evaporator before extracting with diethyl ether (4 × 100 mL). The combined ether extracts were then washed with water (3 × 100 mL), washed with saturated aqueous NaCl (2 × 150 mL), dried over potassium carbonate, filtered, and evaporated under reduced pressure. The product was purified by passing through a short silica gel plug; impurities were removed by elution with petroleum ether (b.p. 40–60 °C) and with petroleum ether/ethyl acetate (100:1); the product was eluted with ethyl acetate and recrystallised from dichloromethane/pentane at −35 °C to give a red-brown solid (1.05 g, 2.0 mmol, 48% yield). Anal. Calc. for $C_{31}H_{26}OFe_2$: C, 71.03; H, 4.61; Fe, 21.31; O, 3.05. Found: C, 70.99; H, 4.97; Fe, 20.78%. ^1H NMR (chloroform-*d*, 300 MHz) δ 7.91 (2H, dd, Ph), 7.36–7.46 (overlapping peaks, 3H, Ph), 4.48 (4H, m, 2 overlapping C_5H_4), 4.22 (10H, s, C_5H_5), 4.20 (4H, m, C_5H_4), 2.87 (1H, s, OH). $^{13}C\{^1H\}$ NMR (chloroform-*d*, 75 MHz) δ 142.6 (Ph quat), 128.6 (Ph*C*H), 128.5 (Ph*C*H), 126.1 (Ph*C*H), 85.9 (alkyne), 84.2 (alkyne), 71.7 (C_5H_4CH), 71.6 (C_5H_4CH), 70.0 (C_5H_5), 69.0 (C_5H_4CH), 66.3 (CPhOH), 63.9 (C_5H_4 quat). EI MS *m*/*z* 525 (M+). IR (KBr) ν 3540 (–O–H), 2228 (alkyne) cm^{-1}.

2.5. $(FcCH{=}CH)_2CH_2$ (**IVa**) and $Fc(CH{=}CH)_2CH_2Fc$ (**IVb**)

According to the scheme described by Tolbert and coworkers [22], *n*-butyllithium (3.4 mL of a 2.5 M hexane solution, 8.4 mmol) was added dropwise to a slurry of $[(Ph_3PCH_2)_2CH_2]^{2+}(Br^-)_2$ (2.9 g, 4 mmol) in THF (30 mL) at −78 °C. After 30 min, the reaction mixture was allowed to warm to room temperature over 1 h; the reaction mixture was then recooled to −78 °C and a solution of FcCHO (4 mmol) in THF (15 mL) added dropwise. The reaction mixture was allowed to warm to room temperature and then refluxed for 12 h. Water (20 mL) and diethyl ether (20 mL) was added and the mixture transferred to a separating funnel. The aqueous layer was extracted with more ether and the combined organics were dried over magnesium sulfate, filtered and evaporated under reduced pressure. The product was purified by eluting a short silica gel plug with 1:10 diethyl ether/pentane, and evaporating the first fraction to give an orange oil, which was an ca. 1:2:1 *E*,*E*:*E*,*Z*:*Z*,*Z* mixture of the isomers of $(FcCH{=}CH)_2CH_2$. Yield: 60%. ^1H NMR (benzene-d_6, 500 MHz) δ 6.26–6.16 (m, overlapping vinyl CHs), 5.92–5.83 (m, overlapping vinyl CHs), 5.52–5.56 (m, overlapping vinyl CHs), 4.28-4.22 (overlapping Cp CHs), 4.04–3.96 (overlapping Cp Chs), 3.29 (t, $J = 7.3$ Hz, minor isomer CH_2), 3.00 (dd, $J = 6.1$, 7.6 Hz, major *E*,*Z* isomer, CH_2), 2.77 (t, $J = 6.5$ Hz, minor isomer CH_2). ^{13}C NMR (benzene-d_6, 125 MHz) δ 127.2 (vinyl CH), 126.6 (vinyl CH), 125.9 (vinyl CH), 125.8 (other vinyl CH resonances presumably obscured by solvent), 84.3 (quat.), 84.2 (quat.), 82.3 (quat.), 82.2 (quat.), 69.6–66.8 (overlapping Fc CHs), 33.2 (CH_2), 32.7 (CH_2), 33.4 (CH_2). Use of KO^tBu as a base in place of ^nBuLi (as described in detail for **VII**) resulted in the isolation of *E*,*E*-$Fc(CH{=}CH)_2CH_2Fc$. ^1H NMR (benzene-d_6, 500 MHz) δ 6.54 (dd, $J = 15.4$, 10.7 Hz, 1H), 6.19 (dd, $J = 15.4$, 10.7 Hz, 1H), 6.18 (d, $J = 15.4$ Hz, 1H), 5.84 (dt, $J = 15.4$, 6.8 Hz, 1H), 4.24 (apparent t, $J =$ ca. 1.8 Hz, 2H), 4.04 (m, 4H), 4.00 (s, 5H), 3.98 (apparent t, $J =$ ca. 1.8 Hz, 2H), 3.96 (s, 5H), 3.02 (d, $J = 6.8$ Hz, 2H). ^{13}C (C_6D_6, 125 MHz) δ 131.8 (vinyl), 131.4 (vinyl), 129.5 (vinyl), 127.3 (vinyl), 87.5 (quat.), 83.9 (quat.), 69.5 (C_5H_5), 69.1 (C_5H_4CH), 68.8 (C_5H_5), 68.5 (C_5H_4CH), 67.8 (C_5H_4CH), 67.0 (C_5H_4CH), 33.1 (CH_2).

2.6. $(FcCH{=}CH)_2CHOH$ (*V*)

FcCH=CHBr (isomeric mixture, 0.58 g, 2 mmol) was dissolved in a 1:1:4 mixture of pentane, diethyl ether, and THF (15 mL). The solution was cooled to −98 °C (MeOH/l · N_2) and treated with ^tBuLi (1.7 M in pentane, 4 mmol). After 30 min, the reaction was allowed to warm to −78 °C over another 30 min. The solution was then treated with ethyl formate (0.2 mL) in THF; after 15 min at −78 °C, the reaction mixture was allowed to warm to room temperature and treated with water (20 mL) and diethyl ether (20 mL). The layers were separated and the aqueous portion was extracted with diethyl ether (3 × 20 mL). Finally, the combined extracts were dried over K_2CO_3, filtered and evaporated under reduced pressure. Attempted purification of the products by column chromatography led to the decomposition of the product; this material was used without further purification for the in situ generation of $[\mathbf{3}]^+$.

2.7. $(FcCH{=}CH)_2CPhOH$ (**VI**)

VI was obtained as a deep-red oil in an analogous way to **V** using ethyl benzoate in place of ethyl formate. Yield: 0.25 g (1 mmol, 45%). ^1H NMR (chloroform-*d*, 300 MHz) δ 8.10 (2H, d, $J = 8$ Hz), 7.40–7.70 (overlapping peaks), 6.40 (1H, br, dd), 5.95 (2H, d, $J = 15$ Hz), 5.60 (1H, br, dd), 4.42 (4H, t, $J = 1.8$ Hz), 4.05–4.15 (4H, overlapping peaks), 4.03 (10H, s). TOF-EI-MS *m*/*z* 528 (46%, M^+), 510 (M^+–OH, 100%). Anal. Calc. for $C_{31}H_{28}Fe_2O$: C, 70.49; H, 5.34. Found: C, 69.20; H, 5.74%.

2.8. $[(PPh_3CH_2)_2CHMe]^{2+}(Br^-)_2$ (**VII**)

1,3-Dibromo-2-methylpropane (6.93 g, 32 mmol), triphenylphosphine (25 g, 96 mmol), and ethanol (30 mL) were deoxygenated in a rotaflo ampoule and then heated to 100 °C for 5 d. The ampoule's contents were transferred to a large conical flask and allowed to cool with stirring; addition of diethyl ether (500 mL) caused a white mixture of oil and solid to separate. After stirring for an additional 1 h, the product fully solidified and was collected on a frit and washed with diethyl ether. After drying in vacuum, the product was obtained as a white powder (20 g, 27 mmol, 84%). ^1H NMR (500 MHz) δ 7.89 (m, 9 H, *ortho*- and *para*-CH), 7.76 (apparent t, $J = 7.0$ Hz, 6 H, Ph *meta*-CH), 4.20 (m, 2H, CH_2), 3.99 (m, 2H, CH_2), 2.26 (m, 1H, CH), 0.99 (d, 3H, $J = 6.3$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (125 MHz) δ 136.4 (s, C_{para}), 134.8 (d, $J_{PC} = 10$ Hz, C_{meta}), 131.7 (d, $J_{PC} = 12$ Hz, C_{ortho}), 119.4 (d, $J_{PC} = 87$ Hz, C_{ipso}), 30.5 (dd, $J_{PC} = 52$, 16 Hz, CH_2), 27.0 (s, CH), 22.1 (s, CH_3). $^{31}P\{^1H\}$ (122 MHz) δ 22.9. ES-MS (MeOH) *m*/*z* 661 (3%, $[C_{40}H_{38}P_2Br]^+$), 290 (100%, $[C_{40}H_{38}P_2]^{2+}$).

2.9. $FcCH{=}CHCHMe{=}CHCH_2Fc$ (**VIII**)

A solution of KO^tBu (7.0 g, 62 mmol) in THF (20 mL) was added dropwise to a suspension of **VII** (3.00 g, 4.05 mmol) in THF (25 mL) at −78 °C. The resulting orange reaction mixture was allowed to warm to room temperature, before recooling to −78 °C and dropwise addition of a solution of FcCHO (1.733 g, 8.1 mmol) in THF (10 mL). The reaction mixture was allowed to warm to room temperature and heated to reflux until TLC showed no further change (38 h). The reaction mixture was poured into water and the organics were extracted with several portions of diethyl ether. The combined extracts were dried on $MgSO_4$, filtered, and evaporated under reduced pressure to afford an orange solid, which was redissolved in dichloromethane and absorbed onto silica gel. The absorbed product was then transferred to a short silica gel plug which was eluted with pentane to yield a small unidentified yellow fraction, followed by a second orange-red fraction (60 mg, 0.24 mmol, 6%), identified as *E*-1-ferrocenyl-3-methyl-butadiene, $FcCH{=}CHC(Me){=}CH_2$. ^1H NMR (benzene-d_6, 300 MHz) δ 6.63 (d, $J = 16$ Hz, 1H, vinyl CH), 6.31 (d, $J = 16$ Hz, 1H, vinyl CH), 5.03 (s, 1H, CH_2), 4.96 (s, 1H, CH_2), 4.26 (apparent t, $J =$ ca. 1.8 Hz, 2H, C_5H_4), 4.06 (apparent t, $J =$ ca. 1.8 Hz, 2H, C_5H_4), 3.97 (s, 5H, C_5H_5). ^{13}C NMR (C_6D_6, 75 MHz) δ 142.5 (vinyl quat.), 129.7 (vinyl CH), 127.4 (vinyl CH), 115.1 (vinyl CH_2), 83.7 (C5H4 quat.), 69.5 (C_5H_5CH), 69.2 (C_5H_4CH), 67.2 (C_5H_4CH), 18.7 (CH_3). TOF-EI-MS *m*/*z* 504 (8%, $2M^+$), 252 (100%, M^+). Elution with a 1:10 mixture of diethyl ether and pentane gave an orange-red oily solid (orange solid after recrystallisation from a mixture of hexane and dichloromethane), shown to be a mixture of the *E*,*E* and *E*,*Z* isomers of $FcCH{=}CHC(Me){=}CHCH_2Fc$ (1.177 g, 2.61 mmol, 64%). Major and minor isomers were found in the approximate ratio 2:1. Major isomer ^1H NMR (benzene-d_6, 300 MHz) δ 6.68 (d, $J = 16.0$ Hz, 1H, $CH{=}CH$), 6.34 (d, $J = 16.0$ Hz, 1H, $CH{=}CH$), 5.80 (t, $J = 7.3$ Hz, 1H, $CMe{=}CH$), ca. 4.32 (m, 2H, C_5H_4), ca. 4.08 (m, 2H, C_5H_4), 4.03 (s, 5H, C_5H_5), ca. 4.00 (s, 7H, C_5H_5 and C_5H_4), ca. 3.97 (m, C_5H_4), 3.11 (d, $J = 7.3$ Hz, 2H, CH_2), 1.83 (s, 3H, CH_3). Minor isomer ^1H NMR (benzene-d_6, 300 MHz) δ 7.07 (d, $J = 15.6$ Hz, 1H, $CH{=}CH$), 6.45 (d, $J = 15.6$ Hz, 1H, $CH{=}CH$), 5.63 (t, $J = 7.3$ Hz, 1H, $CMe{=}CH$), 4.32–3.94 (C_5H_5 and C_5H_4 resonances overlapping with those of the major isomer, but s at 4.05 may be attributed to C_5H_5 of this isomer), 3.24 (d, $J = 7.3$ Hz, 2H, CH_2), 1.83 (s, 3H, CH_3). TOF-EI-MS *m*/*z* 450 (100%, M^+).

2.10. $[\mathbf{2}]^+[CF_3CO_2]^-$, $[\mathbf{2}]^+[BF_4]^-$, $[\mathbf{3}]^+[CF_3CO_2]^-$ and $[\mathbf{4}]^+[CF_3CO_2]^-$

$[\mathbf{2}]^+[CF_3CO_2]^-$ and $[\mathbf{2}]^+[BF_4]^-$ were generated in situ for UV–Vis–NIR studies by addition of a drop of CF_3CO_2H (0.1 mL) or HBF_4 (0.1 mL, 85% in diethyl ether) respectively to ca. 0.1 mM solutions of **III** in dry dichloromethane. UV–Vis–NIR (CH_2Cl_2) λ_{max} (ε_{max}) 355 (9100), 455 (14000), 522 (20000), 1127 (11000) nm (M^{-1} cm^{-1}). Solutions for NMR studies were generated in the same way by addition of TFAD or TFAH by syringe to a dichloromethane-d_2 solution of **III**. ^1H NMR (dichloromethane-d_2/CF_3CO_2D, 300 MHz) δ 8.38 (d, $J = 8.0$ Hz, 2H, Ph *o*-H), 8.17 (t, $J = 8.0$ Hz, 1H, Ph *p*-H), 7.50 (t, $J = 8.0$ Hz, 2H, Ph *m*-H), 5.81 (t, $J = 1.8$ Hz, 4H, C_5H_4), 5.33 (t, $J = 1.8$ Hz, 4H, C_5H_4), 4.75 (s, 10H, C_5H_5). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2/CF_3CO_2H, −25 °C, 125 MHz; assigned using DEPT-135 and GHSQC experiments) δ 176.5 (quat.), 143.1 (quat.), 132.4 (Ph*m*–CH), 131.2 (Ph*p*–CH), 126.7 (Ph*o*–CH), 120.1 (quat.), 114.4 (quat.), 82.8 (C_5H_4CH corresponding to 5.81 ppm ^1H resonance), 77.0 (C_5H_5), 76.9 (C_5H_4CH corresponding to 5.33 ppm ^1H resonance), 70.9 (quat.).

Solutions containing $[\mathbf{3}]^+[CF_3CO_2]^-$ and $[\mathbf{4}]^+[CF_3CO_2]^-$ were obtained in the same way from **V** and **VI**, respectively, and were considerably more stable than those of $[\mathbf{2}]^+[CF_3CO_2]^-$.

2.11. $[\mathbf{3}]^+[BF_4]^-$

A solution of trityl tetrafluoroborate (185 mg, 0.56 mmol) in dichloromethane (10 mL) was added dropwise to a stirred solution of **IVa** (260 mg, 0.60 mmol) in dichloromethane (10 mL); the reaction mixture instantly darkened. After 30 min, the solution was filtered and diethyl ether (150 mL) added. The resulting precipitate was washed with diethyl ether (2 × 20 mL) and dried in vacuo to afford the salt as a dark microcrystalline powder (217 mg, 0.42 mmol, 75%). ^1H NMR (dichloromethane-d_2, 300 MHz) δ 8.17 (d, 2H, $J = 14.2$ Hz, FcC*H*), 8.07 (t, 1H, $J = 12.6$ Hz, FcCHCHC*H*), 6.60 (apparent t, 2H, $J = 13.3$ Hz, FcCHC*H*), 5.47 (m, 4H, C_5H_4), 5.02 (m, 4H, C_5H_4), 4.51 (s, 10H, C_5H_5). $^{13}C\{^1H\}$ NMR (dichloromethane-d_2, 75 MHz) δ 155.6 (Fc*C*H), 154.9 (FcCHCH*C*H), 130.2 (FcCH*C*H), 88.5 (C_5H_4 quat.), 81.9 (C_5H_4CH), 75.5 (C_5H_4CH), 73.3 (C_5H_5). UV–Vis–NIR (CH_2Cl_2) λ_{max} (ε_{max}) 256 (11000), 506 (23000), 904 (16000) nm (M^{-1} cm^{-1}). UV–Vis–NIR (MeCN) λ_{max} 491, 832 nm. UV–Vis–NIR (Me_2CO) λ_{max} 493, 842 nm. UV–Vis–NIR (DMSO) λ_{max} 862 nm. UV–Vis–NIR (DMF) λ_{max} 892 nm. IR (KBr) 3094, 1548 (s), 1494 (s), 1421, 1194 (s), 1149, 1060 (s, br), 1034 (s, br), 927, 834, 644, 513, 479, 440, 427 cm^{-1}. Anal. Calc. for $C_{25}H_{23}BF_4Fe_2$: C, 57.53; H, 4.44. Found: C, 56.98; H, 4.77%.

2.12. [**3**]$^+$[PF$_6$]$^-$

This salt was obtained in an analogous fashion to its [BF$_4$]$^-$ analogue, using [Ph$_3$C]$^+$[PF$_6$]$^-$ in place of [Ph$_3$C]$^+$[BF$_4$]$^-$. UV (CH$_2$Cl$_2$) λ_{max} 505, 900 nm. Anal. Calc. for $C_{25}H_{23}F_6Fe_2P$: C, 51.76; H, 4.00. Found: C, 52.13; H, 4.46%.

2.13. [**4**]$^+$[BF$_4$]$^-$

This salt (0.27 g, 0.45 mmol, 49%) was obtained from **VI** using the method we have previously described for the synthesis of [Mc(CH)$_3$Mc]$^+$[BF$_4$]$^-$ salts from McCH=CHCH-OHMc [7]. ^{1}H NMR (dichloromethane-d_2, 300 MHz) δ 7.77 (2H, d, J = 13.2 Hz, FcC*H*), 7.66 (1H, t, J = 5.0 Hz, Ph), 7.58 (2H, t, J = 5.0 Hz, Ph), 7.34 (1H, d, J = 5.0 Hz, Ph), 6.83 (2H, d, J = 13.2 Hz, CPhC*H*), 5.54 (4H, apparent s, C$_5$H$_4$), 5.08 (4H, apparent s, substituted C$_5$H$_4$), 4.52 (10H, s, C$_5$H$_5$). ^{13}C{^{1}H} NMR (dichloromethane-d_2, 75 MHz) δ 161.5 (*C*Ph), 153.5 (CPh*C*H), 136.8 (Ph quat.), 132.4 (Ph CH), 130.4 (Fc*C*H), 129.3 (Ph CH), 129.2 (Ph CH), 89.4 (C$_5$H$_4$ quat.), 82.2 (C$_5$H$_4$ CH), 75.5 (C$_5$H$_5$), 73.4 (C$_5$H$_4$ CH). ES-MS (MeOH) m/z 510 (100%, M$^+$). UV–Vis (CH$_2$Cl$_2$) $\lambda_{max}(\varepsilon_{max})$ 515 (21000), 926 (14000) nm (M^{-1} cm^{-1}). Anal. Calc. for $C_{31}H_{27}F_4Fe_2B$: C, 62.26; H, 4.55; B, 1.81. Found: C, 61.03; H, 4.66; B, 1.88 (1.81)%.

2.14. [**5**]$^+$[BF$_4$]$^-$

This salt was obtained from **VII** using [Ph$_3$C]$^+$[BF$_4$]$^-$ in the same way as [**3**]$^+$[BF$_4$]$^-$. ^{1}H NMR (dichloromethane-d_2, 300 MHz) δ 8.29 (d, J = 14.2 Hz, 2H, FcC*H*), 6.47 (d, J = 14.2 Hz, 2H, FcCHC*H*), 5.56 (m, 4H, C$_5$H$_4$), 5.11 (m, 4H, C$_5$H$_4$), 4.56 (s, 10H, C$_5$H$_5$), 1.84 (s, 3H, CH$_3$). ^{13}C{^{1}H} NMR (dichloromethane-d_2, 300 MHz) δ 159.4 (*C*Me), 149.4 (Fc*C*H), 132.5 (FcCH*C*H), 89.8 (C$_5$H$_4$ quat), 82.1 (C$_5$H$_4$CH), 75.7 (C$_5$H$_5$), 73.5 (C$_5$H$_4$CH), 16.6 (CH$_3$). ES-MS (MeOH) m/z 449 (100%, M$^+$). UV–Vis (CH$_2$Cl$_2$) λ_{max} 255, 514, 922 nm. Anal. Calc. for $C_{26}H_{25}F_4Fe_2B$: C, 58.27; H, 4.70. Found: C, 56.53; H, 4.44%.

2.15. [**5**]$^+$[PF$_6$]$^-$

This salt was obtained from **VII** using [Ph$_3$C]$^+$[PF$_6$]$^-$ in the same way as [**3**]$^+$[PF$_6$]$^-$. IR (KBr) 3112, 1520 (s), 1494 (s), 1412, 1368, 1351, 1239 (s), 1106, 1050, 1015, 964, 928, 834 (s, br), 642, 558, 497, 467 cm^{-1}. Anal. Calc. for $C_{26}H_{25}F_6Fe_2P$: C, 52.56; H, 4.24. Found: C, 52.69; H, 4.26%.

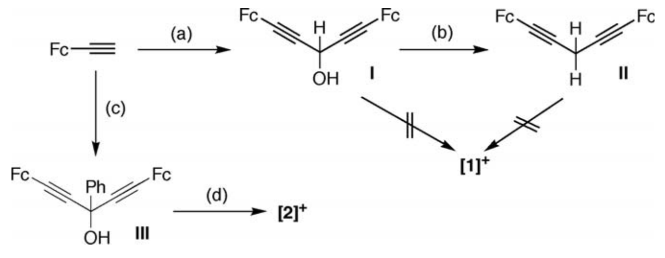
3. Results and discussion

3.1. Synthesis of (FcCC)$_2$CROH and (FcCC)$_2$CH$_2$

Two principal strategies can be identified for the synthesis of bis(ferrocenyl) cations. Brønsted or Lewis acids have been used to generate carbocations stabilised by one or more group 8 metallocenes from alcohol precursors [7,23–36]. Indeed, [Fc$_2$CCCFc]$^+$ – related to our target cations in featuring a ferrocenylalkynyl group – was obtained from protonation of Fc$_2$C(OH)C≡CFc, itself obtained from the reaction of FcC≡CLi and Fc$_2$CO [32,37]. Alternatively, hydride can be abstracted from methylene units in the bridging group using reagents including [Ph$_3$C]$^+$ [22,38,39], DDQ [40–45], and [Cp$_2$RuHal]$^+$ [46,47]. Hence we identified bis(ferrocenylethynyl)methanol (**I**) and bis(ferrocenylethynyl)methane (**II**) as potential precursors to our target cations. We synthesised **I** as shown in Scheme 1 from the reaction of lithiated ethynylferrocene [20] with FcC≡CCHO, which was itself obtained by the reaction of FcC≡CLi and DMF according to a literature procedure [21]. **I** is a new compound, although an isomer, FcC≡CC(O)CH=CHFc has previously been reported [48]. The alcohol **I** was readily converted to **II** by reduction with LiAlH$_4$/AlCl$_3$. Due to our inability to characterise the [**1**]$^+$ cation (vide infra), we synthesised **III** as a precursor to [**2**]$^+$ through the reaction of FcC≡CLi with ethyl benzoate (Scheme 1). Compounds **I**–**III** are oxidized at potentials of +0.14, +0.11 and +0.14 V, respectively, vs. ferrocenium/ferrocene in CH$_2$Cl$_2$/0.1 M [^{n}Bu$_4$N]$^+$[PF$_6$]$^-$. No separation was resolved between first and second oxidation; this is not surprising in view of the length of bridge and the lack of complete conjugation between the two ferrocene groups in these species. The positive values of these potentials are consistent with the alkynyl fragment exerting an electron-withdrawing effect on the iron centers, as has previously been observed for, example, FcC≡CH, for which a value of +0.14 V vs. ferrocenium/ferrocene (CH$_2$Cl$_2$/0.1 M [nBu$_4$N]$^+$[PF$_6$]$^-$) has been reported [49].

3.2. Synthesis of [(FcCC)$_2$CR]$^+$ and [(FcCHCH)$_2$CR]$^+$ cations

We attempted to obtain salts of [(FcCC)$_2$CH]$^+$, [**1**]$^+$, using the methods we and others have used for synthesis of [Fc(CH)$_n$Fc]$^+$ cations, i.e. reaction of **I** with Brønsted and Lewis acids (ethereal HBF$_4$, aqueous HPF$_6$, [Ph$_3$C]$^+$[BF$_4$]$^-$) and reaction of **II** with [Ph$_3$C]$^+$[BF$_4$]$^-$. Invariably the isolable products were dark NMR-silent paramagnetic species [50]. Whilst attempts to isolate salts of [(FcCC)$_2$CPh]$^+$, [**2**]$^+$, from **III** in the ways attempted for [**1**]$^+$ from **I** were also unsuccessful, we were able to



Scheme 1. *Reagents and conditions:* (a) ^{n}BuLi, THF, −78 °C, then FcC≡CCHO; (b) LiAlH$_4$, AlCl$_3$, Et$_2$O; (c) ^{n}BuLi, THF, −78 °C, then PhCO$_2$Et; (d) CF$_3$CO$_2$H or HBF$_4$, CH$_2$Cl$_2$.

observe a room temperature ^{1}H NMR spectrum consistent with the proposed structure in dichloromethane-d_2 on the addition of deuterated trifluoroacetic acid to **III** (CF_3CO_2H has previously been used by others to generate ferrocenyl carbocations [51–53]). The UV–Vis–NIR spectrum (vide infra) obtained under similar conditions can, therefore, be identified with that of [**2**]$^+$. Both NMR and UV–Vis–NIR spectra (Fig. 3) are found to change over time, clearly indicating the instability of this species in solution, consistent with our inability to isolate pure salts of this cation. The peak observed at ca. 750 nm in the decomposition product (Fig. 3) could potentially be due to a ferrocenium-containing product (λ_{max} for unsubstituted ferrocenium and for $[FcCCH]^+$ are 628 and 698 nm, respectively, in dichloromethane [49]); this is consistent with NMR spectra which reveal appearance of a paramagnetic species. The same UV–Vis–NIR spectrum is obtained on addition on ethereal tetrafluoroboric acid to **III** in dichloromethane, but decays more rapidly than that generated using CF_3CO_2H. The formation of ferrocenium products is reminiscent of that observed for many mononuclear ferrocenyl carbocations where the reactivity can be understood in terms of a redox tautomer in which the ferrocene is oxidised and the “carbocation” center is a radical; for example, the dimagnetic Fe^{II} species $[FcCH_2]^+$ has been shown to dimerise to the paramagnetic Fe^{III} dimer $[FcCH_2CH_2Fc]^{2+}$ [54].

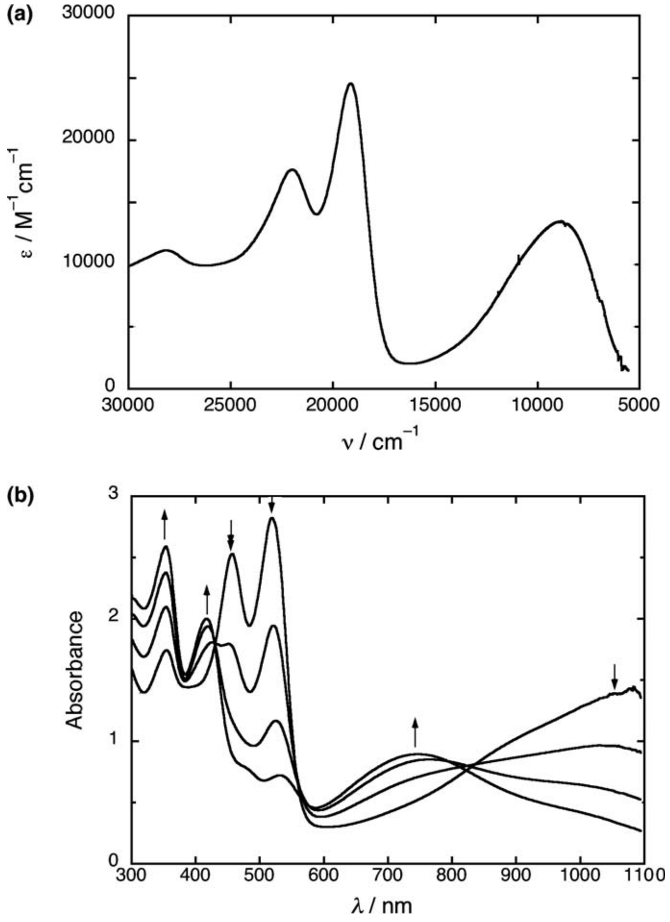


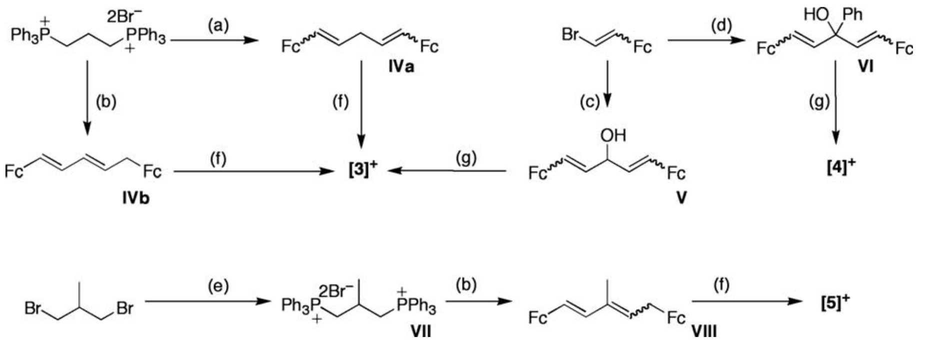
Fig. 3. UV–Vis–NIR spectra of [**2**]$^+$ generated by addition of CF_3CO_2H to **III** in dichloromethane. Above: spectrum with approximate absorptivity determined. Below: spectra taken at ca. 0, 30, 100 and 400 min showing decomposition.

While solutions were sufficiently unstable to permit acquisition of ^{13}C spectra at room temperature, we were able to acquire such spectra at −25 °C if the sample was inserted into the pre-cooled spectrometer immediately after preparation [55]. The ^{13}C resonance corresponding to the central carbon of the π bridge is presumably that at 176.5 ppm; this is considerably upfield from that of the central carbon of trityl cation (211.6 ppm in H_2SO_4 [56]) suggesting the FcCC groups allow for considerable more delocalisation of positive charge than phenyl groups. However, this resonance is somewhat downfield from that of the corresponding resonance in [**4**]$^+$ (161.5 ppm in CD_2Cl_2), suggesting FcCC is a less effective donor than FcCHCH.

We also synthesised the pentamethine cations [**3**]$^+$, [**4**]$^+$, and [**5**]$^+$ for comparison (Scheme 2) with [**1**]$^+$ and [**2**]$^+$ and with the 1,3-ferrocenylallylium cation. We were able to obtain [**3**]$^+$[X]$^-$ {X = BF_4, PF_6} using the previously reported hydride abstraction with $[Ph_3C]^+[X]^-$ from 1,5-bis(ferrocenyl)-1,4-pentadiene (**IVa**) which was obtained as a mixture of *E*,*E*, *E*,*Z*, and *Z*,*Z* isomers from the Wittig reaction of FcCHO and $[(Ph_3PCH_2)_2CH_2]^{2+}(Br^-)_2$ using stoichiometric *n*-butyllithium as a base [22]. Use of excess potassium *tert*-butoxide as base in the Wittig reaction leads to the pure *E*,*E* isomer of 1,5-bis(ferrocenyl)-1,3-pentadiene (**IVb**) which is presumably the thermodynamic product and which is presumably formed due to equilibration via [**3**]$^-$. We were also able to obtain 1,5-bis(ferrocenyl)-3-methyl-1,3-pentadiene (**VIII**) as a mixture of *E*,*E* and *E*,*Z* isomers in the same way as **IVb** and convert it to [**5**]$^+$[X]$^-$ {X = BF_4, PF_6} using trityl salts. In addition, [**3**]$^+$ can be obtained by the action of various acids on $(FcCH{=}CH)_2CHOH$ (**V**) which was obtained in turn, as a mixture of geometric isomers, from FcCH=CHBr (isomer mixture) using lithium-bromine exchange followed by quenching with excess ethyl formate (the intermediate FcCH=CHCHO is expected to be more reactive with FcCH=CHLi than ethyl formate [57]). FcCH=CHCHOHFc and similar species have previously been reported to be rather unstable with respect to oxidation to the corresponding ketones [7,32]; **V** is also rather unstable and was, therefore, used without further purification for the synthesis of [**3**]$^+$. The precursor to [**4**]$^+$, $(FcCH{=}CH)_2CPhOH$ (**VI**) was obtained in the same way as **V**, using ethyl benzoate in place of ethyl formate, and is considerably more stable.

3.3. Spectra of the cations

The isolated salts of [**3**]$^+$–[**5**]$^+$ all form stable solutions in CH_2Cl_2 and were studied using UV–Vis–NIR spectroscopy (see Table 1) [58]. For direct comparison to [**2**]$^+$, solutions of [**3**]$^+$ and [**4**]$^+$ were also generated in situ by treatment of **V** and **VI**, respectively, with CF_3CO_2H; spectra obtained in



Scheme 2. Reagents and conditions: (a) ^{n}BuLi, THF, −78 °C, then FcCHO; (b) excess KO^{t}Bu, THF, −78 °C, then FcCHO; (c) 2 equiv. ^{t}BuLi, pentane/diethyl ether/THF, −98 °C, then HCO$_2$Et, −78 °C; (d) 2 equiv. ^{t}BuLi, pentane/diethyl ether/THF, −98 °C, then PhCO$_2$Et, −78 °C; (e) excess Ph$_3$P, EtOH, 100 °C; (f) [Ph$_3$C]$^+$[X]$^-$ {X = BF$_4$, PF$_6$}, CH$_2$Cl$_2$; (g) HBF$_4$ or CF$_3$CO$_2$H, CH$_2$Cl$_2$.

Table 1
Wavelengths and frequencies corresponding to absorption maxima for the high-energy (HE) and low-energy (LE) transitions seen for bis(ferrocenyl)-terminated cations in CH$_2$Cl$_2$

Cation	λ_{max} (nm)		ν_{max} (10^3 cm^{-1})	
	HE	LE	HE	LE
[**2**]$^+$	522	1127	19.2	8.9
[**3**]$^+$	506	904	19.8	11.1
[**4**]$^+$	515	926	19.4	10.8
[**5**]$^+$	514	922	19.5	10.9

this way were essentially identical to those obtained from solutions of [BF$_4$]$^-$ or [PF$_6$]$^-$ salts. The spectra of [**3**]$^+$–[**5**]$^+$ are qualitatively similar to one another and to the previously reported spectrum of [Fc(CH)$_3$Fc]$^+$ [7,32]. All show two prominent transitions in the Vis–NIR region: we have previously assigned the lower energy of these transitions to a charge transfer from Fe filled d orbitals to the π^* orbital associated with the conjugated bridge, and the higher energy feature to a π–π^* transition [7,59]. Accordingly, both transitions for [**3**]$^+$ are red-shifted relative to those for [Fc(CH)$_3$Fc]$^+$, but the high energy band shows more bridge-length dependence (the energies of the high and low-energy bands of [**3**]$^+$, [Fc(CH)$_3$Fc]$^+$, and [Fc(CH)Fc]$^+$ have been compared in Fig. 7 of Ref. [59]). Introduction of a phenyl or methyl group into the central part of the bridge leads to a slight red shift of both high and low-energy bands.

The optical spectrum of the alkynyl species, [**2**]$^+$ (Fig. 3), shows some qualitative differences from those of [**3**]$^+$–[**5**]$^+$. There is a much more prominent additional band on the high-energy side of the higher energy band, although [**3**]$^+$–[**5**]$^+$ also show weak shoulders in this region. The low-energy band for [**2**]$^+$ is considerably broader ($\Delta\nu_{1/2}$ = ca. 5300 cm^{-1}) than that for [**3**]$^+$–[**5**]$^+$ (ca. 4000 cm^{-1}). While this broadness might be interpreted as evidence for symmetry breaking in the alkynyl cation (the localised species referred to in the introduction show broad low-energy absorptions [4–7]), in that case one would also expect the high-energy band would also be expected to be broad, whereas in [**2**]$^+$ it has a similar bandwidth to [**3**]$^+$–[**5**]$^+$. Moreover, we have attributed the low-energy band to an Fe → π^* charge transfer, in principle consisting of a superposition transitions from each of the three filled d orbitals (xy, x^2–y^2 and z^2) to π^*; hence, the lineshape of this transition will depend to some extent on the energy difference between these transitions. The spectral differences may possibly reflect a structure for [**2**]$^+$ differing from that of [**3**]$^+$–[**5**]$^+$ in that the charge is more localised on the central carbon atom of the bridge, the π^* orbital is less destabilised through interaction with the metal, and in that the Fe orbitals are less stabilised through interaction with the α-carbon. This possibility is consistent with ^{13}C NMR evidence (vide supra).

Acknowledgement

We thank for the Royal Society for partial support and Les Gelbaum for acquiring low-temperature NMR data.

References

[1] C. Kuhn, Synth. Met. 41–43 (1991) 3681.
[2] J.S. Craw, J.R. Reimers, G.B. Bacskay, A.T. Wong, N.S. Hush, Chem. Phys. 167 (1992) 77.
[3] L.M. Tolbert, M.E. Ogle, Synth. Met. (1992) 391.
[4] L.M. Tolbert, X. Zhao, J. Am. Chem. Soc. 119 (1997) 3253.
[5] S.L. Lepkowicz, O.V. Przhonska, J.M. Hales, J. Fu, D.J. Hagan, E.W. Van Stryland, M.V. Bondar, Y.L. Slominsky, A.D. Kachkovski, Chem. Phys. 305 (2004) 259.
[6] S. Barlow, L.M. Henling, M.W. Day, S.R. Marder, Chem. Commun. (1999) 1567.
[7] S. Barlow, L.M. Henling, M.W. Day, W.P. Schaefer, J.C. Green, T. Hascall, S.R. Marder, J. Am. Chem. Soc. 124 (2002) 6285.
[8] S.F. Nelsen, H.Q. Tran, M.A. Nagy, J. Am. Chem. Soc. 120 (1998) 298.
[9] C. LeVanda, K. Bechgaard, D.O. Cowan, J. Org. Chem. 41 (1976) 2700.
[10] A.C. Ribou, J.-P. Launay, M.L. Sachtleben, H. Li, C.W. Spangler, Inorg. Chem. 35 (1996) 3735.
[11] J.E. Sutton, H. Taube, Inorg. Chem. 20 (1981) 3125.
[12] S.V. Rosokha, D.-L. Sun, J.K. Kochi, J. Phys. Chem. A 106 (2002) 2283.
[13] Other donor–acceptor interactions have also been found to be more strongly mediated through alkenes; for example, in *E*-FcCH=CHB(mes)$_2$ {Fc = ferrocenyl, mes = 2,4,6-trimethylphenyl} shows a lower-energy and more intense donor–acceptor CT transition than FcC≡CB(mes)$_2$ Z. Yuan, G. Stringer, I.R. Jobe, D. Kreller, K.

Scott, L. Koch, N.J. Taylor, T.B. Marder, J. Organomet. Chem. 452 (1993) 115.

[14] S. Barlow, C. Risko, V. Coropceanu, N.M. Tucker, S.C. Jones, Z. Levi, V.N. Khrustalev, M.Y. Antipin, T.L. Kinnibrugh, T. Timofeeva, S.R. Marder, J.L. Brédas, Chem. Commun. (2005) 764.

[15] S. Barlow, C. Risko, S.-J. Chung, N.M. Tucker, V. Coropceanu, S.C. Jones, Z. Levi, J.L. Brédas, S.R. Marder, J. Am. Chem. Soc. 127 (2005) 16900.

[16] H.P. Xia, W.F. Wu, W.W. Ng, I.D. Williams, G. Jia, Organometallics 16 (1997) 2940.

[17] K.G. Migliorese, Y. Tanaka, S.I. Miller, J. Org. Chem. 39 (1974) 739.

[18] S. Nakatsuji, K. Nakashima, K. Yamamura, S. Akiyama, Tetrahedron Lett. 25 (1984) 5143.

[19] A. Mendiratta, S. Barlow, M.W. Day, S.R. Marder, Organometallics 18 (1999) 454.

[20] M. Rosenblum, N. Brown, J. Papenmeir, N. Applebaum, J. Organomet. Chem. 6 (1966) 173.

[21] G. Doisneau, G. Balvoine, T. Fillebeen-Khan, J. Organomet. Chem. 94 (1992) 441.

[22] L.M. Tolbert, X. Zhao, Y. Ding, L.A. Bottomley, J. Am. Chem. Soc. 117 (1995) 12891.

[23] C.U. Pittman, Tetrahedron Lett. 37 (1967) 3619.

[24] V.I. Boev, A.V. Dombrovskii, Zh. Obshch. Khim. 50 (1980) 2520.

[25] V.I. Boev, A.V. Dombrovskii, Zh. Obshch. Khim. 55 (1985) 1173.

[26] E.I. Fedin, A.L. Blumenfeld, P.V. Petrovskii, A.Z. Kreindlin, S.S. Fadeeva, M.I. Rybinskaya, J. Organomet. Chem. 292 (1985) 257.

[27] A.Z. Kreindlin, P.V. Petrovskii, M.I. Rybinskaya, A.I. Yanovskii, Y.T. Struchkov, J. Organomet. Chem. 319 (1987) 229.

[28] M.I. Rybinskaya, A.Z. Kreindlin, S.S. Fadeeva, J. Organomet. Chem. 358 (1988) 363.

[29] M.I. Rybinskaya, A.Z. Kreindlin, Y.T. Struchkov, A.I. Yanovsky, J. Organomet. Chem. 359 (1989) 233.

[30] A.I. Yanovsky, Y.T. Struchkov, A.Z. Kreindlin, M.I. Rybinskaya, J. Organomet. Chem. 369 (1989) 125.

[31] C. Zou, M.S. Wrighton, J. Am. Chem. Soc. 112 (1990) 7578.

[32] J. Lukasser, H. Angleitner, H. Schottenberger, H. Kopacka, M. Schweiger, B. Bildstein, K.-H. Ongania, K. Wurst, Organometallics 14 (1995) 5566.

[33] B. Bildstein, P. Denifl, K. Wurst, J. Organomet. Chem. 496 (1995) 175.

[34] B. Bildstein, A. Hradsky, H. Kopacka, R. Malleier, K.-H. Ongania, J. Organomet. Chem. 540 (1997) 127.

[35] A.Z. Kreindlin, F.M. Dolgushin, A.I. Yanovsky, Z.A. Kerzina, P.V. Petrovskii, M.I. Rybinskaya, J. Organomet. Chem. 616 (2000) 106.

[36] S. Barlow, A.R. Cowley, J.C. Green, T.J. Brunker, T. Hascall, Organometallics 20 (2001) 5351.

[37] [FcCCCFc$_2$]$^+$ forms stable crystalline salts; the greater stability relative to that of our target cations is not too surprising since it can be regarded as a FcCC-substituted variant of the stable [Fc$_2$CH]$^+$ cation.

[38] M.J.A. Habib, J. Park, W.E. Watts, J. Chem. Soc. C (1970) 2556.

[39] U.T. Mueller-Westerhoff, A. Nazzal, W. Prössdorf, J.J. Meyerle, R.L. Collins, Angew. Chem. Suppl. (1982) 686.

[40] U.T. Mueller-Westerhoff, Angew. Chem., Int. Ed. Engl. 25 (1986) 702.

[41] U.T. Mueller-Westerhoff, A. Nazzal, W. Prössdorf, J.J. Meyerle, R.L. Collins, Angew. Chem., Int. Ed. Eng. 21 (1982) 293.

[42] B.G. Gavini, T.J. Haas, K.L. Pluorde, U.T. Mueller-Westerhoff, Synth. React. Inorg. Metal-Org. Chem. 22 (1992) 481.

[43] M.F. Moore, S.R. Wilson, D.N. Hendrickson, U.T. Mueller-Westerhoff, Inorg. Chem. 23 (1984) 2918.

[44] M.F. Moore, S.R. Wilson, M.J. Cohn, T.-Y. Dong, U.T. Mueller-Westerhoff, D.N. Hendrickson, Inorg. Chem. 24 (1985) 4559.

[45] S. Ito, N. Morita, T. Asao, J. Org. Chem. 61 (1996) 5077.

[46] M. Watanabe, I. Motoyama, T. Takayama, Bull. Chem. Soc. Jpn. 69 (1996) 2877.

[47] M. Watanabe, I. Moyoyama, T. Takayama, J. Organomet. Chem 524 (1996) 9.

[48] H. Egger, K. Schloegel, Monatsh. Chem. 95 (1964) 1750.

[49] H. Fink, N.J. Long, A.J. Martin, G. Opromolla, A.J.P. White, D.J. Williams, P. Zanello, Organometallics 16 (1997) 2646.

[50] One possible product is the 2,6-bis(ferrocenyl)pyrylium cation, at least in reactions where water is present (the formation of pyrylium species is described in Ref. [18] for reaction of some organic analogues of **I** on treatment with aqueous HClO$_4$). However, the elemental analysis and the paramagnetic NMR spectra rule this out; 2,6-bis(ferrocenyl)pyrylium perchlorate has been synthesised by a different method and is diamagnetic G.N. Dorofeenko, C.V.V. Krasnikov, Zh. Org. Khim. 8 (1972) 2620;
Translated in G.N. Dorofeenko, C.V.V. Krasnikov, J. Org. Chem. USSR 8 (1972) 267.

[51] R. Herrmann, I. Ugi, Tetrahedron 37 (1981) 1001.

[52] J.J. Dannenberg, Angew. Chem., Int. Ed. Engl. 14 (1975) 641.

[53] G.K.S. Prakesh, H.A. Buchholz, J.F.S. Vaughan, Q. Wang, G.A. Olah, J. Braz. Chem. 10 (1999) 313.

[54] K.L. Rinehart, C.J. Michejda, P.A. Kittle, J. Am. Chem. Soc. 81 (1959) 3162.

[55] Attempts to obtain spectra at lower temperatures were complicated by precipitation.

[56] B. Abarca, G. Asensio, R. Ballesteros, T. Varea, J. Org. Chem. 56 (1991) 3224.

[57] J. March, Advanced Organic Chemistry, Wiley, New York, 1985.

[58] We have also studied the electrochemistry of [**3**]$^+$ in CH$_2$Cl$_2$/0.1 M [^{n}Bu$_4$N]$^+$[PF$_6$]$^-$ and found qualitatively similar behavior to that we have previously reported for [Fc(CH)$_3$Fc]$^+$ and methylated analogues in Ref. [6]. The [**3**]$^{2+/+}$ couple is reversible and observed at $E_{1/2}$ = +0.11 V vs. ferrocenium/ferrocene (+0.21 V for [Fc(CH)$_3$Fc]$^+$); the [**3**]$^{3+/2+}$ and [**3**]$^{+/0}$ couples are EC-type processes and are observed at +0.72 and −0.60 V, respectively (+0.82 and −0.64 V, respectively, for [Fc(CH)$_3$Fc]$^+$). In both cases decomposition products, presumably derived from the unstable trication or neutral species, are also observed to grow in at close in potential to ferrocene; this could account with the much lower value of 0.14 V reported for $\Delta E_{1/2}$ ($E_{1/2}^{3+/2+} - E_{1/2}^{2+/+}$) of [**3**]$^+$ by others in Ref. [22].

[59] S. Barlow, S.R. Marder, Chem. Commun. (2000) 1555.