

Synthetic, structural and electrochemical studies
on some ferrocenylazines: crystal structures
of [4](1)(1,4-dimethyl-2,3-diazabuta-1,3-dien) ferrocenophane
and [4₂](1,1') bis(1,4-dimethyl-2,3-diazabuta-1,3-dien) ferrocenophane

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Abstract

By reaction of the hydrazones of mono- and 1,1'-diacetylferrocene with mono- and diketones a series of ferrocenylazines has been prepared. The crystal structures of the monobridged ferrocenophane [4](1)(1,4-dimethyl-2,3-diazabuta-1,3-dien) ferrocenophane (**II**) and of the dibridged ferrocenophane [4₂](1,1')bis-(1,4-dimethyl-2,3-diazabuta-1,3-dien) ferrocenophane (**VII**) have been determined. **II** exists as a centrosymmetric molecule with eclipsed cyclopentadienyl rings and a planar MeC=NN=CMe bridge whereas **VII** has staggered cyclopentadienyl rings and non-planar bridges. In **II** and **VII** the bridges are in the E,E configuration. The electrochemical results show that the ferrocenium ions of the acetylferrocene and the azines are stable in solution whereas those of the hydrazones are unstable. In agreement with a slightly increasing electronic communication between the two ferrocene units, **II** undergoes two almost overlapping one-electron oxidations ($\Delta E^{\circ} = 0.09$ V) whereas **VII** displays two more widely separated one-electron oxidations ($\Delta E^{\circ} = 0.12$ V).

Keywords: Iron; Ferrocenyl azines; Ferrocenophane; Crystal structure; Electrochemistry

1. Introduction

Ferrocene compounds have aroused much interest recently as redox-active entities with potential applications in areas such as materials for molecular electronics [1] and as biologically active compounds [2]. In these contexts there has been considerable interest shown in ferrocenylamines and imines as ligands to transition metals. As a continuation of our studies on the chemistry of main group element derivatives of ferrocene [3a] and their redox behaviour [3b] we have commenced a study of some ferrocenylazines.

We now report high-yielding methods for the synthesis of the hydrazones of acetyl and 1,1'-diacetylferrocene, the condensation reactions of these hydrazones

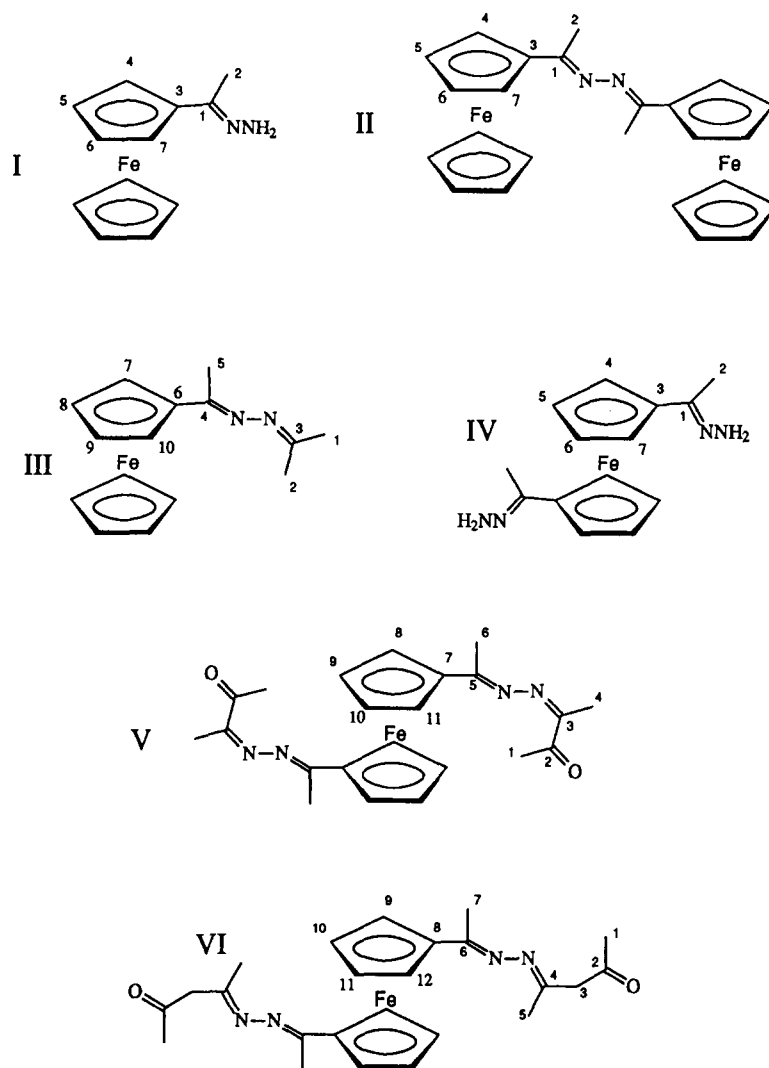
with mono and diketones, the crystal structures of [4](1)(1,4-dimethyl-2,3-diazabuta-1,3-dien)ferrocenophane and [4₂](1,1')bis(1,4-dimethyl-2,3-diazabuta-1,3-dien) ferrocenophane, and electrochemical studies of the compounds. Very few electrochemical studies have been reported for azine-substituted ferrocenes [4,5]. In particular, the oxidation process of complexes **IV** and **VII** unexpectedly displayed ill-shaped responses [6].

2. Experimental details

2.1. General

All preparations were carried out by standard Schlenk techniques [7]. All solvents were freshly distilled, dried and degassed before use and all reactions were performed under purified nitrogen.

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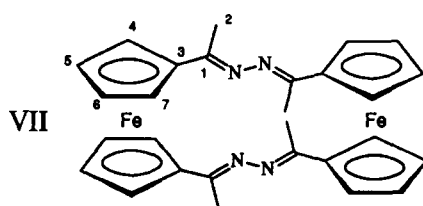
Elemental analysis was performed by Butterworth Laboratories Ltd., Teddington, Middlesex, UK. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AM250 spectrometer operating at 250.13 and 62.90 MHz respectively.

Mass spectra were recorded on a Kratos Profile HV3 instrument. Infrared spectra were recorded on a Perkin–Elmer 881 spectrometer. Materials and apparatus for electrochemistry have been previously described

[8]. Potential values are referred to the saturated calomel electrode (SCE).

2.2. Acetylferrocenehydrazone (I)

A solution of acetylferrocene (1 g, 4.38 mmol) and concentrated hydrochloric acid (0.05 cm³) in ethanol (20 cm³) was added slowly to hydrazine hydrate (10 cm³, 210 mmol) in refluxing ethanol (10 cm³). After 2 h at reflux the ethanol was evaporated under reduced pressure and the product extracted from excess hydrazine with dichloromethane (2 × 30 cm³). Evaporation of the dichloromethane at 85°C under reduced pressure followed by a crystallisation of the residual solid from diethyl ether produced yellow needles (0.99 g, 93%, m.p. 115–117°C. Ref. [9] 110–115.5°C). Anal. Found: C, 59.72; H, 5.97; N, 11.43. C₁₂H₁₄FeN₂. Calc.: C,



59.56; H, 5.78; N, 11.58%. Mass spectrum m/z 242 (M^+). IR(KBr) (C=N) 1639 cm^{-1} .

2.3. [4](1)(1,4-Dimethyl-2,3-diazabuta-1,3-dien) ferrocenophane (II)

Concentrated hydrochloric acid (0.075 cm^3) was added dropwise to a stirred solution of acetylferrocene (4.45 g, 200 mmol) and hydrazine hydrate (20 cm^3) in ethanol (100 cm^3). The solution was heated under reflux for 3 h and then allowed to stand for 2 days. The solvent was evaporated at 85°C under reduced pressure and the solid residue was washed with pentane ($3 \times 30\text{ cm}^3$) and methanol (25 cm^3). A recrystallisation from dichloromethane produced red-carmine needles (2.12 g, 47%, m.p. $216\text{--}217^\circ\text{C}$. Ref. [10] $218\text{--}220^\circ\text{C}$). Anal. Found: C, 63.68; H, 5.26; N, 6.31. $\text{C}_{24}\text{H}_{24}\text{Fe}_2\text{N}_2$. Calc.: C, 63.74; H, 5.36; N, 6.31%. Mass spectrum m/z 452 (M^+). IR(KBr)(C=N) 1599 cm^{-1} .

2.4. 1-Ferrocenyl-1,4-dimethyl-2,3-diazapenta-1,3-diene (III)

Acetylferrocenehydrazone (0.25 g, 0.1 mmol) in acetone (15 cm^3) was stirred for 24 h. The solvent was

evaporated under reduced pressure and the solid extracted with hexane ($2 \times 60\text{ cm}^3$). The solvent was reduced in volume to approximately 40 cm^3 and the product allowed to crystallise as orange-red needles (0.22 g, 75%, m.p. $118\text{--}120^\circ\text{C}$). Anal. Found: C, 63.77; H, 6.42; N, 9.73. $\text{C}_{15}\text{H}_{18}\text{FeN}_2$. Calc.: C, 63.84; H, 6.44; N, 9.93%. Mass spectrum m/z 282 (M^+). IR(KBr)(C=N) 1625 cm^{-1} .

2.5. 1,1'-Diacetylferrocenedihydrazone (IV)

To a solution of 1,1'-diacetylferrocene (0.5 g, 1.89 mmol) and concentrated hydrochloric acid (0.05 cm^3) in ethanol (30 cm^3) at 80°C , hydrazine hydrate (5 cm^3) in ethanol (10 cm^3) was added slowly. After 12 h under reflux the solvent was evaporated and the solid extracted from unreacted hydrazine with dichloromethane ($2 \times 20\text{ cm}^3$). The solvent was evaporated under reduced pressure and the product dried in vacuum as an orange-red powder (0.43 g, 76%, m.p. $150\text{--}152^\circ\text{C}$). Anal. Found: C, 56.2; H, 5.93; N, 18.44. $\text{C}_{14}\text{H}_{18}\text{FeN}_4$. Calc.: C, 56.38; H, 6.09; N, 18.79%. Mass spectrum m/z 298 (M^+). IR(KBr)(C=N) 1600 cm^{-1} .

Table 1

Crystal data and details of data collection and refinement for $[\text{C}_{24}\text{H}_{24}\text{Fe}_2\text{N}_2]$ (II) and $[\text{C}_{28}\text{H}_{28}\text{Fe}_2\text{N}_4]$ (VII) ^a

Compound	(II)	(VII)
Formula	$\text{C}_{24}\text{H}_{24}\text{Fe}_2\text{N}_2$	$\text{C}_{28}\text{H}_{28}\text{Fe}_2\text{N}_4$
M.W.	452.15	532.24
Crystal system	Monoclinic	Monoclinic
a (Å)	10.488(2)	9.744(2)
b (Å)	7.7647(14)	10.2197(7)
c (Å)	12.813(2)	12.225(2)
β (deg)	108.471(8)	102.951(6)
Space group	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
V (Å ³)	989.7(3)	1186.4(3)
D_c (g cm ⁻³)	1.517	1.490
$F(000)$	468	552
μ (Mo K α) (cm ⁻¹)	14.77	12.47
Crystal size (mm ³)	$0.25 \times 0.20 \times 0.12$	$0.30 \times 0.18 \times 0.15$
θ range for cell and data collection/°	2.20–29.85	2.14–24.96
h_{\min}, h_{\max}	–14, 8	–10, 11
k_{\min}, k_{\max}	–9, 8	–12, 9
l_{\min}, l_{\max}	–15, 17	–13, 12
Total data measured	4821	3899
Total unique (R_{int})	2450 (0.0386)	2507 (0.0458)
Absorption correction factors, min, max.	0.874, 0.998	0.898, 1.002
No. of parameters/data/restraints	137/2450/0	340/2507/1
ρ_{\min}, ρ_{\max} (e Å ⁻³)	–0.311, +0.268	–0.318, +0.240
$(\Delta/\sigma)_{\max}$	0.002	0.004
Goodness-of-fit	0.972	0.836
R_1	0.0795 (0.0297) ^b	0.0396 (0.0332)
wR_2	0.1279 (0.0691) ^b	0.0955 (0.0842)

^a Details in common: cell parameters from 250 reflections; crystal system, monoclinic; $Z = 2$, 293 K, Mo K α radiation, $\lambda = 0.71069\text{ \AA}$, Refinement method: full-matrix least squares on F_o^2 .

^b The R_1 and wR_2 values calculated for observed data [$F_o^2 > 2\sigma(F_o^2)$] only (1010 for II and 1784 for VII) are given in parentheses; $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $w = 1/[\sigma^2(F_o^2)]$.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_{24}\text{H}_{24}\text{Fe}_2\text{N}_2]$ (II)

	x	y	z	U_{eq}
Fe	112.3(5)	-3250.6(6)	2946.6(4)	37(1)
N(1)	78(3)	-50(4)	565(2)	45(1)
C(1)	822(4)	-1319(5)	1055(3)	40(1)
C(2)	1479(6)	-2583(6)	512(4)	77(2)
C(3)	1055(4)	-1520(4)	2242(3)	38(1)
C(4)	2011(4)	-2629(5)	2976(3)	43(1)
C(5)	1905(4)	-2464(5)	4034(3)	51(1)
C(6)	891(5)	-1251(5)	3981(3)	54(1)
C(7)	350(4)	-649(5)	2878(3)	45(1)
C(8)	-1219(4)	-4595(5)	1700(3)	51(1)
C(9)	-286(5)	-5725(5)	2417(4)	58(1)
C(10)	-416(5)	-5548(6)	3460(4)	69(1)
C(11)	-1403(6)	-4310(7)	3411(5)	77(2)
C(12)	-1903(4)	-3721(6)	2315(4)	64(1)

 U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.6. 1,1'-Ferrocenebis(1,4-dimethyl-2,3-diazahexa-1,3-dien-5-one) (V)

A suspension of 1,1'-diacetylferrocenedihydrazone (0.20 g, 0.67 mmol) in 2,3-butanedione (5 cm³) was

stirred for 24 h. The suspension was evaporated to dryness and then extracted with hexane (2 \times 30 cm³). The hexane was evaporated under reduced pressure and the residual solid crystallised from diethyl ether as red microcrystals (0.21 g, 64%, m.p. 106–108°C). Anal.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $[\text{C}_{28}\text{H}_{28}\text{Fe}_2\text{N}_4]$ (VII)

	x	y	z	U_{eq}
Fe(1)	7023.4(8)	4632.9(8)	4676.2(7)	44(1)
Fe(2)	13067.7(7)	5922.2(7)	10422.8(6)	43(1)
N(1)	8578(4)	4136(5)	7852(4)	43(1)
C(1)	8555(5)	3479(5)	6974(4)	41(1)
C(2)	9751(6)	2685(7)	6746(5)	59(2)
C(3)	7246(5)	3523(6)	6088(4)	43(1)
C(4)	6923(7)	2716(6)	5102(5)	53(2)
C(5)	5599(7)	3129(8)	4463(6)	67(2)
C(6)	5110(7)	4215(8)	5022(6)	64(2)
C(7)	6132(5)	4440(7)	6022(5)	50(2)
N(2)	10525(5)	6177(5)	6316(4)	45(1)
C(8)	9262(5)	6593(5)	5983(4)	41(1)
C(9)	8519(6)	7541(7)	6595(5)	58(2)
C(10)	8501(5)	6092(6)	4897(4)	39(1)
C(11)	7177(6)	6527(7)	4245(5)	49(1)
C(12)	6816(6)	5769(8)	3279(5)	56(2)
C(13)	7890(6)	4821(7)	3300(5)	55(2)
C(14)	8919(6)	5027(6)	4309(5)	46(1)
N(3)	9853(4)	4051(5)	8671(4)	42(1)
C(15)	9996(5)	4889(5)	9465(4)	40(1)
C(16)	8954(6)	5931(7)	9582(6)	63(2)
C(17)	11283(5)	4800(6)	10337(4)	42(1)
C(18)	11624(6)	5534(6)	11352(5)	52(2)
C(19)	12972(7)	5171(8)	11957(5)	64(2)
C(20)	13513(7)	4221(6)	11330(5)	57(2)
C(21)	12485(6)	3986(6)	10323(5)	46(1)
N(4)	11213(4)	6706(5)	7359(4)	45(1)
C(22)	12368(5)	6136(6)	7804(4)	44(1)
C(23)	12974(7)	4982(7)	7323(6)	63(2)
C(24)	13151(5)	6669(6)	8887(4)	40(1)
C(25)	14519(6)	6333(7)	9508(5)	54(2)
C(26)	14800(6)	7087(8)	10511(5)	62(2)
C(27)	13631(7)	7881(7)	10542(6)	61(2)
C(28)	12611(7)	7620(6)	9552(5)	53(2)

 U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4
Selected bond lengths (Å) and angles (deg) for [C₂₄H₂₄Fe₂N₂] (II)

Fe–C(9)	2.036(4)	Fe–C(6)	2.037(4)
Fe–C(10)	2.038(4)	Fe–C(4)	2.038(4)
Fe–C(11)	2.039(5)	Fe–C(3)	2.041(4)
Fe–C(7)	2.041(4)	Fe–C(12)	2.043(4)
Fe–C(8)	2.044(3)	Fe–C(5)	2.047(4)
N(1)–C(1)	1.290(4)	N(1)–N(1') ^a	1.406(6)
C(1)–C(3)	1.471(5)	C(1)–C(2)	1.492(6)
C(1)–N(1)–N(1') ^a	113.5(4)	N(1)–C(1)–C(3)	117.5(3)
N(1)–C(1)–C(2)	125.0(4)	C(3)–C(1)–C(2)	117.5(3)
C(4)–C(3)–C(1)	126.7(4)	C(7)–C(3)–C(1)	126.3(3)

^a The primed atom belongs to one and the same molecule and is generated by the centre of symmetry at (–x, –y, z).

C–C bond lengths and C–C–C angles (internal) in the cp rings: 1.392(7)–1.432(5), average 1.411(7) Å and 107.0(3)–109.1(4), average 108.0(4)° respectively.

Found: C, 60.84; H, 6.03; N, 12.90. C₂₂H₂₆FeN₄O₂. Calc.: C, 60.86; H, 5.99; N, 12.91%. Mass spectrum *m/z* 434 (M⁺). IR(KBr)(C=N) 1600, (C=O) 1551 cm⁻¹.

2.7. 1,1'-Ferrocenebis(1,4-dimethyl-2,3-diazahexa-1,3-dien-6-one) (VI)

Concentrated hydrochloric acid (0.03 cm³) was added to a mixture of 1,1'-diacetylferrocenedihydrazone (0.15 g, 0.5 mmol) and 2,4-pentanedione (5 cm³) in tetrahy-

drofuran (15 cm³) at –41°C). The suspension was stirred for 12 h and then allowed to warm to –10°C during 12 h and stirred at this temperature for a further 5 h. The solvent was evaporated under reduced pressure, the solid was washed with hexane (2 × 15 cm³), ether (2 × 10 cm³) and then recrystallised from dichloromethane–hexane (0.09 g, 42.5%, m.p. 162–163°C). Anal. Found: C, 61.44; H, 6.49; N, 12.12. C₂₄H₃₀FeN₄O₂. Calc.: C, 62.34; H, 6.54; N, 12.12%. Mass spectrum *m/z* 462 (M⁺). IR(KBr)(C=N) 1611, (C=O) 1578 cm⁻¹.

Table 5
Selected bond lengths (Å) and angles (deg) for [C₂₈H₂₈Fe₂N₄] (VII)

Fe(1)–C(11)	2.021(7)	Fe(1)–C(7)	2.035(6)
Fe(1)–C(4)	2.035(7)	Fe(1)–C(3)	2.036(5)
Fe(1)–C(14)	2.036(5)	Fe(1)–C(12)	2.037(7)
Fe(1)–C(6)	2.046(7)	Fe(1)–C(5)	2.048(7)
Fe(1)–C(10)	2.049(6)	Fe(1)–C(13)	2.053(5)
Fe(2)–C(28)	2.032(6)	Fe(2)–C(25)	2.034(6)
Fe(2)–C(18)	2.035(6)	Fe(2)–C(24)	2.045(5)
Fe(2)–C(19)	2.047(6)	Fe(2)–C(26)	2.048(6)
Fe(2)–C(21)	2.055(6)	Fe(2)–C(20)	2.055(6)
Fe(2)–C(17)	2.066(6)	Fe(2)–C(27)	2.072(7)
N(1)–C(1)	1.262(7)	N(1)–N(3)	1.413(6)
C(1)–C(3)	1.477(7)	N(2)–C(8)	1.279(6)
N(2)–N(4)	1.409(6)	C(8)–C(10)	1.460(7)
N(3)–C(15)	1.279(6)	C(15)–C(17)	1.455(7)
N(4)–C(22)	1.276(6)	C(22)–C(24)	1.476(7)
C(1)–N(1)–N(3)	114.5(4)	N(1)–C(1)–C(3)	117.0(5)
N(1)–C(1)–C(2)	125.5(5)	C(3)–C(1)–C(2)	117.5(5)
C(7)–C(3)–C(1)	125.8(5)	C(4)–C(3)–C(1)	126.0(5)
C(8)–N(2)–N(4)	112.9(5)	N(2)–C(8)–C(10)	115.4(5)
N(2)–C(8)–C(9)	126.3(5)	C(10)–C(8)–C(9)	118.3(5)
C(14)–C(10)–C(8)	126.0(5)	C(11)–C(10)–C(8)	127.6(5)
C(15)–N(3)–N(1)	115.2(4)	N(3)–C(15)–C(17)	116.3(5)
N(3)–C(15)–C(16)	125.9(5)	C(17)–C(15)–C(16)	117.8(5)
C(18)–C(17)–C(15)	126.8(5)	C(21)–C(17)–C(15)	126.7(5)
C(22)–N(4)–N(2)	114.0(5)	N(4)–C(22)–C(24)	116.3(5)
N(4)–C(22)–C(23)	125.4(5)	C(24)–C(22)–C(23)	118.3(5)
C(25)–C(24)–C(22)	128.6(5)	C(28)–C(24)–C(22)	125.1(5)

C–C bond lengths and C–C–C angles (internal) in the cp rings: 1.390(9)–1.441(8), average = 1.420(9) Å and 106.2(5)–109.6(6), average 108.0(6)° respectively. C–C (Me): 1.496(7)–1.506(8), average 1.500(8) Å.

Table 6
¹H and ¹³C chemical shifts^a for the ferrocene compounds I to VII in CDCl₃

Compound	Nucleus	Structural position or group											
		1	2	3	4	5	6	7	8	9	10	Other	
I	H	-	2.03(s)	-	4.49(s)	4.25(s)	-	-	-	-	-	-	4.14(s), cp; 5.06(s), NH ₂
	C	148.11	12.64	85.24	66.17	69.13	-	-	-	-	-	-	68.88, cp
II	H	-	2.19(s)	-	4.79(t)	4.39(t)	-	-	-	-	-	-	4.21(s), cp
	C	158.82	15.69	83.63	(1.8)	69.90	-	-	-	-	-	-	69.23, cp
III	H	1.89(s)	2.06(s)	-	64.43	2.12(s)	-	4.69(t)	4.33(t)	-	-	-	4.16(s), cp
	C	18.27	25.05	159.48	158.48	15.28	69.90	(1.7)	69.90	-	-	-	69.21, cp
IV	H	-	1.97(s)	-	4.50(s)	4.24(s)	-	-	-	-	-	-	5.07 (br s), NH ₂
	C	147.58	12.44	86.07	66.69	69.88	-	-	-	-	-	-	-
V	H	2.48(s)	-	-	1.94(s)	-	2.11(s)	-	4.76(t)	4.44(t)	-	-	-
	C	24.86	199.30	149.10 ^b	11.32	158.96 ^b	16.11	85.97	(1.8)	71.90	-	-	-
VI	H	2.09(s)	-	2.15(s)	-	2.15(s)	-	2.14(s)	68.98	4.58(t)	-	-	4.32(t)
	C	28.85	195.61	95.93	149.06 ^b	17.94	159.68 ^b	14.49	84.68	(1.8)	68.12	-	70.98
VII	H	-	2.48(s)	-	4.70(ddd)	4.22(ddd)	4.53(ddd)	5.10(ddd)	-	-	-	-	-
	C	164.11	15.64	88.20	(2.5, 1.3, 1.4)	(2.5, 2.5, 1.4)	(2.5, 2.5, 1.3)	(2.5, 1.4, 1.4)	72.10	-	-	-	-

^a Relative to SiMe₄ (internal) δ = 0; s = singlet, br = broad, d = doublet, t = triplet; coupling constants (J/Hz) in parentheses. ^b Assignments may be reversed.

2.8. $[4_2](1,1')$ Bis(1,4-dimethyl-2,3-diazabuta-1,3-dien)ferrocenophane (VII)

Concentrated hydrochloric acid (0.15 cm³) was added to a stirred solution of freshly prepared 1,1'-diacetylferrocenedihydrazone (0.2 g, 0.67 mmol) in ethanol (20 cm³) at 80°C. This solution was stirred for 5 min, the solvent was reduced to approximately 15 cm³ and the solution was allowed to stand overnight at room temperature. A precipitate was separated, washed with ethanol (2 cm³) and then recrystallised from ethanol–hexane to produce carmine-red crystals (0.06 g, 17%, m.p. 250–253°C). Anal. Found: C, 62.31; H, 5.08; N, 10.00. C₂₈H₂₈Fe₂N₄. Calc.: C, 63.21; H, 5.26; N, 10.53%. Mass spectrum m/z 532 (M⁺). IR(CHCl₃)(C=N) 1597 cm⁻¹.

2.9. X-ray structure determinations

Crystals of compounds **II** and **VII** suitable for X-ray work were grown from dichloromethane and ethanol–hexane respectively. Crystallographic measurements were made at 293(2) K on a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating anode generator using Mo K α radiation ($\lambda = 0.71069$ Å) by following procedures described elsewhere [11]. The structures were solved by direct methods (SHELXS86) [12] and difference syntheses, and refined by full-matrix least-squares (SHELXL93) [13] using all unique F_o^2 data corrected for Lorentz and polarisation factors, and also for absorption effects (DIFFABS) [14]. In both cases, the non-hydrogen atoms were refined anisotropically; the hydrogen atoms were included in calculated positions (riding model) with U_{iso} refined freely. Compound **VII** was found to be a racemic twin (69/31%); the model presented in the paper represents the major component in the crystal as indicated by the refinement of the Flack's absolute structure parameter [15] to 0.31(4). The source of scattering factors was Ref. [13]. The diagrams were drawn with SNOOP [16]. The calculations were done on a 486DX2/66 personal computer. The crystal data and details of data collection and structure refinement are presented in Table 1. The atomic co-ordinates and selected bond lengths and angles are given in Tables 2–5. Anisotropic displacement coefficients, hydrogen atom parameters, and full tables of bond lengths and angles, have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

Acetylferrocene and 1,1'-diacetylferrocene react with hydrazine hydrate in acidified ethanol to produce in good yields acetylferrocenedihydrazone (**I**) and 1,1'-diacetylferrocenedihydrazone (**IV**) respectively. Both

compounds are unstable to moisture and slowly decompose in solution. To convert them to potentially more useful materials as ligands they were both subjected to condensation reactions with carbonyl compounds. The monohydrazone was reacted with acetylferrocene and with acetone to produce the azines (**II**) and (**III**) respectively. Compound (**II**) can also be formed by the direct reaction of acetylferrocene with hydrazine hydrate. The dihydrazone reacted smoothly with the diketones 2,3-butanedione and 2,4-pentanedione to form compounds (**V**) and (**VI**) respectively. No evidence was observed of the reactions proceeding further to form ferrocenophanes. Heating the dihydrazone (**IV**) in ethanol led to the formation of the novel ferrocenophane (**VII**) but in a lower yield than when metal salts were employed [6]. All the azines are air-stable crystalline solids, they exhibit a molecular ion in the mass spectrometer and show characteristic C=N vibrations in the infrared. The ¹H and ¹³C NMR data (Table 6) were consistent with the proposed structures.

To fully characterise the materials, to establish the configurations of the bridges, and to enable comparisons to be made with the structures of related Schiff base derivatives of acetylferrocenes, the crystal structures were determined of the two ferrocenophanes (**II**) and (**VII**). After completion of this work we discovered that the structure of **VII** had been reported [6]. Our cell dimensions and space group are the same as those reported but our work has identified the fact that the crystals are racemic twin. When allowance was made for this, the R value obtained was 0.0396 for all unique data. In the earlier paper the R value was reported as 0.067 for data with $F_o > 4\sigma(F_o)$. We suggest that the crystal used then was also a racemic twin but it was not noted at the time. In view of this we consider it relevant to report our work in full.

The molecular structures of **II** and **VII** together with the crystallographic atom numbering schemes used are shown in Figs. 1 and 2 respectively. Molecules of **II** are strictly centrosymmetric with a pair of (cp)(C₅H₄)Fe moieties bridged by a –C(Me)NN(Me)C– unit. In molecules of **VII**, which are dimeric, two (C₅H₄)Fe(C₅H₄) moieties are bridged by two –C(Me)NN(Me)C– units and related by an approximate two-fold axis of symmetry. The present study also shows that compound **VII** crystallizes in the non-centrosymmetric space group $P2_1$ with molecules of one hand alternating with molecules of the other hand in the ratio of 69:31.

The Fe–C distances in both compounds (2.036(4)–2.047(4), average 2.040(4) Å in **II**, 2.021(7)–2.072(7), average 2.044(7) Å in **VII**) are similar and fall within the range commonly found for ferrocene compounds [17]. The dimensions of the cyclopentadienyl rings are also very similar in the two compounds (C–C distances and C–C–C angles: 1.392(7)–1.432(5), average 1.411(7) Å and 107.0(3)–109.1(4), average 108.0(4)°

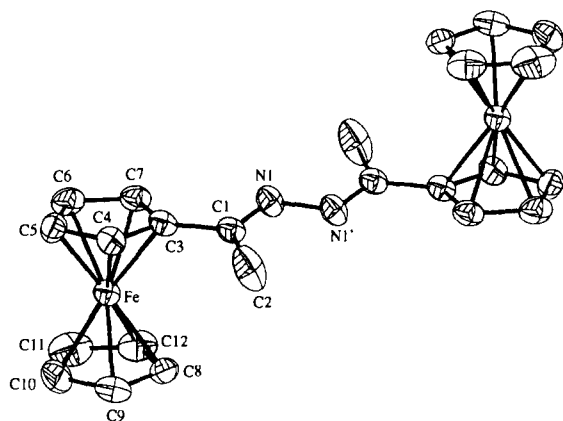


Fig. 1. Molecular structure of (II) showing the atom labelling in the asymmetric unit. Thermal ellipsoids are drawn at 45% probability level. The hydrogen atoms are omitted for clarity.

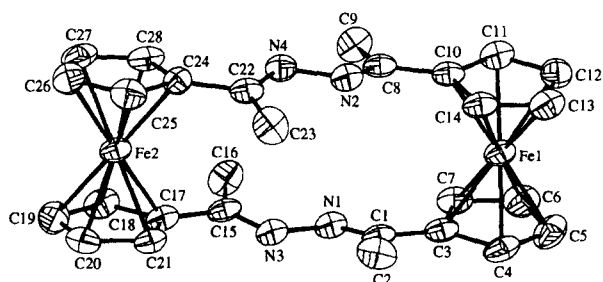


Fig. 2. Molecular structure of (VII) showing the atom labelling. Thermal ellipsoids are drawn at 45% probability level. The hydrogen atoms are omitted for clarity.

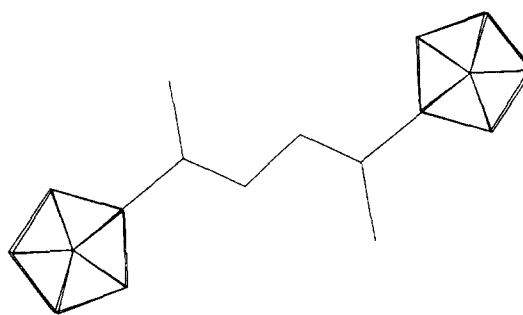


Fig. 3. View of the structure of (II) showing the eclipsed configurations of the cyclopentadienyl rings.

(II); 1.390(9)–1.441(8), average 1.420(9) Å and 106.2(5)–109.6(6), average 108.0(6)° (VII)]. It is interesting to note that the cyclopentadienyl rings in II are eclipsed, whilst in VII they are staggered which is quite uncommon in ferrocene compounds. These arrangements are better illustrated in Figs. 3 and 4 respectively. The cyclopentadienyl rings in both compounds are each planar within experimental error; those bonded to the same Fe atom are also parallel as indicated by the dihedral angles between them 1.3(3)° (II) and 0.7(5), 0.9(5)° (VII). In II, the bridging –CNNC– unit is accurately planar with the methyl carbons also lying on the plane (within only 0.007(4) Å). In VII, however, these units are significantly non-planar with large displacements of atoms (–0.063 to +0.063(7) Å) from

Table 7

Electrochemical characteristics for the oxidation processes of the present monoferrocenes in dichloromethane solution

Complex	$E_{0/+}^a$ (V)	i_{pc}/i_{pa}^a	ΔE_p^a (mV)	Coulometric results
Acetylferrocene	+0.66	1	88	1e ^b yellow-to-blue ^c stable ^d
1,1'-Diacetylferrocene	+0.89	1	82	> 1.5e ^b orange-to-green ^c unstable ^d
(I)	+0.41	0.4	75	1e ^b yellow-to-violet ^c unstable ^d
(III)	+0.50	1	76	~ 1.5e ^b yellow-to-brown ^c unstable ^d
(IV)	+0.38	0.4	63	1e ^b yellow-to-violet ^c unstable ^d
(V)	+0.67	1	90	1e ^b orange-to-brown ^c not fully stable ^d
(VI)	+0.67	1	86	1e ^b orange-to-purple ^c not fully stable ^d
Ferrocene	+0.44	1	90	1e ^b yellow-to-blue ^c stable ^d

^a Measured at 0.2 V s⁻¹. ^b Number of electrons spent in the exhaustive electrolysis. ^c Colour variation upon electrolysis. ^d The extent of stability of the oxidized species is defined as: (i) 'stable' when the cationic species are indefinitely stable; (ii) 'not fully stable' when at the end of electrolysis only 30–50% of the expected amount of cation has been detected; (iii) 'unstable' when the cation underwent full decomposition.

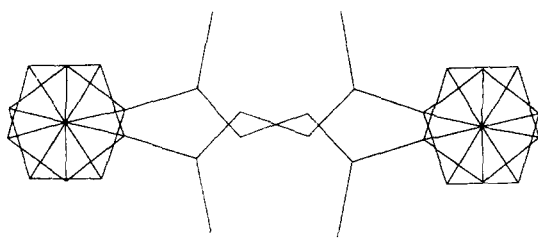


Fig. 4. View of the structure of (VII) showing the staggered configurations of the cyclopentadienyl rings.

the mean plane; displacements of the methyl carbons are even larger (about 0.23 Å). In fact, the two NC(Me) moieties in each bridge in this compound are mutually rotated by 12.9(6) and 13.7(6)°. The –NC(Me) moieties are also non-coplanar with the respective ring planes and mutually rotated by 11.6(5)° (II) and 7.2(5)–13.1(5)° (VII). These deviations from planarity seem to have

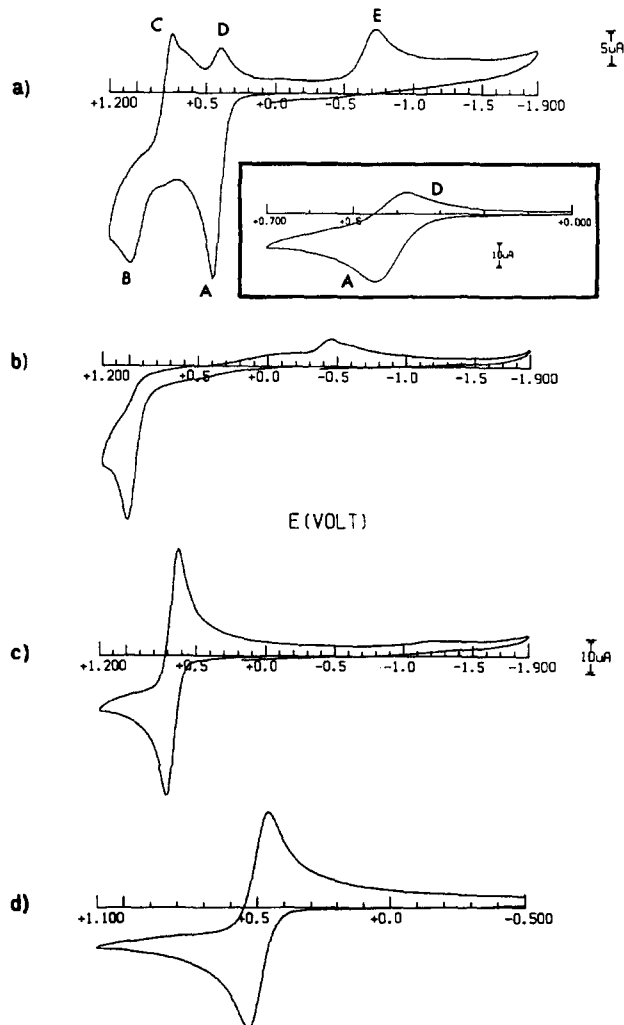


Fig. 5. Cyclic voltammograms recorded at a platinum electrode in CH_2Cl_2 solutions containing $[\text{NBu}_4][\text{ClO}_4]$ (0.2 mol dm^{-3}): (a) (I) ($1.4 \times 10^{-3} \text{ mol dm}^{-3}$); (b) acetylbenzenehydrazone ($2.7 \times 10^{-3} \text{ mol dm}^{-3}$); (c) acetylferrocene ($1.8 \times 10^{-3} \text{ mol dm}^{-3}$); (d) (III) ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$). Scan rate 0.2 V s^{-1} .

resulted from the need to avoid any close non-bonded contacts in the molecules. In both compounds, the molecules are held together in the crystal by van der Waals' forces only.

Fig. 5 shows a comparison of the cyclic voltammetric responses of acetylferrocenehydrazone (I) with the related species, acetylferrocene, acetylbenzenehydrazone, and the related azine (III). It can be seen that the stability of the ferrocenium forms of acetylferrocene and of (III) are considerably greater than that of the hydrazone (I) (peaks A,D). We can confidently assign peaks B and E to the redox processes of the pendant hydrazone group.

An analysis [18] of the oxidation of acetylferrocene and of (III), with scan rate varying from 0.02 to 10.2 V s^{-1} is diagnostic of an essentially electrochemically reversible one-electron process ($i_{\text{pc}}/i_{\text{pa}}$ always unity; $i_{\text{pa}} V^{-1/2}$ constant; $\Delta E_p = 75 \text{ mV}$ at 0.2 V s^{-1}). In contrast to this the first anodic step of (I) is complicated by the ensuing chemical reactions in that $i_{\text{pc}}/i_{\text{pa}} < 1$ at low scan rates, e.g. 0.4 at 0.2 V s^{-1} , and progressively increases with scan rate to reach unity at 10.2 V s^{-1} . Assuming a first order chemical reaction results in a value of $t_{1/2} \approx 1 \text{ s}$ for the $[(\text{I})]^+$ monocation. Similar contrasting behaviour is observed for 1,1'-diacetylferrocene, the dihydrazone (IV) and the azines (V) and (VI). The presence of chemical reactions following the anodic oxidation of IV has been previously pointed out [6], even though the use of a glassy carbon working electrode in tetrahydrofuran solution afforded ill-shaped responses. In Table 7 the formal redox potentials are collected, together with a summary of the results from the controlled-potential macroelectrolysis experiments. The stability of the electrogenerated cations was checked

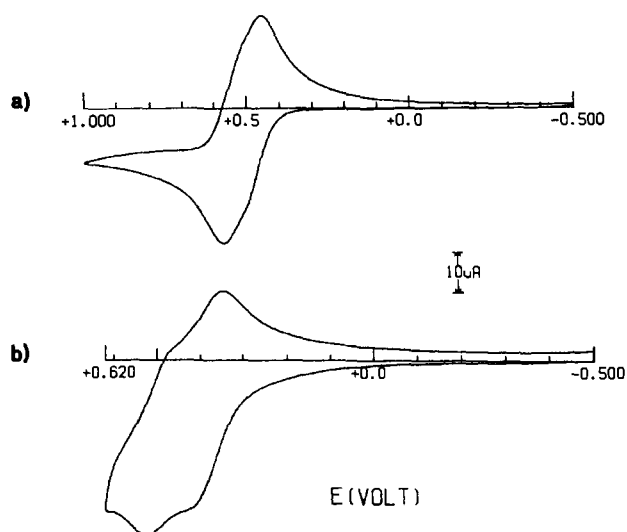


Fig. 6. Cyclic voltammograms recorded at a platinum electrode in CH_2Cl_2 solutions containing $[\text{NBu}_4][\text{ClO}_4]$ (0.2 mol dm^{-3}): (a) (II) ($1.5 \times 10^{-3} \text{ mol dm}^{-3}$), scan rate 0.1 V s^{-1} ; (b) (VII) ($1.3 \times 10^{-3} \text{ mol dm}^{-3}$), scan rate 0.5 V s^{-1} .

Table 8
Electrochemical characteristics for the oxidation processes of the present diferrocenes in dichloromethane solution

Complex	$E_{0/+}^{\circ}$ (V)	$E_{+/2+}^{\circ}$ ^a (V)	Coulometric results
(II)	+0.47	+0.56	2e ^b orange-to-brown ^c not fully stable ^d
(VII)	+0.37	+0.49	2e ^b orange-to-purple ^c unstable ^d

^a Calculated according to Ref. [19]. ^b Number of electrons spent in the exhaustive electrolysis at the second oxidation process. ^c Colour variation upon electrolysis. ^d Extent of stability of the oxidized species (see the corresponding footnote of Table 7).

by cyclic voltammetric measurements performed on the exhaustively oxidised solutions.

It is readily seen that in the mono- and disubstituted ferrocenes, the hydrazone and the azine grouping render the oxidation easier than that of the precursor acetyl ferrocenes, hence indicating that the electron attracting power of the nitrogen-based groups are significantly less than that of the acetyl group. In addition it can be supposed that for the two acetylferrocenes the normal assumption holds that the electron removed on oxidation is derived from an iron-based HOMO orbital, whereas for the other compounds the colour of the ferrocenium indicates that the nitrogen-based substituents make a significant contribution to the character of the orbital.

In Fig. 6 are shown the cyclic voltammetric responses of the two diferrocene complexes (II) and (VII) in the anodic region. The monobridged compound (II) gives rise to two almost overlapping one-electron oxidations, whereas (VII) generates two more widely-separated one-electron steps. This means that the electronic communication between the two ferrocene sub-units is rather small in the singly-bridged compound (II) but is increased with the addition of the second bridge in (VII). Nevertheless, based on the conproportionation constant calculated on the basis of the separation between the formal electrode potentials (Table 8) of the two oxidation processes [19], both cations [II]⁺ ($K_{\text{con}} \approx 33$) and [VII]⁺ ($K_{\text{con}} \approx 100$), should belong to the 'slightly delocalised', class II mixed-valence species, of the classification by Robin and Day [20]. Also, in the case of complex VII the previously used experimental conditions prevented an accurate interpretation of its oxidation process [6].

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