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1,1-Bis(1″,2″,3″,4″,5″-pentamethylferrocen-1′-yl)ethene☆

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Abstract

1,1-Bis(1″,2″,3″,4″,5″-pentamethylferrocen-1′-yl)ethene (**6**) was synthezised as a prototype of two metallocenes that are bridged by the sp^2-carbon center of a vinylidene group. Starting from 6-*N*,*N*-dimethylamino-6-methylfulvene, the iron-containing intermediates were a pentamethylferrocenyl-substituted fulvene and an ethene that was geminally disubstituted by a Cp anion and a pentamethylferrocenyl moiety. Besides other methods, the ferrocenes were characterized by NMR spectroscopy including full signal assignment. The bimetallic compound **6** showed moderate interactions between the two ferrocenes in the cyclic voltammogram ($\Delta E_{1/2} = 150$ mV). According to X-ray crystal structure analysis compound **6** is a twisted molecule; the vinylidene moiety and the Cps of the neighboring ferrocenes are not coplanar. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocenes; Bimetallic compounds; Cyclic voltammetry

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1. Introduction

The title compound 1,1-bis(1″,2″,3″,4″,5″-pentamethylferrocen-1′-yl)ethene is a new member of the family of bridged ferrocenes which has been the focus of many research projects [1]. The reason for the widespread interest is that, with certain bridges, the ferrocenes are no longer independent of each other. Rather interactions occur that bring about new properties.

The ultimate goal of the approach would be to transfer some of these properties to high-nuclear compounds or even polymeric materials. However, it is advisable to perform a property tuning with di- and trinuclear model compounds in order to reduce the number of interfering parameters such as the bonding within and the length and the rigidity of the bridge. The shortest bridge is just one bond, and we have recently terminated work on bimetallocenes (**A**) which feature striking differences in the magnetic behavior all the way from weakly antiferromagnetic to strongly ferromagnetic interaction [2]. When one sp^3-hybridized atom per bridge is introduced, as for instance by using $SiMe_2$ groups in **B** [3], considerable damping of the interaction is observed. A good candidate for further testing the tuning bandwidth of the interaction should be a one-sp^2-carbon bridge as present in vinylidene-bridged metallocenes (**C**). In contrast to the intensively studied ferrocenes separated by conjugated chains (**D**) [4] only little is known about **C**. An isomeric iron derivative of **C** was mentioned in a series of products that demonstrated the usefulness of a new $CpFe^+$ transfer reaction [5a]. A ferrocene having the bridging ligand of **C** was reported recently [5b], and corresponding *t*-butyl-sub stituted ligands are also known [5c]. Here we report the syntheses, the redox properties, and the structure of vinylidene-bridged pentamethylferrocenes.

☆ In honor of the late Professor Rokuro Okawara.

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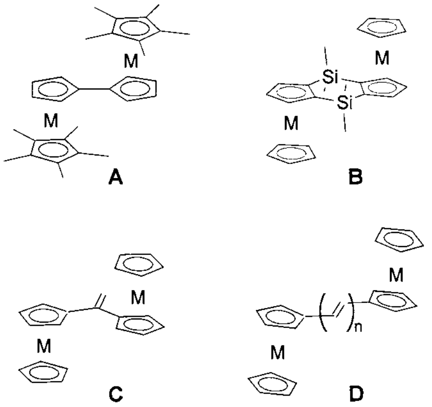
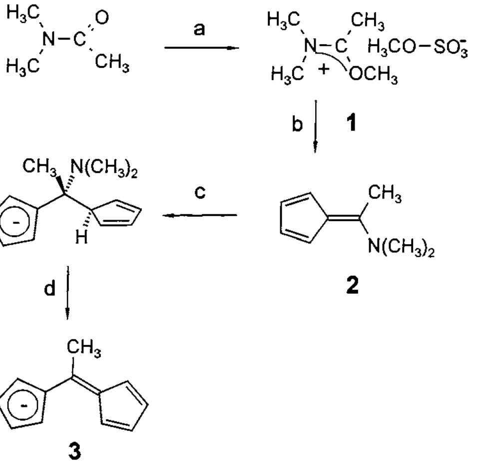


2. Results and discussion

2.1. Synthesis

With a more generally applicable synthesis in view we decided to prepare the bridging ligand first and to subsequently attach the Cp*Fe moieties rather than starting from a substituted ferrocene [5b]. Thus, the fulvene-substituted Cp anion **3** was prepared as depicted in Scheme 1. The aminofulvene **2**, which belongs to a well known class of π-systems [6], was prepared by analogy to the non-methylated compound [7]. Its conversion to **3** proceeded in an equilibrium reaction which was pushed by the addition of crown ether [8]. The isolation of **3** was hampered by polymerization.

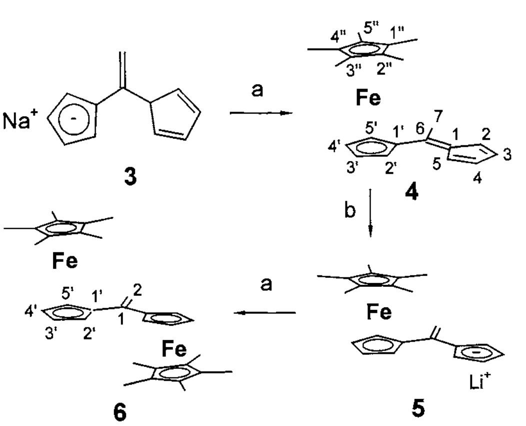
In a stepwise reaction (Scheme 2) the anion **3** was first converted into the mixed-ligand ferrocene **4** by reaction with the TMEDA adduct of Cp*FeCl [9]. Subsequent deprotonation of **4** with the lithium salt of 2,2,6,6-tetramethylpiperidide, and renewed reaction with the iron half-sandwich afforded the desired vinylidene-bridged pentamethylferrocene **6** which was obtained in an analytically pure form in an overall yield of 27% starting from **2**.



Scheme 1. Synthesis of the bridging ligand **3**. (a) $(CH_3O)_2SO_2$, ΔT; (b) NaCp; (c) 18-crown-6, NaCp; (d) $-(CH_3)_2NH$.

2.2. Spectroscopic characterisation and cyclic voltammetry

Besides mass spectroscopy, which showed the expected isotopic patterns of the molecular ions of **4** and **6**, NMR spectroscopy was applied to establish the ferrocene derivatives. The ^{1}H-NMR signals could be assigned straightforwardly except for those of the five-membered ring protons of **4**, **5**, and **6**. H-2′,5′ and H-3′,4′ were distinguished by recording a NOE-difference spectrum of **6**. The signal at 4.11 ppm was assigned to H-2′,5′, because it experienced a NOE enhancement when the signal of the neighboring methylene protons was irradiated. The same signal sequence of H-2′,5′ and H-3′,4′ was assumed for **4** and **5**. The fulvene protons of **4** were assigned according to literature precedents [10]. All five-membered ring protons appeared as pseudo triplets for which the sum $^3J_{H,H} + {}^4J_{H,H}$ [11] is given in the Section 3. Based on the ^{1}H-NMR results the non-trivial assignments of the ^{13}C-NMR signals were assured by H,C-HMQC and H,C-HMBC experiments [12]. Interestingly, in **6** the nuclei H-2′,5′, H-3′,4′, C-2′,5′ and C-3′,4′ are equivalent thus implying C_2 symmetry which is higher than that found in the crystal (see below). We conclude that in solution the two ferrocene moieties of **6** undergo a rapid oscillation about the bonds C-1–C-6 and C-6–C-8 with the coplanar arrangement being energetically less favorable. Similarly, the ferrocene **4** has a dynamic structure in solution owing to torsional flexibility about the bond C-1–C-6. This follows from the fact that for the nuclei in positions 2′-5′ of **4** only two ^{1}H- and ^{13}C-NMR signals were found. Temperature-dependent ^{1}H-NMR spectra down to 185 K did not show any splitting or even a selective broadening of the signals of H-2′,5′ and H-3′,4′. Hence the corresponding energy barriers must be low. The NMR data of **4** and **6** may serve as a basis for the signal assignment of similar compounds; examples are 6-(pentamethylferro-



Scheme 2. Synthesis of the bridged ferrocene **6**. (a) Cp*FeCl(TMEDA); (b) lithium 2,2,6,6-tetramethylpiperidide.

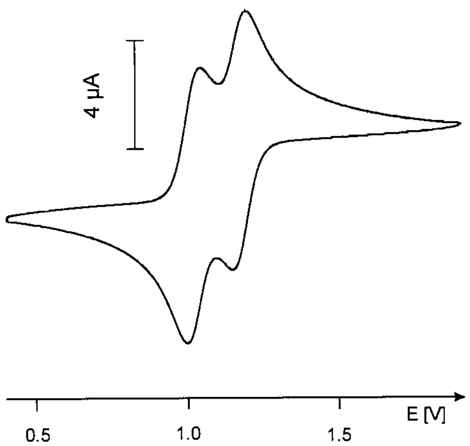


Fig. 1. Cyclic voltammogram of **6** in EtCN (0.86 mmol l^{-1}) at 295 K. Scan rate 200 mV s^{-1}. Potential scale given relative to internal Cp_2Co/Cp_2Co^+.

cenyl)fulvene and bis(pentamethylferrocenyl)ketone [13] for which too many signals were reported and most NMR signals were not assigned.

The cyclic voltammogram of **6** (Fig. 1) displayed two reversible electron transfers (ETs) at 1.02 and 1.17 V (relative to the ET of internal Cp_2Co/Cp_2Co^+) with $\Delta E_p = 55$ and 60 mV, respectively (ΔE_p = separation of the anodic and cathodic peak potentials). It follows that, upon increasing the potential, the expected successive formation of the mono- and dication of **6** was observed, which in turn established the interaction between the ferrocene moieties. The ET separation of $\Delta E_{1/2} = 150$ mV is moderate; stronger interactions are known for decamethylbiferrocene (molecule **A** with M = Fe; $\Delta E_{1/2} = 375$ mV in EtCN [2a] and 240 mV in THF [14]), while they are similar in *E*-1,2-bis(ferrocenyl)ethene (molecule **D** with $n = 1$; $\Delta E_{1/2} = 170$ mV in CH_2Cl_2 [4]), and in diferrocenylmethane ($\Delta E_{1/2} = 100$ mV in EtOH [15]). Although the $\Delta E_{1/2}$ values are modulated by solvent effects, it is evident that the metallocene interactions, as seen by cyclic voltammetry, do not change very much on passing from a bridge containing one sp^3-carbon to a bridge containing one or two sp^2-carbons.

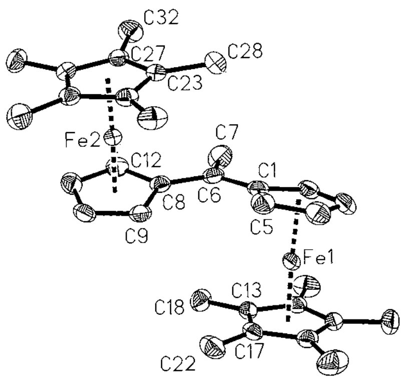


Fig. 2. Molecular structure of **6** (ORTEP plot, displacement ellipsoids at the 50% probability level). For clarity the H-atoms were omitted and only the basic numbering is given.

2.3. Molecular structure of 6

The vinylidene-bridged biferrocene **6** is a rather distorted molecule (Fig. 2). Not only are there angles of 5.0 and 5.4° between the two Cp planes at Fe(1) and Fe(2), respectively; but also, and more strikingly, the bridging ligand is twisted. Relative to the plane C(1), C(6), C(7), C(8) the twist angle of the Cp planes C(1)–C(5) and C(8)–C(12) is 11.0 and 10.3°, respectively. The molecular symmetry in the crystal is C_1 as opposed to C_2 in solution (see above). In the end, the distorsion of **6** is related to that of the thoroughly investigated biphenyl [16], because in **6** the steric interference of H(7) and H(2)/H(12) (and H(5)/H(9) after rotation about the bonds C(1)–C(6) and C(6)–C(8)) resembles that of the 2,2′,6,6′-protons of biphenyl. Probably the closest relative of **6** is 1,1-di(*p*-tolyl)ethene which is twisted in much the same way [17]. This structural feature is also present in diferrocenylketones [13,18] and some more complicated bridged ferrocenes [19].

It is worth noting that C(6)–C(7) (1.338(3) Å) is an isolated double bond while the bonds between C(6) and the ferrocenyl carbons C(1) and C(8) (1.472(3) and 1.480(3) Å, respectively) are normal single bonds between sp^2-carbons. The metal-Cp distances (1.646(4)–1.653(4) Å) are in the usual range, the Fe...Fe distance is 5.602(4) Å, and the other bond lengths and angles do not deviate from what is known from the plethora of ferrocenes.

3. Experimental section

The synthetic work and the physical measurements were carried out under purified dinitrogen, and dry, oxygen-free solvents were used. The mass spectra were obtained from a Varian Mat 50 instrument and the NMR spectra from Jeol JNM 270 and Jeol Lambda 400 spectrometers. The signal shifts (δ) were measured relative to the solvent signals of C_6D_6 (δ (^1H) = 7.15, δ (^{13}C) = 128.0) and DMSO-d_6 (δ (^1H) = 2.49) and calculated relative to TMS. The digital resolution of the 1D spectra was 0.23 Hz/data point, and for the HMQC and HMBC spectra 1024 × 1024 and 2048 × 512 data points, respectively, were used. Cyclic voltammetry experiments were run with equipment described previously [20]. Before adding the compound the 0.1 M solution of n-Bu_4NPF_6 in EtCN was dried in the cell by passing it several times over activated Al_2O_3. The elemental analyses were carried out by the in-house Microanalytical Laboratory.

Table 1
Crystal data and structure refinement of **6**

Molecular formula	$C_{32}H_{40}Fe_2$
Molecular weight	536.34
Temperature (K)	193(2)
Wavelength (pm)	71.073
Crystal system	Monoclinic
Space group	$C2/c$
a (pm)	2890.4(3)
b (pm)	830.4(1)
c (pm)	2209.6(2)
β (°)	92.87(1)
V (nm^3)	5.296(1)
Z	8
$D_{calc.}$ (mg m^{-3})	1.345
Absorption coefficient (mm^{-1})	1.114
$F(000)$	2272
Crystal size (mm)	$0.55 \times 0.26 \times 0.20$
θ range of measurement (°)	3 to 26
Index ranges	$0 \leq h \leq 35$, $0 \leq k \leq 10$, $-27 \leq l \leq 26$
Reflections collected	5274
Independent reflections	5169 [$R_{int} = 0.0183$]
Reflections observed	4213
Absorption correction	Empirical
Max. and min. transmission	1.000 and 0.595
Refinement	Full-matrix least squares on F^2
Data, parameters	5169, 317
Goodness-of-fit	1.097
Final R values [$F_o > 4\sigma(F_o)$]	$R_1 = 0.0287$, $wR_2 = 0.0678$
R values (all data)	$R_1 = 0.0464$, $wR_2 = 0.0736$
Residual electron density ρ_{min}, ρ_{max} (e nm^{-3})	−253 and 311

The X-ray data were obtained from an automated four-circle diffractometer CAD4 (NONIUS) working with Mo–K_α ($\lambda = 0.71073$ Å) radiation. Experimental details and the atomic positional parameters are given in Tables 1 and 2, respectively. The structure was solved and refined by using the program package SHELXTL, version 5.03 (Brucker-AXS). Further data may be obtained on request from the Director, Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 lEW, UK.

3.1. *6-Methyl-6-(1″,2″,3″,4″,5″-pentamethylferrocen-1′-yl)fulvene (**4**)*

A solution of the sodium salt of 6-cyclopentadienyl-6-methylfulvene (**2**) was prepared from 1.45 g (10 mmol) 6-dimethylamino-6-methylfulvene in 60 ml of THF, 290 mg (1 mmol) of 18-crown-6 and 6.0 ml of a 1.71 M solution of NaCp (10 mmol) in THF as described for the non-methylated analogue [8]. The resulting reaction mixture was cooled to −78°C, and 2.06 g (60 mmol) of Cp*FeCl(TMEDA) [9] was added with stirring. The reaction was accompanied by a color change from brown–red to dark violet. The reaction mixture was allowed to come to room temperature (r.t.) overnight, THF was stripped under reduced pressure, and the remaining solid was extracted with hexane. The solution was cooled to −78°C, and a precipitate of unreacted **2** was filtered off. Subsequently, the solvent was removed in vacuo, and the oily residue was freed from the by-products deca- and pentamethylferrocene by sublimation (1 mbar, 100°C) leaving behind 1.31 g of deep violet **4** which contained little impurities according to ^{1}H-NMR spectroscopy.

CI–MS: m/z 347 ([MH]$^+$, 100%), 210 ([MH-Cp*]$^+$, 3%); isotope pattern of [MH]$^+$: m/z (% exptl./calc.) 349 (5.1/3.5), 348 (23.6/27.4), 347 (100.0/100.0), 346 (4.6/1.6), 345 (8.9/6.3). ^{1}H-NMR (400.05 MHz, 295 K, C_6D_6, numbering see Scheme 2): δ 6.90 (1H, m, H-2), 6.75 (1H, m, H-5), 6.70 (1H, m, H-3), 6.66 (1H, m, H-4), 4.12 (2H, ψt, $^3J_{H,H} + {}^4J_{H,H} = 3.4$ Hz, H-2′,5′), 3.80 (2H, ψt, $^3J_{H,H} + {}^4J_{H,H} = 3.8$ Hz, H-3′,4′), 2.22 (2H, s, H-7), 1.59 (15H, s, $C_5(C\underline{H}_3)_5$). $^{13}C\{^1H\}$-NMR (100.50

Table 2
Atomic coordinates ($\times 10^4$) and isotopic displacement parameters (pm^2 10^{-1}] of **6**[a]

Atom	x/a	y/b	z/c	U_{eq}
Fe(1)	1502(1)	3164(1)	3525(1)	24(1)
Fe(2)	870(1)	2212(1)	5854(1)	21(1)
C(1)	1664(1)	2497(3)	4410(1)	30(1)
C(2)	2063(1)	2473(3)	4048(1)	38(1)
C(3)	1988(1)	1379(3)	3565(1)	43(1)
C(4)	1540(1)	707(3)	3609(1)	41(1)
C(5)	1343(1)	1385(3)	4126(1)	35(1)
C(6)	1625(1)	3497(3)	4955(1)	30(1)
C(7)	1999(1)	4259(4)	5193(1)	47(1)
C(8)	1178(1)	3708(3)	5246(1)	27(1)
C(9)	719(1)	3274(3)	5026(1)	29(1)
C(10)	400(1)	3778(3)	5452(1)	33(1)
C(11)	650(1)	4527(3)	5940(1)	34(1)
C(12)	1125(1)	4488(3)	5815(1)	31(1)
C(13)	1246(1)	5478(2)	3524(1)	25(1)
C(14)	1670(1)	5398(3)	3217(1)	27(1)
C(15)	1607(1)	4287(3)	2725(1)	30(1)
C(16)	1144(1)	3678(3)	2727(1)	29(1)
C(17)	923(1)	4418(2)	3222(1)	26(1)
C(18)	1151(1)	6547(3)	4046(1)	38(1)
C(19)	2099(1)	6348(3)	3383(1)	44(1)
C(20)	1961(1)	3844(3)	2282(1)	47(1)
C(21)	921(1)	2510(3)	2286(1)	50(1)
C(22)	424(1)	4233(3)	3360(1)	41(1)
C(23)	1243(1)	103(2)	5957(1)	26(1)
C(24)	764(1)	−242(2)	5824(1)	26(1)
C(25)	505(1)	481(2)	6282(1)	26(1)
C(26)	822(1)	1287(2)	6700(1)	24(1)
C(27)	1278(1)	1049(2)	6495(1)	25(1)
C(28)	1642(1)	−500(3)	5611(1)	41(1)
C(29)	576(1)	−1286(3)	5316(1)	37(1)
C(30)	−12(1)	394(3)	6340(1)	40(1)
C(31)	701(1)	2161(3)	7263(1)	36(1)
C(32)	1716(1)	1622(3)	6814(1)	40(1)

[a] U_{eq} is calculated as one third of the trace of the orthogonal U_{ij} tensor.

MHz, 299 K, C_6D_6): δ 149.1 (C-6), 141.7 (C-1), 131.0 (C-3), 128.8 (C-4), 122.2 (C-2), 122.0 (C-5), 85.0 (C-1′), 81.2 ($\underline{C}_5(CH_3)_5$), 76.4 (C-3′,4′), 73.0 (C-2′,5′), 21.3 (C-7), 10.7 ($C_5(\underline{C}H_3)_5$).

3.2. Deprotonation of **4**

A total of 3.66 g (10 mmol) of compound **4** was dissolved in diethyl ether and cooled to −78°C. When 2.21 g (15 mmol) of lithium 2,2,6,6-tetramethylpiperidide was added to the stirred solution, and when the mixture was warmed to r.t. within 2 h, the color changed from deep violet to light orange. The excess piperidide was filtered off, and the solvent was removed in vacuo. After the remaining solid was washed with hexane and dried 2.5 g (7.3 mmol, 73%) of orange spectroscopically pure (^{1}H-NMR) **5** was obtained.

^{1}H-NMR (270.17 MHz, 298 K, DMSO-d_6, numbering see Scheme 2): δ 5.49 (2H, m, H-2,5), 5.27 (2H, m, H-3,4), 4.69 (2H, s, H-7), 4.16 (2H, m, H-2′,5′), 4.02 (2H, m, H-3′,4′), 1.76 (15H, s, $C_5(C\underline{H}_3)_5$).

3.3. 1,1-Bis(1″,2″,3″,4″,5″-pentamethylferrocen-1′-yl)ethene (**6**)

To a solution of 40 mg (0.12 mmol) of **5** in diethyl ether at −78°C was added 40 mg (0.13 mmol) of Cp*FeCl(TMEDA) [9]. The mixture was stirred for 5 h at −78°C and another 12 h after removal of the cooling bath; the reaction may be monitored by a color change from orange to red. Precipitated LiCl was filtered off, the solvent was removed in vacuo, and the black residue was extracted with hexane. Upon cooling of the yellow–orange solution to −20°C yellow crystals of Cp_2^*Fe were formed and separated by filtration. Further cooling of the remaining solution to −78°C gave a crystalline product from which residual Cp_2^*Fe was removed by sublimation (1 mbar, 100°C) leaving behind 37 mg (0.07 mmol, 58%) of red crystals of **6**. One of these crystals was used for X-ray crystal analysis.

Mp: 177–178°C (slow decomposition above 150°C). Found: C, 71.52; H, 7.59%, $C_{32}H_{40}Fe_2$ requires: C, 71.62; H, 7.52; Fe 20.84%. CI–MS: m/z 536.5 ($[MH]^+$, 100%), 346.5 ($[MH-Cp^*Fe]^+$, 27%), 256.3 ($[MH-Cp^*FeC_7H_6]^+$, 72%); isotope pattern of $[MH]^+$: m/z (% exptl./calc.) 539 (8.6/9.7), 538 (39.5/37.3), 537 (100.0/100.0), 536 (5.4/4.9), 535 (12.7/14.5). ^{1}H-NMR (400.05 MHz, 295 K, C_6D_6, numbering see Scheme 2): δ 5.49 (2H, s, H-2), 4.11 (4H, ψt, $^3J_{H,H}+{}^4J_{H,H}=3.6$ Hz, H-2′,5′), 3.71 (4H, ψt, $^3J_{H,H}+{}^4J_{H,H}=3.8$ Hz, H-3′,4′), 1.74 (15H, s, $C_5(C\underline{H}_3)_5$). $^{13}C\{^1H\}$-NMR (100.5 MHz, 297 K, C_6D_6): δ 141.1 (C-1), 107.9 (C-2), 86.4 (C-1), 80.0 ($\underline{C}_5(CH_3)_5$), 72.8 (C-3′,4′), 71.0 (C-2′,5′), 10.9 ($C_5(CH_3)_5$).

Acknowledgements

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