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From dihydropentafulvalenes to asymmetric biferrocene and terferrocene

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Dedicated to Professor Dieter Sellmann on the occasion of his 60th birthday

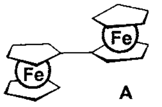
Abstract

In order to realize a step-by-step synthesis of terferrocenes tetramethyldihydropentafulvalene has been mono-deprotonated and further converted to ferrocene and pentamethylferrocene which are both substituted by tetramethylcyclopentadiene (**4** and **9**, respectively). In these syntheses the intermediate half-sandwich $(C_5Me_5)Fe(hfa)(MeCN)$ (hfa = hexafluoroacetylacetonate) proved to be a useful reagent. Compounds **4** and **9** could be deprotonated to corresponding ferrocenes which are substituted by tetramethylcyclopentadienyl anions (**5** and **10**, respectively). Anions **5** and **10** are building blocks for termetallocenes which has been demonstrated by the synthesis of octamethylated terferrocene from **5** and $FeCl_2$. Tetradecamethylbiferrocene has been obtained by reaction of tetramethylpentafulvalene dianion with $FeCl_2$. NMR features and redox properties of the new compounds have been analyzed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Biferrocene; Terferrocene; Iron(II) half-sandwich; Cyclic voltammetry

1. Introduction

Biferrocene (**A**) [1] and biferrocenylene (**B**) [2] are the most simple molecules that result when two ferrocenes are coupled formally. Further coupling leads to terferrocene (**C**) [3] and quarterferrocene [3], and eventually one ends up with poly(ferrocenylene) [4]. Among these compounds biferrocenes have received special attention, because they represent the link of ferrocenylene chains, and because oxidation yields a mixed-valence species [5]. Poly(ferrocenylenes) continue to attract chemists owing to their redox and conducting properties [6], and one would therefore like to study details by using biferrocenes as model compounds. Another topic is tailoring mixed-valence biferrocenium monocations in such a way that the valence is localized or delocalized [7]. Besides biferrocene we are interested in bimetallocenes quite generally, because unusually varying magnetic interaction is observed in addition when the two metal centers carry unpaired electrons [8]. With deliberate changes of the magnetic and other properties in view we wanted to limit delocalization between the two metallocene moieties. However, since paramagnetic bimetallocenes are rather reactive we wanted to explore a suitable approach with more stable biferrocenes.



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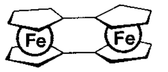

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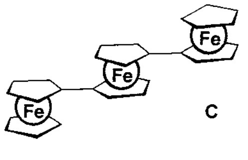

C

The properties of biferrocene (and its mixed-valence cation) can be changed by substitution which has been achieved by the following general approaches: (i) substitution of the parent compound **A** [9]; (ii) coupling of substituted ferrocenes which have an additional substituent like Br, I, and $B(OH)_2$ [10], and (iii) assembly of cyclopentadiene substituents at ferrocene on classical

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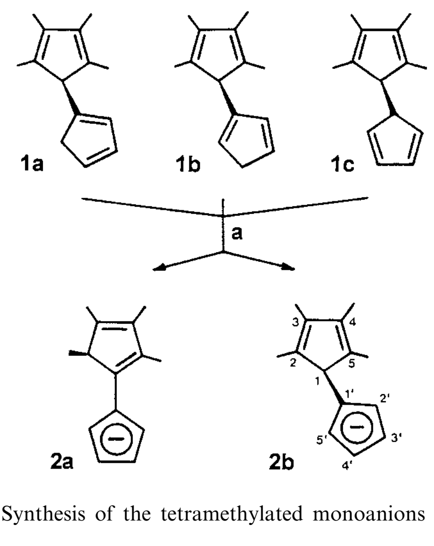
organic routes, deprotonation [11], and reaction with a $[CpFe]^+$ fragment (Cp = cyclopentadienyl) [11c]. Asymmetric substitution would be desirable for the above-mentioned localization of electrons in one half of a bimetallocene. While this is possible by all methods only (iii) is selective. Another serious limitation is that paramagnetic metallocenes would not survive under the reaction conditions of methods (i)–(iii). Therefore, we have investigated a new method which starts from dihydropentafulvalenes having one methylated and one non-methylated five-membered ring [12].

Deprotonation of the parent dihydropentafulvalene has been applied early for the synthesis of biferrocene [13]. A limitation of this method is that the monoanion does not seem to be accessible by deprotonation [14], a result which is in keeping with the virtually identical pK_s values of the rather similar biindenyl [15]. It follows that a selective step-by-step synthesis of bi- and termetallocenes would not be possible. However, the desired monoanion, i.e. a Cp^- anion coupled to a cyclopentadiene should be stable if both five-membered rings are substituted differently such as in the present study.

2. Results and discussion

2.1. Syntheses

The methylated dihydropentafulvalenes **1a**, **1b**, and **1c** (Scheme 1) are susceptible to deprotonation of both the methylated and the non-methylated cyclopentadienyl moiety. Indeed, we have shown that the corresponding dianion (**11** in Scheme 4) is accessible in virtually quantitative yield [12]. The reaction of **1a**–**c** with one equivalent of *n*-BuLi led to the monoanion **2a** as lithium salt in more than 80% yield (Scheme 1). A few batches contained small quantities of isomer **2b** besides **2a** as was indicated by the ^{1}H-NMR spectrum. Signals appeared at 1.70 ppm (CH_3), 3.93 ppm (H-1), 5.01 and 5.16 ppm (H-2′, 5′ and H-3′, 4′); integration confirmed that the signal shifts of the methyl groups were accidentally degenerate. Owing to the low yield and the fact that **2b** slowly rearranged to **2a** isolation of **2b**Li was not attempted. The regioselectivity of the deprotonation is ascribed to the destabilization of Cp^- anion by methyl groups which entails high and low pK_s values for the methylated and non-methylated rings of **1a**–**c**, respectively. It is worth noting that the expected primary deprotonation product **2b** undergoes a 1,5-sigmatropic proton shift to **2a** where additional delocalization of the negative charge into the diene system is more efficient.

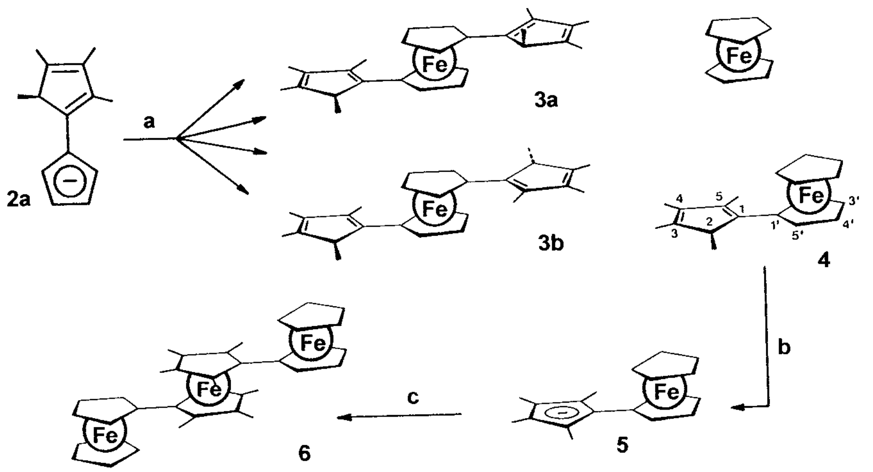


Scheme 1. Synthesis of the tetramethylated monoanions **2a** and **2b**. (a) *n*-BuLi.

Like all Cp-alkali derivatives **2a**Li decomposes in the presence of oxygen and/or moisture. It is insoluble in nonpolar solvents which facilitates purification. THF or DMSO solutions can be used for recording ^{1}H- and ^{13}C-NMR spectra which show that the anion has no plane of symmetry. The conceivable isomer whose methylene group is in position 4 was excluded by comparison with the corresponding ferrocene **9** (vide infra) which gave better resolved spectra.

A simple conversion of anion **2a** into ferrocenes is illustrated in Scheme 2. Thus reaction of a mixture of **2a**Li and CpNa with solvated irondichloride gave Cp_2Fe and the ferrocenes **3a**/**b** and **4** which are substituted by two and one tetramethylcyclopentadiene, respectively. A fourfold excess of CpNa was chosen in order to disfavor the formation of **3a**/**b** which would complicate subsequent reactions. Indeed, the NMR spectra of the mixture of resulting ferrocenes showed **4** besides an excess of Cp_2Fe and a small amount of **3a**/**b**. **3a** is a known compound [11a] whose NMR data could be confirmed approximately except that two sets of signals rather than one were observed. This proves that reaction of two anions **2a** with $FeCl_2$ (Scheme 1) leads to two diastereoisomers (**3a** and **3b**) whereas reaction of 1,1′-dilithioferrocene with tetramethylcyclopentenone [11a] gives **3a** alone.

While the mixture of ferrocenes was used for further reaction a small quantity of **4** could be isolated by chromatography after step c of Scheme 2. It proved to be a key compound for the NMR characterization of other molecules (vide infra). Cp_2Fe could be removed straightforwardly from **3a**/**b** and **4** by reaction of the mixture with *n*-BuLi in hexanes. This led to the insoluble anion **5** together with a small quantity of the anions of **3a**/**b** as dilithium salts while Cp_2Fe stayed in solution. When the lithium salts where dissolved in DMSO-d_6 only the signals of **5** could be detected (see NMR features below). We ascribe this to the low solubility of the lithium salts of **3a**/**b** which were detected indirectly after step c in Scheme 2. Thus, reaction of **5** with



Scheme 2. Synthesis of octamethylterferrocene (**6**). (a) CpNa, $FeCl_2(THF)_{1.5}$; (b) *n*-BuLi; (c) $FeCl_2(THF)_{1.5}$. Molecules shown here and elsewhere in this paper have arbitrary relative orientations of their Cp ligands.

irondichloride gave the octamethylated terferrocene **6** and three side products in small quantity as established by chromatography: (i) Cp_2Fe, which was still left after extraction with hexanes in step b of Scheme 2; (ii) compound **4**, presumably from reprotonation of **5** by traces of water, and (iii) octamethylbiferrocenylene, a known [11a] derivative of **B**, which proves that **3a**/**b** had been deprotonated. The NMR spectra of the terferrocene **6** show sets of signals for the central and terminal ferrocene moieties, respectively. Alkylation of the central ferrocene is reflected in larger ^{13}C-NMR signal shifts of the ring carbon atoms as compared to the terminal ferrocenes. This feature is known for many simple alkylated ferrocenes [16]. Other methylated terferrocenes reported so far are the tetra- [11a] and decamethyl [8b] derivatives.

In order to make the synthesis of the ferrocenyl-substituted cyclopentadiene more selective the CpFe fragment was replaced by $(C_5Me_5)Fe$. The acetylacetonate derivative $(C_5Me_5)Fe(acac)$ has been suggested as a suitable starting compound for mixed-ligand ferrocenes [17]. We have applied the reagent with varying success. The reason is that the precursor $Fe(acac)_2$ usually contains appreciable amounts of $Fe(acac)_3$ [18]. This can be checked by ^{1}H-NMR spectroscopy. Fig. 1 shows the proton spectrum of a representative batch which contained $Fe(acac)_2$ (signals at -19.5 and 20.3 ppm) and $Fe(acac)_3$ (signals at 13.6 and -23.7 ppm) in the ratio 4/1. Different spin delocalization and magnetic interaction evident from temperature-dependent spectra will be reported elsewhere.

Unlike $Fe(acac)_2$, the hexaflouroacetylacetonate analogue $Fe(hfa)_2$ [19] proved to be pure and gave only one set of NMR signals (^{1}H-NMR: δ 18.0, width 1080 Hz; ^{13}C-NMR: δ/width in Hz 854/1450 (CH_3), 884/1400 (CH), 1640/1150 (CO); ^{19}F-NMR: δ -7.4, width 420 Hz; all shifts at 298 K and relative to the signals of C_6D_6 except for external CF_3COOH used for ^{19}F-NMR). Reaction of $Fe(hfa)_2$ with $(C_5Me_5)Li$ in THF gave a brown mixture of $(C_5Me_5)_2Fe$ and $Fe(hfa)_2$ whereas a dark blue solution was obtained when acetonitrile was used as solvent. So far we were unable to crystallize a well-defined compound, while removal of acetonitrile led to $(C_5Me_5)_2Fe$ and $Fe(hfa)_2$. Treatment of the blue solution with 1,2-dimethylcyclopentadienyllithium gave the corresponding heptamethylferrocene in 76% (non-optimized) yield (Scheme 3, step b). On these evidences the donor-stabilized 18-electron species $(C_5Me_5)Fe(hfa)(NCMe)$ (**7**) is suggested to result in solution after step a of Scheme 3.

Freshly prepared solutions of **7** proved very useful for the synthesis of more complicated mixed-ligand ferrocenes. Thus reaction with anion **2a** (Scheme 3, step c) afforded a pentamethylferrocene which is substituted by tetramethylcyclopentadiene (**9**). As expected, the NMR spectra established **9** as pentamethyl-analogue of **4**. However, the advantage over the synthesis of **4** is that **9** is pure (^{13}C-NMR) after flash chromatography

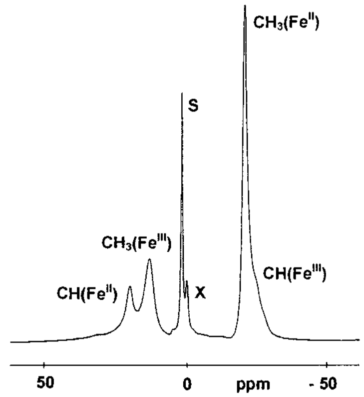
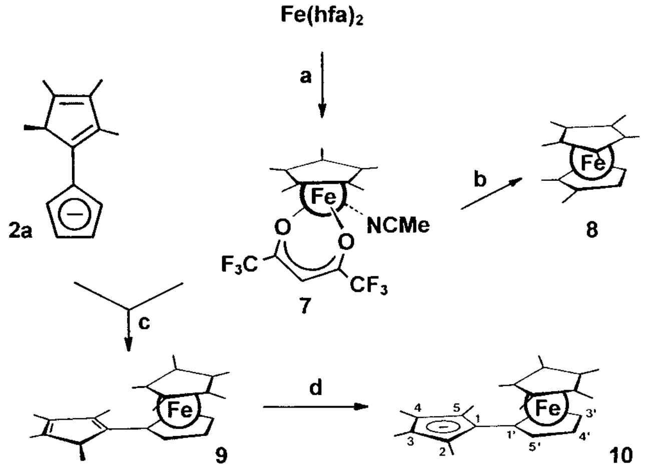
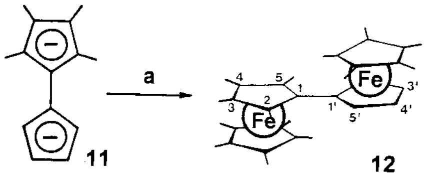


Fig. 1. ^{1}H-NMR spectrum of a 4/1-mixture of $Fe(acac)_2$ and $Fe(acac)_3$ in dioxane-d_8 at 375 K. S = solvent, X = impurity.



Scheme 3. Synthesis of the anion **10** starting from the half-sandwich **7**. (a) $(C_5Me_5)Li$, MeCN; $(Me_2C_5H_3)K$; (c) reaction of **2a** with **7**; (d) *n*-BuLi.



Scheme 4. Synthesis of tetradecabiferrocene (**12**). (a) $(C_5Me_5)Fe(hfa)(MeCN)$.

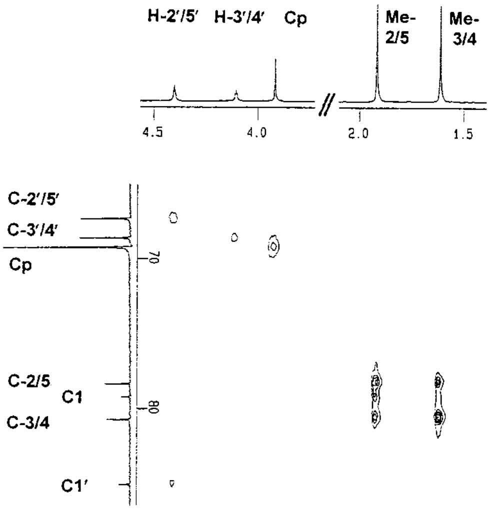


Fig. 2. C, H-HMBC of **6** optimized for $^{2/3}J_{C,H}$.

and that the procedure gives a yield of about 60%. Deprotonation of **9** furnished the air-sensitive anion **10** as lithium salt in 88% yield so that this sequence of reactions is promising for the synthesis of homo- and heterometallic termetallocenes other than **6**.

The use of **7** as valuable $(C_5Me_5)Fe$-transfer reagent was also confirmed by reaction with dianion **11** [12] (Scheme 4). After flash chromatography the highly methylated unsymmetric biferrocene **12** was isolated in 68% yield.

2.2. NMR features

Most of the NMR signals could be assigned by analyzing standard criteria like signal areas, nuclear couplings, and characteristic signal shift ranges of ferrocenes and cyclopentadienyl anions. Note, for example, that **5** and **10** correspond to the tetramethylated pentafulvalene dianion **11** supplemented by Cp and (C_5Me_5), respectively, and modified by replacing one lithium by iron. The distinction of nuclei in positions 2,5 and 3,4 or 2′,5′ and 3′,4′ of the pentafulvalene skeleton has been established for **6** with a gradient-selected Heteronuclear Multiple Bond Correlation (HMBC) experiment optimized for C,H correlations over two and three bonds [20]. As shown in Fig. 2 there are two key correlations: (i) that including signals at 84.7 ppm and 4.40 ppm which identifies C-1′ and H-2′,5′; (ii) that including the ^{13}C-NMR signals at 80.7, 79.3, and 78.5 ppm and the ^{1}H-NMR signal at 1.92 ppm which identifies Me-2,5. The protons of Me-2,5 show a stronger correlation with the carbon signal at 78.5 ppm than with that at 80.7 ppm, and hence the latter signal belongs to C-3,4. The residual cross peaks due to $^1J_{C,H}$ (not shown in Fig. 2) establish the carbon signal of Me-2,5. For compounds **5**, **10**, and **12** nuclei in positions 2,5 and 3,4 were distinguished by comparison with the NMR data of **6**.

From the synthesis it was not clear whether the cyclopentadiene moiety of **2a**, **4**, and **9** had the methylene carbon atom in position 2 or 3 (Schemes 1–3). The ^{1}H-NMR spectrum of **9** was resolved well enough to uncover the methylene proton as quartet of triplets. We ascribe the 2.0-Hz triplet splitting to the long-range coupling with protons 2′,5′ which establishes the 4-methylene isomer of **9** and hence of **2a** and **4**. The methylene group renders nuclei 2′,5′ and 3′,4′ of **2a**, **4**, and **9** nonequivalent. This was not reflected in the NMR spectra of **2a** probably owing to accidental equivalencies not least in the ^{13}C-NMR spectrum where the signals of the pairs C-2′,5′ and C-3′,4′ are separated by only 0.1 ppm. Rapid 1,5-sigmatropic proton shifts could be excluded, because the methyl groups and the ring carbon atoms of the cyclopentadiene moiety gave sharp separate signals. The situation is different for the ferrocenes **4** and **9** where planar chirality must be considered in addition to the asymmetric carbon C4. The pair of diastereomers is best reflected by more than two signals for C2′-5′.

A quite efficient strategy of signal assignment was found for tetradecamethylbiferrocene **12**. Since **12** is asymmetric, the two ferrocene moieties give rise to separate signals with similar shifts. They can be distinguished based on the fact that **12** is oxidized to ferroce-

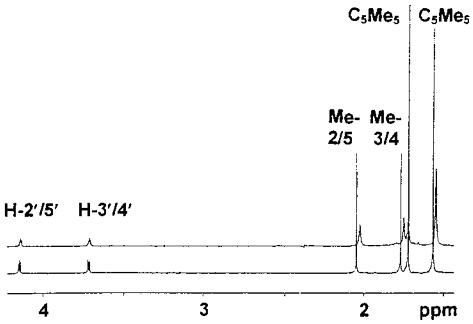


Fig. 3. ^{1}H-NMR spectra of **12** in C_6D_6 at 305 K. Top and bottom: with and without partial oxidation, respectively (see text).

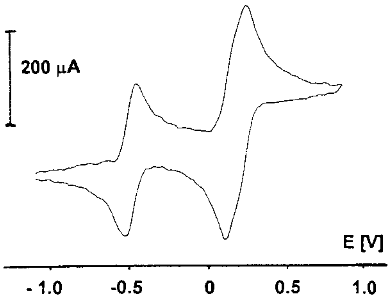


Fig. 4. Cyclic voltammogram of **6** in propionitrile at 298 K. Scan rate 200 mV s^{-1}, potential scale relative to $[Cp_2Fe]^{0/+1}$.

nium step by step in the nona- and pentamethyl half (see Section 2.3). Because of the unpaired electron the NMR signals of ferrocenium ions are broad and strongly shifted; ring and methyl protons are found at high and low frequency, respectively [21]. Thus, upon partial oxidation, some of the NMR signals of **12** underwent changes which are illustrated by the proton spectra in Fig. 3. When pure **12** (bottom trace of Fig. 3) was treated with a small amount of $AgNO_3$ three methyl signals broadened and moved to low frequency (top trace of Fig. 3). It follows that these signals belong to the nonamethylated half of **12**. By contrast, the signal at 1.72 ppm remained virtually unaffected so that it must be assigned to (C_5Me_5) of the pentamethylated half of **12**. It is noteworthy that, quite expectedly, the signals of H-2′,5′ and H-3′,4′ do not move while a slight broadening occurs. This is due to some intermolecular relaxation enhancement which is less efficient than the intramolecular enhancement that influences three of the methyl signals. The same phenomena were observed in the ^{13}C-NMR spectrum, and the carbon signals were assigned accordingly.

2.3. Redox behavior

An attractive aspect of bi- and terferrocenes is the possibility of oxidizing them to mono-, di- and (for the latter) trications [22]. In this respect it was surprising that the cyclic voltammogram of octamethylterferrocene **6** seemed to indicate only two electron transfers (ETs) involving one and two electrons at low and high potential, respectively (Fig. 4). Closer inspection reveals shoulders at the anodic and cathodic waves near 200 mV and hence two overlapping ETs. Their separation is calculated to be 60 mV if one assumes that the distance between the anodic and cathodic current peaks is $\Delta E =$ 70 mV, the value which has been measured for the ET near -450 mV and which is commonly encountered for substituted ferrocenes. Details are given in Table 1 where selected literature data have been added for comparison.

Coupling of two or more ferrocenes is associated with a lowering of the first oxidation potential which amounts to about 90 mV per ferrocenyl group for bi- and terferrocene [3,23] and 145 mV when two pentamethylferrocenes [8c] are coupled to decamethylbiferrocene [8a]. This is illustrated in Fig. 5 and can be ascribed to 'substitution' of ferrocene, to delocalization of the created charge, and to differential solvation. It is

Table 1
Electrochemical data [a] of **6**and **12**

	6	Terferrocene [d]	**12**	Decamethylbiferrocene [e]	Biferrocene [f]
$E_{1/2}(0/1)$ [b]	−455	−180	−535	−410	−100
$\Delta E_p(0/1)$	70		70	65	
$E_{1/2}(1/2)$	150	40	−65	−35	250
$\Delta E_p(1/2)$	[c]		80	65	
$\Delta E_{1/2}(1/2-0/1)$	605	220	470	375	350
$E_{1/2}(2/3)$	210	420			
$\Delta E_p(2/3)$	[c]				
$\Delta E_{1/2}(2/3-1/2)$	60	180			

[a] In propionitrile at 20°C, unless stated otherwise, scan rate 200 mV s^{-1}, potentials in mV are relative to $[Cp_2Fe]^{0/+1}$.

[b] External charges of the species involved are given in parentheses.

[c] Overlapping ETs, see text.

[d] In CH_2Cl_2 [3].

[e] Ref. [8a].

[f] In MeCN [24].

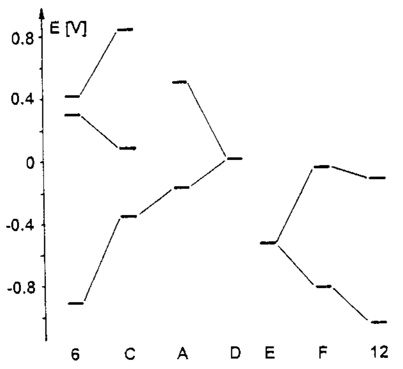


Fig. 5. Shift of redox potentials on passing from ferrocenes to bi- and terferrocenes. A = biferrocene, C = terferrocene, D = ferrocene, E = pentamethylferrocene, F = decamethylbiferrocene; **6** and **12** see Schemes 2 and 4.

also clear from Fig. 5 that the potential-splitting scheme of the pair pentamethylferrocene/decamethylbiferrocene is 265 mV lower than that of the pair ferrocene/biferrocene. The potential shift is due to the electron release of the CH_3 groups, and the value of 53 mV per CH_3 confirms previous findings [24].

The first ET of **12** is only 125 mV lower than that of decamethylbiferrocene while about 200 mV is expected from four additional CH_3 groups. The difference of 75 mV must be ascribed to the fact that charge delocalization in $\mathbf{12}^+$ is much less efficient than in biferrocene (90 mV) and decamethylbiferrocene (145 mV), because the energy of the two oxidation-state isomers of $\mathbf{12}^+$, $(C_5Me_5)Fe^+(C_5H_4)$–$(C_5Me_4)Fe(C_5Me_5)$ and $(C_5Me_5)Fe(C_5H_4)$–$(C_5Me_4)Fe^+(C_5Me_5)$, should differ by about 200 mV (again due to four CH_3 groups). Actually, the numbers do not quantitatively reflect the reasoning as changes of the differential solvation of the engaged species is expected to modulate all data. The second ET of **12** creates a charge in its pentamethylferrocene half, and, therefore, the potential should be similar to that of decamethylbiferrocene. This is indeed found approximately (Fig. 5); the additional moderate stabilization may be due to a long-range effect of the neighboring nonamethylferrocene moiety.

It is gratifying that the octamethylterferrocene **6** can be analyzed in much the same way. When **6** is compared to the parent terferrocene it turns out that the first ET is 270 mV lower whereas a 400-mV shift is expected from eight CH_3 groups. Again this shift is reduced, because in $\mathbf{6}^+$ the charge is trapped at the central ferrocene moiety. The second ET of **6** is 110 mV higher than for terferrocene. In the present case localization of the first charge entails *adjacent* charges in $CpFe^+(C_5H_4)$–$(C_5Me_4)Fe^+(C_5Me_4)$–$(C_5H_4)FeCp$ $(\mathbf{6}^{2+})$, while they are *distant* in terferrocene dication: $CpFe^+(C_5H_4)$–$(C_5H_4)Fe(C_5H_4)$–$(C_5H_4)Fe^+Cp$. The destabilization of 110 mV measured for $\mathbf{6}^{2+}$ confirms the value of 120 mV which has been estimated for passing from distant to adjacent charges in terferrocene dication [3]. Finally, the third ET of **6** is stabilized by 210 mV relative to that of terferrocene. On the one hand the stabilization is due to the long-range methyl effect mentioned with the second ET of **12**. On the other hand oxidation to $\mathbf{6}^{3+}$ is easier than to terferrocene trication, because the incoming charge meets one and two next-neighbor charges, respectively.

2.4. Conclusions

A building block strategy for assembling terferrocenes has been realized. Building blocks are ferrocenes which are substituted by tetramethylcyclopentadienyl anion. The strategy is expected to be applicable to metals other than iron since the synthesis starts from a tetramethylated pentafulvalene anion (**2a**) rather than from the parent metallocene. An octamethylterferrocene (**6**) has been synthesized as pilot compound. The redox potentials of **6** and the hitherto unknown tetradecamethylbiferrocene (**12**) (synthesized from tetramethylpentafulvalene dianion) have been shown to shift upon substitution. While coupling of ferrocene lowers the first potential methylation has two effects: (i) electron release lowers the potential; (ii) charge localization within the cations increases it.

3. Experimental

Synthetic work and characterization were carried out under purified dinitrogen in oxygen-free and dry solvents by using standard Schlenk equipment. Mass spectroscopy data were obtained from a Varian MAT 311A instrument (EI, 70 eV), and NMR spectra were recorded with Jeol GMX 270, Jeol Lambda 400, and Bruker MSL 300 spectrometers. Signal shifts were measured relative to internal solvent peaks and calculated relative to standard values [25]; signal multiplicities given with the ^{13}C-NMR data refer to $^1J_{C,H}$ coupling if not stated otherwise. For cyclic voltammetry measurements a EG&G Princeton Applied Research potentiostat, 173/276 was used. Home-made cells were equipped with a small column for final drying of the solvent over activated Al_2O_3, with platinum wire working and counter electrodes, and with an Ag/AgCl reference electrode. $[n\text{-}Bu_4N]PF_6$ (0.1 molar in propionitrile) served as supporting electrolyte. The potentials were referenced relative to that of internal $[CpCo]PF_6$ and calculated relative to $[Cp_2Fe]^{0/+1}$. Elemental analyses were carried out by the Microanalytical Laboratory of the authors' institution. 1,2-Dimethylcyclopentadienylpotassium was obtained by reaction of the corresponding diene [26] with KH. Other starting compounds were synthesized as described previously: dihydrotetramethylpentafulvalenes **1a**, **1b,** and **1c** [12], dihydrotetramethylpentafulvalene dianion **7** [12], Fe(hfa)$_2$ [19].

*3.1. 4,8-Dihydro-1,2,3,4-tetramethylpentafulvalene-8-yllithium (**2a**Li)*

A mixture of isomers **1a**, **b, c** (5.46 g, 29.3 mmol) was dissolved in 200 ml of pentane and cooled to −30°C. Subsequently, 9 ml of a 1.6 molar solution of *n*-BuLi in hexanes (14.4 mmol) was added from a dropping funnel to the stirred solution. First the reaction mixture became cloudy, later a white precipitate formed when the cooling bath was removed and the mixture was stirred for 12 h. Filtration, washing of the solid with pentane, and drying in vacuo gave 2.25 g (81% yield) of **2a**Li as a lumpy white solid which proved to be NMR-spectroscopically pure.

^{1}H-NMR (DMSO-d_6): δ 1.01 (3H, d, $^3J_{\mathrm{H,H}} = 7.4$ Hz, Me-2), 1.69, 1.79, 1.88 (all 3H, s, Me-3,4,5), 2.78 (1H, q, $^3J_{\mathrm{H,H}} = 7.4$ Hz, H-2), 5.39, 5.54 (both 2H, AA′BB′ pattern, $^3J_{\mathrm{H,H}} + {}^4J_{\mathrm{H,H}} = 3.7$ Hz, H-2′,5′ and H-3′,4′). ^{13}C-NMR (DMSO-d_6): δ 11.4, 12.1, 13.2 (all q, $^1J_{\mathrm{C,H}} = 124.5$ Hz, Me-3,4,5), 19.4 (q, $^1J_{\mathrm{C,H}} = 124.4$ Hz, Me-2), 48.9 (d, $^1J_{\mathrm{C,H}} = 154.1$ Hz, C-5), 105.0, 105.1 (both d, $^1J_{\mathrm{C,H}} = 154.0$ Hz, C-2′,5′ and C-3′,4′), 116.8, (s, C-1′), 118.3, 129.5, 134.8 146.6 (all s, C-1, C-2, C-3, and C-4).

*3.2. Reaction of **2a**Li and CpNa with irondichloride*

To a solution of CpNa (2.15 molar, 80 ml, 172 mmol) in THF was added 7.9 g (41 mmol) of **2a**Li, the mixture was diluted with 200 ml of THF and cooled to 0°C. Further addition of 25.1 g (107 mmol) of FeCl$_2$(THF)$_{1.5}$ gave a black mixture which was stirred for 24 h at 25°C. Then the solvent was removed under reduced pressure, and the remaining solid was extracted with 500 ml of hexanes. A small portion of the resulting orange–brown solution was freed from the solvent, and the solid was redissolved in C$_6$D$_6$. ^{1}H and ^{13}C-NMR spectroscopy showed the signals of Cp$_2$Fe, **3a**, **3b**, and **4**; integration of the ^{1}H-NMR spectrum gave the ratio of 32/1/1/16, respectively.

3a and **3b**: ^{1}H-NMR (C$_6$D$_6$): δ 1.08, 1.11 (both 3H, Me-2), 1.74, 1.75 (both 3H), 1.79 (6H), 1.91, 1.99 (both 3H) (last five signals: Me-3, Me-4, and Me-5), 2.70, 2.80 (1H, H-2), 4.09, 4.30, 4.38, 4.39 (all 1H, H-2′ and H-5′), 4.13, 4.19 (both 2H, H-3′,4′). ^{13}C-NMR (C$_6$D$_6$): δ 11.2 (2C), 12.06, 12.09, 13.2, 13.3 (all 1C) (last five signals: Me-3, Me-4, and Me-5), 16.5, 16.7 (Me-2), 50.5, 50.7 (C-2), 67.9, 68.2, 68.8, 69.02, 69.07, 69.10, 69.17, 69.7 (C-2′, C-3′, C-4′, C-5′), 83.5, 83.6 (C-1′), 135.3 (2C), 136.1, 136.2 (both 1C), 138.6 (2C) 139.6, 139.7 (both 1C) (last six signals: C-3, C-4, and C-5).

A NMR-spectroscopically pure sample of **4** was obtained by chromatography as described in Section 3.3.

^{1}H-NMR (C$_6$D$_6$): δ 1.12 (3H, d, $^3J_{\mathrm{H,H}} = 7.4$ Hz, Me-2), 1.76, 1.80, 2.01 (all 3H, s, Me-3, Me-4, and Me-5), 2.84 (1H, q, $^3J_{\mathrm{H,H}} = 7.3$ Hz, H-2), 4.01 (5H, s, C$_5$H$_5$), 4.11 (2H, br, H-3′,4′), 4.30, 4.35 (both 1H, br, H-2′ and H-5′). ^{13}C-NMR (C$_6$D$_6$): δ 11.2, 12.1, 13.2 (all q $^1J_{\mathrm{C,H}} = 125.2$ Hz, Me-3, Me-4, and Me-5), 16.4 (q, $^1J_{\mathrm{C,H}} = 128.5$ Hz, d, $^2J_{\mathrm{C,H}} = 6.6$ Hz, Me-2), 50.7 (d, $^1J_{\mathrm{C,H}} = 171.8$ Hz, q, $^2J_{\mathrm{C,H}} = 4.9$ Hz, C-2), 67.0, 67.7 (d, $^1J_{\mathrm{C,H}} = 171.8$, C-2′,5′ or C-3′,4′), 68.3, 68.4 (d, $^1J_{\mathrm{C,H}} = 170.3$ Hz, C-3′,4′ or C-2′,5′), 69.3 (d, $^1J_{\mathrm{C,H}} = 175.7$ Hz, ψquin $^{2,3}J_{\mathrm{C,H}} = 6.5$ Hz, C$_5$H$_5$), 83.1 (s, C-1′), 135.4, 136.1, (both s, C-4, and C-5), 139.4, (s, C-1 or C-3) 139.6 (d, $^2J_{\mathrm{C,H}} = 12.5$ Hz, C-3 or C-1).

*3.3. Deprotonation of **3a**, **3b**, and **4***

Into the hexane solution of the ferrocenes described in the previous section was poured 16.4 ml of a 2.5 molar solution of *n*-BuLi in hexanes (4.1 mmol). After 12 h of stirring the orange solution (Cp$_2$Fe) was removed from the red–brown precipitate. The solid was washed with 50-ml portions of hexanes until the solution was colorless. Drying in vacuo gave 8.0 g of an orange powder. The dianion derived from **3a** and **3b** could not be detected by NMR spectroscopy (see Section 2.2). If the ratio of 1/8 for the precursors **3a** + **3b**/**4** (see Section 3.2) is considered the yield of 1′-(2,3,4,5-tetramethylcyclopenta-1,3-dien-1-yl)ferrocene-5-yllithium (**5**Li) was 53%.

^{1}H-NMR (DMSO-d_6): δ 1.84 (3H, s, Me-3,4), 2.11 (3H, s, Me-2,5), 3.86 (5H, s, C$_5$H$_5$), 4,17 (2H, br, H-3′,4′),3.60 (2H, br, H-2′,5′). ^{13}C-NMR (DMSO-d_6): δ 12.3 (q, $^1J_{\mathrm{C,H}} = 121.3$ Hz, Me-3,4), 14.1 (q, $^1J_{\mathrm{C,H}} = 121.7$ Hz, Me-2,5), 63.6 and 63.7 (both d, $^1J_{\mathrm{C,H}} = 172.2$ Hz, C-2′,5′ and C-3′,4′), 67.8 (d, $^1J_{\mathrm{C,H}} = 173.9$ Hz, ψquin, $^{2,3}J_{\mathrm{C,H}} = 6.6$ Hz, C$_5$H$_5$) 96.7 (s, C-1′), 104.3 (s, C-1), 107.3, 107.8 (both s, C-2,5 and C-3,4).

*3.4. 1,1′-Diferrocenyl-2,2′,33′,4,4′-octamethylferrocene (**6**)*

An amount of 1.95 g (6.3 mmol) of **5**Li was dissolved in 100 ml of THF and cooled to 0°C. Then 0.75 g (3.2 mmol) of FeCl$_2$(THF)$_{1.5}$ was added, and the black mixture was stirred for 12 h while being allowed to warm to room temperature. The solvent was stripped from the resulting mixture, and the remaining solid was extracted with hexanes for 4 h in a Soxhlet apparatus. Reducing the volume of the dark red solution to 40 ml and cooling to −40°C for 24 h gave a light orange precipitate which was filtered off and dried under vacuum. 70.5 mg of the solid was treated with 5 ml of hexanes, and the saturated solution was subjected to chromatography (column length 20 cm, diameter 2 cm, basic Al$_2$O$_3$, Fluka 5016A). When hexanes were used for elution two bands appeared. After stripping the solvent a few mg of Cp$_2$Fe and **4** were obtained from the first and second band, respectively; the spectroscopic data of **4** are listed in Section 3.2. Addition of 5% of diethylether to hexanes gave another two bands. The third band contained a small amount of the known octamethylbiferrocenylene [11a] while the fourth band gave 20 mg of **6** as orange needles (yield 28% based on the material used for chromatography, mp 259 °C, decomposition).

MS: *m*/*z* 667 (MH^+, 0.3%), 306 ($[FcMe_4CpH]^+$, 100%), 186 (Fc^+, 45%), 121 ($[MeCpH]^+$, 22%), 56 (Fe^+, 14%), (Fc = ferrocenyl). Found: C, 67.15; H, 6.07; Fe, 24.82%, $C_{38}H_{42}Fe_3$ requires: C, 68.50; H, 6.35; Fe, 25.15%. ^{1}H-NMR (C_6D_6): δ 1.61 (12H, s, Me-3,4), 1.92 (12H, s Me-2,5), 3.91 (10H, s, C_5H_5), 4.10 (4H, ψt, $^3J_{H,H} + {}^4J_{H,H} = 4.0$ Hz, H-3′,4′), 4.40 (4H, ψt, $^{2+4}J_{H,H} = 4.0$ Hz, H-2′,5′). ^{13}C-NMR (C_6D_6): δ 9.6 (q, $^1J_{C,H} = 125.6$ Hz, Me-3,4), 12.5 (q, $^1J_{C,H} = 125.9$ Hz, Me-2,5), 67.3 (d, $^1J_{C,H} = 174.9$ Hz, C-2′,5′), 68.5 (d, $^1J_{C,H} = 174.6$ Hz, C-3′,4′), 69.2 (d, $^1J_{C,H} = 174.6$ Hz, ψquin, $^{2,3}J_{C,H} = 6.6$ Hz, C_5H_5), 78.5 (s, C-2,5), 79.3 (s, C-1), 80.7 (s, C-3,4), 85.1 (s, C-1′).

3.5. *1,2-Dimethylcyclopentadienyl(pentamethylcyclopentadienyl)iron (**8**)*

A dark red solution of $Fe(hfa)_2$ (1.26 g, 2.6 mmol) in 100 ml of acetonitrile was stirred and cooled to −40°C; then 0.37 g (2.6 mmol) of $(C_5Me_5)Li$ was added. Upon further stirring and slowly warming to room temperature the color of the mixture turned to dark blue which was ascribed to the formation of $(C_5Me_5)Fe(hfa)(MeCN)$ (**7**). Cooling back to −40°C and addition of 1,2-dimethylcyclopentadienylpotassium (1.05 g, 8.0 mmol) in 20 ml of THF gave a brown mixture. The cooling bath was removed, and after the mixture had reached room temperature the solvents were stripped. The remaining solid was extracted with 150 ml of hexanes, the solvent was removed under reduced pressure, and the solid recrystallized from acetonitrile to give 0.5 g (76% yield) of **8** as an orange powder.

MS: *m*/*z* 284 (M^+, 100%), 269 ($[M{-}Me]^+$, 5%), 188 ($[(C_5Me_5)Fe]^+$, 4%), 142 (M^{2+}, 5%), 92 ($[Me_2C_5H_4]^+$, 9%). Anal. Found: C, 72.30; H, 8.42; Fe, 18.72%, Calc. for $C_{17}H_{24}Fe$: C, 71.84; H, 8.42; Fe, 19.65%. ^{1}H-NMR (C_6D_6): δ 1.70 (6H, s, Me-1,2), 1.77 (15H, s, C_5Me_5), 3.42 (2H, d, $^3J_{H,H} = 2.3$ Hz, H-3,5), 3.46 (2H, t, $^3J_{H,H} = 2.3$ Hz, H-4). ^{13}C-NMR (C_6D_6): δ 10.6 (q, $C_5\mathit{Me}_5$), 11.1 (q, Me-1,2), 70.0 (d, C-4), 72.3 (d, C-2,3), 79.4 (s, C_5Me_5), 81.2 (s, C-1,2).

3.6. *Pentamethyl-1′-(2,3,4,5-tetramethylcyclopenta-1,3-dien-1-yl)ferrocene (**9**)*

A solution of **7** was prepared from 0.32 g (0.68 mmol) of $Fe(hfa)_2$ and 50 ml of acetonitrile as described in Section 3.5. After cooling to −40°C 0.17 g (0.88 mmol) of solid **2a**Li was added. The mixture was stirred and allowed to reach room temperature within 12 h. The solvent was removed under reduced pressure, and the remainder was extracted with 150 ml of hexanes. The resulting orange–brown solution was reduced and subjected to flash chromatography (basic Al_2O_3/hexanes). Stripping the solvent and drying in vacuo gave 0.15 g (59% yield) of **9** as orange–brown powder which did not show other ^{13}C-NMR signals than those given below.

^{1}H-NMR (C_6D_6): δ 1.17 (3H, d, $^3J_{H,H} = 7.4$ Hz, Me-2), 1.74 (15H, s, C_5Me_5), 1.81, 1.82, 1.98 (all 3H, s, Me-3, Me-4, and Me-5), 2.85 (1H, q, $^3J_{H,H} = 7.4$ Hz, t, $^5J_{H,H} = 2.0$ Hz, H-2), 3.71 (2H, m, H-3′,4′), 3.81, 4.10 (both 1H, m, H-2′,5′). ^{13}C-NMR (C_6D_6): δ 10.1 (q, $C_5\mathit{Me}_5$), 11.0, 11.3, 12.2 (all q, Me-3, Me-4, and Me-5), 17.7 (q, Me-2), 50.4 (d, C-2), 69.8, 70.2, 72.4, 73.0 (all d, C-2′, C-3′, C-4′, and C-5′), 80.0 (s, C_5Me_5), 83.1 (s, C-1′), 134.5, 135.4, (both s, C-4 and C-5) 138.8, 139.2 (both s, C-1 and C-3).

3.7. *Pentamethyl-1′-(2,3,4,5-tetramethylcyclopenta-1,3-dien-1-yl)ferrocene-5-yllithium (**10Li**)*

Compound **9** (0.15 g, 0.40 mmol) obtained in the previous reaction was dissolved in 200 ml of hexanes and treated with 0.5 ml of a 1.6 molar solution of *n*-BuLi (0.8 mmol). After an induction period an orange precipitate formed which was filtered off, washed with 100 ml of hexanes and dried in vacuo to yield 0.13 g (88%) of **10**Li as a moisture- and oxygen-sensitive orange powder which was shown to be pure by NMR spectroscopy.

^{1}H-NMR (DMSO-d_6): δ 1.56 (15H, s, C_5Me_5), 1.76 (3H, s, Me-3,4), 1.97 (3H, s, Me-2,5), 3.19 (2H, br, H-3′,4′), 3.59 (2H, br, H-2′,5′). ^{13}C-NMR (DMSO-d_6): δ 10.6 (q, $^1J_{C,H} = 125.0$ Hz, $C_5\mathit{Me}_5$), 12.4 (q, $^1J_{C,H} = 121.5$ Hz, Me-3,4), 15.4 (q, $^1J_{C,H} = 121.5$ Hz, Me-2,5), 65.2, (d, $^1J_{C,H} = 176.0$, C-2′,5′), 68.4 (d, $^1J_{C,H} = 168.0$ Hz, C-3′,4′), 77.5 (s, C_5Me_5), 96.9 (quin, $^{2/3}J_{C,H} = 6.0$ Hz, C-1′), 101.4 (s, C-1), 107.80 and 107.84 (both s, C-2,5 and C-3,4).

3.8. *Pentamethyl-1′-(nonamethylferrocen-1-yl)ferrocene (**12**)*

To a solution of **7** (prepared from 1.26 g (2.6 mmol) of $Fe(hfa)_2$ and 100 ml of acetonitrile as described in Section 3.5) was added under stirring at −40°C 0.54 g (2.7 mmol) of the dilithium salt of tetramethylpentafulvalene dianion (**11**Li_2) The mixture changed color from blue to brown while it was allowed to warm to room temperature during 12 h. The solvent was removed in vacuo, and the residue was extracted with 250 ml of hexanes. Flash chromatography (basic Al_2O_3/hexanes), stripping of the solvent, and drying in vacuo gave 0.50 g (68% yield) of spectroscopically pure (^{1}H and ^{13}C-NMR) **12** as orange–brown powder.

MS: *m*/*z* 566 (M^+, 100%, 376 ($[M-(C_5Me_5)Fe]^+$, 31%), 326 ($[(C_5Me_5)_2Fe]^+$, 63%). Found: C, 72.87; H, 8.09; Fe, 19.74%, $C_{34}H_{46}Fe_2$ requires: C, 72.10; H, 8.19; Fe, 19.72%. ^{1}H-NMR (C_6D_6): δ 1.56 (15H, s, C_5Me_5 of nonamethylferrocenyl), 1.72 (15H, s, C_5Me_5 of pentamethylferrocenyl), 1.77 (6H, s, Me-3,4), 2.05 (6H, s, Me-2,5), 3.71 (2H ψt, $^{3+4}J_{H,H} = 3.6$ Hz, H-3′,4′), 4.15 (2H ψt, $^{3+4}J_{H,H} = 3.6$ Hz, H-2′,5′). ^{13}C-NMR (DMSO-d_6): δ 9.4 (q, $C_5\mathit{Me}_5$ of nonamethylferrocenyl), 10.1 (q, Me-3,4), 11.2 (q, $C_5\mathit{Me}_5$ of pentamethylferrocenyl), 13.4 (q, Me-2,5), 69.7 (d, C-2′,5′), 71.9 (d, C-3′,4′), 77.3 (s, C-2,5), 78.8 (s, C_5Me_5 of nonamethylferrocenyl), 79.67 (s, C-3,4), 79.70 (s, C_5Me_5 of pentamethylferrocenyl), 80.6 (s, C-1′), 85.5 (s, C-1).

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