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Functionalized pentamethylferrocenes: synthesis, structure, and electrochemistry [1]

Benno Bildstein [a,*], Andreas Hradsky [a], Holger Kopacka [a], Richard Malleier [a], Karl-Hans Ongania [b]

[a] *Institut für Allgemeine, Anorganische, und Theoretische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*
[b] *Institut für Organische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*

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Abstract

The advantageous properties of the Cp* ligand – intensified electron donation, steric bulk, and enhanced solubility in comparison to the ubiquitous Cp ligand – are finding increasing use in organometallic chemistry. A systematic evaluation of synthetic routes to pentamethylferrocene compounds with a wide range of functionalities, including carboxyl, carbonyl, aminomethyl, vinyl, ethynyl, fulvenyl, cyclopentadienylmethyl, and others is reported. Spectroscopic, structural, and electrochemical properties of such functionalized pentamethylferrocenes Fc*$^{/2}$–R are compared to those of non-methylated ferrocenes Fc–R. The electronic influence of the Cp* ligand in these unsymmetrical ferrocenes Fc*$^{/2}$–R has been studied by cyclic voltammetry measurements, demonstrating a decrease in oxidation potential of −0.276 V in direct comparison to non-methylated ferrocenes Fc–R. © 1997 Elsevier Science S.A.

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1. Introduction

The reactivity and chemical properties of functional ferrocene derivatives have been explored in much detail and are well known. The on-going interest in ferrocene chemistry stems from the increasing use and application of such compounds in organic synthesis, homogeneous catalysis, and materials science [1]. In comparison, the analogous chemistry of 1′-substituted pentamethylferrocene derivatives is quite limited [2–4], although the presence of one pentamethylcyclopentadienide (Cp*) ligand in these metallocenes should result in favorable properties in terms of increased stability and solubility [5] and lowered oxidation potential, due to the amplified donor capacity of the Cp* ligand. In addition, the usually encountered 1,1′-substitution pattern of ferrocene derivatives prepared by aromatic electrophilic substitution or by reaction of metallated intermediates with electrophiles [6,7] is of course not possible in the case of the pentamethylferrocene moiety, which might be of advantage with regard to a selective 1′-monofunctionalization or a simplified synthesis of 1′,2′- and 1′,3′-disubstituted compounds. In spite of these anticipated useful features, the paucity of reported functionalized pentamethylferrocenes in the literature is rather surprising. The reasons for this underdeveloped chemistry are the synthetic difficulties which one encounters when trying to adapt from ferrocene chemistry well established synthetic transformations. In this contribution we report how and to what extent such functionalization is possible. Besides these synthetic results, the wide range of functional derivatives available by this study allows the quantification of the donor effect of the Cp* ligand by cyclic voltammetric comparison of Cp*FeCp–R to CpFeCp–R (R = functional substituent).

2. Results and discussion

2.1. General synthetic approach

There are two main routes to substituted 'normal' ferrocenes and the same methods should also be appli-

* Corresponding author. E-mail: benno.bildstein@uibk.ac.at.

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cable for the synthesis of 1'-substituted pentamethylferrocenes. (i) 'Indirect route': the functional substituent can either be introduced by electrophilic substitution or via 1'-metallated pentamethylferrocenes, therefore the parent compound 1,2,3,4,5-pentamethylferrocene and its possible transformation by such methods is of prime interest in the context of this work. (ii) 'Direct route': an appropriately substituted cyclopentadienide is converted to the 1'-substituted pentamethylferrocene by reaction with a pentamethylcyclopentadienide–iron(II) complex, similar to the synthesis of pentamethylferrocene itself. First we address the 'indirect' route (i), and second, because there are major limitations to this approach, the 'direct' route (ii), which proves to be superior in terms of ease of operation and accessibility of differently substituted target compounds.

2.2. Synthesis by the 'indirect route' starting from pentamethylferrocene

Although pentamethylferrocene is a known compound [8–14], we were not able to reproduce the published procedures. Specifically, we never came close to the reported yields of up to 90%, and we always observed the ligand-coupling product decamethyl(dihydro)fulvalene [15,16] as an unavoidable side-product, which is never mentioned [8–14] in the reported syntheses of pentamethylferrocene. In addition, depending on stoichiometry and reaction period, ferrocene and decamethylferrocene [17] were also obtained, which is an indication of the sensitivity of this reaction to ligand scrambling. No difference in product composition or relative yields of these products has been observed when using Cp^*Fe(II)benzoylacetonate [11] instead of Cp^*Fe(II)acetylacetonate [10] as the Cp^*–iron(II) source, and similarly, no improvements were found with different combinations of lithium or sodium cyclopentadienide as reactants and THF or DME as solvent. Published purification procedures for mixtures of ferrocene, pentamethylferrocene, and decamethylferrocene are selective fractional sublimation [9] and selective oxidation of decamethylferrocene [12]. These methods were also of no preparative value because of mainly thermal destruction during sublimation at 0.05 mbar, and because of only preferential, but not selective, oxidation. Therefore, our reaction conditions have been adjusted to minimize ligand exchange and to avoid formation of decamethylferrocene and ferrocene (by low reaction temperature and relatively short reaction time). In this way, pentamethylferrocene was obtained in yields of 75–80%, together with decamethyl(dihydro)fulvalene (20–25%), which can be removed by chromatography, although with heavy losses due to the very similar retention values, giving the pure products in low yield. Fortunately, the presence of decamethyl(dihydro)fulvalene does not interfere with most reactants in the following syntheses, so the chromatographic separation is mostly unnecessary. For both compounds single crystals could be obtained and the X-ray structures (Figs. 1 and 2) are included in this paper for completeness and for comparison to other substituted pentamethylferrocenes in the following. The structure of pentamethylferrocene has been published but is only with difficulty available [13] and the structure has also recently been calculated by lattice-energy minimization [14].

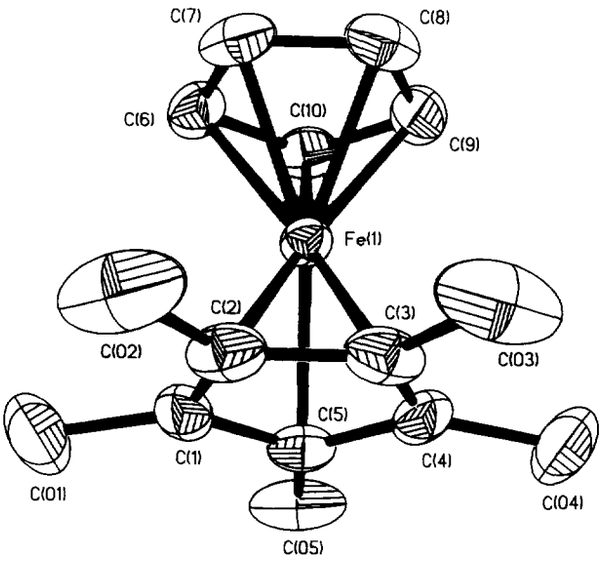


Fig. 1. Molecular structure of pentamethylferrocene, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity. Distances Fe(1) to Cp plane 165.8(1)pm; Fe(1) to Cp^* plane 164.2(1)pm; angle Cp plane to Cp^* plane 0.81(0.16)°.

The distances of the iron atom to the planes of the cyclopentadienyl and pentamethyl-cyclopentadienyl ring are 165.8(1) pm and 164.2(1) pm respectively, and might be attributed to a very small structural *trans* effect [11], indicating the tighter bonding of the more electron-rich Cp^* ligand. As expected, the two ligand planes are essentially parallel [angle of Cp plane to Cp^* plane 0.81(0.16)°]. In the case of decamethyl(dihydro)fulvalene, two independent molecules are in the asymmetric unit (only molecule A is shown in Fig. 2) with bond lengths of 159.1(3) pm and 159.4(3) pm for the bond between the two Cp^* groups, indicative of steric crowding and elongation of this bond in comparison to the standard $C(sp^3)$–$C(sp^3)$ bond length of 153 pm, which is in accord with the reported low enthalpy of dissociation of the Cp^*–Cp^* dimer to Cp^* radicals [16].

The metallation of pentamethylferrocene (Scheme 1) proved to be quite difficult. No reaction is observed with common deprotonating reagents, including methyl lithium, n-butyl lithium, t-butyl lithium, in hexane, ether or THF as solvent, and with or without added TMEDA [18] or HMPA [19] as metal chelating co-solvent. In comparison to ferrocene, where some of these metallat-

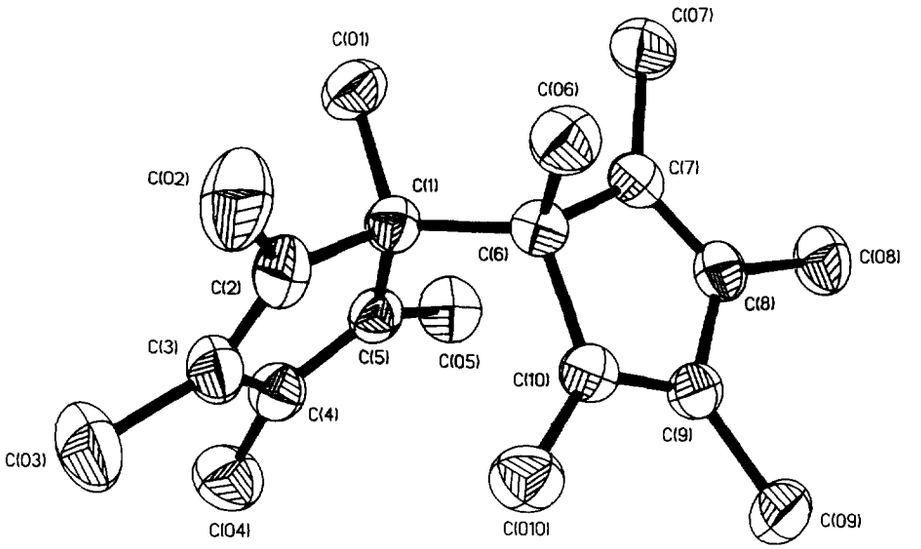
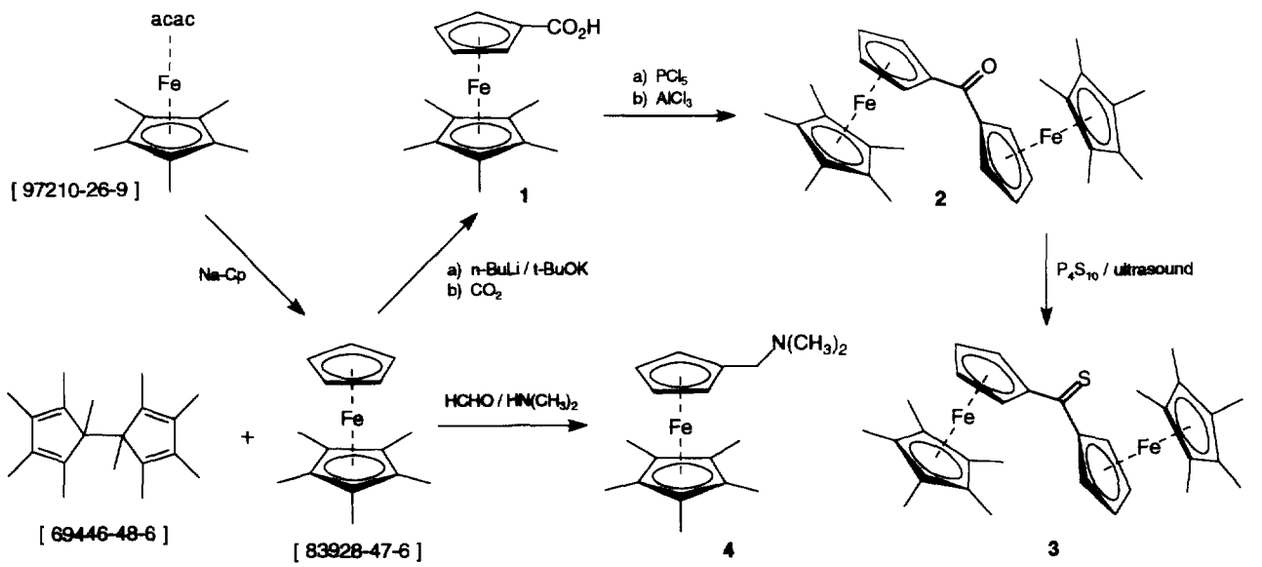


Fig. 2. Molecular structure of decamethyl(dihydro)fulvalene, showing the atom numbering scheme for molecule A. Hydrogen atoms are omitted for clarity. Bond length C(1)–C(6) 159.1(3) pm.

ing agents are sufficiently basic to effect mono- or dimetallation [6,7], even stronger bases are obviously necessary, due to the combined donor effect of the five methyl groups of pentamethylferrocene (compare Section 2.4). The reported dimetallation [9] of pentamethylferrocene with an excess of n-butyl lithium and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) as activator could be reproduced, but no carboxylation occurred upon reaction with dry ice, therefore this method did not allow the preparation of the desired 1,2,3,4,5-pentamethylferrocene-1′-carboxylic acid (**1**). In contrast to these failures, deprotonation of pentamethylferrocene and subsequent carboxylation is possible with a mixture of n-butyl lithium and potassium t-butoxide as 'superbase' [20], affording **1** in 86% overall yield starting from pure pentamethylferrocene.

Despite this successful functionalization of the intermediate 1′-metallated pentamethylferrocene with carbon dioxide, other attempted reactions did not provide the expected products at all or only in poor yield. No 1′-boronic acid could be obtained (after aqueous work-up) from the reaction with excess trimethylborate [21], and no 1′-chloropentamethylferrocene could be isolated from the reaction with excess hexachloroethane [22] as halogenating agent. Similarly, only a 35% conversion to 1,2,3,4,5-pentamethyl-1′-formylferrocene was possible in the reaction with DMF as formylating agent [23], but this compound is more conveniently accessible by the



Scheme 1. Synthesis of **1**–**4** (acac = acetylacetonate).

'direct route' (ii). In addition, metallation of pentamethylferrocene seems to be limited to the superbasic mixture of organyl lithium compounds with potassium alkoxides, because attempted mono- or pentamercuration with an excess of mercuric acetate according to procedures developed by Rausch and coworkers [24] and Winter and coworkers [25] failed to produce any low soluble 1'- or 1',2',3',4',5'-mercurated pentamethylferrocene.

Pentamethylferrocene carboxylic acid (**1**) can be converted to the corresponding acid chloride, which affords bis(pentamethylferrocenyl)ketone (**2**) under Friedel–Crafts conditions (Scheme 1). Besides **2** as the main product other higher acylated and rearranged side-products are formed in this reaction (see Section 4), probably due to the known aluminum chloride catalyzed ligand exchange [26].

The crystal structure of **2** (Fig. 3) shows no unexpected features in regard to bond lengths and angles; overall the structure is very similar to that of diferrocenyl ketone [27] with similar non-planarity [angle of plane of CpFe(1) to plane of CpFe(2) 8.30(47)°] of the two carbonyl-substituted Cp ligands, due to steric hindrance by the inner *ortho* hydrogens. Fig. 3 also gives

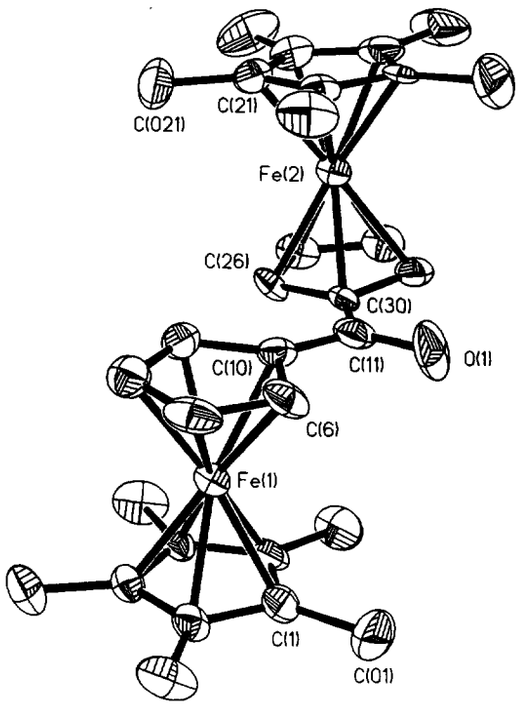


Fig. 3. Molecular structure of **2**, showing the atom numbering scheme; Cp and Cp* carbons are numbered analogously to pentamethylferrocene (see Fig. 1). Hydrogen atoms are omitted for clarity. Distances: Fe(1) to Cp plane [C(6)–C(10)] 165.1(3)pm; Fe(1) to Cp* plane [C(1)–C(5)] 164.6(3)pm; Fe(2) to Cp plane [C(26)–C(30)] 165.3(3)pm; Fe(2) to Cp* plane [C(21)–C(25)] 164.5(3)pm. Angles: Cp plane [C(6)–C(10)] to Cp* plane [C(1)–C(5)] 2.47(48)°; Cp plane [C(26)–C(30)] to Cp* plane [C(21)–C(25)] 2.88(47)°; Cp plane [C(6)–C(10)] to Cp plane [C(26)–C(30)] 8.30(47)°.

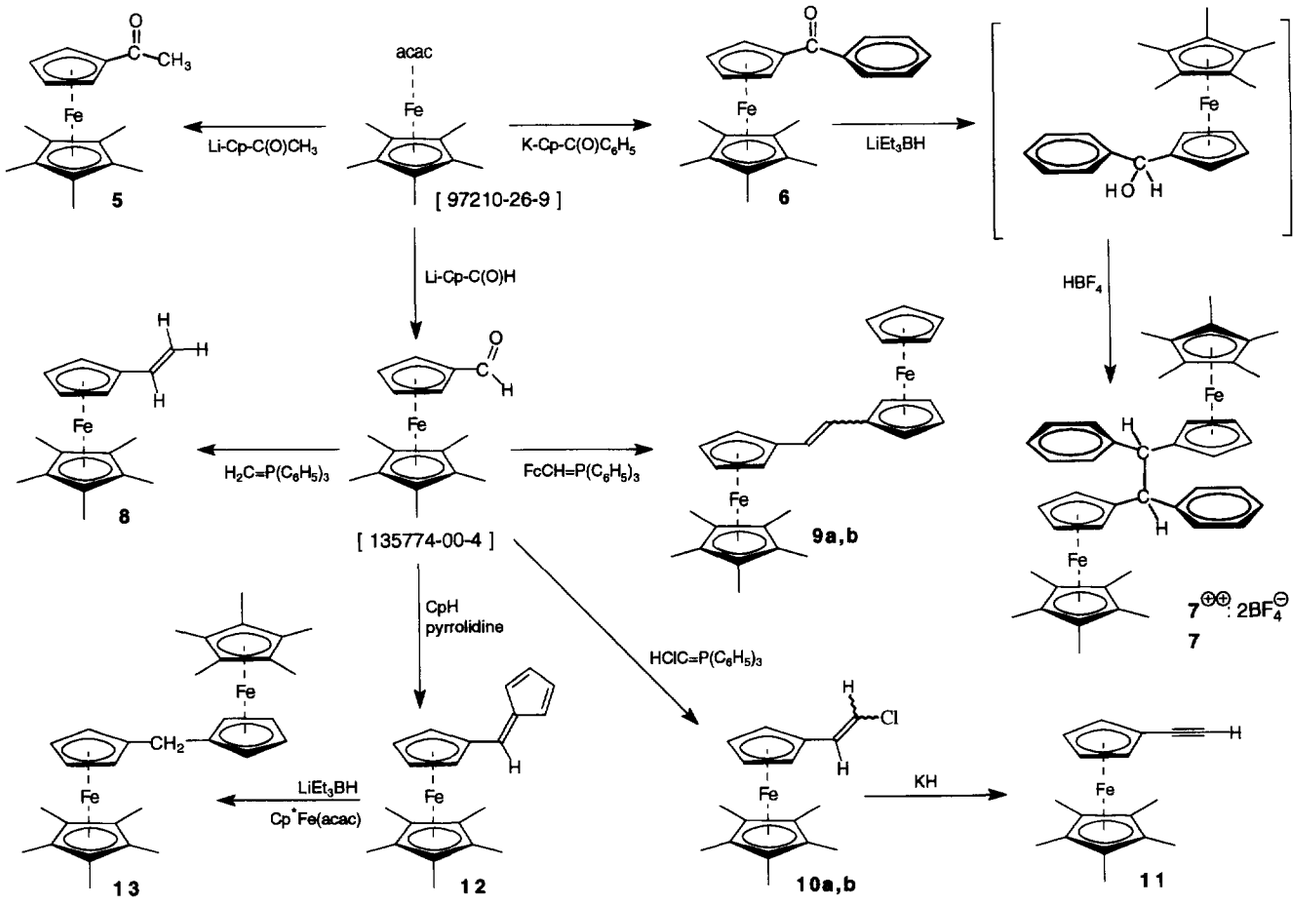
an impression of the considerable steric bulk of the two Cp* units, which prevents standard carbonyl chemistry of this ketone: no reduction to the corresponding alcohol (the precursor of bis(pentamethylferrocenyl)methylium cation [28]) by $LiAlH_4/AlCl_3$ or by lithium triethylborohydride is possible, no tetra(pentamethylferrocenyl)ethylene can be obtained under McMurry reaction conditions [29,30] or with Zn/trimethylchlorosilane [31], and only a very low yield of the unstable purple thioketone (**3**) can be obtained in the reaction with P_4S_{10} with ultrasonic activation [32].

Whereas metallation and subsequent derivatization of pentamethylferrocene is limited in scope and in yield of products, the aminomethylation (Mannich reaction) under standard reaction conditions [33] affords **4** in 79.5% yield as a dark red mobile liquid. In principle and in analogy to dimethylaminomethyl ferrocene, **4** can serve as a synthon for 1',2'-disubstituted 1,2,3,4,5-pentamethylferrocenes by directed orthometallation [6,34], and as a synthon for pentamethylferrocenyl methylation by nucleophilic displacement of trimethylamine from the corresponding methiodide [6]. For example, (pentamethylferrocenyl)methyl-triphenylphosphonium iodide (as a precursor of the corresponding Wittig ylide) can be prepared in low yield from the methiodide by displacement of trimethylamine with triphenylphosphine [35], but this phosphonium salt is more readily accessible from 1,2,3,4,5-pentamethyl-1'-hydroxymethyl-ferrocene [5].

2.3. Synthesis by the 'direct route' starting from functionalized cyclopentadienides

Since the direct route (i) affords only a limited number of the desired pentamethylferrocene derivatives, the alternative indirect route (ii) was investigated (Scheme 2). As noted above, the formylation of metallated pentamethylferrocene with DMF gives only a 35% yield of pentamethylferrocenyl aldehyde, whereas this compound is more conveniently prepared from a preformed formylcyclopentadienide [36] in accord with published results by Cheng and coworkers [4]. This one-pot procedure is advantageous in terms of ease of operation and simplicity in comparison to the direct route (i) which necessitates cumbersome chromatography of the pentamethylferrocene/decamethyl-(dihydro)fulvalene mixture (see above). The synthesis of acetylpentamethylferrocene (**5**) starting from acetylcyclopentadienide [36] proves that route (ii) is not limited to formyl-functionalized cyclopentadienide, and could possibly be extended to other functional group-substituted cyclopentadienides (vinyl, halogeno, amino, hydroxyl, alkoxyl, and carbamoyl), in analogy to chemistry developed by Rausch and coworkers [37], Plenio and coworkers [38], and Erker and coworkers [39].

In contrast to pentamethylferrocenyl aldehyde, which



Scheme 2. Synthesis of compounds **5–13**.

is obtained as a red oil, acetylpentamethylferrocene (**5**) is a solid compound and X-ray quality crystals could be obtained (Fig. 4). In comparison to the structure of the parent compound pentamethylferrocene, where a small structural *trans*-effect with non-equivalent iron–ligand distances can be observed, the corresponding distances in **5** are indistinguishable (Fe–Cp* 165.2(1) pm; Fe–Cp–C(O)CH_3 165.3(1) pm), although the presence of the acetyl group as an acceptor should increase such an effect; therefore we attribute these small observed differences in the ligand–iron bonding distances mainly to solid state packing effects.

For the preparation of benzoylpentamethylferrocene (**6**), a slight modification (with regard to Rausch's procedure [36,37]) of the synthesis of the intermediate benzoylcyclopentadienide proved necessary: whereas no reaction was observed between methylbenzoate and cyclopentadienide, the use of benzoyl chloride with subsequent deprotonation of benzoylcyclopentadiene by potassium t-butoxide afforded **6** in 20% yield. Reduction of ketone (**6**) with lithium triethylborohydride gives access to an unstable alcohol, which either decomposes in solution to 1,2-bis-pentamethylferrocenyl-1,2-diphenylethane (**7**) and pentamethylferrocenyl(phenyl)methane, or can be converted in situ with tetrafluoroboric acid to

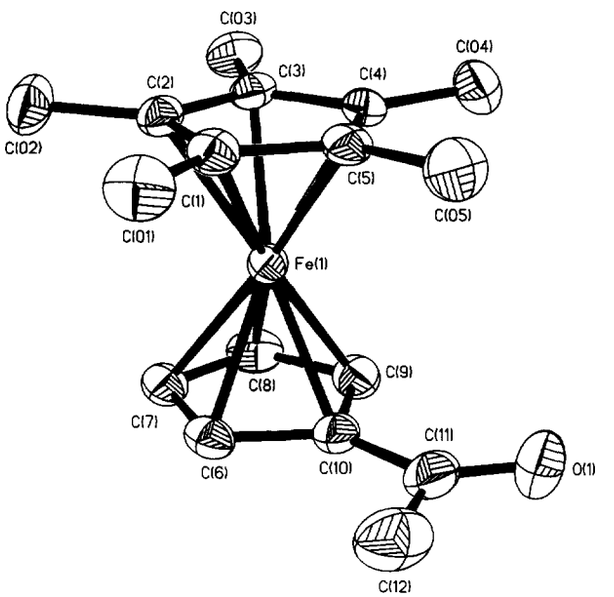
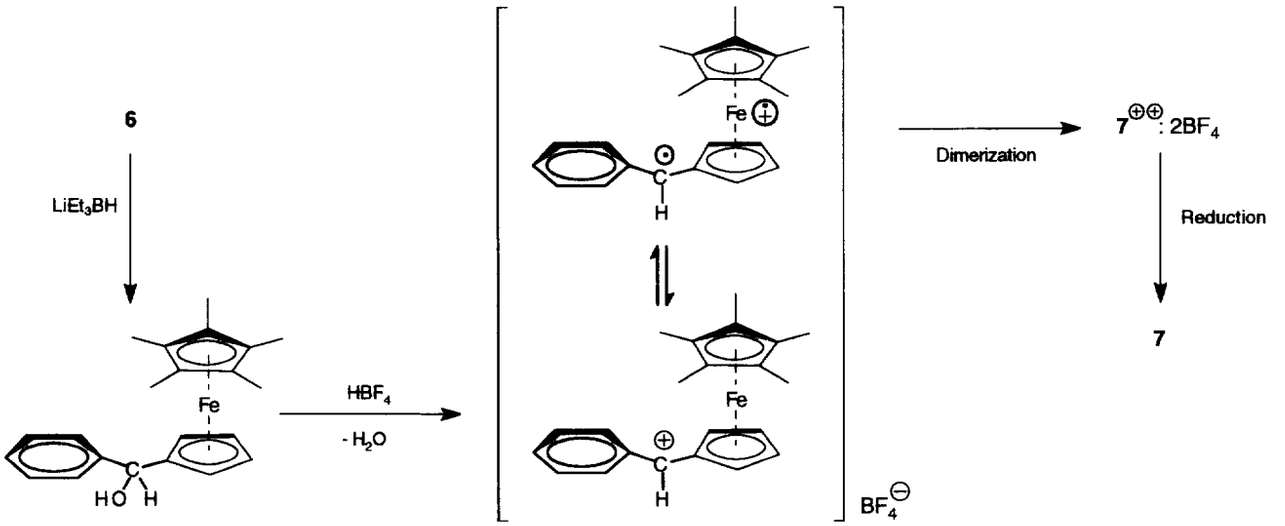


Fig. 4. Molecular structure of **5**, showing the atom numbering scheme; Cp and Cp* carbons are numbered analogously to pentamethylferrocene (see Fig. 1). Hydrogen atoms are omitted for clarity. Distances: Fe(1) to Cp plane [C(6)–C(10)] 165.3(1) pm; Fe(1) to Cp* plane [C(1)–C(5)] 165.2(1) pm. Angles: Cp plane [C(6)–C(10)] to Cp* plane [C(1)–C(5)] 2.14(14)°; O(1)–C(11)–C(10)–C(9) −3.92(44)°.



Scheme 3. Mechanism of formation of 7.

the corresponding pentamethylferrocenyl(phenyl)methylium tetrafluoroborate, which is unstable and dimerizes to the paramagnetic 1,2-bis-pentamethylferrocenium-1,2-diphenylethane $7^{(2+)} \cdot (BF_4)_2$ by an intramolecular redox disproportionation ('electron tautomerism' [40]) followed by intermolecular radical coupling, similar to

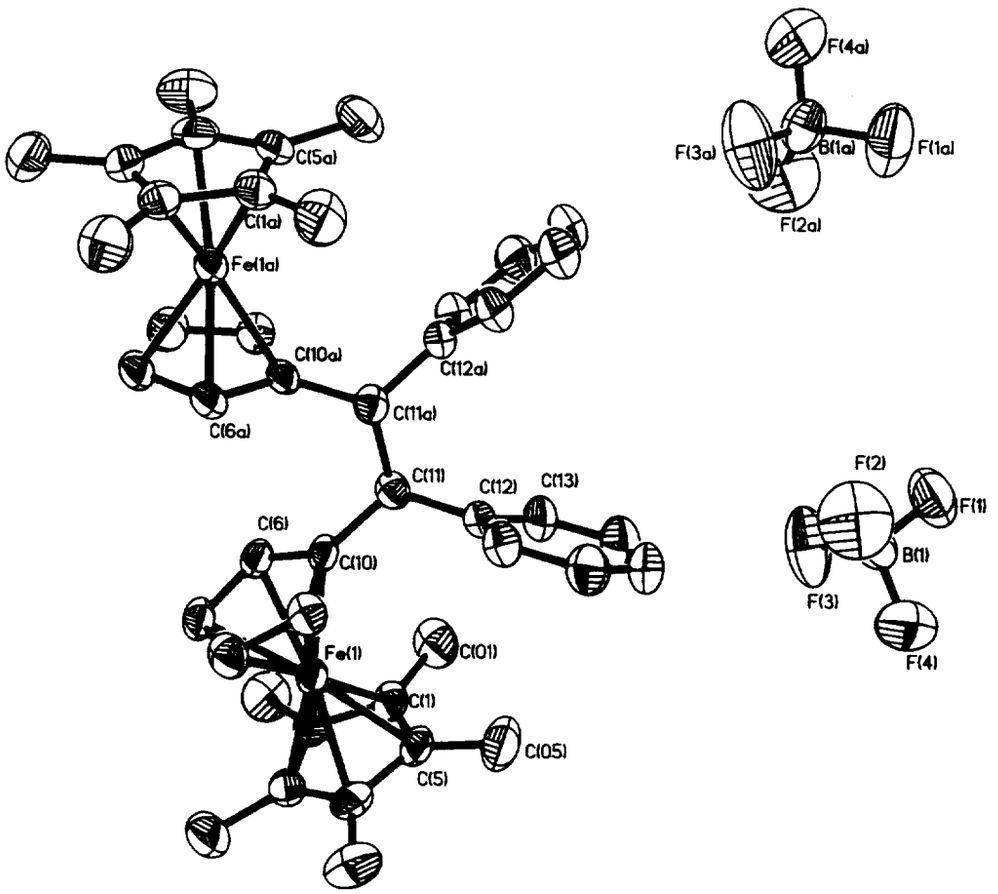


Fig. 5. Molecular structure of $7^{(2+)} \cdot (BF_4)_2$, showing the atom numbering scheme; Cp and Cp* carbons are numbered analogously to pentamethylferrocene (see Fig. 1). Hydrogen atoms are omitted for clarity. Distances: Fe(1) to Cp plane [C(6)–C(10)] 142.7(2) pm; Fe(1) to Cp* plane [C(1)–C(5)] 141.7(2) pm; bond length C(11)–C(11a) 158.7(8) pm. Angles: Cp plane [C(6)–C(10)] to Cp* plane [C(1)–C(5)] 11.50(86)°; C(10)–C(11)–C(11a)–C(10a) 61.67(47)°; H–C(11)–C(11a)–H 171.21(98)°.

other carbon-centered organometallic radicals formed from the corresponding carbenium ions [40,41] (Scheme 3).

Interestingly, the paramagnetic $7^{(2+)} \cdot (BF_4)_2$ can be isolated without difficulty (in contrast to all other reported examples in the literature [40,41]), corroborating the increased stability of pentamethylated ferrocenium ions, and the X-ray single crystal structure (Fig. 5) is, according to our knowledge, the first direct proof of a dicationic dimerization product in such reactions. In comparison to the neutral pentamethylferrocene derivatives (see Figs. 1, 3, 4 and 6) with Fe(II)–Cp and Fe(II)–Cp* distances of 165 pm, the metal-to-ligand distances of $7^{(2+)} \cdot (BF_4)_2$ are shortened (Fe(III)–Cp 143 pm and Fe(III)–Cp* 142 pm respectively), as anticipated. Due to steric congestion, the tilt angle of the planes of the Cp and Cp* ligands is increased to 11.50(86)°. From a stereochemical point of view, one might expect the formation of a stereoisomeric mixture of *meso* and *racemic* ethanes (compare the analogous 1,2-diferrocenyl-1,2-diphenyl-ethanes [42]) with the *meso* isomer, as shown in Scheme 2, favored due to electrostatic repulsion of the two ferrocenium cations and due to the steric bulk of the pentamethylmetallocene substituents. Contrary to these expectations, the *racemic* isomer is obtained with 100% diastereoselectivity. From this paramagnetic dicationic salt the neutral *rac*-1,2-bis-pentamethylferrocenyl-1,2-diphenylethane (**7**) can easily be obtained by reduction with hydrazine.

Pentamethylferrocenyl aldehyde [4] serves as a convenient starting material for Wittig olefinations to obtain further functionalized metallocenes. The aldehyde can be olefinated with methylene ylide to afford vinylpentamethylferrocene (**8**), which is a new organometallic monomer with potential interesting properties of its polymer in comparison to poly(vinylferrocene) ([1], Chapter 10.2 and references cited therein). The unsymmetrical biferrocene (**9a,b**) is obtained by reaction with ferrocenylmethylene ylide [35]. Interestingly, in the solid state the *E*-configurated **9a** adopts an unprecedented [43] *cis* conformation of the two metallocenyl termini with respect to the vinylene bridge (Fig. 6) as opposed to the usually observed *trans* conformation [5].

This unusual *cis* conformation of **9a** might be attributed to crystal forces, which also effect a rather large twisting of the Cp–CH=CH–Cp framework [angle C(12)–C(11)–C(10)–C(9) 13.12°; angle C(11)–C(12)–C(13)–C(14) −26.48°] in comparison to other 1,2-dimetallocenylolefins [5].

Olefination of pentamethylferrocenyl aldehyde with chloromethylene-ylide [44,45] affords chlorovinyl(pentamethylferrocene) (**10a,b**), and subsequent treatment with potassium hydride as base yields ethynyl(pentamethylferrocene) (**11**), which has a limited shelf-life but might be used as a starting compound in the numerous ethyne group transformations, following such established chemistry of ethynylferrocene [44,46,47]. [Polymerization of ethynylpentamethylferrocene in an analogous manner as in Ref. [47] is possible; the polymer has properties as expected (low molecular weight, prone to oxidation) [48].]

Condensation of pentamethylferrocenyl aldehyde with cyclopentadiene yields fulvenyl(pentamethylferrocene) (**12**) as a dark purple oil. Nucleophilic addition of hydride to the exocyclic fulvenic double bond generates an intermediate (pentamethylferrocenyl)methylcyclopentadienide, which can be converted to bis(pentameth-

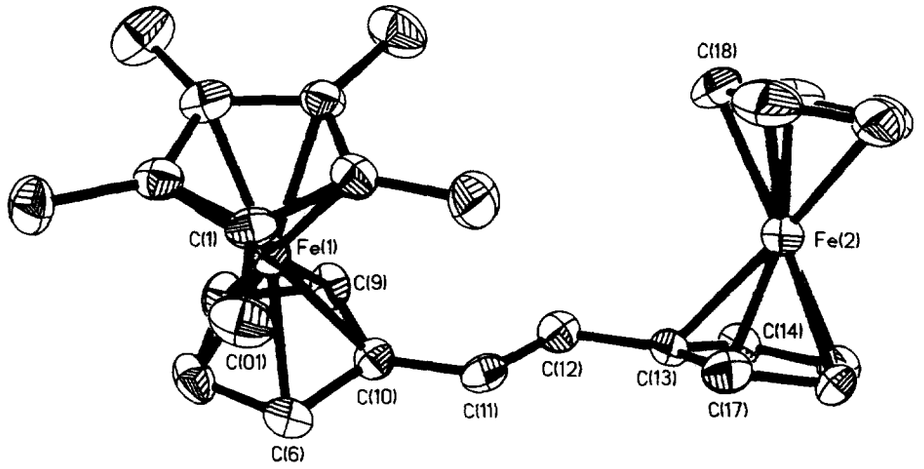


Fig. 6. Molecular structure of **9a**, showing the atom numbering scheme; Cp and Cp* carbons of ferrocene [Fe(1)] are numbered analogously to pentamethylferrocene (see Fig. 1), and Cp carbons of ferrocene [Fe(2)] are numbered from C(13)–C(17) and C(18)–C(22) respectively. Hydrogen atoms are omitted for clarity. Distances: Fe(1) to Cp plane [C(6)–C(10)] 165.4(2) pm; Fe(1) to Cp* plane [C(1)–C(5)] 164.8(2) pm; Fe(2) to Cp plane [C(13)–C(17)] 164.9(2) pm, Fe(2) to Cp plane [C(18)–C(22)] 165.9(2) pm. Angles: Cp plane [C(6)–C(10)] to Cp* plane [C(1)–C(5)] 0.23(30)°; Cp plane [C(13)–C(17)] to Cp plane [C(18)–C(22)] 2.31(43)°; Cp plane [C(6)–C(10)] to Cp plane [C(13)–C(17)] 38.40(22)°; C(12)–C(11)–C(10)–C(9) −13.12(73)°; C(11)–C(12)–C(13)–C(17) −26.48(70)°.

ylferrocenyl)methane (**13**) with Cp* Fe(acac) and might also be converted to termetallocenes, in analogy to published work on the respective octamethylferrocene compounds [49]. Like the congested bis(pentamethylferrocenyl)ketone (**2**), where reduction of the carbonyl group is prevented by the steric bulk of the Cp* ligands (see above), the alternative pathway to the desired bis(pentamethylferrocenyl)methylium cation by abstraction of hydride from bis(pentamethylferrocenyl)methane (**13**) with trityl cation [50] was also unsuccessful, probably due to steric hindrance. Trityl tetrafluoroborate does react with **13**, but only the green mixed-valence iron(II)/iron(III) oxidation product $\mathbf{13}^+ \cdot \mathbf{BF_4}$ was observed, which is only stable in the solid state, according to mass spectroscopy. Crystallization afforded green single crystals of decamethylferrocenium tetrafluoroborate as shown by X-ray analysis and cyclic voltammetry, indicative of decomposition in solution and ligand scrambling of $\mathbf{13}^+ \cdot \mathbf{BF_4}$.

To summarize these preparative results, a wide variety of functionally substituted pentamethylferrocenes is synthetically available, either by the indirect route (i) or by the direct route (ii). In analogy to established chemistry of the respective unmethylated ferrocenes, further derivatizations of these new metallocenes seems feasible, as indicated above, and might give access to improved materials according to the effects of the Cp* ligand as implied in the Introduction.

2.4. Electrochemistry

Qualitatively, the presence of one pentamethylated cyclopentadienyl ring in these compounds is expected to have steric and electronic consequences, in comparison to non-methylated ferrocenes. Whereas the steric bulk of the Cp* ligand is easily recognized in the crystal structures described in the sections above, and is for example also evidenced by the failure of the attempted synthesis of bis(pentamethylferrocenyl)methylium cation, electronically the Cp* ligand is generally considered to be more electron-rich in comparison to Cp. Hence cyclic voltammetric measurements were performed to quantify the combined donor effect of the five methyl substituents (Table 1, Fig. 7).

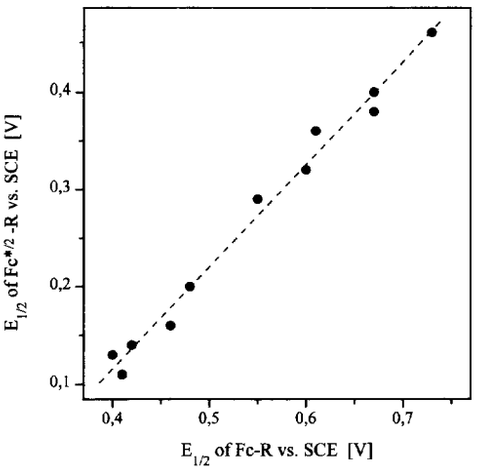


Fig. 7. Linear correlation of the half-wave potentials of pentamethylferrocenes $Fc^{*/2}$–R versus those of ferrocenes Fc–R with the same substituent R: $E_{1/2}[Fc^{*/2}\text{–R}] = 1.049 \cdot E_{1/2}[\text{Fc–R}] - 0.304$. Correlation coefficient 0.9933.

Fig. 7 shows the direct comparison of penta- and non-methylated ferrocenes with the same functional group attached to the metallocenyl moiety. The slope of 1.049 suggests that in both series of compounds ($Fc^{*/2}$–R and Fc–R) the electronic effect of the functional substituent R contributes to the same extent to the measured Fe(II)/Fe(III) couple, justifing the division of the half-wave potential into additive contributions by the different ligands Cp–R and Cp*. The intercept of −0.304 V corresponds to the electronic contribution of the five methyl groups, but this value should be regarded as an estimate only, because of the slope of

Table 1
Electrochemical data of ferrocene and pentamethylferrocene derivatives

Substituent R	$E_{1/2}$ of Fc–R [a]	Ref. [b]	Compound	$E_{1/2}$ of $Fc^{*/2}$–R [a,c]	$\Delta E_{1/2}$ [d]
CH=CH (*trans*)	0.41 and 0.55	[51]	$Fc^{*/2}$–CH=CH–$Fc^{*/2}$ [5]	0.11 and 0.29	0.30 and 0.26
CH_2–OH	0.40	[52]	$Fc^{*/2}$–CH_2–OH [5]	0.13	0.27
H	0.42	this work	$Fc^{*/2}$–H	0.14 [e]	0.28
CH_2–$N(CH_3)_2$	0.46	this work	**4**	0.16	0.29
CH=CH_2	0.48	[53]	**8**	0.20	0.28
C≡C–H	0.60	this work	**11**	0.32	0.28
CO_2H	0.61	[54]	**1**	0.36	0.25
COC_6H_5	0.67	this work	**6**	0.38	0.29
$COCH_3$	0.67	[55]	**5**	0.40	0.27
CHO	0.73	[53]	$Fc^{*/2}$–CHO	0.46	0.27

[a] Half-wave potentials for the reaction $[(Fc \text{ or } Fc^{*/2})\text{–R}]^+ + e^- \leftrightarrow [(Fc \text{ or } Fc^{*/2})\text{–R}]$ in volts vs. SCE; Fc = CpFeCp, $Fc^{*/2}$ = Cp* FeCp.
[b] In CH_3CN solution; solvent correction according to Ref. [53] where applicable.
[c] Determined by cyclic voltammetry in CH_3CN solution with 0.1 M $[(nBu)_4N]PF_6$ electrolyte with a scan rate of 100 mV s^{-1} at 20 °C.
[d] $\Delta E_{1/2} = |E_{1/2}(\text{Fc–R}) - E_{1/2}(Fc^{*/2}\text{–R})|$.
[e] Compare Refs. [2,12,56].

1.049 which is not exactly unity. Therefore this contribution of the Cp^* ligand is more accurately calculated from the mean difference of the potentials of $Fc^{*/2}$–R and Fc–R.

As can be seen from inspection of Table 1, the oxidation potentials increase with increasing acceptor strength of the functional group attached to the pentamethylferrocene moiety, as expected. In comparison of pentamethylferrocenes $Fc^{*/2}$–R to non-methylated ferrocenes Fc–R with the same functional group R, the half-wave potentials differ by 0.30 to 0.25 V, corresponding to a combined contribution of −0.276 V (mean $\Delta E_{1/2}$ with standard deviation 0.014) per Cp^* and an averaged contribution of −0.055 V per methyl group. The electrochemical parametrization in sandwich complexes by a linear ligand parameter approach has recently been published [57] and the measured and calculated oxidation potentials for compounds **1** [$E_{1/2}$(exp) = 0.36 V; $E_{1/2}$(calc) = 0.38 V], **6** [$E_{1/2}$(exp) = 0.40 V; $E_{1/2}$(calc) = 0.38 V], and pentamethylferrocenyl aldehyde [$E_{1/2}$(exp) = 0.46 V; $E_{1/2}$(calc) = 0.43 V] (where the ligand parameters [57] are available) are in reasonable agreement. It is also noteworthy that the calculated difference (ΔE_L = 0.27 V) in the ligand parameters of Cp (E_L = 0.33 V) and Cp^* (E_L = 0.06 V) [57] matches the experimentally found combined contribution of 0.276 V per Cp^* ligand. Also, the half-wave potentials of the pentamethylferrocene derivatives correlate linearly with the dual substituent F parameter of Swain and Lupton [58] (correlation coefficient 0.9705) and with the Hammett σ_m parameter [58] (correlation coefficient 0.9676), similar to other series of ferrocene compounds [59].

3. Conclusions

A systematic investigation of the possible derivatizations of pentamethylferrocene $Fc^{*/2}$ has been carried out, affording a range of functionalized ferrocenes $Fc^{*/2}$–R with the solubilizing and electron-donating Cp^* ligand, which might be of use for further chemistry in analogy to non-methylated ferrocenes Fc–R. Although the target compounds $Fc^{*/2}$–R can mostly be synthesized in an analogous manner as the corresponding unmethylated ferrocenes Fc–R, in some cases the increase in steric bulk and electron-donation caused by the Cp^* ligand either prevents the synthesis of the desired compounds (bis(pentamethylferrocenyl methylium cation and tetra(pentamethylferrocenyl)ethylene, for example) or affords unexpected follow-up products (dimerization of pentamethylferrocenyl(phenyl)methylium cation, for example). This electronic influence of the five methyl groups of the Cp^* ligand in these unsymmetrical ferrocenes $Fc^{*/2}$–R has been studied by cyclic voltammetry measurements, demonstrating a decrease in oxidation potential of −0.276 V in direct comparison to non-methylated ferrocenes Fc–R.

4. Experimental section

Standard techniques and instrumentation for spectroscopic and physical measurements have been described elsewhere [28,29,31].

Cyclic voltammetric measurements were performed at room temperature with a POS 88 potentiostat (Bank Elektronik), using a standard three-electrode apparatus, an atmosphere of purified argon, acetonitrile as solvent, and 0.1 M tetrabutylammonium hexafluorophosphate ([TBA]PF_6) as the conducting salt. The signals were referenced to the saturated calomel electrode (SCE) by calculating the correspoding half-wave potentials from cobaltocenium/cobaltocene as an internal standard versus SCE (SCE; $E_{1/2}$ = −0.93 V).

X-ray structure determinations of pentamethylferrocene (CA Reg. No. 83928-47-6), decamethyl(dihydro)fulvalene (CA Reg. No. 69446-48-6), **2**, **5**, $\mathbf{7}^{(2+)} \cdot (\mathbf{BF_4})_2$, and **9a** (Tables 2–8, Figs. 1–6). General procedures of data collection, structure solution, and refinement were as recently published [31]. The authors have deposited atomic coordinates for all structures with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, Lensfield Road, Cambridge CB2 1EW, UK.

4.1. Pentamethylferrocene (CAS Reg. No. 83928-47-6) and decamethyl(dihydro)fulvalene (CAS Reg. No. 69446-48-6)

Since the reported synthesis and yield [2,8–14] are at variance with our results, full details for the preparation of pentamethylferrocene are given. A Schlenk vessel was charged with 50 ml dry, deoxygenated THF and 6.4 ml (39.4 mmol) pentamethylcyclopentadiene [60] under an atmosphere of argon. The contents was cooled by means of an N_2(l)/EtOH cooling bath to −80 °C and 19.8 ml of a 2.0 molar solution of n-butyl lithium in hexane (39.4 mmol) was added. The cooling bath was removed and the mixture was allowed to warm to room temperature with magnetic stirring. The resulting solution of lithium pentamethylcyclopentadienide was cooled to −80 °C and 10 g (39.4 mmol) iron(II)bis(acetylacetonate) [10] was added in one portion under efficient stirring. After removal of the cooling bath the mixture was allowed to warm to room temperature and stirred for a further 30 min. At −80 °C 19.8 ml (39.4 mmol) sodium cyclopentadienide (2.0 M in THF) was added and stirring was continued for a further 2 h during which time the mixture was allowed to warm to room temperature. Solvents and volatile

materials were removed in vacuo and the resulting crude product mixture was filtered through a short column of basic alumina with hexane as eluent to remove inorganic salts. After removal of hexane on a rotary evaporator the crude product (5.5 g) was shown by TLC and NMR to consist of a mixture of pentameth-

Table 2
Crystal data and structure refinement for pentamethylferrocene, decamethyl(dihydro)fulvalene, **2**, **5**, $\mathbf{7}^{(2+)} \cdot (\mathbf{BF_4})_2$, **9a**

	Pentamethylferrocene	Decamethyl(dihydro)fulvalene	**2**
Molecular formula	$C_{15}H_{20}Fe$	$C_{40}H_{60}$	$C_{31}H_{38}Fe_2O$
Formula weight	256.16	540.88	538.31
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a (pm)	776.6(2)	1101.1(4)	1232.9(2)
b (pm)	817.2(2)	1230.2(2)	1598.8(3)
c (pm)	1218.1(3)	1340.4(3)	1448.6(3)
α (°)	72.55(1)	78.21(2)	90
β (°)	84.73(1)	78.82(2)	113.59(2)
γ (°)	62.03(1)	84.32(2)	90
Volume (nm^3)	0.6502(3)	1.7403(8)	2.6168(8)
Z	2	2	4
Temperature (K)	213	293	223
Density, calc. ($Mg\,m^{-3}$)	1.308	1.032	1.366
Absorption coefficient (mm^{-1})	1.130	0.057	1.130
$F(000)$	272	600	1136
Color, habit	yellow column	colorless block	orange prism
Crystal size (mm^3)	$0.20 \times 0.25 \times 0.60$	$0.8 \times 0.6 \times 0.4$	$0.28 \times 0.15 \times 0.09$
θ range for data collection (°)	3.07 to 24.00	3.05 to 23.50	2.55 to 19.99
Index ranges	$-1 \le h \le 8$, $-8 \le k \le 8$, $-13 \le l \le 13$	$-1 \le h \le 12$, $-13 \le k \le 13$, $-14 \le l \le 15$	$-1 \le h \le 11$, $-1 \le k \le 15$, $-13 \le l \le 13$
Reflections collected	2490	5425	3139
Independent reflections	1989 ($R_{int} = 0.0183$)	5118 ($R_{int} = 0.0123$)	2429 ($R_{int} = 0.0425$)
Reflections with $I > 2\sigma(I)$	1767	4075	1606
Absorption correction	none	none	none
Max. and min. transmission	—	—	—
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1989/0/225	5110/0/602	2427/0/317
Goodness-of-fit on F^2	1.079	1.051	1.020
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0294$, $wR_2 = 0.0709$	$R_1 = 0.0478$, $wR_2 = 0.1163$	$R_1 = 0.0491$, $wR_2 = 0.0868$
R indices (all data)	$R_1 = 0.0367$, $wR_2 = 0.0746$	$R_1 = 0.0641$, $wR_2 = 0.1339$	$R_1 = 0.0957$, $wR_2 = 0.1039$
Largest diff. peak and hole ($e\,nm^{-3}$)	254 and −235	202 and −177	282 and −271
	5	$\mathbf{7}^{(2+)} \cdot (\mathbf{BF_4})_2$	**9a**
Molecular formula	$C_{17}H_{22}FeO$	$C_{44}H_{52}B_2F_8Fe_2 \cdot (CH_2Cl_2)_{1/2}$	$C_{27}H_{30}Fe_2$
Formula weight	298.20	913.93	466.21
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_1/c$ (No. 14)
a (pm)	749.4(2)	2565.4(4)	1415.2(4)
b (pm)	1547.2(2)	1514.1(3)	1286.8(2)
c (pm)	1302.2(2)	1293.4(2)	1285.1(3)
α (°)	90	90	88.24(1)
β (°)	103.25(2)	116.72(2)	90
γ (°)	90	90	108.34(2)
Volume (nm^3)	1.4697(5)	4.4874(13)	90
Z	4	4	4
Temperature (K)	213	213	223
Density, calc. ($Mg\,m^{-3}$)	1.348	1.353	1.394
Absorption coefficient (mm^{-1})	1.016	0.742	1.316
$F(000)$	632	1898	976
Color, habit	yellow platelet	green platelet	orange prism
Crystal size (mm^3)	$0.6 \times 0.5 \times 0.6$	$0.6 \times 0.3 \times 0.1$	$0.3 \times 0.22 \times 0.1$
θ range for data collection (°)	3.08 to 24.00	3.16 to 23.94	3.03 to 22.00
Index ranges	$-1 \le h \le 8$, $-1 \le k \le 17$, $-14 \le l \le 14$	$0 \le h \le 28$, $-1 \le k \le 17$, $-14 \le l \le 13$	$-13 \le h \le 14$, $-1 \le k \le 13$, $-1 \le l \le 13$

Table 2 (continued)

	5	$7^{(2+)} \cdot (BF_4)_2$	9a
Reflections collected	3132	3362	3486
Independent reflections	2311 ($R_{int} = 0.0228$)	3242 ($R_{int} = 0.0322$)	2719 ($R_{int} = 0.0302$)
Reflections with $I > 2\sigma(I)$	1917	2418	1961
Absorption correction	ψ-scan	ψ-scan	ψ-scan
Max. and min. transmission	0.930 and 0.813	0.913 and 0.756	0.919 and 0.812
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2311/0/260	2964/0/285	2719/0/322
Goodness-of-fit on F^2	1.042	1.061	1.045
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0311$, $wR_2 = 0.0708$	$R_1 = 0.0557$, $wR_2 = 0.1302$	$R_1 = 0.0383$, $wR_2 = 0.0738$
R indices (all data)	$R_1 = 0.0437$, $wR_2 = 0.0767$	$R_1 = 0.0843$, $wR_2 = 0.1530$	$R_1 = 0.0693$, $wR_2 = 0.0844$
Largest diff. peak and hole (e nm^{-3})	221 and −231	550 and −281	262 and −312

ylferrocene (75–80% yield by NMR), decamethyldihydrofulvalene [15,16] (20–25% yield) and negligible traces of ferrocene (the calculated yield, corresponding to 80% pentamethylferrocene, is 86.7%). These two compounds can be separated by chromatography, but due to similar retention values most fractions contain both compounds and only a small amount of pure pentamethylferrocene can be obtained in this manner. Attempted separation by fractional sublimation according to a reported procedure [9] was unsuccessful and selective oxidation [12] of pentamethylferrocene with various oxidation agents to remove unoxidized and hence apolar dihydrofulvalene by liquid/liquid extraction with dichloromethane/n-hexane was also of no preparative value, because of fast symmetrization of pentamethylferricenium to ferrocene and ferricenium within a few minutes (see Section 2). For analytical purposes the chromatographed pure pentamethylferrocene was used and for most further reactions, where no interference with dihydrofulvalene seemed possible,

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm$^2 \times 10^{-1}$) for pentamethylferrocene (CA Reg. No. 83928-47-6)

Atom	x	y	z	U_{eq}
Fe(1)	1852(1)	1247(1)	7285(1)	26(1)
C(1)	4761(4)	−515(4)	7704(2)	36(1)
C(2)	3703(4)	−345(4)	8720(2)	40(1)
C(3)	2726(4)	1655(5)	8665(2)	41(1)
C(4)	3190(4)	2692(4)	7620(2)	37(1)
C(5)	4436(4)	1351(4)	7027(2)	34(1)
C(6)	902(4)	52(4)	6371(2)	37(1)
C(7)	−116(4)	221(5)	7384(3)	42(1)
C(8)	−1086(4)	2189(5)	7344(3)	44(1)
C(9)	−660(4)	3244(4)	6299(3)	41(1)
C(10)	564(4)	1920(4)	5707(2)	35(1)
C(01)	6063(6)	−2387(6)	7427(5)	72(1)
C(02)	3635(9)	−1955(9)	9690(4)	85(2)
C(03)	1467(7)	2540(11)	9555(4)	85(2)
C(04)	2550(7)	4844(5)	7215(5)	72(1)
C(05)	5300(6)	1818(7)	5880(3)	60(1)

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

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (pm$^2 \times 10^{-1}$) for decamethyl(dihydro)fulvalene (CA Reg. No. 69446-48-6)

Atom	x	y	z	U_{eq}
Molecule A				
C(1)	2555(2)	1896(2)	4484(1)	36(1)
C(2)	1310(2)	2131(2)	4117(2)	44(1)
C(3)	407(2)	1709(2)	4887(2)	47(1)
C(4)	934(2)	1204(2)	5815(2)	43(1)
C(5)	2162(2)	1325(2)	5613(1)	36(1)
C(6)	3322(2)	2956(2)	4380(1)	34(1)
C(7)	4590(2)	2710(2)	4719(1)	36(1)
C(8)	4642(2)	3288(2)	5456(1)	37(1)
C(9)	3451(2)	3929(2)	5690(1)	36(1)
C(10)	2676(2)	3743(1)	5096(1)	35(1)
C(01)	3291(2)	1011(2)	3892(2)	48(1)
C(02)	1141(3)	2611(3)	3022(2)	67(1)
C(03)	−949(2)	1710(3)	4858(3)	74(1)
C(04)	182(3)	605(2)	6797(2)	65(1)
C(05)	3051(2)	914(2)	6342(2)	49(1)
C(06)	3564(2)	3637(2)	3261(2)	45(1)
C(07)	5677(2)	2066(2)	4198(2)	52(1)
C(08)	5728(2)	3336(2)	5963(2)	50(1)
C(09)	3244(2)	4706(2)	6449(2)	50(1)
C(010)	1400(2)	4280(2)	5045(2)	48(1)
Molecule B				
C(11)	2492(2)	6652(2)	413(1)	38(1)
C(12)	1565(2)	6808(2)	1388(1)	37(1)
C(13)	403(2)	6827(2)	1210(2)	42(1)
C(14)	442(2)	6662(2)	149(2)	43(1)
C(15)	1622(2)	6575(2)	−334(1)	43(1)
C(16)	3388(2)	7654(2)	37(1)	39(1)
C(17)	4315(2)	7696(2)	742(2)	41(1)
C(18)	4142(2)	8671(2)	1068(2)	43(1)
C(19)	3095(2)	9326(2)	657(2)	45(1)
C(20)	2653(2)	8770(2)	59(2)	43(1)
C(011)	3197(2)	5502(2)	626(2)	53(1)
C(012)	1938(2)	6862(2)	2391(2)	50(1)
C(013)	−798(3)	6994(3)	1934(2)	72(1)
C(014)	−703(3)	6573(3)	−274(2)	65(1)
C(015)	2040(3)	6283(3)	−1393(2)	70(1)
C(016)	4150(3)	7653(2)	−1057(2)	60(1)
C(017)	5386(2)	6859(2)	900(3)	64(1)
C(018)	4893(3)	9091(2)	1716(2)	64(1)
C(019)	2646(3)	10465(2)	885(3)	73(1)
C(020)	1649(3)	9183(2)	−558(2)	67(1)

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

the mixture (5.5 g, 75–80% pentamethylferrocene by NMR) was employed as starting material.

4.1.1. Data for pentamethylferrocene

M.p. 92–93 °C. MS (EI, 70 eV): *m/z* (%) 256 (M^+, 100); 135 ($M^+ - FeCp$, 90). IR data (KBr, cm^{-1}): 3099m, 2966m, 2902m, 2858m, 1380s, 1106s, 1071s, 1032s, 1000s, 805s. ^1H NMR ($CDCl_3$): δ 1.94 (15H, s, CH_3), 3.70 (5H, s, Cp). ^{13}C NMR ($CDCl_3$): δ 11.4 (CH_3), 71.1 (Cp), 80.1 (Cp^*). CV (CH_3CN, 273 K) (V): 0.14. X-ray structure (Tables 2 and 3, Fig. 1): single crystals were obtained from CH_2Cl_2/EtOH.

4.1.2. Data for decamethyldihydrofulvalene

M.p. 53 °C. MS (EI, 70 eV): *m/z* (%) 270 (M^+, 100); 135 ($M^+ - Cp^*$, 93). IR data (KBr, cm^{-1}): 2959w, 2914w, 2860w, 1767m, 1652m, 1634m, 1559m, 1507m, 1443s, 1380s, 1262s, 1191m, 1106s, 1063s, 1023s, 863s, 695s. ^1H NMR ($CDCl_3$): δ 1.03 (6H, s, CH_3), 1.60 (12H, s, CH_3), 1.63 (12H, s, CH_3). ^{13}C NMR ($CDCl_3$): δ 10.86 (CH_3), 19.29 (CH_3). X-ray structure (Tables 2 and 4, Fig. 2): single crystals were obtained from n-hexane.

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **2**

Atom	*x*	*y*	*z*	U_{eq}
Fe(1)	2166(1)	1789(1)	2875(1)	26(1)
Fe(2)	−2320(1)	479(1)	2305(1)	28(1)
O(1)	−969(5)	1962(3)	970(4)	60(2)
C(11)	−551(7)	1562(5)	1757(6)	36(2)
C(1)	2741(7)	1769(5)	1735(5)	36(2)
C(2)	3699(6)	1965(5)	2676(5)	31(2)
C(3)	3835(6)	1293(5)	3347(5)	31(2)
C(4)	2959(7)	673(5)	2826(6)	32(2)
C(5)	2283(7)	969(6)	1834(6)	39(2)
C(6)	940(7)	2714(5)	2549(6)	36(2)
C(7)	1894(7)	2878(5)	3476(7)	42(2)
C(8)	1976(7)	2224(5)	4144(6)	39(2)
C(9)	1092(7)	1631(5)	3632(5)	34(2)
C(10)	418(6)	1933(5)	2623(5)	29(2)
C(21)	−2383(7)	843(5)	3635(5)	35(2)
C(22)	−3232(8)	207(5)	3172(6)	41(2)
C(23)	−4029(7)	504(6)	2199(6)	44(2)
C(24)	−3645(7)	1313(6)	2070(6)	37(2)
C(25)	−2642(7)	1531(4)	2960(6)	29(2)
C(26)	−640(6)	78(5)	2556(5)	30(2)
C(27)	−1443(7)	−593(5)	2219(6)	40(2)
C(28)	−2328(7)	−392(5)	1261(6)	39(2)
C(29)	−2075(7)	416(5)	999(5)	37(2)
C(30)	−1022(6)	718(5)	1800(5)	24(2)
C(01)	2309(7)	2303(5)	793(6)	69(3)
C(02)	4437(7)	2738(5)	2910(6)	54(3)
C(03)	4759(6)	1217(5)	4393(5)	49(2)
C(04)	2817(7)	−167(4)	3240(6)	51(3)
C(05)	1311(6)	506(5)	1005(5)	56(3)
C(021)	−1403(7)	803(5)	4682(5)	55(3)
C(022)	−3307(9)	−621(5)	3631(6)	73(3)
C(023)	−5086(7)	24(6)	1468(6)	79(3)
C(024)	−4209(8)	1869(6)	1156(6)	83(3)
C(025)	−1987(7)	2354(4)	3166(6)	52(3)

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

Table 6
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **5**

Atom	*x*	*y*	*z*	U_{eq}
Fe(1)	8257(1)	720(1)	2421(1)	23(1)
O(1)	11092(3)	2537(2)	1655(2)	59(1)
C(1)	7258(4)	1099(2)	3695(2)	29(1)
C(2)	6352(3)	331(2)	3229(2)	27(1)
C(3)	5485(3)	515(2)	2152(2)	27(1)
C(4)	5856(3)	1400(2)	1945(2)	29(1)
C(5)	6936(3)	1758(2)	2899(2)	30(1)
C(6)	10966(4)	418(2)	2932(2)	29(1)
C(7)	9999(4)	−311(2)	2446(2)	32(1)
C(8)	9153(4)	−85(2)	1391(2)	35(1)
C(9)	9591(4)	779(2)	1220(2)	33(1)
C(10)	10739(3)	1109(2)	2178(2)	28(1)
C(11)	11402(4)	1996(2)	2356(2)	40(1)
C(12)	12507(5)	2227(3)	3438(3)	54(1)
C(01)	8272(5)	1202(3)	4817(2)	43(1)
C(02)	6261(5)	−514(2)	3780(3)	40(1)
C(03)	4356(4)	−111(2)	1396(3)	38(1)
C(04)	5163(5)	1875(3)	927(3)	47(1)
C(05)	7539(6)	2683(2)	3049(4)	50(1)

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

*4.2. 1,2,3,4,5-Pentamethylferrocene-1'-carboxylic acid (**1**)*

2.75 g (10 mmol) pentamethylferrocene was dissolved in 20 ml n-hexane and cooled to −50 °C; 3.0 ml (20 mmol) TMEDA (tetramethylethylendiamine), freshly distilled from sodium under an atmosphere of argon, and 2.40 g (20 mmol) potassium t-butoxide were added, and the mixture was stirred for a few minutes. After addition of 10.0 ml (20 mmol) n-butyl lithium (2.0 M in hexane) during the course of 10 min the mixture was stirred further for 1 h at a temperature of −20 °C, during which time the color changed from yellow to red. An excess of solid carbon dioxide was added in one portion, the cooling bath was removed, and stirring was continued for 30 min until the mixture changed its color from red to yellow. Work-up: the reaction mixture was hydrolized with ice/water, solid potassium hydroxide was added until the solution was strongly alkaline, the organic layer (containing 1.67 g, 6.5 mmol unreacted pentamethylferrocene) was separated, the alkaline aqueous layer was acidified with concentrated hydrochloric acid until neutral, the precipitated orange crude **1** was filtered off, and dried at 40 °C in vacuo, yielding 0.9 g (3.0 mmol, 86% yield, based on 3.5 mmol reacted pentamethylferrocene).

4.2.1. Data for 1

M.p. 170 °C (dec.). Anal. Found: C, 63.93; H, 6.69; O, 10.71. $C_{16}H_{20}FeO_2$ Calc.: C, 64.02; H, 6.72; O, 10.66%. MS (FAB): *m/z* (%) 300.08 (M^+, 100); 256.11 ($M^+ - CO_2H$, 27). IR data (KBr, cm^{-1}): 3200–2500m, br, 2970w, 1679s, 1382m, 1295s, 1092s, 1026s, 812s. ^1H NMR (acetone-d_6): δ 1.81 (15H, s, CH_3); 3.99, 4.02, 4.46, 4.76 (each signal: 1H, m, subst. Cp); 7.34 (1H, s, CO_2H). ^{13}C NMR analysis was attempted in various solvents but due to poor solubility no conclusive spectra were obtained. CV (CH_3CN, 273 K) (V): 0.36.

4.3. Bis(1,2,3,4,5-pentamethylferrocen-1'-yl)ketone (2)

To a solution of 350 mg (1.16 mmol) **1** in 50 ml dry deoxygenated toluene was added 245 mg (1.16 mmol) phosphorus pentachloride in three portions with external cooling by an ice/water bath. The mixture was stirred for 4 h, the dark red solution was concentrated in vacuo, and the residue was dissolved in dry dichloromethane. To the cooled (4 °C) red solution were added three portions of aluminum trichloride (194 mg, 1.46 mmol) and 375 mg (1.46 mmol) pentamethylferrocene, resulting in a dark blue solution, which was refluxed for 2 h. Work-up: the mixture was hydrolized with argon-saturated water, the organic layer was separated, washed with 10% sodium carbonate solution, dried with sodium sulfate, solvents were removed in vacuo, the crude product was chromatographed on neutral aluminum oxide with hexane/ether (v/v 2/1) as eluent, yielding 200 mg (0.78 mmol) unreacted pentamethylferrocene and 150 mg (0.28 mmol, 24% yield) **2**. With dichloromethane as eluent minor amounts of the following side-products were obtained: 1',3'-bis(1,2,3,4,5-pentamethyl-1'-ferrocenoyl)-1,2,3,4,5-pentamethylferrocene (35 mg, 0.04 mmol, 3.4% yield), ferrocenyl(1,2,3,4,5-pentamethylferrocen-1'-yl)ketone (20 mg, 0.04 mmol, 3.4% yield), and 1'-ferrocenoyl-3'-(1,2,3,4,5-pentamethylferrocenoyl-1'-yl)-1,2,3,4,5-pentamethylferrocene (5 mg, 0.007 mmol, 0.6% yield).

Table 7
Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for $7^{(2+)} \cdot (BF_4)_2$.

Atom	x	y	z	U_{eq}
Dication				
Fe(1)	1135(1)	8270(1)	242(1)	34(1)
C(1)	1128(2)	7577(3)	1645(4)	42(1)
C(2)	1144(2)	8509(3)	1842(4)	42(1)
C(3)	1660(2)	8850(3)	1836(4)	47(1)
C(4)	1961(2)	8136(3)	1621(4)	48(1)
C(5)	1635(2)	7348(3)	1517(4)	45(1)
C(6)	317(2)	8586(3)	−1109(4)	41(1)
C(7)	711(2)	9291(3)	−903(4)	45(1)
C(8)	1180(2)	8972(3)	−1096(4)	50(1)
C(9)	1070(2)	8070(3)	−1429(4)	40(1)
C(10)	530(2)	7827(3)	−1441(3)	32(1)
C(11)	195(2)	6971(3)	−1819(4)	35(1)
C(12)	556(2)	6130(3)	−1468(4)	38(1)
C(13)	452(2)	5504(3)	−802(4)	53(1)
C(14)	759(3)	4722(4)	−501(6)	77(2)
C(15)	1179(3)	4546(4)	−851(6)	77(2)
C(16)	1286(2)	5149(4)	−1525(6)	67(2)
C(17)	975(2)	5944(3)	−1850(5)	51(1)
C(01)	666(3)	6967(4)	1639(5)	64(2)
C(02)	696(3)	9019(4)	2032(5)	66(2)
C(03)	1863(3)	9797(4)	2063(5)	70(2)
C(04)	2533(2)	8200(4)	1575(5)	75(2)
C(05)	1825(3)	6438(4)	1373(5)	70(2)
Anion				
B(1)	1044(3)	2022(4)	501(6)	56(2)
F(1)	743(2)	1244(2)	367(4)	99(1)
F(2)	1063(2)	2258(4)	−492(4)	127(2)
F(3)	796(2)	2671(2)	847(4)	108(2)
F(4)	1605(2)	1888(3)	1359(4)	123(2)
Solvent molecule				
C(18)	2338(15)	2890(45)	−498(47)	125(18)
Cl(1)	2712(7)	3907(14)	−3(12)	211(9)
Cl(2)	2439(9)	2040(20)	−436(17)	206(9)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z-1/2$; #2 $-x+1/2, -y+1/2, -z$.

Table 8
Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters ($pm^2 \times 10^{-1}$) for **9a**

Atom	x	y	z	U_{eq}
Fe(1)	1550(1)	−1621(1)	−1330(1)	26(1)
Fe(2)	4218(1)	1225(1)	−3607(1)	34(1)
C(1)	1274(3)	−497(3)	−335(4)	28(1)
C(2)	450(3)	−1204(4)	−682(3)	30(1)
C(3)	89(3)	−1171(4)	−1860(4)	34(1)
C(4)	689(3)	−455(4)	−2231(4)	31(1)
C(5)	1416(3)	−34(3)	−1284(4)	28(1)
C(6)	2865(3)	−2320(3)	−490(4)	32(1)
C(7)	2081(3)	−3045(3)	−692(4)	36(1)
C(8)	1628(3)	−3118(4)	−1849(4)	37(1)
C(9)	2139(3)	−2424(3)	−2344(4)	30(1)
C(10)	2921(3)	−1930(3)	−1512(3)	27(1)
C(11)	3625(3)	−1157(3)	−1649(3)	29(1)
C(12)	3775(3)	−915(3)	−2593(4)	29(1)
C(13)	4494(3)	−140(3)	−2712(4)	29(1)
C(14)	4973(3)	−137(4)	−3538(4)	33(1)
C(15)	5638(3)	713(4)	−3352(4)	41(1)
C(16)	5569(3)	1254(4)	−2420(4)	39(1)
C(17)	4856(3)	741(4)	−2030(4)	35(1)
C(18)	2723(3)	1370(4)	−4408(5)	56(2)
C(19)	3264(4)	1410(5)	−5160(5)	60(2)
C(20)	3907(4)	2247(5)	−4882(5)	59(2)
C(21)	3792(4)	2732(4)	−3956(5)	56(2)
C(22)	3054(4)	2190(5)	−3653(5)	59(2)
C(01)	1861(5)	−243(5)	835(5)	41(1)
C(02)	16(5)	−1843(5)	31(5)	43(2)
C(03)	−794(5)	−1774(6)	−2560(6)	53(2)
C(04)	548(5)	−160(6)	−3401(5)	49(2)
C(05)	2181(4)	767(5)	−1288(6)	45(2)

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

4.3.1. Data for 2

M.p. 98–100 °C. Anal. Found: C, 69.04; H, 7.13; O, 2.96. $C_{31}H_{38}Fe_2O$ Calc.: C, 69.17; H, 7.11; O, 2.97%. MS (EI, 70 eV): *m/z* (%) 538.5 (M^+, 100); 510.5 ($M^+ - 2CH_3$, 15); 255 ($M^+ - CO–CpFeCp^*$, 55). IR data (KBr, cm^{-1}): 2966w, 1655s, 1259s, 1045s, 972s, 810s. ^1H NMR ($CDCl_3$): δ 1.69 (30H, s, CH_3); 4.00, 4.14, 4.39, 4.47 (each signal: 2H, m, subst. Cp). ^{13}C NMR ($CDCl_3$): δ 10.5 (CH_3); 70.6, 72.4, 72.6, 75.6 (Cp); 81.3 (Cp^*), not observed: carbonyl-C. X-ray structure (Tables 2 and 5, Fig. 3): single crystals were obtained from acetone.

4.3.2. Data for 1',3'-bis(1,2,3,4,5-pentamethyl-1'-ferrocenoyl)-1,2,3,4,5-pentamethylferrocene

M.p. 65 °C. MS (EI, 70 eV): *m/z* (%) 820.5 (M^+, 25); 630.5 ($M^+ - FeCp^*$, 93); 495.5 ($M^+ - FeCp^* - Cp^*$, 74). IR data (KBr, cm^{-1}): 2966m, 1663s, 1382m, 1262m, 1027s, 803s. ^1H NMR ($CDCl_3$): δ 1.68 (45H, s, CH_3); 4.06, 4.12, 4.39, 4.42, 4.49, 4.81 (10H, each signal: m, subst. Cp); 4.10 (1H, s, 2'-H of subst. Cp). ^{13}C NMR ($CDCl_3$): δ 10.8 (CH_3); 69.9–76.4 (Cp and Cp^*), not observed: carbonyl-C.

4.3.3. Data for ferrocenyl(1,2,3,4,5-pentamethylferrocen-1'-yl)ketone

M.p. not available, oily liquid. MS (EI, 70 eV): *m/z* (%) 468.5 (M^+, 100). HR-MS (FAB): *m/z* 468.07888 (M^+; exact mass calc. for $C_{26}H_{28}Fe_2O$, 468.08389). IR data (KBr, cm^{-1}): 2966m, 1680s, 1382m, 1258m, 1090s, 1042s, 975m, 810s. ^1H NMR ($CDCl_3$): δ 1.70 (15H, s, CH_3); 4.05, 4.44, 4.46, 4.87 (8H, each signal: m, subst. Cp); 4.10 (5H, s, unsubst. Cp of ferrocenyl). ^{13}C NMR ($CDCl_3$): δ 10.5 (CH_3); 69.9–81.5 (Cp and Cp^*), not observed: carbonyl-C.

4.3.4. Data for 1'-ferrocenoyl-3'-(1,2,3,4,5-pentamethylferroceno-1'-yl)-1,2,3,4,5-pentamethylferrocene

Due to only 5 mg material available, only MS and IR analysis was possible. MS (EI, 70 eV): *m/z* (%) 750.5 (M^+, 45), 630 ($M^* - FeCp$, 100). HR-MS (FAB): *m/z* 750.15478 (M^+; exact mass calc. for $C_{42}H_{46}Fe_3O$, 750.15458). IR data (KBr, cm^{-1}) 2966m, 1675s, 1381m, 1262m, 1088m, 1027s, 803s.

4.4. Bis(1,2,3,4,5-pentamethylferrocen-1'-yl)thioketone (3)

A Schlenk vessel was charged with 100 mg (0.19 mmol) bis(1,2,3,4,5-pentamethylferrocen-1'-yl)ketone (**2**), 129 mg (0.29 mmol) P_4S_{10}, 96 mg (1.14 mmol) $NaHCO_3$, and 20 ml dry deoxygenated acetonitrile. The vessel was immersed in an ultrasonic cleaning bath and sonicated for 12 h. Chromatographic work-up (aluminum oxide, n-hexane) yielded **3** as dark blue oil (30 mg, 0.054 mmol, 18.5%) and 95 mg starting ketone (**2**). Thioketone (**3**) is only of limited stability, preventing NMR analysis due to decomposition in solution.

4.4.1. Data for 3

Anal. Found: C, 66.87; H, 6.89. $C_{31}H_{38}Fe_2S$ Calc.: C, 67.16; H, 6.91%. MS (EI, 30 eV): *m/z* (%) 554 (M^+, 16); 524 ($M^+ - S$, 35). IR data (KBr, cm^{-1}): 2964w, 2927w, 2856w, 1263s, 1096s, 1027s, 805s.

4.5. 1'-(N,N-dimethylaminomethyl)-1,2,3,4,5-pentamethylferrocene (4)

The experimental procedure was adapted from the synthesis of N,N-dimethylaminoferrocene [33]. A Schlenk vessel was charged with 150 ml glacial acetic acid, 10 ml 85% phosphoric acid, 2.64 ml (19.5 mmol) bis(dimethylamino)methane, and 3.0 g (11.7 mmol) pentamethylferrocene. The mixture was refluxed for 5 h, during which time the color changed from yellow to green. After cooling to room temperature the solution was diluted with 100 ml water and the aqueous phase was extracted with diethylether, to recover unreacted pentamethylferrocene (480 mg). The aqueous layer was made alkaline by careful addition of approximately 5.0 g solid sodium hydroxide with external cooling, causing separation of a yellowish gel, which was made fluid by adding the same volume of water. Extraction with ether, drying with sodium sulfate, and removal of solvent in vacuo afforded 2.9 g (9.3 mmol, 79.5% yield) of **4** as a dark red mobile liquid.

4.5.1. Data for 4

Anal. Found: C, 69.22; H, 8.70; N, 4.45. $C_{18}H_{27}FeN$ Calc.: C, 69.01; H, 8.69; N, 4.47%. MS (EI, 70 eV): *m/z* (%) 313 (M^+, 100); 298 ($M^+ - CH_3$, 22); 283 ($M^+ - 2CH_3$, 6); 268 ($M^+ - N(CH_3)_2$, 86); 256 ($M^+ - CH_2N(CH_3)_2$, 6). IR data (KBr, cm^{-1}): 2968w, 2908w, 2858w, 2817w, 1457w, 1264s, 911s. ^1H NMR ($CDCl_3$): δ 1.85 (15H, s, CH_3); 2.14 (6H, s, $N(CH_3)_2$); 3.10 (2H, s, CH_2); 3.56, 3.62, (4H, each signal: m, subst. Cp). ^{13}C NMR ($CDCl_3$): δ 11.1 (CH_3); 44.5 ($N(CH_3)_2$); 58.1 (CH_2); 72.2, 72.4, 80.0 (Cp and Cp^*). CV (CH_3CN, 273 K) (V): 0.16.

4.6. 1,2,3,4,5-Pentamethylferrocen-1'-yl aldehyde (CAS Reg. No. 135774-00-4)

Although this is a known compound, the reported synthesis [4] gives only a product mixture and only ^1H NMR spectral data are reported, therefore we describe the preparation in detail. According to a published procedure [36], lithium cyclopentadienide (1 g, 13.9 mmol) and methyl formate (1.25 ml, 20.9 mmol) were refluxed in THF for 2 h. In the meantime, pentamethylcyclopentadiene (4.3 ml, 27.8 mmol) was lithiated with n-butyl lithium (13.9 ml of a 2.0 M solution in

hexane, 27.8 mmol), converted with iron(II)bis(acetylcetonate) (7.1 g, 27.8 mmol) to the corresponding pentamethylcyclopentadienyl-iron(II)acetylacetonate [10], and added to the solution containing lithium formylcyclopentadienide (from above) at a temperature of −80 °C. The mixture was allowed to warm to room temperature under efficient stirring. Work-up: volatile materials and solvents were removed in vacuo, the resulting crude product mixture was chromatographed on neutral aluminum oxide with diethylether/n-hexane (v/v 1/1) as eluent, yielding two fractions. The first yellow fraction (1.95 g in total) consisted of pentamethylferrocene, decamethyl(dihydro)fulvalene, and decamethylferrocene. The second red fraction yielded 1.82 g (6.4 mmol, 46.1%) pure 1,2,3,4,5-pentamethylferrocen-1′-yl aldehyde as a red oil.

4.6.1. Data for 1,2,3,4,5-pentamethylferrocen-1′-yl aldehyde

MS (EI, 70 eV): *m/z* (%) 284.5 (M^+, 100); 255.5 ($M^+ - CHO$, 54). IR data (KBr, cm^{-1}): 2968w, 2914w, 2861w, 1690s, 1455m, 1383m, 1246s, 1034s, 822s. ^1H NMR ($CDCl_3$): δ 1.81 (15H, s, CH_3); 4.14, 4.23 (each signal: 2H, m, subst. Cp); 9.67 (1H, s, CHO). ^{13}C NMR ($CDCl_3$): δ 10.9 (CH_3); 71.8, 76.3 (Cp); 82.2 (Cp^*), 193.8 (CHO). CV (CH_3CN, 273 K) (V): 0.46.

4.7. 1,2,3,4,5-Pentamethyl-1′-acetyl-ferrocene (5)

According to a published procedure [36], lithium cyclopentadienide (400 mg, 5.5 mmol) and ethyl acetate (0.69 ml, 7 mmol) were refluxed in THF for 2 h. In the meantime, pentamethylcyclopentadiene (1.7 ml, 11.0 mmol) was lithiated with n-butyl lithium (5.5 ml of a 2.0 M solution in hexane, 11.0 mmol), converted with iron(II)bis(acetylcetonate) (3.3 g, 11.0 mmol) to the corresponding pentamethylcyclopentadienyl-iron(II)acetylacetonate [10], and added to the solution containing lithium acetylcyclopentadienide (from above) at a temperature of −80 °C. The mixture was allowed to warm to room temperature under efficient stirring. Similar work-up as described for 1,2,3,4,5-pentamethylferrocenyl aldehyde yielded two fractions. The first yellow fraction (1.11 g in total) consisted of pentamethylferrocene, decamethyl(dihydro)fulvalene, and decamethylferrocene. The second red fraction yielded 600 mg (2.1 mmol, 39%) pure 1,2,3,4,5-pentamethyl-1′-acetyl-ferrocene (**5**) as red crystals.

4.7.1. Data for 5

M.p. 101–103 °C. Anal. Found: C, 68.35; H, 7.43; O, 5.35. $C_{17}H_{22}FeO$ Calc.: C, 68.47; H, 7.44; O, 5.37%. MS (EI, 70 eV): *m/z* (%) 298 (M^+, 100); 255.5 ($M^+ - COCH_3$, 74). IR data (KBr, cm^{-1}): 2972w, 2916w, 1617s, 1454m, 1380m, 1277s, 1084s, 1014s, 820s. ^1H NMR ($CDCl_3$): δ 1.79 (15H, s, CH_3); 2.22 (3H, s, $COCH_3$); 4.02, 4.22 (each signal: 2H, m, subst. Cp). ^{13}C NMR ($CDCl_3$): δ 10.5 (CH_3); 27.6 ($COCH_3$); 72.0, 76.4 (Cp); 81.4 (Cp^*), not observed: ($COCH_3$). CV (CH_3CN, 273 K) (V): 0.40. X-ray structure (Tables 2 and 6, Fig. 4): single crystals were obtained from n-hexane/ether.

4.8. Phenyl(1,2,3,4,5-pentamethylferrocen-1′-yl)ketone (6)

To a solution of 1.02 ml (8.81 mmol) benzoyl chloride in 20 ml THF was added dropwise 2.94 ml of 2.0 molar THF solution of sodium cyclopentadienide (5.87 mmol). After stirring the yellow–orange suspension for 30 min at room temperature, 790 mg (7.04 mmol) potassium t-butoxide was added and the red mixture was stirred for a further 1 h. In the meantime, pentamethylcyclopentadiene (1.81 ml, 11.74 mmol) was lithiated with n-butyl lithium (5.88 ml of a 2.0 M solution in hexane, 11.74 mmol), converted with iron(II)bis(acetylcetonate) (3.0 g, 11.74 mmol) to the corresponding pentamethylcyclopentadienyl-iron(II)acetylacetonate [10], and added to the solution containing potassium benzoylcyclopentadienide (from above) at a temperature of −80 °C. The mixture was allowed to warm to room temperature overnight under efficient stirring. Work-up: volatile materials and solvents were removed in vacuo, the resulting crude product mixture was chromatographed on neutral aluminum oxide with diethylether/n-hexane (v/v 1/2) as eluent, yielding as the first fraction dekamethyl(dihydro)fulvalene and pentamethylferrocene, and as the second fraction 420 mg (1.17 mmol, 19.9%) **6** as a red crystalline material.

4.8.1. Data for 6

Anal. Found: C, 73.10; H, 6.98; O, 4.44. $C_{22}H_{25}FeO$ Calc.: C, 73.14; H, 6.97; O, 4.43%. M.p. 93–96 °C. MS (EI, 70 eV): *m/z* (%) 362 (M^+, 100); 255.5 ($M^+ - COC_6H_5$, 62). IR data (KBr, cm^{-1}): 2966m, 2908m, 2860w, 1634s, 1600m, 1578m, 1476m, 1449s, 1438s, 1374s, 1316m, 1073m, 1048s, 1027s, 862m, 849s. ^1H NMR ($CDCl_3$): δ 1.70 (15H, s, CH_3); 4.10, 4.40 (each signal: 2H, m, subst. Cp); 7.40–7.81 (5H, m, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 10.3 (CH_3); 73.6, 76.9, 79.6 (Cp); 81.5 (Cp^*); 127.8–131.1 (C_6H_5); 197.2 (COC_6H_5). CV (CH_3CN, 273 K) (V): 0.38.

4.9. 1,2-Bis-(1,2,3,4,5-pentamethylferrocen-1′-yl)-1,2-diphenyl-ethane^{2+}·(BF_4)$_2$ ($7^{(2+)}$·(BF_4)$_2$) and 1,2-bis-(1,2,3,4,5-pentamethylferrocen-1′-yl)-1,2-diphenylethane (7)

To a solution of 100 mg (0.28 mmol) phenyl(1,2,3,4,5-pentamethylferrocen-1′-yl)ketone (**6**) in THF was added 0.56 ml of a 1.0 molar THF solution of

lithium triethylborohydride (0.56 mmol) at a temperature of 0 °C and the mixture was allowed to warm to room temperature within 90 min, during which period the color of the mixture gradually changed from red to yellow, indicating formation of the corresponding lithium alcoholate. After aqueous quench with argon-saturated water the air-sensitive crude alcohol was rapidly extracted with dry ether; the solution was filtered through a short plug of aluminium oxide and solvents were removed in vacuo, affording the crude phenyl(pentamethylferrocenyl)methanol as a yellow oil, which was dissolved in a Schlenk vessel in glacial acetic acid and treated with 1 ml of a 54% solution of tetrafluoroboric acid in ether. After stirring the green mixture for 1 h the product was precipitated by addition of dry deoxygenated ether, filtered off, washed with five portions of ether, and dried in vacuo, yielding 85 mg (0.1 mmol, 71.4%) $\mathbf{7}^{(2+)} \cdot (\mathbf{BF_4})_2$ as a green microcrystalline solid.

4.9.1. Conversion of $7^{(2+)} \cdot (BF_4)_2$ to 7

To a solution of 50 mg (0.058 mmol) $\mathbf{7}^{(2+)} \cdot (\mathbf{BF_4})_2$ in 5 ml acetonitrile was added 1 ml $H_2NNH_2 \cdot H_2O$ causing an immediate color change from green to yellow. After 30 min the mixture was extracted with H_2O/CH_2Cl_2, the organic layer was dried with Na_2SO_4, and solvents were removed in vacuo, yielding 40 mg (0.058 mmol, 100%) of **7** as a yellow oil which slowly crystallized.

4.9.2. Data for $7^{(2+)} \cdot (BF_4)_2$

M.p. 120 °C (dec.). Anal. Found: C, 60.74; H, 6.03. $C_{44}H_{52}B_2F_8Fe_2$ Calc.: C, 61.01; H, 6.05%. MS (EI, 70 eV): m/z (%) 345 ($M^+/2$ of dication, 100). IR data (KBr, cm^{-1}): 2964m, 2904s, 2858m, 1493m, 1476m, 1455m, 1382s, 1300m, 1262s, 1096s, 1073s, 1030s, 812s. ^1H NMR and ^{13}C NMR spectroscopy showed only broad signals due to paramagnetism. CV (CH_3CN, 273 K) (V): −1.57, −0.89, +0.05, +0.13. X-ray structure (Tables 2 and 7, Fig. 5): single crystals were obtained from dichloromethane.

4.9.3. Data for 7

M.p. 78–80 °C. Anal. Found: C, 76.23; H, 7.58. $C_{44}H_{52}Fe_2$ Calc.: C, 76.31; H, 7.57%. MS (EI, 70 eV): m/z (%) 691 (M^+, 4); 345 ($M^+/2$, 100). IR data (KBr, cm^{-1}): 2964m, 2903s, 2858m, 1493m, 1455m, 1381s, 1262s, 1096s, 1032s, 807s. ^1H NMR ($CDCl_3$): δ 1.24–1.49 (30H, m, CH_3); 3.57–3.97 (10H, m, 8H of subst. Cp and 2H of ethane); 6.68–7.14 (10H, m, C_6H_5). ^{13}C NMR ($CDCl_3$): δ 11.0 (CH_3); 29.6 (CH–CH); 72.1, 74.3 (Cp); 81.1 (Cp*); 81.9 (Cp); 125.7–141.3 (C_6H_5).

4.10. 1,2,3,4,5-Pentamethyl-1′-vinyl-ferrocene (8)

79 mg (0.7 mmol) potassium t-butoxide was added in one portion to a stirred suspension of 250 mg (0.7 mmol) methyltriphenylphosphonium bromide in 25 ml dry deoxygenated THF at a temperature of −80 °C; the mixture was allowed to warm to room temperature and stirred for a further 1 h. After the solution of the phosphorus ylide was cooled to −80 °C, 200 mg (0.7 mmol) 1,2,3,4,5-pentamethylferrocenyl aldehyde was added, the cooling bath was removed, and stirring was continued for 2 h. Aqueous work-up and chromatography (aluminum oxide, n-hexane as eluent) afforded 100 mg (0.35 mmol, 50% yield) **8** as a yellow oil.

4.10.1. Data for 8

Anal. Found: C, 72.24; H, 7.84. $C_{17}H_{22}Fe$ Calc.: C, 72.35; H, 7.86%. MS (EI, 70 eV): m/z (%) 282 (M^+, 100); 267 ($M^+ - CH_2$, 69). HR-MS (FAB): m/z 282.10290 (M^+; exact mass calc. for $C_{17}H_{22}Fe$, 282.10709). IR data (KBr, cm^{-1}): 2965w, 2905w, 1626w, 1381w, 1261s, 1096s, 1026s, 804s. ^1H NMR (CD_2Cl_2): δ 1.84 (15H, s, CH_3); 3.79 (4H, s, subst. Cp); 5.11 (1H, d, $^3J_{cis}(^1H-^1H) = 10$ Hz, CH=CH_2); 5.19 (1H, d, $^3J_{trans}(^1H-^1H) = 20$ Hz, CH=CH_2); 6.26 (1H, dxd, $^3J_{cis}(^1H-^1H) = 10$ Hz, $^3J_{trans}(^1H-^1H) = 20$ Hz, CH=CH_2). ^{13}C NMR ($CDCl_3$): δ 10.8 (CH_3); 69.4, 73.1 (Cp); 80.6 (Cp*); 82.0 (C_1' of subst. Cp); 109.9 (CH=CH_2); 134.5 (CH=CH_2). CV (CH_3CN, 273 K) (V): 0.20.

4.11. 1-Ferrocenyl-2-(1,2,3,4,5-pentamethylferrocen-1′-yl)-ethylene (9a,b)

To a suspension of 412 mg (0.7 mmol) ferrocenylphosphonium iodide [39] in 20 ml THF at a temperature of −80 °C was added 79 mg (0.7 mmol) potassium t-butoxide. The cooling bath was removed and the color of the mixture changed gradually from orange to intense red upon warming to room temperature, indicating formation of the corresponding ylide. After 40 min the mixture was cooled to −80 °C and 200 mg (0.7 mmol) 1,2,3,4,5-pentamethylferrocenyl aldehyde was added. After stirring for 1 h at room temperature, aqueous work-up and chromatography (silica, n-hexane as eluent) gave three fractions. The first two fractions consisted of 20 mg (0.045 mmol, 12.9% yield) *trans*-1-ferrocenyl-2-(1,2,3,4,5-pentamethylferrocen-1′-yl)-ethylene (**9a**) and (0.045 mmol, 12.9% yield) *cis*-1-ferrocenyl-2-(1,2,3,4,5-pentamethylferrocen-1′-yl)-ethylene (**9b**) respectively, and from the third fraction 95 mg (0.33 mmol) unreacted pentamethylferrocenyl aldehyde could be recovered. Yields of **9a,b** are based on recovered aldehyde. *Cis*-ethylene (**9b**) is not very stable, upon storage it is slowly converted to *trans*-ethylene (**9a**).

4.11.1. Data for 9a

Red crystals, m.p. 147–150 °C. Anal. Found: C, 69.60; H, 6.48. $C_{27}H_{30}Fe_2$ Calc.: C, 69.56; H, 6.49%.

MS (EI, 70 eV): m/z (%) 466.5 (M^+, 100); 329 ($M^+ - Cp^*$, 60); 256 ($M^+ - CH{=}CH{-}CpFeCp$, 37). IR data (KBr, cm^{-1}): 3093w, 2964w, 1636w, 1382m, 1106s, 1025s, 810s. ^1H NMR ($CDCl_3$): δ 1.81 (15H, s, CH_3); 3.83 (4H, m, subst. Cp); 4.13 (5H, unsubst. Cp); 4.21, 4.35 (each signal: 2H, m, subst. Cp); 6.23 (2H, s, CH=CH). ^{13}C NMR ($CDCl_3$): δ 11.02 (CH_3); 65.9–80.9 (Cp and Cp^*); 123.5, 123.9 (CH=CH). X-ray structure (Tables 2 and 8; Fig. 6): single crystals were obtained from n-hexane.

4.11.2. Data for ***9b***

Yellow oil, m.p. not available. MS (EI, 70 eV): m/z (%) 466.5 (M^+, 100); 412 ($M^+ - Cp$, 35); 328 ($M^+ - Cp^*$, 62); 256 ($M^+ - CH{=}CH{-}CpFeCp$, 29). IR data (KBr, cm^{-1}): 3093w, 2964w, 1636w, 1382m, 1106s, 1025s, 810s. ^1H NMR ($CDCl_3$): δ 1.53 (15H, s, CH_3); 3.77 (2H, m, subst. Cp); 4.04 (5H, unsubst. Cp); 4.06 (4H, m, subst. Cp); 4.13, 4.30 (each signal: 2H, m, subst. Cp); 5.81 (1H, s, CH=CH); 6.11 (1H, s, CH=CH). ^{13}C NMR ($CDCl_3$): δ 11.00 (CH_3); 66.0–80.9 (Cp and Cp^*); 124.3, 124.9 (CH=CH).

*4.12. 1,2,3,4,5-Pentamethyl-1′-chlorovinyl-ferrocene (**10a,b**)*

45 mg (1.2 mmol) sodium amide was added to a stirred suspension of 365 mg (1.05 mmol) chloromethyl-triphenylphosphonium chloride in 25 ml dry deoxygenated THF at a temperature of 0 °C and the mixture was allowed to warm to room temperature and stirred for a further 30 min. After the solution of the phosphorus ylide was cooled to 0 °C, 200 mg (0.7 mmol) 1,2,3,4,5-pentamethylferrocenyl aldehyde was added, the cooling bath was removed, and stirring was continued overnight. To the solution was added n-hexane and triphenylphosphine oxide precipitated, which was filtered off. Solvents were removed in vacuo and the crude product was purified by chromatography (aluminum oxide, n-hexane as eluent), yielding two fractions. The first fraction afforded 50 mg (0.16 mmol, 23% yield) 1,2,3,4,5-pentamethyl-1′-*trans*-chlorovinyl-ferrocene (**10a**) as an orange solid, and the second fraction afforded 1,2,3,4,5-pentamethyl-1′-*cis*-chlorovinyl-ferrocene (**10b**) as a yellow solid, which is not very stable, eliminating HCl to give 1,2,3,4,5-pentamethyl-1′-ethynyl-ferrocene (**11**); see the data for **10b** and the following preparation of **11**.

4.12.1. Data for ***10a***

M.p. 45 °C. Anal. Found: C, 64.62; H, 6.70. $C_{17}H_{21}ClFe$ Calc.: C, 64.48; H, 6.68%. MS (EI, 70 eV): m/z (%) 316.5 (M^+, 100); 281 ($M^+ - Cl$, 76); 265 ($M^+ - CH{-}Cl$, 99). IR data (KBr, cm^{-1}): 2966w, 2948w, 2908w, 2858w, 1611w, 1382m, 1092s, 1073s, 1031s, 812s, 807s. ^1H NMR (CD_2Cl_2): δ 1.83 (15H, s, CH_3); 3.73, 3.79 (each signal: 2H, m, subst. Cp); 6.08 (1H, d, $^3J_{trans}(^1H{-}^1H) = 13.43$ Hz, CH=CClH); 6.38 (1H, d, $^3J_{trans}(^1H{-}^1H) = 13.43$ Hz, CH=CClH). ^{13}C NMR (CD_2Cl_2): δ 11.0 (CH_3); 69.4, 73.5 (Cp); 80.5 (C_1' of subst. Cp); 81.3 (Cp^*); 112.2 (CH=CClH); 131.3 (CH=CClH). CV (CH_3CN, 273 K) (V): 0.22.

4.12.2. Data for ***10b***

M.p. 45 °C. MS (EI, 70 eV): m/z (%) 316 (M^+, 46); 281 ($M^+ - Cl$, 100); 265 ($M^+ - CH{-}Cl$, 78). IR data (KBr, cm^{-1}): 2966w, 2906w, 2856w, 2107m ($\nu_{C\equiv C}$ of **11**!), 1646w, 1382m, 1094s, 1071s, 1027s, 817s, 807s. ^1H NMR (CD_2Cl_2): δ 1.87 (15H, s, CH_3); 2.82 (0.5H, s, C≡C–H of **11**!); 3.73, 3.82 (each signal: 2H, m, subst. Cp); 7.35 (1H, br s, CH=CClH); 6.26 (1H, br s, CH=CClH). ^{13}C NMR (CD_2Cl_2): δ 10.5 (CH_3); 73.0, 74.6 (Cp); 81.0 (Cp^*); 128.9 (CH=CClH); 133.9 (CH=CClH).

*4.13. 1,2,3,4,5-Pentamethyl-1′-ethynyl-ferrocene (**11**)*

210 mg (0.66 mmol) *cis / trans*-1,2,3,4,5-pentamethyl-1′-chlorovinyl-ferrocene (**10a,b**) was dissolved in 20 ml dry deoxygenated dimethoxyethane; 132 mg (3.3 mmol) potassium hydride was added, and the mixture was refluxed overnight. Aqueous work-up and chromatography (aluminum oxide, n-hexane as eluent) afforded 165 mg (0.59 mmol, 89.4% yield) 1,2,3,4,5-pentamethyl-1′-ethynyl-ferrocene (**11**) as a brown, partially oily solid, which decomposes upon storage under an atmosphere of argon at a temperature of −20 °C within a few weeks.

4.13.1. Data for ***11***

Anal. Found: C, 72.61; H, 7.21. $C_{17}H_{20}Fe$ Calc.: C, 72.87; H, 7.19%. MS (EI, 70 eV): m/z (%) 280 (M^+, 100); 266 ($M^+ - CH$, 22). IR data (KBr, cm^{-1}): 2964w, 2910w, 2856w, 2107m ($\nu_{C\equiv C}$), 1382m, 1262s, 1096s, 1023s, 864s. ^1H NMR (CD_2Cl_2): δ 1.87 (15H, s, CH_3); 2.81 (1H, s, C≡C–H); 3.75, 3.83 (each signal: 2H, m, subst. Cp). ^{13}C NMR (CD_2Cl_2): δ 10.5 (CH_3); 30.1 (C≡CH); 72.9, 74.6 (Cp); 73.9 (C≡CH); 81.1 (Cp^*). CV (CH_3CN, 273 K) (V): 0.32.

*4.14. 6-(1,2,3,4,5-Pentamethylferrocen-1′-yl)-fulvene (**12**)*

A Schlenk tube was charged with 200 mg (0.7 mmol) 1,2,3,4,5-pentamethylferrocenyl aldehyde, 0.22 ml (2.8 mmol) cyclopentadiene, 0.1 ml (1.17 mmol) dry deoxygenated pyrrolidine as base, and 30 ml dry methanol as solvent. The mixture was stirred overnight, changing color from red to purple. Solvents and volatile materials were removed in vacuo, the crude product was dissolved in n-hexane, filtered through a short column of aluminum oxide, n-hexane was removed in vacuo, af-

fording 150 mg (0.45 mmol, 99.1% yield) pure fulvene (**12**) as a dark purple oil.

*4.14.1. Data for **12***

Anal. Found: C, 76.20; H, 7.31. $C_{21}H_{24}Fe$ Calc.: C, 75.91; H, 7.28%. MS (EI, 70 eV): *m/z* (%) 332 (M^+, 100). UV–vis (THF [λ_{max} (nm)/lg ε]): 284.0/3.66; 345.5/4.01; 522/3.41. IR data (KBr, cm^{-1}): 2964s, 2927m, 2858m, 1621s, 1611s, 1438s, 1382m, 1262s, 1096s, 1028s, 803s. ^1H NMR (C_6D_6): δ 1.60 (15H, s, CH_3); 3.83, 3.96 (each signal: 2H, m, subst. Cp); 6.39–6.43 (1H, m, fulvene-H); 6.59–6.61 (2H, m, fulvene-H); 6.73–6.75 (2H, m, fulvene-H). ^{13}C NMR (C_6D_6): δ 10.7 (CH_3); 73.6, 76.3 (Cp); 80.4 (C_1' of subst. Cp); 81.7 (Cp^*); 120.0, 126.6, 128.2, 133.0, 140.1, 141.4 (fulvene-C). CV (CH_3CN, 273 K) (V): 0.29.

*4.15. Bis-(1,2,3,4,5-pentamethylferrocen-1'-yl)-methane (**13**)*

A Schlenk vessel was charged with 20 ml THF, 100 mg (0.3 mmol) 6-(1,2,3,4,5-pentamethylferrocen-1'-yl)-fulvene (**12**), 0.6 ml (0.6 mmol) lithium triethylborohydride (1.0 molar solution in THF); the solution was refluxed for approximately 3 h, until the disappearence of the purple color of the fulvene (**12**) indicated complete hydride addition to the exocyclic fulvenic bond. In the meantime, pentamethylcyclopentadiene (0.1 ml, 0.6 mmol) was lithiated with n-butyl lithium (0.3 ml of a 2.0 M solution in hexane, 0.6 mmol), converted with iron(II)bis(acetylcetonate) (153 mg, 0.6 mmol) to the corresponding pentamethylcyclopentadienyl-iron(II)acetylacetonate [10], and added to the solution containing lithium pentamethylferrocenylmethyl-cyclopentadienide (from above) at a temperature of −80 °C. The mixture was allowed to warm to room temperature under efficient stirring. Similar work-up as described for pentamethylferrocenyl aldehyde yielded two fractions. The first yellow fraction consisted of decamethyl(dihydro)fulvalene. The second yellow fraction yielded 120 mg (0.23 mmol, 76.7%) pure bis-(1,2,3,4,5-pentamethylferrocen-1'-yl)-methane (**13**) as orange crystals.

*4.15.1. Data for **13***

M.p. 193–194 °C. Anal. Found: C, 70.87; H, 7.68. $C_{31}H_{40}Fe_2$ Calc.: C, 71.01; H, 7.69%. MS (EI, 70 eV): *m/z* (%) 524.5 (M^+, 100); 335 ($M^+ - FeCp^*$, 56). IR data (KBr, cm^{-1}): 2964s, 2943s, 2858s, 1476m, 1449m, 1428m, 1380s, 1262m, 1069s, 1034s, 1021s, 808s. ^1H NMR (CD_2Cl_2): δ 1.93 (30H, s, CH_3); 3.08 (2H, s, CH_2); 3.46, 3.53 (each signal: 4H, m, subst. Cp). ^{13}C NMR (CD_2Cl_2): δ 11.3 (CH_3); 27.3 (CH_2); 70.8, 71.8 (Cp); 80.1 (Cp^*); 88.8 (C_1' of subst. Cp).

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