

# Redox-responsive surfactants: synthesis of 1,1-diferrocenyl-*n*-alkanes ( $C_1, C_5, C_7, C_{19}$ ) via reaction of (diferrocenyl) methyl carbocation with carbanions

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## Abstract

Diferrocenylmethyl cation with chloride or tetraphenylborate as counter-ion is prepared from diferrocenylmethanol by dehydration with strong acids. Treatment with trimethylchlorosilane removes residual water to afford anhydrous methyl cation salts, which are highly reactive electrophiles for alkylation of group 14 (carbanions), group 15 (amines), group 16 (alkoxides), and, remarkably, group 17 (fluoride) nucleophiles. Reaction with long-chain carbanions yields 1,1-diferrocenyl substituted *n*-alkanes, which are of potential interest as redox-responsive surfactants. Single crystal structure analyses reveal a tendency for amphiphilic behavior to increase with increasing chain length. Medium chain length 1,1-diferrocenyl-*n*-alkanes show the expected intermolecular stacking, whereas for the longest *n*-alkane synthesized, 1,1-diferrocenyl-*n*-nonadecane, intermolecular complexation with *n*-octadecane is observed.

**Keywords:** Iron; Diferrocenylmethyl cation; Surfactants; X-ray diffraction; 1,1-Diferrocenyl-*n*-alkane; Diferrocenylfluoromethane

## 1. Introduction

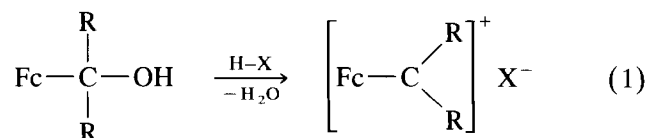
The efficient stabilization of carbenium ions by adjacent aromatic organometallic  $\pi$ -complexes is well known and has been extensively reviewed [1]. The ferrocenyl moiety is a potent donor for these isolable methyl cation salts, which can be viewed as either  $\alpha$ -ferrocenyl carbenium ions or  $\eta^6$ -fulvene- $\eta^5$ -cyclopentadienyl iron(II) cations (Scheme 1). Synthetically, these cations are very reactive electrophiles which readily alkylate nitrogen [2,3,4], sulfur [5], and phosphorus [6] nucleophiles. Analogous reactivity was reported for the isoelectronic diphenylmethylbis( $\pi$ -chromium tricarbonyl) carbenium ion [7]. Alkylation of carbon nucleophiles has been limited so far to the cyanide ion [2,4],  $\alpha$ -nitro carbanions [8], and recently to silyl enol ethers [9]. Although this chemistry seems to be well established for the aforementioned nucleophiles, no successful reactions with simple carbanions which contain no activating group have been reported. We found that carbanions, hydride, alkoxides, and, remarkably, fluoride are readily alkylated by the diferrocenylmethyl

ion. The reaction with carbanions is of particular interest for the synthesis of molecules which incorporate an electrochemically active, polar ferrocene “head” and an apolar, lipophilic hydrocarbon “tail” with potential applications as redox-responsive surfactants [10–13] or as liquid crystal materials [14].

## 2. Results and discussion

### 2.1. Diferrocenylmethyl cation salts

Synthesis of  $\alpha$ -ferrocenylmethyl cation salts is generally achieved by dehydration of the corresponding carbinols with strong acids [1,15,16] (Eq. 1). In this



R = H, alkyl, aryl, X = conjugate base of acid H-X

manner, diferrocenylmethyl fluoride (**1a**), chloride (**1b**), and tetraphenylborate (**1c**) are prepared in 90% yield (Table 1). These salts precipitate from the reaction

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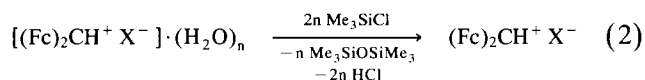
mixture as dark blue microcrystalline solids, which are fairly air-stable for a limited time (a few hours) but should be protected from moisture and light under an inert atmosphere.

The existence of diferrocenylfluoromethane (**6**), which will be discussed later, makes the formulation of (**1a**) as a methylium cation with fluoride as counterion extremely unlikely. The NMR and IR data of (**1a**) are in accord with an HF-solvated fluoride anion: The broad signal located at 1.7 ppm corresponds to the equilibrium  $F(HF)_2^- = HF + FHF^-$  [17]. Only traces of water seem to be involved in this exchange process, because no  $H_2O$  could be detected in the IR spectrum of (**1a**). Attempted removal of solvating HF by prolonged treatment in vacuo leaves (**1a**) unchanged; no bifluoride  $FHF^-$ , which would be easily detectable by NMR [17], is obtained under these conditions.

In contrast to earlier reports [18], chloride (**1b**) does not equilibrate with diferrocenylchloromethane in solution; the  $^1H$  chemical shift ( $\delta = 8.87$  ppm) and the  $^{13}C$  chemical shift ( $\delta = 147.5$  ppm) clearly indicate a cationic  $\alpha-C-H$  moiety [1]. No indications of an HCl-solvated anion,  $ClHCl^-$  or  $Cl(HCl)_n^-$ , respectively, are observed in (**1b**) after drying with trimethylchlorosilane (see below). The difference in the strength of hydrogen bonding of fluorine versus chlorine allows for methylium salts (**1a**) only the existence of a solvated salt, whereas for (**1b**) a methylium salt with chloride as counterion does exist.

Use of these salts as electrophiles for reactions with strongly basic nucleophiles such as carbanions or hydride necessitates complete removal of water and acid, which are inherently present or formed during synthesis

(Eq. 1). Conventionally, repeated washings with dry ether and drying in vacuo affords methylium salts which have been used in subsequent alkylation reactions [2–9]. To ensure complete removal of water we use trimethylchlorosilane as the drying agent, analogously to a published procedure for obtaining unsolvated anhydrous metal chlorides from metal chloride hydrates [19] (Eq. 2). This is an experimentally simple procedure: the



**1b**: X = Cl

**1c**: X = B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>

Fc = Ferrocenyl

solvent dichloromethane, the excess trimethylchlorosilane, and the by-products hexamethyldisiloxane and hydrogen chloride are conveniently removed from the anhydrous diferrocenylmethylium salts (**1b**) and (**1c**) under reduced pressure. This method is not applicable for drying fluoride (**1a**) because of possible formation of trimethylfluorosilane and methylium salt (**1b**) by exchange of fluoride versus chloride driven by formation of the very strong silicon–fluorine bond. Therefore, fluoride (**1a**) was not used for alkylation reactions.

## 2.2. Substituted 1,1-diferrocenylmethanes

The anhydrous methylium salts (**1b**) and (**1c**) are very reactive electrophiles. In terms of convenience of handling and stability, compound (**1c**) is preferred over (**1b**) as the reagent for alkylation reactions with nucle-

Table 1  
Spectral data of diferrocenyl methylium salts (**1a**), (**1b**), (**1c**)

	$^1H$ -NMR <sup>a</sup>	$^{13}C\{^1H\}$ -NMR <sup>a</sup>	IR <sup>b</sup>
<b>1a</b>	1.72 (s, 1.5 H, HF) 4.55 (s, 10 H, unsubst. Cp), 4.99 (t, 4 H, subst. Cp), 5.57 (t, 4 H, subst. Cp), 8.87 (s, 1 H, $\alpha$ -C-H)	74.8 (subst. Cp), 75.8 (unsubst. Cp), 83.8 (subst. Cp), 86.3 (subst. Cp, C1), 147.5 ( $\alpha$ -C-H)	3103w, 3046w, 3073w, 1630w, 1538s, 1414m, 1369w, 1263w, 1107m, 1084s, 1032m, 943w, 825w, 746m, 654w, 515w, 484m, 470m
<b>1b</b>	4.52 (s, 10 H, unsubst. Cp), 4.97 (t, 4 H, subst. Cp), 5.54 (t, 4 H, subst. Cp), 8.92 (s, 1 H, $\alpha$ -C-H)	74.9 (subst. Cp), 76.4 (unsubst. Cp), 84.4 (subst. Cp), 86.9 (subst. Cp, C 1),	3086w, 1635w, 1534s, 1412m, 1370w, 1329w, 1287w, 1265m, 1107w, 1051m, 1007w, 947w, 835s, 745w, 652w, 598w,
<b>1c</b>	4.42 (s, 10 H, unsubst. Cp), 4.70 (t, 4 H, subst. Cp), 5.49 (t, 4 H, subst. Cp), 6.9–7.4 (m, 20 H, arom. H), 8.06 (s, 1 H, $\alpha$ -C-H)	74.8 (subst. Cp), 76.1 (unsubst. Cp), 84.8 (subst. Cp), 87.2 (subst. Cp, C1), 122.2, 126.1, 136.3 (arom. C), 146.4 ( $\alpha$ -C-H)	3115w, 3091w, 3056m, 3031m, 3006w, 2983w, 1578m, 1530s, 1479m, 1452w, 1432m, 1412m, 1368w, 1352w, 1325w, 1263m, 1132m, 1057w, 1036w, 1001w, 943m, 899m, 833m, 746m, 735s, 667w, 654w, 613m, 509m, 461s, 414m

<sup>a</sup> ppm, from TMS, solvent CD<sub>2</sub>Cl<sub>2</sub>;

<sup>b</sup> cm<sup>-1</sup>, KBr. s, singlet; t, triplet; m, multiplet; Cp, cyclopentadienyl.

Table 2  
Spectral data of compounds **2b**, **2c**, **2d**, **3**, **4**, **5a**, **5b**, **6**

	<sup>1</sup> H-NMR <sup>a</sup>	<sup>13</sup> C-NMR <sup>a</sup>	MS <sup>b</sup>	IR <sup>c</sup>
<b>2b</b>	0.95 (t, 3 H, -CH <sub>3</sub> ), 1.35–1.43 (m, 4 H, -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub> ) 1.92–1.96 (m, 2 H, (Fc) <sub>2</sub> CH-CH <sub>2</sub> -) 3.19 (t, 1 H, (Fc) <sub>2</sub> CH-), 3.99–4.02 (m, 2 H, subst. Cp), 4.04–4.09 (m, 6 H, subst. Cp), 4.06 (s, 10 H, unsubst. Cp)	142., 23.0, 30.7, 37.2 (aliph. C) 37.9 ((Fc) <sub>2</sub> CH-), 66.4, 66.6, 67.1, 67.7 (subst. Cp, C2–C5), 68.5 (unsubst. Cp), 95.4 (subst. Cp, C1)	440 (100): M <sup>+</sup> , 383(67): (Fc) <sub>2</sub> CH, 375(7): M <sup>+</sup> - Cp, 318(11): (Fc)(CpFe)CH, 262(11): (Fc)(Cp)CH	3093m, 2954m, 2917m, 2855m, 1757w, 1686w, 1638w, 1458m, 1105s, 1028m, 999m, 805s, 484s
<b>2c</b>	0.88 (t 3 H, -CH <sub>3</sub> ), 1.23–1.51 (m, 8 H, -CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub> ), 1.88–1.96 (m, 2 H, CH <sub>2</sub> -(CH <sub>2</sub> ) <sub>4</sub> -CH <sub>3</sub> ), 3.19 (t, 1 H, (Fc) <sub>2</sub> CH-), 4.00 (m, 2 H, subst. Cp), 4.04–4.07 (m, 6 H, subst. Cp), 4.06 (s, 10 H, unsubst. Cp)	14.2, 22.7, 28.5, 29.7, 31.9, 37.5 (aliph. C), 38.0 ((Fc) <sub>2</sub> CH-), 66.4, 66.6, 67.1, 67.8 (subst. Cp, C2–C5), 68.5 (unsubst. Cp), 95.4 (subst. Cp, C1)	468(100): M <sup>+</sup> , 440(26): M <sup>+</sup> - C <sub>2</sub> H <sub>5</sub> + H, 383(77): (Fc) <sub>2</sub> CH, 318(14): (Fc)(CpFe)CH, 262(63): (Fc)(Cp)CH	3096w, 2961m, 2925m, 2859m, 1636w, 1460m, 1410w, 1261s, 1105s, 1026s, 1001s, 920w, 816s, 607w, 493s, 480s, 463m
<b>2d</b>	0.88 (t, 12 H, -CH <sub>3</sub> ), 621(1): M <sup>+</sup> - CH <sub>3</sub> , 1.25 (broad s, 96 H, -(CH <sub>2</sub> ) <sub>16</sub> -), 1.91 (m, 4 H, (Fc) <sub>2</sub> CH-CH <sub>2</sub> -), 3.18 (t, 2 H, (Fc) <sub>2</sub> CH-CH <sub>2</sub> -), 4.00 (m, 4 H, subst. Cp), 4.06 (m, 32 H, Cp)	14.2, 22.7, 28.6, 29.4, 30.0, 30.01, 31.9, 37.5 (aliph. C), 37.9 (Fc) <sub>2</sub> CH-), 66.4, 66.7, 67.1, 67.8 (subst. Cp, C2–C5), 68.5 (unsubst. Cp), 95.5 (subst. Cp, C1)	636(100): M <sup>+</sup> , 607(2): M <sup>+</sup> - C <sub>2</sub> H <sub>5</sub> , 593(1): M <sup>+</sup> - C <sub>3</sub> H <sub>7</sub> , 579(1): M <sup>+</sup> - C <sub>4</sub> H <sub>9</sub> , 565(1): M <sup>+</sup> - C <sub>5</sub> H <sub>11</sub> ,..., 383(44): (Fc) <sub>2</sub> CH, 319(50): (Fc)(CpFe)CH, 262(13): (Fc)(Cp)CH	3093w, 2954s, 2917s, 2871s, 2851s, 1638w, 1472s, 1412w, 1377w, 1261w, 1105m, 1022m, 999m, 816m, 717m, 480m
<b>3</b>	0.35 (s, 9 H, -Si(CH <sub>3</sub> ) <sub>3</sub> ), 4.08 (m, 4 H, subst. Cp), 4.14 (m, 2 H, subst. Cp), 4.21 (s, 10 H, unsubst. Cp), 4.23 (m, 2 H, subst. Cp), 4.47 (s, 1 H, (Fc) <sub>2</sub> CH-C≡C-)	0.3 (-Si(CH <sub>3</sub> ) <sub>3</sub> ), 33.8 (Fc) <sub>2</sub> CH-), 66.9, 67.2, 67.4, 67.6 (subst. Cp, C2–C5), 68.9 (unsubst. Cp), 85.5 (ethinyl C), 89.9 (subst. Cp, C1), 1071. (ethinyl C?)	481(89): M <sup>+</sup> + H, 480(82): M <sup>+</sup> , 465(3): M <sup>+</sup> - CH <sub>3</sub> , 414(100): M <sup>+</sup> - Cp - H, 407(16): M <sup>+</sup> - Si(CH <sub>3</sub> ) <sub>3</sub> , 342(16): M <sup>+</sup> - Si(CH <sub>3</sub> ) <sub>3</sub> - Cp, 383(4): (Fc) <sub>2</sub> CH, 382(4): (Fc) <sub>2</sub> C	3091m, 2959m, 2900w, 2869w, 2176s, 1643w, 1410m, 1250s, 1105s, 1059m, 1018s, 854s, 760m, 634w, 575w, 478s
<b>4</b>	2.40 (broad s, 2 H, -NH-), 2.84 (s, 4 H, -NH-(CH <sub>2</sub> ) <sub>2</sub> -NH-), 4.09 (m, 30 H, Cp + (Fc) <sub>2</sub> CH-), 4.14 (m, 4 H, subst. Cp), 4.25 (m, 4 H, subst. Cp),	48.8 (-NH-(CH <sub>2</sub> ) <sub>2</sub> -NH-), 56.9 (Fc) <sub>2</sub> CH-), 67.0, 67.0, 67.1, 67.7 (subst. Cp, C2–C5), 68.5 (unsubst. Cp), 93.7 (subst. Cp, C1)	824(6): M <sup>+</sup> - 4 H, 441(99): M <sup>+</sup> - (Fc) <sub>2</sub> C - 4 H, 399(24): (Fc) <sub>2</sub> C-N, 383(100): (Fc) <sub>2</sub> CH	3442m (broad), 3326m, 3089m, 2921w, 2820m, 1636w, 1435m, 1410m, 1310w, 1250m, 1105s, 1020m, 999m, 918w, 818s, 721w, 478s
<b>5a</b>	3.44 (s, 3 H, -OCH <sub>3</sub> ), 4.10 (s, 10 H, unsubst. Cp), 4.13–4.16 (m, 6 H, subst. Cp), 4.24 (m, 2 H, subst. Cp), 4.75 (s, 1 H, (Fc) <sub>2</sub> CH-)	57.0 (-OCH <sub>3</sub> ), 67.04, 67.2, 67.3, 68.7 (subst. Cp, C2–C5), 68.7 (unsubst. Cp), 77.8 ((Fc) <sub>2</sub> CH-), 90.3 (subst. Cp, C1)	414(100): M <sup>+</sup> , 398(2): M <sup>+</sup> - CH <sub>3</sub> - H, 383(18): (Fc) <sub>2</sub> CH, 317(17): (Fc) <sub>2</sub> C - Cp, 262(87): (Fc)(Cp)CH	3096m, 2977m, 2939w, 2921m, 2900m, 2873w, 2811m, 1647m, 1398m, 1283m, 1107s, 1088s, 1041m, 1026m, 999m, 939m, 912m, 818s, 762m, 667w, 522m, 499s, 484s, 451w
<b>5b</b>	1.19 (s, 9 H, -OC(CH <sub>3</sub> ) <sub>3</sub> ), 4.03 (s, 10 H, unsubst. Cp), 4.12 (m, 4 H, subst. Cp), 4.29 (m, 4 H, subst. Cp), 5.06 (s, 1 H, (Fc) <sub>2</sub> CH-)	29.5 (-OC(CH <sub>3</sub> ) <sub>3</sub> ), 66.9, 67.0, 68.1, 68.2 (subst. Cp, C2–C5), 67.6 (-OC(CH <sub>3</sub> ) <sub>3</sub> ), 68.9 ((Fc) <sub>2</sub> CH-), 69.2 (unsubst. Cp), 95.1 (subst. Cp, C1)	456(43): M <sup>+</sup> , 399(8): (Fc) <sub>2</sub> CH - O, 383(32): (Fc) <sub>2</sub> CH, 318(5): (Fc) <sub>2</sub> CH - Cp, 262(100): (Fc)(Cp)CH	3004w, 2925m, 2849w, 1634w, 1451m, 1412m, 1286w, 1261w, 1223w, 1107s, 1041s, 1003s, 818s, 740w, 549w, 480s

Table 2 (continued)  
Spectral data of compounds **2b**, **2c**, **2d**, **3**, **4**, **5a**, **5b**, **6**

	<sup>1</sup> H-NMR <sup>a</sup>	<sup>13</sup> C-NMR <sup>a</sup>	MS <sup>b</sup>	IR <sup>c</sup>
<b>6</b>	4.17 (s, 10 H, unsubst. Cp), 4.17–4.21 (m, 6 H, subst. Cp), 4.29 (m, 2 H, subst. Cp), 6.02 (d, 1 H, <sup>1</sup> J( <sup>1</sup> H– <sup>19</sup> F) = 47.9 Hz, (Fc) <sub>2</sub> CH–F),	67.1, 67.9, 68.0, 68.2, 68.67, 68.72 (subst. Cp, C2–C5, + (Fc) <sub>2</sub> CH–F), 69.2 (unsubst. Cp), 91.7 (subst. Cp, C1)	402(15): M <sup>+</sup> , 383(100): (Fc) <sub>2</sub> CH, 318(17): (Fc) <sub>2</sub> CH – Cp, 262(74): (Fc)(Cp)CH, 186(25): FcH	– <sup>d</sup>

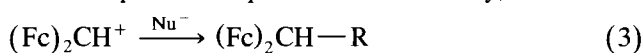
<sup>a</sup> ppm, from TMS, solvent CDCl<sub>3</sub>, except for compound **6**: solvent CD<sub>2</sub>Cl<sub>2</sub>;

<sup>b</sup> m/e (%);

<sup>c</sup> cm<sup>-1</sup>, KBr;

<sup>d</sup> not measured because of the high air-sensitivity of **6**. s, singlet; d, doublet; m, multiplet; Cp, cyclopentadienyl; Fc, ferrocenyl.

ophiles, although comparable results are obtained for both compounds (Eq. 3). Mechanistically, these reac-



<b>1b</b> , <b>1c</b>	<b>2a</b> : R = –H
	<b>2b</b> : R = –(CH <sub>2</sub> ) <sub>3</sub> –CH <sub>3</sub>
	<b>2c</b> : R = –(CH <sub>2</sub> ) <sub>5</sub> –CH <sub>3</sub>
	<b>2d</b> : R = –(CH <sub>2</sub> ) <sub>17</sub> –CH <sub>3</sub> *
	<b>3</b> : R = –C≡C–Si(CH <sub>3</sub> ) <sub>3</sub>
	<b>4</b> : R = –NH–CH <sub>2</sub> –CH <sub>2</sub> –NH–
	<b>5a</b> : R = –OCH <sub>3</sub>
	<b>5b</b> : R = –OC(CH <sub>3</sub> ) <sub>3</sub>
	<b>6</b> : R = –F

Fc = ferrocenyl, Nu = nucleophile; \* **2d** is a 2:1-complex of 1,1-diferrocenyl-*n*-nonadecane with *n*-octadecane (see text).

tions may either be described as “true” S<sub>N</sub>1 substitutions or as nucleophilic additions to the exocyclic, fulvenic double bond (Scheme 1). All reactions proceed rapidly in good yields in the course of a few minutes at –70 °C as indicated by a color change from dark blue to yellow. Alkylation of hydride (in the form of Me<sub>3</sub>AlH<sup>-</sup>; see Experimental) yields diferrocenylmethane (**2a**) with analytical and spectroscopic data in accord with published data [20,21].

Alkylation of sp<sup>3</sup>-carbanions is exemplified by conversion of *n*-butyl, *n*-hexyl-, and *n*-octadecyl carbanions to the C<sub>1</sub>-homologous diferrocenyl-*n*-alkanes (**2b**), (**2c**), and (**2d**), which are characterized by spectroscopic methods (Table 2) and by single crystal structure analysis (Tables 3, 4, 5, and 7; Figs. 1 and 2). Clearly, the diferrocenylmethyl moiety exhibits similar spectroscopic patterns in all compounds (Table 2). In the solid state, the increasing chain length in diferrocenyl-*n*-alkanes (**2b**), (**2c**), and (**2d**) leads to a gradual preferential co-alignment of the *n*-alkyl groups with formation of intermolecular stacks (Figs. 3 and 4). Interestingly, compound (**2d**) is actually an adduct or a molecular

complex between two equivalents of 1,1-diferrocenyl nonadecane (the expected product of the reaction) and one equivalent of *n*-octadecane. The octadecane is most likely formed by hydrolysis of complexed octadecyl magnesium bromide, which is one of the reactants to prepare (**2d**) according to Eq. 3.

The conformation of the diferrocenylmethyl moiety in the solid state is nearly the same for all three compounds; the dihedral angle of the *n*-alkane-linked cyclopentadienyl rings differs from 81.2° to 84.4° (Table 7). This conformation leads to an analogous intermolecular stacking of the molecules in the crystal lattice. Figs. 3 and 4 show the important sections along these layers. Compound (**2d**) has three periodic layers, two diferrocenyl substituted *n*-alkane molecules which co-align with one *n*-octadecane molecule. These layers are not at the same level; they are displaced to each other at 1/3 of the layer distance (Fig. 4). A similar molecular packing shows (**2c**). The layers of the two co-aligned molecules are displaced to each other at 1/2 of the layer distance (Fig. 3).

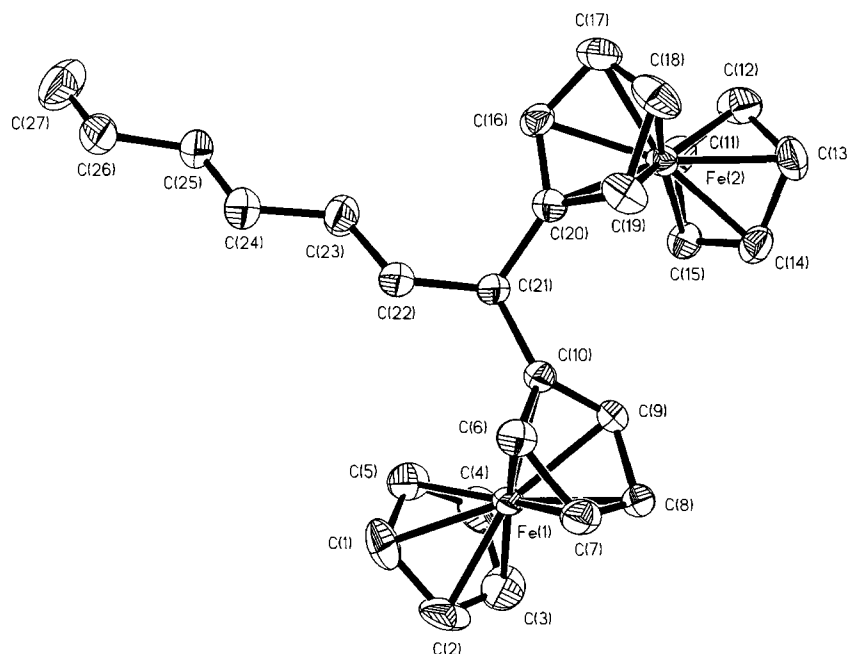
The complex (**2d**) is not only observed in the solid state but also in solution, as shown by NMR (Table 2). Mass spectroscopy, on the other hand, shows only a molecular ion attributable to uncomplexed 1,1-diferrocenyl nonadecane. Obviously, adduct (**2d**) survives conventional purification procedures such as column chromatography and recrystallization. This can be interpreted as relatively strong Van der Waals or London forces between 1,1-diferrocenyl nonadecane and *n*-octadecane. DSC (Differential Scanning Calorimetry) measurements reveal a broad peak ( $\Delta H_{\text{VanderWaals}} = 3.4$  kJ/mol [22.0 J/g]) in the range 120 °C to 170 °C on heating (**2d**) (melting point 74 °C,  $\Delta H_{\text{melting}} = 198$  kJ/mole [129.6 J/g]), which may be assigned to the dissociation of complex (**2d**) into its components. The potential surface-active properties of diferrocenyl-*n*-alkanes, especially in combination with controlled electrochemical oxidation of the ferrocenyl moieties, need further exploration and are beyond the scope of this work.

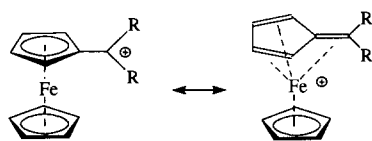
Reaction of methylum salt (**1c**) with lithium trimethylsilylacetylide yields the alkyne (**3**) (Table 2), illustrat-

Table 3

Crystal data and structure refinement for **2c**, **2d**, **5b**

	<b>2c</b>	<b>2d</b>	<b>5b</b>
Molecular formula	C <sub>27</sub> H <sub>32</sub> Fe <sub>2</sub>	C <sub>96</sub> H <sub>150</sub> Fe <sub>4</sub>	C <sub>25</sub> H <sub>28</sub> Fe <sub>2</sub> O
Formula weight	468.23	763.78	456.17
Crystal system	monocline	triclinic	orthorhombic
Space group	P2 <sub>1</sub> /c (No. 14)	P1 (No. 2)	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (No. 19)
<i>a</i> (pm)	1525.3(3)	600.4(2)	762.50(10)
<i>b</i> (pm)	765.3(2)	1125.9(2)	1535.0(3)
<i>c</i> (pm)	1919.3(4)	3167.0(4)	1764.8(2)
$\alpha$ (°)	90	82.070(10)	90
$\beta$ (°)	98.54(3)	88.88(2)	90
$\gamma$ (°)	90	82.81(2)	90
Volume (nm <sup>3</sup> )	2.2156(9)	2.1037(8)	2.0656(5)
<i>Z</i>	4	1	4
Temperature (K)	198	198	233
Density, calc. (mg m <sup>-3</sup> )	1.404	1.206	1.467
Absorption coefficient (mm <sup>-1</sup> )	1.320	0.721	1.417
<i>F</i> (000)	984	830	952
Color, habit	orange platelet	yellow platelet	red block
crystal size (mm)	0.7 × 0.45 × 0.15	0.65 × 0.25 × 0.07	1.0 × 0.8 × 0.7
$\theta$ range for data collection (°)	5.06 to 26.03	3.25 to 21.00	5.12 to 25.99
Index ranges	-1 ≤ <i>h</i> ≤ 18, -1 ≤ <i>k</i> ≤ 9, -23 ≤ <i>l</i> ≤ 23	-6 ≤ <i>h</i> ≤ 5, -10 ≤ <i>k</i> ≤ 11, -31 ≤ <i>l</i> ≤ 31	-1 ≤ <i>h</i> ≤ 9, -1 ≤ <i>k</i> ≤ 18, -1 ≤ <i>l</i> ≤ 21
Reflections collected	5506	5896	2979
Independent reflections	4304 ( <i>R</i> <sub>int</sub> = 0.0257)	4422 ( <i>R</i> <sub>int</sub> = 0.0302)	2820 ( <i>R</i> <sub>int</sub> = 0.0107)
Reflections with <i>I</i> > 2σ( <i>I</i> )	3434	3343	2664
Absorption correction	$\psi$ -scan	none	$\psi$ -scan
Max. and min. transmission	0.994 and 0.722	—	0.928 and 0.800
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	4302/0/262	4416/0/451	2820/0/253
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.035	1.033	1.044
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0334, <i>wR</i> <sub>2</sub> = 0.0753	<i>R</i> <sub>1</sub> = 0.0377, <i>wR</i> <sub>2</sub> = 0.0791	<i>R</i> <sub>1</sub> = 0.0274, <i>wR</i> <sub>2</sub> = 0.0620
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0517, <i>wR</i> <sub>2</sub> = 0.0841	<i>R</i> <sub>1</sub> = 0.0638, <i>wR</i> <sub>2</sub> = 0.0952	<i>R</i> <sub>1</sub> = 0.0302, <i>wR</i> <sub>2</sub> = 0.0633
Largest diff. peak and hole (e nm <sup>-3</sup> )	477 and -347	232 and -256	306 and -275

Fig. 1. Molecular structure of **2c**.

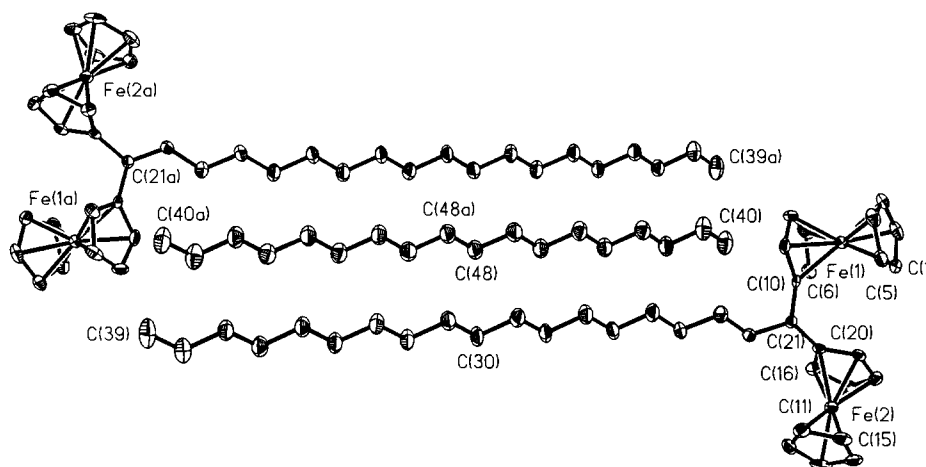
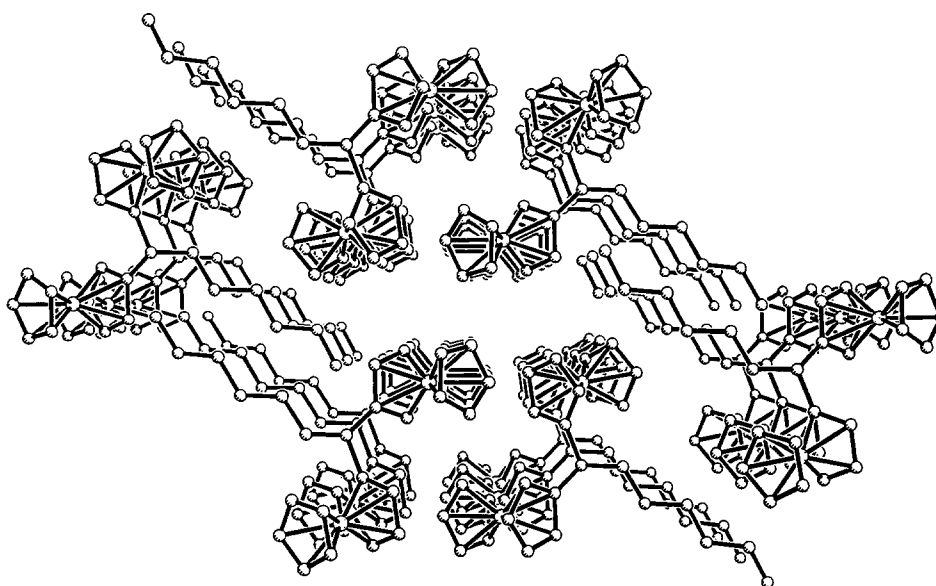


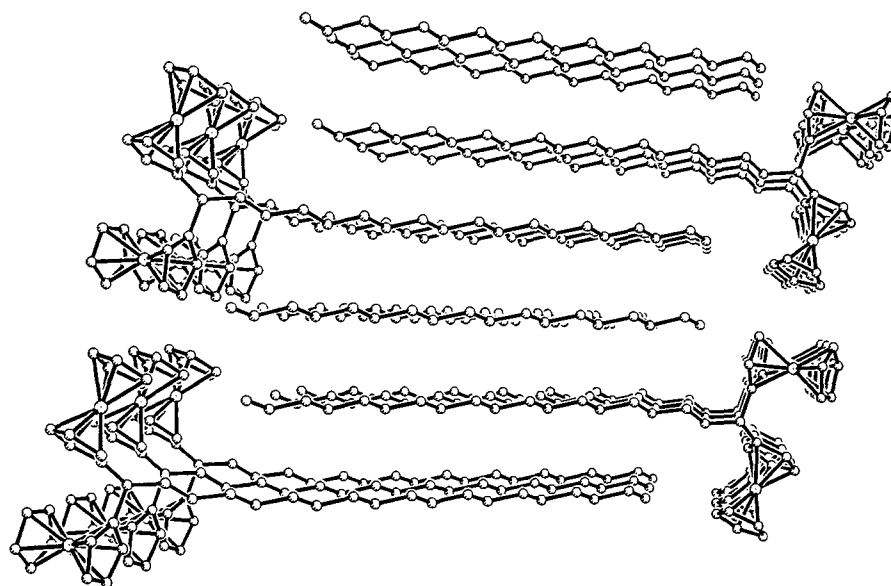
Scheme 1. R = H, alkyl, aryl.

ing the applicability of alkylation of sp-carbanions by diferrocenylmethyl cation. Compound (**3**) is of interest as a precursor for further substituted alkynes: deprotection of the trimethylsilyl group by fluoride should generate 1,1-diferrocenyl-2-propynide, which allows further derivatisation. Surprisingly, an attempted analogous reaction of (**1c**) with lithium acetylide–ethylendiamine complex does not yield any alkyne; instead *N,N'*-bis-diferrocenylmethyl ethylendiamine (**4**) is formed in 69% yield (Table 2). The preferential N-alkylation versus

C-alkylation can be understood in terms of the superior nucleophilicity of primary amines compared to sp-carbanions. Additionally, only the bis-N-alkylated product is formed. In a similar reaction (bis-(octamethylferrocenyl)methylation of 1,4-phenyldiamine), this has been explained by an electronic activation of the second amine group due to the greater electron density upon adding the first octamethylferrocenyl moiety [4].

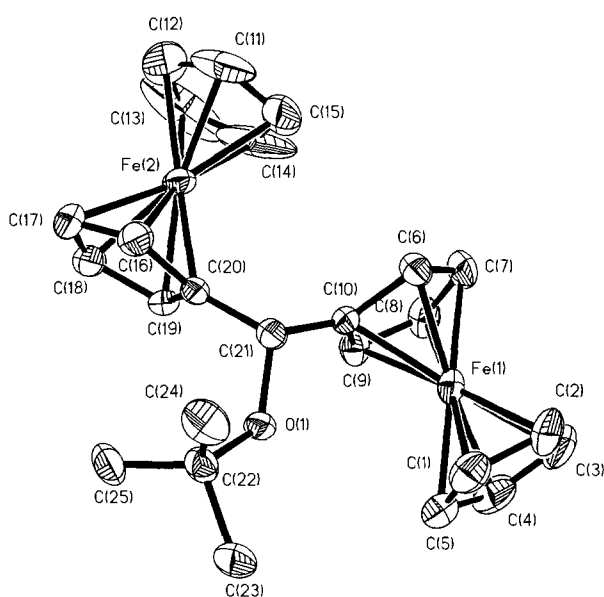
Alkylation of nucleophiles by methyl cation salts (**1b**) or (**1c**) is not limited to carbon- and nitrogen-donor nucleophiles: methanol and potassium *t*-butoxide are alkylated to the corresponding 1,1-diferrocenylmethyl ethers (**5a**) and (**5b**), respectively (Table 2). Reactions of sodium methoxide and methanol with ferrocenyl substituted methyl cation salts have been reported previously [22]. Compounds (**5a**) and (**5b**) are characterized by spectroscopic methods (Table 2) and for (**5b**) also by

Fig. 2. Molecular structure of **2d**.Fig. 3. Stacking of molecules for **2c**.

Fig. 4. Stacking of molecules for **2d**.

X-ray crystallography (Tables 3, 6, and 7; Fig. 5). 1,1-Diferrocenyl-dimethylether (**5a**) forms a calamitic mesophase (m.p.: 79–80 °C, clearing temperature: 100 °C) as revealed by preliminary investigations with a polarizing microscope equipped with a hot stage. The mesogenic properties of (**5a**) are rather surprising; we expected mesomorphism for compounds (**2b**), (**2c**), or (**2d**), which incorporate a long alkyl chain which should favour an orientationally ordered liquid. These compounds show no mesomorphism, whereas in contrast (**5a**), a compound with a “short” methoxy-substituent, does form a mesophase.

To further test the alkylating ability of the diferrocenylmethyl cation, (**1c**) was reacted with fluoride,

Fig. 5. Molecular structure of **5b**.

which is generally known to be a poor nucleophile in substitution reactions. Anhydrous potassium fluoride, complexed by 18-crown-6 to solubilize the fluoride, is readily converted to diferrocenylfluoromethane (**6**) in 96% yield. Although the reaction takes about one hour, as compared to the almost instantaneous alkylations with other nucleophiles, this result underlines the extraordinary reactivity of (**1c**). Fluoromethane (**6**) is very air-sensitive and hydrolyzes instantaneously as is easily indicated by a color change from yellow to the dark blue diferrocenylmethyl cation. Therefore we were not able to record an IR spectrum or obtain reliable C, H elemental analyses. The NMR spectra (Table 2) show the expected coupling to fluorine in the  $^1\text{H}$  spectrum ( $d$ ,  $^1J(^1\text{H}-^{19}\text{F}) = 47.9$  Hz), whereas in the  $^{13}\text{C}$  spectrum the expected number of signals are observed (one carbon is split into a doublet), but, owing to signal overlapping with the carbon resonances of the substituted cyclopentadienyl ring, no value for the coupling  $^1J(^{13}\text{C}-^{19}\text{F})$  could be ascertained. The consequence of the existence of fluoromethane (**6**) is the non-existence of a hypothetical diferrocenylmethyl fluoride; only in a solvated form (compound **1a**) does such a salt exist.

Attempting the same reaction with potassium chloride, complexed by 18-crown-6, led to failure. No reaction occurred. This is in agreement with the existence of diferrocenylmethyl chloride (**1b**).

### 3. Experimental

All manipulations involving air-sensitive materials were carried out by using standard Schlenk techniques under an atmosphere of argon. Solvents were dried and deoxygenated and distilled under argon prior to use.  $^1\text{H}$

and  $^{13}\text{C}$  NMR spectra were obtained on a Bruker AC 200. IR spectra were recorded on a 510 FT-IR Nicolet spectrometer. Mass spectra were recorded on a Varian CH-7 spectrometer. Melting points were determined on a Kofler hot plate apparatus. DSC measurements were obtained with a Perkin Elmer DSC4. Microanalyses were performed by the Analytical Department of Lenzing AG, A-4860 Lenzing, Austria.

### 3.1. $[(\text{Fc})_2\text{CH}]^+[\text{F}(\text{HF})_n]^-$ (**1a**)

Diferrocenylmethanol [23] (190 mg, 0.47 mmol) was dissolved in 40 ml  $\text{Et}_2\text{O}$ , and 0.2 ml of a 46% aqueous HF solution was added by syringe under magnetic stirring. The dark blue precipitate was filtered under argon, and washed three times with small portions of  $\text{Et}_2\text{O}$  and two times with *n*-hexane. After removing all volatiles in vacuo at ambient temperature overnight 167 mg (88.4% yield based on non-solvated diferrocenylmethylum fluoride) were obtained with spectral parameters listed in Table 1.

### 3.2. $[(\text{Fc})_2\text{CH}]^+\text{Cl}^-$ (**1b**)

Diferrocenylmethanol [23] (1.5 g, 3.75 mmol) was similarly dehydrated in  $\text{Et}_2\text{O}$  solution with 0.5 ml (5.6 mmol) concentrated aqueous HCl. The crude product was washed with  $\text{Et}_2\text{O}$  and *n*-hexane and dried in vacuo for 3 h. The resulting blue oily solid was dissolved in 30 ml dichloromethane and stirred for 3 h at room temperature with 3.0 ml of freshly distilled trimethylchlorosilane. The blue solution was evaporated to dryness on a vacuum line and 50 ml *n*-hexane were added to the solid dark blue residue. After stirring for 30 min the product was filtered under argon, washed with  $\text{Et}_2\text{O}$  and *n*-hexane, and dried in vacuo. 1.29 g (82% yield) microcrystalline hygroscopic (**1b**) was obtained with spectral data listed in Table 1. (**1b**) has to be stored under argon with protection from light and should be used within days.

### 3.3. $[(\text{Fc})_2\text{CH}]^+[\text{B}(\text{C}_6\text{H}_5)_4]^-$ (**1c**)

In a Schlenk tube 1.71 g (5 mmol) sodium tetrphenylborate was dissolved in 10 ml glacial acetic acid and 1.0 g (2.5 mmol) diferrocenylmethanol [23] was added under argon. After addition of 0.2 ml (2.5 mmol) trifluoromethanesulfonic acid a dark blue solution was obtained, which was stirred for 1.5 h. Crude (**1c**) precipitated as a blue solid, which was filtered, washed, and dried with trimethylchlorosilane analogously as for (**1b**), yielding 1.40 g (80%) anhydrous diferrocenylmethylum tetraphenylborate (**1c**) with spectral parameters listed in Table 1. (**1c**) is less air-sensitive compared to (**1b**) and can be handled for short periods in air without apparent hydrolysis or oxidation

and is therefore preferred as an alkylating agent in the following reactions. Under an atmosphere of argon (**1c**) can be stored for weeks.

### 3.4. $(\text{Fc})_2\text{CH}_2$ (**2a**)

Solid potassium hydride (38 mg, 0.95 mmol), obtained from a KH mineral oil suspension by removing all volatiles on a vacuum line, was added to 2 ml toluene. After addition of 0.53 ml (0.95 mmol) of a 1.8 molar trimethylaluminum toluene solution and stirring for 3 h a colorless suspension of potassium trimethylaluminum hydride was obtained. The addition of 5 ml THF gave a clear solution, which was cooled to  $-50^\circ\text{C}$  under an atmosphere of argon. Solid (**1c**) (110 mg, 0.16 mmol) was added in one portion under stirring. After 10 min the resulting yellow solution was allowed to warm to room temperature and worked up by pouring into ice/water, separating the organic phase, extracting the aqueous phase with two portions of  $\text{Et}_2\text{O}$ , washing the combined organic phases with three portions of water, drying with  $\text{Na}_2\text{SO}_4$ , and evaporating to dryness on a rotary evaporator, yielding a mixture of the crude product and potassium tetraphenylborate. Extraction with *n*-hexane and evaporating to dryness yielded 34 mg (93%) pure diferrocenylmethane (**2a**) with analytical and spectroscopic properties as reported [20,21].

### 3.5. $(\text{Fc})_2\text{CH}-(\text{CH}_2)_3-\text{CH}_3$ (**2b**)

500 mg (0.71 mmol) (**1c**) were dissolved in 20 ml THF and cooled to  $-70^\circ\text{C}$ ; 0.47 ml of a 2.0 molar hexane-*n*-BuLi solution (0.94 mmol, 1.3 mole equivalents) was added and an immediate color change from blue to yellow indicated complete reaction. Workup as for (**2a**) gave crude (**2b**), which was purified by flash chromatography on silica and recrystallized from *n*-hexane to afford 246.8 mg (79%) orange 1,1-diferrocenyl-*n*-pentane (**2b**), m.p.  $104.5\text{--}105^\circ\text{C}$ , (spectral data: Table 2). Analysis: calcd. for  $\text{C}_{25}\text{H}_{28}\text{Fe}_2$ : C, 68.21; H, 6.41; found: C, 68.03; H, 6.52. The crystal structure of (**2b**), which shows no unusual features, has been deposited at the Cambridge Crystallographic Data Centre, together with the crystal structures of (**2c**), (**2d**), and (**5b**).

### 3.6. $(\text{Fc})_2\text{CH}-(\text{CH}_2)_5-\text{CH}_3$ (**2c**)

326 mg (0.46 mmol) (**1c**) were reacted with 0.5 mmol *n*-hexyl lithium (0.2 ml of a 2.5 molar solution in hexane) in a similar manner as for (**2b**): 1,1-diferrocenyl-*n*-heptane (**2c**), orange crystals, 129 mg (60%), m.p.  $75\text{--}76.5^\circ\text{C}$ , (spectral data: Table 2; crystal structure: Tables 3, 4, and 7; Figs. 1 and 3). Analysis: calcd. for  $\text{C}_{27}\text{H}_{32}\text{Fe}_2$ : C, 69.26; H, 6.89; found: C, 69.61; H, 7.10.



Table 4

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Fe(1)	228(1)	1166(1)	5838(1)	26(1)
Fe(2)	4169(1)	3402(1)	3681(1)	25(1)
C(1)	990(2)	568(4)	5872(2)	49(1)
C(2)	1545(2)	-106(5)	6475(2)	57(1)
C(3)	2149(2)	-1259(4)	6243(2)	58(1)
C(4)	1983(2)	-1320(4)	5510(2)	52(1)
C(5)	1270(2)	-197(4)	5280(1)	44(1)
C(6)	2426(2)	3809(3)	5741(1)	30(1)
C(7)	2984(2)	3198(4)	6373(1)	33(1)
C(8)	3556(2)	1955(4)	6198(1)	34(1)
C(9)	3413(2)	1786(4)	5443(1)	30(1)
C(10)	2713(2)	2931(3)	5161(1)	25(1)
C(11)	4452(2)	1153(4)	3189(1)	41(1)
C(12)	5102(2)	2433(4)	3132(2)	45(1)
C(13)	5500(2)	2897(4)	3822(2)	43(1)
C(14)	5081(2)	1908(4)	4304(1)	35(1)
C(15)	4434(2)	826(3)	3916(1)	32(1)
C(16)	2938(2)	4182(3)	3240(1)	30(1)
C(17)	3588(2)	5370(4)	3075(1)	39(1)
C(18)	4039(2)	6042(3)	3716(2)	41(1)
C(19)	3663(2)	5267(3)	4277(1)	33(1)
C(20)	2970(2)	4122(3)	3989(1)	25(1)
C(21)	2341(2)	3122(3)	4386(1)	24(1)
C(22)	1414(2)	3971(3)	4281(1)	31(1)
C(23)	892(2)	3657(4)	3553(1)	40(1)
C(24)	-54(2)	4313(4)	3439(2)	39(1)
C(25)	-532(2)	3851(4)	2701(2)	39(1)
C(26)	-1463(2)	4521(4)	2532(2)	50(1)
C(27)	-1942(2)	3893(5)	1823(2)	68(1)

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

### 3.7. $2[(Fc)_2CH-(CH_2)_{17}-CH_3][CH_3-(CH_2)_{16}-CH_3]$ (**2d**)

496 mg (0.71 mmol) (**1c**) were reacted with 0.85 mmol (0.85 ml of a 1.0 molar octadecylmagnesium chloride solution in THF, 1.2 mole equivalents) in a similar manner as for (**2b**):  $2[1.1\text{-diferrocenyl-}n\text{-nonadecane}] \cdot [n\text{-ocatadecane}]$  (**2d**), orange needles, 390 mg (72%), m.p. 74–74.5 °C, (spectral data: Table 2; crystal structure: Tables 3, 5, and 7; Figs. 2 and 4). Analysis: calcd. for  $C_{96}H_{150}Fe_4$ : C, 75.48; H, 9.90; found: C, 74.98; H, 10.01.

### 3.8. $(Fc)_2CH-C \equiv C-Si(CH_3)_3$ (**3**)

445 mg (0.63 mmol) (**1c**) were reacted with 76 mg (0.73 mmol) lithium trimethylsilylacetylide (prepared from trimethylsilylacetylene with *n*-butyl lithium) in a similar manner as for (**2b**). 1,1-Diferrocenyl-3-trimethylsilyl-2-propyne (**3**), orange crystals, 221 mg (75.4%), m.p. 138–139 °C, (spectral data: Table 2). Analysis: calcd. for  $C_{26}H_{28}Fe_2Si$ : C, 65.02; H, 5.88; found: C, 64.25; H, 5.98.

### 3.9. $[(Fc)_2CH-NH-CH_2]_2$ (**4**)

451 mg (0.64 mmol) (**1c**) were reacted with 150 mg (1.6 mmol, 2.5 mole equivalents) lithium acetylide–eth-

Table 5

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Fe(1)	4775(1)	2663(1)	4147(1)	22(1)
Fe(2)	1254(1)	7626(1)	4029(1)	21(1)
C(1)	4332(7)	3158(3)	4742(1)	33(1)
C(2)	4062(7)	1925(4)	4753(1)	33(1)
C(3)	6079(7)	1328(3)	4607(1)	32(1)
C(4)	7591(7)	2181(4)	4507(1)	33(1)
C(5)	6516(7)	3311(3)	4590(1)	31(1)
C(6)	2042(6)	3340(3)	3767(1)	25(1)
C(7)	2719(7)	2113(3)	3727(1)	33(1)
C(8)	4942(8)	1989(3)	3581(1)	34(1)
C(9)	5688(7)	3152(4)	3532(1)	27(1)
C(10)	3883(6)	4002(3)	3645(1)	20(1)
C(11)	3415(7)	8733(3)	3730(1)	35(1)
C(12)	1216(9)	9075(4)	3570(1)	38(1)
C(13)	-214(7)	9369(3)	3911(2)	38(1)
C(14)	1152(8)	9200(3)	4280(1)	35(1)
C(15)	3346(7)	8808(3)	4168(1)	34(1)
C(16)	-202(6)	6278(3)	3809(1)	24(1)
C(17)	-1272(6)	6589(3)	4188(1)	26(1)
C(18)	359(7)	6390(3)	4512(1)	28(1)
C(19)	2450(6)	5968(3)	4336(1)	21(1)
C(20)	2128(6)	5889(3)	3896(1)	19(1)
C(21)	3840(6)	5360(3)	3598(1)	19(1)
C(22)	3411(6)	5922(3)	3128(1)	25(1)
C(23)	5352(7)	5628(4)	2833(1)	34(1)
C(24)	5084(7)	6293(3)	2381(1)	32(1)
C(25)	7183(7)	6111(4)	2111(1)	36(1)
C(26)	7081(7)	6852(4)	1676(1)	35(1)
C(27)	9281(7)	6731(4)	1431(1)	38(1)
C(28)	9255(7)	7496(4)	999(1)	36(1)
C(29)	11485(7)	7404(4)	765(1)	38(1)
C(30)	11464(7)	8161(4)	331(1)	37(1)
C(31)	13709(7)	8068(4)	99(1)	38(1)
C(32)	13694(7)	8821(4)	-332(1)	37(1)
C(33)	15929(7)	8734(4)	-564(1)	38(1)
C(34)	15930(7)	9484(4)	-996(1)	39(1)
C(35)	18157(7)	9387(4)	-1230(1)	38(1)
C(36)	18142(7)	10151(4)	-1662(1)	40(1)
C(37)	20353(7)	10059(4)	-1898(1)	37(1)
C(38)	20327(8)	10823(4)	-2330(1)	47(1)
C(39)	22546(8)	10705(5)	-2565(1)	59(2)
C(40)	-49(8)	2407(5)	2750(1)	57(1)
C(41)	2169(8)	2339(4)	2535(1)	51(1)
C(42)	2211(8)	3116(4)	2106(1)	45(1)
C(43)	4432(7)	3016(4)	1880(1)	41(1)
C(44)	4451(7)	3763(4)	1447(1)	41(1)
C(45)	6680(7)	3652(4)	1217(1)	40(1)
C(46)	6665(7)	4400(4)	783(1)	41(1)
C(47)	8890(7)	4300(4)	549(1)	44(1)
C(48)	8888(7)	5042(4)	115(1)	41(1)

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

ylendiamine complex in a similar manner as for (2b). Chromatographic purification using neutral aluminum oxide as stationary phase instead of silica was necessary to avoid protonation or immobilization on the stationary phase, indicated by a color change to blue due to formation of  $\alpha$ -ferrocenyl- $\alpha$ -ammonium compounds: 1,2-bis-diferrocenylmethylamino-ethane (4), orange crystals, 183 mg (69%), m.p. 186–186.5 °C, (spectral data: Table 2). Analysis: calcd. for  $C_{44}H_{44}Fe_4N_2$ : C, 64.12; H, 5.38; N, 3.40; found: C, 63.87; H, 5.60; N, 3.80.

### 3.10. $(Fc)_2CH-OCH_3$ (5a)

500 mg (0.71 mmol) (1c) were reacted with 80 mg (2.5 mmol) methanol in a similar manner as for (2b). Analogous workup and chromatographic purification on neutral aluminum oxide afforded 1,1-diferroceny-dimethyl-ether (5a), orange crystals, 256 mg (87%), m.p. 79–80 °C, (spectral data: Table 2). Analysis: calcd. for  $C_{22}H_{22}Fe_2O$ : C, 63.81; H, 5.35; O, 3.86; found: C, 62.81; H, 5.60; O, 3.53.

### 3.11. $(Fc)_2CH-OC(CH_3)_3$ (5b)

277 mg (0.39 mmol) (1c) were reacted with 72.3 mg (0.59 mmol, 1.5 mole equivalents) potassium *t*-butoxide in a similar manner as for (5a): 1,1-diferroceny-methyl-*t*-butyl-ether (5b), orange crystals, 152 mg (85%), m.p. 141–142 °C, (spectral data: Table 2; crystal structure: Tables 3, 6, and 7; Fig. 5). Analysis: calcd. for  $C_{25}H_{28}Fe_2O$ : C, 65.82; H, 6.19; O, 3.51; found: C, 65.04; H, 6.70; O, 3.40.

### 3.12. $(Fc)_2CH-F$ (6)

300 mg (0.42 mmol) (1c) were dissolved in 20 ml dichloromethane in a Schlenk tube. To this solution were added at ambient temperature 250 mg (4.3 mmol) dry potassium fluoride and 250 mg (0.69 mmol) dibenzo-18-crown-6, purified and dried by converting into the acetonitril adduct [24] and removing the complexed acetonitrile under high vacuum. After stirring for 1 h the color of the solution changed from blue to yellow, indicating complete reaction. Workup was performed under exclusion of air, because (6) immediately turns blue on exposure to air. Dichloromethane was removed in vacuo, and the residue was dissolved in *n*-hexane and filtered under argon to remove the non-hexane soluble byproducts dibenzo-18-crown-6, potassium tetraphenylborate, and the excess potassium fluoride. Evaporating the yellow *n*-hexane solution to dryness yielded (6), which was > 98% pure according to NMR analysis (Table 2): diferrocenylfluoromethane (6), yellow powder, 162 mg (96%). Due to the high air-

Table 6

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$
Fe(1)	711(1)	8794(1)	8964(1)	28(1)
Fe(2)	4704(1)	7318(1)	6615(1)	28(1)
O(1)	351(3)	9142(1)	7086(1)	27(1)
C(1)	-319(6)	10011(2)	8830(2)	43(1)
C(2)	395(7)	9919(3)	9566(2)	54(1)
C(3)	-490(7)	9221(3)	9926(2)	61(1)
C(4)	-1758(5)	8894(3)	9412(2)	52(1)
C(5)	-1632(5)	9381(2)	8741(2)	41(1)
C(6)	3248(4)	8655(2)	8616(2)	33(1)
C(7)	2892(5)	8093(3)	9229(2)	40(1)
C(8)	1521(5)	7530(2)	9016(2)	39(1)
C(9)	1017(4)	7741(2)	8268(2)	31(1)
C(10)	2076(4)	8438(2)	8012(2)	24(1)
C(11)	7186(5)	7409(4)	7017(3)	73(2)
C(12)	7070(9)	6749(6)	6557(3)	114(3)
C(13)	5865(13)	6183(3)	6814(6)	141(4)
C(14)	5214(6)	6542(5)	7497(5)	112(3)
C(15)	6080(6)	7308(4)	7598(2)	68(1)
C(16)	4029(4)	8437(2)	6065(2)	35(1)
C(17)	4114(5)	7725(3)	5548(2)	42(1)
C(18)	2907(5)	7095(2)	5784(2)	40(1)
C(19)	2063(4)	7408(2)	6455(2)	29(1)
C(20)	2759(4)	8246(2)	6629(2)	25(1)
C(21)	2103(4)	8854(2)	7239(2)	25(1)
C(22)	21(4)	9748(2)	6464(2)	31(1)
C(23)	-1723(5)	10157(2)	6694(2)	44(1)
C(24)	1411(5)	10438(2)	6392(2)	44(1)
C(25)	-212(6)	9251(2)	5716(2)	44(1)

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

sensitivity of (6) no satisfactory elemental analysis could be obtained.

### 3.13. X-ray analyses of (2b), (2c), (2d), and (5b)

A Siemens P4 diffractometer with graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 71.073$  pm) was used for data collection (Table 3). The unit cell parameters were determined and refined from 20 to 25 randomly selected reflections, obtained by P4 automatic routines. Data were measured via  $\omega$ -scan and corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [25]. For (2b), (2c) and (5b) an empirical absorption correction [26] was done. The structures were solved by direct methods, SHELXS-86 [27], and refined by a full matrix least-squares procedure using SHELXL-93 [28]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions. Tables of thermal parameters and hydrogen positions have been

Table 7  
Selected bond lengths <sup>a</sup> and angles <sup>b</sup> for 2c, 2d, 5b

	2c	2d	5b
<b>Bond lengths</b>			
Fe(1)–C(1–5) <sup>c</sup>	203.7(3)	203.8(4)	204.2(4)
Fe(1)–C(6–10) <sup>c</sup>	204.2(3)	204.5(4)	204.2(3)
Fe(2)–C(11–15) <sup>c</sup>	204.2(3)	203.6(4)	200.9(5)
Fe(2)–C(16–20) <sup>c</sup>	204.4(3)	204.2(4)	204.1(3)
C <sub>ring</sub> –C <sub>ring</sub> in Cp[C1–C5] <sup>c</sup>	140.4(5)	141.0(6)	141.1(6)
C <sub>ring</sub> –C <sub>ring</sub> in Cp[C6–C10] <sup>c</sup>	142.1(4)	141.8(5)	141.5(5)
C <sub>ring</sub> –C <sub>ring</sub> in Cp[C11–C15] <sup>c</sup>	141.6(4)	140.8(6)	135.2(9)
C <sub>ring</sub> –C <sub>ring</sub> in Cp[C16–C20] <sup>c</sup>	142.1(4)	142.0(5)	142.0(5)
Fe(1)–cent(Cp[C1–C5])	165.1(2)	164.7(2)	165.1(0)
Fe(1)–cent(Cp[C6–C10])	164.5(1)	165.1(2)	164.5(0)
Fe(2)–cent(Cp[C11–C15])	164.9(2)	164.7(2)	164.7(0)
Fe(2)–cent(Cp[C16–C20])	164.7(1)	164.6(2)	164.5(0)
C(10)–C(21)	151.9(3)	151.3(5)	150.6(4)
C(20)–C(21)	151.6(3)	150.6(5)	151.0(4)
C(21)–C(22)	154.2(3)	154.9(5)	– <sup>d</sup>
C(22)–C(23)	152.1(4)	151.2(5)	
C(23)–C(24)	151.4(4)	152.2(5)	
C(24)–C(25)	153.5(4)	151.7(5)	
C(25)–C(26)	149.9(4)	150.8(5)	
C(26)–C(27)	151.5(5)	152.0(5)	
C(27)–C(28)		151.2(5)	
C(28)–C(29)		151.7(6)	
C–C[C(30)–C(39)] <sup>c</sup>		151.2(5)	
C–C[C(40)–C(48a)] <sup>c</sup>		150.5(6)	
<b>Angles</b>			
plane(Cp[C6–C10])–plane(Cp[C16–C20])	84.46(8)	81.23(15)	56.37(0)
C(20)–C(21)–C(10)	111.7(2)	110.2(3)	112.9(2)
C(22)–C(21)–C(20)	110.9(2)	112.2(3)	– <sup>e</sup>
C(22)–C(21)–C(10)	111.8(2)	110.5(3)	
C(23)–C(22)–C(21)	113.5(2)	113.7(3)	
C(24)–C(23)–C(22)	116.0(2)	114.5(3)	
C(25)–C(24)–C(23)	111.6(2)	113.1(3)	
C(26)–C(25)–C(24)	115.1(3)	115.1(3)	
C(27)–C(26)–C(25)	112.6(3)	113.6(3)	
C–C–C[C(28)–C(39)] <sup>c</sup>		114.6(3)	
C–C–C[C(40)–C(48a)] <sup>c</sup>		114.7(4)	

<sup>a</sup> pm;

<sup>b</sup> degrees;

<sup>c</sup> mean value;

<sup>d</sup> C(21)–O(1) = 143.3(4), O(1)–C(22) = 146.1(3), C–C[C(22)–C(23,24,25)] <sup>c</sup> = 152.1(5);

<sup>e</sup> C(22)–O(1)–C(21) = 119.9(2).

deposited at the Cambridge Crystallographic Data Centre.

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