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Synthesis and characterization of new perfluoroalkylated side-chain ferrocenes and ferricinium salts

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Abstract

The synthesis and characterization of various mono- and 1,1′-bis-[ω-(*F*-alkyl)acyl]ferrocenes, 1,1′-bis-[ω-(*F*-alkyl)alkyl]ferrocenes and 1,1′-bis-[ω-(*F*-alkyl)-α-(hydroxy)-alkyl]ferrocenes are described (where *F*-alkyl denotes perfluoroalkylation). The [(*F*-alkyl)acyl]ferrocenes were obtained by Friedel–Crafts acylation of ferrocene with (*F*-alkyl)acyl chlorides. The (*F*-alkyl)alkyl and (*F*-alkyl)-α-(hydroxy)alkyl analogues were selectively prepared by reduction of the acyl derivatives with $LiAlH_4$–$AlCl_3$ and $LiAlH_4$ respectively. These reactions illustrate the chemical inertness of (*F*-alkyl)acyl and (*F*-alkyl)alkyl chains under strongly reducing conditions. When the acylation of ferrocene was performed with ω-[2-(*F*-alkyl)ethenyl]acyl chlorides, acylferrocenes were obtained but their side chains contained the (*Z*)–CF=CH–CH(Cl)– sequence. Formation of these chains resulted from a highly stereospecific (*E*)–CF_2–CH=CH– to (*Z*)–CF=CH–CH(Cl) transformation, which involves an F–Cl exchange and a double-bond migration in the [2-(*F*-alkyl)ethenyl]acyl chain. The 1,1′-bis-[11-(*F*-alkyl)undecanoyl]ferrocenes were found to be most effectively oxidized to the corresponding ferricinium species by HBF_4–*p*-benzoquinone, while their hydrocarbon analogue 1,1′-bis-[undecanoyl]ferrocene underwent a Michael addition to give benzofuranylferrocenes.

Keywords: Perfluoroalkylated ferrocene; Ferricinium; Benzofuranylferrocene; Iron

1. Introduction

The discovery of the anticancer properties of *cis*-platin and its successful introduction into the clinic has served to focus attention on inorganic and organometallic compounds as potential chemotherapeutic agents [1]. The tremendous interest in new transition metal complexes as anticancer drugs arises partly from the drawbacks associated with the use of platinum complexes to treat tumors. The disadvantages of *cis*-platin, such as its extreme nephrotoxicity and its limited efficacy against several human tumors, have prompted an intensive search for platinum complexes [2] and non-platinum [3] analogues with a lower toxicity, an improved therapeutic index or a completely different activity spectrum from that of *cis*-platin. A variety of metallocene compounds have thus been synthesized that display antitumor activities against various experimental and human tumors and unusual spectra of organ toxicity [3–6].

An alternative approach to modifying the therapeutic index of a drug may be to use drug carrier and delivery systems, among which liposomes and/or injectable fluorocarbon emulsions (to be used simultaneously as drug and oxygen-delivering systems) are particularly attractive. Liposomes have been used as drug carriers [7,8] to improve the therapeutic index of several anticancer agents, to enhance their bioavailability, to modify their biodistribution, and even to target tumoral cells and to induce antitumor activity against resistant cells. The use of fluorocarbon emulsions is expected to combine the numerous advantages of a drug delivery system with the considerable benefits brought by fluorocarbon emulsions to therapy, among which are (i) their ability to activate the reticuloendothelial system and to increase cell oxygenation, thus enhancing the tumoricidal effects of radiation or of cytotoxic drugs [9,10], and (ii) their high intravascular persistence and tendency to concentrate around tumors [11].

Our goal is thus to develop new amphiphilic analogues of metal complexes known to have biological and/or therapeutic properties, which may be transported by liposomes and more particularly by fluorocar-

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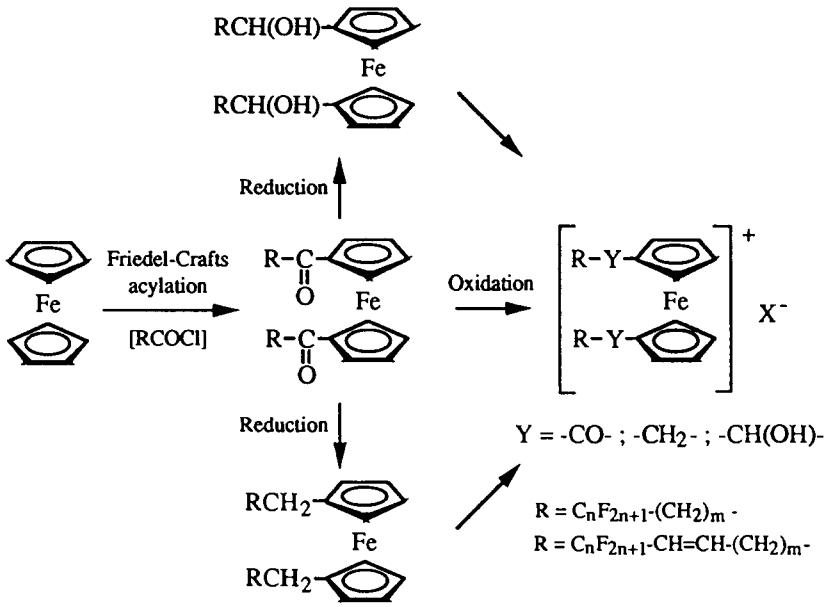


Scheme 1. Route to perfluorakylated side-chain ferrocenes and ferricinium complexes.

bon emulsions. With this objective, we recently synthesized perfluoroalkylated amphiphilic bipyridine ligands [12] and their platinum and palladium complexes [13], which, when incorporated into liposomes, exhibited an in-vitro antitumor activity comparable with that of *cis*-platin [14]. In order to extend the range of amphiphilic cytotoxic drugs, we have selected perfluoroalkylated ferrocene–ferricinium analogues of complexes that have been shown to constitute a class of potential chemotherapeutic agents [5,6]. The novel features of our complexes lie in the long hydrophobic chain consisting of a hydrocarbon spacer terminated by a perfluoroalkyl (or *F*-alkyl) [1] tail of various lengths which is linked to the cyclopentadienyl ligand through a carbonyl or a C–C bond. The perfluoroalkylated chains in these compounds are intended to increase their hydrophobic and fluorophilic character, in order to facilitate their incorporation into liposomes and fluorocarbon emulsions, respectively.

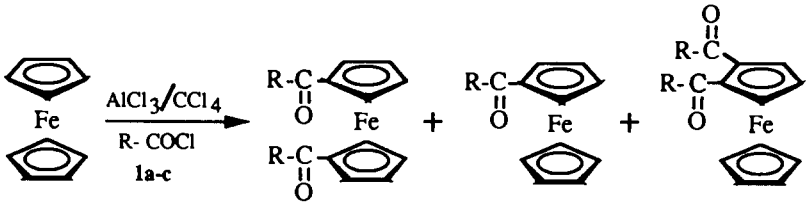
In addition to their potential in biomedical applications, these new ferrocenes and ferriciniums could also, because of this unusual ferrocene–ferricinium electrochemical behavior, act as reliable mediators for some redox reactions [15]. Such amphiphilic ferrocene derivatives are also of considerable interest in view of their multiple possibilities as self-organized molecular systems (micelles, monolayers, Langmuir–Blodgett films, vesicles etc.) and thermotropic liquid crystals, with applications in electronics and non-linear optic for example [16]. Furthermore, the presence of highly fluorinated long chains is expected to confer on these systems some of the specific features that make up the uniqueness of fluorinated materials, e.g. their hydrophobicity and lipophobicity. This should result in new systems with properties substantially different from those known up to now.

We describe here the synthesis and characterization of three series of ferrocene derivatives including 1,1′-bis-[ω-(*F*-alkyl)acyl]ferrocenes, 1,1′-bis-[ω-(*F*-alkyl)alkyl]ferrocenes and 1,1′-bis-[ω-(*F*-alkyl)-α-(hydroxy)alkyl]ferrocenes (Scheme 1). We also describe our attempts to prepare ω-[2-(*F*-alkyl)ethenyl]acylferrocenes which differ from the former metallocenes in respect of the presence of a double bond between the fluorinated tail and hydrocarbon spacer. The chemical oxidation of some of these perfluoroalkylated ferrocenes to their ferricinium analogues has also been investigated.

2. Results and discussion

In view of their potential future applications, it was desirable that the new perfluoroalkylated amphiphilic ferrocenes–ferriciniums (Scheme 1) possess a modular structure (with variable *F*-alkyl tail lengths, hydrocarbon spacers (saturated or unsaturated), and hydroxyls group in proximity to the ferrocene–ferricinium head) to allow for stepwise adjustment of their physicochemical properties (e.g. their fluorophilicity, lipophilicity and consequently hydrophobicity, and hydrophilicity). The carbonyl or C–C bond connectors between the hydrophobic chains and cyclopentadienyl ring were specifically selected for modulating the electronic and redox properties of the complexes and consequently their biological activity.

[1] *F*-alkyl means that all hydrogen atoms attached to the carbon atoms of the alkyl radical are replaced by fluorine atoms.



a: R = C_8F_{17}-$(CH_2)_{10}$-
b: R = C_6F_{13}-$(CH_2)_{10}$-
c: R = C_4F_9-$(CH_2)_{10}$-

Scheme 2. Synthesis of (*F*-alkyl)acylferrocenes.

Aiming at these goals, it was necessary to develop a flexible synthetic strategy for the preparation of the complexes. This strategy (Scheme 1), starting from ferrocene, involves the synthesis of the perfluoroalkylated acyl-substituted ferrocenes from which it should be possible to obtain the perfluoroalkylated alkylferrocenes and α-(hydroxy)alkylferrocenes by selective reduction. Chemical (or electrochemical) oxidation of these ferrocenes should then give the corresponding ferricinium species. This route to perfluoroalkyl-substituted ferrocenes appears to be capable of being generalized to any desired length of the perfluoroalkyl tail and of the spacer between the functional tail and the cyclopentadienyl ring.

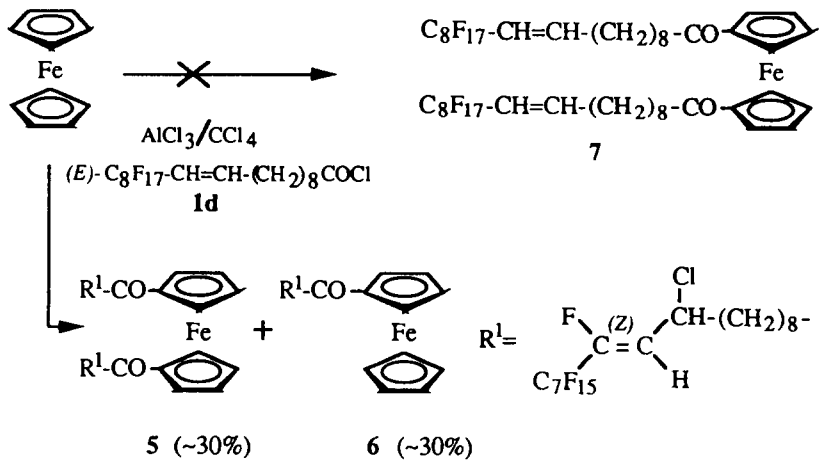
2.1. Synthesis of (F-alkyl)acyl-ferrocenes

The 1,1′-bis-[ω-(*F*-alkyl)acyl]ferrocenes **2a–2c** were synthesized through a standard Friedel–Crafts reaction between ferrocene and the corresponding, readily accessible ω-(*F*-alkyl)acyl chlorides **1a–1c** in the presence of $AlCl_3$; yields ranged from 45 to 60% (Scheme 2). Although the syntheses were performed under conditions which were expected to yield preferentially disubstituted to monosubstituted ferrocenes, the formation of **2** was found to be accompanied by that of the monosubstituted analogues **3** (less than 10%), with the rest almost accounted for by unchanged ferrocene. We also isolated and identified the disubstituted 1,2-isomer **4b** (less than 1%); the formation of the **4a** and **4c** analogues, with very low yields, was shown to occur by thin layer chromatography (TLC) and NMR spectroscopy, by comparison with the data for **4b**. Most importantly, the ^{19}F NMR spectra of **2–4** indicated that the (*F*-alkyl)acyl chains were not affected by the reaction conditions (e.g. no F–Cl exchange occurred; vide infra).

The 1,1′-disubstitution in **2** is more specifically confirmed by the presence of the characteristic ^1H and ^{13}C NMR patterns for the protons (A_2X_2 system) and carbons (three ^{13}C resonances) of the monosubstituted cyclopentadienyl (Cp) ligands.

The monosubstituted compounds **3** show ^1H and ^{13}C NMR spectra that exhibit the characteristic patterns of an unsubstituted Cp ring (a singlet at 4.20 ppm for the Cp protons and a single ^{13}C line at 69 ppm for the Cp carbon atoms) in addition to the above-mentioned characteristic NMR patterns of a monosubstituted Cp ring.

The structure of **4b**, with the two fluorinated acyl chains connected on the same cyclopentadienyl ring in



Scheme 3. Friedel–Crafts reaction between ferrocene and 11-(*F*-octyl)undec-10-enoyl chloride.

position 1 and 2, is also confirmed by NMR spectroscopy. The ^{13}C NMR spectrum exhibits only two ^{13}C lines for the eight cyclopentadienyl CH carbon atoms but in an intensity ratio of about 1/3, very different from the 1/1 ratio observed for the cyclopentadienyl CH carbon atoms in the 1,1'-disubstituted derivatives **2**. This pattern is in agreement with a series of two CH groups and one CH group for the disubstituted Cp ring, the latter being coincidentally equivalent to the CH groups for the unsubstituted Cp ring. Accordingly, the ^1H NMR spectrum displays a sharp singlet at 4.20 ppm and two larger singlets at 4.68 and 4.87 ppm which integrate for five, one and two Cp protons respectively. In view of the electronic effects on the ^1H chemical shifts expected for a carbonyl group, the respective location and integration of the two downfield singlets measured for the protons of the disubstituted Cp ring most likely indicate a 1,2 isomer (**4b**) rather than a 1,3 isomer, for which the most downfield signal is expected to integrate for two protons.

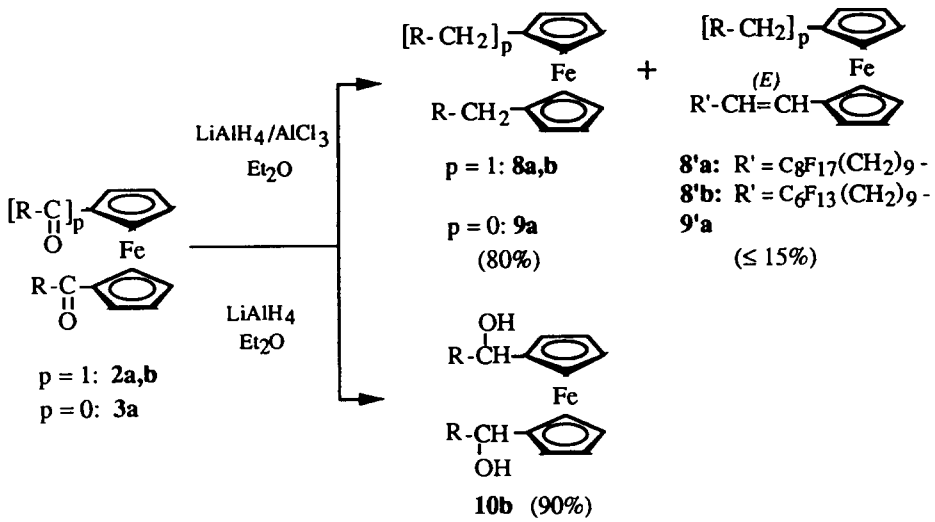
2.2. *Synthesis of ferrocenes containing (F-alkyl)–CF=CH–CH(Cl)acyl side-chains*

During our attempts to prepare 1,1'-bis-[ω-[(2-*F*-alkyl)ethenyl]acyl]ferrocenes such as **7** by Friedel–Crafts acylation of ferrocene with ω-[2-(*F*-alkyl)ethenyl]acyl chlorides, such as **1d**, a more complex reaction occurred (Scheme 3). Mono- and 1,1'-bis-(perfluoroalkylated-acyl)ferrocenes were indeed obtained as a result of an electrophilic substitution reaction on the cyclopentadienyl ring. However, the NMR spectra were not consistent with the expected ω-[2'-(*F*-alkyl)ethenyl]acyl side chains as in **7**. In order to gain further insight into this reaction and to characterize the compounds formed, we performed the reaction without ferrocene. As already reported, we found that the action of $AlCl_3$ on (*E*)-C_8F_{17}–CH=CH–$(CH_2)_8$COCl led, after ethanolysis, to the formation of (*Z*)–CF_3–$(CF_2)_6$–CF=CH–CH(Cl)–CH_2–COOEt, as a result of the highly stereospecific (*E*)-CF_2–CH=CH– to (*Z*)–CF=CH–CH(Cl) (F and H are in *trans*) transformation which involves an F–Cl exchange and double-bond migration [17].

When the reaction between $AlCl_3$ and (*E*)-C_8F_{17}–CH=CH–$(CH_2)_8$–COCl was performed in the presence of ferrocene, the isolated monosubstituted (**6**) and 1,1'-disubstituted (**5**) ferrocenes (about 30% each) did indeed contain chains in which the (*Z*)–CF=CH–CH(Cl)– sequence was present, as shown in Scheme 3.

The IR and NMR data for **5** and **6** clearly indicate that (i) both are ketones, (ii) one of the two Cp rings in **6** and each Cp ring in **5** is connected to a substituent through a carbonyl group, (iii) both substituents in **5** and one in **6** are identical, and (iv) each substituent in **5** and **6** contains the (*Z*)–CF=CH–CH(Cl)– sequence. Compounds **5** and **6** display the ^1H and ^{13}C NMR patterns for the Cp rings characteristic of a 1,1' substitution (**5**) and a monosubstitution (**6**), as described for **2** and **3** respectively. They also exhibit the ^{19}F, ^1H and ^{13}C NMR patterns observed for the (*Z*)–CF_3–$(CF_2)_6$–CF=CH–CH(Cl)–CH_2– sequence found in (*Z*)–CF_3–$(CF_2)_6$–CF=CH–CH(Cl)–CH_2–COOEt [17], except for the signal of the CH(Cl) proton which is overlapped by the A_2X_2 system of the Cp protons. The occurrence of F–Cl exchange is, however, confirmed by elemental analyses and by the presence in the mass spectrum of **6**, of the molecular peak $[M]^{\cdot+}$ at $m/e = 786$ (^{35}Cl) and 788 (^{37}Cl) and of $[M - Cl]^{\cdot+}$ at $m/e = 751$.

It should be noted that the presence of a single ^{19}F resonance for the CF_2 in α to CF=CH and of a single series of ^{13}C resonances for the CF_2–CF=CH–CH_2 moiety in **5** and **6** indicates that the isolated compounds are present as single isomers with respect to the double-bond configuration [17], but in the case of **5** this



Scheme 4. Synthesis of (*F*-alkyl)alkylferrocenes and ω-(*F*-alkyl)-α-(hydroxy)alkylferrocenes (*R* is as defined in Scheme 2).

does not exclude a mixture of diastereoisomers with respect to the two asymmetric CH(Cl) carbon atoms. The large value (about 30 Hz) of the ^{19}F–^{1}H coupling constant between the ethylenic fluorine and proton shows furthermore that the double bonds in **5** and **6** are of *Z* configuration [17].

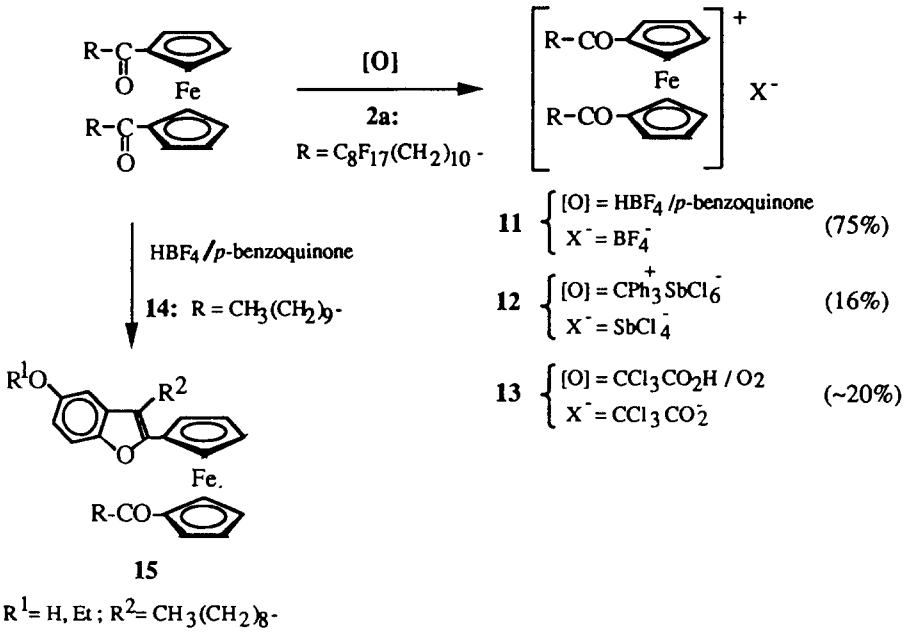
2.3. Synthesis of ω-(F-alkyl)alkyl- and of ω-(F-alkyl)-α-(hydroxy)alkylferrocenes

Mono- and bis-[ω-(*F*-alkyl)alkyl]ferrocenes and ω-(*F*-alkyl)-α-(hydroxy)alkylferrocenes are two other families of compounds expected to be obtainable by relatively simple and direct methods, namely by total and partial reduction of the carbonyl group in the (*F*-alkyl)acylferrocenes **2** and **3**.

Full reduction of the latter derivatives with $LiAlH_4$–$AlCl_3$ gave their (*F*-alkyl)alkylferrocenes **8** and **9** respectively with yields reaching 80% (Scheme 4). Their formation is accompanied by that of the unsaturated derivatives **8′** and **9′** (15% or less), as a result of an elimination of water from a monohydroxy intermediate, and by minor amounts of hydroxy derivatives (such as **10b** confirmed by its selective synthesis from **2b**; vide infra) as a result of incomplete reduction. Most importantly, the ^{19}F NMR spectra of all these compounds, which are identical with those of their respective precursors, showed that the fluorinated tail remained intact, and thus that the strong reducing agent did not induce F–H or F–Cl exchange or HF elimination.

The simultaneous presence in **8′** of a saturated–$(CH_2)_{11}$– spacer linked to one Cp ring and of an unsaturated –CH=CH–$(CH_2)_9$– spacer linked in α of its double bond to the other Cp ring is unambiguously confirmed by the ^{1}H and ^{13}C NMR spectra. Thus the NMR spectra of **8′** exhibit the various signals corresponding to the Cp–$(CH_2)_{11}$ moiety that are observed for **9**. The presence of a Cp–CH=CH–(CH_2)– sequence is attested by the presence in their ^{1}H NMR spectra of (i) a doublet at 6.03 ppm (J = 16 Hz) for the ethylenic proton in α to the Cp ring, (ii) a doublet of triplets (J = 16 and 7 Hz respectively) at 5.80 ppm for the other ethylenic proton and (iii) a doublet of triplets (both J = 7 Hz) at 2.1 ppm for the CH_2 in α to the double bond. The high value of the coupling constant between the ethylenic protons indicates further that the double bond is of *E* configuration. In addition, their ^{13}C NMR spectra with (iv) two resonances (126.3 and 128.5 ppm) characteristic of ethylenic carbons, (v) one signal for the CH_2 in α of the double bond at 33.1 ppm and (vi) two sets of three ^{13}C lines for the two Cp rings undoubtedly confirm the proposed structure for **8′**.

Partial reduction of the carbonyl groups in **2b** with $LiAlH_4$ alone as the reducing agent (Scheme 4) afforded the expected bis-[ω-(*F*-alkyl)-α-(hydroxy)alkyl] ferrocenes(**10b**) almost quantitatively (90% yield). The spectroscopic data (IR, ^{1}H and ^{13}C NMR) for **10b** are fully consistent with the proposed structure. Owing to the presence of the two chiral CH(OH) carbons, **10b** exists as a mixture of diastereoisomers, as shown by the splitting of all the ^{13}C resonances corresponding to the Cp–CH(OH)CH_2 moiety.



Scheme 5. Oxidation of 1,1′-bis-[(*F*-alkyl)acyl]ferrocenes into their ferriciniums ions and formation of benzofuranylferrocenes from 1,1′-bis-(undecanoyl)ferrocene.

2.4. Chemical oxidation of the perfluoroalkylated ferrocenes

Among the ferrocene–ferricinium complexes, only the ferricinium species display antitumor activity. Their activity is furthermore related to the nature of the anion X^- associated with the cationic ferricinium [5,6]. Numerous systems are known for the oxidation of ferrocene derivatives to their ferriciniums [18]. It was therefore judicious to select the systems which combine efficiency and the most interesting X^- anions in terms of antitumor activity which include, among others, $FeCl_4^-$, $SbCl_4^-$, BF_4^-, I_3^-, $CCl_3CO_2^-$ or 2,4,6-trinitrophenolate anions. Several oxidants namely 2,4,6-trinitrophenol–*p*-benzoquinone, iodine, $Ph_3C^+SbCl_6^-$, CCl_3CO_2H, HBF_4–*p*-benzoquinone (all of which are known to oxidize ferrocene [18]) were therefore tried. In order to demonstrate the feasibility of chemical oxidation of ferrocenes bearing perfluoroalkylated side chains, the tests were performed on the 1,1′-bis-(*F*-alkyl)acylferrocenes **2**; owing to the electronic effects of the carbonyl functions on the redox potential of ferrocenes [19], these fluorinated acylferrocenes were expected to be oxidized, for a given oxidizing system, with more difficulty than any of the other fluorinated ferrocenes described here.

We found that the HBF_4–*p*-benzoquinone system was the most efficient for the oxidation of the 1,1′-bis-(*F*-alkyl)acylferrocene **2a** (Scheme 5). The blue ferricinium salt **11a** ($X = BF_4^-$) was indeed obtained with 75% yield by oxidation of the orange 1,1′-bis-[(F-alkyl)-acyl]ferrocene **2a** using HBF_4–*p*-benzoquinone. By contrast, yields of **12a** ($X = SbCl_4^-$), which was also obtained as a blue powder when $Ph_3C^+SbCl_6^-$ was used, were much lower (16%). The reaction with O_2–CCl_3CO_2H as oxidant was not very selective; it gave a black powder (about 20% in **13a** ($X = CCl_3CO_2^-$)) difficult to purify and analyze. The formation of a ferricinium species could not even be detected when 2,4,6-trinitrophenol–*p*-benzoquinone or iodine was used; after 3 days at room temperature, almost all the starting **2a** was recovered unchanged.

Elemental analyses and IR confirmed the structure of the ferricinium complexes **12a** and **13a**. Thus the bathochromic shift of the carbonyl vibration from 1669 cm^{-1} in **2a** to 1703 and 1693 cm^{-1} in **12a** and **13a** respectively agrees with the Fe(II)–Fe(III) oxidation. These ferricinium derivatives were found to be stable only when stored under nitrogen (and in the dark for **13a**). The moisture present in air or in KBr discs caused partial reconversion to the ferrocene analogues, as shown by IR, TLC and NMR.

The presence of a fluorinated tail in the acyl side chains of 1,1′-bis-acylferrocenes was found to play a decisive role in the oxidation of these ferrocenes with HBF_4–*p*-benzoquinone. We previously reported that, as illustrated in Scheme 5, reaction of the lipophilic 1,1′-bis-(undecanoyl)ferrocene (**14**), the hydrocarbon analogue of **2a** with HBF_4–*p*-benzoquinone gave the novel benzofuranylferrocene derivatives **15** [20]; this results from a Michael addition between ketone **14** and *p*-benzoquinone, most probably through the intermediary formation of the corresponding soluble ferricinium ion [21]. This is in marked contrast with the behavior of the "lipophobic" perfluoroalkylated derivative **2a** and of the much less lipophilic acetylferrocene, which were both oxidized to the corresponding, almost insoluble ferricinium complexes; this insolubility of the perfluoroalkylated ferricinium species is likely to protect them from a further Michael addition.

2.5. Conclusion

A general route to various perfluoroalkylated acylferrocenes, alkylferrocenes and α-(hydroxy)alkylferrocenes has been developed. The (*F*-alkyl)acylferrocenes were obtained by a classical Friedel–Crafts acylation of ferrocene with (*F*-alkyl)acyl chlorides. The (*F*-alkyl)alkyl and ω-(*F*-alkyl)-α-(hydroxy)alkyl analogues were selectively prepared by controlled reduction of the acyl derivatives. These reactions illustrate the chemical inertness of (*F*-alkyl)acyl and (*F*-alkyl)alkyl chains under strongly reducing conditions.

However, Friedel–Crafts acylation of ferrocene could not be used for the preparation of [2-(*F*-alkyl)ethenyl]acylferrocenes from [2-(*F*-alkyl)ethenyl]-acyl chlorides, owing to the reactivity of the CF_2–CH=CH– sequence in these latter derivatives towards strong Lewis acids. The substituted acylferrocenes which we did obtain contained the (*Z*)-CF=CH–CH(Cl)– sequence in their acyl side chains, an outcome that opens up new synthetic possibilities.

The oxidation of perfluoroalkylated ferrocenes to the corresponding ferricinium species has been demonstrated. The presence of fluorinated tails in the acyl side chains of 1,1′-bis-acylferrocenes was found to play a decisive role in the oxidation of these ferrocenes with HBF_4–*p*-benzoquinone. Whereas benzofuranylferrocene derivatives were formed from a lipophilic hydrocarbon 1,1′-bis-(acyl)ferrocene, the "lipophobic" perfluoroalkylated analogue was oxidized to the ferricinium complex.

3. Experimental section

3.1. General procedures

3.1.1. Physical methods

Analytical TLC were performed on precoated silica gel 60 F_{254} plates (Merck) with detection by UV (254 nm). Silica gel 60 (Merck, 70–230 mesh) columns were

used for preparative separations which were carried out in the air. IR spectra were recorded on a Bruker IFS spectrometer as KBr discs for the cristalline samples. ^{1}H, ^{13}C (50.3 MHz) and ^{19}F (188.3 MHz) NMR spectra were recorded on a Bruker AC 200 spectrometer (chemical shifts are given relatively to Me_4Si and $CFCl_3$ respectively). Elemental analyses were performed by the Service Central de Microanalyses of the CNRS.

3.1.2. Compound preparation

All reactions were performed under dry nitrogen and under anhydrous conditions using standard Schlenk-type vessels. All solvents were deoxygenated and dried by standard procedures. Triphenylcarbenium hexachloroantimonate ($Ph_3C^+SbCl_6^-$) was prepared by the published procedure. Aluminum trichloride, ferrocene, *p*-benzoquinone and trichloroacetic acid were purified by sublimation under reduced pressure and kept under dry nitrogen. The perfluoroalkylated acid chlorides **1a–1d** were prepared as described in [22]. All other reagents ($LiAlH_4$, $SOCl_2$ and HBF_4–Et_2O) were used as received from commercial sources.

3.2. Synthesis of (F-alkyl)acylferrocenes

Compounds **2a–2c** were made by the procedure described for **2a**. The monosubstituted **3a** and **3b** and disubstituted **4b** derivatives were isolated from the reaction mixtures leading to **2a** and **2b** respectively. Formation of **3c**, **4a** and **4c** was only demonstrated by TLC and NMR analyses of the relevant reaction mixture by comparison with the data for **3a**, **3b** and **4b** respectively.

3.2.1. 1,1'-bis-[11-(F-octyl)undecanoyl]ferrocene (2a)

A CCl_4 solution (5 ml) of 11-(*F*-octyl)undecanoyl chloride (4.27 g, 6.85 mmol) was added dropwise to a suspension of $AlCl_3$ (1.15 g, 8.62 mmol) in CCl_4 (10 ml) at 0°C. The mixture was stirred for 45 min at 0°C. Ferrocene (0.637 g, 3.42 mmol) was gradually added in small portions at room temperature. The resulting violet solution was stirred for 1 h at 40–50°C and then treated with ice-cooled 0.1 N HCl (100 ml). The resulting mixture was extracted with chloroform and the extract was washed with water. After removal of the solvents from the extract, the residue was carefully chromatographed on silica gel (elution with chloroform) to give successively unreacted ferrocene, the monosubstituted derivative **3a** and the 1,1'-disubstituted derivative **2a**. The fractions containing a mixture of **2a** and **3a** were rechromatographed on silica gel (elution with ethyl acetate : petroleum ether 1 : 9). Recrystallization from chloroform yielded pure **2a** as orange–red crystals (2.10 g, 1.55 mmol (45%)).

2a: Melting point (m.p.), 95°C; $R_F = 0.6$ (chloroform). Anal. Found: C, 41.88; H, 3.44; Fe, 4.16. $C_{48}H_{48}O_2F_{34}Fe$ calc: C, 42.43; H, 3.56; Fe, 4.11%. IR (KBr): ν 1216, 1253 (CF_2, CF_3), 1669 (C=O), 3093, 3127 (–CH=) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.32 (br s, 14H, $(CH_2)_7$), 1.63 (m, 2H, CH_2CH_2CO), 2.05 (tt, $^{3}J_{HF} = 19$ Hz, $^{3}J_{HH} = 7$ HZ, 2H, CF_2CH_2), 2.69 (t, $^{3}J_{HH} = 8$ Hz, 2H, CH_2CO), 4.53 (t, $^{3}J = 1.9$ Hz, 2H, Cp CHβ), 4.87 (t, $^{3}J = 1.9$ Hz, 2H, Cp CHα) ppm. ^{13}C NMR ($CDCl_3$): δ 20.0 (t, $^{3}J_{CF} = 4$ Hz, $CF_2CH_2CH_2$), 24.3, 29.1, 29.2, 29.3, 29.4, 29.5 (all s, $(CH_2)_7$), 30.9 (t, $^{2}J_{CF} = 22$ Hz, CF_2CH_2), 40.0 (s, CH_2CO), 70.6, 73.3 (s, s, Cp CHβ and CHγ) 80.5 (s, COC), 203.8 (s, CO) ppm. ^{19}F NMR ($CDCl_3$): δ −81.3 (3F, CF_3), −114.9 (2F, CF_2CH_2), −122.4, −123.2, −124.0 (6F, 2F, 2F, $CF_3CF_2(CF_2)_5$), −126.6 (2F, CF_3CF_2) ppm.

3.2.2. 1,1'-bis-[11-(F-hexyl)undecanoyl]ferrocene (2b)

Orange crystals (yield, 57%); $R_F = 0.6$ (chloroform). Anal. Found: C, 45.75; H, 4.29; Fe, 4.74. $C_{44}H_{48}O_2F_{26}Fe$ calc.: C, 45.61; H, 4.18; Fe, 4.82%. IR (KBr): ν 1217, 1256 (CF_2, CF_3), 1666 (C=O), 3096, 3127 (=CH–) cm^{-1}. ^{1}H and ^{13}C NMR ($CDCl_3$) are identical with those of **2a**, respectively. ^{19}F NMR ($CDCl_3$): δ −81.4 (3F, CF_3), −114.9 (2F, CF_2CH_2), −122.5, −123.4, −124.1 (2F, 2F, 2F, $CF_3CF_2(CF_2)_3$), −126.7 (2F, CF_3CF_2) ppm.

3.2.3. 1,1'-bis-[11-(F-butyl)undecanoyl]ferrocene (2c)

Orange crystals (yield, 60%); $R_F = 0.6$ (chloroform). Anal. Found: C, 50.01; H, 5.09; Fe, 5.68. $C_{40}H_{48}O_2F_{18}Fe$ calc.: C, 50.12; H, 5.05; Fe, 5.83%. IR (KBr): ν 1227 (CF), 1666 (C=O), 3105, 3128 (=CH) cm^{-1}. ^{1}H and ^{13}C NMR ($CDCl_3$) are identical with those of **2a** respectively. ^{19}F NMR ($CDCl_3$): δ −81.5 (3F, CF_3), −115.1 (2F, CF_2CH_2), −125.0 (2F, $CF_3CF_2CF_2$), −126.5 (2F, CF_3CF_2) ppm.

3.2.4. [11-(F-octyl)undecanoyl]ferrocene (3a)

Orange solid (yield, about 10%); $R_F = 0.8$ (chloroform). IR (KBr): ν 1205, 1245 (CF_2, CF_3), 1665 (C=O), 3100 (–CH=) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.35 (br s, 14H, $(CH_2)_7$), 1.66 (m, 2H, CH_2CH_2CO), 2.05 (tt, $^{3}J_{HF} = 19$ Hz, $^{3}J_{HH} = 7$ Hz, 2H, CF_2CH_2), 2.70 (t, $^{3}J_{HH} = 8$ Hz, 2H, CH_2CO), 4.19 (s, 5H, Cp), 4.50 (t, $^{3}J = 1.9$ Hz, 2H, Cp' CHβ), 4.79 (t, $^{3}J = 1.9$ Hz, 2H, Cp' CHα) ppm. ^{13}C NMR ($CDCl_3$): δ 20.1 (t, $^{3}J_{CF} = 4$ Hz, $CF_2CH_2CH_2$), 24.6, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6 (all s, $(CH_2)_7$), 30.9 (t, $^{3}J_{CF} = 22$ Hz, CF_2CH_2), 39.8 (s, CH_2CO), 69.3 and 72.1 (s, s, Cp' CHα and CHβ), 69.7 (s, Cp), 79.2 (s, COC), 204.5 (s, CO) ppm. ^{19}F NMR ($CDCl_3$) identical with that of **2a**.

3.2.5. [11-(F-hexyl)undecanoyl]ferrocene (3b)

Orange solid (yield, about 10%). $R_F = 0.8$ (chloroform). IR (KBr): ν 1205, 1245 (CF_2, CF_3), 1665 (C=O), 3100 (–CH=) cm^{-1}. ^{1}H and ^{13}C NMR ($CDCl_3$) are identical with those of **3a** respectively. ^{19}F NMR identical with that of **2b**.

3.2.6. 1,2-bis-[11-(F-hexyl)undecanoyl]ferrocene (4b)

Orange solid (yield, about 1%). $R_F = 0.7$ (chloroform). Compound **4b** was isolated after several chromatographic treatments of the fractions eluted between **3b** and **2b**. IR (KBr): ν 1215, 1245 (CF_2, CF_3), 1660 (C=O), 3100 (=CH–) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.32 (br s, 28H, $(CH_2)_7$), 1.65 (m, 4H, CH_2CH_2CO), 2.06 (tt, $^3J_{HF} = 19$ Hz, $^3J_{HH} = 7$ Hz, 4H, CF_2CH_2), 2.80 (t, $^3J_{HH} = 8$ Hz, 4H, CH_2CO), 4.30 (s, 5H, Cp), 4.68 (s, 1H, Cp' CHβ), 4.87 (s, 2H, Cp' CHα) ppm. ^{13}C NMR ($CDCl_3$): δ 20.1 (t, $^3J_{CF} = 4$ Hz, $CF_2CH_2CH_2$), 24.6, 29.1, 29.2, 29.3, 29.4, 29.5 (all s, $(CH_2)_7$), 30.9 (t, $^2J_{CF} = 23$ Hz, CF_2CH_2), 42.0 (s, CH_2CO), 71.6 (s, Cp and CHα or CHβ of Cp'), 74.2 (s, CHα or CHβ of Cp'), 82.6 (s, COC), 204.8 (s, CO) ppm. ^{19}F NMR ($CDCl_3$) identical with that of **2b**.

3.3. Synthesis of 1,1'-bis-[10-chloro,12-fluoro-12-(F-heptyl)-11-(Z)-dodecenoyl]ferrocene (5) and [10-chloro-12-fluoro-12-(F-heptyl)-11-(Z)-dodecenoyl]ferrocene (6)

The procedure described for the preparation of **2a** was applied to 11-(*F*-octyl)-10-undecenoyl chloride (0.75 g, 1.25 mmol), $AlCl_3$ (0.27 g, 2.03 mmol) and ferrocene (0.12 g, 0.63 mmol) to give, after hydrolysis with a 1 N NaOH, silica gel chromatography (elution with petroleum ether: ethyl acetate 9:1) and recrystallization from chloroform, **5** (0.38 mmol, 30%) and **6** (0.40 mmol, 32%) as orange crystals.

5: Anal. Found: C, 41.27: H, 3.11; Cl, 5.18; Fe, 4.18. $C_{48}H_{44}Cl_2O_2F_{32}Fe$ calc.: C, 41.51; H, 3.20; Cl, 5.11; Fe, 4.02%. IR (KBr): ν 1215, 1240 (CF_2, CF_3, CF), 1676 (CO), 1708 (CF=CH), 3096 (–CH=) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.35 (br s, 10H, $(CH_2)_5$), 1.69 (m, 2H, CH_2CH_2CO), 1.87 (m, 2H, $CH(Cl)CH_2$), 2.65 (t, $^3J_{HH} = 7.2$ Hz, 2H, CH_2CO), 4.49 (t, $^3J = 1.9$ Hz, 2H, Cp CHβ), 4.77 (m, 3H, Cp CHα and CHCl), 5.75 (dd, $^3J_{HH} = 10.2$ Hz, $^3J_{HF} = 30.6$ Hz, 1H, –CH=) ppm. ^{13}C NMR ($CDCl_3$): δ 24.3, 26.1, 28.9, 29.3, 29.4, 29.8 (all s, $(CH_2)_6$), 38.1 (s, CH_2CHCl), 40.0 (s, CH_2CO), 51.4 (d, $^3J_{CF} = 4$ Hz, CHCl), 70.6, 73.4 (s, s, Cp CHα,β), 80.6 (s, COC), 117.1 (dt, $^2J_{CF} = 7$ Hz, $^3J_{CF} = 5$ Hz, –CH=), 146.2 (dt, $^1J_{CF} = 266$ Hz, $^2J_{CF} = 30$ Hz, CF), 203.6 (CO) ppm. ^{19}F NMR ($CDCl_3$): δ −81.2 (3F, CF_3), −118.6 (2F, CF_2CF), −122.4, −123.3 (4F, 4F, $CF_3CF_2(CF_2)_4$), −126.6 (2F, CF_3CF_2), −127.5 (1F, CF) ppm.

6: Anal. Found: C, 44.15; H, 3.51; Cl, 4.59; Fe, 6.76. $C_{29}H_{27}ClOF_{16}Fe$ calc.: C, 44.27; H, 3.46; Cl, 4.51; Fe, 7.10%. IR (KBr): ν 1215, 1240 (CF_2, CF_3, CF), 1666 (CO), 1707 (CF=CH), 3096, 3111 (–CH=) cm^{-1}. Mass spectroscopy (MS): *m/z* 787, 789 $[(M+1)^{\cdot+}$, ^{35}Cl, $^{37}Cl]$, 786, 788 ($M^{\cdot+}$, ^{35}Cl, ^{37}Cl), 751 $(M-Cl)^{\cdot+}$, 186 ($FeCp_2^{+\cdot}$). ^1H NMR ($CDCl_3$): δ 1.35 (sl, 10H, $(CH_2)_5$), 1,69 (m, 2H, CH_2CH_2CO), 1.87 (m, 2H, $CH(Cl)CH_2$), 2.74 (t, $^3J_{HH} = 7.9$ Hz, 2H, CH_2CO), 4.20 (s, 5H, Cp'), 4.56 (s, 2H, Cp Hβ), 4.87 (m, 3H, Cp Hα and CHCl), 5.91 (dd, $^3J_{HH} = 10.6$ Hz, $^3J_{HF} = 30.4$ Hz, 1H, CH=). ppm. ^{13}C NMR ($CDCl_3$): δ 24.5, 26.0, 28.7, 29.2, 29.3, 29.4 (all s, $(CH_2)_6$), 38.0 (s, CH_2CHCl), 39.6 (s, CH_2CO), 51.3 (d, $^3J_{CF} = 4$ Hz, CHCl), 69.3, 72.0 (s, s, Cp CHα,β), 69.7 (s, Cp'), 79.3 (s, COC), 117.1 (dt, $^2J_{CF} = 6$ Hz, $^3J_{CF} = 5$ Hz, CH), 146.3 (dt, $^1J_{CF} = 266$ Hz, $^2J_{CF} = 30$ Hz, CF), 204.3 (CO) ppm. ^{19}F NMR ($CDCl_3$) identical with that of **5**.

3.4. Synthesis of (F-alkyl)alkylferrocenes

3.4.1. 1,1'-bis-[11-(F-octyl)undecyl]ferrocene (8a)

A mixture of **2a** (300 mg, 0.23 mmol) and $AlCl_3$ (30 mg, 0.23 mmol) in diethyl ether (10 ml) was added dropwise at room temperature, to a suspension of $LiAlH_4$ (34 mg, 0.90 mmol) and $AlCl_3$ (30 mg, 0.23 mmol) in diethyl ether (10 ml). The mixture was stirred for 10 h at 50°C. After hydrolysis, extraction with diethyl ether, chromatography on silica gel (elution with pentane then chloroform) and recrystallization from chloroform, **8a** was obtained as yellow crystals (250 mg, 0.19 mmol (80%)). According to the ^1H NMR spectrum (presence of the characteristic pattern for the ethylenic protons observed for **8b'**; vide infra), the crude reaction mixture contained compound 1-[11-(*F*-octyl)undecyl]-1'-[11-(F-octyl)-1-(*E*)-undecenyl]ferrocene (**8a'**) (about 10%).

8a: Anal. Found: C, 43.28; H, 4.13; Fe, 3.96 $C_{48}H_{52}F_{34}Fe$ calc. C, 43.32; H, 3.94; Fe, 4.20%. IR (KBr): ν 1218, 1251 (CF_2, CF_3), 3091 (=CH) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.31 (br s, 18H, $(CH_2)_9$), 2.05 (tt, $^3J_{HF} = 19$ Hz, $^3J_{HH} = 7$ Hz, 2H, CF_2CH_2), 2.30 (t, $^3J_{HH} = 7.5$ Hz, 2H, CH_2Cp), 3.97 (s, 4H, Cp) ppm. ^{13}C NMR ($CDCl_3$): δ 20.0 (t, $^3J_{CF} = 4$ Hz, $CF_2CH_2CH_2$), 29.1, 29.2, 29.3, 29.4, 29.5, 29.7 (all s, $(CH_2)_8$), 30.9 (t, $^2J_{CF} = 22$ Hz, CF_2CH_2), 31.2 (s, CH_2Cp), 67.0, 68.1 (s, s, Cp CHα,β), 89.7 (s, CH_2C (Cp)) ppm. ^{19}F NMR ($CDCl_3$) identical with that of **2a**.

Compounds **8b** and **9a** were obtained as yellow crystals by the procedure described for **8a**.

3.4.2. 1,1'-bis-[11-(F-hexyl)undecyl]ferrocene (8b) (80%)

Anal. Found: C, 46.73; H, 4.68; Fe, 5.00 $C_{44}H_{52}F_{26}Fe$ calc.: C, 46.74; H, 4.64; Fe, 4.94%. IR (KBr): ν 1210, 1251 (CF_2, CF_3), 3091 (=CH) cm^{-1}. ^1H and ^{13}C NMR ($CDCl_3$) identical with those of **8a** respectively. ^{19}F NMR ($CDCl_3$) identical with that of **2b**.

3.4.3. [11-(F-octyl)undecyl]ferrocene (9a) (80%)

Anal. Found: C, 46.58; H, 4.10; Fe, 7.25. $C_{29}H_{31}F_{17}Fe$ calc.: C, 45.93; H, 4.12; Fe, 7.36%. IR (KBr): ν 1216, 1250 (CF_2, CF_3), 3093 (=CH) cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 1.31 (br, s, 18H, $(CH_2)_9$), 2.07 (tt, $^3J_{HF}$ = 19 Hz, $^3J_{HH}$ = 7 Hz, 2H, CF_2CH_2), 2.34 (t, $^3J_{HH}$ = 7.6 Hz, 2H, (CH_2Cp), 4.07 (s, 4H, $CH_2C_5H_4$), 4.12 (s, 5H, C_5H_5) ppm. ^{13}C NMR ($CDCl_3$): δ 20.1 (t, $^3J_{CF}$ = 4 Hz, $CF_2CH_2CH_2$), 29.1, 29.2, 29.4, 29.5, 29.6, 29.7 (all s, $(CH_2)_8$), 30.9 (t, $^2J_{CF}$ = 22 Hz, CF_2CH_2), 31.2 (s, CH_2Cp'), 67.1, 68.1 (s, s, Cp' CHα,β), 68.5 (s, Cp), 89.7 (s, CH_2C(Cp)) ppm. ^{19}F NMR ($CDCl_3$) identical with that of **2a**.

Minor amounts of 11-(*F*-octyl)-1-(*E*)-undecenylferrocene (**9a'**) were also found in the crude reaction mixture, according to the ^{1}H NMR, spectrum, which showed the characteristic pattern for the ethylenic protons observed for **8b'**.

3.4.4. *1-[11-(F-hexyl)undecyl]-1'-[11-(F-hexyl)-1-(E)-undecenyl]ferrocene (8b')*

This compound (about 15%) was separated by chromatography from the reaction mixture that gave **8b**. IR (KBr): ν 1210, 1250 (CF_2, CF_3), 1652 (C=C), 3095 (=CH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.29, 1.33 (br s, 32H, $(CH_2)_9$ and $(CH_2)_{7'}$), 2.05 (m, 6H, CH_2CH=CH and CF_2CH_2), 2.26 (t, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2Cp), 4.15 (m, 4H, CH_2Cp), 4.11, 4.19 (s, s, 4H, =CH–*Cp*), 5.76 (td, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 15.6 Hz, 1H, =C*H*-CH_2), 6.03 (d, $^3J_{HH}$ = 15.6 Hz, 1H, =C*H*-Cp) ppm. ^{13}C NMR ($CDCl_3$): δ 20.1 (t, $^3J_{CF}$ = 4 Hz, $CF_2CH_2CH_2$), 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7 (all s, $(CH_2)_8$ and $(CH_2)_6$), 31.1 (t, $^2J_{CF}$ = 22 Hz, CF_2CH_2), 33.0 (s, CH_2Cp), 34.1 (s, CH_2CH=CH), 66.9, 68.3, 68.9, 69.3 (all s, Cp CHα,β), 84.6 (s, CH=CH*C* (Cp) 90.0 (s, CH_2C (Cp)), 126.3 and 128.5 (s, *C*H=*C*H) ppm. ^{19}F NMR ($CDCl_3$) identical with that of **2b**.

3.4.5. *1,1'-bis[11-(F-hexyl)-1-hydroxy-undecyl]ferrocene (10b)*

A solution of **2b** (0.50 g, 0.43 mmol) in diethyl ether (10 ml) was added dropwise to a suspension of $LiAlH_4$ (72 mg, 1.89 mmol) in diethyl ether (10 ml). After 12 h at 50°C, hydrolysis, usual work-up and chromatography on silica gel (elution with pentane then chloroform), **10b** was obtained as a yellow solid (0.45 g, 0.39 mmol (90%)). Anal. Found: C, 45.44; H, 4.75; Fe, 4.69. $C_{44}H_{52}O_2F_{26}Fe$ calc.: C, 45.45; H, 4.51; Fe, 4.80%. IR (Nujol): ν 1215, 1244 (CF_2, CF_3), 3092 (=CH–), 3358 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.27 (br s, 16H, $(CH_2)_8$), 1.59 (br s, 2H, CH_2CH), 2.05 (tt, $^3J_{HF}$ = 19 Hz, $^3J_{HH}$ = 7 Hz, 2H, CF_2CH_2), 3.97 (br s, 1H, OH), 4.13–4.26 (m, 4H, Cp), 4.39–4.47 (m, 1H, (HO)CH–) ppm. ^{13}C NMR ($CDCl_3$): δ 20.1 (t, $^3J_{CF}$ = 4 Hz, $CF_2CH_2CH_2$), 25.7, 25.8, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7 (all s, $(CH_2)_7$), 30.9 (t, $^2J_{CF}$ = 22 Hz, CF_2CH_2), 39.3 and 40.1 (s, s, CH_2CH), 65.4, 66.1, 66.5, 67.0, 67.5, 67.7, 69.5 and 70.2 (all s, CH (Cp) and CHOH), 94.2 and 94.4 (s, s, CH*C*(Cp) ppm. ^{19}F NMR ($CDCl_3$) identical with that of **2b**.

3.5. *Oxidation of the (F-alkyl)acylferrocene (2a)*

3.5.1. *1,1'-bis-[11-(F-octyl)undecanoyl]ferricinium tetrafluoroborate (11)*

A solution of **2a** (0.50 g, 0.37 mmol) in chloroform (20 ml) was added dropwise to a mixture of *p*-benzoquinone (80 mg, 0.74 mmol) in 0.3 ml (1.50 mmol) of 54% HBF_4 in Et_2O at −10°C. The mixture was stirred for 45 min at room temperature. The blue precipitate formed was filtered off, washed with chloroform and vacuum dried to give 0.41 g (0.28 mmol (76%)) of **11** as a blue powder insoluble in most common organic solvents. Anal. Found: C, 40.57; H, 3.35; B, 0.75; Fe, 3.45. $C_{48}H_{48}O_2BF_{38}Fe$ calc.: C, 39.88; H, 3.35; B, 0.75; Fe, 3.86%. IR (Nujol): ν 1072, 1050 (BF_4^-), 1200 (CF), 1703 (C=O), 3120 (=CH) cm^{-1}. In KBr discs, the CO vibration at 1703 cm^{-1} disappears slowly and is replaced by a new CO stretch at 1670 cm^{-1} which corresponds to the CO vibration of the ferrocene derivative. This transformation is complete within 1 day.

3.5.2. *1,1'-bis-[11-(F-octyl)undecanoyl]ferricinium tetrachloroantimonate (12)*

A solution of **2a** (0.39 g, 0.29 mmol) in methylene dichloride (25 ml) was added dropwise to a solution of $Ph_3C^+SbCl_6^-$ (0.18 g, 0.30 mmol) in methylene dichloride (5 ml). The resulting blue precipitate of **12** (75 mg, 0.05 mmol (16%)) was filtered off, washed with methylene chloride and dried under vacuum. Unchanged ferrocene (30%) was also recovered from the filtrate. Compound **12** is insoluble in most common organic solvents. IR (KBr): ν 1205, 1250 (CF_2, CF_3), 1693 (C=O), 3107 (=CH) cm^{-1}. The CO band progressively disappears and is replaced by a new CO stretch at 1670 cm^{-1}, as observed for **11**.

3.5.3. *1,1'-bis-[11-(F-octyl)undecanoyl]ferricinium trichloroacetate (13)*

A solution of trichloroacetic acid (44 mg, 0.27 mmol) in methylene dichloride (10 ml) was added dropwise under nitrogen to a solution of **2a** (120 mg, 0.09 mmol) in methylene chloride (10 ml). Dioxygen was bubbled through the solution for 30 min which was then stirred for 60 h in the dark and allowed to stand in the dark for 3 days. The resulting black precipitate (35 mg, 0.02 mmol (22%) if it consists of **13**) was then filtered off, washed with methylene chloride and dried under vacuum. Attempted further purification was unsuccessful. IR (Nujol): ν 721,736 (CCl), 1204, 1242 (CF_2, CF_3), 1577 (CO_2^-), 1667 (C=O) cm^{-1}.

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