

Alkylferrocenes: A simple preparation from lithioferrocenes and their aqueous electrochemistry

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Abstract

Mono- and dialkylferrocenes are readily prepared by the nucleophilic substitution of *n*-alkyl halides with lithioferrocenes. The products can be purified by short-path distillation or recrystallization. Three alkylferrocenes were prepared by this synthetic strategy and characterized by cyclic voltammetry in aqueous solution. © 1997 Elsevier Science S.A.

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1. Introduction

Ferrocene derivatives are versatile reagents for use in areas such as materials and catalysis [1]. Alkyl substituted ferrocenes are being investigated for potential use as electrode surface modifiers [2], in the construction of redox active dendrimers [3], redox-switchable surfactants [4], and others. We were interested in preparing new alkyl metallocenes for use as redox-switchable surfactants. When ferrocenes with long alkyl chains are oxidized, they are structurally similar to cationic surfactants (the ferrocene is the cationic head group and the alkyl chain the lipophilic tail). These molecules are water soluble with the appropriate counterion and can form micelles above the critical micelle concentration (cmc). If the ferrocene-based surfactant is then reduced the surfactant-like behavior (micelle) is broken. Redox-switchable surfactants based on ferrocenes have been used to prepare thin films by micelle disruption and may also find uses in separations. Through our investigation of redox-switchable surfactants based on alkylferrocenes, we have demonstrated that alkylation of lithioferrocenes is a general, simple, and effective method for the preparation of alkyl-substituted ferrocenes.

The direct alkylation of ferrocene by Friedel–Crafts

alkylation gives poor yields and produces an intractable mixture of mono- and polyalkylferrocenes [5]. For this reason, alkylferrocenes are typically prepared by first synthesizing mono- and diacyl ferrocenes which can be prepared in moderate yields with good selectivity. The acylferrocene can then be transformed to the corresponding alkylferrocene by Clemmensen reduction or other means [6]. The disadvantages of this procedure are that it is a two-step synthesis that requires purification after each step.

In order to simplify and significantly shorten the time needed for the preparation of alkylferrocenes, we have developed an improved synthesis based on lithioferrocenes. The cyclopentadienyl rings of ferrocene can be dilithiated by *t*-butyllithium in diethyl ether at room temperature or by *n*-BuLi in the presence of tetramethylethylenediamine (tmeda) [7] and the structure of the dilithioferrocene-tmeda adduct has been determined [8]. Monolithioferrocene can be obtained in high yields from the reaction of ferrocene with *t*-BuLi in THF [9]. In early studies of ferrocene chemistry it was shown that carboxy, triphenylsilyl, and amino ferrocene derivatives could be prepared from lithioferrocenes [10]. Also, lithioferrocenes have been shown to readily react with ketones and aldehydes [11], as well as chlorotrimethylsilane [12] and chlorophosphine [13]. In this paper we describe a general method to prepare alkylferrocenes, previously prepared by reduction of acylferrocenes [14], by the reaction of mono- and dilithioferrocenes with

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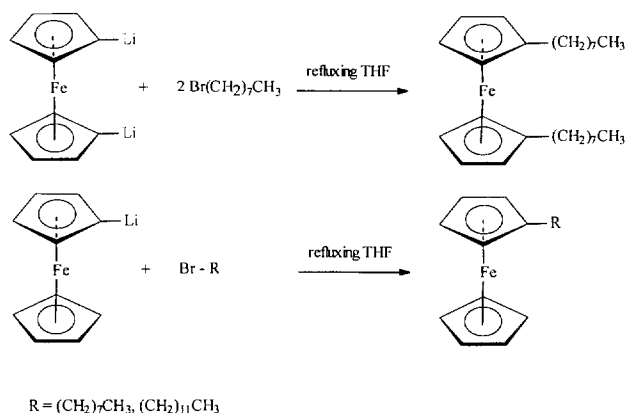


Fig. 1. Synthesis of alkylferrocenes from lithioferrocenes.

alkyl halides (Fig. 1) and briefly describe their electrochemical behavior in aqueous solutions.

2. Results

To prepare 1,1'-di(octyl)ferrocene, the cyclopentadienyl rings of ferrocene were lithiated by two equivalents of *n*-BuLi in the presence of tmeda to give dilithioferrocene. Excess 1-bromooctane was added without purification and the solution refluxed overnight. The products consisted mostly of 1,1'-di(octyl)ferrocene along with some unreacted ferrocene and (1-octyl)ferrocene as a byproduct. The residual ferrocene is removed by vacuum sublimation and the alkylferrocene purified by vacuum distillation to give a red oil of 1,1'-di(octyl)ferrocene.

The mono-substituted compounds (1-octyl)ferrocene and (1-dodecyl)ferrocene were prepared by addition of the appropriate alkylhalide to monolithioferrocene prepared by the addition of *tert*-butyllithium to ferrocene. For these reactions the product mixture consisted only of residual unreacted ferrocene and the desired product. The ferrocene was removed by sublimation and the product purified by vacuum distillation or recrystallized depending on its melting point. Although these yields are not high (Table 1), we believe that they can be improved with further optimization of the reaction conditions. Overall, we found that by using this one pot preparation method, we were able to synthesize multi-gram quantities of alkylferrocenes within 24 h, saving considerable time over the traditional two-step method.

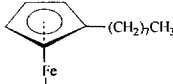
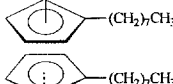
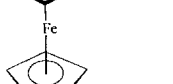
It has been well established that ferrocene derivatives are easily oxidized by either electrochemical or chemical methods and the electrochemistry of many alkylferrocene have been studied [15]. To use these compounds as redox-switchable surfactants, the iron must be oxidized to the ⁺³ state in order for the metallocene to exhibit surfactant-like behavior. We tried several chemical oxidants and found that bromine or hydrogen perox-

ide gave products that were soluble in THF but insoluble in water. Oxidation with sulfuric acid did not give rise to any soluble products. However, oxidation of the alkylferrocenes with silver nitrate gave water-soluble ferricinium complexes. Chemical oxidation of the octyl-substituted ferrocenes and the dodecylferrocene by silver nitrate was accompanied by a color change in the surfactant-containing solutions. The original red colored solution is converted to blue, consistent with the presence of the positively charged ferricinium ion.

We then examined the cyclic voltammetry of the octyl- and dodecylferricinium ions in aqueous 0.5 M NaNO₃ electrolyte. Since the alkylferrocenes are not soluble in water, the ferricinium ions were prepared by adding a 10-fold excess of silver nitrate to the alkylferrocene suspended in 0.5 M NaNO₃ to give an alkylferricinium concentration of 5 × 10⁻⁴ M. The solution color became blue and metallic silver plated out on the inside of the flask. Using a syringe filter, 20 milliliters of the alkylferricinium solution was transferred to the electrochemical cell where cyclic voltammograms were obtained.

The electrolyte was distilled water with 0.5 M NaNO₃ as the supporting electrolyte. The working electrode was electrochemically cleaned by cycling the potential between the electrolyte limits before the start of each experiment. A cyclic voltammogram of the blank electrolyte was recorded prior to the experiment to verify that the working electrode surface or the electrolyte solution are free of impurities.

Table 1

Product	Yield (%) ^a	E _p (reduction) vs Ag/AgCl _b
	41	0.11
	30	0.27
	18	0.23

^a Yields based on ferrocene. ^b 0.05 M NaNO₃.

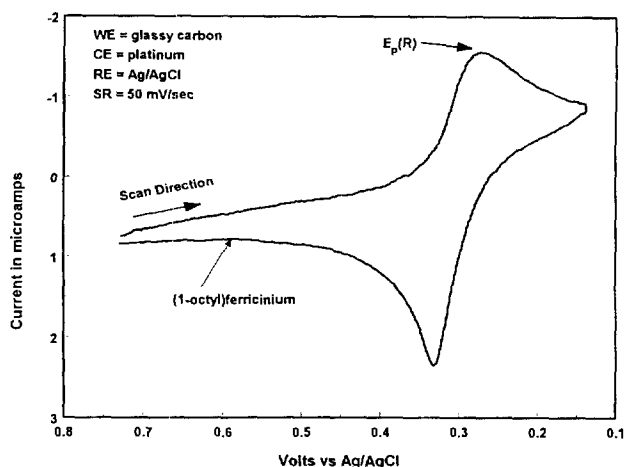


Fig. 2. Cyclic voltammogram of (1-octyl)ferrocinium in 0.5 M NaNO_3 .

Fig. 2 shows a cyclic voltammogram (CV) of (1-octyl)ferrocinium in the 0.5 M NaNO_3 electrolyte. The reduction wave shows a typical diffusion-controlled shape, however the sharpness of the reoxidation wave suggests that the reduced (neutral) species had adsorbed onto the electrode. Since the reduced (1-octyl)ferrocene is insoluble in aqueous electrolytes, partitioning of the alkylferrocene to the electrode surface would be expected and is consistent with the observed CV. We do not expect that the peak shapes observed for the octyl or dodecylferrocenes are a function of disruption of a micelle, since the 10^{-4} M concentrations used were below the critical micelle concentrations (CMC) for these materials [16].

E_p (reduction) for the (1-octyl)ferrocinium ion is 0.23 V (versus Ag/AgCl). The voltammometric results of for (1-dodecyl)ferrocinium ion were essentially identical to those obtained with (1-octyl)ferrocinium ion, except that the E_p (reduction) was 0.23 V (versus Ag/AgCl). For the 1,1'-(dioctyl)ferrocinium ion the CV was qualitatively the same as the mono-octylferrocene, and the E_p (reduction) was found to be 0.11 V (versus Ag/AgCl).

The similarities of the potentials for the octyl- and dodecylferrocene are expected since the primary difference is the longer chain length of the dodecyl substituent. For electronic effects, carbons further than three or four atoms away from the ferrocene ring have little effect on the redox potentials. The shift in potential (compared to the mono-octylferrocene) for the dioctyl substituted ferrocene is due to the presence of the second electron-donating group on the ferrocene rings.

3. Conclusions

We have demonstrated a simple and general synthetic strategy for preparing alkylferrocenes from fer-

rocene by reactions of lithioferrocenes with alkylhalides. This method is an alternative to the two-step method now commonly used that requires the synthesis and purification of an acylferrocene followed by reduction to the hydrocarbon. Also, the cyclic voltammetry of these materials was studied in aqueous solution.

4. Experimental section

4.1. General comments

All reactions were carried out under a prepurified nitrogen atmosphere using standard Schlenk, glovebox and vacuum line techniques. All solvents were distilled under nitrogen over appropriate drying agents. All of the alkylferrocene samples showed a single spot in reverse-phase TLC (RP-18 F₂₅₄s Merck; acetonitrile). Ferrocene, 1-bromooctane (99%), 1-bromododecane (97%), TMEDA (99%), and alkyllithium reagents (all from Aldrich) were used as received.

4.2. General procedure for the preparation of alkylferrocenes from lithioferrocenes

To a stirred suspension of lithioferrocene (prepared from ferrocene (3.0 g, 16.1 mmol) and *t*-BuLi (8.5 mL, 1.7 M in hexanes) in 20 mL THF) or dilithioferrocene (prepared from ferrocene (3.0 g, 16.1 mmol), *n*-BuLi (16.1 mL, 2.5 M in hexanes), and tmeda (6.1 mL, 40.3 mmol) in 80 mL hexanes) was added alkylhalide (16.1 and 40.3 mmol respectively). A condenser was added and the solution refluxed overnight giving a cloudy orange solution. Hexanes (50 mL) was added to the solution, the solution was washed with water, and the aqueous portion extracted with hexanes (20 mL). The organic fractions were dried over magnesium sulfate, filtered, and the solvent removed in vacuo. The residue was placed in a sublimator and excess ferrocene was sublimed at 60°C under vacuum. The product was then purified either by short-path distillation or recrystallization depending on its melting point [17].

(1-Dodecyl)ferrocene

^1H NMR data (CDCl_3 , 20°C) δ = 4.08 (s, 5 H, Cp), 4.04 (m, 2 H, Cp), 4.03 (m, 2 H, Cp), 2.29 (m, 2 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.48 (m, 2 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 1.27 (m, 18 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$), 0.88 (m, 3 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$). Calc.: C 74.55, H 9.67; Found: C 75.28, H 10.25.

(1-Octyl)ferrocene

^1H NMR data (CDCl_3 , 20°C) δ = 4.09 (s, 5 H, Cp), 4.05 (m, 2 H, Cp), 4.04 (m, 2 H, Cp), 2.31 (m, 2 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.50 (m, 2 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.29 (m, 10 H,

$\text{CpCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$, 0.90 (m, 3 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$). Calc.: C 72.49, H 8.79; Found: C 73.20, H 8.92.

1,1'-Di(octyl)ferrocene

^1H NMR data (CDCl_3 , 20°C) δ = 4.04 (br s, 8 H, Cp), 2.25 (m, 4 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.47 (m, 4 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 1.28 (m, 24 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$), 0.89 (m, 6 H, $\text{CpCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_3$). Calc.: C 76.08, H 10.31; Found: C 75.99, H 10.24.

4.3. Electrochemistry

The cyclic voltammograms (CV) were obtained using a four-neck 50 mL flask as the electrochemical cell. The typical three-electrode cell configuration included a glassy carbon working electrode, a platinum counter electrode and a Ag/AgCl reference electrode. The electrochemical cell was air-tight, providing a controlled atmosphere. The solution was deaerated using a nitrogen sweep gas for 15 minutes prior to obtaining the CV scan. The glassy carbon working electrode was polished with alumina, cleaned in an ultrasonic bath with distilled water, and finally rinsed with distilled water prior to use. The platinum counter electrode was cleaned with concentrated sulfuric acid, rinsed with distilled water, cleaned in the ultrasonic bath, and again rinsed with distilled water.

Acknowledgements

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