ARTICLE IN PRESS

C. R. Chimie xxx (2016) 1–9

Contents lists available at ScienceDirect

Comptes Rendus Chimie

www.sciencedirect.com

Full paper/Mémoire

Synthesis of new binuclear ferrocenyl compounds by hydrosilylation reactions

Reza Teimuri-Mofrad*, Farzaneh Mirzaei, Hassan Abbasi, Kazem D. Safa

Department of Organic and Biochemistry, Faculty of Chemistry, University of Tabriz, P.O. Box 51666-16471, Tabriz, Iran

ARTICLE INFO

Article history:
Received 10 February 2016
Accepted 28 June 2016
Available online xxxx

Keywords:
Ferrocene
Silane
Hydrosilylation
Cyclic voltammetry
Butenylferrocene

ABSTRACT

Ferrocenyl silanes are prepared by treatment of Grignard reagents produced from 4-chlorobutylferrocene derivatives and chlorodimethylsilane in THF. Butenylferrocenes are prepared by the elimination reaction of 4-chlorobutylalkylferrocenes by sodium *tert*-butoxide in DMSO. A hydrosilylation reaction between a butenyl compound and ferrocenylsilane occurred in dry toluene at room temperature in the presence of the Karstedt catalyst to produce the desired binuclear ferrocenyl compound in good to high yields. The electrochemical behavior of new ferrocenyl compounds were studied by cyclic voltammetry in CH_3CN/0.1 M $LiClO_4$, and the relation between the peak currents and the square root of the scan rate, showed that the redox process is diffusion-limited.

1. Introduction

Hydrosilylation is a powerful tool to functionalize organic molecules, and it represents one of the most important routes in obtaining organosilicon compounds [1]. The addition of Si–H bonds to unsaturated compounds could be carried out by free radical chain reactions or more traditionally by the use of different catalysts such as platinum or other transition metals. For this reaction, the Karstedt catalyst of the empirical formula $[Pt_2(CH_2{-}CH{-}Si{-}(Me)_2OSi(Me)_2CH{-}CH_2)_3]$, which follows a mechanism involving colloids, has predominated in recent years [2]. Recent discoveries in a broad range of applications such as electrical, magnetic, optical, biomedical, coatings, aerospace, and catalysis greatly increased the interest in incorporation of transition metals into organic monomers and polymers [3,4].

Since its discovery in 1951, ferrocene has quickly attracted the attention of the scientific and technical community on account of its interesting chemistry [5–7]. Researchers started to develop synthetic strategies leading to ferrocene derivatives and explored their applications in a wide range of scientific areas [8]. Due to the favorable electronic properties of ferrocene and its ease of functionalization, these compounds have found many applications in materials science, including sensors, [9–15] catalysts, [16–19] electroactive materials [20–22] and aerospace materials.

Ferrocene derivatives are a well-known class of one-electron donors which exhibit well established reversible redox couples. As a consequence, ferrocene derivatives, particularly those possessing functionalized tethers, have emerged as strong candidates for molecular electronic devices, electro-optical materials, multielectron redox catalysts and electrode surface modifiers [23,24]. There are several methods known for the formation of vinyl or propenylferrocene. Derivatives with longer alkenyl chains are hardly known in the literature. Previous methods for the synthesis of alkenylferrocenes were based on the dehydration and dehydrohalogenation reactions of the corresponding ferrocenylalkanols and ferrocenylalkylhalides with a suitable reagent, respectively [25,26].

Based on our interest in ferrocenyl chemistry here, we report the synthesis of binuclear ferrocenyl compounds

---

* Corresponding author.
E-mail address: teymouri@tabrizu.ac.ir (R. Teimuri-Mofrad).

http://dx.doi.org/10.1016/j.crci.2016.06.011
1631-0748/© 2016 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

Please cite this article in press as: R. Teimuri-Mofrad, et al., Synthesis of new binuclear ferrocenyl compounds by hydrosilylation reactions, Comptes Rendus Chimie (2016), http://dx.doi.org/10.1016/j.crci.2016.06.011

using the hydrosilylation strategy. Besides the electrochemical properties of the synthesized ferrocenyl compounds are reported in the present article.

2. Result and discussion

Alkylferrocenes (**3a**–**c**) were synthesized by acylation of ferrocene with acyl chlorides in dry CH_2Cl_2 in the presence of $AlCl_3$ as the catalyst. The reaction was subsequently followed by the reduction of carbonyl compounds (**2a**–**c**) by adding $NaBH_4$ in diglyme to produce the desired compounds in good yields (Scheme 1).

4-Chlorobutylferrocene (**5a**) was synthesized by the acylation reaction as reported in the literature [27,28]. Acylation of alkylferrocenes (**3a**–**c**) with 4-chlorobutanoyl chloride in dry CH_2Cl_2 and $AlCl_3$ as the catalyst which subsequently continues by in situ reduction of carbonyl compounds (**4b**–**d**) in the presence of $NaBH_4$ in diglyme, produces 4-chlorobutylalkylferrocenes (**5b**–**d**) in high yields (Table 1 and Scheme 1).

3-Butenylferrocene (**6a**) and 3-Butenylalkylferrocenes (**6b**–**d**) were synthesized with the elimination reaction of 4-chlorobutylferrocene (**5a**) and 4-chlorobutylalkylferrocene derivatives (**5b**–**d**) by sodium *tert*-butoxide in DMSO at 60 °C in good yields, respectively [26]. This reaction also was carried out by simple bases such as KOH or NaOH in diglyme and DMSO, but the rate of conversion was less than when sodium *tert*-butoxide was used (Scheme 2). In 48 h, compound **6a** was obtained in 80% yield using KOH at 80 °C while at 60 °C the output decreases to 65% yield in the same reaction time (Table 2, Entry 3).

Similarly, the reaction in diglyme was not successful and only 5% product was obtained (Table 2, Entry 1). By NaOH in DMSO, 3-butenylferrocene was obtained in 10% yield after 36 h (Table 2, Entry 2).

(4-Ferrocenylbutyl)dimethylsilane derivatives were synthesized by the Grignard reaction between 4-chlorobutylferrocene (**5a**) [29], (4-chlorobutyl)ethylferrocene (**5b**) and chlorodimethylsilane in THF in 89 and 91% yields, respectively (Scheme 3) [30,31].

Table 1
Synthesis of 4-chlorobutylalkylferrocenes (**5a**–**d**).

Entry	Product	Yield%
1	**5a**	90
2	**5b**	89
3	**5c**	88
4	**5d**	88

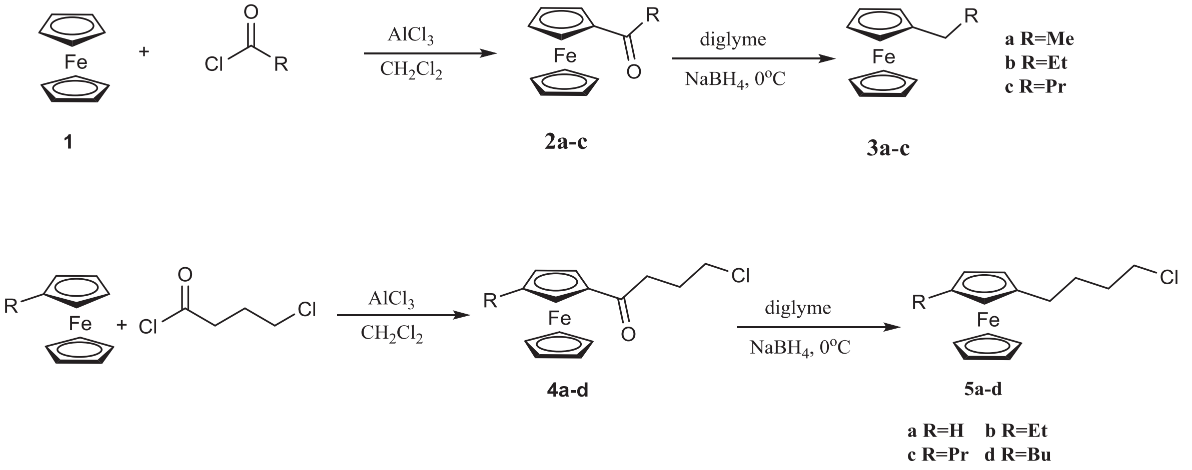
For the synthesis of binuclear ferrocenyl based organosilane compounds initially we treated the 3-(butenylferrocene) (**6a**) with (4-ferrocenylbutyl)dimethylsilane (**7a**) in dry hexane with the Karstedt catalyst at room temperature. After 3 days the desired product was obtained in low yield (Table 3, Entry 1); in this case (4-ferrocenylbutyl)dimethylsiloxane was formed as the main product under reflux conditions. Using THF gave the desired bis(4-ferrocenylbutyl)dimethylsilane (**8a**) in 10% yield.

Finally in dry toluene at room temperature after 24 h the product (**8a**) was obtained with 91% yield (Table 3, Entry 3). The novel binuclear ferrocenyl based organosilane compounds **8a**–**g** were synthesized according to this procedure in 80–91% yields (Table 4). The results showed that alkyl substituted ferrocenyl moieties are less reactive than others present in this reaction. ^1H NMR spectra of the obtained compound showed that the only formed product was alpha and no beta type was observed (Scheme 4).

Symmetrical binuclear ferrocenyl based organosilane compounds **8a** and **8e** were also synthesized by the Grignard reaction between **5a** and **5b** with dimethyldichlorosilane in THF under reflux conditions in 92 and 84% yields, respectively (Scheme 5).

3. Cyclic voltammetry

The electrochemical behavior of the synthesized compounds has been studied by cyclic voltammetry at different scan rates (mV/s) 25, 50, 100, 150, 200 and 250 in CH_3CN/0.100 M $LiClO_4$. The resulting diagrams represent pseudo-



Scheme 1. Synthesis of 4-chlorobutylalkylferrocenes (**5a**–**d**).

Please cite this article in press as: R. Teimuri-Mofrad, et al., Synthesis of new binuclear ferrocenyl compounds by hydrosilylation reactions, Comptes Rendus Chimie (2016), http://dx.doi.org/10.1016/j.crci.2016.06.011