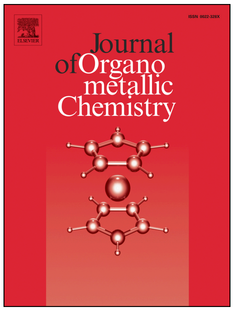

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Synthesis, characterization and electrochemical behaviour of dimethyleneamine-bridged methylated and non-methylated biferrocenyl derivatives

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KEYWORDS. Ferrocene; octamethylferrocene; electrochemistry; modified electrodes; electronic communication.

Abstract

Two dimethyleneamine-bridged octamethylated and non-methylated biferrocenyl complexes, compounds **1** and **2**, have been synthesized and characterized by ^{1}H, $^{29}Si\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectroscopy, and mass spectrometry. The redox activity of the ferrocenyl centers in **1** and **2** has been characterized by cyclic voltammetry in dichloromethane containing [*n*-Bu$_4$N][PF$_6$], [*n*-Bu$_4$N][B(C$_6$F$_5$)$_4$] or [*n*-Bu$_4$N]Cl as electrolyte support. Their electrochemistry is not only strongly dependent on the solvent/electrolyte medium but also on the substituents of the ferrocenyl moieties. Studies of the electrochemical oxidation of **1** provide evidence of the grafting of a ferrocene species onto platinum electrode surfaces.

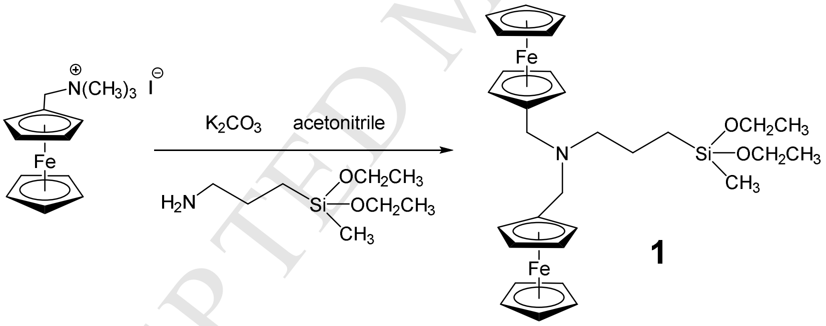
1. Introduction

Organometallic mixed-valence species have long been the subject of a plethora of studies.[1-7] Among them, complexes bearing linked ferrocenyl units have emerged as an important category of materials due to the high thermal stability and interesting electrochemistry of ferrocene.[8-19] However, complexes containing chemically equivalent ferrocenyl centers bridged by a dimethyleneamine group have been comparatively much less developed. In most of these studies, modulation and control of the degree of electronic communication between the ferrocene centers have been investigated by different means such as protonation or alkylation of the nitrogen bridge and by changing the solvent polarity and electrolyte nature.[20-23] Nevertheless, to the best of our knowledge, no examples have been reported to date on alkylamine linked bis(polymethylatedferrocenyl) complexes. In the present work, we report our findings on the electrochemistry of two new dimethyleneamine-bridged octamethylated and non-methylated biferrocenyl derivatives using three electrolytes with anions of different coordinating properties. $\Delta E_{1/2}$ values and the corresponding comproportionation constants, K_c, will be used as a guide to compare the degree of the electronic interaction between the organometallic centers. We will also examine the formation of a ferrocene derivative layer persistently attached to the electrode surface.

2. Results and discussion

2.1. Synthesis and characterization

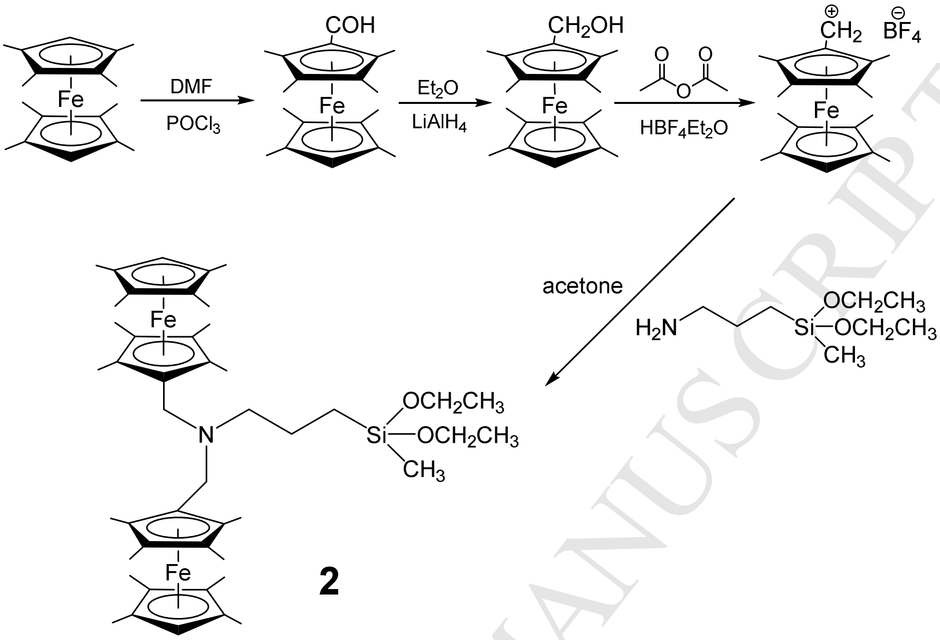
N,N-bis((ferrocenyl)methyl)N-propyldiethoxymethylsilylamine, **1**, has been synthesized following a literature procedure,[20,21] by refluxing (ferrocenylmethyl)trimethylammonium iodide and 3-aminopropyldiethoxymethylsilane in acetonitrile (Scheme 1).



Scheme 1. Synthesis of 1.

The synthesis of the bis(octamethylatedferrocenyl) complex was not so straightforward (Scheme 2). The key starting step in the preparation of the new compound is the previous synthesis of the (octamethylferrocenyl)methyl carbocation.[24] This organometallic fragment was prepared by Vilsmeier reaction of octamethyl ferrocene to give octamethylferrocenyl aldehyde, which was then reduced to (octamethylferrocenyl)methyl methanol by treatment with $LiAlH_4$. Finally, it was converted into (octamethylferrocenyl)methyl carbocation by treatment with acetic anhydride and $HBF_4.Et_2O$.

N,N-bis((octamethylferrocenyl)methyl)N-propyl diethoxymethylsilylamine, **2**, was then prepared via nucleophilic attack of 3-aminopropyldiethoxymethylsilane on the BF_4^- salt of (octamethylferrocenyl)methyl carbocation in acetone.



Scheme 2. Synthesis of 2.

1 and **2** were characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy and FAB or MALDI-TOF MS. ^{1}H NMR spectra of **1** and **2** show key signals arising from the organometallic moieties in the ranges 4.2−4.0 ppm and 1.9−1.6 ppm, respectively, along with resonances corresponding to the adjacent methylene group at around 3.3 ppm, and those of the protons of the propyl chain $-(CH_2)_3-$, in the region 2.4−0.5 ppm, which have been unambiguously assigned. The signals of the ethoxysilyl groups appear at around 3.7 and 1.2 ppm and that of the Si-CH_3 group at 0.1 ppm. The structures of **1** and **2** were also confirmed by the ^{13}C NMR spectra, which display exclusively the resonances expected for the different carbon atoms (see the Experimental Section). The ^{29}Si{^{1}H} NMR spectra display only the signal expected for the silicon atom in the molecules. The FAB mass spectrum of **1** showed the protonated molecular ion at m/z 588.2, and the MALDI-TOF mass spectrum of **2**, the molecular ion at m/z 811.5, in both cases with isotopic patterns matching exactly the calculated values.

2.2. Electrochemistry

Cyclic voltammetry (CV) of **1** and **2** was recorded on Pt in CH_2Cl_2 solution, between 0 and 0.9 V and -0.6 and 0.6 V, respectively, with [*n*-Bu_4N][PF_6] (Figures 1A and 1C) and [*n*-Bu_4N][$B(C_6F_5)_4$] (Figures 1B and 1D) 0.1 M as supporting electrolytes. In agreement with the results reported by Geiger and co-workers, in a low polarity solvent such as dichloromethane, replacement of a 'traditional' anion such as hexafluorophosphate, PF_6^-, by the weakly coordinating tetrakis(pentafluorophenyl) borate, $B(C_6F_5)_4^-$, minimizes ion-pairing interactions, thus causing an important effect on the electrochemical properties.[25-28] The voltammetric behavior of **1** with [*n*-Bu_4N][PF_6] as supporting electrolyte, resembles that observed by Kaifer and co-workers for closely related complexes.[21] As shown in Figure 1A, oxidation of **1** occurs as a chemically reversible voltammetric composite wave, indicating that the two ferrocenyl moieties are oxidized in two almost overlapped one-electron processes at 0.45 V, revealing that the electronic communication between the ferrocenyl units can be considered essentially negligible. However, CVs of **1** recorded using [*n*-Bu_4N][$B(C_6F_5)_4$] as supporting electrolyte (Figure 1B) show two well-separated and reversible oxidation waves at $E_{1/2}^1 = 0.390$ V and $E_{1/2}^2 = 0.570$ V ($\Delta E_{1/2} = 180$ mV, $K_c = 1106$). This wave splitting, in the absence of electronic interactions, has to be the result of a considerable through-space electrostatic effect between the ferrocenium centers, in the presence of the weakly-coordinating $B(C_6F_5)_4^-$ anion.

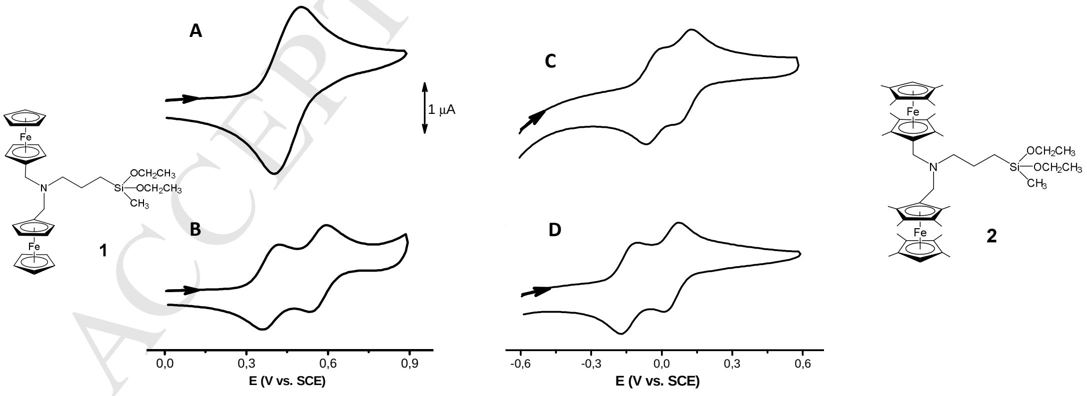


Figure 1. CVs at a Pt-disk electrode in CH_2Cl_2/0.1 M supporting electrolyte of (A) **1** with [*n*-Bu_4N][PF_6], (B) **1** with [*n*-Bu_4N][$B(C_6F_5)_4$], (C) **2** with [*n*-Bu_4N][PF_6], (D) **2** with [*n*-Bu_4N][$B(C_6F_5)_4$]. Scan rate = 100 mV s^{-1}.

On the other hand, in the CVs of **2** measured with [*n*-Bu_4N][PF_6] as supporting electrolyte (Figure 1C) two partially overlapping waves are observed at $E_{1/2}^1$ = -0.029 V and $E_{1/2}^2$ = 0.100 V ($\Delta E_{1/2}$ = 129 mV, K_c = 152). As expected, there is a negative shift in the redox potentials due to the electron donating ability of the methyl groups. When [*n*-Bu_4N][$B(C_6F_5)_4$] is used as supporting electrolyte, the two redox waves for **2** appear completely resolved at $E_{1/2}^1$ = -0.141 V and $E_{1/2}^2$ = 0.043 V ($\Delta E_{1/2}$ = 184 mV, K_c = 1293) (Figure 1D). This behavior contrasts with that observed by Astruc and co-workers[10,11] in rigid ferrocenyl-terminated redox stars and dendrimers with and without methyl substituents on the ferrocenyl groups, for which in all cases no splitting is observed in the presence of the strongly ion-pairing PF_6^-, and overlapping waves are obtained with the weakly coordinating anion, $B[C_6H_3(CF_3)_2]_4^-$.

With the aim of minimizing the electrostatic repulsion between the electrogenerated charges, by increasing the ion pairing interactions between the oxidized ferrocenes and the electrolyte anions, we decided to take advantage of the strong ion-pairing ability of chloride[27] and examine the electrochemical properties of **2** using [*n*-Bu_4N]Cl as supporting electrolyte. Surprisingly, two overlapped, but clearly distinguishable waves were still observed (Figure 2).

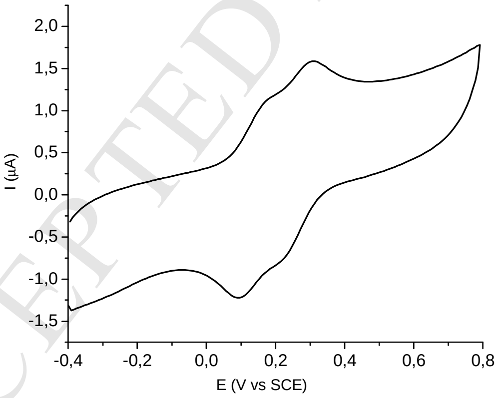


Figure 2. Cyclic voltammogram at a Pt-disk electrode of **2** in CH_2Cl_2 /[*n*-Bu_4N]Cl 0.1M solution. Scan rate 100 mV s^{-1}.

The voltammograms of **2** in the three electrolytes show a progression of the splitting from the smaller to the larger counter anion. This fact is most probably the result of the electrostatic effect due to the increased steric bulk of the methylated ligands. The octamethylation of the cyclopentadienyl ligands shields and weakens the influence of the electrolyte counter anion in **2** compared to **1**.

We had envisaged taking advantage of the –Si(OEt)$_3$ groups in **1** and **2** to immobilize the complexes on platinum oxide surfaces. However, all our efforts to obtain the corresponding derivatized electrodes following the procedure we have previously used,[29] were unsuccessful. On the other hand, unexpectedly, when the potential was held fixed at 1 V vs SCE, for 5 min in a degassed solution of **1** in CH_2Cl_2/[n-Bu_4N][PF_6] 0.1 M, using a freshly polished platinum disk electrode, this resulted in detectable electroactive material persistently attached to the electrode surface. Figure 3 shows the voltammetric response of this electrode in fresh CH_2Cl_2 containing only [n-Bu_4N][PF_6] 0.1 M. A single well-defined oxidation-reduction wave is observed, with a formal potential value of +0.59 V vs SCE and the expected linear relationship of peak current with potential sweep rate, characteristic of a surface-confined redox species. The fact that no splitting in the wave was detected, even in the presence of the non-coordinating electrolyte $B(C_6F_5)_4^-$, was a surprising point. All our previous studies in CH_2Cl_2 solution, on compounds containing interacting ferrocenyl units confined onto electrode surfaces, lead to two wave redox responses,[15,29-31] which suggests that in this case the rupture of the molecule has occurred.

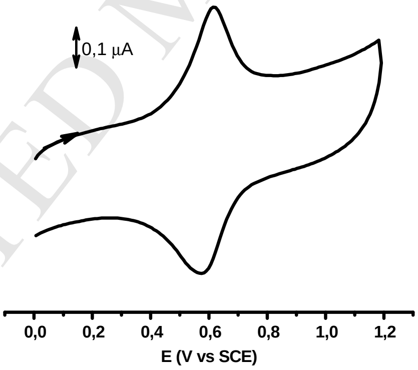


Figure 3. CV recorded in CH_2Cl_2 /[n-Bu_4N][PF_6] 0.1 M, of a Pt disk-electrode previously modified by holding it at a fixed potential of 1 V for 5 min in a degassed solution of **1** in CH_2Cl_2 /[n-Bu_4N][PF_6] 0.1 M. Scan rate = 100 mV s^{-1}.

The electrochemical behaviour of **1** was then studied in a broader potential range, up to 1.2 V vs SCE. In contrast to that observed when the potential scan is reversed at a lower value, a CV characteristic of an ECE’ mechanism is obtained. In the first scan an additional adsorption reduction peak appears at 0.6

V (vs SCE),[32] with an associate anodic wave that arises in the second scan (Figure 4).

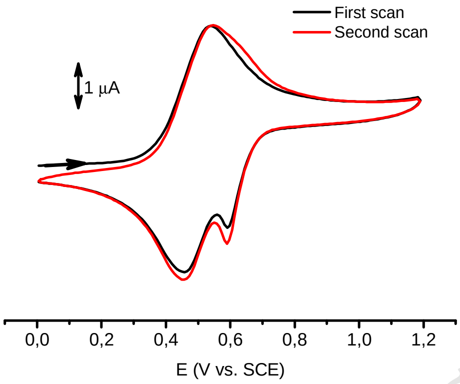


Figure 4. CV of **1** at a Pt electrode in CH_2Cl_2 /[n-Bu_4N][PF_6] 0.1 M. Scan rate = 100 mV s^{-1}.

The reduction potential of the new adsorbed system generated after the oxidation of **1** is very close to that observed for the species attached on the electrode surface mentioned above (Figure 3), and so we have tried to find an explanation to this fact. It is known that oxidation of aliphatic amines requires rather positive potentials,[33] however, as described by Torriero, Bond and co-workers, the ferrocenium ion has shown to act as mediator in the catalytic oxidation of aliphatic amines.[34] On the other hand, in the early seventies, Mann et al reported the cleavage of carbon-nitrogen bonds in tertiary aliphatic amines upon electro-chemical oxidation.[35] Therefore, it can be conceived that some of the electrochemically generated ferrocenium ions in **1** trigger the electron-transfer reaction with the amine group. This oxidation process could then be followed by the cleavage of the carbon-nitrogen bond, to afford a new ferrocenyl species that remains adsorbed on the electrode surface. ~~The reduction potential of the new reversible system generated after the oxidation of **1** is very close to that observed for the species attached on the electrode surface mentioned above (Figure 3).~~

In order to evaluate this surmise, we also performed an analogous electrochemical study with a degassed solution of N,N-dimethylferrocenylmethylamine in CH_2Cl_2 /[n-Bu_4N][PF_6] 0.1 M. After holding the potential fixed at 1 V vs SCE for 5 min, the platinum disk electrode was washed thoroughly with CH_2Cl_2. A CV recorded in fresh CH_2Cl_2 containing only [n-

$Bu_4N][PF_6]$ 0.1 M shows a single well-defined oxidation-reduction wave, with a formal potential value of +0.59 V vs SCE (Figure 5). This result sustains our assumption of the intramolecular electron transfer process between the amine group and the ferrocenium center followed by the rupture of the N-C bond, leading to the formation of a ferrocenyl species that can derivatize electrode surfaces.

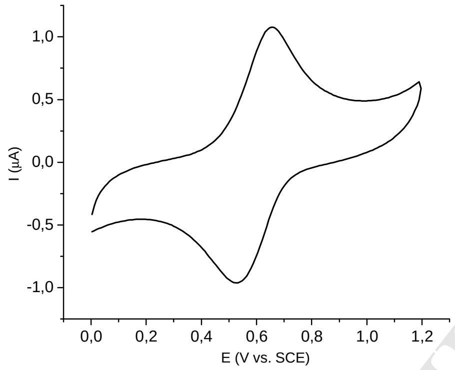


Figure 5. Voltammetric response of a Pt disk electrode modified with N,N-dimethylferrocenylmethylamine in CH_2Cl_2 /[*n*-$Bu_4N][PF_6]$ 0.1 M. Scan rate 100 mV s^{-1}.

3. Experimental

3.1. Materials and methods

All reactions were performed under an inert atmosphere using Schlenk techniques. Solvents were dried by standard procedures over the appropriate drying agents and distilled immediately prior to use. Reagents were purchased from Aldrich, Fluka, Panreac and Alfa Aesar and used as received without further purification. Silica gel 60 silanized (0.063-0.200 mm) was used for column chromatographic purifications. (Octamethylferrocenyl)methanol was prepared according to literature procedures.[24] NMR spectra were recorded on a FT BRUKER AMX-300 spectrometer or on a FT BRUKER DRX-500 spectrometer. Chemical shifts are reported in ppm (δ) relative to residual solvent resonances. FAB mass spectrum was obtained using a VG AutoSpect mass spectrometer and 3-Nitrobenzyl alcohol (m-NBA) as matrix. MALDI-TOF mass spectrum was collected on a Reflex III (Bruker) mass spectrometer and trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) was used as matrix. Electrochemical experiments were performance using an Autolab PGSTAT 128N potentiostat. Electrochemical measurements were carried out in freshly distilled CH_2Cl_2 from calcium hydride under argon. A conventional three-electrode cell was used with a platinum-disk working electrode (A=0.020 cm^2), SCE as the reference electrode and a coiled platinum wire as a counter electrode. Under our conditions the FcH/FcH^+ couple was at 0.42 V vs SCE. The supporting electrolytes used were tetra-*n*-butylammonium hexafluorophosphate ([*n*-Bu_4N][PF_6]), tetra-*n*-butylammonium chloride ([*n*-Bu_4N]Cl), and tetra-*n*-butylammonium tetrakis(pentafluorophenyl)borate ([*n*-Bu_4N][B$(C_6F_5)_4$]), which was synthesised as described in the literature.[36,37] The supporting electrolyte concentration was typically 0.1 M. Solutions for cyclic voltammetry were deoxygenated by purging with prepurified nitrogen and contained 0.5 mM in the redox-active species.

3.2. Synthetic procedures

3.2.1. **Synthesis of N,N-bis((ferrocenyl)methyl)N-propyldiethoxymethylsilylamine (1).** In a Schlenk flask, 3-aminopropyldiethoxymethylsilane (123 µl, 0.59 mmol) and (ferrocenyl)trimethylammonium iodide (0.50 g, 1.29 mmol) were dissolved in 12 mL of acetonitrile and stirred at 85º C for 24 h in the presence of potassium carbonate K_2CO_3 (0.81 g, 5.86 mmol). After cooling to room temperature, the potassium carbonate excess was removed by filtration and the solid was washed with dichloromethane. The solvent of the filtrates was removed under vacuum to give an orange residue, which was purified by silanized silica column chromatography using hexane as eluent and triethylamine 2%. **1** was obtained as a yellow oil (0.11 g, 32%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.16 (m, 4H, C_5H_4), 4.11 (m, 4H, C_5H_4), 4.08 (s, 10H, C_5H_5), 3.75 (q, 4H, J = 7, OCH_2CH_3), 3.40 (s, 4H, Fc-CH_2), 2.28 (t, 2H, J = 7.5, $NCH_2CH_2CH_2Si$), 1.48 (m, 2H, $NCH_2CH_2CH_2Si$), 1.22 (t, 6H, J = 7, OCH_2CH_3), 0.52 (m, 2H, $NCH_2CH_2CH_2Si$), 0.10 (s, 3H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 83.80, 70.14 (C_5H_4), 68.47 (C_5H_5), 67.73 (C_5H_4), 58.07 (OCH_2CH_3), 55.46 ($NCH_2CH_2CH_2Si$), 52.56 (Fc-CH_2), 20.59 ($NCH_2CH_2CH_2Si$), 18.44 (OCH_2CH_3), 11.32 ($NCH_2CH_2CH_2Si$), 4.77 ($SiCH_3$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$, 60 MHz): δ -4.50. MS (FAB; m/z): 588.2 $(M+H)^+$.

3.2.2. **Synthesis of *N*,*N*-bis((octamethylferrocenyl)methyl)*N*-propyldiethoxymethylsilyl amine (2).** Acetic anhydride (215 µL, 2.28 mmol) was added to a stirred solution of (octamethylferrocenyl)methanol (0.43 g, 1.30 mmol) in Et_2O (40 mL) and then $HBF_4 \cdot Et_2O$ (345 µL, 2.54 mmol) was added to lead a precipitate. After removing the solvent by filtration, the solid was washed twice with pentane and dried under vacuum, affording the BF_4^- salt of [(octamethylferrocenyl)methyl carbocation] as a reddish-orange solid. This solid was immediately dissolved in acetone (30 mL) and 3-aminopropyl(diethoxy)methylsilane (2.9 mL, 13.96 mmol) was then added. After stirring for 45 minutes, the solvent was evaporated under vacuum and a greenish yellow residue was obtained. This residue was subjected to column chromatography on silanized silica using hexane/methanol (20:1) as eluents and triethylamine 2%. After removal of the solvent, the compound **2** was obtained as a yellow solid (0.24g, 45%). ^{1}H NMR (C_6D_6, 500 MHz): δ 3.66 (q, 4H, J = 7, OCH_2CH_3), 3.28 (s, 4H, $Fc^{\#}$-CH_2), 3.20 (s, 2H, $C_5(CH_3)_4H$), 2.44 (t, 2H, J = 7, $NCH_2CH_2CH_2Si$), 1.88 (s, 12H, $C_5(CH_3)_4$), 1.74 (s, 12H, $C_5(CH_3)_4$), 1.73 (s, 12H, $C_5(CH_3)_4$), 1.65 (s, 12H, $C_5(CH_3)_4$), 1.16 (t, 6H, J = 7, OCH_2CH_3), 0.62 (m, 2H, $NCH_2CH_2CH_2Si$), 0.08 (s, 3H, $SiCH_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 80.60 ($C_5(CH_3)_4$), 58.07 (OCH_2CH_3), 56.71 ($NCH_2CH_2CH_2Si$), 49.13 ($Fc^{\#}$-CH_2), 20.51 ($NCH_2CH_2CH_2Si$), 18.49 (OCH_2CH_3), 11.38 ($NCH_2CH_2CH_2Si$), 11.04, 10.03, 9.75, 9.21 ($C_5(CH_3)_4$), -4.90 ($SiCH_3$). ^{29}Si{^{1}H} NMR ($CDCl_3$, 100MHz): δ -3.68. MS (MALDI-TOF; m/z): 811.5 $(M)^+$.

4. Conclusions

Two dimethyleneamine-bridged octamethylated and non-methylated biferrocenyl complexes, **1** and **2**, have been synthesized and characterized. As far as we know, **2** constitutes the first example of an alkylamine linked bis(polymethylatedferrocenyl) complex. The voltammetric behaviour of the non-methylated **1** with different supporting electrolytes, resembles that observed before for related complexes, with negligible electronic communication in the presence of the strongly ion-pairing PF_6^-, and a significant through-space electrostatic effect between the ferrocenium centers, when the anion is the weakly-coordinating $B(C_6F_5)_4^-$. In contrast, the voltammetric behavior of **2** measured with [*n*-Bu_4N][PF_6] or even [*n*-Bu_4N]Cl as supporting electrolytes shows in both cases a noticeable through-space electrostatic effect between the octamethylated ferrocenium centers, as a result of the steric bulk of the methylated ligands, which shield the influence of the electrolyte counter anion.

A stable ferrocenyl specie that remains persistently attached to the electrode surface upon electrochemical studies of the dimethyleneamine-bridged biferrocenyl complex **1** is reported.

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Synthesis, characterization and electrochemical behaviour of dimethyleneamine-bridged methylated and non-methylated biferrocenyl derivatives

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HIGHLIGHTS

We report the synthesis and complete characterization of two dimethyleneamine-bridged octamethylated and non-methylated biferrocenyl complexes:

1. As far as we know, this is the first example of an alkylamine linked bis(polymethylatedferrocenyl) complex.
2. Its voltammetric behaviour differs from that of the non-methylated derivative due to the steric bulk of the methylated ligands, which shield the influence of the electrolyte counter anion.
3. A stable ferrocenyl species that remains persistently attached to the electrode surface upon electrochemical studies of the dimethyleneamine-bridged biferrocenyl complex is also reported.