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# Synthesis, characterization and electrochemical behaviour of new bis(fluoroalkyl) ferrocenylphosphonates and their tin tetrachloride complexes

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## Abstract

The synthesis and characterization of new fluoroalkyl and non-fluorinated long chain alkyl ferrocenylphosphonates from reaction of ferrocene with corresponding phosphorochloridates are reported. These phosphonates were used as ligands for the preparation of new tin(IV) chloride complexes. All these ferrocenylphosphonate derivatives were characterized with multinuclear ($^{1}H$, $^{13}C$, $^{19}F$, $^{31}P$ and $^{119}Sn$) NMR, IR and UV-vis spectroscopic techniques. The electrochemical behavior of these compounds was also investigated using cyclic voltammetry; the results show that fluoroalkyl groups render the reverse one-electron transfer oxidation reaction more difficult ($\Delta E_{1/2}$ = 310-330 mV) as compared to non fluorinated alkyl groups ($\Delta E_{1/2}$ = 215-261 mV).

**Keywords:** Ferrocenylphosphonates, fluoroalkyl alcohols, cyclic voltammetry.

## 1. Introduction

Organophosphorus chemistry have gained considerable interest due to their widespread applications in various areas such as agriculture [1,2], biology [3,4], pharmaceuticals [5-7] and chemical synthesis [8,9]. Among these, one of the most common classes are phosphonates, which are attracting increasing interest as important structural motifs that are found in a variety of naturally occurring compounds [10-12], as anticancer [13,14], inhibitors of hepatitis C virus [15,16], anti-HIV [17] and antimalarial agents [18].

On the other hand, ferrocene and ferrocenyl derivatives are well known for their ability to undergo reversible one-electron oxidation, they have been used extensively as single-electron transfer (SET) reagents in organometallic and coordination chemistry to switch the redox state of complexes [19-22]. Ferrocenene-containing organophosphorus compounds are increasingly

investigated in organic synthesis as synthetic intermediates [23,24], potential ligands, in catalysis [25] and as sensitizers in dye sensitized solar cells [26].

The incorporation of fluoroalkyl groups has been shown to modify the physical and chemical properties of molecules giving them special applications in the fields of pharmaceutics, catalysis and materials science [27-29]. It was also shown that fluoroalkyl chains generally provide a higher thermal stability to the molecule, facilitating both hitsstorage and handling [30,31]. They are also used as biocompatible surfactants as emulsion stabilizers and vesicle-forming components [32,33] .

In continuation of our exploration in the synthesis of variously substituted phosphoramidates [34,35], we describe, herein, the synthesis of a series of new fluoroalkyl and alkyl ferrocenylphosphonates and corresponding tin tetrachloride complexes. The products were obtained in good yields and fully characterized by multinuclear ($^{1}$H, $^{13}$C, $^{19}$F, $^{31}$P and $^{119}$Sn NMR) NMR, IR, cyclic voltammetry (CV), HRMS for phosphonates and elemental analysis for the corresponding tin(IV) complexes. The effect of fluoroalkyl and non-fluorinated long chain groups on the electrochemical behavior of these phosphonate derivatives is also investigated.

## 2. Experimental

All reactions were carried out under an inert atmosphere. Solvents were carefully dried by conventional methods and distilled under argon before use. All commercially available chemicals ferrocene, tBuLi 1.7 M solution in pentane and tBuOK were used as received from their suppliers. Dialkyl and bis(fluoroalkyl) chlorophosphates [36] and diethyl ferrocenylphosphonate (**3**) [37] were prepared following literature procedures.

### *2.1 General procedure for the preparation of ferrocenylphosphonates FcP(O)(OR)$_2$ (1-6)*

The phosphonates (**1-6**) were prepared in a similar manner to the method reported by Oms *et al.* [37] with some modifications: KO*t*Bu (72 mg, 0.65 mmol) was added to a solution of ferrocene (1.0 g, 5.38 mmol) in THF (20 mL) at room temperature and stirred for 30 min. The solution was then cooled to –78 °C and *t*-BuLi (6.32 mL, 10.76 mmol, 1.7 M in pentane) was added dropwise. The reaction mixture was stirred at -78 °C for 1 h. The chlrorphosphate (6.73 mmol) in THF was added to the orange solution at -78 °C. The solution slowly warmed to room temperature and left until the reaction was complete. The resulting deep brown solution was concentrated under vacuo; water (50 mL) was added to the residue and solution extracted

with diethyl ether (3x20 mL). The combined organic fractions were dried over $Na_2SO_4$, filtered and evaporated *in vacuo*. The crude product was purified by flash column chromatography.

***FcP(O)(OCH$_2$CF$_3$)$_2$ (1)***

Flash chromatography Pentane to $Et_2O$. Yellow solid, MP = 54°C. FT-IR (υ/cm$^{-1}$) 3019, 2401, 1712, 1421, 1215(P=O), 1175, 1106, 1075, 984, 751, 668. RMN $^1$H (400 MHz, $CDCl_3$) δ 4.55 (s, 5H), 4.47 – 4.37 (m, 4H), 4.34 (d, *J* = 4.3 Hz, 4H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -75.10 (t, *J* = 7.9 Hz). $^{13}$C NMR (101 MHz,$CDCl_3$) 122,73(qd, $^1J_{C\text{-}F}$ = *278.76 Hz*, $^3J_{C\text{-}P}$ = *9 Hz*), 72.27 (d, *J* = 15.0 Hz, C3), 71.68 (d, *J* = 16.8 Hz, C2), 70.17 (s, $C_PC$), 62.65 (d, $J\,^1{}_{P\text{-}C}$= 225,23 Hz, C1), 61.68 (q (d, $J_{P\text{-}O\text{-}C}$ = 3.0 Hz), P(OCH$_2$CF$_3$)$_2$). $^{31}$P NMR (162 MHz,$CDCl_3$) δ 30.23 (s). Anal. calcd for Anal. calcd for $C_{14}H_{13}F_6FeO_3P$: C, 39.10; H, 3.05 %. Found:

***FcP(O)(OCH$_2$C$_2$F$_5$)$_2$ (2)***

Flash chromatography Pentane to $Et_2O$/MeOH (9:1). Brown liquid. FT-IR (υ/cm$^{-1}$) 3020, 2401, 1704, 1423, 1215 (P=O), 1156, 1027, 749, 668. $^1$H NMR (400 MHz, $CDCl_3$) δ 4.58 – 4.45 (m, 8H), 4.34 (s, 5H). $^{19}$F NMR (377 MHz, $CDCl_3$) δ -83.56 (s), -124.49 (s). $^{13}$C NMR (101 MHz, $CDCl_3$) δ111,86 (tq, $^1J_{C\text{-}F}$ = *248.46 Hz*, $^2J_{C\text{-}F}$ = *29 Hz*, $CF_2$), 118,35 (qt, $^1J_{C\text{-}F}$ = *286.84 Hz*, $^2J_{C\text{-}F}$ = *35 Hz*, $CF_3$), 72.29 (d, *J* = 15.2 Hz, C3), 71.57 (d, *J* = 17.1 Hz, C2), 70.12 (s, $C_PC$), 62.29 (d, $J\,^1{}_{P\text{-}C}$= 225,23 Hz, C1), 61 (t (d, $J_{P\text{-}O\text{-}C}$ = 5.0 Hz), P(OCH$_2$C$_2$F$_5$)$_2$). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 30.34 (s). Anal. calcd for Anal. calcd for $C_{16}H_{13}F_6FeO_3P$: C, 39.25; H, 2.47 %. Found:

***FcP(O)(OHex)$_2$ (4)***

Flash chromatography hexane gradient to hexane/EtOAc 9:1. Pale brown liquid. $^1$H NMR (400 MHz, $CDCl_3$) δ 4.50 – 4.45 (m, 2H), 4.39 – 4.34 (m, 2H), 4.27 (s, 5H), 4.10 – 3.94 (m, 4H), 1.71 – 1.58 (m, 4H), 1.41 – 1.21 (m,12H), 0.86 (t, *J* = 6.7 Hz, 6H).$^{13}$C NMR (101 MHz, $CDCl_3$) 71.50 (d, *J* = 15.4 Hz, C3), 71.11 (d, *J* = 13.9 Hz, C2), 69.79 (s, $C_PC$), 66.88 (d, $J\,^1{}_{P\text{-}C}$= 216,14 Hz, C1), 65.64 (d, $J_{P\text{-}O\text{-}C}$ = 6.0 Hz))., 31.31 (s), 30.48 (d, *J* = 6.6 Hz), 25.24(s), 22.91 (s), 22.51 (s), 13.97 (s).$^{31}$P NMR (162 MHz, $CDCl_3$) δ 25.79 (s). Anal. calcd for $C_{22}H_{35}FeO_3P$: C, 60.84; H, 8.12 %. Found:

***FcP(O)(OHep)$_2$ (5)***

Flash chromatography hexane/EtOAc gradient to EtOAc/MeOH (4:1). Pale Brown liquid. $^1$H NMR (400 MHz, $CDCl_3$) δ 4.52 (t, *J* = 4.4 Hz, 2H), 4.41 (t, *J* = 4.6 Hz, 2H), 4.32 (s, 5H), 4.25 – 3.80 (m, 5H), 1.77 – 1.64 (m, 5H), 1.49 – 1.28 (m, 10H), 0.92 (t, *J* = 7.1 Hz, 7H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 25.77 (s).

***FcP(O)(OOct)$_2$ (6)***

Flash chromatography hexane/EtOAc gradient to EtOAc/MeOH (4:1). Brown liquid. $^1$H NMR (400 MHz, $CDCl_3$) δ 4.52 (d, *J* = 10.4 Hz, 2H), 4.40 (s, 2H), 4.31 (s, 5H), 4.18 – 4.08 (m, 5H), 1.76 – 1.58 (m, 5H), 1.30 (ddd, *J* = 18.7, 9.4, 4.8 Hz, 27H), 0.89 (t, *J* = 6.9 Hz, 7H). $^{31}$P NMR (162 MHz, $CDCl_3$) δ 25.75 (s).

***2.2 General procedure for the preparation of complexes (7-10)***

A solution of ferrocenyphosphonates (0.46 mmol) in dry $CH_2Cl_2$ (10 mL) was slowly added to $SnCl_4$ (0.06 g, 0.23 mmol) in $CH_2Cl_2$ (20 mL) and the mixture stirred under $N_2$ for 24 h. The volatiles were then removed *in vacuo* and the complex [$SnCl_4L_2$] washed with anhydrous hexane and dried *in vacuo* to give the complexes as brown oils.

***[SnCl$_4$(1)$_2$] (7)***

Yield: 0.20 g (80%); FT-IR (cm$^{-1}$) υ = 1159 (P=O), 1077 (P-O-C), 749, 668; $^1$H NMR (300 MHz, $CDCl_3$) δ 4.93 – 4.60 (m, 8H), 4.52 (s, 5H). $^{31}$P NMR (121 MHz, $CDCl_3$) δ 28.06 ($^1J_{P-C}$ = 223 Hz), 27.67. $^{119}$Sn NMR (112 MHz, $CDCl_3$) -714.89. Anal. calcd for $C_{28}H_{26}Cl_4F_{12}Fe_2O_6P_2Sn$: C, 30.86; H, 2.41 %. Found:

***[SnCl$_4$(2)$_2$] (8)***

Yield: 0.27 g (90%); FT-IR (cm$^{-1}$) υ = 1177 (P=O), 1126 (P-O-C), 754, 668; $^1$H NMR (300 MHz, $CDCl_3$) δ 5.03 – 4.7 (m, 8H), 4.52 (s, 5H). $^{31}$P NMR (121 MHz, $CDCl_3$) δ 28.19 ($^1J_{P-C}$ = 216.25 Hz), 25.06 . $^{119}$Sn NMR (112 MHz, $CDCl_3$) −714.19, -647.97. Anal. calcd for $C_{32}H_{26}Cl_4F_{20}Fe_2O_6P_2Sn$: C, 29.80; H, 2.03 (%); Found:

***[SnCl$_4$(3)$_2$] (9)***

Yield: 0.18 g (90%); $^1$H NMR (400 MHz): δ = 4.50-4.38 (m,4H), 4.30 (s, 5H), 4.12 (m, 4H),1.33 (t, *J* = 7.1 Hz, 6H). RMN $^{31}$P (121 MHz, $CDCl_3$) δ 21.83($^1J_{P-C}$ = 232.32 Hz). NMR $^{119}$Sn (112 MHz, $CDCl_3$) -728.82.

***[SnCl$_4$(4)$_2$] (10)***

Yield:0.18 g (71 %); FT-IR (cm$^{-1}$) υ = 1126 (P=O), 1159 (P-O-C), 738, 668; $^1$H NMR (300 MHz, $CDCl_3$) δ 5.20 (s, 5H), 5.57-6.5 (m,4H), 3.81-3.94 (m, 4H), 1.17-137 (m, 12H), 0.85-

0.87 (m, 6H). $^{31}P$ NMR (121 MHz, $CDCl_3$) δ 19.47, 16.01. $^{119}Sn$ NMR (112 MHz, $CDCl_3$) -660. Anal. calcd for $C_{44}H_{70}Cl_4F_{20}Fe_2O_6P_2Sn$: C, 48.12; H, 6.42 (%). Found:

### *2.3 Physical measurements*

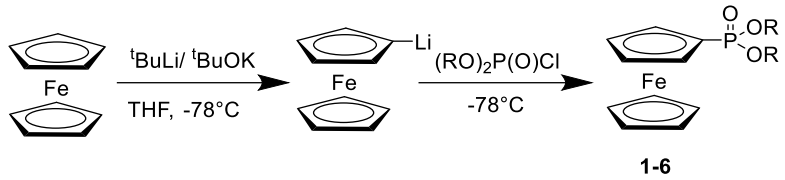
Melting points were measured using an "Electrothermal 9100 : apparatus and are uncorrected. $^1H$ (300 MHz), $^{13}C$ (75.4 MHz), $^{19}F$ NMR (282 MHz) and $^{31}P$ (121 MHz) NMR spectra were recorded with a Bruker ACIII-300 spectrometer. TMS was used as the internal standard for $^1H$ and $^{13}C$, $CFCl_3$ for $^{19}F$ and $H_3PO_4$ for $^{31}P$ NMR spectroscopy. HRMS data were obtained from a high resolution MicromassmicrOTOF-Q II 10027 spectrometer with electron spray ionization method. Infrared spectra were recorded on a YL2000 FT-IR spectrometer using KBr pellets. Cyclic voltammograms and potential square wave voltammograms were obtained in a three-electrode cell. A GCE working electrode, a platinum wire auxiliary electrode and an Ag/AgCl reference electrode were used to record voltammograms. The electrolyte was $nBu_4NPF_6$ (0.1 M in dichloromethane). The concentration of electro-active species was 0.001 M. Pulse amplitude of 25 mV and a scan rate of 5 $mVs^{-1}$ were used to record the potential square wave voltammograms. UV/Vis spectra were recorded on a Unico 2802 spectrophotometer using chloroform as solvent.

## 3. Results and discussion

### *3.1. Synthesis of ferrocenylphosphonates and their complexes*

The synthesis of the new ferrocenylphosphonates $FcP(O)(OR)_2$ (**1**, **2** and **4-6**) was performed using the $^tBuLi/^tBuOK$ system at low temperature, following a similar methodology reported by Oms *et al.* [37]. Thus, the reaction of ferrocene (Fc), using the Schlosser–Lochmann base (tBuLi/KOtBu) in THF at -78°C, with different phosphorochloridates gave the phosphonates **1-6** in yields of 30–79% (Table 1). The isolated yields were, in general, better for fluoroalkyl derivatives. The previously known phosphonate (**3**), $FcP(O)(OEt)_2$ [37], was prepared in the same way and used for comparison purposes.

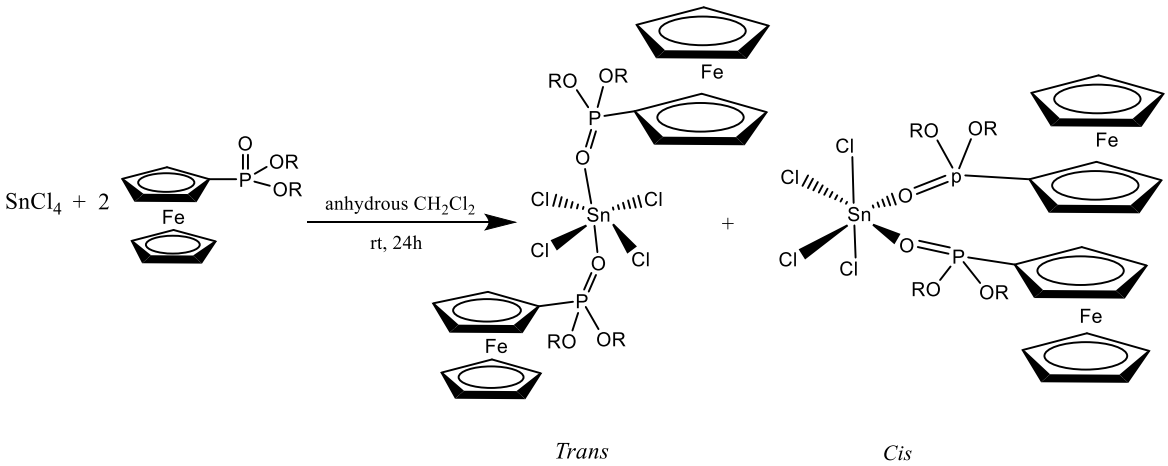
**Table 1:** Synthesis of ferrocenylphosphonates, $FcP(O)(OR)_2$ (**1-6**).




| Phosphonate | R | t (h) | Yield (%)[a] |
|---|---|---|---|
| **1** | $CH_2CF_3$ | 4 | 60 |
| **2** | $CH_2C_2F_5$ | 4 | 44 |
| **3** | Et | 12 | 76[b] |
| **4** | n-Hex | 12 | 56 |
| **5** | n-Hep | 12 | 30 |
| **6** | n-Oct | 12 | 40 |

[a] Yields after purification, [b] 79% [37].

The coordination chemistry of ferrocenyl phosphophonates (**1-4**) as potential phosphoryl ligands (L) was examined. Therefore, the reaction of these phosphonates with tin tetrachloride in anhydrous dichloromethane affords, after 12 h, the new complexes $[SnCl_4L_2]$ (**7-10**) in 71-90 yields (Scheme 1, Table 2). These adducts were obtained as brown viscous oils, which are fairly soluble in dichloromethane and chloroform.




**Scheme1**. Synthesis of ferrocenylphosphonate complexes, $[SnCl_4(FcP(O)(OR)_2)_2]$ (**7-10**).

**Table 2:** Synthesis of ferrocenylphosphonate complexes, $[SnCl_4(FcP(O)(OR)_2)_2]$ (**7-10**).

| Complex | Yield (%) |
|---|---|
| $[SnCl_4(FcP(O)(OCH_2CF_3)_2)_2]$ (**7**) | 80 |
| $[SnCl_4(FcP(O)(OCH_2C_2F_5)_2)_2]$ (**8**) | 90 |
| $[SnCl_4(FcP(O)(OEt)_2)_2]$ (**9**) | 90 |
| $[SnCl_4(FcP(O)(OHex)_2)_2]$ (**10**) | 71 |

### *3.2. IR and NMR Spectroscopic characterization*

The strong bands observed in the infrared spectra within the range 1214-1250 $cm^{-1}$ for ferrocenylphosphonates (**1-4**) are assigned to $\upsilon_{P=O}$. The P-O stretching vibrations display relatively strong absorptions in the range 1067-1075 $cm^{-1}$. These stretching vibration values are in good agreement with literature data for related derivatives [38,39]. Interestingly, the P=O stretching vibrations for complexes (**7-10**) are shifted to lower frequencies while the P-O vibrations are shifted to higher frequencies upon coordination with tin tetrachloride compared to that in the free ligands (**1-4**) (Table 3). This suggests that the P=O bond is weakened upon complexation, consistent with the coordination to the tin center through the P=O group. The magnitude of the coordination shift ($\Delta\nu_{(P=O)}$) in such complexes is in the range 38-88 $cm^{-1}$ and would be directly proportional to the stability of the complex, which deponds upon the donor ability of the parent ligand. Thus, the most pronounced coordination shift (88 $cm^{-1}$) is observed for non alkyl phosphonate complexes **9** and **10**, in agreement with the expected weakening effect of fluoroalkyl groups on the donor ability of fluoroalkyl phosphonates in complexes **7** and **8** (See Table 3).

**Table 3** : IR data (($\nu$/cm$^{-1}$) for ferrocenylphosphonate complexes (**7-10**).

| Complex | $\nu_{(P=O)}$ | | $\nu_{(P-O)}$ | |
|---|---|---|---|---|
| | L | Complex ($\Delta\nu_{(P=O)}$) | L | Complex ($\Delta\nu_{(P-O)}$) |
| $[SnCl_4(FcP(O)(OCH_2CF_3)_2)_2]$ (**7**) | 1215 | 1159 (56) | 1074 | 1177 (103) |
| $[SnCl_4(FcP(O)(OCH_2C_2F_5)_2)_2]$ (**8**) | 1215 | 1177 (38) | 1075 | 1126 (51) |
| $[SnCl_4(FcP(O)(OHex)_2)_2]$ (**10**) | 1214 | 1126 (88) | 1074 | 1159 (85) |

All ferrocenylphosphonates (**1-6)** were also characterized by their NMR ($^1$H, $^{13}$C, $^{19}$F and $^{31}$P) spectra, which are all consistent with the proposed structures. Indeed, the $^{31}$P NMR spectra show that the resonances of fluoroalkyl phosphonates (**1** and **2**) are shifted downfield (30 ppm) as compared to non fluorinated derivatives (**3-6**) (25 ppm) [40].

The $^{31}$P NMR spectra of corresponding tin(IV) complexes (**7-10**) show a shift of the resonance signals towards the strong fields compared to those of the free ligands. Such a behaviour is explained by electron effects resulting from a modification in electron density at the phosphorus due to the coordination of the P=O oxygen atom of the ligand to the tin atom. This coordination shift is more pronounced for non fluoroalkyl phosphonate derivatives, in agreement with our above mentioned IR data. It is important to note that the $^{31}$P-{$^1$H} NMR spectra of complexes (**7-10**) show two types of signals: the high frequency major resonance flanked with Sn satellites is assigned to the *trans* isomer and the low frequency signal which is relatively broad due to fast expected ligand exchange is attributed to the *cis* form (Figures 1(a and c)).

In order to gain more insights into the structure of complexes (**7-10**) in solution and in addition to $^{31}$P NMR, we examined these adducts using $^{119}$Sn NMR spectroscopy. The corresponding $^{119}$Sn NMR spectra of complexes **7** and **8** in $CDCl_3$ display at room temperature only one triplet feature at -715 ppm ($^2J_{P-Sn}$ = 227 Hz) for **7** (Figure 1(b)) and a triplet at -714 ppm ($^2J_{P-Sn}$ = 222 Hz) together with a broad signal at -648 ppm in the region of hexacoordinated tin species for **8** (Figure 1(d)). The triplet resonance observed in the $^{119}$Sn NMR spectra is due to $^{119}$Sn-$^{31}$P coupling in the *trans* isomers, while the large signal is ascribed to the labile *cis* ismer. This is consistent with the $^{31}$P NMR spectra where signals

displaying Sn satellites with the corresponding coupling constants were observed. The results are also in fair agreement with the related bidentate ferrocenyl phosonate tin(VI) complexes $[(Fc^{1,1'})_2SnCl_4]$ and $[(Fc^{1,2})_2SnCl_4]$ [41] in which the $^{119}Sn$ NMR spectra display one triplet at 707 ppm ($^2J_{P\text{-}Sn}$ = 215 Hz) and -694 ppm ($^2J_{P\text{-}Sn}$ = 176 Hz) for $Fc^{1,1'}$ and $Fc^{1,2}$ complexes, respectively.

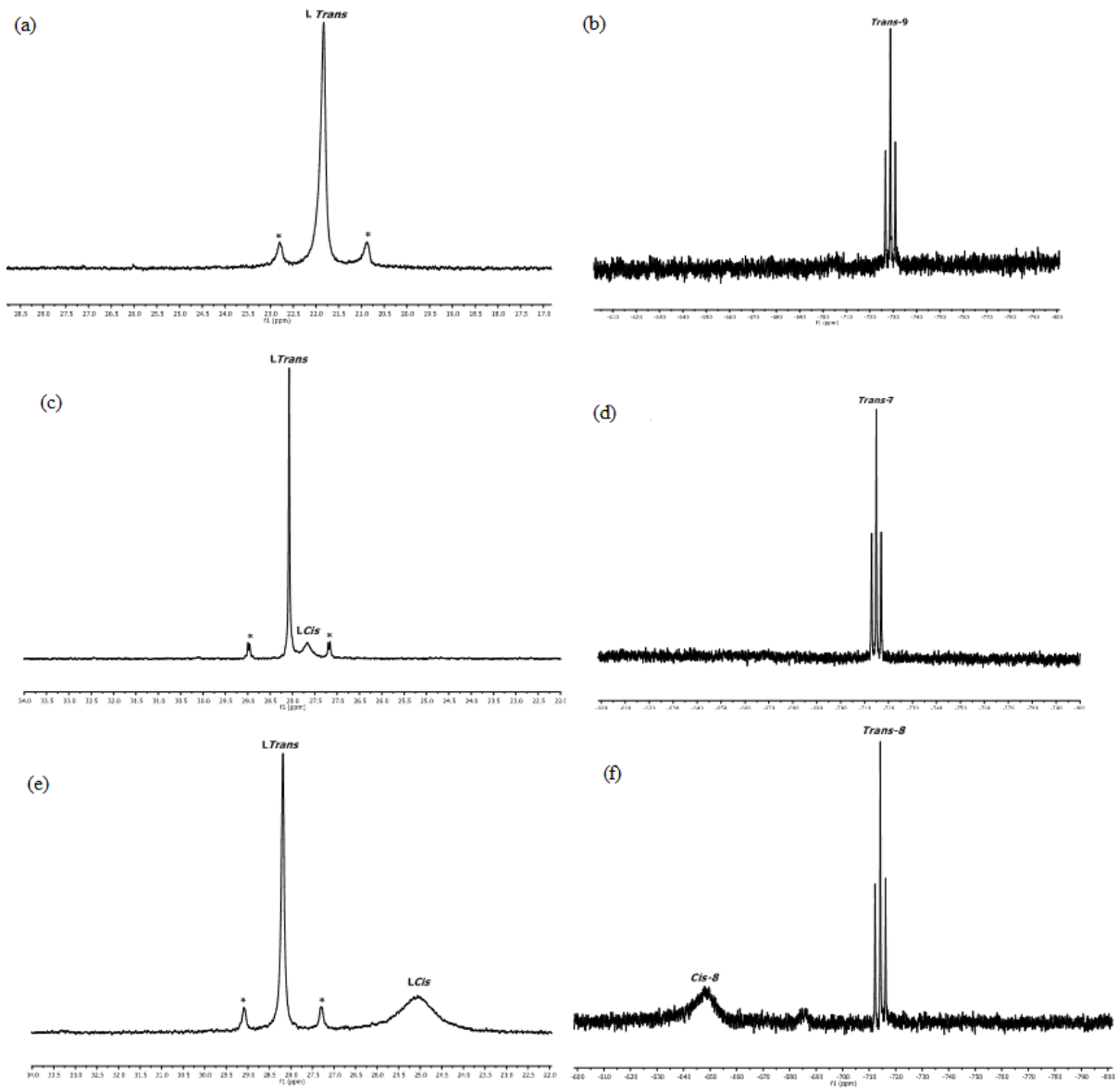



**Figure 1** $^{31}P$ NMR spectra for ferrocenyl phosphonate complexes **9** (a), **7** (c) and **8** (e)**;** $^{119}Sn$ NMR spectra for **9** (b), **7** (d) and **8** (f) in $CDCl_3$ at 25 °C.

**Table 4**: NMR data (δ/ppm and *J*/Hz) for ferrocenylphosphonate (L = **1-4**) and ferrocenylphosphonate complexes $[SnCl_4(L)_2]$ (**7-10**).

| Compound | $^{31}P$ | | | $\Delta\delta\ ^{31}P$ [a] | | $^{119}Sn$ ($^2J_{P-Sn}$) | | *Trans* (%) [b] |
|---|---|---|---|---|---|---|---|---|
| | L | *Cis* | *Trans* | *Cis* | *Trans* | *Cis* | *Trans* | |
| $[SnCl_4(\mathbf{1})_2]$ (**7**) | 30.23 | 27.67 | 28.06 | 2.56 | 2.17 | - | -715 (227) | 79 |
| $[SnCl_4(\mathbf{2})_2]$ (**8**) | 30.34 | 25.06 | 28.19 | 5.28 | 2.15 | -648 | −714 (222) | 52 |
| $[SnCl_4(\mathbf{3})_2]$ (**9**) | 26.70 | - | 21.83 | - | 4.87 | - | -729 (236) | 100 |
| $[SnCl_4(\mathbf{4})_2]$ (**10**) | 25.79 | 19.47 | - | 6.32 | - | -660 | -714 (224) | - |

[a] $\Delta\delta\ ^{31}P = \delta(^{31}P)_L - \delta(^{31}P)_{comp.}$; [b] measured from $^{31}P$ NMR.

The above NMR data show that the ferrocenyl phosphonate complexes exist in solution as mixtures of *trans* and *cis* isomers. Complexes **7** and **9** exist as almost a single isomer with a significant predominance of the *trans* form, whereas complex **8** and **10** exists as two isomers with an observed predominance for the *cis* isomer. The difference observed in closely related complexes **7** and **8** could be interpreted by the weakening effect of the $OCH_2C_2F_5$ groups on the donor ability of the ligand in the latter adduct.

### *3.3. Electrochemical behaviour*

Cyclic voltammetry and potential square wave experiments were carried out in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. The cyclic voltammogram of $FcP(O)(OCH_2CF_3)_2$ (**1**) (1 mM) at a scan rate of 100 $mVs^{-1}$ is shown in Fig. 2. The half wave potentials of different compounds prepared are given in Table 5, along with the direct comparison with ferrocene. As observed before, the presence of phosphonate group directly linked to the ferrocenyl ring renders the oxidation more difficult ($\Delta E_{1/2}$ = 215-261 mV) [37], consistent with the electron-withdrawing effect of the phosphonate substituent. This effect is enhanced by the presence of fluoroalkyl groups in our case for **1** and **2** and their related tin complexes **7** and **8**. For example, comparison of the electrochemical behaviour of fluoroalkyl and non-fluorinated long chain group

ferrocenylphosphonates shows that the presence of fluoroalkyl groups renders the reverse one-electron transfer oxidation reaction approximately 100 mV more difficult as compared to that of non fluorinated alkyl group ($\Delta E_{1/2}$ = 310-330 mV for **1** and **2** vs. 215 mV for **4**). Complex **7** is easier to oxidize than its related ligand (**1**), whilst complex **8** shows no difference with its ligand (**2**) (Table 5). This could be explained by a more pronounced ligand dissociation associated to its exchange with *cis* isomer in the latter complex (**8**), in fair agreement with NMR data discussed above. The potential square wave voltammetry (PWSV) was used to determine the have wave potential of complex 9 (Fig. 3). Complexes **9** and **10** containing non fluorinated ligands **3** and **4** display, in general, the same electrochemical trends as those observed for related non fluorinated ferrocenyl phosphonte derivatives [36].

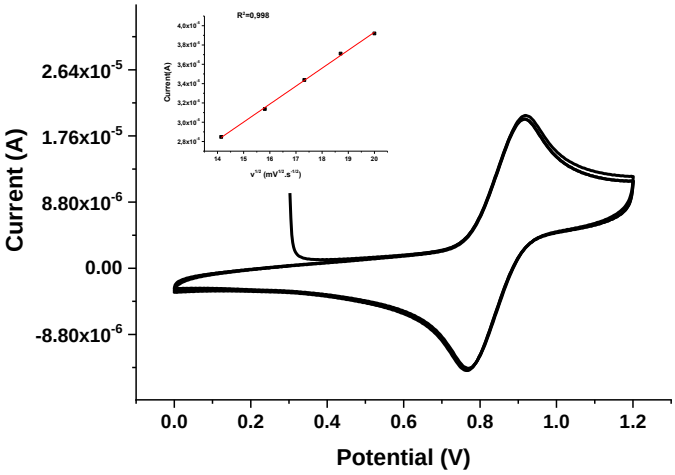



**Figure 2** Cyclic voltammogram of ferrocenylphosphonate derivative **1** and $I = f(v^{1/2})$.

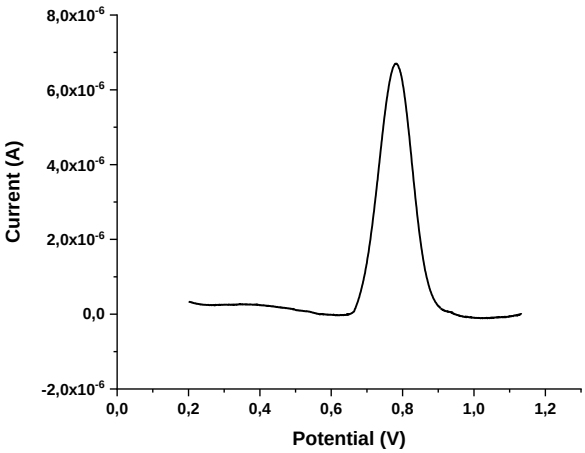



**Figure 3** PSWV curve of the complex [$SnCl_4(FcP(O)(OEt)_2)_2$] (**9**).

**Table 5** Oxidation of ferrocenyl phosphorus derivatives by voltammetry, in DCM, 0.1 M.

| Compound | Epa (mV) /(Ag/AgCl) | Epc (mV) /(Ag/AgCl) | $\Delta E^a$ (mV) | $E_{1/2}{}^b$ (mV) | $\Delta E_{1/2}{}^c$ (mV) /FcH |
|---|---|---|---|---|---|
| FcH | 700 | 330 | 370 | 515 | 0 |
| $FcP(O)(OCH_2CF_3)_2$ (**1**) | 910 | 770 | 140 | 840 | 325 |
| $FcP(O)(OCH_2C_2F_5)_2$ (**2**) | 880 | 780 | 100 | 830 | 315 |
| $FcP(O)(OEt)_2$ (**3**) [d] | 648 | 581 | 67 | 614 | 261 |
| $FcP(O)(OHex)_2$ (**4**) | 810 | 650 | 160 | 730 | 215 |
| $[SnCl_4(\mathbf{1})_2]$ (**7**) | 875 | 756 | 119 | 815 | 300 |
| $[SnCl_4(\mathbf{2})_2]$ (**8**) | 880 | 780 | 100 | 830 | 325 |
| $[SnCl_4(\mathbf{3})_2]$ (**9**) | - | - | - | 780[e] | 265 |
| $[SnCl_4(\mathbf{4})_2]$ (**10**) | 790 | 690 | 100 | 740 | 225 |

[a] $\Delta E$ = Epa-Epc; [b] $\Delta E_{1/2}$ = (1/2)(Epa+Epc); [c] $\Delta E_{1/2} = E_{1/2}$/(Ag/AgCl)-$E_{1/2}$(FcH+/FcH)/(Ag/AgCl),
[d] Values taken from [32]; [e] Determined with PSWV.

### *3.4. UV-vis characterization*

To gain more insights into the electronic structues of phosphonates **1**–**4** and related tin(IV) complexes **7**-**10**, their UV-vis spectra were recorded in chloroform, which display bands at 580-651 nm, 436–463 nm, shoulders at 332-356 nm and strong bands at 297-331 nm (Fig. 4). This trend is in general consistent with related ferrocenyl phosphonates [24]. The low energy absorption is most probably assigned to ferrocene [42]. The absorption bands of phosphonates are slightly bathochromic shifted upon coordination to the tin center (Fig. 4)

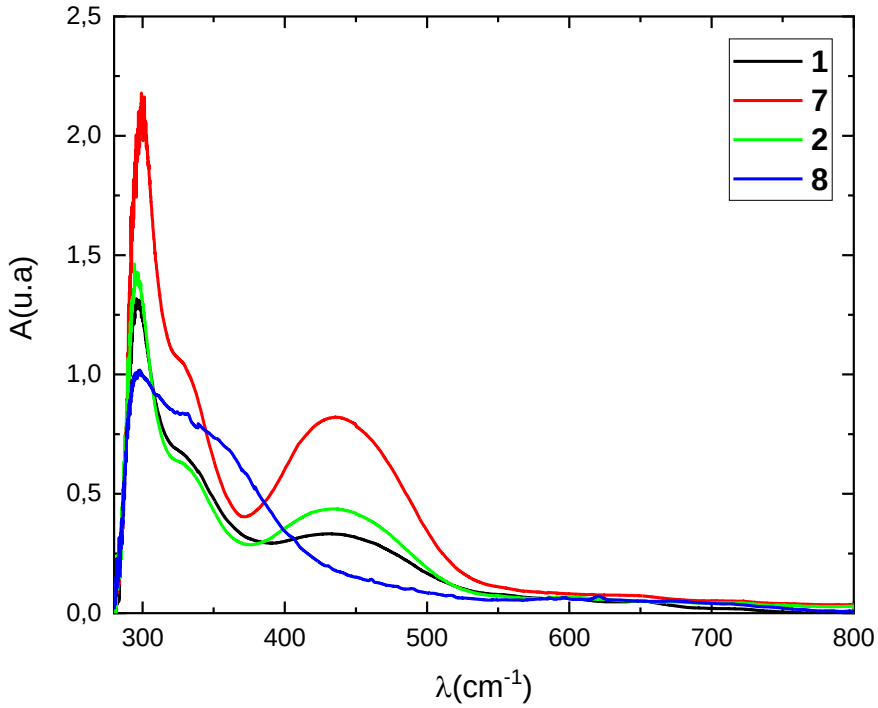



**Figure 4** UV-Vis spectra of fluoroalkyl ferrocenylphosphonates **1** (black) and **2** (green); and their tin complexes **7** (red) and **8** (blue) in $CHCl_3$.

## 4. Conclusion

We have synthesized a series of new ferrocenylphosphonates and related tin tetrachloride complexes. These were characterized by NMR, IR, CV and UV-vis techniques. The results show that the presence of fluoralkyl groups affects more significantly both the reactivity and electrochemical behavior of ferrocenylphosphonates and corresponding tin(IV) adducts as compared to non fluorinated counterparts. The biological activity of these ferrocenyl phosphonate derivatives as well as their coordination chemistry towards other metal cations are already under investigation.

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## Disclosure statement

No potential conflict of interest was reported by the author(s).

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