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Improved synthesis of diethyl ferrocenylphosphonate, crystal structure of $(FcPO_3Et_2)_2 \cdot ZnCl_2$, and electrochemistry of ferrocenylphosphonates, $FcP(O)(OR)_2$, $FcCH_2P(O)(OR)_2$, 1,1′-fc$[P(O)(OR)_2]_2$ and $[FcP(O)(OEt)_2]_2 \cdot ZnCl_2$ (Fc = $(\eta^5C_5H_5)Fe(\eta^5C_5H_4)$, fc = $(\eta^5C_5H_4)Fe(\eta^5C_5H_4)$, R = Et, H)

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Abstract

An improved synthesis of diethyl ferrocenylphosphonate using the ^{t}BuLi/^{t}BuOK system at low temperature is reported and the structure of $[FcPO_3Et_2]_2 \cdot ZnCl_2$ complex is described. The electrochemical behaviour of $FcP(O)(OEt)_2$, 1,1′-fc$[P(O)(OEt)_2]_2$, $FcCH_2P(O)(OEt)_2$, and their corresponding acids were compared. Each of them shows a reversible one-electron transfer reaction. Ferrocenylbisphosphonate is more difficult to oxidize than ferrocenylphosphonate due to the presence of two electron-withdrawing substituents. A methylene spacer between the ferrocenyl unit and the phosphonate group renders the compound easier to oxidize. The acids are easier to oxidize than the esters, and their salts, in which the phosphonate group behave as an electron-donating group, are even easier to oxidize than the ferrocene. The ferrocenylphosphonic acid may be, then, considered as a redox-active pH responsive molecule.

Keywords: Diethyl ferrocenylphosphonate; Ferrocenylphosphonic acid; Electrochemistry

1. Introduction

Ferrocene and ferrocenyl derivatives are well known for their ability to undergo reversible one-electron oxidation [1]. The redox potential depends on the electronic effect of the ring substituents on ferrocene. Electron-withdrawing substituents increase the oxidation potential (decrease the reactivity towards oxidation), while electron-donating substituents decrease the oxidation potential and thus enhance the reactivity of ferrocene [2–9]. This change of the oxidation potential of the ferrocenyl centre with the electronic effect of the substituent (chelating ligand) has been used to electrochemically sense neutral or ionic guest molecules allowing their amperometric or potentiometric titration [1,10–14]. Phosphines substituents on the ferrocenyl unit allow incorporation of a redox-active moiety into transition metal complexes, often

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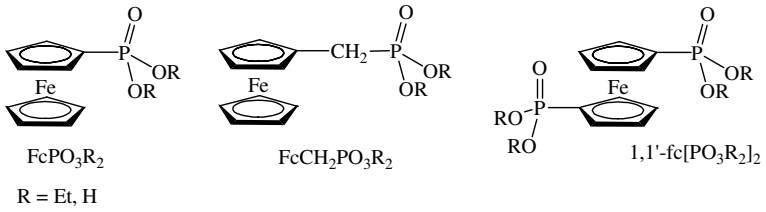


Scheme 1. The ferrocenylphosphonates.

leading to an increase in the reactivity of the complex [1]. Coordinated ferrocenylphosphine ligands usually exhibit simple, reversible electrochemistry arising from one-electron oxidation of the ferrocenyl centre, while free ferrocenylphosphine displays complex redox chemistry [9,15]. By contrast, there are few reports about the electrochemistry of ferrocenylphosphine oxide [9,16], and ferrocenylphosphonates [17–20], despite their potential for co-ordination chemistry [21–23], for preparation of redox-active metal phosphonates materials and surface modification of metals and metal oxides [24].

In this work, we report the electrochemical behaviour of the ferrocenyl unit linked to:

(i) one phosphonate group, $FcPO_3R_2$,
(ii) two phosphonate groups in the 1,1′ position, 1,1′-$fc[PO_3R_2]_2$,
(iii) one phosphonate group through a methylene spacer, $FcCH_2PO_3R_2$ (Scheme 1).

The influence of the change from the ester to the acid and their salts on the electrochemistry of the ferrocenyl unit is discussed. The crystal structure and the electrochemistry of the complex of diethyl ferrocenylphosphonate with zinc chloride are presented.

The preparation of most of these phosphonates derivatives has been already reported [25]. However, the low yield obtained in the preparation of diethyl ferrocenylphosphonate prompted us to search for a more efficient method for its preparation. The preparation of diethyl ferrocenylmethylphosphonate, which was not reported by Alley and Henderson [25] is given.

2. Experimental

2.1. Solvents and reagents

Ferrocene (Aldrich) was sublimed before use. ^{t}BuLi (Acrõs) 1.5 M solution in pentane was titrated prior to use. THF was distilled first over CaH_2 and then over Na/benzophenone. CH_2Cl_2 was dried over P_2O_5.^{t}BuOK (Avocado), diethyl chlorophosphate (Acrõs), dicyclohexylamine (Merck) were used as received. Ethyl ferrocenylmethylphosphonic acid, ferrocenylmethylphosphonic acid, 1,1′-ferrocenylbisphosphonic acid, and diphenyl ferrocenylmethylphosphonate were prepared according to Henderson et al. [19,25].

All experiments were performed under an inert atmosphere.

2.2. Syntheses

2.2.1. Diethyl ferrocenylphosphonate

In a three-necked flask, 100 ml of THF was added to 5 g of ferrocene (27 mmol) and 0.54 g of potassium *tert*-butoxide (5 mmol). The solution was stirred for 20 min at room temperature before being frozen at −78 °C. ^{t}BuLi (19 mmol) in pentane was added drop-wise from a dropping funnel. Stirring was maintained 30 min before the drop-wise addition of 27 mmol of chlorodiethylphosphate dissolved in 10 ml of THF. After 20 min, the mixture was left to return to room temperature. The black solution was washed with 200 ml of NaOH 1M. The organic phase was extracted with CH_2Cl_2 (3×30 ml), dried over $MgSO_4$, filtered and the solvents were removed under vacuum. The black residue was dissolved in CH_2Cl_2 (ca. 2 ml) and purified with silica column chromatography, using first CH_2Cl_2 as eluting solvent to removed excess ferrocene and the mixture of CH_2Cl_2/THF (70/30) to obtain 4.9 g (15 mmol) of $FcP(O)(OEt)_2$ as a brown oil (79% yield). ^{1}H NMR ($CDCl_3$, δ ppm): 1.37 (t, 6H, $^3J_{HH}$ = 7.1 Hz); 4.16 (m, 4H); 4.34 (s, 5H); 4.42 (m, 2H); 4.54 (m, 2H); ^{31}P NMR ($CDCl_3$, δ ppm): 27.0; (CD_3OD, δ ppm) 28.5; ^{13}C NMR ($CDCl_3$, δ ppm): 16.85 (d, $^3J_{CP}$ = 6.5 Hz); 62.04 (d, $^2J_{CP}$ = 6 Hz); 67.28 (d, $^1J_{CP}$ = 215.3 Hz); 70.24 (s); 71.6 (d, $^2J_{CP}$ = 14.1 Hz); 71.92 (d, $^3J_{CP}$ = 15.6 Hz). IR ν (cm^{-1}) (P═O) 1245. Anal. Calc. for $C_{14}H_{19}FePO_3$: C, 52.17; H, 5.90. Found: C, 52.16; H, 6.26%.

2.2.2. Ferrocenylphosphonic acid

From Me_3SiBr: 4.14 g (13 mmol) of diethyl ferrocenylphosphonate was dissolved in 25 ml of CH_2Cl_2 in a Schlenk tube. 5.1 g (39 mmol) of Me_3SiBr was drop-wise added with stirring at room temperature. After 12 h, the solvent was evaporated to dryness and the oil dissolved in 25 ml CH_3CN. 4 ml of water was added to precipitate $FcPO_3H_2$, which was filtered and washed successively with CH_2Cl_2 and Et_2O, leading to 2.82 g (11 mmol) of ferrocenylphosphonic acid (yield: 85%).

From Me_3SiCl: In a two-necked flask, 6.24 g (19 mmol) of diethyl ferrocenylphosphonate and 5.79 g (39 mmol) of NaI were dissolved in 70 ml of CH_3CN. Me_3SiCl (5 ml, 39 mmol) was added drop-wise leading to the precipitation of NaCl. After stirring for 12 h, 20 ml of MeOH was added. After filtration, the solvents were evaporated under vacuum, leading to a yellow powder, which was washed, successively by CH_2Cl_2 and Et_2O giving 3.65 g (14 mmol) of ferrocenylphosphonic acid (74% yield).

M.p. 201 °C (dec.) (198–205 °C dec. [25]); ^{1}H NMR (CD_3OD, δ ppm): 4.33 (s, 5H); 4.44 (m, 2H); 4.51 (m, 2H); ^{31}P NMR (CD_3OD): 24.6 ppm; IR (KBr); ν (cm^{-1}) (P═O) 1201. Anal. Calc. for $C_{10}H_{11}FePO_3$: C, 45.11; H, 4.13; P, 11.65, Fe, 20.97. Found: C, 45.16; H, 4.09; P, 10.98, Fe, 20.30%.

2.2.3. Mono dicyclohexylammonium salt of ferrocenylphosphonic acid, $FcPO_3H^-(C_6H_{11})_2NH_2^+$

To 0.532 g (2 mmol) of ferrocenylphosphonic acid dissolved in 20 ml of methanol was added 0.724 g (4 mmol) of dicyclohexylamine with stirring. After 4 h, the solution was filtered, leading to 0.85 g of the dicyclohexylammonium salt (95% yield), m.p. = 208–209 °C, ^{1}H NMR (200 MHz, CD_3OD) δ (ppm) 4.45 (2H, m), 4.28 (5H, s), 4.25 (2H, m), 3.21 (2H, m), 1.89 ($10H_{eq}$, m), 1.37 ($10H_{ax}$, m); ^{31}P NMR (81 MHz, CD_3OD) 17.7 ppm; FAB$^-$ *m/z* 265 ($FcPO_3H^-$). Anal. Calc. for $C_{22}H_{34}NFePO_3$ (446.85): C, 59.08; H, 7.61; N, 3.13; Fe, 12.50; P, 6.94. Found: C, 58.89; H, 7.75; N, 3.27; Fe, 12.22; P, 7.10%.

2.2.4. Sodium salts of ferrocenylphosphonic acid

190 mg (0.71 mmol) of ferrocenylphosphonic acid was added to 28.5 mg (0.71 mmol) of NaOH dissolved in 10 ml of water. After stirring for 2 h, the water was evaporated in vacuum leading to 179 mg (0.62 mmol) of the monosodium salt (87% yield): ^{1}H NMR (200 MHz, CD_3OD, δ ppm) 4.47 (2H, m), 4.30 (5H, s), 4.27 (2H, m); ^{31}P NMR (81 MHz, CD_3OD) 17.9 ppm.

Reaction of 200 mg of ferrocenylphosphonic acid with 30 mg of NaOH dissolved in 20 ml water gave 227 mg (97% yield) of the di sodium salt: ^{1}H NMR (200 MHz, CD_3OD, δ ppm) 4.43 (2H, m), 4.27 (5H, s), 4.13 (2H, m); ^{31}P NMR (81 MHz, CD_3OD) 16.1 ppm (15.3 ppm, D_2O [25]).

2.2.5. Diethyl ferrocenylmethylphosphonate

The procedure of Alley and Henderson [25] for the preparation of $FcCH_2P(O)(OEt)(OH)$ was followed. In a three-necked flask 6.39 g (46 mmol) of diethylphosphite $H(O)P(OEt)_2$ were added drop-wise to a suspension of 1.105 g (46 mmol) of sodium hydride in 90 ml of toluene at 0 °C under stirring. After stirring for 45 min, the solution was allowed to return to room temperature and then refluxed until the solution became uncoloured. About 5 g (23 mmol) of hydroxymethylferrocene powder was added in 1 g portions and the reflux was maintained for 3 h. The solution was left to return to room temperature and 0.95 g (11 mmol) of $NaHCO_3$ in 120 ml of water was added and stirred for 10 min. The organic and aqueous phases were separated.

The aqueous phase was washed with 30 ml of ether and acidified with a few drop of concentrated HCl to precipitate a yellow powder. 20 ml of CH_2Cl_2 was added to dissolve the powder, the two phases were separated and the aqueous phase was extracted with 2×20 ml of CH_2Cl_2. The organic phases were combined, dried over $MgSO_4$, and concentrated to about 10 ml and a large amount of acetone was added to precipitate 0.86 g (3 mmol) of ethyl ferrocenylphosphonic acid $FcCH_2P(O)(OEt)OH$ (13% yield). ^{1}H NMR ($CDCl_3$, δ ppm) 1.28 (t, 3H, $3J_{HH} = 6.8$ Hz); 2.88 (d, 2H, $^2J_{HP} = 20.5$ Hz), 3.99 (q, 2H), 4.14 (s, 5H), 4.14 (m, 2H), 4.28 (m, 2H). ^{31}P NMR ($CDCl_3$) 29.6 ppm.

The organic phase was washed with 30 ml water and dried over $MgSO_4$. The solvent was evaporated under vacuum and the product purified by silica column chromatography using first CH_2Cl_2/hexane (80/20) followed by CH_2Cl_2/THF (75/25) as eluant, leading to 4.42 g (13 mmol) of diethyl ferrocenylmethylphosphonate as a brown oil (56.5% yield). ^{1}H NMR ($CDCl_3$, δ ppm) 1.28 (t, 6H, $^3J_{HH} = 7$ Hz); 2.95 (d, 2H, $^2J_{HP} = 18.5$ Hz); 4.02 (q, 4H); 4.15 (s, 5H); 4.14 (m, 2H); 4.26 (m, 2H); ^{31}P NMR ($CDCl_3$) 26.5 ppm.

2.2.6. Ferrocenylmethylphosphonic acid

In a Schlenk tube containing 0.86 g (2.6 mmol) of diethyl ferrocenylmethylphosphonate was added 0.52 g (5 mmol) of triethylamine dissolved in 20 ml of CH_2Cl_2. 0.78 g (5 mmol) of trimethylbromosilane was added drop-wise and the stirring was maintained for 12 h. 30 ml of a saturated solution of $NaHCO_3$ was added. After 3 h of stirring the two phases were separated and the aqueous phase washed with 20 ml of CH_2Cl_2, and acidified with concentrated HCl to precipitate a yellow powder which was washed successively with 2×20 ml of water and 20 ml of ether leading to 0.6 g (2.1 mmol) of ferrocenylmethylphosphonic acid (83% yield). ^{1}H NMR (DMSO D_6, δ ppm) 2.69 (d, 2H, $^2J_{HP} = 19.5$ Hz), 4.05 (m, 2H), 4.13 (s, 5H), 4.19 (m, 2H). ^{31}P NMR (DMSO D_6) 21.8 ppm (23.1 ppm [25]). ^{13}C NMR ($CDCl_3$, δ ppm) 30.6 (d, $^1J_{CP} = 134.2$ Hz), 67.8 (s), 69.5 (s), 70.1 (d, $^3J_{CP} = 3.6$ Hz), 81.2 (d, $^2J_{CP} = 3.5$ Hz). IR (KBr) ν (cm^{-1}) (P═O) 1225.

2.2.7. 1,1′-Ferrocenylbis(diethyl phosphonate)

The procedure of Alley and Henderson [25] was followed, but we failed to obtain an as good yield as the 88% reported and only a 24% yield was obtained. ^{1}H NMR ($CDCl_3$, δ ppm) 1.33 (t, 12H, $^3J_{HH} = 6.9$ Hz), 4.11 (q, 8H), 4.59 (m, 8H); ^{31}P NMR ($CDCl_3$, δ

ppm) 25.9; ^{13}C NMR ($CDCl_3$, δ ppm) 16.9 (d, $^3J_{CP}=6.6$ Hz), 62.3 (d, $^2J_{CP}=6.6$ Hz), 68.8 (d, $^1J_{CP}=214$ Hz), 73.4 (d, $^3J_{CP}=15.6$ Hz), 74.3 (d, $^2J_{CP}=13.6$ Hz).

2.2.8. 1,1′ Ferrocenylbisphosphonic acid

It was obtained in 67% yield following Alley and Henderson [25].

^1H NMR (CD_3OD, δ ppm) 4.61 (4.5–4.7, Na salt, D_2O [25]); ^{31}P NMR (CD_3OD, δ ppm) 23.6 (21.7, Na salt, D_2O [25]); IR (KBr) ν (cm^{-1}) (P═O) 1197.

2.2.9. [FcP(O)(OEt)$_2$]$_2$·ZnCl$_2$ complex

To a solution of 1.08 g (3.3 mmol) of diethyl ferrocenylphosphonate dissolved in 5 ml of MeOH was added drop-wise, at 0 °C 0.23 g (1.7 mmol) of $ZnCl_2$ in 5 ml of MeOH. After stirring overnight at room temperature, the solvent was evaporated to dryness to give 1.19 g (1.5 mmol) of an orange brown powder, which crystallized on slow evaporation of an ether solution; m.p. = 66.6–72.7 °C. Anal. Calc. for $C_{28}H_{38}Fe_2P_2O_6ZnCl_2$: C, 43.05; H, 4.87; P, 7.94; Fe, 14.30; Zn, 8.38; Cl, 9.10. Found: C, 43.17; H, 4.73; P, 7.57; Fe, 13.87; Zn, 8.16; Cl, 8.90%. ^1H NMR ($CDCl_3$, δ ppm) 1.40 (t, 6H), $^3J_{HH}=6.7$ Hz), 4.31 (m, 4H), 4.40 (s, 5H), 4.47 (m, 2H), 4.67 (m, 2H); ^{31}P NMR (CD_3OD, δ ppm) 29.2; IR (KBr) ν (cm^{-1}) (P═O) 1207.

2.3. Physical measurements

The NMR spectra were performed on a Bruker Avance DPX 200, chemical shifts for ^1H and ^{13}C–{^1H} are referenced to $SiMe_4$ and deuterated solvents and for ^{31}P to H_3PO_4 (85%) and deuterated solvent. Infrared spectra were taken on a Thermo Nicolet Avatar 320 FT-IR spectrophotometer as KBr pellets. Cyclic voltammograms and potential square wave voltammograms were obtained with a Voltalab 10 in a three-electrode cell. A 0.20 cm diameter platinum disc working electrode, a platinum wire auxiliary electrode and a saturated calomel reference electrode were used to record voltammograms. The electrolyte was nBu$_4$NPF$_6$(0.1 M in methanol). 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.

2.4. Structure determinations

Single-crystals of bis(diethyl ferrocenylphosphonate)zinc chloride complex were obtained by slow evaporation of a diethyl ether solution at ambient temperature. A suitable crystal was mounted on a glass fibre at 173 K and X-ray data collected on a CAD 4 Nonius diffractometer, using Mo Kα radiation (λ 0.71069 Å). The structure solution was carried out with the SHELXS-86 program [26]. Hydrogen atoms positions were calculated (SHELXL) [27]. The H atoms were not refined but taken in account in the last cycle of the refinement. The refinement (with F^2s) converged to the final R_1 and wR_2 values of 0.0428 and 0.1140, respectively.

3. Results and discussion

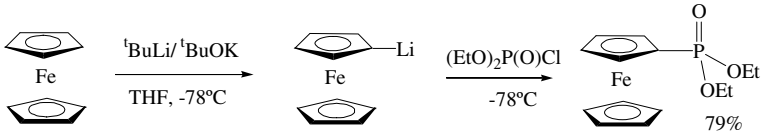
3.1. Synthesis

Diethyl ferrocenylphosphonate FcP(O)(OEt)$_2$ has been prepared in 33% yield by reaction of mono lithioferrocene with diethylchlorophosphate (EtO)$_2$P(O)Cl at 0 °C [25].

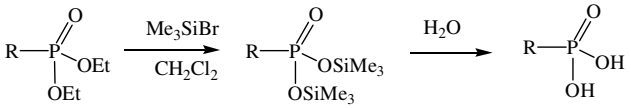
To improve the reactivity of the system, we used a "super base" as proposed by Sanders and Mueller-Westerhoff [28]. ^{t}BuOK activated, at low temperature, both ^{t}BuLi for the mono-lithiation of ferrocene and the lithiated ferrocene for the substitution of diethyl chlorophosphate. The addition of 0.26 equivalent of ^{t}BuOK and an excess of ferrocene and diethylchlorophosphate versus ^{t}BuLi gave diethyl ferrocenylphosphonate in 79% yield after purification by silica column chromatography (Scheme 2).

In the reaction of ferrocenylmethanol with sodium diethylphosphite, FcCH$_2$P(O)(OEt)OH was extracted from the aqueous phase according to Alley and Henderson [25], but in lower yield (13% instead of 65%). The low yield in FcCH$_2$P(O)(OEt)(OH) prompted us to look at the organic phase, from which diethyl ferrocenylmethylphosphonate FcCH$_2$P(O)(OEt)$_2$ was isolated in 56% yield.

Ferrocenylphosphonic acids were prepared by conversion of the corresponding esters under mild conditions using Me$_3$SiBr and water (Scheme 3) [29].



Scheme 2. Synthesis of diethyl ferrocenylphosphonate.



Scheme 3. Synthesis of ferrocenylphosphonic acid from its ester.

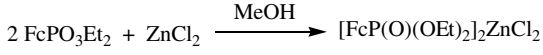
3.2. Complexation

The complexation property of the diethyl ferrocenylphosphonate has been studied by its reaction with zinc chloride. Addition of zinc chloride to diethyl ferrocenylphosphonate in methanol gave, after evaporation of the solvent, an orange brown solid (Scheme 4).

Suitable crystals for X-ray crystallography were grown by slow evaporation of a diethyl ether solution. The crystallographic data are given in Table 1.

A view of the molecule is presented in Fig. 1, with selected bond distances and angles listed in Table 2.

The crystal structure consists of discrete $ZnCl_2(O\text{-}P(OEt)_2Fc)_2$ complex units without any solvent molecule. Two chlorine atoms and two oxygen atoms from the phosphoryl groups define a distorted tetrahedral arrangement around the zinc centre. The Fe–C distances, which lie in the range 2.002(6)–2.071(6) Å (mean 2.038 Å), are similar to those of other ferrocene compounds.



Scheme 4. Complexation of zinc dichloride by diethyl ferrocenylphosphonate.

Table 1
Crystallographic data

Formula	$C_{28}H_{38}Cl_2Fe_2O_6P_2Zn$
Formula weight	780.46
Colour, habit	Orange brown plate
Crystal size (mm)	0.55×0.30×0.11
Temperature (K)	173
System	Monoclinic
Space Group	*C*2/*c*
a (Å)	22.935(4)
b (Å)	7.708(2)
c (Å)	18.920(4)
β (°)	104.73(2)
V (Å^3)	3235.0(14)
Z	4
λ (Å)	0.71069
μ (cm^{-1})	19.24
D (g cm^{-3})	1.603
T (K)	173
Total number of Reflections (1)	1909
Total number of Reflections $I>2\sigma(I)$(2)	1524
R_{F^2} (1)	0.0575
R_{F^2} (2)	0.0428
wR_{F^2} (1)	0.1161
wR_{F^2} (2)	0.1140
Residual density maximum/minimum	0.490/−0.870

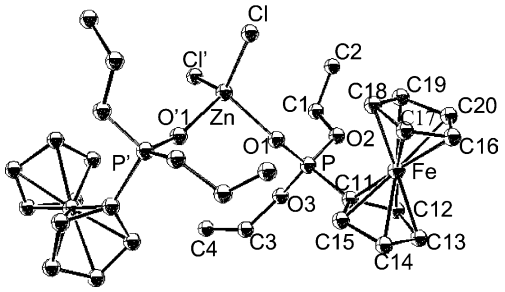


Fig. 1. Ortep view of the environment of Zn atom. The H atoms have been omitted for clarity.

The P–C (Cp) distance (1.770(6) Å) is comparable with those reported for $fc(P(O)Ph_2)_2$ and $fc(P(O)(^iPr)_2)_2$ (1.785–1.780 Å) [30]. The P–OZn distance (1.467 Å) is shorter than the P–OR distances (1.555–1.568 Å).

The complexation of metal by alkyl phosphonates has been reported to be equilibrated in solution [31]. The ^{31}P NMR chemical shift of diethyl ferrocenylphosphonate in deuterated methanol was 28.5 ppm while it was 29.2 ppm for the complex. Addition of 5 equivalents of $ZnCl_2$ to the phosphonate solution shifted the chemical shift to 29.9 ppm, indicating that an equilibrium really took place.

3.3. Electrochemistry

Cyclic voltammetry and potential square wave experiments were carried out in methanol containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte. Fig. 2 presents, as example, cyclic voltammograms (CV) of $FcP(O)(OEt)_2$ (1 mM) at a scan rate of 100 mV s^{-1}.

The separation of the anodic and cathodic potential is nearly constant at 67 mV as found for ferrocene under the same condition and the ratio I_{pa}/I_{pc} is almost unity. The peak currents vary linearly with $v^{1/2}$ indicating a diffusion-controlled process. These results are in good agreement with a reversible one-electron transfer reaction. The value of ΔE higher than 59 mV, also observed for ferrocene (FcH), is possibly due to uncompensated solution resistance between the working and reference electrodes. The half wave potentials of the different compounds prepared are displayed in Table 3, 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 ($\Delta E_{1/2}=261$ mV), consistent with the electron-withdrawing effect of the phosphonate substituent (entry1) [9,30]. This effect is enhanced by the presence of two phosphonate units (entry 11) and becomes twice as great as for the mono-substituted compound ($\Delta E_{1/2}=485$ mV). The presence of the methylene spacer between the cyclopentadienyl ring and the P atom shields and/or counter-balances this

Table 2
Selected bond lengths (Å) and angles (°) for complex $[FcP(O)(OEt)_2]_2 \cdot ZnCl_2$

Zn–Cl	2.223(2)	O(3)–C(3)	1.470(7)
Zn–O(1)	1.978(4)	C(1)–C(2)	1.432(10)
P–O(1)	1.467(4)	C(11)–C(12)	1.386(8)
P–O(2)	1.555(4)	C(11)–C(15)	1.435(8)
P–O(3)	1.568(4)	C(12)–C(13)	1.432(8)
P–C(11)	1.770(6)	C(13)–C(14)	1.407(9)
O(2)–C(1)	1.453(8)	C(16)–C(17)	1.389(9)
Cl–Zn–Cl′	123.26(10)	O(1)–P–O(2)	116.7(3)
O(1)–Zn–O(1′)	98.0(3)	O(1)–P–O(3)	111.4(3)
O(1)–Zn–Cl	106.52(13)	O(2)–P–O(3)	102.0(2)
O(1)–Zn–Cl′	109.81(14)	O(1)–P–C(11)	110.6(2)
P–O(1)–Zn	154.0(3)	O(2)–P–C(11)	104.8(2)
P–O(2)–C(1)	121.8(4)	O(3)–P–C(11)	111.0(3)
P–O(3)–C(3)	119.9(4)	P–C(11)–C(12)	130.1(4)
C(12)–C(11)–C(15)	108.2(5)	P–C(11)–C(15)	121.7(4)

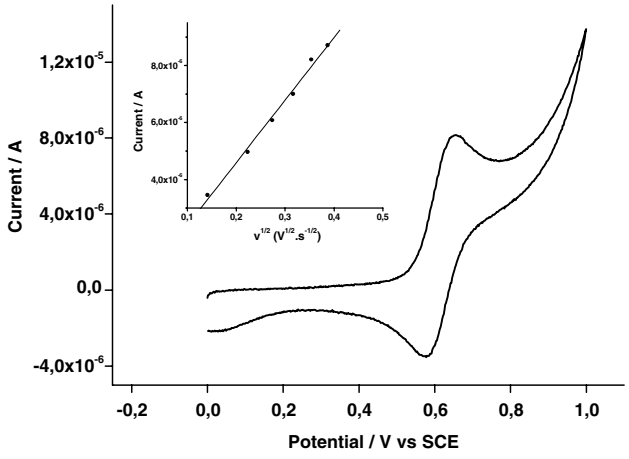


Fig. 2. Cyclic voltammogram of $FcP(O)(OEt)_2$ and $I=f(v^{1/2})$.

effect due to its electron donating effect ($\Delta E_{1/2}=24$ mV, entry 7). Note that the diphenyl ferrocenylphosphonate is slightly more difficult to oxidize ($\Delta E_{1/2}=57$ mV, entry 6).

The phosphonic acids are easier to oxidize than the esters. The variation of the half wave potential from diethyl ferrocenylphosphonate (entry 1) to ferrocenylphosphonic acid (entry 2) is +104 mV, and doubles on going from $fc(PO_3Et_2)_2$ to $fc(PO_3H_2)_2$ (180 mV). The methylene spacer renders this variation from the ethyl ester (entry 10) to acid (entry 11) less marked: 42 mV. The change of the first ethyl group (entries 7, 8) gives rise to a greater variation (32 mV) than the second (entry 9) (10 mV). It is noteworthy that this variation decreases with the length of the spacer even for phosphonates containing π conjugated ferrocenyl units

Table 3
Oxidation of ferrocenyl phosphorus derivatives by voltammetry, in methanol, 0.1 M Bu_4NPF_6, scan rate = 100 mV s^{-1}, Pt working electrode, SCE reference, 22 ± 2 °C

Entry	Compounds	E_{pa} (mV)/SCE	E_{pc} (mV)/SCE	ΔE[a] (mV)	$E_{1/2}$[b] (mV)/SCE	$\Delta E_{1/2}$[c] (mV)/FcH
0	FcH	390	316	74	353	0
1	$FcPO_3Et_2$	648	581	67	614	+261
2	$FcPO_3H_2$	548	471	77	510	+57
3	$FcPO_3H^-DCHAH^+$	380	312	68	344	−9
4	$FcPO_3H^-\ Na^+$	372	311	61	341	−12
5	$FcPO_3^{2-}2\ Na^+$	206	140	66	173	−180
6	$FcCH_2PO_3Ph_2$	441	379	62	410	+57
7	$FcCH_2PO_3Et_2$	408	346	62	377	+24
8	$FcCH_2PO_3EtH$	381	310	71	345	−8
9	$FcCH_2PO_3H_2$	367	303	64	335	−18
10	$fc[PO_3Et_2]_2$[d]				838	+485
11	$fc[PO_3H_2]_2$[d]				658	+305
12	$[FcPO_3Et_2]_2 \cdot ZnCl_2$[d]				603	+250

[a] $\Delta E = E_{pa} - E_{pc}$.
[b] $E_{1/2} = (1/2)(E_{pa} + E_{pc})$.
[c] $\Delta E_{1/2} = E_{1/2}/SCE - E_{1/2}(FcH^+/FcH)/$ SCE.
[d] Determined by PSWV.

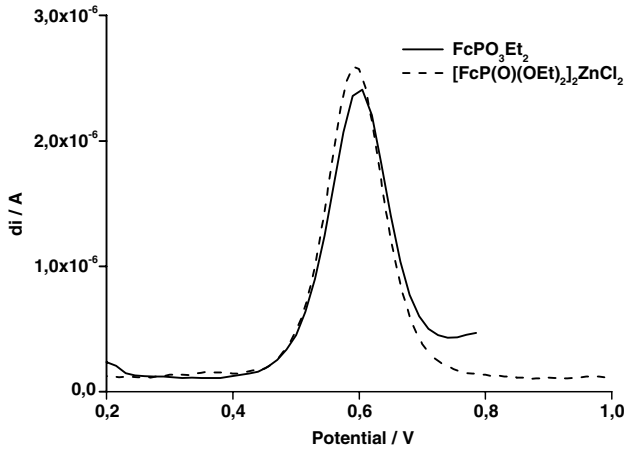


Fig. 3. PSWV curves of de $FcPO_3Et_2$ and of the zinc complex $[FcP(O)(OEt)_2]_2 \cdot ZnCl_2$.

[20], and does not exist for ferrocenyl carboxylate [32]. A huge effect is observed during the neutralisation of the ferrocenylphosphonic acid, the salts being easier to oxidize than ferrocene (entries 3–5). An identical variation of the half wave potential of −169 mV is observed for the conversion of the acid to the mono-salt and to the di-salt. The nature of the cation, sodium or cyclohexyl ammonium, has little effect on the half wave potential. The negatively charged phosphonate group is no longer an electro-withdrawing group and renders the ferrocenyl unit easier to oxidize than ferrocene. The differences of −169 and −337 mV between the half wave potentials of the ferrocenylphosphonic acid and of its mono and di-sodium salt show that the ferrocenylphosphonic acid can act as a redox-active pH responsive molecule. This aspect is currently under investigation.

The potential square wave voltammetry (PSWV) was used to determine the half wave potential of the complex $[FcP(O)(OEt)_2]_2 \cdot ZnCl_2$ (Fig. 3).

$\Delta E_{1/2}$ between diethyl ferrocenylphosphonate and the complex is only 11 mV, showing the small effect of the coordination of the phosphoryl group on the potential of the ferrocene/ferrocenium couple. However, we have seen, by ^{31}P NMR, that in solution the complex exists in equilibrium with the starting compounds. The presence of only one peak in the ^{31}P NMR spectrum and PSWV voltammogram indicates that the equilibrium is fast. Diethyl ferrocenylphosphonate does not appear to be efficient as an amperometric sensor of metal ions.

4. Conclusion

Ferrocenylphosphonic acid has been prepared in good yield employing a ^{t}BuLi/^{t}BuOK "super base" pair at low temperature. Its half wave potential shows that the phosphonate group acts as an electron-withdrawing group, which may be modulated by the nature of the substituents around the phosphorus centre. The presence of only one peak and the low variation of $E_{1/2}$ from diethyl ferrocenylphosphonate to the zinc complex show that this kind of complexation cannot be useful for electrochemically recognise metal ions. However, the large variation of the half wave potential of the ferrocenylphosphonic acid and its di-sodium salt indicates that it is a redox-active pH responsive molecule, which may be considered as a new potential electrochemical sensor.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 231570. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44 1223 336033, or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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