

# Electroactive poly zinc, cadmium, manganese ferrocenylphenylphosphinates

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Received 26 July 2004; accepted 20 September 2004

## Abstract

The synthesis of ferrocenylphenylphosphinic acid in high yield is reported. The electrochemical behaviour of ethyl ferrocenylphenylphosphinate, ferrocenylphenylphosphinic acid and its sodium salt are compared. The preparation and characterization of zinc, cadmium and manganese ferrocenylphenylphosphinates are reported. They are anhydrous and show a high thermal stability. The iso-structurality of these compounds is settled, and a structure involving double bridging phosphinate groups is proposed. Their half wave potentials, determined by cyclic voltammetry using a cavity micro electrode are similar to each other, and are close to that of the sodium salt of ferrocenylphenylphosphinic acid, and even to those of the related metal ferrocenylphosphonates  $M(II)(HO_3PFC)_2 \cdot xH_2O$ .

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**Keywords:** Ferrocenylphenylphosphinic acid; Poly metalphosphinate; Electrochemistry

## 1. Introduction

Polymeric metal phosphinates,  $[MO_2PRR']_n$ , among which the most studied are divalent metal phosphinates, form a unique class of inorganic polymers with fully inorganic one-dimensional framework [1].

The linear chain of structurally characterized polymeric metal(II) phosphinates consists of metal atoms linked either by alternating single and triple bridging phosphinate groups [2–4], or by double bridging phosphinate groups [5–8]. The two modes of bridging have also been found in related poly Zinc(II) (dialkyl)phosphates [9–12] (see Scheme 1).

The coordination number of the metal is usually four; however, it can reach six in the presence of coordinating substituents in the organic chain of the phosphonates

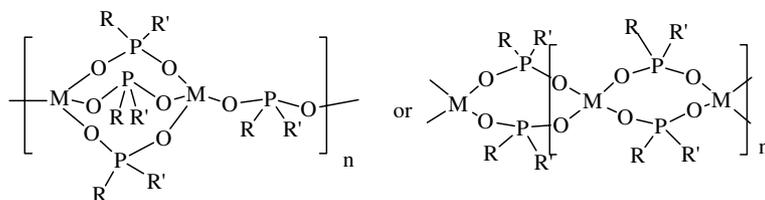
[13] or by coordination of solvent molecules [11,14]. The mode of coordination of the phosphinate groups involves always the coordination of one oxygen to one metal, even if the linkage of one oxygen to two metals, currently observed for metal phosphonates [15], has been postulated in some cases to explain the six-fold coordination of the metal [13,16].

Metal phosphinates are usually resistant to oxidation and hydrolysis, the phosphinate groups acting as solid bridging ligands. Their properties result from both the nature of the metal atom and the nature of the organic substituents on the phosphorus atom.

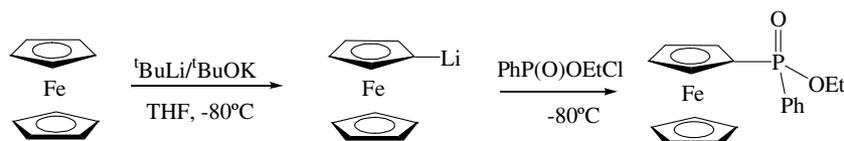
Moreover, ferrocene derivatives are of interest in many fields such as homogeneous catalysis, medicine due to their antitumour activity, materials due to their conducting, magnetic or non-linear optical properties, electrochemical sensors, luminescent devices, and polymers [17–28]. This is related to the specific geometries that the ferrocenyl moiety can enforce and its electronic (redox) properties. Their covalent attachment into

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Scheme 1. Modes of coordination of the bridging phosphinates.



Scheme 2. Synthesis of ethyl ferrocenylphenylphosphinate.

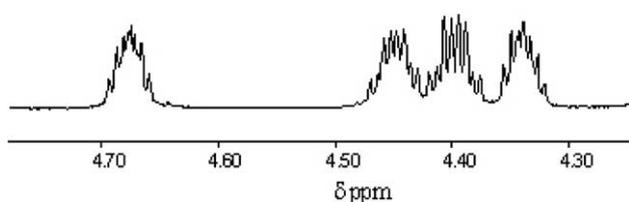
hybrid organic–inorganic materials, such as polymetalphosphinates is an important step in the development of molecular-level devices. We report here a simple and convenient method for the preparation of ferrocenylphenylphosphinic acid in high yield, and the characterization of the metal phosphinates obtained by its reaction with zinc, cadmium and manganese salts. The mode of coordination of the phosphinate group and the coordination number of the metal are discussed on the basis of the spectroscopic data.

## 2. Results and discussion

### 2.1. Synthesis and characterization of ferrocenylphenylphosphinic acid

Ethyl ferrocenylphenylphosphinate was prepared by reaction of monolithioferrocene with chloroethyl phenylphosphonate (Scheme 2), which was obtained by chlorination of ethyl phenylphosphinate  $\text{PhP(O)(OEt)H}$  prepared by ethanolsis of  $\text{PhPCl}_2$  [29]. The high yield, after purification by chromatography, (88%) results from the use of a “super base”  $^t\text{BuLi}/\text{BuOK}$  at  $-80^\circ\text{C}$  as we have reported for the preparation of ferrocenylphosphonic acid [30].

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of  $\text{FcPhP(O)(OEt)}$  showed the non-equivalence of the pairs of protons and carbons in the substituted cyclopentadienyl ring,

Fig. 1.  $^1\text{H}$  NMR spectrum of the protons of the substituted Cp ring.

as a consequence of the chiral nature of the phosphorus centre (Fig. 1) [31,32]. The diastereotopy introduced by a chiral substituent into the cyclopentadienyl ring is usually observed by  $^{13}\text{C}$  NMR, but rarely by  $^1\text{H}$  NMR. [33–35] The presence of a phosphorus centre seems to favour the distinction between the four protons of the cyclopentadienyl ring [35,36].

The assignment of the NMR chemical shifts of the substituted Cp ring (Table 1) was made considering that: (i) the P(V) is a withdrawing substituent, leading to a downfield shift for the 2 and 5 positions [37,38], (ii) the non-equivalence of the carbon atoms of the substituted Cp is a direct result of the asymmetric substituent, the greater separation of the  $^{13}\text{C}$  resonance having to be attributed to the  $\text{C}_2/\text{C}_5$  atoms [31], (iii)  $^2J_{\text{CP}} < ^3J_{\text{CP}}$  [39]. It has not yet been possible to ascertain the assignment of  $\text{C}_2$  and  $\text{C}_5$  and of  $\text{C}_3$  and  $\text{C}_4$  atoms.

Ferrocenylphenylphosphinic acid was prepared in 92% yield by conversion of the ester under mild conditions using  $\text{Me}_3\text{SiBr}$  followed by hydrolysis [40].

The ferrocenyl compounds were characterized by cyclic voltammetry using 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  $n\text{Bu}_4\text{NPF}_6$  (0.1 M in methanol). The concentration of the electro-active species was 0.001 M (see Table 2).

As referred to the ferrocene, the electron-withdrawing effect of the phosphinate substituents leads to an increase of the half wave potential of the ferrocene/ferrocenium couple. The transformation of the ester into the acid leads to a 65 mV decrease of the half wave potential. It is noteworthy that a greater effect has been observed for ferrocenylphosphonates [30], whereas it does not exist for carboxylate derivatives [41]. The neutralisation of the acid leads to a decrease of 162 mV of the half wave potential. Again, this effect is more pronounced in the case of ferrocenylphosphonic acid [30].

Table 1  
 $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shift of ethyl ferrocenylphenylphosphinate

	$\delta$ (ppm)	$^1\text{H}$ NMR	$^{13}\text{C}$ NMR ( $J_{\text{CP}}$ Hz)
	H-C (2/5)	4.69/4.44	72.27 (11.6)/71.52 (11.1)
	H-C (3/4)	4.40/4.35	71.71 (21.6)/71.99(16.9)
	H-C (6)	4.21	70.15
	H-C (7)	3.98	61.16 (5.5)
	H-C (8)	1.36	16.98 (6.5)
	H-C (10, 14)	7.89	131.84 (9.8)
	H-C (11, 13)	7.53	128.77 (12.6)
	H-C (12)	7.53	132.28 (2.4)
	C (1)		71.46(178)
	C (9)		133 (131)

Table 2  
 Electrochemical data of diethyl ferrocenylphenylphosphinate, ferrocenylphenylphosphinic acid, and its sodium salt in methanol (scan rate: 100  $\text{mV s}^{-1}$ )

Compounds	$E$ oxidation (mV)/SCE	$E$ reduction (mV)/SCE	$\Delta E$ (mV)	$E_{1/2}$ (mV)/SCE	$\Delta E_1/2$ (mV)/FcH
FcH	390	316	74	353	0
FcPhPO <sub>2</sub> Et	644	565	79	604	251
FcPhPO <sub>2</sub> H	577	499	78	538	186
FcPhPO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>	406	347	59	377	24

## 2.2. Metal ferrocenylphenylphosphinates

### 2.2.1. Syntheses of metal ferrocenylphenylphosphinates

Due to the low solubility of ferrocenylphenylphosphinic acid in acidic water, the reactions were made at  $\text{pH} > 8$ . Metal ferrocenylphenylphosphinates were obtained by addition of metal nitrates to phosphinic acid in water. The compositions of the powders obtained corresponded to  $\text{M}(\text{O}_2\text{PPhFc})_2$ .

### 2.2.2. IR spectroscopy of metal ferrocenylphenylphosphinates

The IR spectra of the three metalferrocenylphenylphosphonates are similar. The IR spectrum of  $\text{Mn}(\text{O}_2\text{PPhFc})_2$  is reported in Fig. 2. No bands related

to water are present. The CH vibrations appear at 3100, 3080, 3050  $\text{cm}^{-1}$  and the two mains bands at 1164 and 1074  $\text{cm}^{-1}$ , 1159 and 1066  $\text{cm}^{-1}$ , 1157 and 1070  $\text{cm}^{-1}$  are related to the symmetric and anti symmetric  $\text{PO}_2$  absorption of Zn, Cd and Mn compounds, respectively. The presence of only two bands indicates that the phosphinates are of symmetric coordination mode, i.e., the oxygen atoms are linked to the same number of metal atoms [16].

### 2.2.3. MAS NMR spectroscopy of metal ferrocenylphenylphosphinates

The  $^{31}\text{P}$  MAS NMR spectra of the diamagnetic compounds ( $\text{M}=\text{Zn}$ , spinning rate, s.r., 10 kHz, scan number, s.n., 360;  $\text{M}=\text{Cd}$ , s.r. 10 kHz, n.s. 480) show

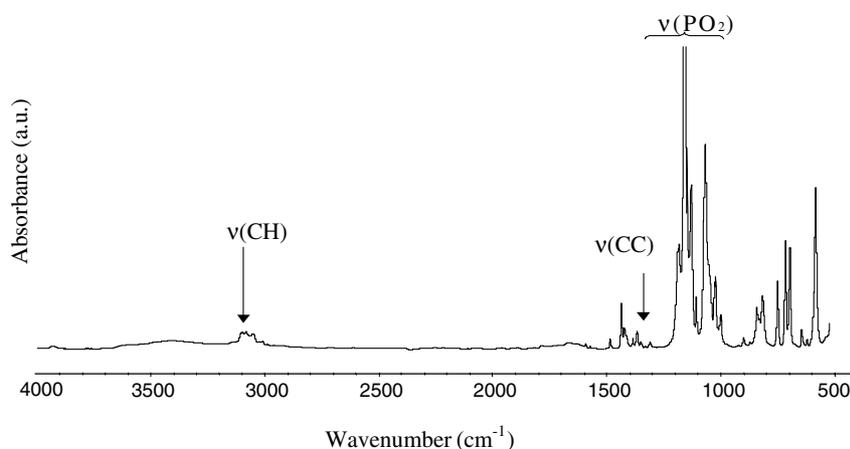


Fig. 2. IR spectrum of  $\text{Mn}(\text{O}_2\text{PPhFc})_2$ .

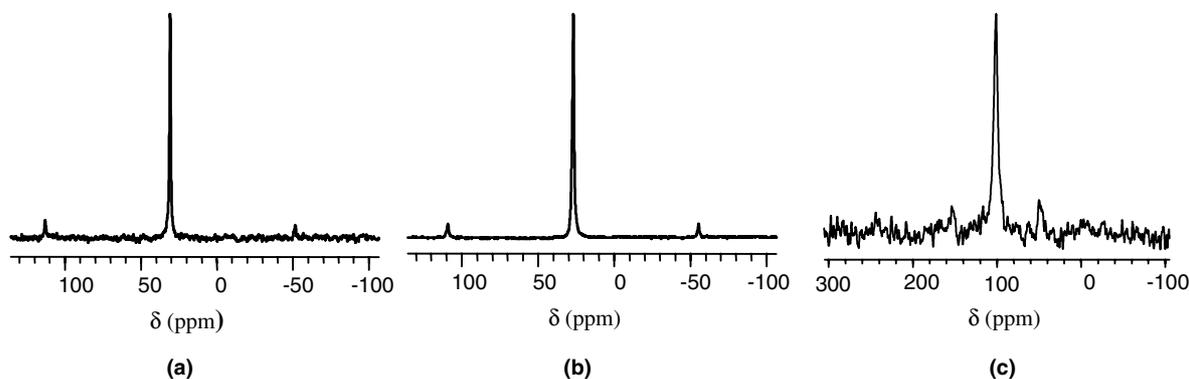


Fig. 3.  $^{31}\text{P}$  MAS NMR of: (a)  $\text{Zn}(\text{O}_2\text{PPhFc})_2$ ; (b)  $\text{Cd}(\text{O}_2\text{PPhFc})_2$ ; (c)  $^{113}\text{Cd}$  MAS NMR of  $\text{Cd}(\text{O}_2\text{PPhFc})_2$  (chemical shift vs.  $\text{Cd}(\text{ClO}_4)_2$  1 M).

one peak (Fig. 3(a) and (b)).  $^{31}\text{P}$  chemical shifts have been correlated with P–O bond lengths and P–O–P bond angles [42,43]. The presence of only one  $^{31}\text{P}$  chemical shift for our compounds indicates that the backbone structure involving mono and triple bridging phosphinates can be ruled out. Indeed, for Zinc butylphenylphosphinate, dibutylphosphinate and related di-ter-butylphosphates, in which the chain consists of single and triple bridging phosphinates, the P–O bond lengths and P–O–P bond angles differ for the mono and triple bridging phosphinates. Therefore, a minimum of two peaks can be expected for a such structure.

The solid state  $^{113}\text{Cd}$  MAS NMR spectrum of  $\text{Cd}(\text{O}_2\text{PPhFc})_2$  (s.r. 4.5 kHz, n.s. 27448) shows the presence of one resonance at 100.8 ppm (Fig. 3(c)).

The  $^{113}\text{Cd}$  chemical shift is very sensitive to the nature of the substituents around the Cd centre and also on its coordination mode, although the isotropic shifts of the oxo-Cd compounds are not sufficiently discriminating to allow structure-chemical shift correlation since the coordination polyhedra around the Cd atom can be very irregular [44]. Nevertheless, a general pattern between  $^{113}\text{Cd}$  chemical shifts and coordination number for oxo-Cd compounds is 50 to 0 ppm for 6-coordinate Cd, 30 to –50 for 7-coordinate Cd [45,46]. A chemical shift of 5-coordinated Cd has been reported at 90.6 ppm (220.2 ppm/ $(\text{CdNO}_3)_2$ ) for cadmium phosphonocarboxylate  $\text{Cd}_2(\text{OH})(\text{O}_3\text{PC}_2\text{H}_4\text{CO}_2)$  [47]. Chemical shifts from 114 to 108 ppm have been found for 4-coordinated Cd in heterometallic isopropoxides  $\text{Cd}(\text{O}^i\text{Pr})_3$ ,  $\text{Ba}(\text{M}_2(\text{O}^i\text{Pr})_9)_2$  ( $\text{M}=\text{Ti}, \text{Zr}, \text{Hf}$ ) [48,49]. The peak observed at 100.8 ppm corresponds to a  $\text{CdO}_4$  site, the same coordination number of cadmium has been found in related cadmium dialkylthiophosphates  $\text{Cd}(\text{S}_2\text{P}(\text{OR})_2)_2$  for both polynuclear and binuclear cadmium compounds [50,51]. A 5-coordinate Cd can be ruled out because it implies the coordination of one oxygen to two Cd atoms, which would give three bands for the stretching of the non-symmetric  $\text{PO}_2$  groups.

#### 2.2.4. X-ray powder patterns of metal phosphinates

No single crystals for structural characterization were obtained. Fig. 4 shows the X-ray powder diffractograms of the compounds.

The positions of the peaks are quite similar for the three compounds. The distance and relative intensity are reported in Table 3.

The similarities in compositions, in X-ray patterns, in IR spectra, as well as in  $^{31}\text{P}$  NMR spectra allow us to assume the iso-structurality of the three phosphinates. The iso-structurality implies the same coordination number for the metals and the same coordination mode for the bridging phosphinate groups. The coordination number of the metals has been determined by  $^{113}\text{Cd}$  NMR to be four. Such coordination is also reported for zinc phosphinates and is in agreement with the symmetry of the  $\text{PO}_2$  groups determined by IR spectroscopy [2,3,7,52–56]. The unique peak observed by  $^{31}\text{P}$  MAS NMR agrees with the two crystallographically equivalent phosphinate bridges, as already reported for  $[\text{Pb}(\text{O}_2\text{PPh}_2)_2]_n$  [6],  $[\text{Zn}(\text{O}_2\text{PHC}_6\text{H}_5)_2]_n$  [7],  $[\text{Zn}(\text{O}_2\text{P}(\text{O}-$

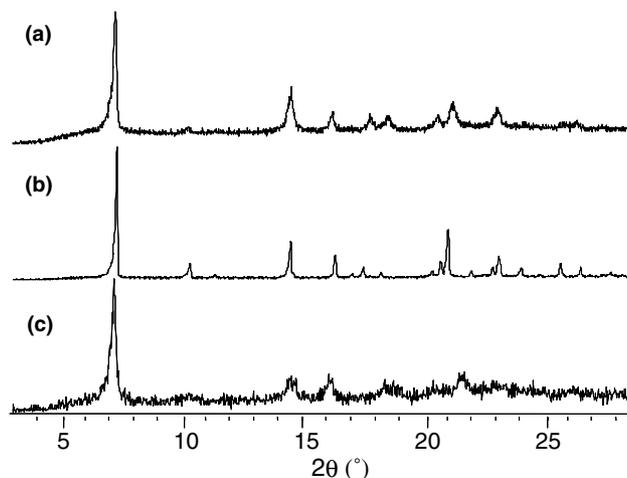


Fig. 4. X-ray diffraction of  $\text{M}(\text{O}_2\text{PPhFc})_2$ : (a)  $\text{M}=\text{Mn}$ ; (b)  $\text{M}=\text{Cd}$ ; (c)  $\text{M}=\text{Zn}$ .

Table 3  
X-ray powder patterns of  $M(O_2PR_2)_2$

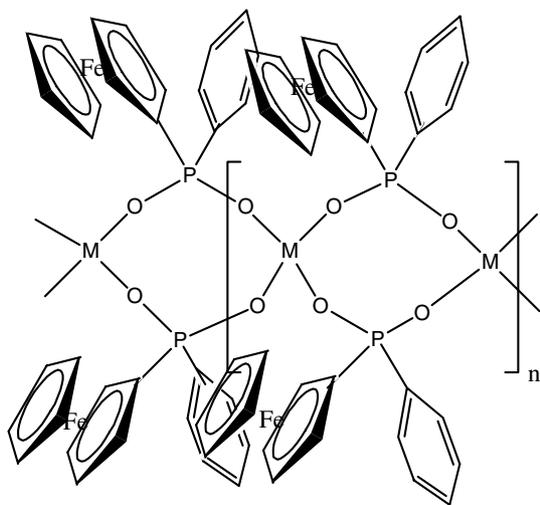
$Mn(O_2PPhFc)_2$	$Zn(O_2PPhFc)_2$	$Cd(O_2PPhFc)_2$
$d$ (Å) (I%)	$d$ (Å) (I%)	$d$ (Å) (I%)
12.15 (100)	12.24 (100)	12.08 (100)
8.62 (4.3)	8.65 (4.0)	8.55 (11.6)
6.08 (36.5)	6.13 (14.4)	6.10 (29.8)
5.45 (16.6)	5.49 (16.8)	5.41 (16.6)
4.78 (10.6)	4.75 (7.9)	4.85 (4.1)
4.18 (20.8)	4.10 (12.3)	4.22 (39)
		3.84 (17.3)

$Me)_2)_n$  [10],  $[Zn(O_2P(OEt)_2)_2]_n$  [9], and  $[Zn(O_2PFcOH)_2 \cdot 2H_2O]_n$  [57].

A structure with tetracoordinated metals and double bridged phosphinate groups can be proposed for the metal ferrocenylphenylphosphinates (Scheme 3). The proposed structure is similar to the structure of  $Zn(HO_3Pfc)_2 \cdot 2H_2O$  [57]

#### 2.2.5. Thermal stability of metalphosphinates

The thermal stability of metal ferrocenylphenylphosphinates has been determined by TGA (Fig. 5). As expected no weight loss corresponding to the loss of water can be observed. Furthermore, the products are stable until 355 °C for cadmium phosphinate, 400 °C for zinc phosphinate, and 445 °C for manganese phosphinate. The weight losses occur in three steps, the second one starting between 450 and 500 °C. This behaviour is in contrast with the ones reported for  $Zn(O_2PPh_2)_2$ ,  $Zn(O_2PMePh)_2$ ,  $Zn(O_2PMe_2)_2$  and  $Zn(O_2P(O^tBu)_2)_2$  for which a substantial weight loss occurs in only one step [12,54,55]. The proposed mode of decomposition of  $Zn(O_2PPh_2)_2$  at 500 °C involves the



Scheme 3. Proposed structure of Zinc, Cadmium and Manganese ferrocenylphenylphosphinates.

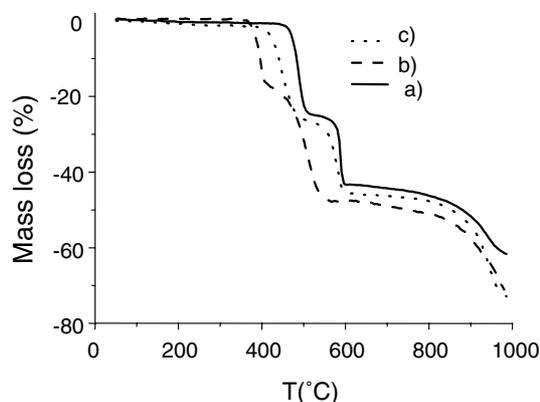


Fig. 5. TGA of  $M(O_2PPhFc)_2$  under Argon,  $5\text{ °C min}^{-1}$ : (a)  $M=Mn$ ; (b)  $Cd$ ; (c)  $M=Zn$ .

initial formation of benzene taking place without rupture of the polymer backbone [55]. For the metal ferrocenylphenylphosphinates, the escape of one equivalent of benzene would lead to weight losses of 10.9%, 10.2% and 11.1% for  $Zn(O_2PPhFc)_2$ ,  $Cd(O_2PPhFc)_2$  and  $Mn(O_2PPhFc)_2$ , respectively. However, the first weight losses are in agreement with the escape of one equivalent of ferrocene 25.1% (calc. 25.9%) for  $Zn(O_2PPhFc)_2$ , 18.6% (calc. 24.4%) for  $Cd(O_2PPhFc)_2$ , and 24.4% (calc. 26.3%) for  $Mn(O_2PPhFc)_2$ . The second weight losses, which are of the same order of magnitude, would result from the escape of the second equivalent of ferrocene.

The thermal stability of metal phosphinates depends on the substituents on the phosphorus atom: a sharp weight loss occurs at 134 °C for  $Zn(O_2P^tBuO)_2$  [12], 550 °C for  $Zn(O_2PPh_2)_2$ , 460 °C for  $Zn(O_2PMe_2)_2$ , 420 °C for  $Zn(O_2PMePh)_2$  [54], whereas, for  $Zn(O_2PFcPh)_2$  a three steps process begins at 400 °C. The thermal stability depends also on the nature of the metal, the order of stability found for metal ferrocenylphenylphosphinates being:  $Mn > Zn > Cd$ .

#### 2.2.6. Electrochemistry of poly metalphosphinates

Cyclic voltammetry experiments were performed in a three electrode cell, in which the working electrode was a cavity microelectrode furnished by the “réseau micro electrode à cavité du CNRS” (France), the counter electrode was a platinum wire, and the reference electrode was a saturated calomel electrode (SCE). The electrolyte was KCl 1 M in water. The cavity microelectrode has been developed to study the electrochemical properties of powdered materials [58]. The low reaction volume ( $10^{-8}\text{ cm}^3$ ) minimizes the distortions due to the large ohmic drop and capacitive current encountered with the composite electrode device [59–62].

Fig. 6 shows the cyclic voltammograms of the three compounds. Their half wave potentials are very close to each other: 261, 255 and 265 mV for  $Zn(O_2PPhFc)_2$ ,

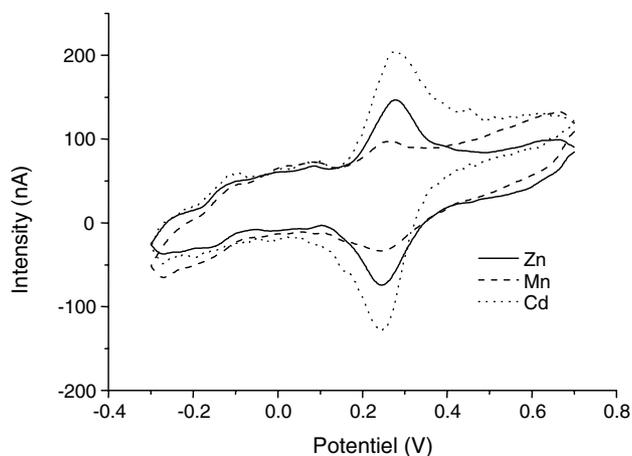


Fig. 6. Cyclic voltammograms of  $M(O_2PPhFc)_2$ ,  $M=Zn$ ,  $Cd$ ,  $Mn$ .

$Cd(O_2PPhFc)_2$  and  $Mn(O_2PPhFc)_2$ , respectively. The value is also close to the one of the sodium salt of the ferrocenylphenylphosphinic acid  $FcPhP(O)O^-Na^+$  (251 mV) measured in water.

The half wave potential of the metal ferrocenylphenylphosphinates are almost insensitive to the nature of the metal.

Unexpectedly, the half wave potential of metal ferrocenylphosphonates  $M(O_2PFCOH) \cdot xH_2O$  containing an unreacted OH group on the phosphorus are also very close: 255 mV for  $Zn(HO_3PFC)_2 \cdot 2H_2O$ , 238 mV for  $Cd(HO_3PFC)_2 \cdot 3.5H_2O$ , and 243 mV for  $Mn(HO_3PFC)_2 \cdot 3H_2O$  and 246 mV for  $Na(HO_3PFC)$  [63]. The substitution of the phenyl group by an OH group has very little effect on the half wave potential of the ferrocene/ferrocenium couple. The influence of the nature of the second substituent on the redox behaviour of  $Fe^{II}/Fe^{III}$  couple is currently under investigation.

### 3. Conclusion

Electroactive polymetal phosphinates have been prepared starting from ferrocenylphenylphosphinic acid synthesized in high yield. The zinc, cadmium and manganese derivatives are iso-structural based on the composition, and on IR and NMR spectroscopy, and on the X-ray powder diffractogramme. The structure proposed involves tetracoordinated metals double bridged by the phosphinate groups. The metal ferrocenylphenylphosphinates possess a great stability in spite of the presence of the ferrocenyl moiety. The half wave potential of the ferrocene/ferrocenium couple remains the same whatever the metal. Thus, ferrocenylphenylphosphinic acid cannot be used to detect metal salts electrochemically.

## 4. Experimental

### 4.1. Solvents and reagents

Ferrocene (Aldrich) was sublimed before use.  $tBuLi$  (Acrōs) 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  $P_2O_5$ .  $tBuOK$  (Avocado), dichlorophenylphosphine (Avocado) were used as received.

### 4.2. Syntheses

#### 4.2.1. Ethyl chlorophenylphosphonate

In a two necked flask was added drop-wise 20 mL (0.147 mol) of dichlorophenylphosphine to 45 mL (0.76 mol) of ethanol at 0 °C under stirring which was maintained over night. The solvent was eliminated in vacuum and the product was distilled

(b.p. 110 °C/3 mm Hg) leading to 22.49 g (0.132 mol, 90% yield) of ethyl phenylphosphonate  $PhP(O)(OEt)H$ .  $^1H$  NMR ( $CDCl_3$ ,  $\delta$  ppm): 7.62 (m, 2H); 7.37 (m, 3H), 7.5 (d, 1H,  $^1J_{PH} = 573$  Hz); 4.07 (m, 2H); 1.37 (t, 3H).  $^{31}P$  NMR ( $CDCl_3$ ,  $\delta$  ppm): 27.42.

22.49 g (0.132 mol) of ethyl phenylphosphonate were dissolved in 150 mL of  $CCl_4$  and frozen to 0 °C.  $Cl_2$  gas was bubbled through the solution until it became green. The excess of chlorine was eliminated by bubbling nitrogen through the solution. The solvent was evaporated under vacuum and the product distilled (b.p. 90 °C/3 mm Hg) giving 16.06 g (0.0785 mol, 59% yield) of ethyl chlorophenylphosphonate.  $^1H$  NMR ( $CDCl_3$ ,  $\delta$  ppm): 7.77 (m, 2H), 7.38 (m, 3H); 4.27 (m, 2H); 1.30 (t, 3H).

#### 4.2.2. Ethyl ferrocenylphenylphosphinate

In a Schlenk tube was added drop-wise, at  $-78$  °C, 14 mmol of  $tBuLi$  in pentane to a solution of 19.6 mmol (3.63 g) of ferrocene and 3.5 mmol (0.39 g) of  $tBuOK$  in 80 mL of THF under stirring. After stirring for 30 min, 19.6 mmol (4 g) of ethyl chlorophenylphosphonate in 10 mL of THF were added drop-wise. The mixture was left to return to room temperature and 10 mL of a 1 M NaOH solution were added. The mixture was extracted with  $3 \times 30$  mL of  $CH_2Cl_2$ . The organic phase was dried over  $MgSO_4$ , filtered, and the solvent evaporated in vacuum. The compound was then purified by silica column chromatography using  $CH_2Cl_2$  to eliminate the excess of ferrocene, and then  $CH_2Cl_2/THF$  (70/30). After evaporation of the solvent under vacuum, 12.3 mmol (4.36 g) of ethyl ferrocenylphenylphosphinate were obtained as a brown solid (88% yield).  $^1H$  NMR ( $CDCl_3$ ,  $\delta$  ppm): 1.36 (t, 3H,  $H_8$ ,  $^3J_{HH} = 7.1$  Hz); 3.98 (m, 2H,  $H_7$ ); 4.21 (s, 5H,  $H_6$ ); 4.35 (m, 1H,  $H_3$ ); 4.40 (m, 1H,  $H_4$ ); 4.44 (m, 1H,  $H_5$ ); 4.69 (m, 1H,  $H_2$ ); 7.53

(m, 3H, H<sub>11</sub>, H<sub>12</sub>, H<sub>13</sub>); 7.89 (m, 2H, H<sub>10</sub>, H<sub>14</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ ppm): 16.98 (d, C<sub>8</sub>, <sup>3</sup>J<sub>CP</sub> = 6.5 Hz); 61.16 (d, C<sub>7</sub>, <sup>2</sup>J<sub>CP</sub> = 5.5 Hz); 70.15 (s, C<sub>6</sub>); 71.46 (d, C<sub>1</sub>, <sup>1</sup>J<sub>CP</sub> = 178.1 Hz); 71.52 (d, C<sub>5</sub>, <sup>2</sup>J<sub>CP</sub> = 11.1 Hz); 71.71 (d, C<sub>3</sub>, <sup>3</sup>J<sub>CP</sub> = 21.6 Hz); 71.99 (d, C<sub>4</sub>, <sup>3</sup>J<sub>CP</sub> = 16.9 Hz); 72.27 (d, C<sub>2</sub>, <sup>2</sup>J<sub>CP</sub> = 11.6 Hz); 128.76 (d, C<sub>11</sub>, C<sub>13</sub>, <sup>2</sup>J<sub>CP</sub> = 12.6 Hz); 131.84 (d, C<sub>10</sub>, C<sub>14</sub>, <sup>3</sup>J<sub>CP</sub> = 9.9 Hz); 132.3 (d, C<sub>12</sub>, <sup>4</sup>J<sub>CP</sub> = 2.4 Hz); 133 (d, C<sub>9</sub>, <sup>1</sup>J<sub>CP</sub> = 131 Hz); <sup>31</sup>P (CDCl<sub>3</sub>, δ ppm): 37.7. IR (KBr) ν (P=O): 1208 cm<sup>-1</sup>. Anal. calc. for C<sub>18</sub>H<sub>19</sub>FePO<sub>2</sub>: C, 61.01; H, 5.37; P, 8.76; Fe, 15.76. Found: C, 61.10; H, 5.61; P, 8.66; Fe, 15.00%.

#### 4.2.3. Ferrocenylphenylphosphinic acid

1.35 g (3.8 mmol) of ethyl ferrocenylphenylphosphinate were dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> in a Schlenk tube. 1 mL (7.6 mmol) of Me<sub>3</sub>SiBr was added drop-wise, the solution was stirred overnight, and 10 mL of water were added leading to the precipitate, which is filtered and washed with CH<sub>2</sub>Cl<sub>2</sub> and Et<sub>2</sub>O. 1.14 g (3.5 mmol) of ferrocenylphenylphosphinic acid was obtained (92% yield). <sup>1</sup>H NMR (CD<sub>3</sub>OD, δ ppm): 4.28 (m, 4H); 4.51 (s, 5H); 7.54 (m, 3H), 7.83 (m, 2H); <sup>13</sup>C NMR (CD<sub>3</sub>OD, δ ppm): 69.8 (s, C<sub>6</sub>); 71.53 (d, C<sub>3</sub>, C<sub>4</sub>, <sup>3</sup>J<sub>CP</sub> = 14.6 Hz); 71.65 (d, C<sub>2</sub>, C<sub>5</sub>, <sup>2</sup>J<sub>CP</sub> = 11.6 Hz); 128.53 (d, C<sub>11</sub>, C<sub>13</sub>, <sup>2</sup>J<sub>CP</sub> = 13.1 Hz); 130.83 (d, C<sub>10</sub>, C<sub>14</sub>, <sup>3</sup>J<sub>CP</sub> = 10.1 Hz); 132.00 (d, C<sub>12</sub>); 134.9 (d, C<sub>9</sub>, <sup>1</sup>J<sub>CP</sub> = 138 Hz); <sup>31</sup>P NMR (CD<sub>3</sub>OD, δ ppm): 35.4. IR (KBr) ν(P=O): 1224 cm<sup>-1</sup>. Anal. Calc. for C<sub>16</sub>H<sub>15</sub>FePO<sub>2</sub>: C, 58.89; H, 4.61; P, 9.51, Fe, 17.11. Found: C, 58.46; H, 4.50; P, 8.96, Fe, 16.69%.

#### 4.2.4. Zinc ferrocenylphenylphosphinate: Zn(O<sub>2</sub>PPhFc)<sub>2</sub>

To 0.1 g (0.31 mmol) of ferrocenylphenylphosphinic acid dissolved in 35 mL of EtOH was added 0.12 g (0.41 mmol) of zinc nitrate hexahydrate. After 6 days, the precipitate was filtered, washed with methanol and ether and dried under vacuum. 0.073 g (0.11 mmol) of a fibrous yellow solid was obtained (73% yield based on the acid). Anal. Calc. for C<sub>32</sub>H<sub>28</sub>Fe<sub>2</sub>P<sub>2</sub>ZnO<sub>4</sub>: C, 53.67; H, 3.91; Fe, 15.60; P, 8.67; Zn, 9.14. Found: C, 53.79; H, 4.03; Fe, 15.28; P, 8.61; Zn, 8.91%. <sup>31</sup>P MAS NMR: 26.8 ppm.

#### 4.2.5. Cadmium ferrocenylphenylphosphinate, Cd(O<sub>2</sub>-PPhFc)<sub>2</sub>

0.1 g (0.31 mmol) of ferrocenylphenylphosphinic acid was dissolved in 27 mL of water. The pH of the solution was adjusted to 8 by addition of NaOH (1 M). 0.096 g (0.31 mmol) of cadmium nitrate tetrahydrate was added and the solution was left for 6 days at room temperature. The precipitate was filtered washed with methanol and ether and dried under vacuum. Yellow needles were obtained (0.55 g, 0.07 mmol, 45% yield). Anal. Calc. for C<sub>32</sub>H<sub>28</sub>Fe<sub>2</sub>P<sub>2</sub>CdO<sub>4</sub>: C, 50.36; H, 3.67; Fe, 14.64; P, 8.13;

Cd, 14.74. Found: C, 50.22; H, 3.68; Fe, 14.40; P, 8.12; Cd, 14.46%. <sup>31</sup>P MAS NMR: 30.6 ppm. <sup>113</sup>Cd MAS NMR 100.8 ppm vs. Cd(ClO<sub>4</sub>)<sub>2</sub> 1 M.

#### 4.2.6. Manganese ferrocenylphenylphosphinate, Mn(O<sub>2</sub>-PPhFc)<sub>2</sub>

The pH of a solution of 0.1 g (0.31 mmol) of ferrocenylphenylphosphinic acid in 30 mL of water was adjusted to 9.4 by addition of NaOH (1 M). 0.069 g (0.28 mmol) of manganese nitrate tetra hydrate was added and the solution was left for 6 days at room temperature. The yellow solid was filtered, washed with CH<sub>3</sub>OH and Et<sub>2</sub>O and dried under vacuum, yielding 0.088 g (0.13 mmol, 84% yield) of yellow powder. Anal. Calc. for C<sub>32</sub>H<sub>28</sub>Fe<sub>2</sub>P<sub>2</sub>MnO<sub>4</sub>: C, 54.47; H, 3.97; Fe, 15.83; P, 8.79; Mn, 7.79. Found: C, 54.53; H, 3.60; Fe, 15.73; P, 8.31; Mn, 7.72%.

#### 4.3. Physical measurements

The NMR spectra of solutions were performed on a Bruker Avance DPX 200, chemical shifts for <sup>1</sup>H and <sup>13</sup>C-<sup>1</sup>H are referenced to SiMe<sub>4</sub> and deuterated solvent and for <sup>31</sup>P to H<sub>3</sub>PO<sub>4</sub> (85%) and deuterated solvent. <sup>31</sup>P MAS <sup>1</sup>H decoupled NMR spectra were recorded on a Bruker DPX 300 operating at 121.5 MHz, chemical shifts are referenced to H<sub>3</sub>PO<sub>4</sub> (85%), the magic angle spinning rates was 10kHz, and the scan numbers were between 360 and 600 with a pulse angle of π/2. <sup>113</sup>Cd MAS <sup>1</sup>H decoupled spectra were recorded on a Bruker AM 400 operating at 88.75 MHz, chemical shifts were referenced to Cd(ClO<sub>4</sub>)<sub>2</sub> 1 M, the spinning rate was 4.5 kHz, the scan number was 27448, with a pulse angle of π/6. Samples (60–80 mg) of the metal ferrocenylphenylphosphinates were placed in a zirconium dioxide rotor 4 mm in diameter. The width of a reference line for crystalline adamantane was used to check the uniformity of the magnetic field. Infrared spectra were taken on a Thermo Nicolet Avatar 320 FT-IR spectrophotometer as KBr pellets. Cyclic 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 of soluble compounds. The electrolyte was *n*Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M in methanol). For the insoluble metal ferrocenylphenylphosphinates, a cavity microelectrode of Pt, furnished by the "réseau microélectrode à cavité du CNRS" France, was used as working electrode. The electrolyte was KCl (1 M in water). The scan rate was 100 mV s<sup>-1</sup>. TGA were recorded on a Netzsch 409 thermobalance. X-ray powder diffraction was performed on an X Pert Philips diffractometer. Elemental analyses were performed by the CNRS "Service central d'analyse" in Vernaison France.

## Acknowledgement

Financial support from the Centre National de la Recherche Scientifique, CNRS, and from the French Minister of Research is gratefully acknowledged.

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