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Synthesis and characterisation of ferrocenyl-phosphonic and -arsonic acids

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Synopsis and graphical abstract

A series of ferrocene-derived phosphonic acids $\text{Fc}(\text{CH}_2)_n\text{P}(\text{O})(\text{OH})_2$ ($n = 0, 1, 2$), bis(phosphonic acids) $1,1'\text{-Fc}'[(\text{CH}_2)_n\text{P}(\text{O})(\text{OH})_2]_2$ [$\text{Fc} = \text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)$; $\text{Fc}' = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2$; $n = 0,1$] and the arsonic acid $\text{FcCH}_2\text{CH}_2\text{As}(\text{O})(\text{OH})_2$ have been synthesized; X-ray crystal structures of $\text{FcCH}_2\text{P}(\text{O})(\text{OH})_2$ and $\text{FcCH}_2\text{CH}_2\text{P}(\text{O})(\text{OH})_2$ are

reported, together with a study of their fragmentation pathways by negative-ion electrospray mass spectrometry.

Abstract

The ferrocene-derived acids $\text{FcCH}_2\text{CH}_2\text{E}(\text{O})(\text{OH})_2$ [**4**, E = P; **10**, E = As; Fc = $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4)$] have been synthesized by reaction of $\text{FcCH}_2\text{CH}_2\text{Br}$ with either $\text{P}(\text{OEt})_3$ followed by hydrolysis, or with sodium arsenite followed by acidification. Reaction of FcCH_2OH with $(\text{EtO})_2\text{P}(\text{O})\text{Na}$ gave $\text{FcP}(\text{O})(\text{OEt})(\text{OH})$, which was converted to $\text{FcCH}_2\text{P}(\text{O})(\text{OH})_2$ **3** by silyl ester hydrolysis using $\text{Me}_3\text{SiBr}/\text{Et}_3\text{N}$ followed by aqueous workup. Similarly, the known phosphonic acid $\text{FcP}(\text{O})(\text{OH})_2$ and the new derivatives $1,1'\text{-Fc}'[\text{P}(\text{O})(\text{OH})_2]_2$ [$\text{Fc}' = \text{Fe}(\eta^5\text{-C}_5\text{H}_4)_2$] and $1,1'\text{-Fc}'[\text{CH}_2\text{P}(\text{O})(\text{OH})_2]_2$ **7** have been synthesized *via* their corresponding esters. X-ray crystal structure determinations have been carried out on **3** and **7**, and the hydrogen-bonding networks discussed. Electrospray mass spectrometry has been employed in the characterization of the various acids. Phosphonic acids give the expected $[\text{M} - \text{H}]^-$ ions and their fragmentation at elevated cone voltages has been found to be dependent on the acid. $\text{FcP}(\text{O})(\text{OH})_2$ fragments to $[\text{C}_5\text{H}_4\text{PO}_2\text{H}]^-$, but in contrast $\text{Fc}(\text{CH}_2)_n\text{P}(\text{O})(\text{OH})_2$ ($n = 1, 2$) give $\text{Fe}\{\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_n\text{P}(\text{O})\text{O}_2\}^-$ ions, which are proposed to have an intramolecular interaction between the Fe atom and the phosphonate group. In contrast, arsonic acid **10**, together with $\text{PhAs}(\text{O})(\text{OH})_2$ for comparison, undergo facile alkylation (in methanol or ethanol solvent), and at elevated cone voltages (e.g. $> 60\text{V}$) undergo carbon-arsenic bond cleavage giving $[\text{CpFeAs}(\text{O})(\text{OR})\text{O}]^-$ ($\text{R} = \text{H, Me, Et}$) and ultimately $[\text{AsO}_2]^-$ ions.

Keywords: Ferrocene; Phosphonic acid; Arsonic acid; Crystal structures; Electrospray mass spectrometry

1. Introduction

Phosphonic and arsonic acids are diprotic acids with the general formula $RE(O)(OH)_2$ ($E = P, As$; $R = \text{alkyl, aryl}$). There has been recent intense interest in the chemistry of phosphonic acids, particularly for the self-assembly of their metal salts into two- and three-dimensional structures, since the resulting phosphonate materials have chemical properties which are highly dependent on the nature of the organic moiety (R) on the phosphonic acid.[1] Indeed, phosphonic acids containing photo-active [2], acidic [3], basic [4], ion-selective [5] and chiral [6] R groups have been prepared for incorporation into metal phosphonate materials.

The aim of this work was to synthesise phosphonic acids derived from the ferrocene moiety, and to ultimately incorporate these redox-active molecules into metal phosphonate materials. In this field, there has been recent interest in phosphonic acids and phosphonates derived from the arene chromium tricarbonyl moiety, where the carbonyl ligands provide a convenient infrared spectroscopic handle for materials characterization.[7,8]. Since its discovery, there has been intense interest in the chemistry of ferrocene and its derivatives [9] however, in the area of organophosphorus derivatives, most work has focused on ferrocenyl-phosphines as ligands.[9,10] Reports of phosphonic acid derivatives of ferrocene are, surprisingly, extremely rare. The phosphonic acid

FcP(O)(OH)_2 has been reported in patent literature as an ingredient in explosives [11] while the monoester $\text{FcCH}_2\text{P(O)(OMe)(OH)}$ has been known for some time.[12] 6-Ferrocenylhexylphosphonic acid, $\text{Fc(CH}_2)_6\text{P(O)(OH)}_2$ has been synthesized by Me_3SiBr -mediated hydrolysis of $\text{Fc(CH}_2)_6\text{P(O)(OEt)}_2$. [13] We have recently reported the synthesis of the phosphinic acid $\text{FcCH}_2\text{P(O)(OH)(CH}_2\text{OH)}$ [14] and the phosphate salt $\text{FcCH}_2\text{CH}_2\text{OPO}_3\text{Na}_2$ is known.[15] Arsonic acids, while weaker acids than phosphonic acids, also form salts with metals [16] and have been widely used as analytical reagents for certain metal ions [17] though their structural chemistry has been less widely studied.[16] Ferrocene-phosphonic (and arsonic) acids have application in the fabrication of functionalised (electroactive) monolayers on metal and oxide surfaces.[13, 18]

2. Results and discussion

2.1 Synthesis and spectroscopic characterisation of ferrocenylphosphonic acids

Synthetic methods for the preparation of phosphonic acids are well-developed and have been the subject of several comprehensive reviews. [19] Phosphonic acids can be prepared from aryl phosphonate esters by hydrogenolysis in the presence of platinum or palladium catalysts. [20] Hydrogenolysis of the recently synthesized $\text{FcCH}_2\text{P(O)(OPh)}_2$ [21] with H_2/PtO_2 led to the isolation of the monoester $\text{FcCH}_2\text{P(O)(OPh)OH}$ **1**, rather than the desired phosphonic acid. We therefore turned to the hydrolysis of alkyl esters, which has been widely used in the synthesis of phosphonic acids. The diethyl ester $\text{FcCH}_2\text{P(O)(OEt)}_2$ has been prepared by reaction of $\text{FcCH}_2\text{NMe}_3\text{I}$ with $(\text{EtO})_2\text{P(O)Na}$ or

$\text{P}(\text{OEt})_3$.^[2] We find that the same product is produced in moderate yield (after chromatographic purification) when FcCH_2OH reacts with $(\text{EtO})_2\text{P}(\text{O})\text{Na}$ in refluxing toluene. Using an excess of $(\text{EtO})_2\text{P}(\text{O})\text{Na}$, the monoester $\text{FcCH}_2\text{P}(\text{O})(\text{OEt})\text{OH}$ **2** was the principal product. The preparation of monoesters by base hydrolysis is well-known, ^[23] and in the present case it seems likely that the excess $(\text{EtO})_2\text{P}(\text{O})\text{Na}$ is effecting ester cleavage. Compound **2** is easily purified by extraction into aqueous base, followed by acidification. This compound is stable, and conveniently prepared in good yield (50-65%).

The ferrocene moiety is prone to acid-catalysed oxidation, so acidic hydrolysis of **2** was not undertaken. Instead, **2** was silylated with $\text{Me}_3\text{SiBr}/\text{Et}_3\text{N}$, followed by hydrolysis of the resulting silyl ester with 10% NaHCO_3 solution. Such silyl ester-mediated hydrolysis of phosphonate esters is a common technique for the preparation of acid-sensitive phosphonic acids.^[8, 13, 24] Acidification of the NaHCO_3 solution resulted in the precipitation of $\text{FcCH}_2\text{P}(\text{O})(\text{OH})_2$ **3** in high (91%) yield, Scheme 1. The acid is a yellow crystalline material, sparingly soluble in water and most organic solvents, though appreciably soluble in lower alcohols and Me_2SO . The yellow colour of the solid slowly fades to pale green upon prolonged exposure (several months) to air at room temperature, characteristic of the ferricinium ion formed as a result of the compound catalyzing its own oxidation.

A similar synthetic method was applied to the preparation of ferrocenylethylphosphonic acid, $\text{FcCH}_2\text{CH}_2\text{P}(\text{O})(\text{OH})_2$, **4**, Scheme 2. $\text{FcCH}_2\text{CH}_2\text{OH}$ [which was unreactive towards $\text{P}(\text{OPh})_3$ or $(\text{EtO})_2\text{P}(\text{O})\text{Na}$] was brominated using PBr_3 to give stable $\text{FcCH}_2\text{CH}_2\text{Br}$, which underwent Michaelis-Arbuzov ^[25] reaction in refluxing

$\text{P}(\text{OEt})_3$ to give $\text{FcCH}_2\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$ in high yield. Silyl ester mediated hydrolysis of $\text{FcCH}_2\text{CH}_2\text{P}(\text{O})(\text{OEt})_2$ proceeded smoothly to give the acid $\text{FcCH}_2\text{CH}_2\text{P}(\text{O})(\text{OH})_2$ **4** as a yellow powder in high yield. Acid **4** is air stable, and is soluble in polar solvents such as lower alcohols and Me_2SO .

Three further ferrocenylphosphonic acids have been prepared, the previously reported $\text{FcP}(\text{O})(\text{OH})_2$ **5** [11] and the novel 1,1'-ferrocenylbis(phosphonic acids), 1,1'- $\text{Fc}'[\text{P}(\text{O})(\text{OH})_2]_2$ **6**, and 1,1'- $\text{Fc}'[\text{CH}_2\text{P}(\text{O})(\text{OH})_2]_2$ **7**. The acids **5** and **6** are synthetically related, both being derived from reaction of lithiated ferrocene (FcLi or $\text{Fc}'\text{Li}_2$ for **5** and **6** respectively) with $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$, Scheme 3. Reactions of lithiated ferrocenes with compounds containing P-Cl bonds are well-established in the synthesis of ferrocenylphosphorus compounds, and the reaction of $\text{Fc}'\text{Li}_2$ with $(\text{EtO})_2\text{PCl}$ has been reported in the literature.[26] The products in the present case are the ferrocenylphosphonates $\text{FcP}(\text{O})(\text{OEt})_2$ and 1,1'- $\text{Fc}'[\text{P}(\text{O})(\text{OEt})_2]_2$, which were purified by flash column chromatography. Silyl ester-mediated hydrolysis was complicated by the solubility of the resulting acids **5** and **6** in water. Hydrolysis was therefore effected by a small excess of water in dichloromethane, rather than by a solution of NaHCO_3 . $\text{FcP}(\text{O})(\text{OH})_2$ is an air-stable, yellow crystalline compound, while **6** is also yellow, but the colour fades with time. Both **5** and **6** are soluble in water and polar organic solvents.

The synthesis of phosphonic acid **7** was accomplished using similar chemistry. Reaction of 1,1'-dilithioferrocene with paraformaldehyde gave the diol 1,1'- $\text{Fc}'(\text{CH}_2\text{OH})_2$ which was chlorinated with PCl_3 in a known procedure [27] to give the reactive dichloride 1,1'- $\text{Fc}'(\text{CH}_2\text{Cl})_2$. This was reacted, without purification, with excess refluxing $\text{P}(\text{OEt})_3$ to give 1,1'- $\text{Fc}'[\text{CH}_2\text{P}(\text{O})(\text{OEt})_2]_2$, which after silyl ester hydrolysis gave **7** as a bright yellow

powder which turns green over a period of weeks in air, and is soluble in water and polar organic solvents.

The phosphonic acids give single resonances in their $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra, e.g. at δ 23.1 for $\text{FcCH}_2\text{P}(\text{O})(\text{OH})_2$ **3**. Spectra recorded in alkaline D_2O give an upfield shift of *ca.* 5 ppm compared to spectra for the free acids.

2.2 Synthesis of diphenyl ferrocenylphosphonate esters

As part of this work, we have also synthesized and characterized the phenyl ferrocenylphosphonate esters $\text{FcP}(\text{O})(\text{OPh})_2$ **8** and $1,1'\text{-Fc}'[\text{P}(\text{O})(\text{OPh})_2]_2$ **9**. The reaction of $(\text{PhO})_2\text{P}(\text{O})\text{Cl}$ with FcLi and $1,1'\text{-Fc}'\text{Li}_2$ gave **8** and **9** respectively, in high yields. The crude products were brown oils, easily purified by silica column chromatography, using ethyl acetate as the eluting solvent. The pure phenyl esters **8** and **9** are orange crystalline solids, unlike the analogous ethyl esters, which are brown oils. They are also appreciably more stable than the analogous ethyl esters, which discolour rapidly in air at room temperature. It was found during the synthesis of **8** that the order of addition of the FcLi and $(\text{PhO})_2\text{P}(\text{O})\text{Cl}$ had some bearing on the outcome of the reaction. If FcLi is added to a solution of $(\text{PhO})_2\text{P}(\text{O})\text{Cl}$ the reaction proceeded as expected. However, the reverse order of addition led to two products (in *ca.* 1:1 ratio by ^{31}P NMR) which were isolated by chromatography and identified as the expected phenyl ester $\text{FcP}(\text{O})(\text{OPh})_2$ **8** and a second product characterised by ^{31}P NMR (δ ^{31}P 42.6) and electrospray ionisation mass spectrometry [M^+ , m/z 510 (100%), MNa^+ , m/z 533 (76%)] as the phosphinate ester $\text{Fc}_2\text{P}(\text{O})(\text{OPh})$.

2.3 X-ray crystal structure determinations of $\text{FcCH}_2\text{P}(\text{O})(\text{OH})_2$ **3** and $1,1'$ - $\text{Fc}'[\text{CH}_2\text{P}(\text{O})(\text{OH})_2]_2$ **7**

To fully characterize the acids **3** and **7**, and compare the differences in the structure of mono- and bis-substituted ferrocenylphosphonic acids, single crystal X-ray diffraction analyses were carried out on both compounds. There has been considerable recent interest in structural features of metallocene-derived carboxylic acids,[**28**] and the structures of **3** and **7** are the first of ferrocenylphosphonic acids.

The molecular structures of **3** and **7** are shown in Figures 1 and 2 respectively, together with the atom numbering schemes. Selected bond lengths and angles are given in Tables 1 and 2 respectively. Of particular interest in both structures are the hydrogen-bonding networks formed between the acid hydroxyl groups and the hydrogen bond accepting P=O group.

The structure of **3** shows no exceptional bond lengths or angles. The cyclopentadienyl rings of the ferrocenyl group are eclipsed and the C(1)-C(11) bond lies in the plane of the cyclopentadienyl rings, as seen in structures of other Fc-CH₂-P systems.[**14,21**] There is no interaction of the phosphonic acid group with the iron atom. Indeed the phosphonic acid is heavily involved in the anticipated hydrogen bonding interactions with adjacent phosphonic acid groups. The compound crystallizes with 8 molecules in the unit cell and forms two-dimensional ferrocenyl bi-layers in the crystallographic *ab* plane. Hydrogen bonding between phosphonic acid groups on the surface of these layers serve to hold the structure together. Individual hydrogen bonding interactions are shown in Figure 3, while the overall lattice is depicted in Figure 4. Each

phosphonic acid group bonds to the P=O oxygen of an adjacent phosphonic acid residue in the same plane along the *b*-axis via an O(3)-H(3) ... O(1') bond. The second hydroxyl group hydrogen bonds to a phosphonic acid residue in an adjacent plane with the formation of an O(2)-H(2) ... O(1'') bond. This second hydrogen bond bridges the bi-layers and results in the formation of eight-membered P-O-H rings, Figure 3. Such rings are a common feature of organophosphorus acid structures [29] and the chain of hydrogen-bonded eight-membered rings is reminiscent of that observed previously in the structure of an aza-crown ether functionalised phosphonic acid derivative [4c]. The P=O group of each molecule of **3** accepts two hydrogen bonds, one from a neighbour in the same plane, and the second from an adjacent plane, Fig. 3.

The two C₅H₄CH₂P(O)(OH)₂ units of **7** adopt an *anti* orientation about the central iron atom. The iron sits at a centre of symmetry and the asymmetric unit contains only half of the molecule. As in the structure of **3** the C(1)-C(11) bond lies in the plane of the cyclopentadienyl ring and there is no indication of any interaction between the iron atom and phosphonic acid groups.

The macrostructure of **7** can be described as infinite chains of hydrogen bonded bisphosphonic acid molecules. These chains run almost at right angles to each other in the structure and are crosslinked by further hydrogen bonding interactions, as shown in Figure 5. A similar infinite chain motif is found in the crystal structures of the bisphosphonic acid series (HO)₂P(O)-(CH₂)_n-P(O)(OH)₂ (*n* = 1, [30] 2 [31] and 3 [32]). The structures adopted by these aliphatic bisphosphonic acids in the solid state are those which maximise the hydrogen bonding interactions. Each phosphonic acid group in the crystal of **7** is involved in four hydrogen bonds, giving a total of eight hydrogen bonding interactions for

each molecule. The P=O bonds accept two hydrogen bonds, one from a neighbour in the same chain, the second from a phosphonic acid in a neighbouring chain. Similarly, each phosphonic acid group forms two donor hydrogen bonds through the two OH groups.

2.4 Synthesis of the ferrocene-derived arsonic acid $\text{FcCH}_2\text{CH}_2\text{As(O)(OH)}_2$ 10

The Meyer reaction [33] has been widely used for the synthesis of aliphatic arsonic acids, and involves the reaction of sodium arsenite (Na_3AsO_3) with alkyl halides, followed by acidification, whereupon the acid separates out.[34] However, reactions of the ferrocenylmethylating agents $\text{FcCH}_2\text{NMe}_3\text{I}$ or FcCH_2OH with sodium arsenite in refluxing aqueous solution, or FcCH_2Cl and sodium arsenite in water-dichloromethane at reflux did not produce the arsonic acid $\text{FcCH}_2\text{As(O)(OH)}_2$. Instead only starting material and FcCH_2OH were obtained on workup. Sodium arsenite solution is strongly basic, and presumably effects hydrolysis of $\text{FcCH}_2\text{NMe}_3^+$ and the reactive chloride FcCH_2Cl to FcCH_2OH . [35]

Reaction of $\text{FcCH}_2\text{CH}_2\text{Br}$ with sodium arsenite was more successful, with the arsonic acid $\text{FcCH}_2\text{CH}_2\text{As(O)(OH)}_2$ being isolated in fair yield as an air-stable yellow powder on acidification. The acid did not decompose in air over time [though neither did the phosphonic acid analogue $\text{FcCH}_2\text{CH}_2\text{P(O)(OH)}_2$], and unlike the phosphonic acids which decomposed on melting, the arsonic acid had a clearly defined melting point and did not decompose.

2.5 Electrospray ionization mass spectrometry (ESMS) study of ferrocene-derived phosphonic and arsonic acids

2.5.1 Phosphonic acids

ESMS is a versatile technique for the characterisation of involatile and thermally sensitive compounds, and there have been several studies applying the technique to ferrocene-derived compounds.[36] Ferrocene and some derivatives can be oxidised to the ferricinium ion under electrospray conditions,[37] while other derivatives bearing protonatable groups show a variable amount of protonation.[21] Phosphonic acids readily deprotonate under ESMS conditions, [38] and as expected, the negative ion ES spectra of the ferrocenylphosphonic acids **3**, **4**, and **5** were dominated at low cone voltages by the $[M-H]^-$ ions.

Of interest are the differing fragmentation pathways at elevated cone voltages. For $FcP(O)(OH)_2$ **5** a peak at m/z 128 appeared, assigned to the ion $[C_5H_4PO_2H]^-$ ion (formally formed by loss of neutral C_5H_5FeOH), which is also observed in the negative ion spectrum of **6** at high cone voltages. No other fragmentation of **5** is observed at cone voltages up to 180 V. Fig. 6(c) shows the spectrum of **5** at a cone voltage of 100 V. The ES spectra for **3** and **4** give a single major fragment ion at high cone voltages (e.g. 100 V, Figure 6(a), (b)), at m/z 213 and 227 respectively, corresponding to loss of C_5H_6 from the pseudo-parent $[M-H]^-$ ion. The resulting ions $[Fe\{\eta^5-C_5H_4(CH_2)_nPO_3\}]^-$ ($n = 1$ or 2) (alternatively written as $[M - H - C_5H_6]^-$) might be stabilized by interaction between the phosphonate group and the exposed iron atom, structures **11** and **12**. Evidence for this comes from the far greater relative intensity of the $[M - H - C_5H_6]^-$ ion in the spectra of **4**

when compared to **3**, as illustrated in Fig. 6 at a cone voltage of 100 V. The extra CH₂ spacer in **4** would enable the phosphonate to interact more easily with the iron; the analogous ion is not observed in the spectra of **5**. A similar, though positively-charged ion, [Fe{η⁵-C₅H₄CH₂P(O)(OPh)₂}]⁺ was observed in high cone voltage spectra of FcCH₂P(O)(OPh)₂, and is thought to be stabilized by interaction of the P=O group with the iron atom.[21]

The ES spectra of the ferrocenylbis(phosphonic acid) **6** are dominated by the [M - H]⁻ (*m/z* 345) and [M - 2H]²⁻ (*m/z* 172) ions. At higher cone voltages, ions at *m/z* 327 and 128 are observed; the former is formed by loss of H₂O from [M - H]⁻ (possibly giving a cyclic P-O-P anhydride) and the latter corresponds to the [C₅H₄PO₂H]⁻ ion. Spectra for **7** are also dominated by the [M - H]⁻ ion (*m/z* 373) at low cone voltages, however the [M - 2H]²⁻ ion (*m/z* 186) was not observed. At higher cone voltages (> 120 V) a more complex fragmentation pattern emerges, though still dominated by [M - H]⁻.

The monoesters **1** and **2** also gave strong [M - H]⁻ ions and weaker [2M - H]⁻ ions at low cone voltages, with pyridine added to aid ionization. At higher cone voltages (> 60 V), fragmentation occurs, with ions [M - H - PhOH]⁻ (*m/z* 261) and [M - H - PhH]⁻ (*m/z* 277) observed for **1**. Positive ion ES spectra of the diester **8** gave both [M]⁺ and [M + H]⁺ ions (*m/z* 418 and 419 respectively), with the latter increasing in intensity at higher cone voltages. At cone voltages greater than 60 V the [M - C₅H₅]⁺ ion appeared and increased in intensity as the cone voltage was increased, similar to the behaviour reported for FcCH₂P(O)(OPh)₂. [21] Positive ion ES spectra of the bis(phosphonate ester) **9** were dominated by the [2M + Li]⁺ (*m/z* 1307) and [2M + Na]⁺ (*m/z* 1323) ions, even when no Li⁺ or Na⁺ ions were added, showing the strong, but not unexpected, propensity of this

compound to coordinate metal ions.[38,39] The $[M]^+$ (m/z 650), $[M + H]^+$ (m/z 651), $[M + Li]^+$ (m/z 657) and $[M + Na]^+$ (m/z 673) ions were also observed. Phosphonate **9** may prove to have an interesting coordination chemistry, given recent interest in this field, such as the ability of $[Fe\{\eta^5-C_5H_4P(O)Ph_2\}_2]$ to stabilize an unusual tetrahedral coordination geometry for palladium(II).[40]

2.5.2 $FcCH_2CH_2As(O)(OH)_2$

The negative-ion ES spectrum of **10** at 20 V in methanol with added pyridine resulted in observation of the expected $[M - H]^-$ ion (m/z 337), together with the $[M - 2H + Me]^-$ ion, i.e. $[FcCH_2CH_2As(O)(OMe)O]^-$ at m/z 351, due to methylation by the solvent. This behaviour is markedly different to that of the analogous phosphonic acid **4**, which showed no methylation. When ethanol is used as the solvent, the analogous $[FcCH_2CH_2As(O)(OEt)O]^-$ ion (m/z 365) was observed. At elevated cone voltages, the spectra are more complex; at 60 V for the methanol system the base peak is $[CpFeAsO_2(OMe)]^-$ (m/z 259) while significant intensity ions $[AsO_2]^-$ (m/z 107) [41] and $[AsO_2 + MeOH]^-$ (m/z 139) are also observed. At very low intensity, ions $[M - H]^-$ (m/z 337) and $[CpFeAsO_2(OH)]^-$ (m/z 245) are also observed. The ions at m/z 245 and 259 are of interest, since they require cleavage of the As-C bond; an analogous process was not observed for the phosphonic acid analogue **4**. At 100 V, the $[AsO_2]^-$ ion was the sole ion observed; as shown by studies described later in this section, this behaviour appears typical of other arsonic acids.

Studies of the positive-ion ES behaviour of organoarsenic acids tend to dominate the published literature [41,42,43] which is rather surprising, given the acidic nature of

such compounds and the equal ability of ES spectrometers to operate in positive or negative ion modes. The acids however have been found to form $[M + X]^+$ ($X = H, Na$ and K) ions under ES conditions [41,42] and positive ion mode has been used in the development of analytical techniques.[43,44] The use of methanolic solvents is commonplace in the reported studies, and methanol is specifically added to increase sensitivity in one study.[45] The positive ion ES behaviour of six organoarsenic acids in a methanol-water solvent system in the presence of acetic acid has been studied.[42] In all cases, the protonated molecule was the most intense ion, however, all spectra contained weak ions due to the respective $[M + H - H_2O + MeOH]^+$ ions, corresponding to monomethylation of the parent acids. Esterification of arsenic acids is known to be a facile process in alcoholic solutions.[46]

Prompted by the lack of negative-ion ES studies of organo-arsenic acids (especially arsonic acids), a brief study of phenylarsonic acid was undertaken, using methanol or ethanol as the solvent, with pyridine added to aid ionisation. $PhAs(O)(OH)_2$ methylated very readily, such that at 20 V the only ion observed was $[PhAs(O)(OMe)O]^-$ (m/z 215). Increasing the cone voltage yielded $[M - H]^-$ (m/z 201), $[M - OH]^-$ (m/z 185), $[AsO_2 + MeOH]^-$ (m/z 139) and $[AsO_2]^-$ (m/z 107), the latter being the base peak at cone voltages greater than 60 V. Spectra in ethanol paralleled the methanol spectra, confirming assignments.

3. Experimental

3.1 Materials and methods

All solvents used were LR grade or better, and (except for ethyl acetate) were distilled under a nitrogen atmosphere from the appropriate drying agent prior to use: THF and diethyl ether (sodium-benzophenone ketyl), dichloromethane and petroleum spirits, boiling range 60-80 °C (CaH₂), toluene (sodium metal). Reactions were carried out in air unless otherwise stated.

Platinum dioxide (BDH), sodium metal (BDH), *n*-butyl lithium, 1.6 M in hexanes (Aldrich), *t*-butyl lithium, 1.7 M in pentane (Aldrich), tetramethylethylenediamine (tmeda) (BDH), diethylphosphite (Aldrich), triethylphosphite (BDH), PCl₃ (Aldrich), As₂O₃ (BDH), TMEDA (BDH), phenylarsonic acid (BDH) and ferrocene (Strem) were used as supplied. The compounds FcCH₂P(O)(OPh)₂ [21], FcCH₂OH [47], FcCH₂CH₂Br [48], FcLi [49], 1,1'-Fc'Li₂ [50], Me₃SiBr [51], (PhO)₂P(O)H [52], (RO)₂P(O)Cl (R = Et, Ph) [53] and FcCH₂Cl [54] were prepared by the literature procedures, or minor variations thereof. 1,1'-Fc'(CH₂OH)₂ was prepared by reaction of 1,1'-Fc'Li₂ with (CH₂O)_n, followed by aqueous workup.

Melting points were measured using a Reichert Thermopan melting point microscope and are uncorrected. IR spectra were recorded using a Bio-Rad FTS-40 spectrometer. Samples of the phosphonic acids were run as KBr disks, while samples of the esters, and the arsonic acid were run in CH₂Cl₂ solution. Electrospray mass spectra (ESMS) were obtained with a VG Platform II mass spectrometer. Samples were dissolved in an appropriate solvent and introduced into the spectrometer via a 10 μL sample loop using a Thermo Separation Products SpectraSystem P1000 LC pump at a flow rate of 0.01 mL min⁻¹. Cone voltages were typically varied from 20 to 120 V to maximise spectral

quality. To aid ionisation, pyridine was added to acidic samples. A Bruker AC300P spectrometer operating at 121.51 MHz was used to acquire all ^{31}P NMR spectra; chemical shifts are relative to an external reference of 85% orthophosphoric acid (δ 0.0). ^{13}C and ^1H NMR spectra were obtained on a Bruker AC300P (^1H , 300.13 MHz; ^{13}C 75.47 MHz) or a Bruker DRX400 (^1H , 400.17 MHz; ^{13}C , 100.62 MHz) spectrometer and referenced to residual solvent lines. Solvents were assigned the following chemical shift values with respect to external SiMe_4 : CDCl_3 , 7.26 (^1H), 77.06 (^{13}C); d^6 -DMSO, 2.6 (^1H), 39.5 (^{13}C); D_2O , 3.5 (MeOH, ^1H), 49.3 (MeOH, ^{13}C). Acid samples were often dissolved in $\text{NaOD}/\text{D}_2\text{O}$ solution, prepared by reaction of a small amount of Na (~1-3 mg) with excess D_2O (~2 mL). Two-dimensional NMR experiments were used to unambiguously assign spectra for compounds **2**, **8**, **9**, **3** and **4**. Comparison of these results with other spectra aided in full assignment of the rest of the compounds. The atom labelling scheme used for assignment of ferrocenyl NMR signals is given in Scheme 4.

3.2 Synthesis of $\text{FcCH}_2\text{P}(\text{O})(\text{OPh})(\text{OH})$ **1**.

To a solution of $\text{FcCH}_2\text{P}(\text{O})(\text{OPh})_2$ (0.55 g, 1.2 mmol), in MeOH (25 mL) was added a catalytic amount (*ca.* 5 mg) of PtO_2 . This solution was placed under a dihydrogen atmosphere (50 p.s.i.) and agitated for four days. The dark green solution was allowed to slowly evaporate resulting in the precipitation of dirty yellow crystals of **1**. The crystals were dissolved in CH_2Cl_2 (10 mL) and extracted with 10% aqueous NaHCO_3 (2 x 10 mL). The combined aqueous fractions were washed with CH_2Cl_2 (10 mL), acidified with

concentrated HCl then extracted with CH₂Cl₂ (2 x 10 mL). The combined organic fractions were dried over MgSO₄ and filtered. The product was precipitated by addition of petroleum spirits, filtered and air dried to give 21.3 mg (4.6%) of **1** as a yellow powder, m.p. 160 °C. Elemental Analyses: Found C, 57.4%; H, 4.9%. Calculated for C₁₇H₁₇FeO₃P: C, 57.3%; H, 4.8%. ³¹P-¹H NMR (CDCl₃): δ 26.5. ¹³C -¹H NMR (CDCl₃): δ 150.18 (d, ²J_{C,P} 11Hz, Ph, *i*-C), 129.62 (s, Ph, *m*-C), 124.86 (s, Ph, *p*-C), 120.76 (s, Ph, *o*-C), 70.10 (s, C2), 69.43 (s, C4), 68.40, (s, C3), 27.67 (d, ¹J_{C,P} 140Hz, CH₂P). ¹H NMR (CDCl₃): δ 7.24-6.90 (5H, m, Ph), 4.24 (2H, br s, H3), 4.13 (7H, br s, H2,H4), 2.95 (d, ²J_{H,P} 21Hz, CH₂P). ESMS: (MeOH/H₂O, cone voltage 20V) *m/z* 355 ([M - H]⁻, 100%), 325 ([M - H + MeOH]⁻, 10%). IR (Solution in CH₂Cl₂) (cm⁻¹): 3053 (s, br), 2926 (w), 1204 (s), 1105, (m), 1071 (w), 1039 (w), 1025 (w), 1000 (w), 985 (w), 923 (m).

3.3 Synthesis of FcCH₂P(O)(OEt)(OH) **2**.

(EtO)₂P(O)Na was prepared by refluxing a mixture of diethyl phosphite (6.97 mL, 0.054 mol) and sodium metal (1.24 g, 0.054 mol) in dry toluene (80 mL) under a nitrogen atmosphere until no trace of the metal was observed (1-2 hours). To the hot solution was added FcCH₂OH (5.85 g, 0.027 mol) in ~1 g portions and reflux continued for three hours. The reaction solution was cooled and 60 mL of 10% NaHCO₃ solution added. The resulting two phase system was stirred for 10 minutes before the layers were separated.

The aqueous layer was washed with Et₂O (40 mL), acidified with concentrated HCl and extracted with CH₂Cl₂ (3 x 30 mL). The combined CH₂Cl₂ fractions were dried over MgSO₄ and filtered. The solution was concentrated (to ~10 mL) and acetone added until no further precipitation occurred. The precipitate was filtered, washed with cold water (10 mL) followed by acetone (5 mL), then air-dried to give 5.43 g (65%) of **2** as a microcrystalline yellow powder, m.p. 183 °C (dec). Elemental Analyses: Found C, 50.3%; H, 5.6%. Calculated for C₁₃H₁₇FeO₃P : C, 50.7%; H, 5.6%. ³¹P-¹H NMR (CDCl₃): δ 29.1. ¹³C-¹H NMR (CDCl₃): δ 16.33 (*d*, ³J_{C,P} 6.4Hz, OCH₂CH₃), 28.24 (*d*, ¹J_{C,P} 142Hz, CH₂P), 61.56 (*d*, ²J_{C,P} 6.9Hz, OCH₂CH₃), 67.87 (*s*, C3), 68.91 (*s*, C4), 69.47 (*d*, ³J_{C,P} 3.1Hz, C2). ¹H NMR (CDCl₃): δ 1.24 (3H, *t*, ³J_{H,H} 7.0Hz, OCH₂CH₃), 2.85 (2H, *d*, ²J_{H,P} 19.9Hz, CH₂P), 3.93 (2H, *m*, OCH₂CH₃), 4.09, (2H, *d*, ³J_{H,H} 1.6Hz H3), 4.11 (5H, *s*, H4), 4.23 (2H, *br s*, H2), 6.7 (1H, *br s*, POH). ESMS: (MeCN/H₂O, cone voltage 20 V) *m/z* 307 ([M - H]⁻, 100%), 325 ([M - H + H₂O]⁻, 9%). IR (Solution in CH₂Cl₂) (cm⁻¹): 3416 (w), 1221 (m), 1204 (s), 1104 (m), 1051 (s), 1024 (s), 966 (m), 806 (m), 609 (w), 493 (m), 475 (m).

3.4 Synthesis of FcCH₂P(O)(OH)₂ **3**.

A solution of triethylamine (0.82 g, 8.1 mmol) and **2** (2.5 g, 8.11 mmol) in dry CH₂Cl₂ (50 mL) was placed under a nitrogen atmosphere in an oven-dried flask. Me₃SiBr (6.2 g, 40 mmol) was added and the mixture refluxed gently for 3 h. The reaction mixture was

cooled to room temperature, saturated aqueous NaHCO₃ solution (50 mL) added and the two-phase system stirred vigorously for a further 3 h. The layers were separated, the aqueous phase was washed with CH₂Cl₂ (2 x 25 mL) and acidified with concentrated HCl. The yellow precipitate was filtered and washed with water (2 x 50 mL) then air-dried to give 2.08 g (91%) of **3**, m.p. 222-228 °C (dec.). Elemental Analyses: Found C, 46.5%; H 4.7%. Calculated for C₁₁H₁₃FeO₃P : C, 47.2%; H, 4.7%. ³¹P-¹H NMR (DMSO): δ 23.1. ¹³C-¹H NMR (DMSO): δ 29.68 (d, ¹J_{P-C} 134Hz, CH₂P), 67.16 (s, C3), 68.66 (s, C4), 69.24 (br s, C2), 80.26 (br s, C1). ¹H NMR (DMSO): δ 2.65 (2H, d, ²J_{P-H} 19Hz, CH₂P), 4.00 (2H, s, H3), 4.07 (5H, s, H4), 4.15 (2H, s, H2). ESMS: (MeCN/H₂O, cone voltage 60 V) *m/z* 279 ([M - H]⁻, 100%). IR (KBr disc) (cm⁻¹): 2753 (br, s), 1264 (m), 1225 (m), 1103 (s), 992 (s), 947 (s), 925 (m), 832 (m), 814 (m), 610 (w), 542 (w), 498 (m), 436 (m).

3.5 Synthesis of FcCH₂CH₂P(O)(OH)₂ **4**.

FcCH₂CH₂Br (0.85 g, 2.9 mmol) was dissolved in triethylphosphite (5 mL) and heated to reflux under nitrogen. After 5 h the solution was cooled and the excess triethylphosphite removed by distillation (*ca.* 0.2 mmHg at room temp.). The residue[¶] was dissolved in CH₂Cl₂ (10 mL) and placed under a nitrogen atmosphere. Triethylamine (1.47 g, 14.5 mmol)[‡] and Me₃SiBr (2.22 g, 14.5 mmol) were added and the reaction stirred for 4 h at room temperature. Sodium hydroxide (1 M, 20 mL) was added and stirring continued for

30 min. The layers were separated and the aqueous layer washed with CH₂Cl₂ (2 x 20 mL), then acidified with concentrated HCl. The yellow precipitate was filtered, washed liberally with cold water and air-dried to give 0.58 g (68%) of **4**, m.p. 185-190 °C (dec.). Elemental Analyses: Found C, 49.1%, H, 5.3% Calculated for C₁₂H₁₅FeO₃P : C 49.1%, H 5.1%. ³¹P-¹H} NMR (d₆-DMSO): δ 26.63. ¹³C-¹H} NMR (d₆-DMSO): δ 22.54 (*d*, ²J_{C-P} 2Hz CH₂CH₂P), 28.66 (*d*, ¹J_{C-P} 101Hz, CH₂P), 66.87 (*s*, C3), 67.33 (*s*, C2), 89.05 (*d*, ³J_{C-P} 16Hz, C1). ¹H NMR (d⁶-DMSO): δ 1.84 (2H, *d*, ²J_{H-P} 18Hz, CH₂P), 2.46 (2H, *br. s.*, CH₂CH₂P), 4.03 (2H, *br s*, H3), 4.09 (9H, *m*, H2 and H4), 7.22 (1.6H, *br. s.*, P-OH). ESMS: (MeCN/H₂O, cone voltage 20 V) *m/z* 293 ([M - H]⁻ 100%), 311 ([M - H + H₂O]⁻ 10%). IR (KBr disc) (cm⁻¹): 3414 (w), 2721 (br, m), 1230 (m), 1195 (m), 1112 (s), 1019 (s), 961 (m), 931 (s), 824 (m), 814 (m), 677 (m), 520 (m), 505 (m), 494 (m).

¶Separation of the diethyl-ester intermediate [FcCH₂CH₂P(O)(OEt)₂] by flash column chromatography (Al₂O₃, EtOAc to MeOH solvent gradient) prior to hydrolysis did not improve the overall yield.

‡The triethylamine can be omitted if the trimethylsilylbromide is freshly distilled and glassware is dry.

3.6 Synthesis of FcP(O)(OH)₂ **5**.

Ferrocene (0.93 g, 5 mmol) was dissolved in dry THF (5 mL) and cooled to 0 °C under nitrogen. ^tBuLi (0.6 mL, 1.7 M, 4.16 mmol) was added and the solution stirred for 15 min. (EtO)₂P(O)Cl (0.718 g, 4.16 mmol) was added dropwise with stirring, and the

solution stirred for 1 h. The solvent was removed under reduced pressure and replaced with H₂O (20 mL) and CH₂Cl₂ (20 mL). The layers were separated and the organic phase washed with H₂O (2 x 20 mL) before being dried over MgSO₄, filtered and the solvent removed under vacuum. The residue was dissolved in EtOAc (*ca.* 2 mL) and purified with alumina flash column chromatography, using EtOAc as the eluting solvent. The resulting red oil [FcP(O)(OEt)₂, 0.45 g, 1.4 mmol] was dissolved in CH₂Cl₂ (10 mL) and placed under a nitrogen atmosphere. Freshly distilled Me₃SiBr (0.64 g, 4.19 mmol) was added and the solution stirred for 4 h. Solvent and excess silane were removed under vacuum and replaced with dry, distilled CH₂Cl₂ (5 mL). To this was added H₂O (0.10 g, 5.56 mmol). Precipitation of the acid began within 5 min. After 30 min. the product was filtered and washed with CH₂Cl₂, then air dried to give 0.31 g (24%) of **5** as a microcrystalline yellow solid, m.p. 198-205 °C (dec.). Elemental Analyses: Found C, 44.5%; H 4.2%. Calculated for C₁₀H₁₁FeO₃P : C, 45.2%; H, 4.1%. ³¹P-¹H NMR (Na salt in D₂O): δ 15.3. ¹³C-¹H NMR (Na salt in D₂O): δ 69.76 (*s*, C4), 70.55 (*d*, ³J_{C,P} 9.6Hz, C3), 71.26 (*d*, ²J_{C,P} 11.3Hz, C2), 73.33 (*d*, ¹J_{C,P} 154Hz, C1). ¹H NMR (d⁶-DMSO): δ 4.14 (2H, br s, H3), 4.21 (5H, br s, H4), 4.28 (2H, br s, H2). ESMS: (MeCN/H₂O, cone voltage 40 V) *m/z* 265 ([M - H]⁻, 100%). IR (KBr disc) (cm⁻¹): 2796 (br, m), 1202 (s), 1130 (s), 1106 (m), 1039 (s), 1013 (s), 944 (s), 889 (w), 816 (w), 667 (w), 585 (m), 472 (m), 452 (m).

3.7 Synthesis of 1,1'-Fc'[P(O)(OH)₂]₂ **6**.

Ferrocene (0.93 g, 5 mmol) was dissolved in petroleum spirits (20 mL) under nitrogen. $n\text{BuLi}$ (6.24 mL, 1.6 M, 10 mmol) and tmeda (0.74 mL, 5 mmol) were added and the reaction stirred for 12 h. The resulting suspension was added slowly with stirring to a solution of $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$ (1.6 mL, 10 mmol) in petroleum spirits (10 mL). The reaction was immediate, resulting in the precipitation of a brown tar. The solvent was decanted off and replaced with water (20 mL) and CH_2Cl_2 (20 mL). The phases were separated and the aqueous layer further extracted with CH_2Cl_2 (2 x 20 mL). The combined organic fractions were dried over MgSO_4 and evaporated to dryness. The residue was dissolved in EtOAc (*ca.* 5 mL) and purified with alumina flash column chromatography, using an EtOAc to MeOH solvent gradient to give 2 g (88%) of 1,1'-ferrocenyl-bis(diethylphosphonate) as a brown oil.

A solution of 1,1'-ferrocenyl-bis(diethylphosphonate) (0.526 g, 1.15 mmol), in dry CH_2Cl_2 (10 mL) was placed under nitrogen, freshly distilled Me_3SiBr (0.88 mL, 9.2 mmol) added dropwise and the reaction mixture stirred overnight. Water (0.3 mL, 0.016 mol) was added and stirring continued until precipitation was complete (*ca.* 30 min). The microcrystalline yellow powder was filtered and washed with acetone to give 0.35 g (89%) of **6**, m.p. 235-238 °C (dec.). Elemental Analyses: Found C, 34.5%; H, 3.3%. Calculated for $\text{C}_{10}\text{H}_{12}\text{FeO}_6\text{P}_2$: C, 34.7%; H, 3.5%. ^{31}P - $\{^1\text{H}\}$ NMR (Na salt in D_2O): δ 21.7. ^{13}C - $\{^1\text{H}\}$ NMR (Na salt in D_2O): δ 72.09 (d, $^1\text{J}_{\text{C,P}}$ 149Hz, C1), 72.52 (d, $^3\text{J}_{\text{C,P}}$ 10Hz, C3), 72.71 (d, $^2\text{J}_{\text{C,P}}$ 12Hz, C2). ^1H NMR (Na salt in D_2O): δ 4.5-4.7 (8H, m, H2,H3), 8.80 (4H, br s, POH). ESMS: (MeCN, cone voltage 80 V) m/z 345 ($[\text{M} - \text{H}]^-$, 100%), 327 ($[\text{M} - \text{H} -$

H₂O]⁻, 17%). IR (KBr disc) (cm⁻¹): 2771 (br, m), 1198 (s), 1058 (s), 1036 (s), 1004 (s), 956 (s), 885 (m), 839 (m), 747 (m), 638 (m), 575 (s), 501 (m), 480 (m), 461 (m), 434 (w).

3.8 Synthesis of 1,1'-Fc'[CH₂P(O)(OH)₂]₂ 7.

In a dry, nitrogen-flushed flask was placed THF (30 mL), 1,1'-ferrocenylbis(methanol) (0.80 g, 3.26 mmol), pyridine (0.52 g, 6.52 mmol) and freshly distilled PCl₃ (0.89 g, 6.52 mmol). The reaction mixture was stirred until precipitation of pyridinium chloride was deemed complete (*ca.* 1 h). The solution was filtered and the solvent removed to give a bright yellow crystalline material, crude 1,1'-Fc'(CH₂Cl)₂. Triethylphosphite (5 mL) was added and the solution refluxed for 2 h. Excess triethylphosphite was distilled off under vacuum and the resulting brown oil purified by alumina flash column chromatography using an EtOAc to MeOH solvent gradient. The 1,1'-ferrocenyl-bis-(diethyl methylphosphonate) was isolated as a viscous brown oil (1.03 g, 65%).

1,1'-ferrocenyl-bis-(diethylmethylphosphonate) (0.53 g, 1.1 mmol) was dissolved in dry CH₂Cl₂ (10 mL) and the solution placed under a nitrogen atmosphere. Me₃SiBr (1.32 g, 8.8 mmol) was added and the reaction stirred for 3 h. Water (0.15 g, 8.8 mmol) was added with stirring, resulting in precipitation of a dark green powder. The solvent was removed and the residue dissolved in 5 mL of 1 M NaOH solution. The green solution was reduced to a yellow colour by the addition of excess potassium metabisulfite, then acidified with concentrated HCl. Slow evaporation over 3 days gave dark brown crystals which were filtered and washed with water (5 mL), then air-dried to give 0.173 g (42%) of 7, m.p. darkens at 203 °C (dec.). Elemental Analyses: Found C, 37.4%; H,

4.4%. Calculated for $C_{12}H_{16}FeO_6P_2$: C, 38.5%; H, 4.3%. ^{31}P - $\{^1H\}$ NMR (Na salt in D_2O): δ 19.0. ^{13}C - $\{^1H\}$ NMR (Na salt in D_2O): δ 32.84 (*d*, $^1J_{C,P}$ 76Hz, $\underline{CH_2P}$), 69.64 (*s*, C2), 72.20 (*s*, C3), 86.50 (*d*, $^2J_{C,P}$ 2Hz C1). 1H NMR (Na salt in D_2O): δ 2.49 (4H, *d*, $^2J_{P,H}$ 12.3Hz, $\underline{CH_2P}$), 3.98 (4H, *br s*, H3), 4.12 (4H, *br s*, H2). ESMS: (MeCN/ H_2O , cone voltage 20 V) *m/z* 373 ($[M - H]^-$, 100%), 325 ($[M - 2H]^{2-}$, 28%). IR (KBr) (cm^{-1}): 2749 (*br, s*), 1265 (*m*), 1225 (*m*), 995 (*s*), 946 (*s*), 920 (*m*), 829 (*m*), 607 (*m*), 483 (*m*), 432 (*m*).

3.9 Synthesis of $FcP(O)(OPh)_2$ **8**.

Ferrocene (0.93 g, 5 mmol) was dissolved in dry THF (5 mL) under nitrogen and cooled to 0 °C. $tBuLi$ (2.9 mL, 1.7M, 5 mmol) was added and the solution stirred for 15 min. This solution was added dropwise to a solution of $(PhO)_2P(O)Cl$ (1.34 g, 5 mmol) in THF (10 mL) and the solution stirred for 1 h. The solvent was removed under reduced pressure and replaced with H_2O (20 mL) and CH_2Cl_2 (20 mL). The layers were separated and the organic phase washed with H_2O (2 x 20 mL) before being dried over $MgSO_4$. The solvent was removed and the resulting brown oil purified by silica flash column chromatography using petroleum spirits : CH_2Cl_2 : MeOH (48 : 50 : 2) as the eluting solvent. This gave 0.83 g (40%) of **8** as a brown oil which crystallised upon standing, m.p. 77-80 °C. Elemental Analyses: Found C, 62.3%; H, 4.7%. Calculated for $C_{22}H_{19}FeO_3P$: C, 63.2%; H, 4.6%. ^{31}P - $\{^1H\}$ NMR ($CDCl_3$): δ 20.6. ^{13}C - $\{^1H\}$ NMR ($CDCl_3$): δ 65.45 (*d*, $^1J_{C,P}$ 166Hz, C1), 70.12 (*s*, C4), 71.90 (*dd*, $^2J_{C,P}$ 12Hz, $^3J_{C,P}$ 11Hz, C2,C3), 120.73 (*d*, $^3J_{C,P}$

3Hz, *o*-C), 124.93 (*s*, *p*-C'), 129.72 (*d*, $J_{C,P}$ 10Hz, *m*-C), 150.86 (*d*, $^2J_{C-P}$ 6Hz, *i*-C). 1H NMR ($CDCl_3$): δ 4.25 (5H, *s*, H4), 4.46 (2H, *s*, H3), 4.62 (2H, *d*, $^2J_{C,P}$ 1.2Hz H2), 7.1-7.4 (10H, *m*, Ph). ESMS: (MeCN/H₂O, positive ion, cone voltage 60 V) *m/z* 419 ([M + H]⁺, 100%), 436 ([M + H₂O]⁺, 31%), 460 ([M + MeCN]⁺, 11%). IR (solution in CH₂Cl₂) (cm⁻¹): 1591 (*s*), 1492 (*s*), 1188 (*m*), 1107 (*m*), 1071 (*m*), 1006 (*m*), 944 (*s*), 828 (*m*), 619 (*m*), 603 (*m*), 496 (*s*).

3.10 Synthesis of 1,1'-Fc[P(O)(OPh)₂]₂ 9.

Ferrocene (1 g, 5.4 mmol) was dissolved in petroleum spirits (20 mL) under nitrogen. ⁿBuLi (6.72 mL, 1.6M, 10.8 mmol) and freshly distilled tmeda (0.8 mL, 0.62 g, 5.4 mmol) were added and the reaction stirred for 12 h. A solution of (PhO)₂P(O)Cl (2.2 mL, 2.9 g, 10.8 mmol) in diethyl ether (10 mL) was then added slowly with stirring. The product precipitated as a brown tar. The solvent was removed under vacuum and the residue washed with petroleum spirits (2 x 10 mL). Water (20 mL) and CH₂Cl₂ (20 mL) were added and the flask agitated until dissolution was complete. The layers were separated and the organic phase washed with water (2 x 20 mL), dried over MgSO₄ and the solvent removed. The resulting brown oil was purified by silica flash column chromatography using a CH₂Cl₂ to EtOAc to MeOH solvent gradient. The mono-substituted byproduct, FcP(O)(OPh)₂ eluted in EtOAc : CH₂Cl₂, 1 : 9, while the desired product eluted in EtOAc : CH₂Cl₂, 3 : 7. Removal of the solvent resulted in 2.45 g (66%) of 1,1'-Fc[P(O)(OPh)₂]₂ 9 as yellow crystals, m.p. 120-121.5 °C. Elemental Analyses: Found C, 62.7%; H, 4.5%.

Calculated for $C_{34}H_{29}FeO_6P_2$: C, 62.8%; H, 4.3%. ^{31}P - $\{^1H\}$ NMR ($CDCl_3$): δ 26.2. ^{13}C - $\{^1H\}$ NMR ($CDCl_3$): δ 73.53 (*d*, $^2J_{C,P}$ 16Hz, C2), 74.60 (*d* $^3J_{C,P}$ 14Hz, C3), 120.63 (*d* $^3J_{C,P}$ 4Hz, *o*-C), 125.14 (*s*, *p*-C), 128.66 (*d*, $^1J_{C,P}$ 61Hz, C1), 129.74 (*s*, *m*-C), 150.59 (*d*, $^2J_{C,P}$ 8Hz, *i*-C). 1H NMR ($CDCl_3$): δ 4.60 (4H, *s*, H3), 4.70 (4H, *d*, $^3J_{H,P}$ 1Hz, H2), 7.1-7.4 (20H, *m*, Ph). ESMS: (positive ion, MeOH, cone voltage 90 V) *m/z* 651 ($[M + H]^+$, 100%), 673 ($[M + Na]^+$, 19%). IR (solution in CH_2Cl_2) (cm^{-1}): 1591 (*s*), 1490 (*s*), 1189 (*m*), 1163 (*m*), 1071 (*w*), 1036 (*m*), 1025 (*m*), 1007 (*w*), 941 (*s*), 837 (*w*), 618 (*w*), 602 (*m*), 403 (*m*).

3.11 Synthesis of $FcCH_2CH_2As(O)(OH)_2$ **10**.

Arsenic(III) oxide (As_2O_3 , 0.213 g, 1.07 mmol) was dissolved in aqueous sodium hydroxide (1.3 mL, 4.98 M, 6.45 mmol) and made up to 5 mL with water. $FcCH_2CH_2Br$ (0.7 g, 2.4 mmol) in CH_2Cl_2 (5 mL) was added, the CH_2Cl_2 removed under reduced pressure and 0.5 mL of EtOH added as a co-solvent. The resulting solution was refluxed for 7 h. After cooling, the reaction solution was extracted with CH_2Cl_2 to remove any unreacted bromide. The aqueous layer was acidified with 1 M HCl, the resulting yellow precipitate filtered, washed with cold water, and dried to give 0.34 g (41%) of **10**, m.p. 149-152 °C. Elemental Analyses: Found C, 42.7%; H, 4.7%. Calculated for

$C_{12}H_{15}AsFeO_3$: C, 42.6%; H, 4.5%. ^{13}C - $\{^1H\}$ NMR (Na salt in D_2O): δ 22.65 (*s*, $\underline{C}H_2Cp$), 31.21 (*s*, $\underline{C}H_2As$), 67.67 (*s*, C3), 68.02 (*s*, C2), 69.06 (*s*, C4), 90.08 (*s*, C1). 1H NMR (Na salt in D_2O): δ 2.30 (2H, *m*, $\underline{C}H_2As$), 2.85 (2H, *m*, $\underline{C}H_2Cp$), 4.24 (2H, *br s*, H3), 4.46 (7H, *br s*, H2, H4). ESMS: (MeOH, cone voltage 40 V) *m/z* 351 ($[M - 2H + Me]^-$, 30%), 337 ($[M - H]^-$, 100%), 259 ($[M - 2H - CpCH_2CH_2 + Me]^+$ 6%), 245 ($[M - H - CpCH_2CH_2]$, 10%). IR (solution in CH_2Cl_2) (cm^{-1}): 2743 (*br, s*), 2385 (*br, m*), 2303 (*br, m*), 1252 (*w*), 1220 (*w*), 881 (*s*), 827 (*m*), 784 (*m*), 486 (*m*).

3.12 X-ray crystal structure determinations for $FcCH_2P(O)(OH)_2$ **3** and $1,1'-Fc'[CH_2P(O)(OH)_2]_2$ **7**.

Single crystals of **3** were obtained serendipitously from a warm methanol solution which also contained urea and zinc chloride in an attempt to prepare the zinc salt of the acid. From this solution, small yellow crystals of **3** precipitated over a period of 2-4 weeks. Crystallographic data for **3** are given in Table 3. The data set was collected on a Nicolet R3 diffractometer. The structure was solved by direct methods and developed routinely using the SHELXL-97 program with full least-squares refinement based on F_o^2 .

All non-hydrogen atoms were refined using anisotropic temperature factors. All hydrogen atoms were found from peaks of residual electron density in the penultimate electron density map and refined in a riding model with isotropic temperature factors. The largest residual electron density peaks in the final electron density map did not exceed +0.279 and -0.305 e Å⁻³.

Crystals of **7** suitable for X-ray crystallographic analysis were obtained by evaporation of an aqueous solution which also contained potassium bisulfite as an antioxidant. Crystallographic data for compound **7** are given in Table 3. The data set was collected on a Siemens SMART CCD diffractometer and corrected for absorption using SADABS.[55]. The structure was solved by direct methods and developed routinely using the SHELXL-97 program with full-matrix least-squares refinement based on F_o². All non-hydrogen atoms were refined using anisotropic temperature factors. All hydrogen atoms were found from peaks of residual electron density in the penultimate electron density map and were refined with isotropic temperature factors. The largest residual electron density peaks in the final density map did not exceed +0.336 or -0.288 e Å⁻³.

Crystallographic data for both structure determinations have been deposited with the Cambridge Crystallographic Data Centre, CCDC, (No. 158654 for **3**, 158655 for **7**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ [FAX +44 (1223) 336033] or e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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Table 1. Selected bond lengths[¶] (Å) and angles (°) for **3**.

Cp Fe-C av	2.054(16)	P(1)-O(2)	1.566(1)
range	2.045-2.064	P(1)-O(3)	1.568(1)
Cp C-C av	1.43(1)	O(2)-H(2)	0.775(1)
range	1.422-1.432	O(3)-H(3)	0.783(1)
C(1)-C(11)	1.514(2)	O(1)----H(2')	1.819(1)
C(1)-P(1)	1.805(1)	O(1)----H(3')	1.829(1)
P(1)-O(1)	1.513(1)		
C(11)-C(15) range	107.57(12)-108.54(12)	O(1)-P(1)-O(2)	113.28(6)
C(21)-C(25) range	107.6(2)-108.2(2)	O(1)-P(1)-O(3)	108.86(6)
C(15)-C(11)-C(1)	126.97(12)	O(2)-P(1)-O(3)	108.26(7)
C(12)-C(11)-C(1)	125.44(12)	P(1)-O(2)-H(2)	119.05(7)
C(11)-C(1)-P(1)	112.18(9)	P(1)-O(3)-H(3)	117.39(7)
O(1)-P(1)-C(1)	112.06(6)	O(2)-H(2)--O(1')	175.92(7)
O(2)-P(1)-C(1)	105.95(6)	O(3)-H(3)--O(1')	166.87(7)
O(3)-P(1)-C(1)	108.25(7)		

[¶]Non-bonded O...O distances: O(1)...O(2a) 2.5932, O(1)...O(3b) 2.5982 Å.

Table 2. Selected bond lengths[¶] (Å) and angles (°) for **7**.

Cp Fe-C av	2.039(2)	P(1)-O(3)	1.548(2)
range	2.037-2.042	P(1)-O(2)	1.551(1)
Cp C-C av	1.420(3)	O(2)-H(2)	0.745(10)
range	1.413-1.427	O(3)-H(3)	0.661(10)
C(1)-C(11)	1.498(2)	O(1)-----H(2')	1.832(10)
P(1)-C(1)	1.785(2)	O(1)-----H(3')	1.923(10)
P(1)-O(1)	1.502(1)		
C(11)-C(15)		O(2)-P(1)-O(3)	108.37(8)
range	107.43-108.37	O(2)-P(1)-O(1)	113.33(7)
C(15)-C(11)-C(1)	126.4(2)	O(3)-P(1)-O(1)	108.98(8)
C(12)-C(11)-C(1)	126.2(2)	P(1)-O(2)-(H2)	119.5(2)
C(11)-C(1)-P(1)	112.68(12)	P(1)-O(3)-(H3)	116.6(2)
C(1)-P(1)-O(2)	106.14(9)	O(2)-H(2)----O(1')	175.1(2)
C(1)-P(1)-O(3)	108.06(9)	O(3)-H(3)----O(1')	164.5(2)
C(1)-P(1)-O(1)	111.77(7)		

[¶]Non-bonded O...O distances: O(1)...O(2a) (in chain) 2.5745; O(1)...O(3b) (cross chain) 2.5662 Å.

Table 3. Crystal data and analysis parameters for
 $\text{FcCH}_2\text{P}(\text{O})(\text{OH})_2$ **3** and $1,1'\text{-Fc}'[\text{CH}_2\text{P}(\text{O})(\text{OH})_2]_2$ **7**.

Empirical formula	$\text{C}_{11}\text{H}_{13}\text{O}_3\text{PFe}$	$\text{C}_{12}\text{H}_{16}\text{O}_6\text{P}_2\text{Fe}$
Crystal size (mm)	0.34 x 0.29 x 0.21	Not recorded.
Formula weight (g mol^{-1})	280.03	374.04
Crystal system	Orthorhombic	Monoclinic
a (Å)	9.859(3)	8.3415(2)
b (Å)	9.231(2)	9.8376(1)
c (Å)	25.017(7)	9.1540(2)
β (°)	90	103.696(1)
V (Å ³)	2276.7(1)	729.82(2)
Space group	Pbca	$\text{P}2_1/\text{c}$
Z	8	2
D_{calc} (g cm^{-3})	1.634	1.702
$F(000)$	1152	384
$\mu(\text{Mo-K}\alpha)$ (mm^{-1})	1.45	1.28
Temperature (K)	293(2)	293(2)
2θ range for data collection	$2 < \theta < 27^\circ$	$2 < \theta < 27^\circ$
Total reflections	23529	4242

Unique reflections	2534 ($R_{\text{int.}} = 0.0224$)	1577 ($R_{\text{int.}} = 0.016$)
T_{min}	0.726	0.758
T_{max}	1.000	0.962
$R_1 [I > 2\sigma(I)]$	0.0216	0.024
wR_2	0.058 [†]	0.0613 [‡]
GOF	1.053	0.971

[†] $w = [\sigma^2(F_o^2) + (0.0313P^2 + 1.2852)]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.

[‡] $w = [\sigma^2(F_o^2) + (0.0328P^2 + 0.4962P)]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.

Captions for Figures

Fig. 1 Molecular structure and atom numbering scheme of $\text{FcCH}_2\text{P}(\text{O})(\text{OH})_2$ **3**; non-hydrogen atom ellipsoids are shown at the 50% probability level.

Fig. 2 Molecular structure and atom numbering scheme of $1,1'\text{-Fc}'[\text{CH}_2\text{P}(\text{O})(\text{OH})_2]_2$ **7**; non-hydrogen atom ellipsoids are shown at the 50% probability level.

Fig. 3 Hydrogen bonding interactions involving **3**, showing the formation of eight-membered $\text{HO-P=O}\dots\text{HO-P=O}$ rings.

Fig. 4 The hydrogen bonded lattice of **3**, showing ferrocene bi-layers held together by hydrogen bonding.

Fig. 5 The hydrogen bonding network in the structure of **7**.

Fig. 6 Negative ion electrospray mass spectra of (a) **3** (b) **4** and (c) **5** at a cone voltage of 100 V, showing the relative intensities of the $[\text{M} - \text{H} - \text{C}_5\text{H}_6]^-$ ions for **3** and **4** (see structures **11** and **12**) and the formation of the $[\text{C}_5\text{H}_4\text{PO}_2\text{H}]^-$ ion for **5**.