Synthesis and characterisation of ferrocenyl-phosphonic and -arsonic acids

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Abstract

The ferrocene-derived acids $FcCH_2CH_2E(O)(OH)_2$ [**4**, E = P; **10**, E = As; Fc = $Fe(\eta^5-C_5H_5)(\eta^5-C_5H_4)$] have been synthesized by the reaction of $FcCH_2CH_2Br$ with either $P(OEt)_3$ followed by hydrolysis, or with sodium arsenite followed by acidification. Reaction of $FcCH_2OH$ with $(EtO)_2P(O)Na$ gave $FcP(O)(OEt)(OH)$, which was converted to $FcCH_2P(O)(OH)_2$ (**3**) by silyl ester hydrolysis using $Me_3SiBr–Et_3N$ followed by aqueous work-up. Similarly, the known phosphonic acid $FcP(O)(OH)_2$ and the new derivatives $1,1'-Fc'[P(O)(OH)_2]_2$ [Fc' = $Fe(\eta^5-C_5H_4)_2$] and $1,1'-Fc'[CH_2P(O)(OH)_2]_2$ (**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 $[M-H]^-$ ions and their fragmentation at elevated cone voltages has been found to be dependent on the acid. $FcP(O)(OH)_2$ fragments to $[C_5H_4PO_2H]^-$, but in contrast $Fc(CH_2)_nP(O)(OH)_2$ ($n = 1, 2$) give $Fe\{\eta^5-C_5H_4(CH_2)_nP(O)O_2\}^-$ ions, which are proposed to have an intramolecular interaction between the Fe atom and the phosphonate group. In contrast, arsonic acid (**10**), together with $PhAs(O)(OH)_2$ for comparison, undergo facile alkylation (in methanol or ethanol solvent), and at elevated cone voltages (e.g. > 60 V) undergo carbon–arsenic bond cleavage giving $[CpFeAs(O)(OR)O]^-$ (R = H, Me, Et) and ultimately $[AsO_2]^-$ ions. © 2001 Elsevier Science B.V. All rights reserved.

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 = 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]. 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 synthesize phosphonic acids derived from the ferrocene moiety, and to ulti-

mately 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 $FcCH_2P(O)(OMe)(OH)$ has been known for some time [12]. 6-Ferrocenylhexylphosphonic acid, $Fc(CH_2)_6P(O)(OH)_2$, has been synthesized by Me_3SiBr-mediated hydrolysis of $Fc(CH_2)_6-P(O)(OEt)_2$ [13]. Synthesis of the phosphinic acid, $FcCH_2P(O)(OH)(CH_2OH)$ [14] and the phosphate salt,

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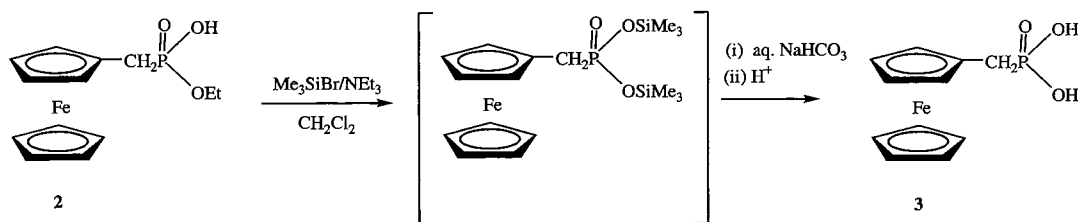
Scheme 1.

FcCH$_2$CH$_2$OPO$_3$Na$_2$ [15] have recently been reported. Arsonic acids, while weaker acids than phosphonic acids, also form salts with metals [16] and have been used widely as analytical reagents for certain metal ions [17] though their structural chemistry has been studied less widely [16]. Ferrocene–phosphonic (and arsonic) acids have application in the fabrication of functionalized (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 FcCH$_2$P(O)(OPh)$_2$ [21] with H$_2$–PtO$_2$ led to the isolation of the monoester FcCH$_2$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 FcCH$_2$P(O)(OEt)$_2$ has been prepared by reaction of FcCH$_2$NMe$_3$I with (EtO)$_2$P(O)Na or P(OEt)$_3$ [22]. We find that the same product is produced in moderate yield (after chromatographic purification) when FcCH$_2$OH reacts with (EtO)$_2$P(O)Na in refluxing toluene. Using an excess of (EtO)$_2$P(O)Na, the monoester FcCH$_2$P(O)(OEt)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 (EtO)$_2$P(O)Na is effecting ester cleavage. Compound 2 is purified easily by extraction into an 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 Me$_3$SiBr–Et$_3$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 FcCH$_2$P(O)(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$_2$SO. 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.


1, R = Ph
2, R = Et

7
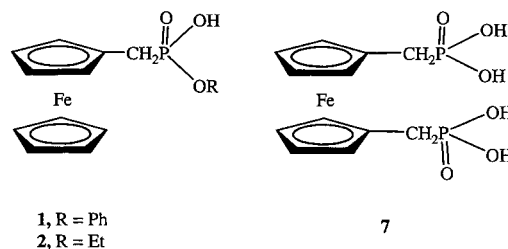
A similar synthetic method was applied to the preparation of ferrocenylethylphosphonic acid, FcCH$_2$CH$_2$P(O)(OH)$_2$ (4) (Scheme 2). FcCH$_2$CH$_2$OH [which was unreactive towards P(OPh)$_3$ or (EtO)$_2$P(O)Na] was brominated using PBr$_3$ to give stable FcCH$_2$CH$_2$Br, which underwent Michaelis–Arbuzov [25] reaction in refluxing P(OEt)$_3$ to give FcCH$_2$CH$_2$P(O)(OEt)$_2$ in high yield. Silyl ester mediated hydrolysis of FcCH$_2$CH$_2$P(O)(OEt)$_2$ proceeded smoothly to give the acid FcCH$_2$CH$_2$P(O)(OH)$_2$ (4) as a yellow powder in high yield. The acid 4 is air stable, and is soluble in polar solvents such as lower alcohols and Me$_2$SO.

Three further ferrocenylphosphonic acids have been prepared, the previously reported FcP(O)(OH)$_2$ (5) [11] and the novel 1,1′-ferrocenylbis(phosphonic acids), 1,1′-Fc′[P(O)(OH)$_2$]$_2$ (6) and 1,1′-Fc′[CH$_2$P(O)(OH)$_2$]$_2$ (7). The acids 5 and 6 are related synthetically, both being derived from reaction of lithiated ferrocene (FcLi or Fc′Li$_2$ for 5 and 6, respectively) with (EtO)$_2$P(O)Cl (Scheme 3). Reactions of lithiated ferrocenes with compounds containing P–Cl bonds are well-established in the synthesis of ferrocenyl–phosphorus compounds, and the reaction of Fc′Li$_2$ with (EtO)$_2$PCl has been reported in the literature [26]. The products in the present case are the ferrocenylphosphonates FcP(O)-
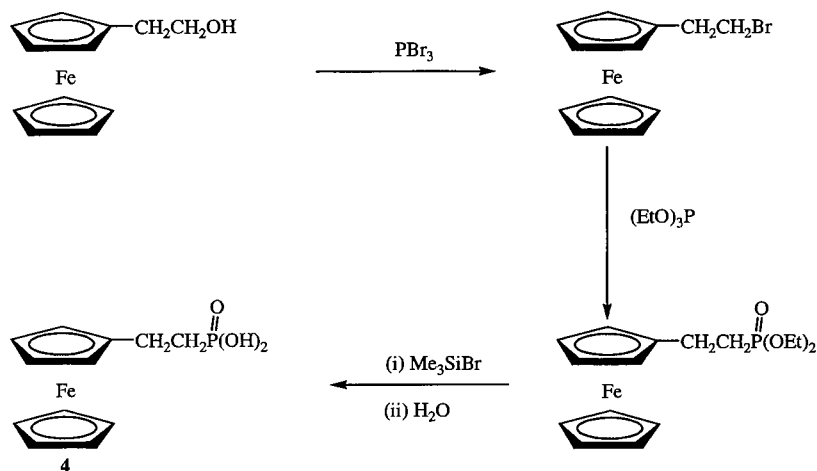
Scheme 2.
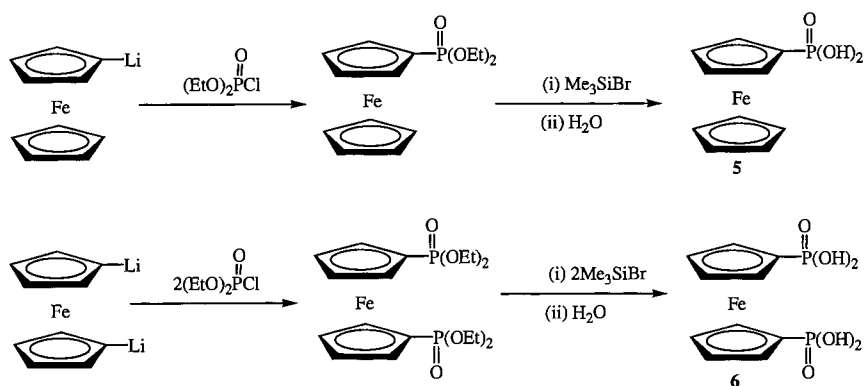
Scheme 3.

(OEt)$_2$ and 1,1′-Fc′[P(O)(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$_3$. FcP(O)(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′-Fc′(CH$_2$OH)$_2$ which was chlorinated with PCl$_3$ in a known procedure [27] to give the reactive dichloride 1,1′-Fc′(CH$_2$Cl)$_2$. This was reacted, without purification, with excess refluxing P(OEt)$_3$ to give 1,1′-Fc′[CH$_2$P(O)(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}P–{^{1}H}-NMR spectra, e.g. at δ 23.1 for FcCH$_2$-P(O)(OH)$_2$ (**3**). Spectra recorded in alkaline D$_2$O 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 FcP(O)(OPh)$_2$ (**8**) and 1,1′-Fc′[P(O)(OPh)$_2$]$_2$ (**9**). The reaction of (PhO)$_2$P(O)Cl with FcLi and 1,1′-Fc′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 (PhO)$_2$P(O)Cl had some bearing on the outcome of the reaction. If FcLi is added to a solution of (PhO)$_2$P(O)Cl the reaction proceeded as expected. However, the reverse order of addition led to
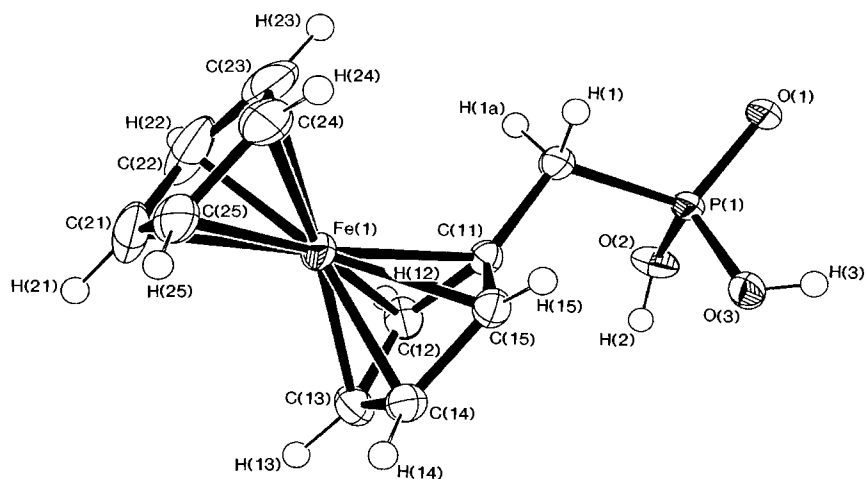
Fig. 1. Molecular structure and atom numbering scheme of FcCH$_2$P(O)(OH)$_2$ (**3**); non-hydrogen atom ellipsoids are shown at the 50% probability level.
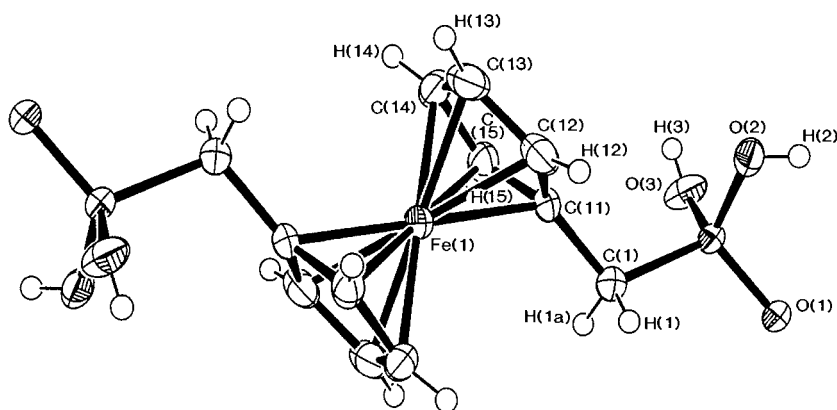

Fig. 2. Molecular structure and atom numbering scheme of 1,1′-Fc′[CH$_2$P(O)(OH)$_2$]$_2$ (**7**); non-hydrogen atom ellipsoids are shown at the 50% probability level.

two products (in ca. 1:1 ratio by ^{31}P-NMR) which were isolated by chromatography and identified as the expected phenyl ester FcP(O)(OPh)$_2$ (**8**) and a second product characterized 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 Fc$_2$P(O)(OPh).

2.3. X-ray crystal structure determinations of FcCH$_2$P(O)(OH)$_2$ (3) and 1,1′-Fc′[CH$_2$P(O)(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 interest recently in structural features of metallocene-derived carboxylic acids [28], and the structures of **3** and **7** are the first of the ferrocenylphosphonic acids.

The molecular structures of **3** and **7** are shown in Figs. 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–CH$_2$–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 eight 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 serves to hold the structure together. Individual hydrogen bonding interactions are shown in Fig. 3, while the overall lattice is depicted in Fig. 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 (Fig. 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

Fig. 3. Hydrogen bonding interactions involving **3**, showing the formation of eight-membered HO–P=O···HO–P=O rings.

Table 1
Selected bond lengths ^{a} (Å) and bond angles (°) for **3**

Bond lengths			
CpFe–C av	2.054(16)	P(1)–O(2)	1.566(1)
Range	2.045–2.064	P(1)–O(3)	1.568(1)
CpC–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)		
Bond angles			
C(11)–C(15)	107.57(12)	O(1)–P(1)–O(2)	113.28(6)
range	–108.54(12)		
C(21)–C(25)	107.6(2)	O(1)–P(1)–O(3)	108.86(6)
range	–108.2(2)		
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)		

^{a} Non-bonded O···O distances: O(1)···O(2a) 2.5932, O(1)···O(3b) 2.5982 Å.

Table 2
Selected bond lengths ^{a} (Å) and bond angles (°) for **7**

Bond lengths			
CpFe–C av	2.039(2)	P(1)–O(3)	1.548(2)
Range	2.037–2.042	P(1)–O(2)	1.551(1)
CpC–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)		
Bond angles			
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)–H(2)	119.5(2)
C(11)–C(1)–P(1)	112.68(12)	P(1)–O(3)–H(3)	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)		

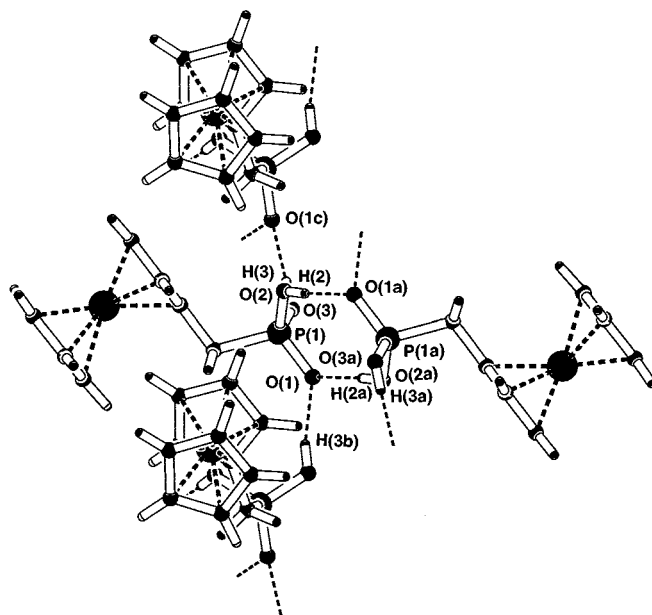^{a} Non-bonded O···O distances: O(1)···O(2a) (in chain) 2.5745; O(1)···O(3b) (cross chain) 2.5662 Å.

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 $C_5H_4CH_2P(O)(OH)_2$ 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 cross-linked by further hydrogen bonding interactions, as shown in Fig. 5. A similar infinite chain motif is found in the crystal structures of the bisphosphonic acid series $(HO)_2P(O)–(CH_2)_n–P(O)(OH)_2$ ($n = 1$, [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.
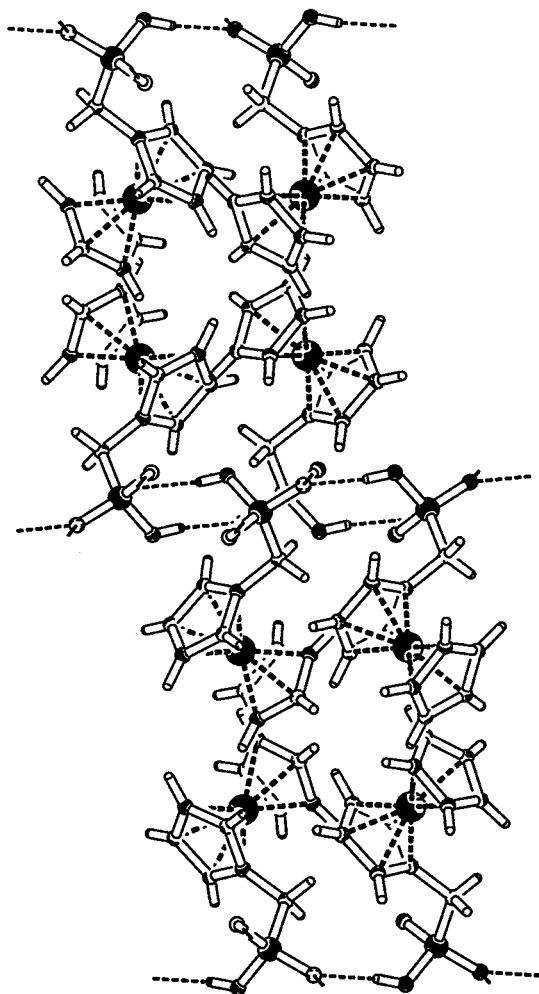
Fig. 4. The hydrogen bonded lattice of 3, showing ferrocene bi-layers held together by hydrogen bonding.

2.4. Synthesis of the ferrocene-derived arsonic acid FcCH₂CH₂As(O)(OH)₂ (10)

The Meyer reaction [33] has been used widely 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 ferrocenyl-methylating agents $FcCH_2NMe_3I$ 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

$FcCH_2As(O)(OH)_2$. Instead only starting material and $FcCH_2OH$ were obtained on work-up. Sodium arsenite solution is strongly basic, and presumably effects hydrolysis of $FcCH_2NMe_3^+$ and the reactive chloride $FcCH_2Cl$ to $FcCH_2OH$ [35].

The reaction of $FcCH_2CH_2Br$ with sodium arsenite was more successful, with the arsonic acid $FcCH_2CH_2As(O)(OH)_2$ being isolated in a 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 $FcCH_2CH_2P(O)(OH)_2$], 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, Fig. 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 $[Fe\{\eta^5\text{-}C_5H_4(CH_2)_nPO_3\}]^-$ ($n = 1$ 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
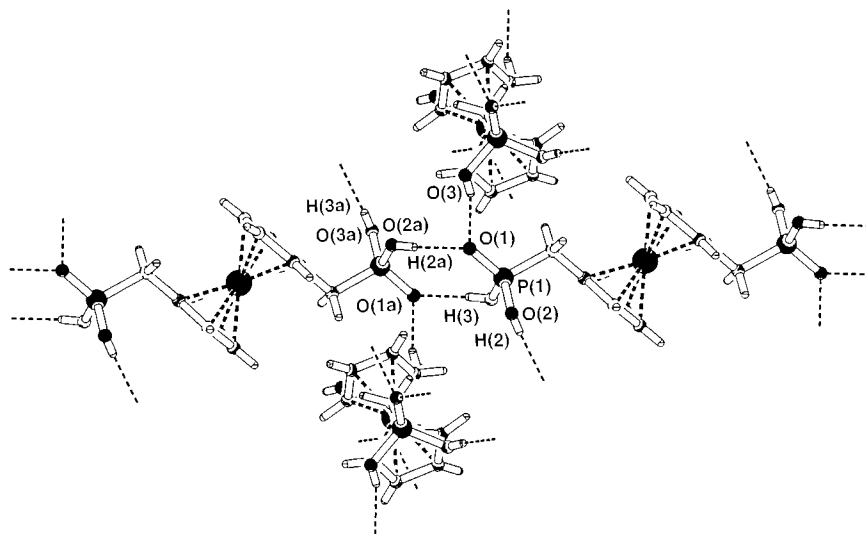

10   11   12
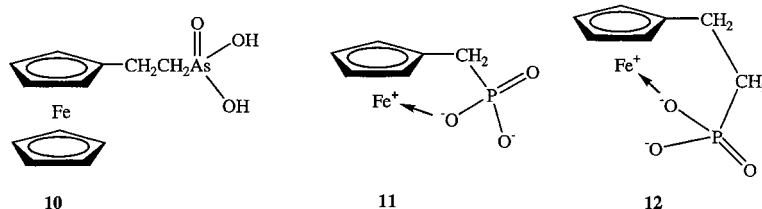
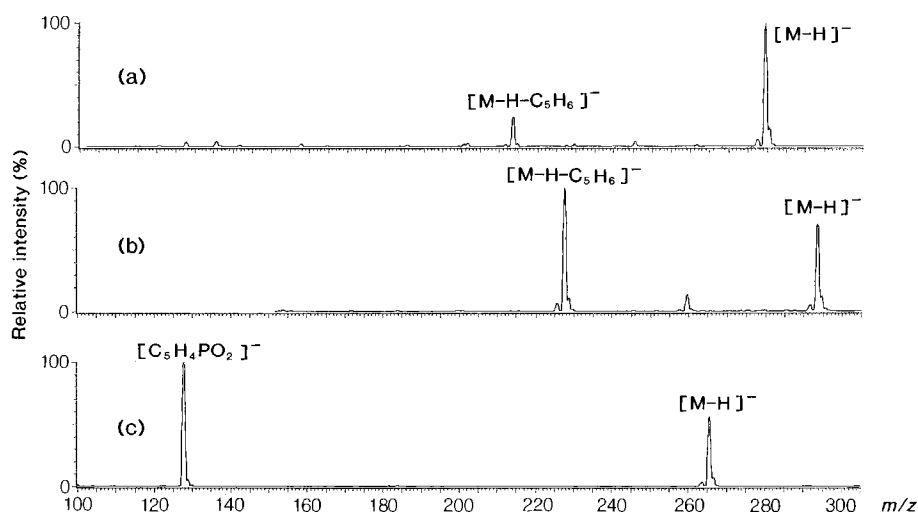Fig. 5. The hydrogen bonding network in the structure of **7**.

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 $[M-H-C_5H_6]^-$ ions for **3** and **4** (see structures **11** and **12**) and the formation of the $[C_5H_4PO_2H]^-$ ion for **5**.

$[M-H-C_5H_6]^-$ ion in the spectra of **4** when compared to **3**, as illustrated in Fig. 6 at a cone voltage of 100 V. The extra CH_2 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, $[Fe\{\eta^5\text{-}C_5H_4CH_2P\text{-}(O)(OPh)_2\}]^+$ was observed in high cone voltage spectra of $FcCH_2P(O)(OPh)_2$, 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 H_2O from $[M-H]^-$ (possibly giving a cyclic P–O–P anhydride) and the latter corresponds to the

$[C_5H_4PO_2H]^-$ 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 $[M-C_5H_5]^+$ ion appeared and

increased in intensity as the cone voltage was increased, similar to the behaviour reported for $FcCH_2P(O)(OPh)_2$ [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 [41–43] 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 added specifically 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 (CaH_2), 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), PCl_3 (Aldrich), As_2O_3 (BDH), TMEDA (BDH), phenylarsonic acid (BDH) and ferrocene (Strem) were used as supplied. The compounds $FcCH_2P(O)(OPh)_2$ [21], $FcCH_2OH$ [47], $FcCH_2CH_2Br$ [48], FcLi [49], 1,1′-Fc′Li_2 [50], Me_3SiBr [51], $(PhO)_2P(O)H$ [52], $(RO)_2P(O)Cl$ (R = Et, Ph) [53] and $FcCH_2Cl$ [54] were prepared according to literature procedures, or minor variations thereof. 1,1′-Fc′$(CH_2OH)_2$ was prepared by reaction of 1,1′-Fc′Li_2 with $(CH_2O)_n$, followed by aqueous work-up.

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 CH_2Cl_2 solution. 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 SpectaSystem 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
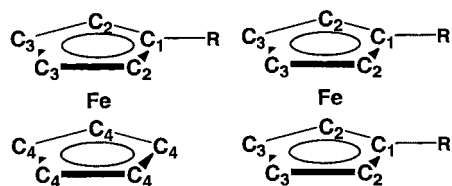
Scheme 4. Atom labeling used in assignment of ferrocenyl NMR signals; hydrogen atoms are numbered according to the carbon to which they are bonded.

all ^{31}P-NMR spectra; chemical shifts are relative to an external reference of 85% orthophosphoric acid (δ 0.0). ^{13}C- and ^{1}H-NMR spectra were obtained on a Bruker AC300P (^{1}H, 300.13 MHz; ^{13}C 75.47 MHz) or a Bruker DRX400 (^{1}H, 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 (^{1}H), 77.06 (^{13}C); Me$_2$SO-d^6, 2.6 (^{1}H), 39.5 (^{13}C); D$_2$O, 3.5 (MeOH, ^{1}H), 49.3 (MeOH, ^{13}C). Acid samples were often dissolved in NaOD–D$_2$O solution, prepared by reaction of a small amount of Na (~ 1–3 mg) with excess D$_2$O (~ 2 ml). Two-dimensional NMR experiments were used to unambiguously assign spectra for compounds **2**, **3**, **4**, **8**, and **9**. 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 FcCH$_2$P(O)(OPh)(OH) (1)

To a solution of FcCH$_2$P(O)(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 psi) and agitated for 4 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$_2$Cl$_2$ (10 ml) and extracted with 10% aqueous NaHCO$_3$ (2 × 10 ml). The combined aqueous fractions were washed with CH$_2$Cl$_2$ (10 ml), acidified with concentrated HCl then extracted with CH$_2$Cl$_2$ (2 × 10 ml). The combined organic fractions were dried over MgSO$_4$ 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. Anal. Found: C, 57.4; H, 4.9. Calc. for C$_{17}$H$_{17}$FeO$_3$P: C, 57.3; H, 4.8%. ^{31}P–{^{1}H}-NMR (CDCl$_3$): δ 26.5. ^{13}C–{^{1}H}-NMR (CDCl$_3$): δ 150.18 (d, $^2J_{C,P}$ 11 Hz, 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, $^1J_{C,P}$ 140 Hz, CH_2P). ^{1}H-NMR (CDCl$_3$): δ 7.24–6.90 (5H, m, Ph), 4.24 (2H, br s, H3), 4.13 (7H, br s, H2, H4), 2.95 (d, $^2J_{H,P}$ 21 Hz, CH_2P). ESMS: (MeOH–H$_2$O, cone voltage 20V) m/z 355 ([M−H]$^-$, 100%), 325 ([M−H + MeOH]$^-$, 10%). IR (solution in CH$_2$Cl$_2$) (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 FcCH$_2$P(O)(OEt)(OH) (2)

(EtO)$_2$P(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 h). To the hot solution was added FcCH$_2$OH (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% NaHCO$_3$ solution added. The resulting two-phase system was stirred for 10 min before the layers were separated.

The aqueous layer was washed with Et$_2$O (40 ml), acidified with concentrated HCl and extracted with CH$_2$Cl$_2$ (3 × 30 ml). The combined CH$_2$Cl$_2$ fractions were dried over MgSO$_4$ 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). Anal. Found: C, 50.3; H, 5.6. Calc. for C$_{13}$H$_{17}$FeO$_3$P: C, 50.7; H, 5.6%. ^{31}P–{^{1}H}-NMR (CDCl$_3$): δ 29.1. ^{13}C–{^{1}H}-NMR (CDCl$_3$): δ 16.33 (d, $^3J_{C,P}$ 6.4 Hz, OCH$_2$$CH_3$), 28.24 (d, $^1J_{C,P}$ 142 Hz, CH_2P), 61.56 (d, $^2J_{C,P}$ 6.9 Hz, OCH_2CH$_3$), 67.87 (s, C3), 68.91 (s, C4), 69.47 (d, $^3J_{C,P}$ 3.1 Hz, C2). ^{1}H-NMR (CDCl$_3$): δ 1.24 (3H, t, $^3J_{H,H}$ 7.0 Hz, OCH$_2$$CH_3$), 2.85 (2H, d, $^2J_{H,P}$ 19.9 Hz, CH_2P), 3.93 (2H, m, OCH_2CH$_3$), 4.09, (2H, d, $^3J_{H,H}$ 1.6 Hz, H3), 4.11 (5H, s, H4), 4.23 (2H, br s, H2), 6.7 (1H, br s, POH). ESMS: (MeCN–H$_2$O, cone voltage 20 V) m/z 307 ([M−H]$^-$, 100%), 325 ([M−H + H$_2$O]$^-$, 9%). IR (Solution in CH$_2$Cl$_2$) (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 FcCH$_2$P(O)(OH)$_2$ (3)

A solution of triethylamine (0.82 g, 8.1 mmol) and **2** (2.5 g, 8.11 mmol) in dry CH$_2$Cl$_2$ (50 ml) was placed under a nitrogen atmosphere in an oven-dried flask. Me$_3$SiBr (6.2 g, 40 mmol) was added and the mixture refluxed gently for 3 h. The reaction mixture was cooled to room temperature (r.t.), saturated aqueous NaHCO$_3$ 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 CH$_2$Cl$_2$ (2 × 25 ml) and acidified with concentrated HCl. The yellow precipitate was filtered and washed with water (2 × 50 ml) then air-dried to give 2.08 g (91%) of **3**, m.p. 222–228 °C (dec.). Anal. Found: C, 46.5; H, 4.7. Calc. for C$_{11}$H$_{13}$FeO$_3$P: C, 47.2; H, 4.7%. ^{31}P–{^{1}H}-NMR (Me$_2$SO): δ 23.1. ^{13}C–{^{1}H}-NMR (Me$_2$SO): δ 29.68 (d,

$^1J_{P-C}$ 134 Hz, CH_2P), 67.16 (s, C3), 68.66 (s, C4), 69.24 (br s, C2), 80.26 (br s, C1). ^{1}H-NMR (Me$_2$SO): δ 2.65 (2H, d, $^2J_{P-H}$ 19 Hz, CH_2P), 4.00 (2H, s, H3), 4.07 (5H, s, H4), 4.15 (2H, s, H2). ESMS: (MeCN–H$_2$O, 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 FcCH$_2$CH$_2$P(O)(OH)$_2$ (4)

FcCH$_2$CH$_2$Br (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 r.t.). The residue[1] was dissolved in CH$_2$Cl$_2$ (10 ml) and placed under a nitrogen atmosphere. Triethylamine (1.47 g, 14.5 mmol)[2] and Me$_3$SiBr (2.22 g, 14.5 mmol) were added and the reaction stirred for 4 h at r.t. Sodium hydroxide (1 M, 20 ml) was added and stirring continued for 30 min. The layers were separated and the aqueous layer washed with CH$_2$Cl$_2$ (2 × 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.). Anal. Found: C, 49.1; H, 5.3. Calc. for C$_{12}$H$_{15}$FeO$_3$P: C, 49.1; H, 5.1%. ^{31}P–{^{1}H}-NMR (Me$_2$SO-d_6): δ 26.6. ^{13}C–{^{1}H}-NMR (Me$_2$SO-d_6): δ 22.54 (d, $^2J_{C-P}$ 2 Hz CH_2CH$_2$P), 28.66 (d, $^1J_{C-P}$ 101 Hz, CH_2P), 66.87 (s, C3), 67.33 (s, C2), 89.05 (d, $^3J_{C-P}$ 16 Hz, C1). ^{1}H-NMR (Me$_2$SO-d^6): δ 1.84 (2H, d, $^2J_{H-P}$ 18 Hz, CH_2P), 2.46 (2H, br s, CH_2CH$_2$P), 4.03 (2H, br s, H3), 4.09 (9H, m, H2, H4), 7.22 (1.6H, br s, P–OH). ESMS: (MeCN–H$_2$O, cone voltage 20 V) m/z 293 ([M−H]$^-$ 100%), 311 ([M−H + H$_2$O]$^-$ 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).

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. ^{t}BuLi (0.6 ml, 1.7 M, 4.16 mmol) was added and the solution stirred for 15 min. (EtO)$_2$P(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 H$_2$O (20 ml) and CH$_2$Cl$_2$ (20 ml). The layers were separated and the organic phase

washed with H$_2$O (2 × 20 ml) before being dried over MgSO$_4$, 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 CH$_2$Cl$_2$ (10 ml) and placed under a nitrogen atmosphere. Freshly distilled Me$_3$SiBr (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 CH$_2$Cl$_2$ (5 ml). To this was added H$_2$O (0.10 g, 5.56 mmol). Precipitation of the acid began within 5 min. After 30 min the product was filtered and washed with CH$_2$Cl$_2$, then air-dried to give 0.31 g (24%) of 5 as a microcrystalline yellow solid, m.p. 198–205 °C (dec.). Anal. Found: C, 44.5; H, 4.2. Calc. for C$_{10}$H$_{11}$FeO$_3$P: C, 45.2; H, 4.1%. ^{31}P–{^{1}H}-NMR (Na salt in D$_2$O): δ 15.3. ^{13}C–{^{1}H}-NMR (Na salt in D$_2$O): δ 69.76 (s, C4), 70.55 (d, $^3J_{C,P}$ 9.6 Hz, C3), 71.26 (d, $^2J_{C,P}$ 11.3 Hz, C2), 73.33 (d, $^1J_{C,P}$ 154 Hz, C1). ^{1}H-NMR (Me$_2$SO-d^6): δ 4.14 (2H, br s, H3), 4.21 (5H, br s, H4), 4.28 (2H, br s, H2). ESMS: (MeCN–H$_2$O, 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}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 (EtO)$_2$P(O)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$_2$Cl$_2$ (20 ml). The phases were separated and the aqueous layer further extracted with CH$_2$Cl$_2$ (2 × 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$_2$Cl$_2$ (10 ml) was placed under nitrogen, freshly distilled Me$_3$SiBr (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.). Anal. Found: C, 34.5; H, 3.3. Calc. for C$_{10}$H$_{12}$FeO$_6$P$_2$: C, 34.7; H, 3.5%. ^{31}P–

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[1] Separation of the diethyl-ester intermediate [FcCH$_2$CH$_2$P-(O)(OEt)$_2$] by flash column chromatography (Al$_2$O$_3$, EtOAc to MeOH solvent gradient) prior to hydrolysis did not improve the overall yield.

[2] The triethylamine can be omitted if the trimethylsilylbromide is freshly distilled and glassware is dry.

{^{1}H}-NMR (Na salt in D$_2$O): δ 21.7. ^{13}C–{^{1}H}-NMR (Na salt in D$_2$O): δ 72.09 (d, $^1J_{C,P}$ 149 Hz, C1), 72.52 (d, $^3J_{C,P}$ 10 Hz, C3), 72.71 (d, $^2J_{C,P}$ 12 Hz, C2). ^{1}H-NMR (Na salt in D$_2$O): δ 4.5–4.7 (8H, m, H2, H3), 8.80 (4H, br s, POH). ESMS: (MeCN, cone voltage 80 V) m/z 345 ([M–H]$^-$, 100%), 327 ([M–H–H$_2$O]$^-$, 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′[CH$_2$P(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 PCl$_3$ (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′(CH$_2$Cl)$_2$. 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 CH$_2$Cl$_2$ (10 ml) and the solution placed under a nitrogen atmosphere. Me$_3$SiBr (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.). Anal. Found: C, 37.4; H, 4.4. Calc. for C$_{12}$H$_{16}$FeO$_6$P$_2$: C, 38.5; H, 4.3%. ^{31}P–{^{1}H}-NMR (Na salt in D$_2$O): δ 19.0. ^{13}C–{^{1}H}-NMR (Na salt in D$_2$O): δ 32.84 (d, $^1J_{C,P}$ 76 Hz, CH_2P), 69.64 (s, C2), 72.20 (s, C3), 86.50 (d, $^2J_{C,P}$ 2 Hz C1). ^{1}H-NMR (Na salt in D$_2$O): δ 2.49 (4H, d, $^2J_{P,H}$ 12.3 Hz, CH_2P), 3.98 (4H, br s, H3), 4.12 (4H, br s, H2). ESMS: (MeCN–H$_2$O, cone voltage 20 V) m/z 373 ([M–H]$^-$, 100%). 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. ^{t}BuLi (2.9 ml, 1.7 M, 5 mmol) was added and the solution stirred for 15 min. This solution was added dropwise to a solution of (PhO)$_2$P(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$_2$O (20 ml) and CH$_2$Cl$_2$ (20 ml). The layers were separated and the organic phase washed with H$_2$O (2 × 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$_2$Cl$_2$: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. Anal. Found: C, 62.3; H, 4.7. Calc. for C$_{22}$H$_{19}$FeO$_3$P: C, 63.2; H, 4.6%. ^{31}P–{^{1}H}-NMR (CDCl$_3$): δ 20.6. ^{13}C–{^{1}H}-NMR (CDCl$_3$): δ 65.45 (d, $^1J_{C,P}$ 166 Hz, C1), 70.12 (s, C4), 71.90 (dd, $^2J_{C,P}$ 12 Hz, $^3J_{C,P}$ 11 Hz, C2, C3), 120.73 (d, $^3J_{C,P}$ 3 Hz, o-C), 124.93 (s, p-C′), 129.72 (d, $J_{C,P}$ 10 Hz, m-C), 150.86 (d, $^2J_{C-P}$ 6 Hz, i-C). ^{1}H-NMR (CDCl$_3$): δ 4.25 (5H, s, H4), 4.46 (2H, s, H3), 4.62 (2H, d, $^2J_{C,P}$ 1.2 Hz, H2), 7.1–7.4 (10H, m, Ph). ESMS: (MeCN–H$_2$O, positive ion, cone voltage 60 V) m/z 419 ([M + H]$^+$, 100%), 436 ([M + H$_2$O]$^+$, 31%), 460 ([M + MeCN]$^+$, 11%). IR (solution in CH$_2$Cl$_2$) (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. ^{n}BuLi (6.72 ml, 1.6 M, 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)$_2$P(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 × 10 ml). Water (20 ml) and CH$_2$Cl$_2$ (20 ml) were added and the flask agitated until dissolution was complete. The layers were separated and the organic phase washed with water (2 × 20 ml), dried over MgSO$_4$ and the solvent removed. The resulting brown oil was purified by silica flash column chromatography using a CH$_2$Cl$_2$: EtOAc:MeOH solvent gradient. The mono-substituted byproduct, FcP(O)(OPh)$_2$ eluted in EtOAc:CH$_2$Cl$_2$, 1:9, while the desired product eluted in EtOAc:CH$_2$Cl$_2$, 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. Anal. Found: C, 62.7; H, 4.5. Calc. for C$_{34}$H$_{29}$FeO$_6$P$_2$: C, 62.8; H, 4.3%. ^{31}P–{^{1}H}-NMR (CDCl$_3$): δ 26.2. ^{13}C–{^{1}H}-NMR (CDCl$_3$): δ 73.53 (d, $^2J_{C,P}$ 16 Hz, C2), 74.60 (d $^3J_{C,P}$ 14 Hz, C3), 120.63 (d $^3J_{C,P}$ 4 Hz, o-C), 125.14 (s, p-C), 128.66 (d, $^1J_{C,P}$ 61 Hz, C1), 129.74 (s, m-C), 150.59 (d, $^2J_{C,P}$ 8 Hz, i-C).

Table 3
Crystal data and analysis parameters for $FcCH_2P(O)(OH)_2$ (3) and $1,1'$-$Fc'[CH_2P(O)(OH)_2]_2$ (7)

Empirical formula	$C_{11}H_{13}O_3Pfe$	$C_{12}H_{16}O_6P_2Fe$
Crystal size (mm)	$0.34 \times 0.29 \times 0.21$	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	$Pbca$	$P2_1/c$
Z	8	2
D_{calc} (g cm^{-3})	1.634	1.702
$F(000)$	1152	384
μ(Mo-K_α) (mm^{-1})	1.45	1.28
Temperature (K)	293(2)	293(2)
2θ Range for data collection (°)	$2 < \theta < 27$	$2 < \theta < 27$
Total reflections	23529	4242
Unique reflections	2534	1577
	($R_{int} = 0.0224$)	($R_{int} = 0.016$)
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 [a]	0.0613 [b]
Goodness-of-fit	1.053	0.971

[a] $w = [\sigma^2(F_o^2) + (0.0313P^2 + 1.2852]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.
[b] $w = [\sigma^2(F_o^2) + (0.0328P^2 + 0.4962P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.

^{1}H-NMR (CDCl$_3$): δ 4.60 (4H, s, H3), 4.70 (4H, d, $^3J_{H,P}$ 1 Hz, 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$_2$Cl$_2$) (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$_2$O$_3$, 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$_2$CH$_2$Br (0.7 g, 2.4 mmol) in CH$_2$Cl$_2$ (5 ml) was added, the CH$_2$Cl$_2$ 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$_2$Cl$_2$ 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. Anal. Found: C, 42.7; H, 4.7. Calc. for C$_{12}$H$_{15}$AsFeO$_3$: C, 42.6; H, 4.5%. ^{13}C–{^{1}H}-NMR (Na salt in D$_2$O): δ 22.65 (s, CH_2Cp), 31.21 (s, CH_2As), 67.67 (s, C3), 68.02 (s, C2), 69.06 (s, C4), 90.08 (s, C1). ^{1}H-NMR (Na salt in D$_2$O): δ 2.30 (2H, m, CH_2As), 2.85 (2H, m, CH_2Cp), 4.24 (2H, br s, H3), 4.46 (7H, br s, H2, H4). ESMS: (MeOH, cone voltage 40 V) m/z 351 ([M$-$2H + Me]$^-$, 30%), 337 ([M$-$H]$^-$, 100%), 259 ([M$-$2H$^-$CpCH$_2$CH$_2$ + Me]$^+$ 6%), 245 ([M$-$H$-$CpCH$_2$CH$_2$), 10%). IR (solution in CH$_2$Cl$_2$) (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 a reducing agent. 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_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 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}.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 158654 for complex 3 and CCDC no. 158655 for complex 7. 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; e-mail: deposit@ ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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