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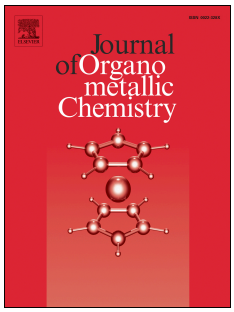

Synthesis and structure of ferrocenylphosphinic acids

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The intermolecular hydrogen bonding in mono-substituted ferrocenylphosphinic acid Fc(P(R)(O)(OH)) (R = H, Me, Et, Ph) proceeds highly stereoselectively with formation of enantiomorphous chains. In disubstituted acids 1,1'-$Fc(P(R)(O)(OH))_2$ (R = Me, Et, Ph) molecular and crystal structure is determined by the competition of intermolecular and intramolecular hydrogen bonding.

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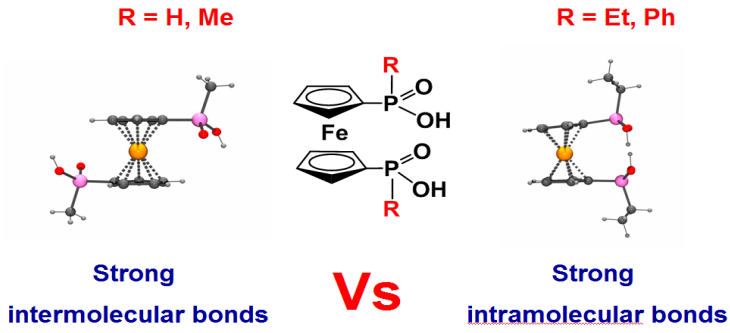

Synthesis and structure of ferrocenylphosphinic acids

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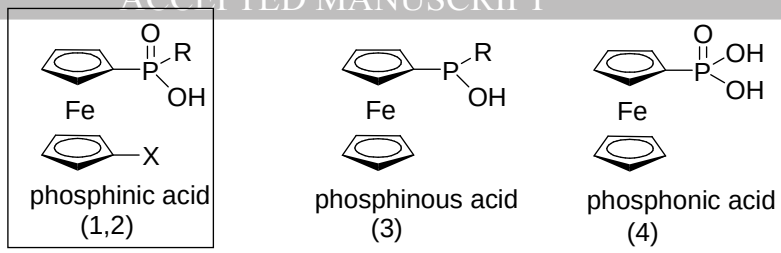
Keywords: Ferrocene / Phosphinic acid / Structure / Hydrogen bond

*The series of ferrocenylphosphinic acids Fc(P(R)(O)(OH)) (**1a-d**) and ferrocene-1,1'-diyl-phosphinic acids Fc(P(R)(O)(OH))$_2$ (**2a-d**) (R = H (a), Me (b), Et (c), Ph (d)) have been obtained and studied using X-ray single crystal diffraction, IR-spectroscopy and quantum chemistry. The intermolecular hydrogen bonding in **1a-d** proceeds highly stereoselectively and results in formation of racemic conglomerate of **1d**. The formation of inter- and intra-molecular hydrogen bonds for disubstituted acids **2c-d** depends on substituent at phosphorus atoms.*

Introduction

The arylphosphinic acids ArP(R)(O)(OH) (R = H, alkyl, aryl) are widely used for the construction of self-assembled two- and three- dimensional structures or single molecular magnets (SMM) based on p- [1], d- [2] and f- [3] metals, e.g., Ru [4] and Mn [5] complexes. The replacement of the aryl fragment in these acids for the cognate ferrocenyl fragment, containing redox-active iron atom, may result in additional interesting properties like enhanced exchange interactions and give the opportunity to make sensors or switchable devices.

However ferrocenylphosphinic acids (**1, 2**) are poorly studied in contrast to other ferrocenyl-containing phosphorus acids. For example, ferrocenylphosphinous acids (**3**) existing as the mixtures of two tautomeric forms have been widely employed as ligands in transition metals catalysis of cross-coupling reactions [6,7], asymmetric hydrogenation [8] etc. Ferrocenylphosphonic acid (**4**) has been considered as redox-active pH-responsive molecule and the redox half-wave potential of ferrocenylphosphonates is sensitive to the bonding mode with metal atoms [9-14].



R = H: X = H (**1a**), P(O)(OH)H (**2a**)
R = Me: X = H (**1b**), P(O)(OH)Me (**2b**)
R = Et: X = H (**1c**), P(O)(OH)Et (**2c**)
R = Ph: X = H (**1d**), P(O)(OH)Ph (**2d**)

The data on the synthesis, structure and redox properties of ferrocenylphosphinic acids are scarcely presented, although their first synthesis dates back to 1962: Solott and Howard found that ferrocene reacts with PCl_3 under Fridel-Crafts reaction conditions in the presence of $AlCl_3$ to form (**1a**) and (**2a**) with the yield of 3.2% and 4.6% respectively after the hydrolysis [15]. Diferrocenylphosphinic acid was also isolated from this mixture [16]. The yield of (**1a**) was slightly improved to 8.6% using Me_2NPCl_2 as starting reagent instead of PCl_3 [17]. The formation of (**1a**) as a side-product has been also observed in the hydrolysis of diphosphene tbtP=PFc (tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]-phenyl, Fc = ferrocenyl) [18]. Ferrocenylphenylphosphinic acid (**1d**) was obtained in high yield of 92% *via* the reaction of ethyl ferrocenylphenylphosphinate Fc(Ph)P(O)OEt with Me_3SiBr and the following hydrolysis [19]. However the preparation of Fc(Ph)P(O)OEt was based on the use of hazardous gas Cl_2 [19].

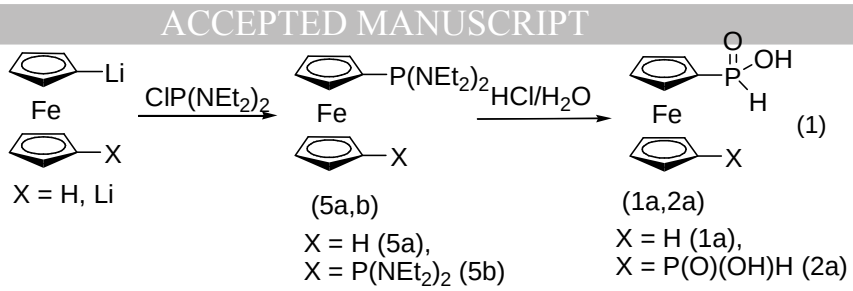
It should be mentioned that no information on the conformational behaviour or hydrogen bonding of ferrocenylphopshinic acids (**1,2**) is available although intra- or intermolecular hydrogen bonding is very important for their coordination properties and self-organization into novel coordination polymers and metal-organic frameworks [20]. In this respect ferrocenylphosphinic acids (**1,2**) are especially attractive due to opportunity to effectively tune both conformation and hydrogen bonding by variations of substituents at phosphorus atoms.

Hereon we report on the preparation and structure of a series of mono- and disubstituted ferrocenylphosphinic acids.

Results and Discussion

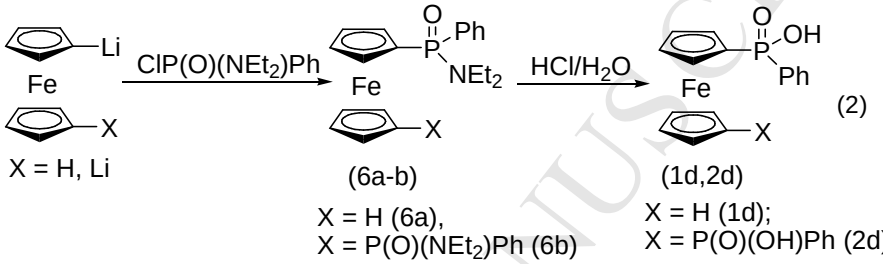
Synthesis

For the preparation of ferrocenylphosphinic acids we have elaborated a new method based on the high reactivity of P-N bond towards acid hydrolysis. Indeed we have found that the heating of ferrocene-1,1'-diyl-bis(diaminophosphine) (**5b**) [21,22] with 10% HCl results in formation of ferrocene-1,1'-diyl-bis(H-phosphinic acids) (**2a**) with good yield (eq.1).

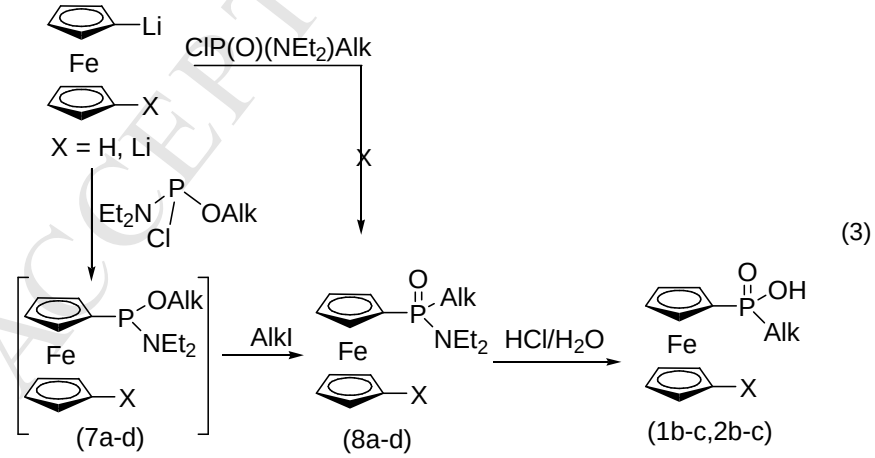


In similar manner the hydrolysis of diaminoferrocenylphosphine (**5a**) obtained by the reaction of mono-lithiated ferrocene FcLi with $ClP(NEt_2)_2$ leads to ferrocenyl(H-phosphinic acid) (**1a**).

In similar manner ferrocenyl(phenyl)phosphinic (**1d**) and ferrocene-1,1'-diyl-bis(phenylphosphinic acid) (**2d**) were obtained in good yield (eq.2) using amidochlorophenylphosphinate $PhP(O)(Cl)NEt_2$ as a starting reagent.



However the reaction of lithiated ferrocene derivatives FcLi or $FcLi_2$ with alkylamidochlorophosphonates $AlkP(O)(NEt_2)Cl$ (Alk = Me, Et) takes place neither at low temperature nor upon heating. Therefore for the preparation of alkyl substituted ferrocenylphosphinic acids (**1b-c**, **2b-c)** we have used a three step route including the reaction of FcLi or $FcLi_2$ with alkyl(diethylamido)(chloro)phosphite to form alkylamidoferrocenylphosphonites (**7**) (eq.3).



Alk=Me: X=H (1b, 7a, 8a),$P(OMe)NEt_2$ (7c),$P(O)(NEt_2)Me$ (8c),P(O)(OH)Me (2b)
Alk=Et; X=H (1c, 7b, 8b),$P(OEt)NEt_2$ (7d),$P(NEt_2)(O)Et$ (8d),P(O)(OH)Et (2c)

The latter treated by iodoalkanes underwent Michaelis-Arbuzov rearrangement [23] to alkyl(ferrocenyl)amidophosphinates (**8**), which were hydrolyzed with 10% HCl to form the corresponding ferrocenyl(alkyl)phosphinic acids (**1b-c**, **2b-c**) with the overall yield ~50%.

Structure

All monosubstituted (**1a-d**) as well as three disubstituted ferrocene-1,1'-diyl-bisphosphinic acids (**2b-d**) gave single crystals suitable for X-ray diffraction study (figures 1-6, see also supplementary materials, figures S1-S2).

Phosphinic acids possess the ability to form strong hydrogen bonds in the solid state by virtue of the very electronegative O atoms bound to an electropositive P atom [24]. Simple phosphinic acids in the gas phase show almost twice the dimerization enthalpy of the analogous carboxylic acids [25].

One might expect the self-assembly of the molecules in the crystalline phase with the formation of acidic dimers typical for phenylphosphinic acid [26], however all the studied monosubstituted compounds (**1a-d**) exhibit the same supramolecular pattern – a hydrogen bonded polymeric chain along the twofold screw axis.

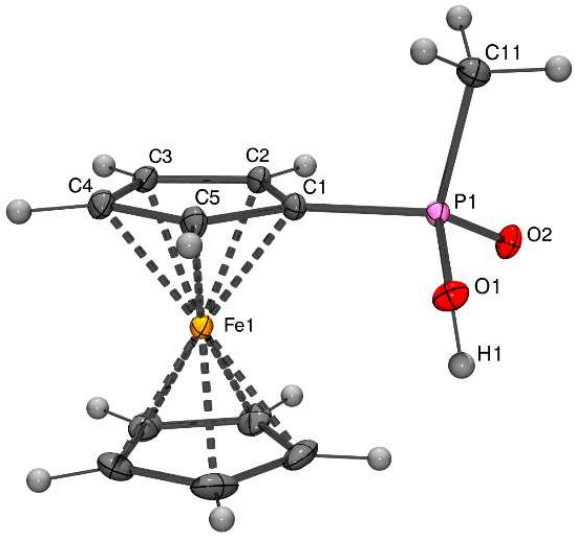


Figure 1. ORTEP view of ferrocenylmethylphosphinic acid (**1b**). Ellipsoids probability 50%.

It should be mentioned that the phosphorus atom in this series of monosubstituted ferrocenylphosphinic acids (**1a-d**) is chiral and the formation of enantiomorphous hydrogen-bonded chains indicates that chiral recognition occurs in these compounds. However, it is not the sufficient condition for the whole crystal to be chiral. The first members of the series (**1a**) and (**1b**) are racemates crystallizing in the centrosymmetric space group $P2_1/c$. The enantiomorphous chains are arranged in alternating fashion, and the secondary weak C-H…O interactions bound the chains consisting of opposite enantiomers (fig. 2).

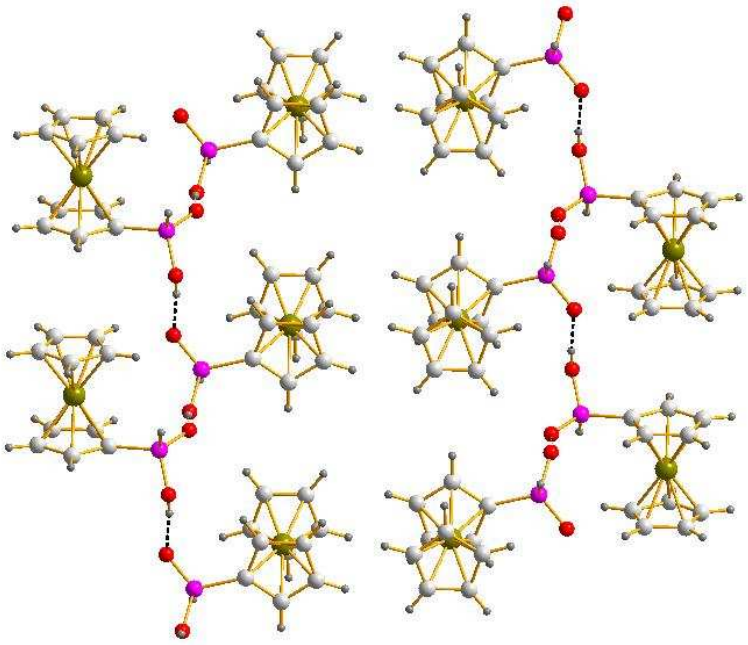


Figure 2 A fragment of crystal packing of ferrocenyl(H-phosphinic acid) (**1a**)

The same phenomena of chiral molecular recognition occurs in the crystals of the substituted acids (**1c, d**) with R= Et and Ph. However, the ethyl derivative (**1c**) was found to be a racemic twin, which means that each unit cell consists of one enantiomer but the crystal is made of both types of unit cells. In the crystals of the phenyl derivative (**1d**) two enantiomers crystallize separately with the Flack parameter being equal to 0.01(2) (fig.3) to form racemic conglomerate.

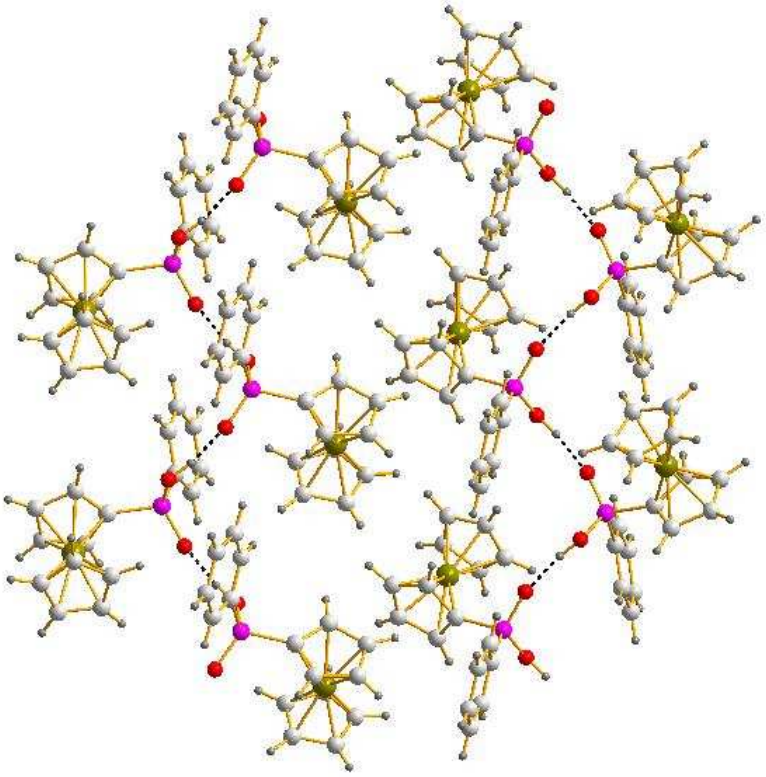


Figure 3 A fragment of crystal packing of ferrocenyl(phenyl)phoshinic acid (**1d**)

The introduction of the second phosphinic acid fragment into ferrocene results in drastically different hydrogen bonding patterns (fig.4,5). Thus the presence of two hydrogen bond donors and several acceptors in **2b** results in two-dimensional intermolecular hydrogen-bonded network in which each molecule is bound to four neighbors *via* strong hydrogen bonds (fig. 5).

These interactions determine the ideal *trans* orientation of two substituents and thus the skewed conformation of the Cp-ring of ferrocene fragment (fig.4).

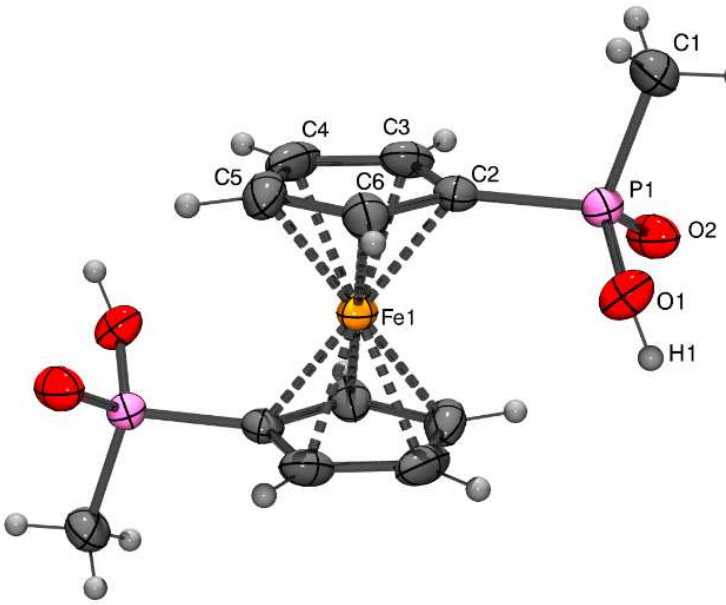


Figure 4. ORTEP view of 1,1'-ferrocenylene bis(methylphosphinic acid) (**2b**). Ellipsoids probability 50%.

It is interesting enough that completely different crystal structure is observed in ethyl and phenyl derivatives (**2c, d**), in which intramolecular contra intermolecular interactions determine the crystal packing.

The strong intramolecular hydrogen bonding between the two acidic fragments is observed in **2c** (fig. 6) and **2d** (fig. S2), that results in perfectly eclipsed conformation and causes a significant tilt of the two cyclopentadienyl rings from the parallel orientation. Oxygen atoms participate in multiple weak C-H…O intermolecular interactions which determine not only the packing motif, but also the molecular structure, in particular the orientation of substituents R respective to the ferrocenyl fragment (fig.6).

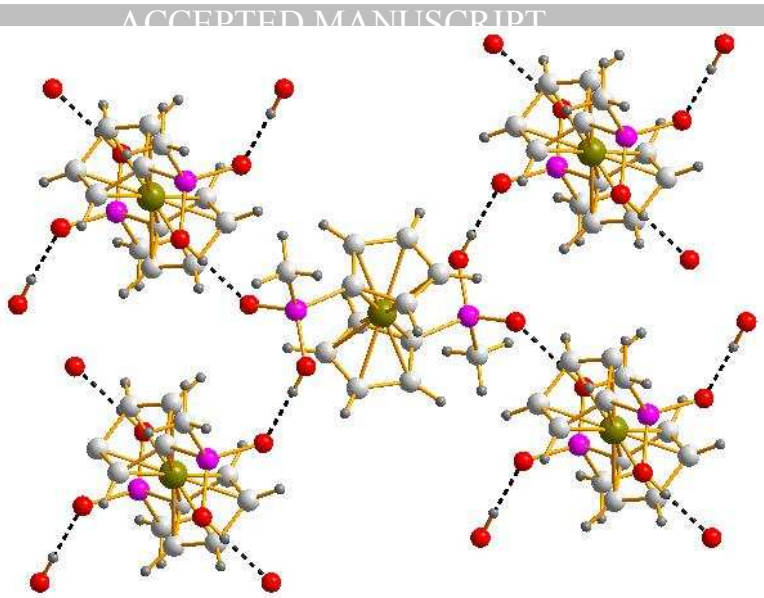


Figure 5. A fragment of crystal packing of **2b** showing hydrogen bonding scheme.

To obtain further information about hydrogen bonding in ferrocenylphosphinic acids (**1,2**) Density Functional Theory (DFT) computations combined with infrared (IR) spectroscopy were carried out. IR spectra of the compounds (fig.7) clearly point to strong hydrogen bonding between POH and P=O groups.

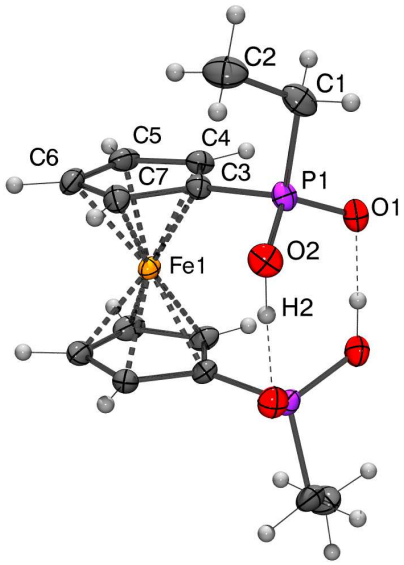


Figure 6. ORTEP view of 1,1'-ferrocenylene bis(ethylphosphinic acid) (**2c**). Ellipsoids probability 50%.

For the case of ferrocene-1,1'-diyl-bis(ethylphosphinic acid) (**2c**), taken as an example of the intramolecularly H-bonded species, DFT computations show that owing to this cooperative H-bonding there arises strong dynamic interaction of two νP=O and two δPOH oscillators. This results in complex vibrations of eight-membered cyclic system $(P{=}O\ldots H\text{-}O\text{-}P)_2$, producing three

bands in the spectral region between 1150 and 1250 cm^{-1} (fig. 7) instead of two bands (νP=O and δPOH) expected for the corresponding independent oscillators.

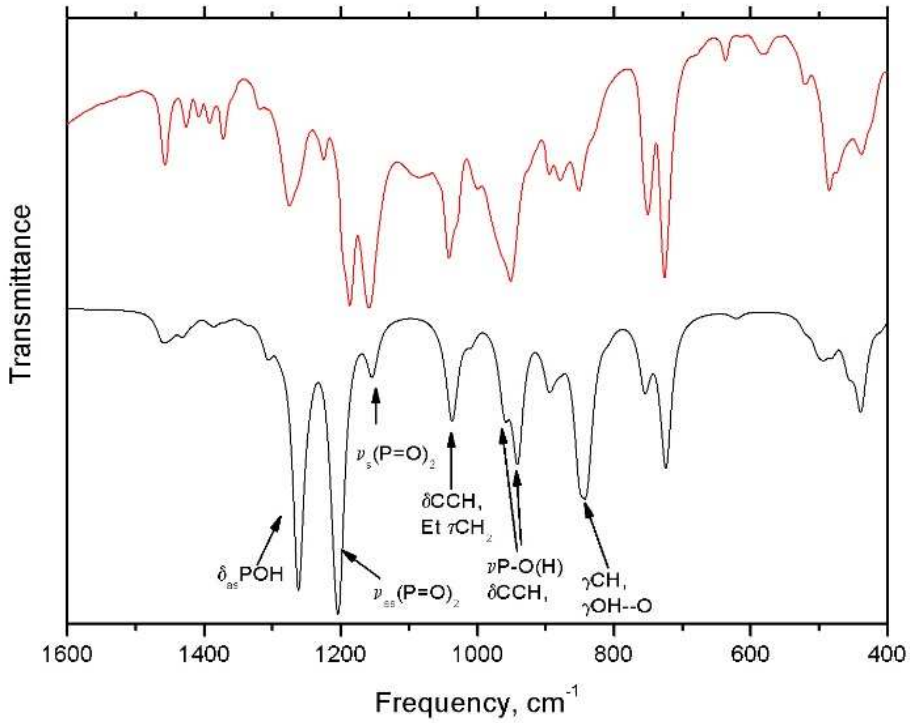


Figure 7. Experimental (red) and DFT simulated (black) IR spectra of ferrocene-1,1'-diyl-bis(ethylphosphinic acid) (**2c**). The simulated spectrum represents the computed frequencies and intensities, plotted with a Lorentzian broadening (f.w.h.m. = 10 cm-1)

We estimated the energy of the intramolecular H-bonds (EHB_{intra}) as the difference between the energies of conformers I and V of molecule **2a** (fig. 8). The former is stabilized by two intramolecular P=O…H-O-P bonds, while in the latter conformer the H-bonding is absent. Thus, the energy of formation of the two H-bonds in molecule **2a** roughly equals to 23 kcal/mol. Very similar values of 23 - 24 kcal/mol were obtained in the same way for the molecules **2b-d**.

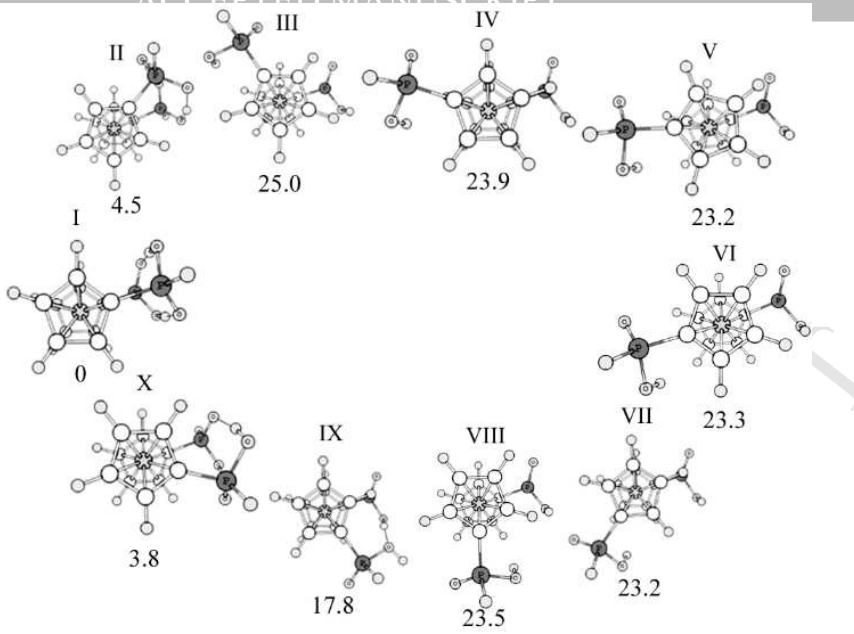


Figure 8. Conformations of ferrocene-1,1'-diyl-bis(H-phosphinic acid) (**2a**) and their computed energies (kcal/mol) relative to the energy of the most stable conformer I. Structures I and V are optimized without any constraints. The structures II, III, IV, VI, VII, VIII, IX, X are optimized with dihedrals (P)CYY'C'(P') fixed at 36°, 108°, 144°, 170°, -144°, -108°, -72° and -36° respectively, where Y designates the center of Cp ring. H-bonds are plotted with dotted lines.

The above approach seems reasonable as in the absence of H-bonds the "immanent" conformational energy of **2** depends on conformation of the ferrocenyl moiety only slightly. For example, the energies of conformations V-VIII (fig. 8) differ by no more than 0.3 kcal/mol. Similar conformational flexibility was found earlier for 1,1'-dimethylferrocene [27]. The barrier to internal rotation of RP(=O)OH moiety relative to ferrocenyl fragment, according to present computations, does not exceed 3 kcal/mol.

The energy of the intermolecular P=O…H-O-P hydrogen bonding (EHB_{inter}), calculated as the energy difference between the H-bonded dimer of molecules **1a** and two corresponding monomer species, amounts to 16.5 kcal/mol. This value, being larger than EHB_{intra} per one P=O…H-O-P bond (~11.5 kcal/mol for **2a**), is smaller than the enthalpy of H-bonding in the dimers of dimethyl-, bis(chloromethyl)- and diphenylphosphinic acids (24, 35 and 50 kcal/mol, respectively) [28].

Conclusions

The series of mono- and disubstituted ferrocenylphosphinic acids $Fc(P(R)(O)(OH))_n$ (n = 1,2; R = H, Me, Et, Ph) were obtained. The intermolecular hydrogen bonding in mono-substituted ferrocenylphosphinic acid Fc(P(R)(O)(OH)) (R = H (**1a**), Me (**1b**), Et (**1c**), Ph (**1d**)) proceeds

highly stereoselectively, with formation of enantiomorphous chains, which results in formation of racemic conglomerate in **1d**. In disubstituted acids 1,1'-Fc(P(R)(O)(OH))$_2$ (R = Me (**2b**), Et (**2c**), Ph (**2d**)) molecular and crystal structure is determined by the competition of intramolecular (**2b**) and intermolecular hydrogen bonding (**2c** and **2d**). Diversity of conformational forms of ferrocenylphosphinic acid along with possibility to adjust the hydrogen bonding by the variation of substituents at phosphorus atom opens a possibility to obtain novel coordination polymers or metal-organic frameworks with tunable properties.

Experimental Section

All reactions and manipulations were carried out under dry pure Ar in standard Schlenk apparatus. Hexane, THF, Et_2O were distilled from sodium/benzophenone and stored under argon before use. MeOH was dried and distilled over Mg [29]. The NMR spectra were recorded with a Bruker Avance-400 spectrometer (^{1}H: 400 MHz; ^{31}P: 161.7 MHz; ^{13}C: 100.6 MHz). $SiMe_4$ was used as the internal reference for ^{1}H and ^{13}C NMR chemical shifts, and 85% H_3PO_4 as the external reference for ^{31}P NMR spectroscopy. IR spectra were recorded on a FTIR spectrometer Bruker Vector-22 in the 400 – 4000 cm^{-1} range at optical resolution of 4 cm^{-1}. Solid samples were prepared as KBr pellets.

Ferrocene (Aldrich), n-butyl lithium (1.6M in hexanes (Aldrich)), t-butyl lithium (1.7M in pentane (Aldrich)), tetramethylethylenediamine (tmeda) (Aldrich), EtI (Aldrich), MeI (Aldrich) were used as supplied. Initial compounds $(Et_2N)_2PCl$ [30,31], $PhP(O)(Cl)NEt_2$ [32], $(EtO)P(Cl)NEt_2$ [33], $(MeO)P(Cl)NEt_2$ [34] were prepared according to literature procedures. Mono- and dilithiated ferrocene FcLi [35], $FcLi_2$ [36] were obtained on known procedure using ^{t}BuLi/KO^{t}Bu and n-BuLi/tmeda systems respectively.

Computational Aspects

All computations reported in this study were carried out using the Gaussian 03 [37] suite of programs. Calculations were performed with Becke's three parameter hybrid exchange functional [38] and the gradient-corrected nonlocal correlation functional of Lee, Yang and Parr (B3LYP) [39]. The ligand atoms H, C, O and P were treated with 6-31G* basis set [40], while for Fe atoms ECP LanL2DZ basis set [41] was used. This method was shown to produce good results when describing structural, energetic and spectroscopic parameters of ferrocenes and their pentaphospholyl analogues [27]. All stationary points were characterized as minima by analysis of the Hessian matrices. The calculated force fields were transformed to internal coordinates, and scaling procedure was applied using the program described in ref [42]. The transferable scaling factors employed in this work are summarized in Table 1S (ESI). The scaling factor of 1.25 was

taken for FeC stretchings as this value resulted in the best agreement between the calculated and the corresponding experimental vibrational frequencies of ferrocenes [27].

X-ray Structure Analyses

Data for crystals **1a-1d** and **2b** were collected on a Bruker Smart Apex II CCD diffractometer, for **2d** on a Bruker Kappa Apex II CCD diffractometer, for **2c** on a Bruker Kappa Apex Duo diffractometer using graphite-monochromated $Mo_{K\alpha}$ (0.71073 Å) radiation. Programs used: data collection APEX2 (Bruker, 2004) [43], COLLECT [44], data reduction SAINT (Bruker, 2004) [43], Dirax/lsq [45], EvalCCD [46], absorption correction SADABS version 2.10 (Sheldrick, Bruker AXS Inc., 2002) [43], structure solution SIR [47], SHELXS97 (Sheldrick, 1997) [48], structure refinement by full-matrix least-squares against F^2 using SHELXL-97 [48] and WinGX [49], graphics ORTEP3 for Windows [50].

1. Ferrocenylphosphonous acid N,N-diethylamide (**5a**). To solution of ferrocenyllithium FcLi obtained from ferrocene (21.1 g, 110 mmol), ^{t}BuOK (2.36 g, 21 mmol) and ^{t}BuLi (47 ml, 80 mmol) in 300 ml THF was added dropwise $(Et_2N)_2PCl$ (16.8 g, 80 mmol) at -78˚C. Reaction mixture was stirred for 6 hours at room temperature. Solvent was removed under reduced pressure and residue was purified by column chromatography to give 17,8 g (62%) of **5a** as orange oil. ^{1}H NMR ($CDCl_3$): δ 1.09 (tr, $^3J_{HH}$ = 7.2 Hz, 12H, CH_3), 2.91 (m, 8H, CH_2), 4.06 (s, 5H, Cp), 4.21 (br s, 2H, Hα-C_5H_4), 4.32 (br s, 2H, Hβ-C_5H_4). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 98.4 (s). Analysis (%). Calc. for $C_{18}H_{29}FeN_2P$ (360.26): C 55.6, H 6.3. Found: C 55.2, H 6.2.

2. Ferrocenyl(phenyl)phosphinic acid N,N-diethylamide (**6a**). In similar manner from ferrocene (21.1 g, 0.11 mmol), ^{t}BuOK (2.36 g, 0.021 mmol), ^{t}BuLi (50 ml, 1.6 M, 0.08 mmol) and PhP(O)(Cl)(NEt_2) (18.5 g, 0.08 mol) was obtained 21.7 g (71 %) of **6a** as orange oil. ^{1}H-NMR (DMSO-d_6): δ 0.91 (t, $^3J_{HH}$ 6.9 Hz, 6H, CH_3), 2.83 (m, 4H, CH_2), 3.88 (s, 5H, Cp), 4.16 (s, 1H, Hα-C_5H_4), 4.44 (s, 1H, Hα-C_5H_4), 4.49 (s, 1H, Hβ-C_5H_4), 4.61 (s, 1H, Hβ-C_5H_4), 7.6 (m, 3H, Ph), 7.88 (dd, $^3J_{HH}$ 6.50 Hz, $^3J_{HP}$ 11.18 Hz, 2H, o-Ph). $^{31}P\{^1H\}$-NMR (DMSO-d_6): δ 33.6 (s). Analysis (%). Calc. for $C_{20}H_{24}FeNOP$ (381.23): C 63.0, H 6.3. Found: C 63.6; H, 6.4.

Table 1 Crystallographic data for ferrocenylphosphinic acids **1,2**

Compound reference	**1a**	**1b**	**1c***	**1d**	**2b**	**2c**	**2d**
Chemical formula	$C_{10}H_{11}FeO_2P$	$C_{11}H_{13}FeO_2P$	$C_{12}H_{15}FeO_2P$	$C_{16}H_{15}FeO_2P$	$C_{12}H_{16}FeO_4P_2$	$C_{14}H_{20}FeO_4P_2$	$C_{22}H_{20}FeO_4P_2$
Formula Mass	250.01	264.03	278.06	326.10	342.04	370.09	466.17
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
a/Å	13.062(13)	10.6190(10)	6.0910(1)	7.689(2)	8.686(6)	13.753(2)	22.98(3)
b/Å	7.556(8)	7.0310(10)	7.6550(1)	8.774(2)	11.506(8)	7.9070(10)	7.918(9)
c/Å	10.554(11)	14.845(2)	25.497(5)	20.840(4)	7.138(5)	14.432(2)	11.096(13)
α/°	90.00	90.00	90.00	90.00	90.00	90.00	90.00
β/°	108.340(10)	105.0750(10)	90.00	90.00	108.786(7)	92.711(4)	106.16(3)
γ/°	90.00	90.00	90.00	90.00	90.00	90.00	90.00
Unit cell volume/Å^3	988.7(18)	1070.2(2)	1188.8(3)	1405.9(6)	675.4(8)	1567.7(4)	1940(4)
Temperature/K	296(2)	100(2)	296(2)	296(2)	296(2)	75(2)	150(2)
Space group	*P2(1)/c*	*P2(1)/c*	*P2(1)2(1)2(1)*	*P2(1)2(1)2(1)*	*P2(1)/c*	*C2/c*	*C2/c*
Z	4	4	4	4	2	4	4
No. of reflections measured	7694	7770	9841	22241	3253	19284	8430
No. of independent reflections	2152	2451	2705	3545	1323	2082	1599
R_{int}	0.0683	0.0786	0.0565	0.0840	0.0320	0.0289	0.1289
Final R_1 values ($I > 2\sigma(I)$)	0.0371	0.0282	0.0464	0.0345	0.0272	0.0224	0.0429
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0817	0.0787	0.0877	0.0539	0.0672	0.0588	0.0847
Final R_1 values (all data)	0.0587	0.0292	0.0743	0.0712	0.0317	0.0307	0.0770
Final $wR(F^2)$ values (all data)	0.0898	0.0794	0.0980	0.0605	0.0690	0.0611	0.0932
Flack parameter			0.5	0.01(2)			

* refined as racemic twin

3. *Ferrocene-1,1'-diyl-bis(phosphonous acid N,N-diethylamide)* (**5b**). To a suspension of 1,1'-ferrocenedilithium $FcLi_2$, obtained from ferrocene (10 g, 54 mmol), n-BuLi (71 ml, 114 mmol) and TMEDA (17 mL, 114 mmol) in 200 ml petroleum ether was added dropwise a solution of $(Et_2N)_2PCl$ (24.8 g, 118 mmol) in petroleum ether (40 mL) at -78°C. Reaction mixture was stirred for 6 hours at room temperature. Solvent was removed under reduced pressure and mixture was dissolved in 150 ml dichloromethane and washed with water. Organic layer was separated, dried over Na_2SO_4, filtered and solvent was evaporated to leave 22.8 g (79 %) of **5b** as orange oil. ^{1}H-NMR (DMSO-d_6): δ 0.98 (t, $^3J_{HH}$ 6.8 Hz, 12H, CH_3), 2.82 (m, 8H, CH_2), 4.51 (br s, 4H, Hα-C_5H_4), 4.69 (br s, 4H, Hβ-C_5H_4). ^{31}P{^{1}H}-NMR (DMSO-d_6): δ 93.4 (s) [51]. Analysis (%).Calc. for $C_{26}H_{48}FeN_4P_2$ (534.48): C, 58.43; H, 9.05%. Found: C, 58.3; H, 9.01.

4. Ferrocene-1,1'-diyl-bis(phenylphosphinic acid N,N-diethylamide) (**6b**). In similar manner from ferrocene (10 g, 54 mmol), n-BuLi (71 ml, 114 mmol), TMEDA (17 mL, 114 mmol) and $PhP(O)(Cl)N(Et)_2$ (26.4 g, 114 mmol) was obtained 22.4 g (72 %) of **6b** as orange oil. ^{1}H-NMR (DMSO-d_6): δ 0.94 (t, $^3J_{HH}$ 6.8 Hz, 12H, CH_3), 2.88 (m, 8H, CH_2), 4.57 (br s, 4H, Hα-C_5H_4), 4.65 (br s, 4H, Hβ-C_5H_4), 7.63 (m, 6H, Ph), 7.88 (m, 4H, o-Ph). ^{31}P{^{1}H}-NMR (DMSO-d_6): δ 33.5 (s). Analysis (%).Calc. for $C_{30}H_{38}FeN_2O_2P_2$ (576.43): C, 62.5; H, 6.6%. Found: C, 62.3; H, 6.4.

5. O-Methyl-ferrocenylphosphonous acid N,N-Diethylamide (**7a**). To solution of ferrocenyllithium FcLi obtained from ferrocene (10 g, 54 mmol), ^{t}BuOK (1.12 g, 10 mmol) and ^{t}BuLi (22.4 ml, 38 mmol) in 150ml THF was added dropwise $(MeO)P(Cl)(NEt_2)$ (6.55 g, 40 mmol) at -78˚C. Reaction mixture was stirred for 6 hours at room temperature. Solvent was evaporated under reduced pressure and residue was dissolved in 150 ml dichloromethane and washed with water. Organic layer was dried over Na_2SO_4, filtered and solvent was evaporated to leave 7.66 g (63 %) of **7a** as orange oil. ^{1}H-NMR ($CDCl_3$): δ 0.97 (t, $^3J_{HH}$ 6.83 Hz, 6H, CH_3), 2.84 (m, 4H, CH_2), 3.42 (s, 3H, OMe), 4.08 (s, 5H, Cp), 4.17 (m, 2H, Hα-C_5H_4), 4.38 (br s, 2H, Hβ-C_5H_4). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 136.2 (s). Analysis (%).Calc. for $C_{15}H_{22}FeOPN$ (319.16): C 56.4, H 6.9. Found: C 56.1, H 6.6.

6. O-Ethyl-ferrocenylphosphonous acid N,N-Diethylamide **(7b**). In similar manner from ferrocene (10 g, 54 mmol), ^{t}BuOK (1.12 g, 10 mmol), ^{t}BuLi (22.4 ml, 38 mmol) and $(EtO)P(Cl)(NEt_2)$ (7.34 g, 40 mmol) was obtained 8.66 g (65 %) of **7b** as orange oil. ^{1}H-NMR ($CDCl_3$): δ 0.91 (t, $^3J_{HH}$ 6.6 Hz, 6H, CH_3), 1.26 (tr, $^3J_{HH}$ 6.9 Hz, 3H, Et), 2.95 (m, 4H, CH_2), 3.74 (m, 2H, CH_2), 4.11(s, 5H, Cp), 4.21 (m, 2H, H_α-C_5H_4), 4.43 (m, 2H, H_β-C_5H_4). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 130.3 (s). Analysis (%). Calc. for $C_{16}H_{24}FeOPN$ (333.19): C 57.6, H 7.2. Found: C, 57.1, H, 7.2.

7. *Ferrocene-1,1'-diyl-bis((O-methyl)phosphonous acid N,N-diethylamide)* (**7c**). To a suspension of 1,1'-dilithiumferrocene $FcLi_2$ obtained from ferrocene (10 g, 54 mmol), n-BuLi (71 ml, 114 mmol) and TMEDA (17 mL, 114 mmol) in petroleum ether (200 ml) was added dropwise at -78°C a solution of (MeO)P(Cl)(NEt_2) (19.32 g, 114 mmol) in petroleum ether (40 mL). Reaction mixture was stirred for 12 hours at room temperature. Solvent was removed under reduced pressure and mixture was dissolved in 150 ml dichloromethane and washed with water. Organic layer was separated, dried over Na_2SO_4, filtered and solvent was evaporated to leave 21.7 g (89%) of **7c** as orange oil. ^{1}H-NMR ($CDCl_3$): δ 0.99 (tr, $^3J_{HH}$ = 6.4 Hz, 12H, CH_3), 2.88 (m, 8H, CH_2), 3.33 (s, 6H, Me), 4.45 (m, 4H, H_α-C_5H_4), 4.55 (m, 4H, H_β-C_5H_4). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 135.7 (s). Analysis (%).Calc. for $C_{20}H_{34}FeO_2P_2N_2$ (452.29): C 53.1, H 7.5. Found: C 53.0, H 7.2.

8. *Ferrocene-1,1'-diyl-bis((O-ethyl)phosphonous acid N,N-diethylamide)* (**7d**). In similar manner from ferrocene (10 g, 54 mmol), n-BuLi (71 ml, 114 mmol), TMEDA (17 mL, 114 mmol) and EtOP(Cl)N($Et)_2$ (20.92 g, 114 mmol) was obtained 22.3 g (86 %) of **7d** as orange oil. ^{1}H-NMR ($CDCl_3$): δ 1.00 (t, $^3J_{HH}$ 6.6 Hz, 12H, CH_3), 1.22 (tr, $^3J_{HH}$ 7.0 Hz, 6H, CH_3), 3.01 (m, 8H, NEt_2), 3.78 (m, 4H, CH_2), 4.40 (m, 4H, H_α-C_5H_4), 4.53 (m, 4H, H_β-C_5H_4). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 130.6 (s). Analysis (%). Calc. for $C_{22}H_{38}FeO_2P_2N_2$ (480.34): C 55.0, H 7.9. Found: C 55.2, H 7.7.

9. *Ferrocenyl(methyl)phosphinic acid N,N-diethylamide* (**8a**). To solution of **7a** (7.66g, 24 mmol) in 50 ml CH_2Cl_2 was added MeI (3.41 g, 24 mmol). Reaction mixture was refluxed for 3 hours. Solvent was evaporated to leave 7.16 g (93%) of **8a** as orange oil. ^{1}H-NMR ($CDCl_3$): δ 1.46 (tr, $^3J_{HH}$ = 7.9 Hz, 6H, CH_3), 1.90 (d, $^2J_{HP}$ 14.8 Hz, 3H, CH_3), 3.06 (m, 4H, CH_2), 4.36 (s, 5H, Cp), 4.49 (s, 2H, H_α-C_5H_4), 4.56 (s, 2H, H_β-C_5H_4). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 56.7 (s). Analysis (%). Calc. for $C_{15}H_{22}FeNOP$ (319.16): C 56.4, H 6.9.Found: C 56.2, H 6.8.

10. *Ferrocenyl(ethyl)phosphinic acid N,N-diethylamide* (**8b**). In similar manner from **7b** (7.99g, 24 mmol) and EtI (4.49 g, 24 mmol) was obtained 7.3 g (91%) of **8b** as orange oil. ^{1}H-NMR ($CDCl_3$): δ 0.94 (tr, $^3J_{HH}$ 7.02 Hz, 6H, CH_3), 1.32 (dt, $^3J_{HH}$ 6.98 Hz, $^3J_{PH}$ 2.14 Hz, 3H, CH_3), 1.88 (m, 2H, CH_2), 2.93 (m, 4H, CH_2), 4.25 (s, 5H, Cp), 4.28 (m, 1H, H_α-C_5H_4), 4.29 (m, 1H, H_α-C_5H_4), 4.34 (m, 1H, H_β-C_5H_4), 4.40 (m, 1H, H_β-C_5H_4). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 43.1 (s). Analysis (%). Calc. for $C_{16}H_{24}FeNOP$ (333.19): C 57.6, H 7.2. Found: C 57.5, H 6.9.

11. *Ferrocene-1,1'-diyl-bis(methylphosphinic acid N,N-diethylamide)* (**8c**). In similar manner from **7c** (21.9g, 48 mmol) and MeI (13.63 g, 96 mmol) was obtained 20.4 g (93 %) of **8c** as orange oil. ^{1}H-NMR ($CDCl_3$): δ 1.43 (tr, $^3J_{HH}$ = 6.5 Hz, 12H, CH_3), 1.95 (d, $^3J_{HP}$ 15.1 Hz, 6H, Me), 2.98 (m, 8H, CH_2), 4.48 (m, 4H, H_α-C_5H_4), 4.52 (m, 4H, H_β-C_5H_4). ^{31}P{^{1}H}-NMR

($CDCl_3$): δ 56.3 (s). Analysis (%).Calc. for $C_{20}H_{34}FeN_2O_2P_2$ (452.29): C 53.1, H 7.5. Found: C 53.1, H 7.0.

12. *Ferrocene-1,1'-diyl-bis(ethylphosphinic acid N,N-diethylamide)* (**8d**). In similar manner from **7d** (22.4g, 47 mmol) and EtI (14.7 g, 94 mmol) was obtained 20.7 g (92%) of **8d** as orange oil. ^{1}H-NMR ($CDCl_3$): δ 1.48 (tr, $^3J_{HH}$ = 6.4 Hz, 12H, CH_3), 1.89 (tr, $^3J_{HH}$ 7.2 Hz, 6H, CH_3), 2.97 (m, 8H, CH_2), 2.28 (m, 4H, CH_2), 4.46 (m, 4H, H_α-C_5H_4), 4.52 (m, 4H, H_β-C_5H_4). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 43.2 (s). Analysis (%).Calc. for $C_{22}H_{38}FeN_2O_2P_2$ (480.34): C 55.0, H 7.9. Found: C 54.8, H 7.6.

13. *Ferrocenyl(H-phosphinic acid)* (**1a**).To solution of **5a** (15.0 g, 41.6 mmol) in 40 ml of EtOH was added 10% HCl (50 ml, 170 mmol) (Caution! Hot!). Precipitate was filtered, washed subsequently with water and petroleum ether and dried on air at 25^{o}C to give 9.1 g (87%) of (**1a**) as a microcrystalline brown solid, m.p. 127°C. ^{1}H-NMR (DMSO-d^6): δ 4.30 (s, 5H, Cp), 4.46 (m, 4H, Cp^p), 7.56 (1H, $^1J_{HP}$ 550.1 Hz, P-H), ^{31}P{-} NMR (DMSO-d^6): δ 19.6 (d, $^1J_{HP}$ 550.1 Hz), ^{13}C{^{1}H}-NMR (DMSO-d^6): δ 69.6 (s, Cp), 71.1 (d, $^2J_{CP}$ 15.4 Hz, C2), 71.6 (d, $^3J_{CP}$ 11.7 Hz, C3), 72.9 (d, $^1J_{CP}$ 145.6 Hz, C1). IR (KBr): 3110 m, 3093 sh (varCH); 2663 w (ν(P)O-H); 2421 w (νPH); 1704 sh (δ(P)OH); 1422 m (νCC); 1386 w (νCC); 1367 w; 1314 vw; 1198 s (δPOH, νP=O); 1106 s (Cp breath); 1091 (sh) (δHPO); 1034 s (δCCH); 977 vs (νP-O(H)); 890 s (δCCC, νP-O(H)); 843 (sh) (γCH, γOH); 819 m; 640 w (δCp in-plane). Analysis (%). Calc. for $C_{10}H_{11}FeO_2P$ (250.01): C 48.0, H 4.4. Found: C 48.1, H 4.3.

In similar manner were prepared following ferrocenylphosphinic acid:

14. From **8a** (7.16 g, 22.4 mmol) was obtained 4.7 g (79%) of *ferrocenyl(methyl)phosphinic acid* (**1b**) as a microcrystalline brown solid, m.p. 163°C. ^{1}H-NMR (DMSO-d^6): δ 1.5 (d, $^3J_{HP}$ 14.5 Hz, 3H, Me), 4.3 (s, 5H, Cp), 4.40 (m, 2H, Cp), 4.41 (m, 2H, Cp), 5.79 (br s, 1H, P-OH); ^{31}P{^{1}H}-NMR (DMSO-d^6): δ 38.4; ^{13}C{^{1}H}-NMR (DMSO-d^6): δ 18.0 (d, $^1J_{CP}$ 101.4 Hz, Me), 69.6 (s, Cp), 70.8 (d, $^2J_{CP}$ 4.7 Hz, C3), 70.9 (s, C2), 75.6 (d, $^1J_{CP}$ 144.1 Hz, C1); IR (KBr): 3083 s (ν_{ar}CH); 2980 w, 2913 w, 2850 w (ν_{alk}CH); 2542 m (ν(P)O-H); 2246 m, 2137 m, 2057 m (2γOH); 1783 w, 1714 m, 1688 m, 1621 m (δ(P)OH); 1427 m (Cp^p νCC); 1409 w (Cp νCC); 1389 w, 1370 w, 1350 vw, 1315 w (Cp^p νCC); 1300 s (Me); 1207 s, 1186 s (δPOH, νP=O, Cp^p breath[e]); 1125 s; 1107 s (Cp breath[f]); 1040 s, 1029 s (Cp^p δCCH); 998 s, 984 vs, 966 s (νP-O(H)); 903 s (Me); 889 ms (Cp^p δCCC, νP-O(H)); 852 s, 824 s (Cp^p γCH, γOH); 812 s; 761 s; 636 mw (δCp^p in-plane). Analysis (%).Calc. for $C_{11}H_{13}FeO_2P$ (264.04): C 50.0, H 4.9. Found: C 49.6, H 5.0.

15. From **8b** (7.3 g, 21.9 mmol) was obtained 5.2 g (83 %) of *ferrocenyl(ethyl)phosphinic acid* (**1c**) as a microcrystalline brown solid, m.p. 178°C. ^{1}H-NMR ($CDCl_3$): δ 1.16 (m, 3H, CH_3), 1.88 (br s, 2H, CH_2), 4.42 (br s, 5H, Cp), 4.51 (br.s., 2H, Cp), 10.75 (br s, 1H, P-OH); ^{31}P{^{1}H}-NMR

($CDCl_3$): δ 43.1 (s); $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 5.8 (d, $^2J_{CP}$ 4.4 Hz, Et), 23.3 (d, $^1J_{CP}$ 108.2 Hz, Et), 72.3 (d, $^3J_{CP}$ 11.0 Hz, $C3_{Cp}$), 72.6 (d, $^2J_{CP}$ 13.5 Hz, $C2_{Cp}$), 74.6 (d, $^1J_{CP}$ 132.4 Hz, $C1_{Cp}$); IR (KBr): 3106 m (ν_{ar}CH); 2981 m, 2928 w, 2855 w (ν_{alk}CH); 2703 vw, 2631 vw (ν(P)O-H); 2319 vw, 2256 vw (2γOH); 1698 w, 1652 m (δ(P)OH); 1477 vw; 1458 w (Et $\delta_{as}CH_3$); 1443 w; 1424 w (Cp^p νCC); 1412 vw (Et $\delta_s CH_3$); 1389 w, 1370 w, 1353 vw, 1313 vw (Cp^p νCC); 1294 vw (Me); 1228 sh (Et τCH_2); 1193 s (δPOH, νP=O, Cp^p breath[e]); 1165 s; 1143 s; 1107 s (Cp breath[f]); 1037 vs (Cp^p δCCH); 1002 s (Et τCH_2); 987 s, 963 s (νP-O(H)); 896 m (Cp^p δCCC, νP-O(H)); 843 sh, 821 m (Cp^p γCH, γOH); 774 w; 751 w (Et ρCH_2); 721 w (νPEt, δPEt, δOPO); 638 vw (δCp^p in-plane). Analysis (%).Calc. for $C_{12}H_{15}FeO_2P$ (278.06): C 51.8, H 5.4. Found: C 51.5, H 5.4.

16. From **6b** (21.7 g, 40.6 mmol) was obtained 17.7 g (95%) of *ferrocenyl(phenyl)phosphinic acid* (**1d**) as microcrystalline brown solid, m.p. 201 °C (dec.). ^{1}H-NMR (DMSO-d^6): δ 4.19 (s, 5H, Cp), 4.39 (m, 4H, Cp^P), 7.48 (m, 3H, Ph), 7.72 (dd, 2H, $^3J_{HH}$=7.22 Hz, $^3J_{HP}$=11.34 Hz, o-Ph); $^{31}P\{^1H\}$-NMR (DMSO-d^6): δ 27.8 (s); $^{13}C\{^1H\}$-NMR (DMSO-d^6): δ 69.7 (s, Cp), 71.2 (d, $^3J_{CP}$ 11.4 Hz, C3), 71.6 (d, $^2J_{CP}$ 13.9 Hz, C2), 74.9 (d, $^1J_{CP}$ 152.6 Hz, C1), 128.5 (d, $^2J_{CP}$ 12.4 Hz, p-C_{Ph}), 130.8 (d, $^3J_{CP}$ 9.5 Hz, m-C_{Ph}), 131.4 (d, $^4J_{CP}$ 1.5 Hz, o-C_{Ph}), 136.8 (d, $^1J_{CP}$ 136.5 Hz, ipso-C_{Ph}). IR (KBr): 3094 w, 3055 w (ν_{ar}CH); 2599 w (ν(P)O-H); 1704 (sh) (δ(P)OH) ; 1593 m (Ph^d ν_{8a}); 1484 w (Ph^d ν_{19a}); 1437 s (Ph^d ν_{19b}); 1422 m (νCC); 1386 m (νCC); 1369 m ; 1312 w ; 1190 s (δPOH, νP=O, Cp^p breath[e]); 1183 s (Ph^d ν_{9a}); 1125 s (Ph^d ν_{15}); 1107 s (Cp breath); 1071 s (Ph^d ν_{18b}); 1028 s (δCCH); 1001 s (Ph^d ν_{12}); 959 vs (νP-O(H)); 894 s (δCCC, νP-O(H)); 840 (sh) (γCH, γOH); 824 s ; 751 m (Ph^d ν_1); 715 s (Ph^d ν_{11}); 695 s (Ph^d ν_4); 637 w (δCp in-plane). Analysis (%).Calc. for $C_{16}H_{15}FeO_2P$ (326.11): C 58.9, H 4.6. Found: C 58.5, H 4.4.

17. From **5b** (14.0 g, 26.2 mmol) was obtained 7.6 g (92%) of *ferrocene-1,1'-diyl-bis(H-phosphinic acid)* (**2a**) as a microcrystalline brown solid, m.p. 188°C. ^{1}H-NMR (DMSO-d^6): δ 4.6 (m, 8H, Cp), 7.5 (d, $^1J_{HP}$ 565.4, 2H, P-H); $^{31}P\{-\}$-NMR (DMSO-d^6): δ 18.5 (d, $^1J_{HP}$ 565.4 Hz); $^{13}C\{^1H\}$-NMR (DMSO-d^6): δ 72.8 (d, $^2J_{CP}$ 15.0 Hz, C2), 73.2 (d, $^3J_{CP}$ 11.0 Hz, C3), 73.8 (d, $^1J_{CP}$ 136.8 Hz, C1); IR (KBr): 3110 (sh), 3093 w (ν_{ar}CH); 2622 w (ν(P)O-H); 2391 m (νPH); 1704 (sh) (δ(P)OH); 1424 m (νCC); 1392 m (νCC); 1364 m; 1313 w; 1196 vs (δPOH, νP=O, Cp breath); 1091 s (δHPO); 1037 s (δCCH); 982 s (νP-O(H)); 890 s (δCCC, νP-O(H)); 841 s (γCH, γOH); 822 (sh); 637 s (δCp in-plane). Analysis (%).Calc. for $C_{10}H_{12}FeO_4P_2$ (313.99): C 38.2, H 3.8. Found: C 38.1, H 3.6.

18. From **8c** (20.4 g, 45.1 mmol) was obtained 12.7 g (82%) of *ferrocene-1,1'-diyl-nebis(methylphosphinic acids)* (**2b**) as microcrystalline brown solid, m.p. 174 °C (subl.). ^{1}H-NMR (DMSO-d^6): δ 1.46 (d, $^2J_{HP}$ 15.15 Hz, 6H, Me), 4.55 (d, $^3J_{HH}$ 1.58 Hz, 4H, Cp), 4.58 (d, $^3J_{HH}$ 1.66 Hz, 4H, Cp); $^{31}P\{^1H\}$-NMR (DMSO-d^6): δ 41.2 (s); $^{13}C\{^1H\}$-NMR (DMSO-d^6): δ 17.7 (d, $^1J_{CP}$ 106.4 Hz, Me), 72.7 (d, $^3J_{CP}$ 6.9 Hz, $C3_{Cp}$), 72.6 (d, $^2J_{CP}$ 33.4 Hz, $C2_{Cp}$), 75.6 (d, $^1J_{CP}$

138.3 Hz, $C1_{Cp}$); IR (KBr): 3099 vw (ν_{ar}CH); 2984 vw, 2916 vw, 2852 vw (ν_{alk}CH); 2575 vw (ν(P)O-H); 2232 vw, 2172 vw, 2045 vw (2γOH); 1790 (sh), 1716 (sh), 1623 s (δ(P)OH); 1472 s; 1424 s (Cp^p νCC); 1390 m, 1370 m, 1312 sh (Cp^p νCC); 1297 s (Me); 1192 s (δPOH, νP=O, Cp^p breath[e]); 1162 sh; 1060 sh; 1034 s (Cp^p δCCH); 976 vs (νP-O(H)); 905 s (Me); 879 s (Cp^p δCCC, νP-O(H)); 853 s, 828 s (Cp^p γCH, γOH); 759 s; 637 mw (δCp^p in-plane). Analysis (%). Calc. for $C_{12}H_{16}FeO_4P_2$ (342.05): C 70.2, H 4.7. Found: C 70.1, H 4.8.

19. From **8d** (20.7 g, 43 mmol) was obtained 13.8 g (86%) of *ferrocene-1,1'-diyl-bis(ethylphosphinic acids)* (**2c**) as a microcrystalline brown solid, m.p. 154 °C (dec.). ^{1}H-NMR ($CDCl_3$): δ 1.05 (dt, $^3J_{HP}$ 19.4 Hz, $^3J_{HH}$ 7.7 Hz, 3H, CH_3), 1.74 (dq, $^1J_{HP}$ 15.6 Hz, $^3J_{HH}$ 7.8 Hz, 2H, CH_2), 4.56 (d, $^3J_{HH}$ 1.4 Hz, 2H, Cp), 4.60 (d, $^3J_{HH}$ 1.4 Hz, 2H, Cp), 11.89 (s, 2H, P-OH); ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 47.6 (s); ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 5.8 (d, $^2J_{CP}$ 4.4 Hz, CH_3), 23.4 (d, $^1J_{CP}$ 108.2 Hz, Et), 72.3 (d, $^3J_{CP}$ 11.0 Hz, $C3_{Cp}$), 72.6 (d, $^2J_{CP}$ 13.6 Hz, $C2_{Cp}$), 74.7 (d, $^1J_{CP}$ 132.4 Hz, $C1_{Cp}$).; IR (KBr): 3093 m (ν_{ar}CH); 2974 m, 2937 m, 2908 m, 2882 m (ν_{alk}CH); 2707 w (ν(P)O-H); 1704 (sh) (δ(P)OH); 1458 m ($\delta_{as}CH_3$); 1426 m (νCC); 1408 m ($\delta_s CH_3$); 1392 m, 1372 m, 1318 w (νCC); 1275 s ($\delta_{as}(POH)_2$); 1225 m (τCH_2); 1187 vs ($\nu_{as}(P=O)_2$); 1159 vs ($\nu_s(P=O)_2$, $\delta_s(POH)_2$); 1042 s (νCC, ρCH_3); 1032 (sh) (δCCH); 1000 w (τCH_2); 951 s (νP-O(H)); 895 m (δCCC, νP-O(H)); 852 m (γCH, γOH); 826 (sh) ; 751 s (ρCH_2); 726 s (νPEt, δPEt, δOPO); 637 vw (δCp in-plane); Analysis (%).Calc. for $C_{14}H_{20}FeO_4P_2$ (370.09): C 56.6, H 4.3. Found: C 56.3, H 4.1.

20. From **6b** (22.4 g, 38.8 mmol) was obtained 17.0 g (94%) of *ferrocene-1,1'-diyl-bis (phenylphopshinic acid)* (**2d**) as a microcrystalline brown solid, m.p. 208 °C (dec.). ^{1}H-NMR (DMSO-d^6): δ 4.60 (m, 4H, Cp), 4.67 (m, 4H, Cp), 7.47 (dd, $^4J_{HP}$ 7.38 Hz, $^3J_{HH}$ 7.02 Hz, 4H, m-Ph), 7.51 (d, $^3J_{HH}$ 7.02 Hz, 2H, p-Ph), 7.69 (dd, $^3J_{HP}$ 12.21 Hz, $^3J_{HH}$ 7.38 Hz, 4H, o-Ph); ^{31}P{^{1}H}-NMR (DMSO-d^6): δ 28.8 (s); ^{13}C{^{1}H}-NMR (DMSO-d^6): δ 73.1 (d, $^3J_{CP}$ 11.4 Hz, C3), 73.4 (d, $^2J_{CP}$ 14.7 Hz, C2), 74.8 (d, $^1J_{CP}$ 144.5 Hz, C1), 128.8 (d, $^4J_{CP}$ 12.8 Hz, p-C_{Ph}), 130.7 (d, $^3J_{CP}$ 10.2 Hz, m-C_{Ph}), 131.9 (s, o-C_{Ph}), 137.8 (d, $^1J_{CP}$ 147.4 Hz, ipso-C_{Ph}); IR (KBr): 3083 w, 3057 vw (ν_{ar}CH); 2622[c] vw (ν(P)O-H); 1704 (sh) (δ(P)OH); 1595 m (Ph^d ν_{8a}); 1485w (Ph^d ν_{19a}); 1436 s (Ph^d ν_{19b}); 1422 (sh) (νCC); 1388 w (νCC); 1365 w ; 1310 vw ; 1188 s (δPOH, νP=O, Cp^p breath); 1179 sh (Ph^d ν_{9a}); 1127 s (Ph^d ν_{15}); 1067 s (Ph^d ν_{18b}); 1037 s (δCCH); 1000 s (Ph^d ν_{12}); 961 vs (νP-O(H)); 894 m (δCCC, νP-O(H)); 844 m (γCH, γOH); 828 (sh) ; 751 m (Ph^d ν_1); 717 s (Ph^d ν_{11}); 693 s (Ph^d ν_4); 640 m (δCp in-plane); Analysis (%).Calc. for $C_{22}H_{20}FeO_4P_2$(466.18): C 56.6, H 4.3. Found: C 56.3, H 4.0.

Supporting Information ORTEP view of **1a, 1c, 1d, 2d**, scaling factors for the force fields, potential of oxidation and re-reduction peaks of ferrocenylphosphinic acids (**1,2**). CCDC 904130

(**1a**), 904133 (**1b**), 904135 (**1c**), 904129 (**1d**), 904132 (**2b**), 904131 (**2c**) and 904134 (**2d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Acknowledgments

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> We synthesized ferrocenylphosphinic acids as ligands for coordination polymers
> Spontaneous racemization takes place for monosubstituted ferrocenylphosphinic acids
> Difference of hydrogen bonding was observed for ferrocen-1,1’-diyl-bisphosphinic acids
> Conformation of ferrocenephosphinic acids depend on substituent’s at phosphorus atoms

Supporting Information

Synthesis and structure of ferrocenylphosphinic acids

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Table 1S. Scaling factors for the force fields

scaling factor		Value
stretch	CC	0.9207[a]
stretch	CH (arom.)	0.915[b]
stretch	CH (aliph.)	0.889[b]
stretch	FeC	1.25
bend	CCC	1.0144[a]
bend	CCH	0.950[a]
bend	HCH	0.9016[a]
torsion	all	0.9523[a]

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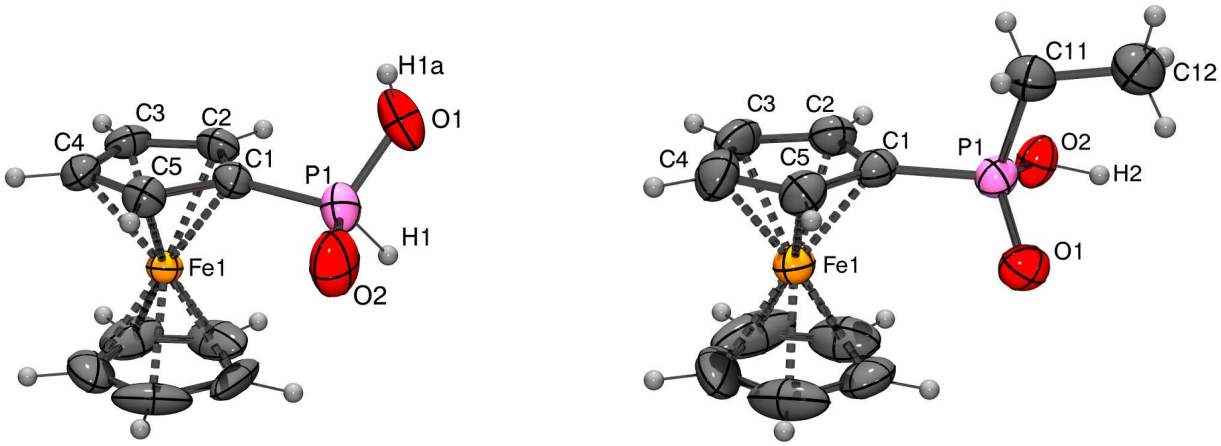

Figure S1. An ORTEP view of ferrocenyl(H-phosphinic acid) (**1a**) (left) and ferrocenyl(ethyl)phosphinic acid (**1c**) (right). Ellipsoids probability 50%.

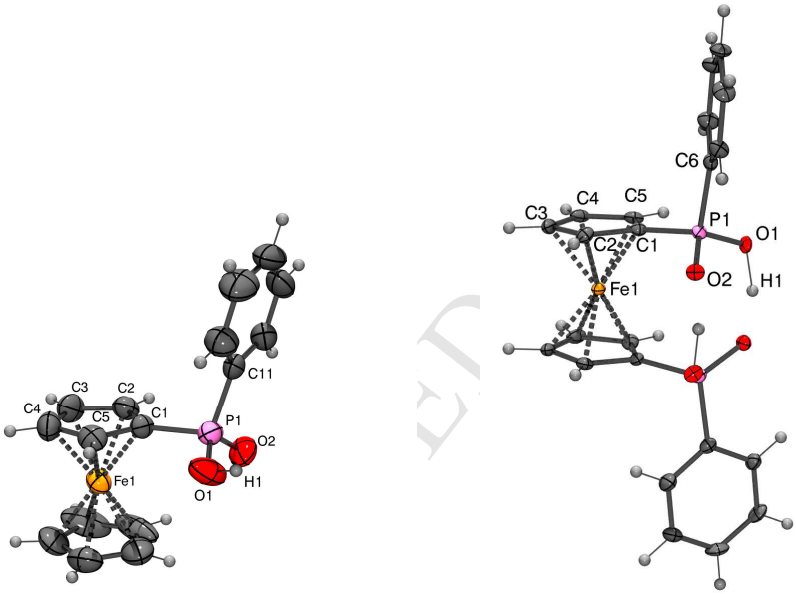

Figure S2. An ORTEP view of ferrocenyl(phenylphosphinic acid) (**1d**) (left) and 1,1'-ferrocenebis(phenylphosphinic acid) (**2d**) (right). Ellipsoids probability 50%.

Electrochemistry.

Cyclic voltammograms were recorded using potentiostat PI-50-1 interfaced to XY-recorder H 307/2 at potential scan rate t = 100 $mV \cdot s^{-1}$ in MeOH / 0.1 M Bu_4NBF_4 media at 295 K. A glassy carbon working electrode (ð = 3.4 mm) embedded in Teflon and Pt wire as counter electrode were used in electrochemical cell. Before each measurement the surface of the working electrode was mechanically polished. The potentials were measured toward formal potential of $Fc^{0/+}$ redox-system (internal standard) using a saturated calomel electrode (SCE) as a reference electrode. The diffusion nature of the peaks currents (i_p) was proved by the theoretical form of voltammograms and by a linear dependence of $i_p \sim$ υ*1/2 in the range of 10–200 $mV \cdot s^{-1}$.

All mono- and disubstituted ferrocenylphosphinic acids experience a reversible one one-electron oxidation and re-reduction (Fig. S3, table S2) similar to other phosphorus containing derivatives of ferrocene [1,2,3]. However the reversibility of oxidation of (1,2) is not sensitive on the to the steric bulk of the substituents on the phosphorus atom in contrast to [1]. The potentials of acid peaks (1,2) are shifted in positive field relative to the corresponding potentials of ferrocene. Mono-substituted acids (1a-d) are easier oxidized in comparison with di-substituted (2a-d) species, which confirms electron-withdrawing character of phosphinic substituentes. For disubstitituted acids the difference between the oxidation and re-reduction potentials ($E_{p,ox}$ - $E_{p,rered}$ = 80÷130 mV) is higher than for monosubstituted species.

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Table S2. Potential (V, vs. Fc0/+) of oxidation and re-reduction peaks of ferrocenylphosphinic acids (**1,2**).

Acid		Potential		
		Alkaline medium	Neutral medium	Acidic medium
1a	$E_{p,ox}$	0.11	0.12, 0.24	0.27
	$E_{p,rered}$	0.05	0.07, 0.18	0.20
1b	$E_{p,ox}$	0.11	0.12, 0.26	0.26
	$E_{p,rered}$	0.04	0.08, 0.18	0.19
1c	$E_{p,ox}$	0.12	0.10, 0.20	0.24
	$E_{p,rered}$	0.02	0.04, 0.13	0.18
1d	$E_{p,ox}$	0.06	0.07, 0.21	0.24
	$E_{p,rered}$	-0.01	0.02, 0.14	0.17
2a	$E_{p,ox}$	0.20	0.41	0.50
	$E_{p,rered}$	0.12	0.30	0.40
2b	$E_{p,ox}$	0.18	0.37	0.45
	$E_{p,rered}$	0.08	0.25	0.36
2c	$E_{p,ox}$	0.19	0.39	0.47
	$E_{p,rered}$	0.02	0.26	0.39
2d	$E_{p,ox}$	0.09	0.34	0.43
	$E_{p,rered}$	0.01	0.26	0.37

Conditions: solvent MeOH, supporting electrolyte 0.1 M Bu_4NBF_4, scan rate υ = 100 mV/s. Concentration of (**1,2**) C = 10^{-3} M. Acidic medium was obtained by addition of equal volume of 0.1 M solution HCl, alkaline conditions was made by addition of two-fold volume of 10^{-3} M solution of Bu_4NOH.

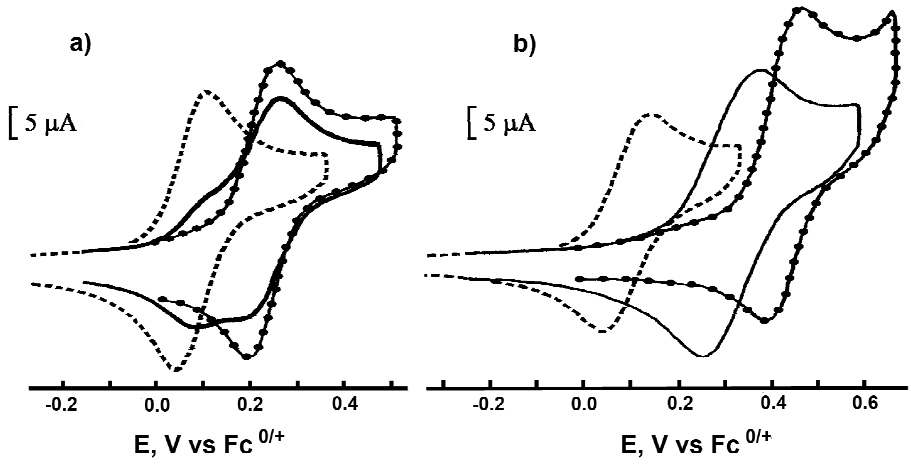

Figure S3. CV of mono- (a) and disubstituted (b) ferrocenylphosphinic acids (**1b** and **2b** respectively) (C = 10^{-3} M) in MeOH/0.1 M Bu_4NBF_4 (solid line), after addition of Bu_4NOH (C = $2{\cdot}10^{-3}$ M for **1b**,C = $8{\cdot}10^{-3}$ M for **2b**) (dotted line) and by following addition of HCl (C = 10^{-1} M for **1b**, C = $2{\cdot}10^{-1}$ M for **2b**) (line with circles).