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Structural Studies of Protonated Monophosphaferrocenes using Mössbauer and NMR Spectroscopy

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Abstract

Some monophosphaferrocenes have been studied in strongly acidic media. In trifluoromethanesulphonic acid (triflic acid) the species are iron-protonated as shown by the presence of a hydrido signal in the ^{1}H NMR spectra between −0.8 and −3.0 ppm. Such systems show novel $^2J_{PH}$ coupling transmitted via the iron centre. Evidence for iron protonation is also found in the ^{57}Fe Mössbauer spectra of triflic acid frozen solutions. Deuteriation of monophosphaferrocenes in triflic acid-d$_1$ is discussed, together with the sulphonation of phenylated derivatives in concentrated sulphuric acid. The ^{13}C NMR spectra of phenyl-substituted phosphaferrocenes are also reported, and compared with known data for diphosphaferrocenes.

Introduction

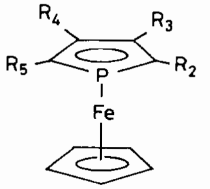
Recently we published some preliminary findings on the ^{57}Fe Mössbauer spectroscopy of diphosphaferrocenes and their protonated derivatives [1].

We have now initiated an extensive investigation into the chemistry of mono- and diphosphaferrocenes and their derivatives in strong acids. Five monophosphaferrocenes have been studied covering a range of ring substitution patterns. The latter tends to govern the behaviour of these ferrocene analogues in strong acids. The five derivatives listed below have been investigated by ^{1}H, ^{31}P NMR and ^{57}Fe Mössbauer spectroscopy.

Results and Discussion

Phosphaferrocenes are prone to atmospheric oxidation, especially in solution, an observation first reported by Mathey [2].

In triflic acid, decomposition of all phosphaferrocenes studied occurred fairly rapidly, and hence NMR spectra were run immediately after preparation. The most stable species were the phenylated derivatives **III** and **IV**. Compound **V** was very unstable in triflic acid and no meaningful results were obtained. Derivatives **I** to **IV** dissolved cleanly in triflic acid to give deep orange/red solutions from which they could be recovered unchanged by dilution with water, provided exposure to the acid was limited.



I, R_2=R_3=R_4=R_5=H
II, R_2=R_5=H, R_3=R_4=CH_3
III, R_3=R_4=H, R_2=R_5=C_6H_5
IV, R_2=R_3=R_4=R_5=C_6H_5
V, R_2=R_4=R_5=H, R_3=CH_3

^{1}H/^{31}P NMR Spectra

The ^{1}H and ^{31}P NMR spectra of **I** → **IV** in triflic acid indicated that protonation occurs at the iron atom (cf. ferrocene in triflic acid) [3]. The ^{1}H and ^{31}P NMR results are given in Table I. The protonated complexes give rise to some novel spin–spin splitting patterns of the phosphorus resonance (J_{PH}) as well as very high upfield chemical shifts (δ^{31}P).

All the derivatives showed upfield shifts over those obtained in CDCl$_3$, ranging from 139 ppm for **I** to 185 ppm for **IV**. The spin–spin coupling patterns precluded phosphorus protonation as did the upfield Fe–H resonance in the ^{1}H NMR spectra.

The range of phosphorus–hydrogen coupling constants ($^1J_{PH}$) commonly found is 400–900 Hz for phosphonium salts and 150–250 Hz for phosphines. Typical P-protonated phosphines such as triphenyl phosphine and 1,2,5-triphenylphosphole have $^1J_{PH}$ of ~500 Hz in triflic acid, thus the coupling constants observed for **I** → **IV** (50–70 Hz) rule out P protonation.

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TABLE I. $^1H^a$ and $^{31}P^b$ NMR Data for Protonated Phosphaferrocenes in Triflic Acid

Compound	^1H NMR						^{31}P	
	αH	βH	βMe	Cp	FeH	J_{PFeH}	$\delta^{31}P$	J_{PFeH}
I	4.00 $(37.5)^c$	6.8		5.00	−2.10	56	−206.0 $(-66.9)^d$	47.9
II	3.78 $(34.1)_c$		2.31	4.95	−2.95	57	−230.5 $(-82.3)^d$	57.5
III	7.1^e			4.70	−1.20	58	−222.5 $(-60.2)^d$	59.6
IV	7.0			4.90	−0.8	72	−245.2 $(-60.2)^d$	71.1

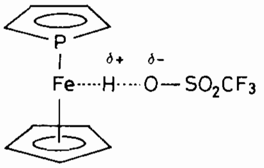
[a] ^1H shifts in ppm from external TMS J_{PH} in Hz. [b] ^{31}P shifts in ppm from 85% H_3PO_4 (+ve downfield). [c] $^2J_{P-H\alpha}$ in Hz. [d] Values in $CDCl_3$. [e] Masked by phenyl resonance.

Both **III** and **IV** gave doublets in triflic acid (^{31}P NMR).

I and **II** gave more complex spectra. The principle coupling was due to P–Fe–H interactions resulting in a doublet (*cf.* **III** and **IV**, ~60 Hz). Each signal was further split by coupling to the α hydrogens (~35 Hz), giving two triplets. The spectrum of **I** is further perturbed by $^3J_{PH}$ from the β protons. Measurement of $^2J_{P-Fe-H}$ was generally in good agreement with that measured from ^1H NMR (see Table I) as is $^2J_{P-C-H}$. The values for **I** and **II** are lower than those measured for the non-protonated form (37–38 Hz) [2], due to the fact that proton exchange takes place at positions α to phosphorus. The perturbation of the ^{31}P spectra was shown to be due to phosphorus– hydrogen coupling since all spectra collapsed to singlets upon broad band proton decoupling.

The magnitude of $\delta^{31}P$ in these systems has been postulated to be dependent on the geometry at the phosphorus atom [5]; protonation at iron would be expected to cause significant changes in the spacial arrangement of the η^5 ligands and is probably the major cause of the large change in $\delta^{31}P$.

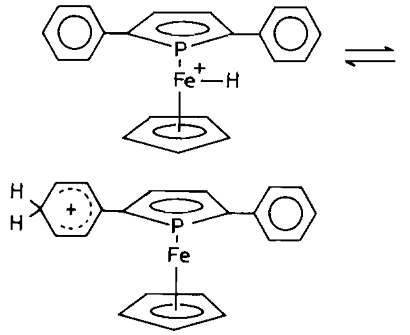
The ^1H NMR spectra of **I** → **IV** in triflic acid support iron protonation. In general, iron protonated metallocenes show signals in the hydrido region (higher field than TMS). The proton attached to iron in protonated ferrocene has δH ~−2.00 ppm [6, 7]. **I** → **IV** showed doublets in the ^1H NMR above TMS, thus confirming iron protonation, the hydrido resonance being split by phosphorus coupling. δH was variable ranging from −2.95 ppm for **II** to −0.80 ppm for **IV**. The change in δH parallels the expected change in iron basicity and steric effects as the ring substitution pattern is varied. This phenomenon may be rationalised in terms of charge separation of the type: which is more complete as the iron becomes more basic. The degree of charge separation and 'ionic character' increases in the order **II** > **I** > **III** > **IV**. Protonation causes a marked deshielding of the β protons where present; with **III** the β resonance overlaps with the arene resonance.



H/D Exchange in the Phosphaferrocene System

Proton exchange of derivatives **I**–**IV** was examined using triflic acid-d_1. This showed that the behaviour of the mono phosphaferrocenes in triflic acid is quite complex. Although the instability of monophosphaferrocenes in triflic acid limits the time of exposure to this medium, interesting deuteriation patterns are observed.

For **II** the α protons undergo rapid exchange with no exchange occurring at the cyclopentadienyl (Cp) ring in the time taken to completely deuteriate at the αH positions (5–10 min). **I** showed similar behaviour although there was some exchange (~40%) at the Cp ring as deduced from the ^1H NMR spectrum of recovered samples. Activation by methyl groups clearly makes exchange on the phospha-Cp ring more favourable in this case. Exchange of the β protons appears to be negligible in the phosphaferrocene system, as shown by the lack of D incorporation in 2,2′ and 3,3′-dimethyl diphosphaferrocenes [8]. **III** and **IV** paralleled the behaviour of 2,2′5,5′-tetraphenyldiphosphaferrocene in triflic acid-d_1. Here, rapid exchange at the phenyl sites occurred. This would indicate that the following equilibrium is involved (or possibly diprotonated species).



III was dissolved in excess triflic acid-d_1 and recovered after 1 h. The deuteriation of the phenyl groups was found to be 53% approaching the theoretical value for the exchange of all the *ortho* and *para* protons (calc. 60%). Similar exchange of the arene protons was noted with **IV**. With **III**, as **I**, some deuteriation of the Cp ring was detected (~18% after 1 h).

Reaction with Other Acids

Both **III** and **IV** were insoluble in neat trifluoroacetic acid (TFA) but dissolved to give orange/red solutions in 98% H_2SO_4. Like its diphosphaferrocene analogue [1], **III** underwent sulphonation at the *para* position of the arene, as did **IV**. Both **III** and **IV** sulphonate very rapidly, as indicated by ^{1}H NMR spectra of reaction solutions. This is followed by a slower sulphonation on a second arene ring. No sulphonation of the Cp ring was observed.

Alkyl monophosphaferrocenes were found to rapidly decompose in 98% H_2SO_4. **I** and **II** dissolved in TFA to give intense purple solutions which were paramagnetic. The colour change indicates that oxidation rather than protonation occurs in TFA.

The reluctance of the Cp ring in monophosphaferrocenes to undergo electrophilic substitution reaction [2] shows clearly that the P Cp ring deactivates the Cp ring. This is borne out by ^{13}C NMR data for the phosphaferrocene system.

^{13}C NMR

The ^{13}C NMR data appar in Table II. The Cp resonances for ferrocene **I** and **IV** appear at 67.8, 70.2 and 75.5 ppm respectively.

This trend indicates a withdrawal of electron density from the Cp ring to the PCp ring. Supporting this is the observation that the Cα and Cβ resonances always occur at higher fields for the mono compared with the corresponding diphosphaferrocene, *i.e.* electron density is withdrawn from the Cp ring into the PCp ring resulting in shielding of the Pcp carbons. Thus shift difference ($\Delta\alpha$) between the α carbons for diphosphaferrocenes compared with monophosphaferrocenes is always positive, as is the corresponding difference ($\Delta\beta$) for the β carbons.

The trend appears common to arsaferrocenes. For azaferrocene very large shift differences occur between the α and β carbons, due to the high electronegativity of nitrogen, although the Cp signal is not markedly perturbed. The shift differences ($\Delta\alpha$, $\Delta\beta$) are listed in Table III.

^{57}Fe Mössbauer Results

The Mössbauer parameters for **I** → **V** appear in Table IV. Quadrupole splittings (*QS*) vary as expected with ring substitution though in a less additive manner than previously noted [1] **I** shows a reduction in *QS* of 0.33 mm s^{-1} compared to ferrocene and is in good agreement with previous estimates [1].

The tetraphenyl derivative (**IV**) has a *QS* identical with that of the parent (**I**) and is clear evidence for the lack of planarity between the Ph and PCp rings removing any strong resonance interaction. Relevant to this are the large interplanar angles found in tetraphenylphosphacyclopentadienylmanganesetricarbonyl (45–50°) [12]. Phenyl substituents have been shown to cause a decrease in *QS* of ~0.08(2) mm s^{-1} in ferrocene systems [13].

The corresponding decrease for phosphaferrocenes is thus lower at about 0.04(2) mm s^{-1}. A major factor which reduces the *QS* of phosphaferrocenes

TABLE II. ^{13}C NMR[a] of Phenyl Phosphaferrocenes.

		C_α	C_β	C_1	C_2	C_3	C_4	C_5	C_6	Cp
A[b]	δ	102.45	83.7	137.7	126.8	128.4	126.5	128.4	126.8	–
	J_{PC}	59.69	5.6	16.3	10.8	–	–	–	10.8	–
III	δ	99.2	79.2	141.25	127.5	128.6	126.7	128.6	127.5	74.0
	J_{PC}	60.1	5.2	16.8	9.3	–	–	–	9.3	–
IV	δ	99.2	99.8	139.2[c]	126.3[c]	127.4[c],d	127.2[c,d]	127.4[c,d]	126.3	75.5
	J_{PC}	57.6	3.9	17.0	10.1	–	–	–	10.1	–
				(137.0)[e]	(130.6)[e]	(132.4)[e]	(127.2)[e]	(132.4)[e]	(130.3)[e]	
				–	–	–	–	–		

[a] A = **IV** in $CDCl_3$; **III** in CS_2. Shifts in ppm from TMS. [b] A = 2,2′,5,5′-tetraphenyldiphosphaferrocene. cResonances for 2,5-phenyl groups. [d] Assignment tentative. [e] Resonances for the 3,4-phenyl groups.

TABLE III. ^{13}C Data for Other Heteroferrocenes and Chemical Shift Differences between α Carbons (Δα^{a}) and β Carbons (Δβ^{a} ppm) for Di and Monoheteroferrocenes

Heteroferrocene	C_α	C_β	Cp	Δ_α	Δ_β	Reference
ferrocene			67.8			9
azaferrocene	90.00	72.60	68.70			9
diphosphaferrocene	79.20	82.00	70.20	2.10	2.2	28
phosphaferrocene	77.20	79.80	70.20			2
2,2'5,5'tetraphenyl-diphosphaferrocene	see Table II			3.1	4.5	this work
2,5-diphenylphospha-ferrocene			74.02			this work
3,3'4,4'tetramethyl diphosphaferrocene	82.10	97.50		3.9	2.7	10
3,4-dimethylphosphaferrocene	78.20	94.80	71.40			2
2,2'5,5'tetramethyl-diarsaferrocene	108.50	86.10		1.9	3.5	11
2,5-dimethyl arsaferrocene	106.60	82.62	71.24			11

$^{a}\Delta_\alpha$ = difference in C_α shift between di and monophosphaferrocenes. Δ_β defined similarly.

TABLE IV. ^{57}Fe Mössbauer Data. (Isomer Shifts *IS*, Quadrupole Splitting *QS* and Linewidth Half Width at Half Height Γ. All in mm s^{-1})

Compound		*IS*	*QS*	Γ	Δ*QS*
I	b	0.51(1)	2.07(1)	0.19(1)	–
	c	0.47(1)	2.10(1)	0.13(1)	0.12(2)
II	b	0.48(1)	2.11(1)	0.19(1)	–
	c	0.45(1)	2.28(1)	0.19(1)	0.17(2)
III^{d}	b	0.51(1)	2.00(1)	0.15(1)	–
	c	0.47(1)	2.21(2)	0.16(1)	0.21(3)
IV	b	0.51(1)	2.07(1)	0.21(1)	–
	c	0.52(2)	2.12(3)	0.18(3)	0.05(4)
V	b	0.50(1)	2.05(1)	0.16(1)	–

^{a}Δ*QS* *QS* acid–*QS* solid. ^{b}Solid at 80 K. ^{c}Triflic acid FSS at 80 K. ^{d}Previously reported in ref. 1.

relative to ferrocene is the ability of the phosphorus atom to reduce the π electron donating power of the ligand. This effect has been well documented using other probes [14]. Variation of *QS* values as a function of ligand π donating power has been discussed in relation to other organoiron complexes [15]. In this context it is interesting to note that the ratios of *QS* values of phosphaferrocene to ferrocene (0.863) is quite similar to the ratio of the force constants for ring metal bonds in phosphacymatrene and cymatrene (0.813) [14]. Azaferrocene has a *QS* comparable to phosphaferrocene [15] and the relative weakness of the aza Cp–metal bond compared with the Cp metal bond has been demonstrated by mass spectral studies [16].

Iron protonation in ferrocenes causes increases in *QS* due to removal of electron density from iron based orbitals (e_{2g}) [3] an effect also occurring in iron mercury bonded species [17]. Derivatives **I** → **IV** all showed increases in *QS* when dissolved in triflic acid and studied as frozen solid solutions (FSS), confirming metal protonation [3]. **I** → **II** also showed a slight reduction in isomer shift (IS) as found with protonated ferrocenes [3].

The increases in *QS* on protonation are on average much smaller (~0 1 mm s^{-1}) than those of the ferrocenes (~0.2 mm s^{-1}). This can be attributed to differences in the basicity of the iron atom in the two systems, (*vide supra*).

MO calculations predict that the charge on the central atom should be greater for the phosphaferrocenes than for ferrocene itself [18] The more basic monophosphaferrocene **II** has a significantly higher Δ*QS* value than the less basic **IV** in triflic acid FSS.

Factors such as steric hindrance to approach of the acid in **IV** will also be important. For **III** such steric problems do not occur since the reagent can approach the iron atom from a direction remote from the phenyl substituents. We had previously interpreted the increased *QS* value for 2,2'5,5'-tetraphenyldiphosphaferrocene in triflic acid as being due to protonation of the *para* position of the Ph ring [1]. This assignment was made based on erroneous ^{31}P NMR data, pointed out to us by Mathey [19]. Although protonation at this position certainly occurs as is evident from deuterium exchange [1], we are nevertheless now of the opinion that the major protonation site is the iron atom.

Both in the parent and protonated forms, Mössbauer spectroscopy indicates that the iron atom is less basic in the phosphaferrocene system compared to ferrocene.

An inverse relationship between the oxidation potential and the *QS* of a series of ferrocenyl derivatives has recently been established [20]. The lowering of *QS* caused by the phosphorus atom indicates, along with other factors previously mentioned, that phosphaferrocenes should be harder to oxidise than ferrocenes and indeed this is found in practice. Mathey and co-workers have shown that the inclusion of a phosphorus atom causes an anodic shift of the oxidation potential [21]. The *QS* values for phosphaferrocenes and the electrochemical oxidation potentials measured by Mathey and co-workers [21] do not fit the correlation established for ferrocenes [20]. This is due to electrochemical data being obtained under different experimental conditions. If the electrochemical data from ref. 21 is compared to the *QS* values for phosphaferrocenes, a correlation does appear to exist, however the electrochemical data on phosphaferrocenes is too limited at present for definite quantitative conclusions.

Conclusions

Both NMR and ^{57}Fe Mössbauer studies show that phosphaferrocenes have an iron protonated structure in triflic acid, thus they parallel the behaviour of ferrocene [3] rather than azaferrocene, which is N-protonated in quite weakly acidic media [22].

The phosphorus atom appears to have lost all Brönsted base activity. The greatly reduced Lewis base activity has been documented by Mathey *et al.* [5] although the phosphorus lone pair can act as a σ donor to low oxidation state metals [23]. The reduced activity of the P lone pair has been explained in phosphaferrocene and phosphacymatrene by MO calculations [18, 24].

Residual electron densities calculated for phosphaferrocene [18] are in accordance with the deuteriation patterns observed. The most electron rich carbon sites are those α to phosphorus which accounts for the marked preference for H/D exchange to occur here in **I** and **II.** In **III** and **IV** where the α positions are phenylated, the arene substituents are the preferred site for electrophilic reactions as in 2,2′5,5′-tetraphenyl diphosphaferrocene [1]. With **III** some H/D exchange is detected on the Cp ring but not at position β to phosphorus. This is exactly the behaviour expected from calculated electron densities [18].

H/D exchange at comparable or faster rates on the arene compared to the Cp ring of **III** strongly supports the ^{13}C evidence that the PCp ring quite strongly deactivates the Cp ring. The question of the structure of the protonated phosphaferrocenes is an interesting one. Compared with the unprotonated species, a much larger difference in ^{1}H shifts occurs for the α and β protons. Bitterwolf [25] has shown that the ring protons nearest the iron bound proton are deshielded by about 0.3 ppm. For monophosphaferrocene the Hα, Hβ shifts are 4.05, 5.30 ppm in $CDCl_3$ and 4.00, 6.80 in CF_3SO_3H. It is thus probable that the proton enters on the side remote from the phosphorus atom.

Experimental

All manipulations involving phosphaferrocenes were performed under Ar or N_2. Solutions for NMR spectroscopy were used immediately after preparation as were solutions in triflic acid solutions for Mössbauer spectroscopy. Triflic acid was purchased from 3M Chemicals. Triflic acid-d$_1$ was prepared from the anhydride and D_2O.

Phosphaferrocenes **I** → **V** were prepared by the reaction of the corresponding phospholyl metal with η^5-cyclopentadienyl η^6-mesitylene iron(II) hexafluorophosphate, full details of which appear elsewhere [26]. Other preparations are given in references [2] (**I, II**), [1] (**III**) and [27] (**IV**). Phosphaferrocenes were stored under N_2 at −20 °C and used as soon as possible after preparation. 2,2′5,5′-tetraphenyldiphosphaferrocene was prepared by literature methods [28]. Deuteriated samples were prepared by dissolving the phosphaferrocene in a 100-fold excess of triflic acid-d$_1$ and recovering by quenching with D_2O (reaction time **I, II** 5–10 min; **III, IV**, 1 h). After neutralisation with Na_2CO_3 the deuteriated product was recovered by extraction with CH_2Cl_2.

^{1}H NMR spectra were obtained on a Varian EM 360 instrument and ^{31}P NMR spectra on a Brucker Spectrospin WP 80 instrument.

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