A Study of Acylmonophosphaferrocenes in Strong Acids

R. M. G. ROBERTS, J. SILVER and A. S. WELLS*

Department of Chemistry and Biological Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, U.K.

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Abstract

The behaviour of a number of acylated monophosphaferrocenes in strong acids has been investigated using ^{1}H and ^{31}P NMR, ^{57}Fe Mössbauer spectroscopy and hydrogen–deuterium exchange. The results show that, as with ferrocenyl ketones and diphosphaferrocenyl ketones, the carbonyl oxygen is protonated in preference to phosphorus or iron-based lone pairs. Monoacylated monophosphaferrocenes were found to undergo facile exchange of their α-protons in deuteriated acids.

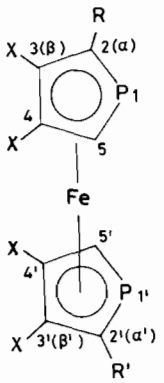
Introduction

We have recently reported the behaviour of acylated diphosphaferrocenes in strong acids [1]. It was found that these compounds reacted in an identical manner to acylated ferrocenes, protonation occurring at the carbonyl oxygen rather than at the iron or phosphorus atoms.

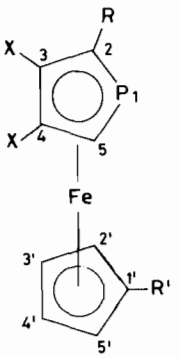
A second important class of phosphorus-containing ferrocenes are the monophosphaferrocenes, which have one Cp and one phosphacyclopentadienyl (PCp) ligand. Acyl derivatives of monophosphaferrocenes are not easily obtained by usual Friedel–Crafts reactions [2], since monophosphaferrocenes are decomposed by $AlCl_3$ [3]. However, we have recently developed a synthetic route which has made available a range of monophosphaferrocenyl ketones [4–6]. The work reported here concerns an investigation of the structure of protonated acylated monophosphaferrocenes together with a comparison with their diphosphaferrocene counterparts.

Results and Discussion

The structures of the mono- and diphosphaferrocenes used in this study appear below.



1a X = Me, R = COMe, R^1 = H
1b X = Me, R = COC_6H_5, R^1 = H
1c X = Me, R = R^1 = COMe
1d X = Me, R = R^1 = COC_6H_5
2 X = H, R = COC_6H_5, R^1 = H



3a X = Me, R = COMe, R^1 = H
3b X = Me, R = COC_6H_5, R^1 = H
3c X = Me, R = H, R^1 = COMe
3d X = Me, R = H, R^1 = COC_6H_5
3e X = Me, R = H, R^1 = COt-Bu
3f X = H, R = H, R^1 = COC_6H_5
3g X = Me, R = R^1 = COMe
3h X = Me, R = COMe, R^1 = COC_6H_5

The range of new compounds covers PCp acylated compounds (**3a, b**), Cp acylated analogues (**3c–f**) and monophosphaferrocenyl diketones (**3g, h**) as well as the new benzoylated diphosphaferrocene (**2**).

*Present address: Smith, Kline and French Research Laboratories, Old Powder Mills, Leigh, Tonbridge, Kent, U.K.

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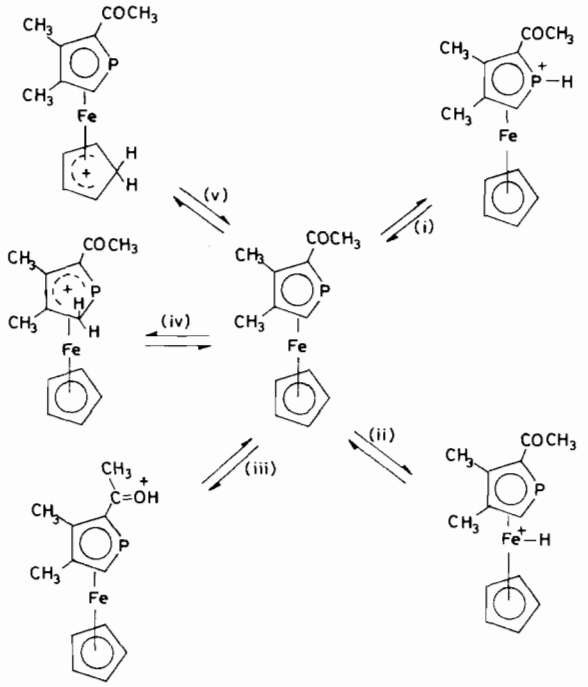


Scheme 1.

Monophosphaferrocenyl ketones can in principal undergo several types of protonation as shown in Scheme 1. In addition to protonation at phosphorus (i) and iron (ii), and the carbonyl oxygen (iii), sigma complexes may also be formed [(iv) and (v)].

In order to determine which equilibrium predominates, solutions of the phosphaferrocenyl ketones in strong acids were examined by ^{1}H and ^{31}P NMR spectroscopy and the results compared with those obtained in $CDCl_3$. The compounds were also examined in deuteriated acids and ^{57}Fe Mössbauer spectra were obtained for selected samples.

The yellow–orange ketones dissolved in strong acids to give intense purple solutions from which they could be recovered unchanged by neutralisation with aqueous Na_2CO_3 followed by extraction into a suitable solvent. ^{31}P NMR spectroscopy provides the most useful structural probe for the phosphaferrocenes, the data for which appear in Table 1. Two general points can be made. The spectra obtained in strong acids do not show any primary phosphorus–hydrogen coupling ($^{1}J_{PH}$ = ~500 Hz), thus ruling out phosphorus protonation (i). Metal-protonated phosphaferrocenes show characteristically large upfield shifts of ~60 to 182 ppm [7]. By contrast, the ^{31}P signals for monophosphaferrocenyl ketones occur markedly downfield in acid media showing the absence of metal protonation. When diphosphaferrocenyl ketones, **1a** to **1d**, are protonated at the carbonyl oxygen in trifluoroacetic acid (TFA) [8], the ^{31}P signals are shifted downfield relative to those in $CDCl_3$ [1]. Thus carbonyl protonation also occurs in the monophosphaferrocenes. 2-Acetyltetramethyldiphosphaferrocene (**1a**) shows two well separated phosphorus resonances with the expected coupling constants ($^{2}J_{PH}$) in both $CDCl_3$ and TFA [1].

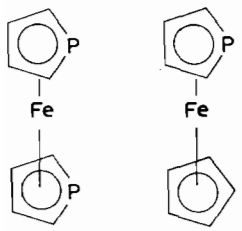
TABLE 1. ^{31}P NMR Data

Compound	Solvent	$\delta^{31}P$ [a]	$^{2}J_{PH}$ [b]	$\Delta\delta^{31}P$ [c]	Reference
2	$CDCl_3$	−40.2(d), −56.8(t)	36, 36	–	
	TFA	−26.4(d), −50.0(t)	36, 36	13.8, 6.80	
3a	$CDCl_3$	−54.4(d)	38	–	4
	TFA	−24.6(d)	38	29.8	
3b	$CDCl_3$	−52.7(d)	36	–	4
	TFA	−20.0(s)	[d]	32.7	
3c	$CDCl_3$	−77.1(t)	36	–	5
	TFA	−63.6(s)	[d]	13.8	
3d	$CDCl_3$	−76.7(t)	36	–	5
	TFA	−55.6(d)	[d]	20.8	
3e	$CDCl_3$	−82.2(t)	37	–	5
	TFA	−70.0(s)	[d]	12.2	
3f	$CDCl_3$	−65.5(t)	37	–	5
	TFA	−52.8(s)	[d]	12.7	
3g	$CDCl_3$	−53.0(d)	36	–	6
	70% H_2SO_4	−24.5(d)	36	28.5	
	CF_3SO_3H	−2.3(d)	36	50.7	
3h	$CDCl_3$	−51.5(d)	36	–	6
	70% H_2SO_4	−21.5(d)	36	30.0	
	CF_3SO_3H	−5.1(d)	36	46.4	

[a] δ in ppm, (s) = singlet, (d) = doublet, (t) = triplet. [b] J in Hertz. [c] $\Delta\delta$ = change in $\delta^{31}P$ in acid solvent compared to $\delta^{31}P$ in $CDCl_3$. [d] $^{2}J_{PH}$ = not resolved due to α-H exchanging with the solvent.

By contrast, the benzoyl analogue, **1b**, shows two distinct resonances in $CDCl_3$ but only one broad signal in TFA. In order to account for this phenomenon, we examined the β-unsubstituted compound, **2**. This compound showed two well defined P resonances in TFA (Table 1). The phosphorus in the protonated ligand was shifted downfield by 13.8 ppm ($\Delta\delta^{31}P$) compared to a value of +23 ppm for **1b**. The smaller $\Delta\delta^{31}P$ value probably reflects a lower degree of protonation of **2** in TFA compared to **1b**, due to the absence of electron releasing methyl groups which would lower the ketone basicity [9]. The absence of the methyl groups would also markedly slow down hydrogen exchange [10, 11]. The broad ^{31}P resonances observed for **1b** in TFA can therefore be explained by the faster hydrogen exchange in **1b** compared with that in **2**, where well resolved signals are found.

The monophosphaferrocenyl ketones that are substituted on the PCp ligands (**3a** and **3b**) show downfield shifts of ~30 ppm in TFA compared to ~22 ppm for their diphosphaferrocenyl counterparts **1a** and **1b**. This may well be due to a somewhat higher basicity for the monophosphaferrocenyl system.



4 **5**

Evidence for this comes from a comparison of the ^{31}P shifts of diphosphaferrocene **4** (−59 ppm, ref. 2) with that of monophosphaferrocene **5** (−67.5 ppm, ref. 12) which indicates a significant transfer of charge from the Cp to the PCp ring with consequent build up of electron density on any acyl oxygens present in the latter ring. Support for this charge redistribution comes from the ^{13}C NMR data for monophosphaferrocene itself where the free Cp resonance is 3.3 ppm downfield from that of ferrocene [3]. As in the case of **1b**, the fine structure of the phosphorus resonance for **3b** is lost in TFA, the signal appearing as a broad singlet rather than the expected doublet. This must be caused by a faster exchange of the α-protons in the benzoyl derivatives compared to that in the acetyl derivatives. This in turn could be linked to the lower basicity of the substrate and a lower degree of protonation at the carbonyl group which results in faster exchange of the α-protons. It would appear from these results that benzoylphosphaferrocenes are in fact weaker bases than acetylphosphaferrocenes which would parallel the relative basicities of benzoyl and acetyl ferrocene (pK_a values of ~3.31 and −2.80 respectively) [9].

A general trend found here and in our initial work is that both mono and diphosphaferrocenyl ketones [1] are much more prone to undergo electrophilic exchange processes of their ring protons than ferrocenyl ketones in media of comparable acid strength. This is in contradistinction to the usual reactivity found for η^5-PCp ligands compared with η^5-Cp ligands. η^5-PCp complexes are less reactive towards Friedel–Crafts substitution compared with their η^5-Cp analogues. This behaviour of the ketones in acidic media is therefore probably due to a lowering of the basicity caused by the inclusion of a phosphorus atom(s) in the Cp ring with concurrently less protonation at the carbonyl group in the phosphaferrocene systems allowing exchange to take place at a faster rate. The Cp substituted ketones (**3c–3g**) generally show lower $\Delta\delta^{31}P$ values in TFA than the PCp acylated compounds; this would be expected since the protonated ketone substituents are on ligands remote from the phosphorus nuclei.

The diketones, **3g** and **3h**, gave downfield shifts of +28.5 and 30.0 ppm respectively in 70% H_2SO_4 compared to +24 ppm for 2,2′-diacetyl-3,3′,4,4′-tetramethyldiphosphaferrocene in the same solvent. In the much stronger acid, trifluoromethanesulphonic acid ($H_0 = -14.6$ [13] *versus* −5.9 for 70% H_2SO_4 [14]), increased downfield shifts are found (Table 1). It is likely that these ketones are monoprotonated in 70% H_2SO_4 and diprotonated in triflic acid. Both ketones therefore show behaviour towards these acids similar to that of 1,1′-diacylferrocenes [15] and 2,2′-diacyldiphosphaferrocenes [1].

^1H NMR Results

The ^1H chemical shifts obtained for the solutions are given in Table 2. The ^1H NMR results confirm that iron protonation does not occur. All spectra in strongly acidic media showed the absence of high field resonances due to iron-bound protons ($\delta Fe^+H = -0.8$ to −2.93 ppm for iron-protonated monophosphaferrocenes [7]). The changes found in the spectra obtained in acid solution are in accord with protonation at the carbonyl groups.

In $CDCl_3$ the signals for the acetylated PCp ligands are readily assigned. The acetyl methyl groups α to phosphorus occur as doublets at ~2.30 ppm ($^4J_{PH}$ ~ 4 Hz). The methyl group at lowest field (~2.4 ppm) is the methyl group at position 3 (βMe_3), since it is deshielded by the anisotropy of the neighbouring carbonyl group [1]. For protonated acetyl groups, the acetyl Me resonance is now the most deshielded. The increased shielding of βMe_3 is caused by a reduction in the anisotropy of the protonated carbonyl group [16]. The J_{PH} coupling of the 2-acyl groups

TABLE 2. ^{1}H NMR Results for Diphosphaferrocenes

Compound	Solvent	δαH [a]	βMe$_3$	βMe$_4$	2-MeCO [b]	Cp	Other
PCp acylated monophosphaferrocenes							
3a	$CDCl_3$	4.16(d)	2.46(d)	2.26(s)	2.35(d)	4.30(s)	
	TFA	3.80(d)	1.91(s)	1.80(s)	1.96(s)	3.97(s)	
3b	$CDCl_3$	4.13(d)	2.38(s)	2.20(s)		4.27(s)	7.50(m), 7.90(m) arene
	TFA	[c]	1.95(s)	1.87(s)		4.35(s)	~7.30(m) arene
		δαH [a]	βMe	MeCO	CpH2,5	CpH3,4	Other
Cp acylated monophosphaferrocenes							
3c	$CDCl_3$	3.87(d)	2.11(s)	2.70(s)	4.90(m)	4.45(m)	
	TFA	[c]	1.55(s)	2.08(s)	4.60(s)		
3d	$CDCl_3$	3.80(d)	2.05(s)		4.97(m)	4.55(m)	7.50(m), 7.90(m) arene
	TFA	[c]	1.48(s)		4.65(s)		~7.20(m) arene
3e	$CDCl_3$	3.70(d)	2.15(s)		4.90(m)	4.34(m)	1.30(s) t-Bu
	TFA	3.40(d)	2.00(s)		4.10(m)	4.50(s)	0.85(s) t-Bu
	80% H_2SO_4	4.30(d)	2.00(s)		5.45(s)		1.60(s) t-Bu
3f	$CDCl_3$	4.00(d)			4.91(m)	4.60(m)	5.15(m) βH, 7.50(m), 7.90(m) arene
	TFA	[c]			4.70(s)		3.95(m) βH, ~7.30(m) arene
		δαH [a]	βMe$_3$	βMe$_4$	2-COMe [b]	1′-COMeCp	Cp	Other
Monophosphaferrocene diketones								
3g	$CDCl_3$	4.10(d)	2.47(s)	2.23(s)	2.37(d)	2.42(s)	4.50(m), 4.68(m), 4.88(m)	
	70% H_2SO_4	4.77(d)	2.05(s)	2.00(s)	2.27(s)	2.35(s)	4.80(m), 4.92(m)	
3h	$CDCl_3$	4.10(d)	2.40(s)	2.20(s)	2.30(d)		4.57(m), 4.85(m), 5.08(m)	7.62(m), 7.94(m) arene
	70% H_2SO_4	4.82(d)	2.10(s)	2.00(s)	2.18(s)		4.97(m)	~7.70(m) arene

Results in $CDCl_3$ taken from refs. 4–6; (s) = singlet, (d) = doublet, (m) = multiplet. [a] $^2J_{PH}$ values 36–38 Hz. [b] $^4J_{PH}$ values ~ 4 Hz. [c] Resonance not observed due to exchange with solvent.

was not resolved in acidic media. However, the signals could be readily identified since they were noticeably broader than signals from βMe groups. The βMe groups for the benzoylated PCp ligands had very similar chemical shifts to their acetyl analogues in acid solution. For the benzoyl compounds in $CDCl_3$ the H_{ortho} and $H_{meta,para}$ of the phenyl groups are well separated (H_{ortho} at lowest field). When protonated, only one broad aromatic multiplet was found; an identical effect is found in benzoylferrocene [15, 17].

Interesting results are obtained from the 1′-acylmonophosphaferrocenes, **3c**–**3f**. In acetylferrocenes H2,5 of the Cp ring is deshielded compared to H3,4 of the Cp ring. This phenomenon is due to the anisotropy of the carbonyl group. Hence H2,5 for the CpCOR ligands of **3c**–**3f** appear at lower fields than H3,4 (Table 2). For protonated acetylferrocenes, the reverse is true due to a reduction in the anisotropy of the CO double bond [16]. In contrast to the two well separated multiplets usually found for protonated acylferrocenes, the Cp resonances for **3c**, **3d** and **3f** collapsed to singlets in TFA. Similar behaviour is also found for protonated ferrocenyl ketones where the other carbonyl substituent is large (t-butyl, 1-adamantyl) [18]. Comparison of these results would suggest that the protonated 1′-acylmonophosphaferrocenes studied here have rather large dihedral angles ($\theta > 40°$) between the Cp ring and carbonyl [18, 19] group.

^{57}Fe Mössbauer spectroscopy (see later) also shows that the protonated acyl groups of **3c**, **3d** and **3f** are not particularly efficient at withdrawing electron density from the Cp ligands.

The 1′-acylmonophosphaferrocene closest in structure to the sterically hindered ferrocenyl ketones is **3e**, the t-butyl derivative. This compound shows two separate multiplets for the Cp ring protons in TFA (Table 2). On steric grounds, it is highly unlikely that this compound has a lower value of θ than the other 1′-ketones. The reason for this behaviour is that **3e** is appreciably less basic than the other 1′-ketones (due to steric hindrance to coplanarity plus electron withdrawal by the PCp ring) and is only weakly

protonated in TFA. In the much stronger acid, 80% H_2SO_4/H_2O, the Cp signal for **3e** did collapse to a singlet. The observed magnetic equivalence of H2′(H5′) and H3′(H4′) of protonated 1′-acylmonophosphaferrocenes is almost certainly fortuitous due to a combination of electron withdrawal by the PCp ring and the reduced anisotropic effect of the $C{=}OH^+$ group.

The H2(H5) protons of **3c**, **3d** and **3f** were not observed in TFA due to exchange with the solvent. The doublet obtained for **3e** in $CDCl_3$ appeared as a singlet in TFA also indicating exchange. However, for **3e** in 80% H_2SO_4 the H2(H5) signal reverts to a doublet with $^2J_{PH}$ in the expected range (36–38 Hz). This result further confirms the hypothesis that increased carbonyl protonation even in the remote ring retards the α-H exchange process and suggests that **3c**, **3d** and **3f** are not fully protonated in TFA. The inclusion of a phosphorus atom again lowers the basicity compared with simple ferrocenyl ketones which are fully protonated in TFA [15].

In general, in the ^{1}H NMR spectra of the PCp ring the diketones **3g** and **3h** in TFA were similar to that of **3a**. However, the Cp ligands in **3g** and **3h** show three resonances in $CDCl_3$ rather than the expected two. The two proton multiplet at lowest field was assigned to H2′,5′ and two multiplets at higher field assigned to H3′ and H4′. The Cp ligand also shows five ^{13}C resonances which is attributed to restricted rotation about the central axis [6] causing magnetic non-equivalence of all the ring carbons. In 70% H_2SO_4 the pattern of Cp resonances for **3g** and **3h** changes. **3g** gives one multiplet and **3h** two multiplets in the ratio 3:1 (high field most intense). We believe that this change is due to an alteration of geometry on protonation. In the neutral form a *trans* orientation of the acyl groups would be preferred on steric grounds. When protonated, the molecule probably adopts a *cis* structure with the proton held between both carbonyl groups [15].

Hydrogen–Deuterium Exchange

Many of the compounds studied here were found to undergo facile exchange of the α-protons in the PCp ring. This was shown by the examination of ^{1}H NMR spectra in deuteriated acids. Both **3a** and **3b** were deuteriated at the α-positions in TFA-d; identical behaviour has been reported for their diphosphaferrocenyl counterparts, **1a** and **1b** [1]. No exchange of the Cp ring protons was detected over the time taken to fully deuteriate the α-positions, even though the PCp rings carry deactivating acyl substituents. This interesting finding further illustrates the highly unreactive nature of the Cp ring in monophosphaferrocenes towards electrophilic substitution reactions [3, 6] and reflects the transfer of electron density from Cp to PCp rings.

The 1′-acylmonophosphaferrocenes, **3c–3f**, also underwent exchange at the α-sites in the PCp ring. With **3f**, which has an unsubstituted PCp ring, no exchange of the β-protons was detected. This result parallels those obtained for hydrogen–deuterium exchange in alkyl and aryl substituted phosphaferrocenes where the β-positions are also inert to deuteriation [7, 8]. It would appear that this is a general feature of coordinated η^5-PCp and its arsenic analogue, η^5-AsCp. A brief report has stated that 2,2′,5,5′-tetramethyldiarsaferrocene undergoes exchange of the β protons in TFA-d [20], however, a more recent kinetic study of the diarsaferrocene has shown that the relative rates of exchange of the α- and β-positions exceeds 10^6:1 [21]. Thus both coordinated η^5-PCp and η^5-AsCp show patterns of exchange identical to those of the aromatic heterocycles furan and thiophen [22]. These observations are in accord with the greatly enhanced aromaticity of coordinated η^5-PCp and η^5-AsCp ligands compared to their heterocyclic cyclopentadiene precursors [23].

The addition of two acyl groups to a diphosphaferrocene (**1c** and **1d**) is sufficiently deactivating to stop exchange of the α-protons in 70% D_2SO_4/D_2O (*w/w*). In the 2,2′-diacetyl compound (**1c**) deuterium exchange was found instead in the acetyl methyl protons. This process is thought to occur via enolisation of the protonated acetyl groups and proceeded at a much faster rate than in 1,1′-diacetylferrocene [1]. As expected, the α hydrogens in both monophosphaferrocenyl diketones, **3g** and **3h**, did not exchange their α-proton in 70% D_2SO_4/D_2O; there was also no measurable exchange of the acetyl methyl protons over the time taken for **1c** to exchange completely with solvent. It would therefore appear that two ring phosphorus atoms are necessary to activate a diacetylferrocene to undergo this type of exchange process.

^{57}Fe Mössbauer Results

^{57}Fe Mössbauer results obtained for **3a**, **3b**, **3c**, **3d** and **3f** as solids and in TFA frozen solution are given in Table 3. The results show that there is negligible change in the chemical isomer shifts (*IS*) of the ketones and the protonated ketones (frozen solution) compared to their α-unsubstituted precursors.

The addition of an acyl group to the ferrocene/diphosphaferrocene nucleus lowers the quadrupole splitting (*QS*) by conjugate electron withdrawal from ring-based molecular orbitals. This effect is increased when the acyl group is protonated. Thus an acetyl group lowers the *QS* of ferrocene by on average 0.12 mm s^{-1} (ΔQS) whereas a protonated acetyl group causes a decrease of 0.30 mm s^{-1} [15] ($\Delta QS[H^+]$). It will be seen from Table 3 that similar reductions in *QS* occur for the monophosphaferrocenes where the

TABLE 3. ^{57}Fe Mössbauer Results

Compound	Phase[a]	*IS* [b]	*QS* [b]	ΔQS [c]
MPF[d, e]	S	0.51(1)	2.07(1)	
3,4-dimethyl MPF[e]	S	0.48(1)	2.11(1)	
3a	S	0.48(1)	1.93(1)	0.18(2)
	FSS	0.50(1)	1.77(1)	0.34(2)
3b	S	0.49(1)	2.00(1)	0.11(2)
	FSS	0.53(1)	1.78(1)	0.33(2)
3c	S	0.51(1)	2.06(1)	0.05(2)
	FSS	0.50(1)	1.96(1)	0.15(2)
3d	S	0.51(1)	2.03(1)	0.08(2)
	FSS	0.51(1)	1.94(1)	0.17(2)
3f	S	0.52(1)	2.00(1)	0.07(2)
	FSS	0.53(1)	1.94(1)	0.13(2)

[a]Phase, S = solid, FSS = frozen solid solution in TFA. All data obtained at 80 K. [b]*IS* = isomer shift; *QS* = quadrupole splitting, both in mm s^{-1}. [c]ΔQS = decrease in *QS* of ketone compared to parent phosphaferrocene; MPF or 3,4-dimethyl MPF. [d]MPF = monophosphaferrocene. [e]Data from ref. 7.

acyl function is on the PCp ring. This is also true for the diphosphaferrocenes **1a** and **1b** ($\Delta QS[H^+]$ are 0.26 and 0.30 mm s^{-1} respectively). However, the ΔQS values for the Cp acylated derivatives are significantly smaller (ΔQS 0.05–0.08 mm s^{-1} and ΔQS-$[H^+]$ 0.13–0.17 mm s^{-1} for **3c**, **3d** and **3f**). This reflects the reduced ability of the substituent to withdraw electrons from a ring already denuded of electron density by the PCp ring.

Experimental

All compounds were prepared by literature methods apart from benzoyldiphosphaferrocene (**2**) [4 - 6]. Owing to the sensitivity of monophosphaferrocenes towards atmospheric oxidation, spectroscopic data were obtained on freshly prepared solutions which were made from substrates purified immediately before dissolution.

^{1}H NMR spectra were obtained on a Varian EM360 spectrometer (reference external TMS) and ^{31}P NMR spectra were obtained on a Bruker WP80 spectrometer (reference 85% H_3PO_4, δ +ve downfield shift). Mössbauer data were obtained and fitted as previously described [24]. Chemical shifts are relative to iron metal at 298 K.

2-Benzoyldiphosphaferrocene

This compound was synthesised in 63% yield by an identical method to that reported for the synthesis of **1b** and **3b** (benzoic anhydride/triflic acid in dichloromethane) [4]. The compound was isolated as a red oil after chromatography on silica gel (70/230 mesh) (eluent benzene). ^{1}H NMR ($CDCl_3$) 4.00m (H2′H5′); 4.47m (H5); 5.40m (H3′H4′); 5.57, 6.30m (H3,H4); 7.50, 7.90m (arene). Molecular weight M^+ 326 (calc. 326) in 70 eV mass spectrum. Other ions *m/e* 139 $[C_4H_4PFe]^+$, 105 $[C_6H_5CO]^+$, 56 $[Fe]^+$.

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