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The Formation and Spectroscopic Identification of some α-Phosphaferrocenyl Carbenium Ions

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Abstract

A number of α-phosphaferrocenyl alcohols have been synthesized and their behaviour in trifluoroacetic acid solution examined by investigating changes in ^{31}P NMR and ^{57}Fe Mössbauer spectra. The results indicate that dehydration occurs and carbenium ions are formed. These were found to have considerably lower stability than α-ferrocenyl carbenium ions.

Introduction

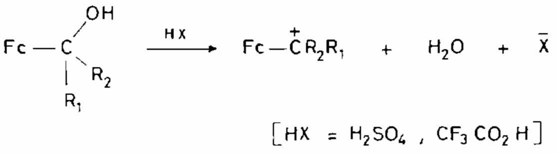
In recent years there has been a growing interest in the synthesis and reactivity of phosphorus-containing analogues of ferrocene. Typical of such compounds are monophosphaferrocene and diphosphaferrocene in which one or both cyclopentadienyl (Cp) ligands are replaced by phosphacyclopentadienyl ligands (PCp).

Recent investigations have shown that two, three and even five phosphorus atoms can be substituted for CH units in the η^5-ligand [1, 2], however, mono- and diphosphaferrocene derivatives remain the most intensively studied of the η^5-PCp systems to date.

We have recently reported the behaviour of such phosphaferrocene derivatives in strong acids and their reactivity towards electrophilic species [3–6]. Alkyl and aryl mono- and diphosphaferrocenes are metal-protonated in strong acids (CF_3SO_3H) [3, 4], and thus they parallel the behaviour of ferrocene rather than azaferrocene which protonates on the hetero atom [7]. As with ferrocene, the iron atom can form metal–metal bonds with such species as Ag(I), Cu(I) and $AlCl_3$ [6]. Groups such as $Fe(CO)_4$ are known to complex to the phosphorus atom [8], but 'hard' electrophiles add to the iron atom, a fact which can be explained by molecular orbital theory [9]. The HOMOs in such complexes are iron-based lone pairs (comparable to the a_{1g} and e_{2g} HOMOs of ferrocene) whereas the phosphorus lone pairs are low lying in energy which explains the ability of some electrophiles to bond to iron rather than phosphorus.

Acyl ferrocenes protonate at the keto oxygen in strong acids [10], as do acyl diphosphaferrocenes [5]. The inclusion of a phosphorus atom in the Cp ring of ferrocene derivatives does not therefore markedly affect the behaviour towards strong acids.

The ability of certain organometallic substituents to stabilise α-carbenium ion centres has been known for many years. The most intensively investigated are the α-ferrocenyl carbenium ions [11]. The high stability of these ions has been shown to be due to electron donation from the iron-based e_{2g} orbitals into the vacant p orbital of the carbenium ion centre [12–14]. The generation of such carbenium ions is most commonly effected by dehydration of the corresponding α-alcohols in strong acids.



$$Fc{-}C(OH)R_1R_2 \xrightarrow{HX} Fc{-}\overset{+}{C}R_2R_1 + H_2O + \overset{-}{X}$$

$$[HX = H_2SO_4,\ CF_3CO_2H]$$

In view of the fact that the P atom in phosphaferrocenes does not protonate, we decided to investigate the possible formation of α-phosphaferrocenyl carbenium ions from the corresponding alcohols in trifluoroacetic acid and report our findings herein.

Results and Discussion

The compounds used in this study are shown below. These three examples were chosen to cover the three possible types of phosphaferrocenyl alcohols

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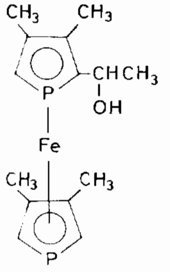

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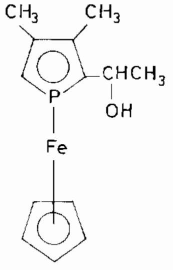
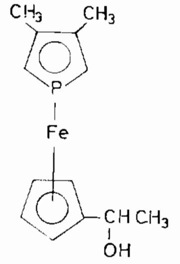


II



III

Because of the chiral carbon atom attached to C_2 of the PCp ring and the resultant asymmetry of the PCp ring, both **I** and **II** exist as diastereomeric mixtures. In the case of **I**, the diastereomers (**IA**, **IB**) were separated, **IA** being the least polar isomer (eluted first from chromatography columns). Some preliminary work with **IA**/**B** mixtures showed that diastereomeric separation was unnecessary hence **II** was examined as a diastereomeric mixture.

The secondary alcohols were synthesized via reduction of their acetyl analogues. The synthesis and separation of **IA** and **IB** was first reported by Mathey and co-workers [15] who used $NaBH_4$ in methanol to reduce 2-acetyl-3,3′,4,4′-tetramethyldiphosphaferrocene. Initially, we used an identical procedure but found that the reaction also produced the methyl ether derivatives of **IA** and **IB** as by products. This problem was eliminated by using $LiAlH_4$ in anhydrous ether which gave the required alcohols in good to excellent yields. This method produced equal amounts of **IA** and **IB**. Whilst the diastereomers of **II** were not separated, the ^1H NMR spectrum showed several signals that were clearly resolved for each diastereomer (notably from the Cp rings and the methyl group of the hydroxyethyl substituents, see 'Experimental'). Integration of these signals showed both diastereomers to be present in equal amounts. These results show that the reduction of 2-acetylphosphaferrocenes by $LiAlH_4$ is not stereoselective.

Reactivity in TFA

I to **III** dissolved in TFA to give intense brown solutions. Owing to concentration problems and some decomposition of some of the derivatives in this medium, ^1H NMR spectra of such solutions did not prove to be a very useful diagnostic probe of the nature of the new species produced. Much more information could be obtained from ^{31}P NMR and ^{57}Fe Mössbauer spectroscopy.

^{31}P NMR Spectroscopy

The ^{31}P NMR results for **I**–**III** are presented in Table 1, together with data for related systems. Before discussing the results, several important points need to be stated. Firstly, for diphosphaferrocenes that have one PCp with a 2-substituent, δ ^{31}P in this ring is readily assigned by the multiplicity of the signal (a doublet due to $P-H_2$ coupling). Secondly in unsymmetrically substituted diphosphaferrocenes, coupling between the two non-equivalent phosphorus nuclei is sometimes observed. Thirdly, both isomers of diastereomeric phosphaferrocenes have quite distinct ^{31}P NMR shifts.

In $CDCl_3$, δ ^{31}P for precursors 3,3′,4,4′-tetramethyldiphosphaferrocene (TMDPF) and 3,4-dimethylmonophosphaferrocene (DMMPF), are found at −70.6 and −82.3 ppm respectively (Table 1, entries 1 and 3). In CF_3SO_3H, where these compounds exist as metal protonated species, very large upfield shifts are found (Table 1, entries 2 and 4). The addition of acetyl groups at the 2 position causes a downfield shift of δ ^{31}P (Table 1, entries 5, 7, 9) because of the well characterised deshielding nature of this substituent. Protonation of the carbonyl oxygen in TFA increases the electron-withdrawing power of the substituent and further downfield shifts of δ ^{31}P are observed (Table 1, entries 6, 8, 10).

In $CDCl_3$, compounds **I**–**III** have δ ^{31}P values close to their parent derivatives (Table 1, entries 11, 13, 15, 17), the hydroxyethyl substituent having a relatively small electronic effect. This is also reflected in the similarity of the ^{31}P shifts of the two phosphorus atoms present. Dramatic changes occur, however, when **IA** and **IB** are dissolved in TFA (Table 1, entries 12, 14). Two important effects can be seen. For each diastereomer, the two phosphorus nuclei become considerably deshielded in TFA relative to $CDCl_3$. The differences between the δ ^{31}P values for the phosphorus nuclei in each diastereomer also increase, that in the 2-substituent PCp ring showing the larger downfield shift. Phosphorus–phosphorus coupling was also observed in these spectra. These observed couplings were characterised by the fact that they were unaffected by decoupling the H_2 proton. These changes in the ^{31}P NMR spectra strongly suggest that α-carbenium ions are indeed formed in TFA. A protonated 2-acetyl group causes a change in δ ^{31}P ($\Delta\delta$) of between 21 and 29 ppm, whereas a full positive charge on C_{exo} gives rise to a much greater $\Delta\delta$ value of 45 ~ 50 ppm. The presence of a strong electron-withdrawing substituent on one PCp ring would also greatly increase the magnetic non-equivalence of the two phosphorus nuclei in each diastereomer. Perhaps the most important piece of evidence for the formation of carbenium ions is that whilst **IA** and **IB** have quite distinct spectra in $CDCl_3$, they produce identical spectra in TFA. The removal of one chiral centre converts the diastereomers into enantiomers, which have identical NMR spectra.

Similar comments apply to **II** and **III**. In $CDCl_3$, **II** gave spectra showing coupling to the α-proton and H_2 (methine); *i.e.* each diastereomer gave a doublet of

TABLE 1. ^{31}P NMR Data

Compound[a]	Entry	Solvent	δ ^{31}P [b]	J(PH) [c]	J(PP) [d]	Δδ ^{31}P [e]	Reference
TMDPF	1	$CDCl_3$	−70.6(t)	36			4
	2	CF_3SO_3H	−146.3(s)	[f]		−75.7	4
DMMPF	3	$CDCl_3$	−82.3(t)	38			3
	4	CF_3SO_3H	−230.5(t × 2)	34, 57.5[g]		−148.2	3
2-Acetyl TMDPF	5	$CDCl_3$	−48.8(d), −66.7(t)	37, 37	12		5
	6	TFA	−27.4(d), −59.7(t)	37, 37	5	+21.4, +8.6	5
2-Acetyl DMMPF	7	$CDCl_3$	−54.4(d)	38			
	8	TFA	−24.6(d)	38		+29.6	
1′-Acetyl DMMPF	9	$CDCl_3$	−77.1(t)	36			
	10	TFA	−63.6(s)	[f]		+13.5	
IA	11	$CDCl_3$	−78.2(m)	[h]	[h]		
	12	TFA	−25.3(d), −38.8(t)	37, 38	6	+52.9, +39.4	
IB	13	$CDCl_3$	−70.7(d), −71.1(t)	36, 34	[i]		
	14	TFA	−25.4(d), −38.1(t)	37, 39	6	+45.3, +33.0	
II	15	$CDCl_3$	−83.2(d × 2), −89.9(d × 2)	36.37[j]			
	16	TFA	−30.3(s)	[k]	[k]	+56.3[l]	
III	17	$CDCl_3$	−88.6(t)	36			
	18	TFA	−37.8(s)	[k]		+50.8	

[a] TMDPF = 3,3′,4,4′-tetramethyldiphosphaferrocene; DMMPF = 3,4-dimethylmonophosphaferrocene. [b] δ in ppm relative to H_3PO_4; (s) = singlet, (d) = doublet, (t) = triplet, (m) = multiplet. [c] ^2J(PH) values in Hz. [d] ^2J(PP) values for unsymmetrically substituted diphosphaferrocenes. [e] Δδ ^{31}P = the change in δ ^{31}P in acidic solvent compared to $CDCl_3$, a +ve value indicates a downfield shift. [f] ^2J(PH) not resolved due to rapid exchange with the solvent. [g] The second, large ^2J(PH) value arises from coupling to the iron-bound proton. [h] Similarity of δ ^{31}P values results in a complex multiplet, J values not resolved. [i] No apparent P–P coupling. [j] ^3J(PH) = 6 Hz. [k] Broad signals, coupling constants not resolved. [l] Average value.

doublets (Table 1, entry 15). In TFA only one signal was detected, with the expected large downfield shift (Table 1, entry 16). For both **II** and **III** in TFA coupling constants were not resolved because of the broad nature of the signals. This is possibly due to the presence of traces of paramagnetic decomposition products. The carbenium ions derived from **II** and **III** were considerably less stable than that obtained from **IA** and **IB**, the ^{31}P NMR spectrum of **III** in TFA showed several signals downfield from H_3PO_4 assigned to decomposition products from decomplexed η^5-PCp ligands.

TABLE 2. ^{57}Fe Mössbauer Data at 80 K

Compound	Phase[a]	IS [b, c]	QS [b]	ΔQS [b]
IA	S	0.48(1)	1.83(1)	
	FSS[d]	0.47(2)	1.92(1)	0.09(2)
IB	S	0.48(1)	1.80(2)	
	FSS[d]	0.46(1)	1.90(1)	0.10(3)
II	S	0.48(1)	2.15(1)	
	FSS	0.48(2)	2.22(1)	0.07(2)
		1.34(2)	3.10(2)	
III	S	0.47(1)	2.15(1)	
	FSS	0.46(2)	2.19(1)	0.04(2)
		1.36(2)	3.07(2)	

[a] Phase S = solid, FSS = frozen solid solution in TFA. [b] IS = isomer shift, QS = quadrupole splitting, ΔQS = increase in QS in TFA. All in mm s^{-1}. [c] Relative to natural iron (foil) at 298 K. [d] Trace of a high spin iron(II) species similar to those of **II** and **III** below.

Mössbauer Spectroscopy

^{57}Fe Mössbauer results obtained for **I**–**III** as solids and in TFA frozen solutions are presented in Table 2.

The major difference in the Mössbauer parameters of phosphaferrocenes compared to ferrocene is the reduction in the quadrupole splitting (QS) of ~0.3 mm s^{-1} for each phosphorus atom [3, 4]. Substituent effects operate in a similar manner to ferrocenes, *i.e.* electron-donating substituents such as methyl groups increase the QS, electron-withdrawing substituents like phenyl and acyl reduce the QS [3–5]. Withdrawal of electron density from the e_{2g} orbitals of ferrocene generally leads to large increases in the QS. For example, iron-protonated ferrocene in triflic acid frozen solution shows a QS increase of 0.23 mm s^{-1} [16], whilst that for $\mathrm{Fc\overset{+}{C}HCH_3}$ increases by 0.25 mm s^{-1} [3]. Metal protonated phosphaferrocenes also usually show increases in the QS [3, 4]. Formation of carbenium ions should therefore be characterised by increases in QS over the parent alcohol. The data in Table 2 shows this to be the case.

The alcohols have QS values close to TMDPF and DMMPF precursors [4, 5]. This is not unexpected in view of the relative electronic neutrality of the hydroxyethyl group. The diastereomers **IA** and **IB** have identical Mössbauer parameters; ^{57}Fe Mössbauer spectroscopy does not distinguish between diastereomeric phosphaferrocenes [5] as the iron electronic environments are identical. All the alcohols gave increased *QS* values in TFA, albeit much smaller than the increase found for 2-hydroxyethylferrocene. This implies that less electron density is withdrawn from the iron atom, which would not be unexpected since the η^5-PCp ligand is known to be electron-withdrawing compared to the η^5-Cp ligand. The reduction of iron participation in stabilising the carbenium ion is also probably the cause of the greatly reduced stability of the α-phosphaferrocenyl carbenium, ions compared to their ferrocene analogues. This instability is evident from the Mössbauer data since Table 2 shows that apart from the iron sites arising from the carbenium ions, a second iron site is apparent in each case. The large *QS* value ($\sim$3.07 mm s^{-1}) and high positive isomer shift ($\sim$1.34 mm s^{-1}) indicate that this second site is due to the presence of high spin iron(II) species. The fact that the second iron(II) electronic environment is high spin shows (i) the absence of η^5-bonded ligands and (ii) that this species must arise from decomposition products of the α-phosphaferrocenyl carbenium ions after decomplexation of the ligands.

Experimental

Acetyl phosphaferrocenes were synthesised by literature methods [17, 18]. All preparations were carried out under dry Ar. Column chromatography was performed on silica gel (70/230 mesh) or acidic alumina/5% H_2O (*w*/*w*), eluent benzene ethyl acetate (95:5 *v*/*v*). ^{1}H NMR spectra were obtained on a Varian EM 360 spectrometer, reference external TMS. ^{31}P NMR spectra were obtained on a Bruker WP80 spectrometer, reference 85% H_3PO_4, δ is +ve for downfield shift. The Mössbauer spectrometer and details of the liquid nitrogen cryostat, and experimental conditions have been described previously [19].

Because of their sensitivity towards atmospheric oxidation, **II** and **III** were characterised only by ^{1}H and ^{31}P NMR. Likewise, solutions of α-phosphaferrocenyl alcohols used for spectroscopic studies were prepared from freshly purified materials; spectra were obtained immediately after dissolution of the substrate.

2-α-Hydroxyethyl-3,3′,4,4′-tetramethylphosphaferrocene (IA and IB)

2-Acetyl-3,3′,4,4′-tetramethyldiphosphaferrocene (2 g, 6.3 mmol) was dissolved in anhydrous ether (80 ml) and solid $LiAlH_4$ in small portions until the ketone could not be detected by TLC analysis. Ethyl acetate (25 ml) was added and the reaction stirred at room temperature for 0.5 h. Water (100 ml) was added and the mixture acidified with concentrated HCl (1 ml). The organic phase was separated, washed with water (100 ml), dried over anhydrous Na_2SO_4, and the solvent removed *in vacuo*. The residue was chromatographed on silica gel. The first red band eluted contained **IA** and unreacted ketone, the second red band was pure **IB**. The first fraction was rechromatographed on alumina. Unreacted ketone was eluted first, followed by pure **IA**. The products were isolated as red solids by slow evaporation of CH_2Cl_2 solution.

IA: yield 0.60 g (30%), melting point 95–97 °C (lit. 100–105 °C [15]).

IB: yield 0.60 g (30%), melting point 65–68 °C (lit. 70–72 °C) [15]).

IA and **IB** gave ^{1}H NMR spectra ($CDCl_3$) in agreement with those previously published [15].

2-α-Hydroxyethyl-3,4-dimethylmonophosphaferrocene (II) and 1′-α-Hydroxyethyl-3,4-dimethylmonophosphaferrocene (III)

The above were synthesised in an identical manner except that $LiAlH_4$ was added as a 1.0 molar solution in tetrahydrofuran (Aldrich Chemical Co.). An exact 0.25 molar equivalent, based on ketone present, was employed. After work up, the products were isolated as yellow–orange air-sensitive oils by chromatography on alumina and gave the following yields and ^{1}H NMR spectra.

***II**, yield 81%*

^{1}H NMR ($CDCl_3$)* $\delta = 1.25$(d) ^3J(HH) = 6 Hz, 1.45(d) ^3J(HH) = 6 Hz CH*Me*, 1.83(s) OH (exchanges with D_2O), 2.20(s), 2.25(s) $Me_{3,4}$, 3.71(d) ^2J(PH) = 37 Hz H_2, 4.10(s), 4.20(s) Cp, 4.55(m) C*H*Me.

***III**, yield 90%*

^{1}H NMR ($CDCl_3$)* $\delta = 1.30$(d) CH*Me* ^3J(HH) = 6 Hz, 2.08(s) $Me_{3,4}$, 2.55(s) OH (exchanges with D_2O), 3.72(d) ^2J(PH) = 37 Hz $H_{2,5}$, 3.88(m) and 4.15(m) $H_{2',5'}$ and $H_{3',4'}$ Cp, 4.38(m) C*H*Me.

In view of the air sensitivity of these derivatives, elemental analysis was not attempted.

References

1 R. Bartsch, P. B. Hitchcock and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1987) 1146.
2 O. J. Schever and T. Brück, *Angew. Chem., Int. Ed. Engl.*, *26* (1987) 59.
3 R. M. G. Roberts, J. Silver and A. S. Wells, *Inorg. Chim. Acta*, *118* (1986) 135.
4 R. M. G. Roberts, J. Silver and A. S. Wells, *Inorg. Chim. Acta*, *119* (1986) 1.

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*δ in ppm, (s) = singlet, (d) = doublet, (m) = multiplet.

5 R. M. G. Roberts, J. Silver and A. S. Wells, *Inorg. Chim. Acta, 119* (1986) 171.

6 R. M. G. Roberts, J. Silver and A. S. Wells, *Inorg. Chim. Acta, 119* (1986) 165.

7 K. K. Joshi, P. C. Pauson, A. R. Qafi and W. H. Stubbs, *J. Organomet. Chem., 1* (1964) 471.

8 B. Deschamps, F. Mathey, J. Fischer and J. H. Nelson, *Inorg. Chem., 23* (1984) 3455.

9 N. M. Kostić and R. F. Fenske, *Organometallics, 2* (1983) 1008.

10 G. Neshvad, R. M. G. Roberts and J. Silver, *J. Organomet. Chem., 236* (1982) 349.

11 W. E. Watts, *J. Organomet. Chem. Lit., 7* (1974) 339.

12 G. Neshvad, R. M. G. Roberts and J. Silver, *J. Organomet. Chem., 221* (1981) 85.

13 G. Neshvad, R. M. G. Roberts and J. Silver, *J. Organomet. Chem., 236* (1982) 237.

14 A. A. Korridze, N. M. Astakhova, P. V. Petrovskii and A. I. Lutsenko, *Dokl. Akad. Nauk SSSR, 242* (1978) 117.

15 G. De Lauzon, B. Deschamps, J. Fischer, F. Mathey and A. Mitschler, *J. Am. Chem. Soc., 102* (1980) 994.

16 R. M. G. Roberts, J. Silver and R. J. Ranson, *J. Organomet. Chem., 219* (1981) 233.

17 R. M. G. Roberts and A. S. Wells, *Inorg. Chim. Acta, 120* (1986) 53.

18 R. M. G. Roberts and A. S. Wells, *Inorg. Chim. Acta, 112* (1986) 167.

19 M. Y. Hamed, R. C. Hider and J. Silver, *Inorg. Chim. Acta, 66* (1982) 13.