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# A $^{57}$Fe Mössbauer Study of Phosphaferricenium Ions

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## Abstract

A number of phosphaferricenium salts have been prepared by oxidation of the corresponding phosphaferrocenes with tetracyanoethylene. Water appears to catalyse the oxidation. In contrast to the ferrocene/ferricenium system, the quadrupole splitting (QS) does not collapse on oxidation of the phosphaferrocene, but remains relatively large (1.6–2.6 mm $s^{-1}$). This indicates that the electron is removed from a phosphaferrocene molecular orbital which has a different Fe 3d orbital composition from that of ferrocene. The phosphaferricenium cations are unstable and appear to decompose via disproportionation reactions giving high spin iron(II) as the initial product. The cation derived from 1′-methyl-2,3,4,5-tetraphenylphosphaferrocene was isolated in a reasonably pure state.

## Introduction

Ferrocene (FcH) is readily oxidised to well defined stable ferricenium derivatives by a range of organic and inorganic oxidants. By contrast, no phosphaferricenium cations ($FcP^+$) have yet been isolated. Phosphaferrocenes (FcP) are more difficult to oxidise than ferrocene as shown by a relative anodic shift of 185 mV per P atom obtained from cyclic voltammetry (CV) studies [1]. This is due to the electron withdrawing nature of the phosphacyclopentadienyl ring. Attempts to produce $FcP^+$ salts by oxidising FcP with strong oxidants such as $H_2O_2$ leads to extensive decomposition. CV studies of Mathey *et al.* [1] have shown that oxidation occurs by removal of an Fe 3d electron as is the case with ferrocene. In both FcH and FcP the highest occupied molecular orbitals are largely non-bonding and have almost 100% metal d character [2, 3].

We report here a $^{57}$Fe Mössbauer spectroscopic study of both mono- and diphosphaferricenium ions with a view to investigating the electronic environment of the central iron atom and to gain insight into the mode of decomposition of these cations.

## Results and Discussion

Phosphaferrocenes can complex with metals at both the P [4] and Fe [5] sites. In order to avoid such behaviour, we chose not to use either metal ion oxidants or strong Lewis acids. Instead, we employed organic oxidants such as chloroanil, tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) all of which have been used to oxidise Fc species [6–9] and examined the oxidation of the following substrates: 3,3′4,4′-tetramethyldiphosphaferrocene (TMDPF), 3,4-dimethylmonophosphaferrocene (DMMPF) and 1′-methyl-2,3,4,5-tetraphenylmonophosphaferrocene (MTPMPF). Initial experiments using TCNE in solvents acetone and acetonitrile resulted in no observable oxidation with any of the above complexes. The addition of water, however, produced instant colour changes from the original red–orange solutions [TMDPF intense green, DMMPF and MTPMPF deep brown]. Water thus appears to catalyse the oxidation process. A similar phenomenon has been noted with the Fe–Ag bonded species, $TMDPF/CF_3SO_3Ag$, which is stable in anhydrous MeCN, but is rapidly and oxidatively decomposed by water [5]. Attempts to isolate the $FcP^+$ salts were only partially successful. We were able to prepare $[MTPMPF]^+[TCNE]^{\cdot-}$ in 54% yield and in a reasonably pure state†. We were also able to isolate $[TMDPF]^+$ salt but it was too unstable to attempt elemental analysis as was $[DMMPF]^+$ salt. The $^{57}$Fe Mössbauer spectra were therefore run on frozen solid solutions prepared immediately after water addition. In some cases, we examined aged solutions to identify the decomposition products.

A 4–5 molar excess of TCNE was used to ensure complete oxidation (*cf.* FcH + TCNE [7]) and to allow for the possible formation of complex anions (oxidation with TCNQ [8] often results in the forma-

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†The anion may be $(CN)_2C{=}C(CN)O^-$ rather than $TCNE^{\cdot-}$ due to hydrolysis.

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tion of (TCNQ)$_2^{\cdot-}$]. Ferrocene, ruthenocene and osmocene form charge transfer (CT) complexes with TCNE prior to oxidation [10, 11]. Such complexes are unstable and decompose rapidly to the metal(III) cations. These complexes appear to be stable only in non-polar solvents such as cyclohexane and it seems highly unlikely that such CT complexes of phosphaferrocenes would exist in the polar solvents (aqueous acetone of MeCN) used here. In order to check this point the $^{31}$P NMR spectra of TMDPF and DMMPF in acetone were examined in the presence of $H_2O$ and TCNE. The only species detected were unreacted starting materials in both cases, and there was no evidence for the existence of diamagnetic CT complexes. TLC analysis (silica plates, eluent $CH_2Cl_2$) also indicated a very polar reaction product. Examination of freshly prepared samples showed the presence of unreacted starting material which was eluted with the solvent front and the green–brown oxidation product which was not eluted. Examination of aged solutions showed numerous other products from the decomposition of the cations.

## $^{57}$Fe Mössbauer Spectroscopy

The Mössbauer results are listed in Table I for both oxidised and unoxidised forms. Ferrocene has a quadrupole splitting (QS) of 2.40 mm s$^{-1}$ which invariably collapses on oxidation to a singlet (or a doublet of very small QS of ~0.2–0.3 mm s$^{-1}$) [9–11]. It is clear from our data that such behaviour does not occur for phosphaferrocenes. [TMDPF]$^+$ shows only a small reduction in QS whereas [DMMPF]$^+$ and [MTPMPF]$^+$ show increases in QS of about 0.5 mm s$^{-1}$. The similarity of TMDPF and [TMDPF]$^+$ appears fortuitous.

TABLE I. $^{57}$Fe Mössbauer Data

| Compound | Phase | IS | QS |
|---|---|---|---|
| TMDPF | S | 0.48(1) | 1.87(1) |
| [TMDPF]$^+$TCNE$^{\cdot-}$ | FSS | 0.49(1) | 1.81(2) |
| Aged solution (Fig. 1) | FSS | 0.50(1) | 1.72(1) |
| | | 1.70(1) | 2.90(1)[a, c] |
| [TMDPF]$^+$TCNE$^{\cdot-}$ (isolated, Fig. 2) | S | 0.50(1) | 1.63(3) |
| | | 0.20(3) | 0[b, c] |
| | | 0.78(7) | 0[b, c] |
| DMMPF | S | 0.48(1) | 2.11(1) |
| [DMMPF]$^+$TCNE$^{\cdot-}$ (Fig. 3) | FSS | 0.51(1) | 2.70(2) |
| | | 0.60(1) | 2.27(4)[c, d] |
| Aged solution (Fig. 4) | FSS | 0.51(1) | 2.68(1) |
| | | 0.60(1) | 0[b] |
| | | 1.38(1) | 3.51(2)[a] |
| MTPMPF | S | 0.52(1) | 2.05(1) |
| [MTPMPF]$^+$TCNE$^{\cdot-}$ | FSS | 0.54(1) | 2.44(1) |
| [MTPMPF]$^+$TCNE$^{\cdot-}$ | S | 0.55(1) | 2.48(1) |
| [MTPMPF]$^+$TCNE$^{\cdot-}$/PF$_6^-$ | S | 0.53(1) | 2.63(2) |

IS = isomer shift, QS = quadrupole splitting, both mm s$^{-1}$, reference Fe foil. All data obtained at 80 K. S = solid, FSS = frozen solid solution. [a] Fe(II) S = 2, [b] Fe(III), decomposition products. [c] Roughly fitted. [d] Unreacted starting material.

The large difference in the QS of the monophosphaferricenium cations and the neutral monophosphaferrocenes leads to a ready identification of product and starting material. With TMDPF and [TMDPF]$^+$ the QS values are however too close to be resolved. The initial value obtained of 1.81 mm s$^{-1}$ for [TMDPF]$^+$ is probably high as a result of the presence of unreacted TMDPF. That obtained from an aged solution is lower (1.72 mm s$^{-1}$) and reflects the loss of TMDPF. Collins [13] has found excellent agreement between the observed QS for FcH and FcH$^+$ and those calculated on the basis of electron removal from $e_{2g}$ Fe-based molecular orbitals ($d_{x^2-y^2}$ or $d_{xy}$). Phosphaferrocenes have a different ordering of the non-bonding Fe-based MOs [2, 3]. The large observed QS values for the FcP$^+$ species indicates that an electron is removed from a different MO than that in FcH. It is, unfortunately, not possible to make a more quantitative analysis at this stage since the two MO schemes presented for diphosphaferrocenes have different sequences of the non-bonding Fe-based orbitals [2, 3], though both treatments give results significantly different from those of FcH. The latter has a degenerate $d_{x^2-y^2}$, $d_{xy}$ pair as the HOMOs followed by $d_{z^2}$ [14]. Both MO schemes for FcP show that the three Fe based orbitals are non-degenerate and that the HOMO is $d_{z^2}$ [2] or a hybrid comprising $d_{z^2} + d_{x^2-y^2}$ [3].

The fact that the magnitude of change in the QS is different between the mono- and diphosphaferrocenyl systems on oxidation suggests a slightly different composition of the HOMOs. This is not entirely unexpected since both have different sets of ligands.

No significant changes in isomer shifts occurred on oxidation which parallels the oxidation of FcH.

Mössbauer spectra of the decomposed FcP$^+$ species are presented in Figs. 1–4. Solutions of [TMDPF]$^+$-[TCNE$^{\cdot}$]$^-$ frozen immediately after preparation show simple quadrupole doublets. After ~20 min a second doublet appears (Fig. 1) which has high IS and QS values (1.70 and 2.90 mm s$^{-1}$ respectively) typical of high spin Fe(II). Figure 2 shows the spectrum of the green solid obtained on precipitation by ether (aged ~10 h at 20 °C). Extensive decomposition has occurred. The outer doublet is that of [TMDPF]$^+$ and the other signals appear to be due to mixtures of Fe(III) species. Figures 3 and 4 illustrate the decomposition of [DMMPF]$^+$. The freshly prepared sample (Fig. 3) shows two doublets and is a mixture of

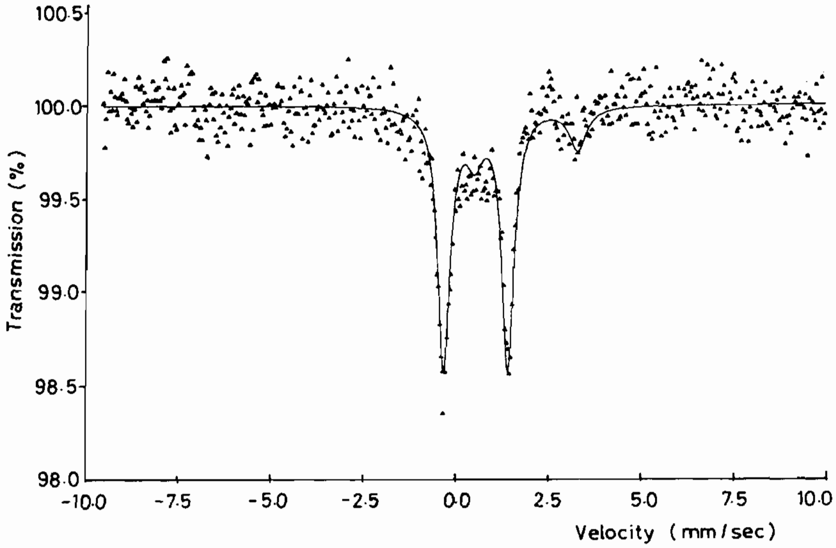

Fig. 1.

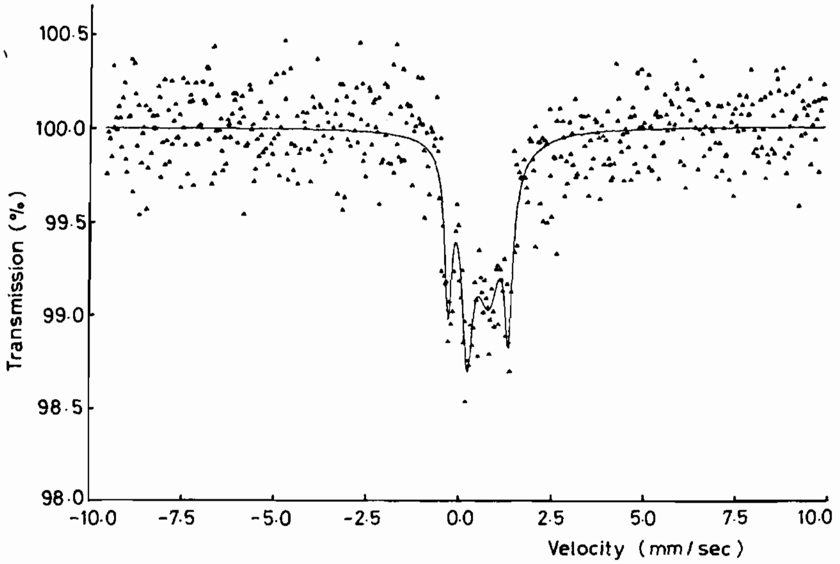

Fig. 2.

DMMPF and [DMMPF]$^+$. On standing the inner doublet (DMMPF) disappears and the [DMMPF]$^+$ breaks down into high spin Fe(II) together with a small amount of Fe(III) (Fig. 4).

We attempted to stabilise the FcP$^+$ cation by using ring phenylated phosphaferrocenes. 2,2′5,5′-tetraphenyldiphosphaferrocene and 2,3,4,5-tetraphenylphosphaferrocene were too insoluble in the aqueous media used to effect the oxidation, hence MTPMPF was used and indeed formed a more stable FcP$^+$ derivative. We tried to exchange the (TCNE$^{\cdot -}$) ion for $PF_6^-$ using aqueous $NH_4PF_6$ and obtained a brown solid containing a mixture of anions as shown from its IR spectrum ($\nu$(CN) 2200 cm$^{-1}$, $\nu$(PF) 840 cm$^{-1}$). [MTPMPF]$^+$ was more stable than the other cations. Its Mössbauer spectrum showed no change over a period of two weeks, displaying a QS of 2.63 mm s$^{-1}$ as the mixed salt (*cf.* 2.05 mm s$^{-1}$ for MTPMPF). Colour changes produced on cooling (*vide infra*) also suggest that the solid has the same structure as that obtained in frozen solid solution. The FcP$^+$ cations at room temperature were green–brown in colour but on cooling to 80 K changed to deep purple, as did the isolated solid.

The use of deoxygenated solvents did not enhance the stability of the FcP$^+$ solutions. Both mono- and

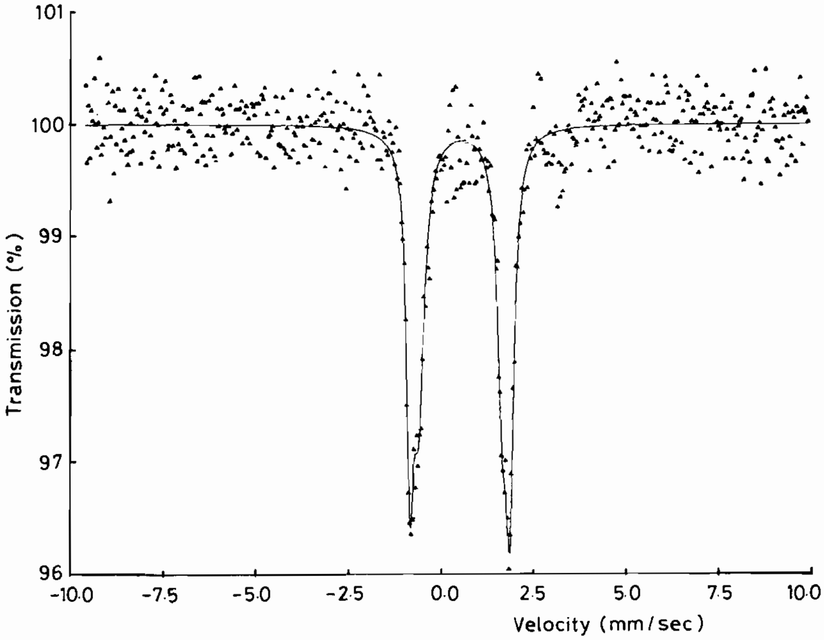

Fig. 3.

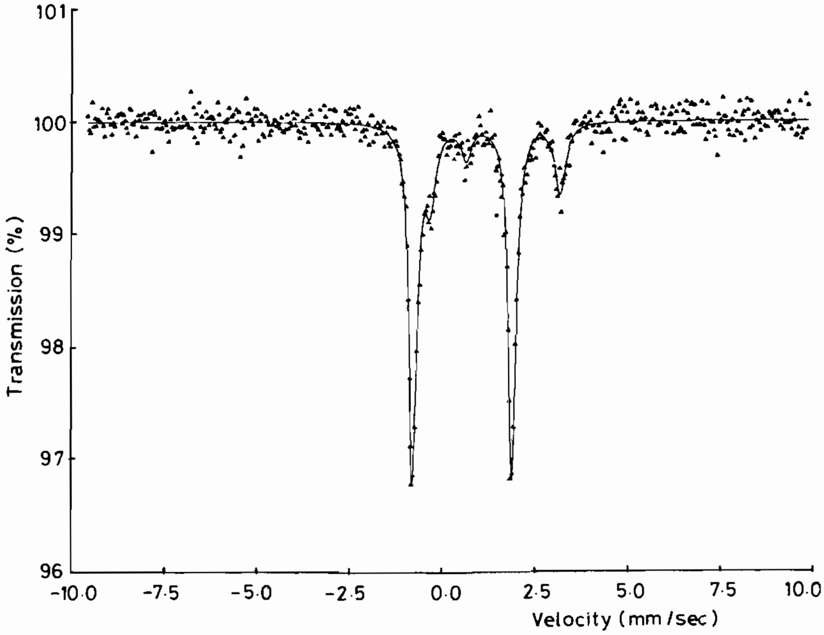

Fig. 4.

diphosphaferricenium cations showed slightly different QS values as solids and frozen solid solution.

The initial decomposition product of $FcP^+$ contains high spin Fe(II) which suggests that the cation does not simply decompose liberating Fe(III). Mathey [1] has concluded that 3,3'4,4'-tetramethylbiphosphole is a product of decomposition of $[TMDPF]^+$. We believe that the $FcP^+$ undergoes a disproportionation reaction in which an electron is transferred from a $PCp^-$ ligand to the Fe(III) atom after which decomposition occurs liberating phospholyl radicals, the dimerisation of which produces biphosphole. The freed Fe(II) is ultimately oxidised back to Fe(III) as shown by Mössbauer spectra of aged materials. We did not detect 3,3'4,4'-tetramethylbiphosphole as a biproduct using $^{31}P$ NMR. This compound is very susceptible to atmospheric oxidation [15] and would not be expected to exist under the strongly oxidising conditions employed here.

## Experimental

Phosphaferrocenes were produced by literature methods [16–18] and were purified immediately prior to use by column chromatography and recrystallisation.

### *1′-Methyl-2,3,4,5-tetraphenylmonophosphaferricenium Tetracyanoethylenate*

1′-Methyl-2,3,4,5-tetraphenylmonophosphaferrocene (0.30 g, 0.57 mmol) was stirred with TCNE (0.29 g, 2.28 mmol) in acetone:water (90:10 *v*/*v*) for 20 min. $Et_2O$ (20 ml) was added and the solution left at room temperature for 2 h. The resulting brown crystals were filtered off, washed with cold ether and benzene and dried *in vacuo*. Yield: 0.20 g (54%), melting point decomposition above 150 °C. *Anal.* Found: C, 71.6; H, 5.1; N, 7.4; Calc. for $C_{40}H_{27}FeN_4P$: C, 73.1; H, 4.2; N, 8.6; Calc. for $C_{39}H_{27}FeN_3OP$*: C, 73.1; H, 4.2; N, 6.6%.

The unstable $[TMDPF]^+[TCNE]^-$ was formed in a similar manner but gave poor analytical data due to decomposition.

Analyses were performed by the Micro Analytical Laboratory, University of Manchester.

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*Calculated for the hydrolysed anion $(CN)_2C{=}C(CN)O^-$.

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