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Mössbauer and NMR Studies of Protonated Acyl Diphosphaferrocenes

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Abstract

The acyl derivatives of 3,3′,4,4′-tetramethyldiphosphaferrocene (TMDPF) have been examined in strong acids by ^{57}Fe Mössbauer, ^{1}H and ^{31}P NMR spectroscopy. As with ferrocenyl ketones, protonation was found to occur at the keto function, the diphosphaferrocenyl ketones having comparable or, in some cases, reduced basicities compared to ferrocenyl ketones.

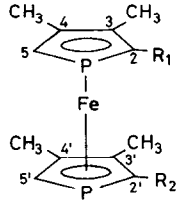
Trends in the ^{57}Fe Mössbauer parameters are not as additive as in ferrocene systems due to steric crowding. The keto derivatives show some unusual deuteriation patterns and these have been compared with those of ferrocenyl ketones. The ^{13}C spectra of several derivatives have been reported to illustrate the rather complex stereochemistry found in these derivatives.

Introduction

Ferrocenyl ketones have a remarkable basicity at the carbonyl oxygen and are readily protonated [1], though the factors causing these high basicities (relative to aryl ketones) are the subject of much speculation. Protonated ferrocenyl ketones have been studied by many probes [2, 3], and pK_a values have been determined for some derivatives [4]. Recently we reported ^{57}Fe Mössbauer spectroscopic studies for some protonated ferrocenyl ketones [5, 6, 7], and have extended these studies to include diphosphaferrocenyl ketones.

The compounds studied here are the acyl derivatives of 3,3′,4,4′-tetramethyldiphosphaferrocene (TMDPF). These are readily prepared by standard Friedel–Crafts acylation of TMDPF [8].

The derivatives examined were:

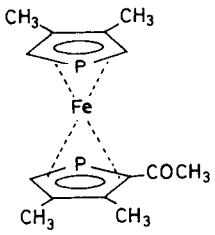


I: $R_1 = COCH_3$, $R_2 = H$
II: $R_1 = COC_6H_5$, $R_2 = H$
IIIa/b: $R_1 = R_2 = COCH_3$
IVa/b: $R_1 = R_2 = COC_6H_5$

Discussion

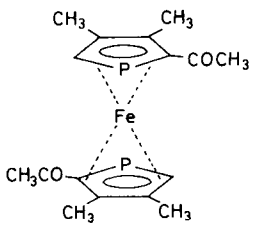
Before discussing the structure of these compounds, an appreciation of their stereochemistry is necessary.

I is a chiral molecule [8] which in theory can exist in a number of conformations arising from the rotation of the phospholyl rings (PCp) about the molecular axis. The most stable conformation is probably that with the methyl substituents in a *trans* orientation with the rings staggered (as is found in TMDPF) [8].

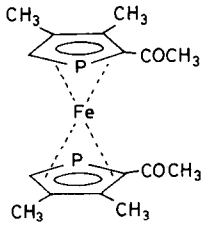


The methyl groups should all be distinct irrespective of ring orientations, as should the α protons.

The diacetyl derivative **III** exists as separable diastereomers [8], whose structures adopt *cis* and *trans* forms,



IIIa



IIIb

We have assigned **IIIa** as the *trans* isomer as it is formed in higher yield and is eluted first from chromatography columns indicating a weaker dipole moment.

IV also exists as a diastereomeric mixture which resisted attempts at chromatographic separation.

Ketones **I**–**IV** dissolved in media of sufficient acidity to give intense purple solutions characteristic of carbonyl protonated species. The lack of primary

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TABLE I. ^{1}H NMR Chemical Shifts (δ in ppm rel. ext. TMS, H_5, H_2', H_5' All Appear as Doublets $^2J_{PH} \sim 37$ Hz)

		H_5	$H_{2',5'}$[a]	Me(3)	Me(4)	Me(3')	Me(4')	COMe[b]
I	$CDCl_3$	4.04	3.74	2.45	2.18	2.12	2.05	2.35
	TFA	4.20	3.65, 3.42	1.93	1.78	1.55	1.55	2.05
								$H_{2,6}$ $H_{3,4,5}$
II	$CDCl_3$	4.04	3.70	2.40	2.33	2.16	2.06	~7.7 ~7.40
	TFA		~ 3.40 (singlet, br)	1.97	1.83	1.44	1.40	~7.10
								COMe
IIIa[c]	$CDCl_3$	3.75		2.24	1.96			2.24
	TFA	3.45		1.78	1.60			1.91
	70% H_2SO_4	4.62		2.20	2.20			2.60
	Triflic acid	4.95		2.15	1.93			2.47
IIIb[c]	$CDCl_3$	4.14		2.35	2.13			2.35
	TFA	3.85		1.82	1.63			1.91
	70% H_2SO_4	4.77		2.20	2.07			2.47
	Triflic acid	4.95		2.06	1.95			2.45
								$H_{2,6}$ $H_{3,4,5}$
IVa[d]	$CDCl_3$	4.18		2.28	2.20			~7.8 ~7.4
IVb	$CDCl_3$	3.97		2.40	2.35			~7.8 ~7.40

[a] αH on non-acylated ring, two sites not resolved in $CDCl_3$ [8]. [b] $^2J_{PH} \sim 3$Hz not resolved in acid solutions. However COMe broader than βMe due to unresolved coupling. [c] βMe_1 and COMe overlap in $CDCl_3$. [d] **IVa/b** assigned on integral values.

P–H coupling and absence of signals at ~−2 ppm [9] in the ^{1}H NMR spectrum rules out both phosphorus and iron as sites for protonation. The strongest acid used in this work (CF_3SO_3H) does not protonate at phosphorus in diphosphaferrocenes [10].

Restricted rotation about the molecular axis has been reported for **I** and **II**, being manifest in the appearance of four separate βMe signals in the ^{1}H NMR spectra [8]. Table I lists the ^{1}H NMR data. The assignments in solvent trifluoroacetic acid (TFA) were made by comparison with those in $CDCl_3$. The most notable features are the downfield shift of H_5 and the upfield shifts of the methyl resonances on protonation. This can be rationalised by the markedly increased electron withdrawal of the C=O$\overset{+}{H}$ group (most affecting the 4, 5 positions) and the reduction of the anisotropy of the carbonyl function by protonation (reducing the deshielding of the 3 position in particular). The appearance of separate signals for H_2' and H_5' indicates restricted rotation about the molecular axis.

Both diacetyl derivatives **IIIa** and **IIIb** dissolve in TFA to give red solutions suggesting only partial protonation. Complete protonation occurs in 70% H_2SO_4, whereas in the much strong triflic acid diprotonation occurs (see ^{31}P NMR section) causing large downfield shifts of H_5. Solutions of the diprotonated species were rather unstable and decomposed extensively after 4 h.

In contrast to **IIIa, b, IVa** or **b** were fully protonated in TFA as shown by the typical deep purple colour produced. Solutions in 98% H_2SO_4 and CF_3SO_3H were unstable.

^{31}P NMR

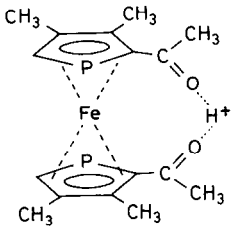
The ^{31}P NMR data for **I** to **IV** are given in Table II. Recently we postulated that diphosphaferrocenes were not iron-protonated in triflic acid [10]. However, as a result of a more detailed study [11], it has become apparent that diphosphaferrocenes are at least partially iron protonated. The Fe–H signal is not always observed at room temperature due to rapid exchange with solvent. Iron protonation causes a pronounced upfield shift of δ^{31}P. In this case, all the derivatives show downfield shifts when protonated and no primary P–H coupling ($^1J_{PH}$) is found, thus confirming keto rather than iron or P protonation. **I** in TFA showed a downfield shift of δ^{31}P of 21.4 ppm compared to that obtained in $CDCl_3$ for the acetyl substituted PCp ring. δ^{31}P for the non-acetylated ring showed a downfield shift of 8.8 ppm. **II** in TFA showed one broad signal at 22.9 ppm downfield from that observed in $CDCl_3$. The equivalence of both P nuclei is surprising in view of the results obtained for **I** and has been attributed to the rapid exchange of the α protons in this solvent. A similar effect was found for the αH resonances in the ^{1}H NMR. Protonation of the keto oxygen thus causes a downfield shift of ~22.0 ppm.

TABLE II. ^{31}P NMR Data[a]

Compound	Solvent	$\delta\ ^{31}P$	$J_{P_1P_2}$	$\Delta\delta$
I	$CDCl_3$	−48.80, −66.68	12	–
	TFA	−27.39, −57.91	5	+21.41, +8.77
II	$CDCl_3$	−46.36, −65.18	10	–
	TFA	−23.50	–	+22.86
IIIa	$CDCl_3$	−48.89		–
	TFA	−38.40		+10.50
	70% H_2SO_4	−25.45	5	+23.44
	CF_3SO_3H	−15.07[b]		+33.82
IIIb	$CDCl_3$	−45.25		–
	TFA	−34.20		+11.05
	70% H_2SO_4	−21.20		+24.05
	CF_3SO_3H	−5.59[b]		+39.66
IVa	$CDCl_3$	−51.85	–	–
	TFA	−6.52	–	+45.33
	98% H_2SO_4	−11.60[b]	–	+40.25
	CF_3SO_3H	−11.26	–	+40.59
IVb	$CDCl_3$	−37.01	–	–
	TFA	−23.15	–	+13.86
	98% H_2SO_4	−3.77[b]	–	+33.24
	CF_3SO_3H	−1.82	–	+35.19

[a] δ in ppm, J in Hz δ +ve downfield shift. Reference 85% H_3PO_4/D_2O. $\Delta\delta$ = downfield shift in acidic solvent. [b] Other minor signals at lower field than H_3PO_4 due to decomposition. For monosubstituted products $\delta\ ^{31}P$ of substituted ring is resonance at lowest field. $\delta\ ^{31}P$ for **IVa/b** assigned on signal integral intensities.

The ^{31}P spectrum of the **IIIa/b** mixture prior to chromatographic separation showed an isomer ratio of 60:40 and was almost identical to that found for **IVa/IVb** (59:41). Both **IIIa** and **b** showed smaller downfield shifts in TFA due to incomplete protonation. In 70% H_2SO_4/H_2O downfield shifts comparable to **I** and **II** in TFA are observed which strongly indicates that monoprotonation has occurred in all derivatives. The proposed *cis* isomer **IIIb** gave a doublet in the ^1H coupled spectrum ($^2J_{PH}$ 37.5 Hz) as would be expected from an intramolecular hydrogen bonded structure with both P nuclei identical (*cf.* monoprotonated diacetylferrocene [5]).



The designated *trans* isomer **IIIa** gave a more complex spectrum consisting of two doublets which we have assigned as two non equivalent P nuclei, $^2J_{PH} \sim 31.5$ Hz and $J_{P_1P_2} = 5$ Hz.

Under proton decoupling, however, the ^{31}P signal appeared as a slightly broad singlet, the low value of $J_{P_1P_2}$ making resolution difficult. The magnetic nonequivalence of the two P nuclei would be much reduced if rapid proton exchange occurs as is likely in this system.

In triflic acid both **IIIa** and **IIIb** showed even larger downfield shifts commensurate with diprotonation. By comparison with **I**, where protonation of the acetyl group causes downfield shifts of 21.4 and 8.8 ppm for the acylated and nonacylated rings respectively, diprotonated species should appear ~30 ppm downfield. The observed shifts were 33.82 and 39.68 ppm respectively.

The results obtained for **IVa/b** were surprising. In TFA **IVb** showed a downfield shift of 13.6 ppm very similar to that found for **IIIa** and **IIIb** and indicates incomplete protonation. **IVa**, by contrast, showed a very large downfield shift of 45.33 ppm, almost identical to the values obtained in 98% H_2SO_4 and triflic acid, where diprotonation is considered to occur. **IVb** showed comparable downfield shifts in both stronger acids. Triflic acid is much stronger that 98% H_2SO_4 ($H_o - 14.6$ [12] *vs.* −10.2) [13], thus the similarity of the downfield shifts shows that 98% H_2SO_4 is strong enough to diprotonate both **IVa** and **IVb**. However, the result for TFA indicates that **IVa**

TABLE III. Deuteration of Protonated Ketones

Compound	Acid[a]	Time (approx.)	%D[b]	Site
I	A	15 h	~90	Hα
FcCOMe	A	3 days	–[c]	–
FcCOMe	B	2 h	64	Free CP
II	A	4 h	>90	Hα
$FcCOC_6H_5$	A	4 h	–[c]	–
IIIa	A	15 h	25	$COCH_3$
IIIa	B	3½ h[d]	35	$COCH_3$
IIIa	C	5½ h	50	$COCH_3$
IIIb	A	15 h	Extensive decomposition	
IIIb	B	3½ h[d]	35	$COCH_3$
IIIb	C	5½ h	70[e]	$COCH_3$
IV	A	15 h	–[c]	–
$Fc(COMe)_2$	C	15 h	20	$COCH_3$
$Fc(COMe)_2$	B	15 h	–[c]	–

[a]Acid A = CF_3CO_2D; B = CF_3SO_3D; C = 70% H_2SO_4, D_2O *w/w*. [b]Determined by ^1H NMR by comparison with non-exchangeable sites, βMe for TMDPF derivatives, acetylated Cp ring for acetyl ferrocenes. [c]None detected by ^1H NMR and mass spectroscopy. [d]Decomposition limits reaction time. [e]Attained isotopic equilibrium with solvent. Acid in large excess in all cases.

is diprotonated in this solvent. TFA is a much weaker acid (H_o – 4.4) [14] and is not strong enough to diprotonate diacyl ferrocenes [5]. The reason for this anomaly is not clear.

^{13}C NMR

The ^{13}C spectra of **I**–**III** are reported in Table V. The chemical shifts of the PCp ring carbons are in the region expected for such derivatives [15]. As in simpler derivatives no phosphorus carbon coupling is detected beyond the β carbons [15]; however such coupling is detected in substituents attached to C_α positions with $^3J_{PC}$ values of ~5–9 Hz and with $^2J_{PCO}$ values of larger magnitude than $^2J_{PC\beta}$.

No $^3J_{PC}$ was detected with C_1 of the phenyl group of **II** and C_2 and C_6 are magnetically non-equivalent. Two of the β methyl resonances overlap. As expected from ^1H NMR results [8] all carbon sites in the PCp rings of **I** and **II** are distinct.

Diastereomer **IIIa** showed eight separate PCp ring carbons indicating rotation about the central ring axis and that the two rings do not exist in an exactly staggered conformation.† Two distinct acetyl groups are also present in **IIIa**. The spectrum of **IIIb** was much simpler indicating a more symmetrical structure; however two distinct acetyl methyl signals were observed.

H/D Exchange of Protonated Ketones

Table III summarises the results of deuterium exchange in the ferrocenyl and TMDPF ketones. The rapid exchange of the ring protons of **II** in TFA lead us to examine the other derivatives in deuteriated acids. In TFA-d_1 both **I** and **II** underwent H/D exchange of the α protons, the latter occurring at a much faster rate. Surprisingly even the αH on the $RC{=}OH^+$ substituted ring exchanged. The rate of exchange of **I** in TFA-d_1 was slow enough to be measurable by ^1H NMR. The rapid rate of exchange in **II** made NMR measurements difficult but samples recovered from 50% deuteriated TFA showed enhanced deuterium uptake in the non acylated PCp ring commensurate with the less deactivated nature of this ring. Under identical conditions no exchange was detected in acetyl or benzoyl ferrocene even after prolonged reaction time (3 days). H/D exchange in the free Cp ring in acetyl ferrocene occurred in the much stronger triflic acid-d_1.

IIIa/b also underwent exchange in deuteriated acids. ^1H NMR and mass spectroscopy indicated no exchange of the α protons but rather of the acetyl-methyl protons. The most likely mechanism for this is via acid catalysed enolisation.

IIIa showed a small deuterium uptake in the acetyl group in TFA-d_1 in keeping with the degree of protonation in this medium. **IIIb** was however too unstable to obtain measurable enrichment. In 70% H_2SO_4/D_2O (in which both appear to be fully mono-protonated) deuterium uptake was found to be much more efficient, the deuterium content of the acetyl methyls reaching that of the solvent after five hours. This process was found to occur to a much lesser extent with diacetyl ferrocene, suggesting a lower concentration of the enol intermediate. The differences in behaviour between the ferrocenes and phosphaferrocenes is highlighted by the fact that **IIIa/b** undergo H/D exchange in the CH_3CO moiety

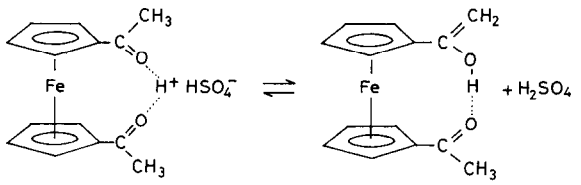
† This is found in the parent TMDPF where the phosphorus of one ring is located over a β carbon of the lower ring [8].

TABLE IV. ^{57}Fe Mössbauer Parameters Recorded. (Isomer Shift (*IS*), Quadrupole Splitting (*QS*), and Linewidth at $\frac{1}{2}$ Height ($\frac{1}{2}h$) All in mm s^{-1}) for Acetyl Derivatives of 3,3',4,4'-tetramethyldiphosphaferrocene (TMDPF)

Compound	Phase[a]	*IS*	*QS*	$\frac{1}{2}h$	ΔQS[b]
TMDPF	s	0.47(1)	1.87(1)	0.19(1)	–
I	s	0.49(1)	1.67(1)	0.18(1)	0.20(2)
I	CF_3CO_2H/FSS	0.49(1)	1.61(1)	0.16(1)	0.26(2)
II	s	0.47(1)	1.84(1)	0.19(1)	0.03(2)
II	CF_3CO_2H/FSS	0.49(1)	1.54(1)	0.16(1)	0.33(2)
IIIa	s	0.47(1)	1.57(1)	0.19(1)	0.30(2)
IIIa	70%/H_2SO_4/H_2O/FSS	0.50(2)	1.38(5)	0.20(4)	0.49(6)
IIIa	CF_3SO_3H/FSS	0.51(2)	1.38(3)	0.13(2)	0.49(4)
IIIb	s	0.47(1)	1.58(1)	0.19(1)	0.29(2)
IIIb	70%/H_2SO_4/H_2O/FSS	0.50(1)	1.34(4)	0.25(3)	0.53(5)
IV	s	0.47(1)	1.74(1)	0.16(1)	0.13(2)
IV	CF_3CO_2H/FSS	0.51(2)	1.65(3)	0.13(2)	0.22(4)

[a] s = solid, FSS frozen solid solution. [b] ΔQS = *QS* TMDPF – *QS* ketone.

in CF_3SO_3D whereas diacetylferrocene does not, although both appear to be diprotonated. This difference is probably the result of electron withdrawal by the PCp ligands, encouraging the removal (exchange) of the acetyl protons. The fact that exchange occurs in 70% H_2SO_4 for diacetyl ferrocene (monoprotonation) suggests that the enol form is stabilised by hydrogen bonding.



H/D exchange of **IIIa/b** in triflic acid-d_1 shows such stabilisation is unnecessary in the phosphaferrocene system. **IVa/b** showed no exchange in TFA-d_1.

Mössbauer Spectroscopy

The ^{57}Fe Mössbauer parameters for **I** → **IV** are presented in Table IV. Ferrocenyl ketones have been extensively studied using Mössbauer spectroscopy [5]. Acyl substitution lowers the quadrupole splitting (*QS*) by electron withdrawal from the ring based e_1 orbital, as expected for conjugated –M substituents. The effects on the magnitude of *QS* have been shown to be roughly additive [5]. The presence of a phosphorus atom in the Cp ring causes a reduction in *QS* of ~0.3 mm s^{-1} [10] whereas methyl substitution causes a small increase in *QS*. **I** → **IV** all displayed reduced *QS* values compared to TMDPF in keeping with ferrocenyl ketones, although the effects are not additive. The major contributing factor here must be steric crowding in the more heavily substituted TMDPF derivatives. Illustrative of this is the very small ΔQS found for **II**. Molecular models suggest that the least sterically crowded conformation is where the benzoyl group is twisted out of the plane of the PCp ring, thus reducing the –M effect of the carbonyl function.

Although ΔQS values are not additive, larger values are found on the addition of a second acyl substituent as expected. Both diastereomers **IIIa** and **IIIb** had identical *QS* values, the linewidth of **IVa/b** was normal indicating that, like **III**, both **IVa** and **IVb** have the same *QS*. Protonation of acylferrocenes causes a further reduction in *QS* in keeping with electron withdrawal from ring based e_1 orbitals, rather than iron based (e_2) *i.e.* the protonated form does not have a ferrocenyl carbonium character [5]. In media in which **I** → **IV** are monoprotonated, **I** → **IV** all showed further reductions in *QS*, *cf.* protonated ferrocenyl ketones. **IIIa** showed no further reduction in QS when diprotonated in triflic acid. **IIIH**$^+$ showed a similar ΔQS value to **IH**$^+$ in contrast to the unprotonated forms. When protonated the benzoyl group probably becomes more planar with the PCp ring, the extra electronic stability overcoming the unfavourable steric factors.

Although the effects on *QS* of **I** and **II** in both solid and protonated form vary considerably, all show a similar reduction in *QS* in going from the parent metallocene to the protonated ketone, {(FcH → $[FcCOCH_3]H^+$ ΔQS = 0.29(2), FcH → $[FcCOC_6H_5]$-H^+ ΔQS = 0.25(2), TMDPF → **IH**$^+$ ΔQS = 0.26(2). TMDPF → **IIIH**$^+$ ΔQS = 0.33(2)}

As with ferrocenyl ketones, no significant changes in the isomer shift values were found for **I** → **IV** compared to TMDPF.

Experimental

All preparations were carried out under dry argon. Unless otherwise stated, reagents were supplied commercially and used without further purification.

TABLE V. ^{13}C NMR Data[a,b] for Acylated 3,3',4,4'-Tetramethyldiphosphaferrocene (TMDPF) in Solvent CS_2 for (I/II) and $CDCl_3$ for (IIIa, b)

Acyl group	Parameter	C2	C5	C2'	C5'	C3	C4	C3'	C4'	Me(3)	Me(4)	Me(3')	Me(4')	MeCO	CO
2-acetyl (I)	δ	90.34	83.95	83.82	83.34	102.67	98.64	98.37	94.14	16.13	14.82	14.51	14.33	13.19	201.65
	J_{P-C}	63.4	61.3	61.3	58.2	7.7	6.7	6.0	5.3	_c	_c	_c	_c	9.7	23.0
2-benzoyl (II)	δ	92.79	84.93	84.42	83.30	100.67	99.33	98.70	98.51	16.95	15.12	15.12	14.75	–	198.11	140.82(C1)[d], 129.26(C2), 128.08(C3, C5),
	J_{P-C}	66.4	60.3	61.0	60.4	7.6	7.3	3.7	3.1	_c	_c	_c	_c	–	19.8	131.78(C4), 129.59(C6)
2,2'-diacetyl (IIIa)	δ	89.82	84.23	89.85	84.30	109.94	98.41	105.12	98.30	14.15	13.02	14.15	13.02	31.04	203.46
														31.34	204.50
	J_{P-C}	64.7	64.7	64.7	64.9	3.6	2.2	3.6	2.2	_c	_c	_c	_c	5.3	11.1
														5.6	10.9
2,2'-diacetyl (IIIb)	δ	91.32	85.25	91.32	85.25	103.69	98.22	103.69	98.22	15.04	12.95	15.04	12.95	31.13	203.0
														31.43	
	J_{P-C}	64.0	59.9	64.0	59.9	3.9	3.9	3.9	3.9	_c	_c	_c	_c	5.8	24.2
														6.2	

[a]Chemical shifts, δ, in ppm from TMS, phosphorous carbon coupling constants, J_{P-C}, in Hz. [b]Assignments of the ring carbons other than the quaternary C atoms must be regarded as tentative. [c]Not observed. [d]Phenyl resonances.

Where necessary solvents were dried by standard laboratory procedures. TMDPF was made by the aluminium chloride modification [15] of Mathey's original method [8]. The precursor 3,4-dimethyl-1-phenylphosphole was made by literature methods [16].

Synthesis of Acyl Derivatives

These were synthesised by the methods given in ref. 8, except that **IIIa/b** were separated on acidic alumina freshly deactivated with 5% H_2O. Eluant benzene/ethyl acetate 97.5:2.5 *v/v*.

The spectroscopic and physical properties conformed with those given in ref. 8.

IV was prepared by a similar method to **IIIa/b** using a four-fold excess of benzoyl chloride and aluminium chloride. A satisfactory separation of **IVa/b** could not be obtained on chromatography columns and the following results refer to the diastereomeric mix. Melting point (m.p.) 96 °C (Pet. ether 60/80). IR $\nu_{C=O}$ 1630 cm^{-1} (nujol). *Anal.* Calc. for $C_{26}H_{24}P_2O_2Fe$: C, 64.2; H, 4.9. Found: C, 63.9; H, 5.0%. Molecular weight 486 (m^+ mass spectroscopy). Yield 69%.

TFA-d_1 and triflic acid-d_1 were prepared from the corresponding anhydrides (10% excess) and D_2O and were fractionated under N_2 before use.

^1H NMR spectra were obtained on a Varian EM360 and ^{31}P and ^{13}C NMR spectra on a Bruker WP80 spectrometer. Micro analyses were performed by the Micro Analytical Laboratory, Manchester University.

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