# Friedel Crafts Acetylations of Alkyl and Phenylphosphaferrocenes

R. M. G. ROBERTS and A. S. WELLS

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

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## Abstract

The acetylation of a number of alkyl phosphaferrocenes has been examined. Methyl groups exert similar directive properties as found with ferrocene systems. A synthetic route to 1′-2-diacyl monophosphaferrocenes has been described and the products obtained from the acetylation of several phenylphosphaferrocenes have been isolated and characterised.

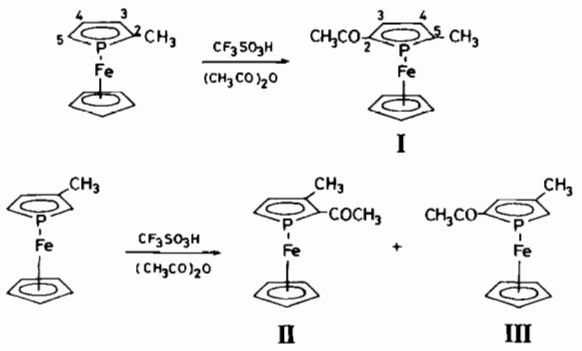
## Introduction

The only phosphorus heterocyclic aromatic compounds that undergo classical C-electrophilic substitution reactions are those containing the $\eta^5$-cyclopentadienyl (Cp) analogue, $\eta^5$-phosphacyclopentadienyl (PCp) ligand. Whilst they are less reactive than their Cp counterparts, Mathey and coworkers have succeeded in functionalising many PCp derivatives via aromatic substitution reactions using standard Friedel Crafts procedures [1–5]. Such compounds include diphosphaferrocenes (DPF), monophosphaferrocenes (MPF), and phosphacymantrenes. In PCp derivatives C-electrophilic substitution predominates due to the low energy level of the phosphorus lone pair which precludes the addition of the electrophile to phosphorus [6]. To date, the only alkyl MPF that has been acylated is the symmetrically substituted 3,4-dimethyl MPF [3]. One problem encountered is the low yields of acylated alkyl MPF due to decomposition by the $AlCl_3$ catalyst. We have recently found that 'triflic acid' ($CF_3SO_3H$) is a much cleaner catalyst than $AlCl_3$ and therefore decided to investigate the acetylation of monomethyl MPFs by this route. Another notable difference between the electrophilic chemistry of MPFs compared to ferrocene is the failure to diacylate 3,4-dimethyl MPF [3]. By contrast ferrocene readily forms 1,1′-diacyl derivatives [8] as does 3,3′,4,4′-tetramethyl DPF [4, 9].

In spite of being readily obtainable, little work has been done on the acylation of phenyl derivatives. We have therefore undertaken a more detailed investigation of the acetylation of several phenyl MPFs and DPFs, and report on the synthesis of diacyl MPF derivatives.

## Results and Discussion

Alkyl substitution activates the ferrocene moiety towards electrophilic attack and directs electrophiles $\beta$ to the alkyl group [10]. For the acetylation of methylferrocene relative product ratios of 1,3:1,2:1,1′ are 1:0.75:0.63 [11], similarly for 1,1′-dimethylferrocene product ratios of 1,3:1,2 of 1:0.44 [12] and 1:0.59 [13] have been reported. Such reactions are usually performed with $AlCl_3$/MeCOCl. We checked the acetylation and benzoylation of 1,1′-dimethylferrocene using $CF_3SO_3H/(RCO)_2O$ and obtained product ratios of 1,3:1,2 of 1:0.5. Hence for alkyl ferrocenes, both electrophiles show similar selectivity. The products obtained on acetylation of monomethyl MPFs are shown in Scheme 1.




Scheme 1.

In both cases no Cp acetylated products were detected which parallels the results obtained for MPF, 3,4-dimethyl MPF and 3,4-dimethyl-2-phenyl MPF [3]. 2-Methyl MPF produced only the 2,5 isomer. The low reactivity of the $\beta$ positions is also shown in MPF in which the isolated monoacetyl derivative contains only 15% of 3-acetyl MPF [3]. The low reactivity of the $\beta$ sites towards electrophiles is apparent in the H/D exchange reactions of MPF and DPF derivatives in triflic acid; d [14–16].

3-Methyl MPF produced both isomers resulting from $\alpha$ acetylation. The ratio of **II**:**III** was 0.86:1, the methyl group thus having very similar directive

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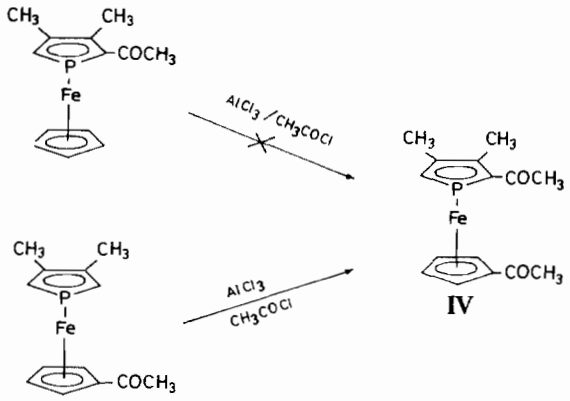
properties to those found in methylferrocene. Obviously the Cp ring in MPFs is considerably less reactive towards electrophiles than in ferrocenes, *viz.* the failure to date to diacetylate MPF. This indicates considerable electron withdrawal by the PCp ligand.

3,4-Dimethyl MPF cannot be diacetylated using $AlCl_3$/MeCOCl [3], the first acetyl group is introduced $\alpha$ to P and decomposition occurs faster than acylation of the less reactive Cp. If an acetyl group is already present on the Cp ring [17] standard Friedel Crafts methods are successful, producing 1′,-2-diketones in good yield (Scheme 2).

The above reaction scheme was also found suitable for making 2-acetyl-1′-benzoyl-3,4-dimethyl MPF (**V**) starting from the 1′-benzoyl derivative.

The $^1H$ NMR spectra of **IV** and **V** strongly suggested that restricted rotation exists in these derivatives (see Table II). The Cp protons appeared as three distinct multiplets rather than two. This was confirmed by $^{13}C$ NMR (see 'Experimental'). Five distinct carbon sites were apparent for the Cp ring. The magnetic non-equivalence of $C_2$ and $C_5$ and $C_3$ and $C_4$ shows that the two rings do not rotate freely about the central axis. For steric reasons a *trans* arrangement of the acetyl groups would seem to be the most favourable conformation. It should be noted that $^1H$ and $^{13}C$ NMR spectroscopy have also shown that restricted rotation exists in the 2-acyl and 2,2′-diacyl derivatives of 3,3′,4,4′-tetramethyl DPF [4, 9].

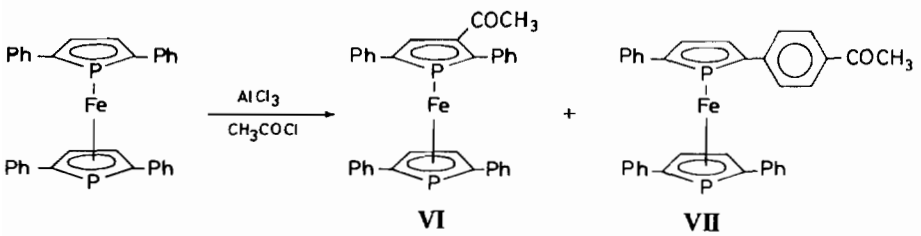



Scheme 2.

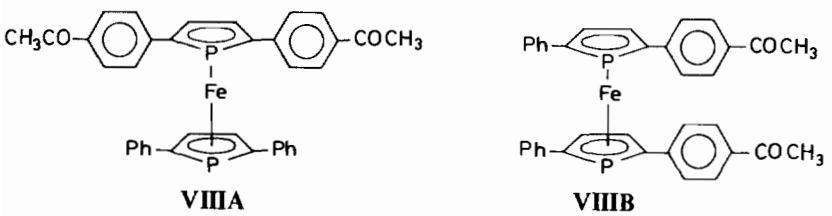
*Reactivity of Phenylphosphaferrocenes*

The addition of a phenyl group to ferrocene deactivates the ferrocene nucleus towards electrophiles. For phenyl and 1,1′-diphenylferrocene, products arising from the substitution of the phenyl group are minor [18, 19]. This is in keeping with the much higher reactivity of ferrocene compared to that of benzene. 2,2′,5,5′-tetraphenyl DPF however gave mainly phenyl substituted products. Using an equimolar amount of MeCOCl the ratio of **VII**:**VI** was found to be ~10.5:1 (Scheme 3). The use of excess MeCOCl lowers this ratio suggesting that **VII** is diacylated faster than **VI** which is also borne out by the structure of the diacetyl products **VIIIA/B** shown in Scheme 4.

The addition of two acetyl groups to TPDPF could in theory produce a large number of isomers. However only **VIIIA/B** appear to be formed (characterised by IR and $^{31}P$ NMR spectroscopy). The mixture showed no $\nu$(C=O) at 1650 $cm^{-1}$ as found with **VI** which shows that the product contains only aryl acetyl groups ($\nu$(C=O) for **VIIIA/B** and **VII** = 1660 $cm^{-1}$). This is confirmed by $^{31}P$ NMR spectroscopy.




Scheme 3.




Scheme 4.

TPDPF has $\delta^{31}P$ at −61.0 ppm. **VI** gave $\delta^{31}P$ values of −33.6 and −57.2 ppm which are assigned to the acylated and non-acylated PCp rings respectively. **VII** gave $\delta^{31}P$ values of −58.9 and −61.1 ppm and are assigned likewise. Thus the addition of a $\beta$ acetyl group deshields $\delta^{31}P$ by 27.4 ppm whereas the addition of a *para* acetyl group to a phenyl substituent causes a downfield shift of only 2.1 ppm. **VIIIA/B** gave $\delta^{31}P$ values of −60.3, −59.3 and −56.4 ppm of relative intensity 1:2:1. The $\delta^{31}P$ values rule out any $\beta$ acetyl products and the $\delta^{31}P$ value of −59.3 ppm can be assigned to **VIIIB** by comparison with **VII**. The signals at −60.3 and −56.4 ppm can be attributed to **VIIIA**, the PCp ring with two *p* acetylated phenyl substituents at −56.4 being very close to that calculated from **VII** ($\delta^{31}P = -56.8$ ppm).

The formation of **VIIIA/B** casts light on the transmission of electronic effects through the different aromatic rings. Clearly the addition of a $\beta$ acetyl group to a PCp ring to give **VI** deactivates all other sites on the molecule to further attack. The addition of an acetyl group to the *para* position of an arene substituent to give **VII** deactivates both PCp rings but not markedly any other phenyl group, as **VIIIA** and **B** are formed in equal amounts. The deactivation of the PCp rings by the addition of electron withdrawing groups at the *para* position of the arene substituent is paralleled in ferrocene chemistry where the Cp rings of 1,1′-di(*p*-bromophenyl)ferrocene are less reactive towards electrophiles than in 1,1′-diphenyl ferrocene [18, 19].

2,3,4,5-Tetraphenyl MPF gave mainly the Cp substituted isomer with $AlCl_3$/MeCOCl (ratio **X**:**IX** 1:5.9)* (Scheme 5).

However TPMPF appeared to be very selective too towards the electrophile. Acylation with $CF_3SO_3H$/$(MeCO)_2O$ gave mainly **X** (ratio **IX**:**X** 1:9)* (Scheme 6).

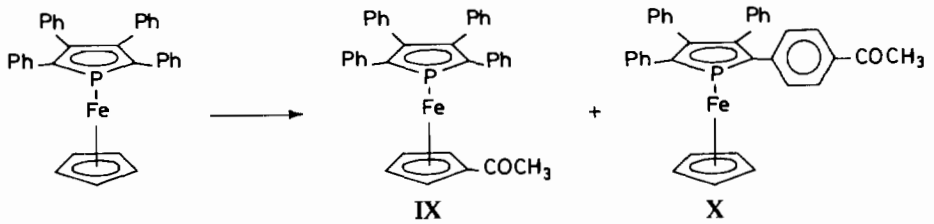
Both arene and Cp substituent products were isolated from the acetylation of 2,5-diphenyl MPF using $AlCl_3$/MeCOCl and $CF_3SO_3H/(MeCO)_2O$.

In this case measured yields and isomeric ratios were found to be variable. One problem encountered was that the low polarity solvents used to effect separation caused some decomposition of **XI** on chromatography columns. Such behaviour was not found with any other compound studied here.

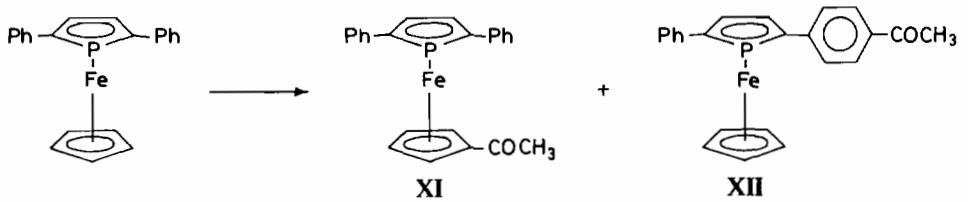
An experiment was performed in which separation was not attempted and the product mixture was instead examined by $^{31}P$ NMR (acetylating reagent $CF_3SO_3H/(MeCO)_2O$). $\delta^{31}P$ for 2,5-diphenyl MPF and **XII** were almost identical, so the relative proportions of unreacted starting material and **XII** were estimated by TLC.

From $^{31}P$ NMR integral ratios, the composition of the mixture was calculated as 13% 2,5-diphenyl MPF, ~43% **XII** and ~45% **XI**. Hence compared to 2,3,4,5-tetraphenyl MPF, the diphenyl derivatives show a more pronounced tendency to undergo Cp ring acetylation. A weak signal at −40.4 ppm of ~2.5% total intensity was also apparent in the $^{31}P$ NMR spectrum. $\delta^{31}P$ for 2,5-diphenyl MPF is at −66.2 ppm in $CDCl_3$. By comparison with **VI**, the

*The product arising from acetylation of a phenyl group in TPMPF could contain products having the acetyl group on the 2,5 or 3,4 phenyl substituents or a mixture of both. Preliminary $^{13}C$ NMR studies show that the product has the structure shown above.




Scheme 5.




Scheme 6.

calculated value for 3-acetyl-2,5-diphenyl MPF would be −38.8 ppm, hence we attribute this to the isomer produced by acetylation β to phosphorus. The very low abundance of this isomer shows why such products are difficult to isolate and characterise.

The substitution patterns of the phenylphosphaferrocenes examined here show that blocking the α positions with phenyl groups does not lead to the production of β acetyl derivatives but rather reaction occurs on the phenyl and/or Cp ring. It is interesting to note that both α positions must be blocked for substitution to occur on an arene ring. Thus, 3,4-dimethyl-2-phenyl MPF reacts with $AlCl_3$/MeCOCl to give acetylation at the free α position [3].

## Experimental

Phosphaferrocenes were prepared by literature methods [4, 20]. All manipulations involving monophosphaferrocenes were carried out under $N_2$ or Ar. Chromatography was performed on deactivated acidic alumina (15% $H_2O$ wt./wt.) or silica gel 70/230 mesh. Reactions that produced isomeric mixtures were rechromatographed.

Melting points, analytical data and ν(CO) values are given in Table I. Where no melting point is given the compound was an oil at room temperature and resisted attempts at recrystallisation. Elemental analysis was performed by the Micro Analytical Department, University of Manchester. Where no analysis is given the product was susceptible to atmospheric oxidation and in such cases molecular weights have been determined ($M^+$ mass spectrum at 70 eV). **IV** and **X** appeared to be air stable, but perfectly satisfactory analytical data were not obtained.

The structural identity of products was determined by NMR spectroscopy (*vide infra*) (Table II). $^1H$ NMR were obtained on a Varian EM360 and $^{13}C$/$^{31}P$ NMR spectra on a Bruker WP80 Spectrometer referenced to TMS and 85% $H_3PO_4$ respectively. Phosphorus–hydrogen coupling constants were typical for such systems [3, 4]. In the case of derivatives where substitution occurred on the arene ring, the disubstituted arene appeared as two symmetrical doublets in the $^1H$ NMR confirming *para* substitution, with coupling constants of the expected magnitude. The protons on the arene closest to the acetyl group and *meta* to the phosphacyclopentadienyl ring (labelled $H_{meta}$ in Table II) were well separated from other aromatics. The $H_{ortho}$ signal tended to be partially obscured by other aromatic signals. The addition of the paramagnetic shift reagent $Eu(FOD)_3$ caused large downfield shifts of $\delta CH_3CO$ and $\delta H_{meta}$, $\delta H_{ortho}$ was also shifted downfield enough to separate it from other resonances and the two doublets from the disubstituted arene could be clearly seen.

### *Acylation Reactions*

#### *2-Acetyl-3-methyl MPF (I)*

**I** was prepared by an identical procedure to 2-acetyl-3,4-dimethyl MPF using triflic acid in excess acetic anhydride [7]. After work up, the product was chromatographed on alumina with $CH_2Cl_2$. The orange band eluted was rechromatographed on alumina with benzene/ethylacetate (97:3 *v/v*). A trace of unreacted 2-methyl MPF was eluted first followed by **I**. 1.2 g (5.5 mmol) 2-methyl MPF gave 0.6 g **I** (42%).

#### *2-Acetyl-3-methyl- and 2-acetyl-4-methyl MPF (II, III)*

3-Methyl MPF (1.5 g, 6.9 mmol) was acetylated as above to give **II** 0.32 g and **III** 0.37 g (total yield

TABLE I. Physical data and IR for Acylated Derivatives

| Product | Melting point (°C) | Analysis[a] (%) | | Molecular weight[b] | ν(C=O) ($cm^{-1}$)[b, c] |
|---|---|---|---|---|---|
| | | C | H | | |
| **I** | | | | 260 | 1675 |
| **II** | | | | 260 | 1675 |
| **III** | | | | 260 | 1663 |
| **IV** | 68–70 | | | 316 | 1600, 1650 |
| **V** | | | | 378 | 1638, 1655[d] |
| **VI** | 138 | 71.1(71.8) | 4.5(4.6) | | 1650 |
| **VII** | 206 | 71.7(71.8) | 4.5(4.6) | | 1660 |
| **VIIIA/B** | ~200 | 70.0(70.8) | 4.6(4.6) | | 1660 |
| **IX** | 90–94 | | | 550 | 1675 |
| **X** | 171–174 | | | 550 | 1680 |
| **XI** | | | | 398 | 1670 |
| **XII** | 130 decomp. | | | 398 | 1660 |

[a]Calculated values in parenthesis. [b]From mass spectra ($M^+$) at 70 eV. [c]In Nujol. [d]Thin film.

TABLE II. $^{31}P/^{1}H$ NMR data for **I** → **XII**

| Product | Solvent | $\delta^{31}P$ | αH [a] | βH [b] | MeCO [c] | α/βMe | Cp | Other |
|---|---|---|---|---|---|---|---|---|
| Alkyl derivatives | | | | | | | | |
| **I** | $CS_2$ | −44.1 | | 5.28m, 5.78m | 2.27[d] | 2.08d | 4.35 | |
| **II** | $CS_2$ | −38.6 | 4.05[d] | 5.15m | 2.32[d] | 2.50s | 4.35s | |
| **III** | $CS_2$ | −45.6 | 4.10[d] | 5.71m | 2.20[d] | 2.40s | 4.36s | |
| **IV** | $CDCl_3$ | −53.0 | 4.10[d] | | 2.37[d], 2.42s | 2.23s, 2.47s | 4.50m, 4.68m, 4.88m | |
| **V** | $CDCl_3$ | −51.4 | 4.10[d] | | 2.30[d] | 2.20s, 2.40s | 4.57m, 4.85m, 5.08m | arene 7.62m, 7.95m |

| | | $\delta^{31}P$ | βH [b] | MeCO | Cp | Arene $H_{meta}$ | Arene (other) |
|---|---|---|---|---|---|---|---|
| Phenyl derivatives | | | | | | | |
| **VI** | $CDCl_3$ | −33.6, −57.2 | 5.30m, 5.95m[d] | 2.05s | | | ~7.20m |
| **VII** | $CDCl_3$ | −58.9, −61.1 | 5.31m, 5.85m | 2.52s | | 7.60[d] | ~7.10m |
| **VIII A** | $CDCl_3$ | −56.4, −60.3 | 6.15m, 5.30m | 2.60s | | 7.60[d] | ~7.15m |
| **B** | | −59.3 | 5.75 | | | | |
| **IX** | $CDCl_3$ | −61.8 | | 2.15s | 4.35m | | 7.05 |

| | | $\delta^{31}P$ | βH | MeCO | Cp | Arene $H_{meta}$ [e] | Arene |
|---|---|---|---|---|---|---|---|
| **X** | $CDCl_3$ | −62.1 | | 2.58s | 4.45s | 7.82[d] | 7.15s |
| **XI** | $CDCl_3$ | −69.7 | 5.50[d] | 1.78s | 4.30m, 4.45m[f] | | ~7.20m |
| **XII** | $CDCl_3$ | −66.9 | 5.75[d] | 2.57s | 4.20s | 7.82[d] | ~7.4m |

δ in ppm, s = singlet, m = multiplet, d = doublet. [a] $^{2}J$(PH) 36–38 Hz. [b] $^{3}J(PH)^{2}$ 5 Hz. [c] $^{4}J$(PH) 4 Hz. [d] = $^{3}J$(PαMe) 10 Hz. [e] $^{3}J$(Hm/Ho) ~ 8 Hz. [f] βH on acetylated ring.

39%). **II** was eluted first on alumina using benzene/ethylacetate (93:3 *v/v*). **I**, **II** and **III** were very air sensitive.

*2,1′-Diacetyl-3,4-dimethyl- and 2-acetyl-1′-benzoyl MPF (IV, V)*

$AlCl_3$ (0.3 g, 2.2 mmol) and MeCOCl (0.18 g, 2.2 mmol) were stirred in dry $CH_2Cl_2$ (~50 $cm^3$) for 0.25 h. 1′-acetyl-3,4-dimethyl MPF (0.61 g, 2.2 mmol) in $CH_2Cl_2$ (~5 $cm^3$) was added and the resulting deep purple solution stirred at room temperature for 0.5 h. The reaction was quenched with $H_2O$ (~50 $cm^3$). After the usual work up, the product was chromatographed on alumina with $CH_2Cl_2$. The isolated diketone was rechromatographed on silica with ethylacetate to give 0.6 g **IV** (65%). Using an identical procedure, 1′-benzoyl-3,4-dimethyl MPF (0.6 g 1.8 mmol) gave 0.4 g **V** (59%).

*$^{13}C$ NMR of IV (solvent Ar saturated $CS_2$)*

14.42, 16.11 $\beta Me_{3,4}$, 27.79, 1′$CH_3CO$, 30.93 ($^{3}J$(PC) 9.3 Hz) 2 $CH_3CO$ 73.82, 74.34, 76.30, 76.87 $CpC_2$–$C_5$, 82.74 ($^{1}J$(PC) 59 Hz) αC, 83.65 $C_pC_1$, 90.50 ($^{1}J$(PC) 52 Hz) αC quat, 96.03 ($^{2}J$(PC) 4.9 Hz), 100.96 ($^{2}J$(PC) 7.8 Hz) $C\beta_{3,4}$ 197.13, ′$COCH_3$, 102.77 ($^{2}J$(PC) 23.1 Hz) 2$COCH_3$.

*$^{13}C$ NMR of V (solvent as IV)*

14.78, 15.90 $\beta Me_{3,4}$, 30.00 ($^{3}J$(PC) 9.0 Hz) 2 $CH_3CO$, 74.91, 76.41, 76.61, 77.62 ($CpC_2$–$C_5$, 82.22 $CpC_1$, 83.47 ($^{1}J$(PC) 59.0 Hz) αC, 90.40 ($^{1}J$(PC) 64.0 Hz) αC quat, 95.93 ($^{2}J$(PC) 5 Hz), 101.33 ($^{2}J$(PC) 8 Hz) $C\beta_{3,4}$ 128.50 arene $C_{3,4}$, 128.73 arene $C_{2,6}$, 132.07 arene $C_4$, 139.36 arene $C_1$, 194.38 $COC_6H_5$, 201.75 ($^{2}J$(PC) 23.0 Hz) $COCH_3$.

*VI, VII and VIII*

2,2′,5,5′-Tetraphenyl DPF (1.2 g, 2.3 mmol) was dissolved in refluxing dry $CH_2Cl_2$ (~80 $cm^3$). To the refluxing solution $AlCl_3$ (0.44 g, 4.6 mmol) and MeCOCl (0.18 g 2.3 mmol) in $CH_2Cl_2$ (~10 $cm^3$) was rapidly added. The resulting purple solution was refluxed for 0.5 h after quenching and work up the product was chromatographed on silica with $CH_2Cl_2$. Unreacted TPDPF was eluted first followed by **VI** then **VII**. The use of excess MeCOCl produced **VIIIA/B** which were eluted with $CHCl_3$. The products were recrystallised from $CH_2Cl_2$/MeOH to give 0.08 g **VI** and 0.66 g **VII** (total yield 57%). Yield **VIIIA/B** depends on mole ratio of MeCOCl added.

*IX and X*

*(a) Via MeCOCl/$AlCl_3$*

TPMPF (1 g, 2.0 mmol) was dissolved in dry $CH_2Cl_2$ and a solution of MeCOCl (0.16 g, 2.0 mmol) and $AlCl_3$ (0.27 g, 2.0 mmol) in dry $CH_2Cl_2$ (~5 $cm^3$) added. The mixture was stirred at room temperature for 0.5 h. After work up the product was

chromatographed on alumina with benzene. Unreacted TPMPF was eluted first followed by **IX** (0.07 g). **IX** was eluted with benzene:$CH_2Cl_2$ (50:50 *v/v*) yield 0.41 g (total yield 44%). Both **IX** and **X** were recrystallised from $CH_2Cl_2$.

*(b) Via $(MeCO)_2O/CF_3SO_3H$*

An identical procedure to that given above was used with $(MeCO)_2O$ (0.2 g, 2.0 mmol) and $CF_3SO_3H$ (0.3 g, 2.0 mmol) as the acylating agent giving 0.18 g **X** and 0.02 g **IX** (total yield 20%).

*XI and XII*

**XI** and **XII** were prepared by the same method as for **IX** and **X**. **XII** was eluted first followed by **XI**. Yields of isolated compounds were variable. In the experiment examined by $^{31}P$ NMR only, the organic phase was dried and evaporated. The residue was dissolved in $CDCl_3$ and the $^{31}P$ NMR spectrum obtained immediately.

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