The Cleavage of Cyclopentadienyl Substituted η^6-Arene η^5-Cyclopentadienyl Iron(II) Cations by Phospholyl Anions. A Facile Route to 1′-Substituted Monophosphaferrocenes

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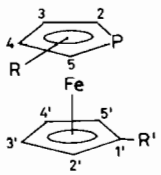
Abstract

η^6-Arene η^5-cyclopentadienyl iron PF_6^- salts bearing substituents on the cyclopentadienyl ring are cleaved by phosphacyclopentadienyl anions (PCp^-M^+) to give 1′-substituted monophosphaferrocenes. Such derivatives are unavailable via chemical modification of monophosphaferrocenes such as Friedel–Crafts reaction or metallation. 1′-Alkyl, acyl, *N,N*-dimethylaminomethyl and 1′-carboxylic acids have been synthesised and characterised. Nucleophilic displacement of chloride by PCp^-M^+ in the η^6-chlorobenzene cation produces novel 1-phenylphospholes one of which has been isolated and characterised. The synthetic route was found to be unsuccessful in the production of azaferrocene.

Introduction

Certain classes of derivatives of monophosphaferrocenes are unavailable via standard methods of modifying metallocenes such as electrophilic substitution, metallation, *i.e.*

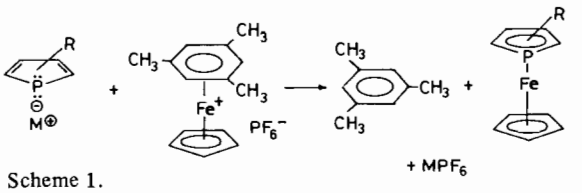


R = Me, H
R′ = COR, CO_2H, alkyl

For the monophosphaferrocene system Friedel–Crafts substitution always introduces the incoming group into the PCp ring with high specificity for substitution α to phosphorus [1]. Cp substitution occurs only where the α positions in the PCp ring are blocked by phenyl groups and even then a large amount of substitution occurs on the phenyl substituent [2], rather than on the Cp ring. The high positional selectivity of such reactions has been shown by chemical reactivity studies [1] and explanations for such behaviour have been offered by molecular orbital calculation [3].

Metallation of phosphaferrocenes does not appear feasible as the phosphorus atom is slightly electrophilic and as such is prone to attack by powerful nucleophiles *i.e.* R^-Li^+ [4–6]. Mercuration has also been reported to fail [7].

We recently discovered that phospholyl anions (PCp^-) reacted with η^6-arene η^5-cyclopentadienyl iron cation to produce monophosphaferrocenes [8] (Scheme 1).

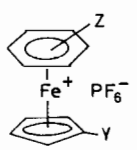


Scheme 1.

We considered that 1′ derivatives may be available via a similar route using cyclopentadienyl substituted arene cations. Accordingly, as a logical extension to our initial work, we have investigated the range of such reactions for both phosphorus and nitrogen (azaferrocene) systems.

Discussion

The reaction of various PCp^-M^+ derivatives with arene complexes of the type:



Z = H or 1,3,5 Me_3
Y = $COCH_3$, COC_6H_5, $COCMe_3$, CO_2H
CH_3, CH_2NMe_2

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TABLE I. Summary of Yields and Analytical Data for 1′-Substituted Monophosphaferrocenes Obtained from the Reaction of Phospholylithium Reagents with η^6-(arene)η^5-(cyclopentadienyl)Fe(II) PF_6 Complexes

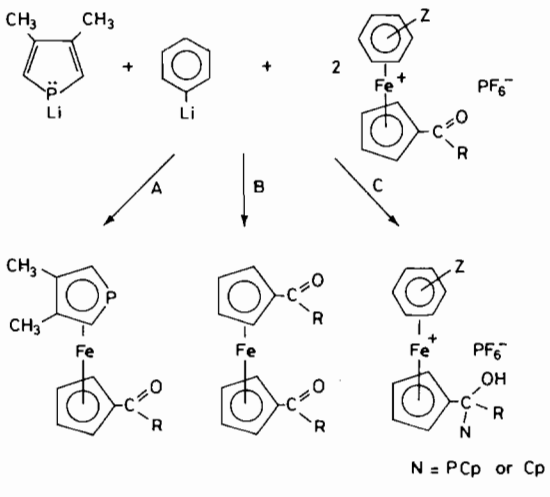
Compound number	PCp substituents	Cp substituents	% yield	Melting point	Analyses[a] (found(calc.))	Molecular weight[b]	ν(CO)[c]
1	3 4-Me_2	COMe	13[d]	45–6		274	1675
2	3 4-Me_2	COMe	34[e]				
3	3,4-Me_2	CoPh	43[e]			336	1640
4	3,4-Me_2	COtBu	50[e]			316	1655
5	3,4-Me_2	CH_2NMe_2	45[d]		[f]		
6	3,4-Me_2	$CH_2N^+Me_3I^-$	93[d]	>150	C, 42.1; H, 5.5; N, 3.0 (C, 41.8; H, 5.3; N, 3.3)		
7	3,4-Me_2	CO_2H	0[d]				
8	3,4-Me_2	CO_2H	52[e]	150	C, 52.2; H, 4.9 (C, 52.9; H, 4.7)		1640
9	3, Me	CO_2H	48[e]	156–8	C, 50.3; H, 4.3 (C, 50.4; H, 4.2)		
10	H	COPh	10[e]			308	1640
11	2,3,4,5-Ph_4	CH_3	62[d,g]	68–70	C, 78.3; H, 4.9 (C, 78.2; H, 5.2)		

[a]Calculated values in parentheses. [b]From M^+ measurement (mass spectra). [c]In cm^{-1}. [d] Using mesitylene complex. [e]Using benzene complex. [f]Analysed as methiodide (compound 6). [g]Using K metal instead of Li.

showed that the method provided a viable route to 1′monophosphaferrocenes.

The reaction of η^6-arene iron cation with nucleophiles/strong bases can be complex [9]. In our original study [8], we postulated that monophosphaferrocenes arise via nucleophilic attack of PCp^- on the positive iron centre. 1,3,5-Trimethyl substitution on the arene was preferred to discourage nucleophilic addition to the arene ring. We started our investigation by synthesising a series of 1′-ketones using 3,4-dimethylPCp^-Li^+ (results are summarised in Table I). The major products of such reactions are shown below in Scheme 2.

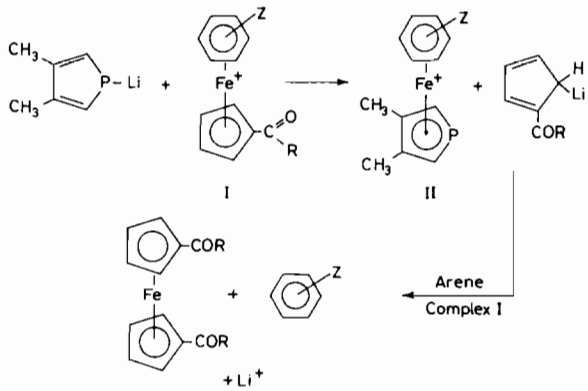
Phenyl lithium (Ph^-Li^+) arises as a biproduct from the production of the PCp^-Li^+ [10]. Since



Scheme 2.

Ph^-M^+ species react with arene complexes and phosphaferrocenes, two equivalents of arene complex are used to remove Ph^-Li^+. Reaction (Scheme 2, A) produces the desired product as in Scheme 1. Considerable amounts of 1,1′-diacyl ferrocenes were found (Scheme 2, B), ranging from 20 to 35% based on arene complex added. Such products arise from a nucleophilic induced rearrangement or reductive disproportionation [11, 12]. This may be caused by either organometallic reagent (PCp^- or Ph^-M^+) but is facilitated by acyl substitution as little or no ferrocene is produced when the Cp ring is unsubstituted [8]. Fortunately the mono and diketone products are readily separated by column chromatography. It is possible that diacylferrocenes arise via displacement of a Cp ligand.

However, this does not occur to any measurable extent since no η^6-benzene η^5-phospholyl iron-cation complexes could be detected. Not unexpectedly, the ionic biproducts contained compounds

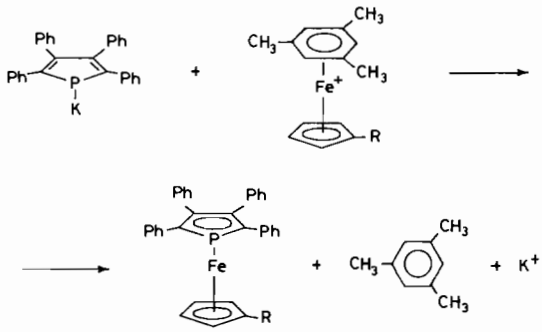


arising from addition of PCp^- and Ph^- to the carbonyl group (Scheme 2, C).

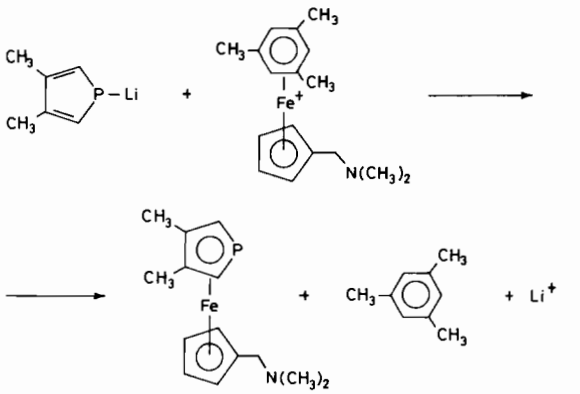
For Z = 1,3,5-Me_3 a considerably lower yield of 1'acetylmonophosphaferrocene was obtained compared to the benzene complex, hence other ketones were synthesised using the benzene complex. The inhibition of A (Scheme 2) by 1,3,5-trimethyl substitution was also found in another case (*vide infra*). Acyl substitution on the Cp ring would activate all sites of the complex towards nucleophile/bases, as well as providing an alternative reaction site. Indeed, the desired product could be detected immediately after the reagents were mixed (TLC analysis) whereas with Cp unsubstituted reactions, refluxing is needed before products can be detected [8]. We suspect that in the more reactive Cp acyl complexes, alkyl substitution on the arene discourages the desired attack at iron and encourages reaction at other sites of the arene cation. For the series Z = H, R = CH_3, C_6H_5, tBu, the yield increased with the bulk of R showing that the side reaction C (Scheme 2) is inhibited by steric hindrance at the carbonyl carbon. Finally we succeeded in producing a PCp unsubstituted 1'-ketone in modest yield.

To investigate whether 1,3,5-trimethyl substitution provided too much steric hindrance we synthesised two Cp unsubstituted monophosphaferrocenes as in our original publication [8] using the *p*-xylene arene complex in place of mesitylene and obtained the following results (yield mesitylene arene complex in parentheses) 3,4-dimethylphosphaferrocene 30% (51%) and 2,5-diphenylphosphaferrocene 75% (61%). In the case of the large phenylated PCp anion, the less hindered *p*-xylene complex gives a rather better yield. However, for the more reactive and less selective dimethyl PCp anion, the loss of alkyl protection on the arene results in lower yields. We therefore concluded that the mesitylene FeCp complex would be the best arene complex overall for use in the synthesis of 1'alkyl Cp derivatives.

The reaction was also found suitable for the synthesis of 1'alkyl monophosphaferrocenes;



and for the production of 1'-alkylphosphaferrocenes with more complex substituents, *i.e.* *N,N*-dimethylaminomethyl.



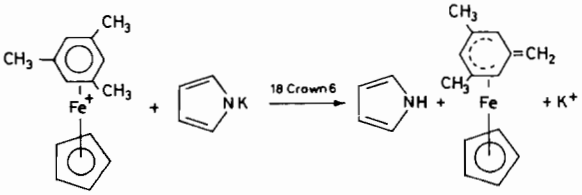
3,4-Dimethylphospholyllithium was also found to react with η^6-benzene η^5-cyclopentadienylcarboxylic acid iron hexafluorophosphate to give the corresponding phosphaferrocene 1'carboxylate, yielding the free acid after protonation with HCl. This interesting finding indicates that PCp^- can attack the metal centre in the zwitterion as the initial reaction is undoubtedly deprotonation of the acid by PCp^-. (These complex acid cations are much stronger acids than their uncharged equivalents $[\eta^6\text{-}C_6H_5CO_2HFe\eta^5C_5H_5]^+PF_6$ and $[\eta^6\text{-}C_6H_6Fe\eta^5\text{-}C_5H_4CO_2H]^+PF_6^-$ have pK_a values of 3.05 and 3.53 respectively compared to 5.69 and 6.11 for benzoic acid and ferrocene carboxylic acid [13, 14].)

Reaction with the mesitylene complex produced no detectable amount of the required product under the above conditions.

The 3-methyl derivative was synthesised in an identical manner. In these cases a 1:1 ratio of phosphole:arene complex was used rather than 1:2 to allow for the loss of PCp^- on protonation, (this does not remove all PCp^- as an equimolar amount of Ph^-Li^+ is present).

Reaction of Potassium Pyrrolidide (NCp^-K^+) with η^6-Arene Complexes

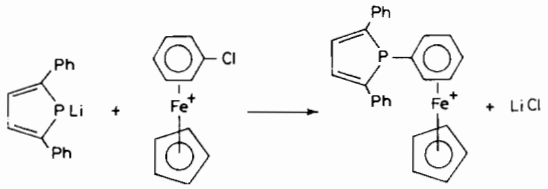
NCp^-K^+ was found to be inert towards the η^6-benzene and η^6-mesitylene complexes at room temperature in DME or THF owing to the insolubility of both reagents. Attempts to reflux such systems resulted in extensive decomposition. The addition of the K^+ selective crown ether (18 crown 6) as a phase transfer catalyst enabled reaction to proceed at room temperature. However, with the η^6-mesitylene complex, NCp^-K^+ acted as a base and deprotonated a methyl substituent, typical behaviour of such systems when treated with strong bases [9].



Reaction with the η^6-benzene complex produced ferrocene and traces of unstable η^5-NCp compounds, (not however azaferrocene), which decomposed before a definite identification could be made.

Nucleophilic Displacement of Chloride

In our initial publication on these cleavage reactions, chloro substitution was shown to inhibit the formation of phosphaferrocenes, the major reaction being nucleophilic displacement of Cl^- by PCp^- [8]. We reported the formation of such a compound with 3,4-dimethylPCp^-Li^+ which was not isolated but characterised only via NMR spectroscopy. We repeated this reaction using another PCp^- anion (2,5-diphenylphospholyl lithium) and found identical behaviour, thus this appears to be the general reaction between PCp^- and (η^6-ClC_6H_5-Feη^5-C_5H_5)$^+PF_6^-$. In this case, we have isolated and fully characterised the new 1-phenylphosphole as formed below.



(No 2,5-diphenylmonophosphaferrocene could be detected from this reaction.)

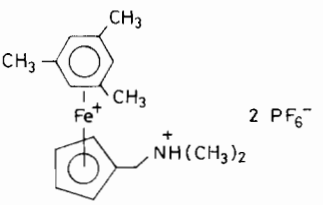
The addition of the $CpFe^+$ unit modifies the properties of 1,2,5-triphenylphosphole (TPP). The strong blue fluorescence of TPP is totally quenched [15]. $\delta^{31}P$ for $TPPFeCp^+PF_6^-$ is very close to that found for TPP (+1.0 and +4.00) which shows no major geometric or electronic changes at P on addition of the $FeCp^+$ unit. The reactivity of the P lone pair is reduced, however, probably due to a direct field influence of the positive charge on Fe. $TPPFeCp^+PF_6^-$ was not quaternised by methyl iodide at room temperature, whereas TPP reacts with MeI in benzene to form the quaternary salt [15]. $TPPFeCp^+PF_6^-$ was sparingly soluble in CF_2CO_2H to give yellow solutions in which $\delta^{31}P$ appeared as a singlet showing no P protonation. $TPPFeCp^+PF_6^-$ dissolved readily in the much stronger CF_3SO_3H to give deep red solutions in which P protonation was apparent. $\delta^{31}P$ appeared as a doublet $^1J_{PH} = 510$ Hz, which collapsed to a singlet with proton decoupling. Finally, as with TPP, the P^V oxide could be formed by treatment with hydrogen peroxide [15].

Table I summarises the results obtained for the synthesis of 1′monophosphaferrocenes. Such reactions are obviously viable as synthetic pathways to Cp substituted monophosphaferrocenes. Although the yields are rather modest in some cases, the method nevertheless affords routes to otherwise intractable derivatives. In some cases unavoidable side reactions obviously reduce yields, however, our chief aim at this stage was to explore the range of general applicability of the reaction and no attempt was made to optimise yields.

Such reactions do not appear to be such a ready source of azaferrocenes, the major drawback being that the NCp^- anion acts as a base rather than a nucleophile, such a change is not entirely unexpected in changing from phosphorus to nitrogen. It is likely that such reactions described here will provide a convenient route to 1′-arsa- and stilbametallocenes whose corresponding MCp^- anions show reactivity similar to PCp^- anions [16, 17].

The nature of arene substitution clearly has a large effect on the course of such reactions described here. The nucleophilic displacement of chloride by PCp^- is the favoured reaction, rather than arene cleavage, and in some cases 1,3,5-trimethyl substitution can provide too much steric hindrance at the iron atom. The Cp substituent also influences the reaction pathway as shown by the production of 1,1′-disubstituted ferrocenes with acyl substituted substrates, negligible amounts of ferrocene are produced with Cp unsubstituted reactions [8], and no 1,1′ disubstituted ferrocenes were detected where the substituent was CO_2H, CH_3 or CH_2NMe_2. The production of 1,1′disubstituted ferrocenes is promoted by electron withdrawing groups in the arene complex. CO_2H produced no 1,1′ferrocene dicarboxylic acid as the substituent exists as CO_2^- when nucleophilic attack by PCp^- occurs. It is interesting to note that even when the arene cation carries a Cp ring substituted with an electron withdrawing group, *i.e.* acyl, no cleavage of the Cp ligand was found. This parallels the recent results of Sutherland *et al.* [18] who investigated the photochemical cleavage of similar arene cations with phosphines and other arenes. It is obviously more favourable to displace the uncharged arene from the positive iron center rather than the negative Cp anion.

A final point to note is that the arene cation used for the synthesis of the *N,N*-dimethylaminomethyl derivative is isolated as the conjugated acid, thus:



We attempted the preparation of the above by a similar method to that given in the experimental section using refluxing mesitylene as the solvent, and isolated only the Cp unsubstituted complex in ~25% yield.

TABLE II. ^{1}H[a] and ^{31}P[b] Chemical Shifts for New Monophosphaferrocenes

Compound	$\delta H_{3,4}$	$\delta H_{2,5}$	$\delta H_{3',4'}$	$\delta H_{2',5'}$	Others	$\delta^{31}P$
1		3.87[d]	4.45m	4.90m	2.11s ($Me_{3,4}$), 2.20s (CH_3CO)	−77.0
3		3.80[d]	4.55m	4.97m	2.05s ($Me_{3,4}$), 7.5–7.9m (arene)	−76.7
4		3.70[d]	4.34m	4.90m	1.30s (tBu), 2.15 ($Me_{3,4}$)	−79.0
5		3.70[d]	4.09m	4.20m	2.20s ($Me_{3,4}$), 2.30s (NMe_2), 3.25s (CH_2)	−83.7
6		3.50[d]	3.90m	4.21m	1.72s ($Me_{3,4}$), 2.77 (N^+Me_3), 4.05s (CH_2)	−79.4
8		3.80[d]	4.60m	4.80m	2.20s ($Me_{3,4}$), 8.6 br.s. (OH)	−75.6
9	5.15m	3.90[d], 4.00m	4.60m	4.91	2.21s (Me_3), 10.4 br.s. (OH)	−64.2
10	5.20m	4.00 (2xd)[c]	4.65m	5.00m	7.5–7.9 (arene)	−64.5
11			4.15m	4.15m	1.75s (Me), 7.1 (arene)	−56.1[d]

[a]Ppm from TMS, solvent $CDCl_3$. [b]Ppm from 85% H_3PO_4 −ve upfield, solvent $CDCl_3$. [c]$J_{H_2H_2}$ ~ 3 Hz. [d]Solvent acetone-d_6/D_2O 85:15 *v/v*.

Experimental

All reactions were carried out under dry Ar, as was the handling and storage of monophosphaferrocenes. Solvents were dried by standard laboratory procedures; aluminium chloride used in the synthesis of acyl Cp arene cation was sublimed before use. Chromatography was performed on acidic alumina with a 5% H_2O content or silica gel 70/230 mesh. ^{1}H NMR were run on a Varian EM360 reference external TMS. ^{31}P NMR were obtained on a Bruker WP80 reference 85% H_3PO_4 (δ +ve downfield). For ^{1}H NMR s = singlet, d = doublet, m = multiplet. All αH $^{2}J_{PH}$ 36–38 Hz, (see Table II).

Most monophosphaferrocenes were susceptible to atmospheric oxidation and elemental analysis has been reported only for the most stable derivatives; molecular weight determination has been reported for derivatives not analysed, (m^+ mass spectrum at 70 eV).

Where no melting point is given, the compounds were oils at room temperature and resisted attempts at recrystallisation. Micro analysis was performed by the Analytical Department, University of Manchester.

The following reagents were prepared by literature methods; 3,4-dimethyl, 3-methyl and 1-phenylphospholes [19], 1,2,5-triphenylphosphole [20], pentaphenylphosphole [21]. η^6-Benzene, mesitylene/xylene chlorobenzene η^5-cyclopentadienyl iron hexafluorophosphates were made by standard procedures [22–24], η^6-benzene and mesitylene η^5-acetyl/benzoylcyclopentadienyl iron hexafluorophosphates [25], η^6-benzene and mesitylene η^5-cyclopentadienylcarboxylic acid iron hexafluorophosphates [26].

Other Arene Complexes

η^6-Mesitylene η^5-methylcyclopentadienyl iron PF_6^-

The above was produced in an identical manner to the Cp unsubstituted complex using 1,1'-dimethylferrocene. Reaction time, 3 h. Yield 19%, melting point (m.p.) decomposition (decomp.) ~250 °C. *Anal.* Calc. for $C_{15}H_{19}FePF_6$: C, 45.0; H, 4.8. Found: C, 44.7; H, 4.7%. ^{1}H NMR (DMSO d_6) 2.00(s) 3H, Me 2.42(s) 9H, Cp 4.85(s) 4H, arene t. 10.0 ppm (s) 3H.

η^6-Benzene η^5-t-butanoylcyclopentadienyl iron PF_6^-

The above was produced in an identical manner to the other keto complexes [25] from t-butyl ferrocenyl ketone. Yield 48% (reaction time = 1h) m.p. decomp. >200 °C ν(CO) 1675 cm^{-1} (nujol). *Anal.* Calc. for $C_{16}H_{19}FeOPF_6$: C, 44.9; H, 4.4. Found: C, 44.1; H, 4.5%. ^{1}H NMR (CD_3CN) tBu 0.95(s) 9H, $H_{3,4}$ 4.90(m) 2H, $H_{2,5}$ 5.17(m) 2H, arene 5.95(s) 6H.

η^6-Mesitylene η^5-(N,N-dimethylaminomethyl)-cyclopentadienyl iron PF_6^-

N,N-dimethylaminomethyl ferrocene (14 g, 0.058 mol); aluminium powder (1.5 g 0.058 mol) aluminium chloride (30.9 g, 0.23 mol) water (1.05 cm^3, 0.058 mol) and excess mesitylene (~30 cm^3) were refluxed in cyclohexane (~150 cm^3) for 5 h. The mixture was cooled and quenched with ice water (150 cm^3). The aqueous layer was separated, filtered, and washed with ether (2 × 150 cm^3). Excess NH_4PF_6 solution was added, and the resulting yellow solid filtered off and washed with cold water. After drying the solid was washed with CH_2Cl_2 and recrystallised from acetone/ether. Yield 16 g (47%) as conjugate acid, bis hexafluorophosphate. M.p. decomp. 214–218 °C. *Anal.* Calc. for $C_{17}H_{25}FeNP_2F_{12}$: C, 34.6; H, 4.2; N, 2.4. Found: C, 33.5; H, 4.4; N, 2.3%. ^{1}H NMR (CD_3CN) Me 2.19(s) 9H, NMe_2 2.46(d)* 6H, CH_2 3.51(d)* 2H Cp 4.70(s) 4H, arene 5.80(s) 3H.

*J-7 Hz observation of coupling to amino proton depends on sample and solvent purity.

The acid was converted to the free base by shaking with aqueous KOH (pH ~ 14) and CH_2Cl_2. The free base dissolved in the organic phase and isolated after drying by the addition of ether. M.p. 170–174 °C. *Anal.* Calc. for $C_{17}H_{24}FeNPF_6$: C, 46.1; H, 5.4; N, 3.2. Found: C, 46.0; H, 5.6; N, 3.0%. ^1H NMR (acetone d_6) NMe_2 1.75(s) 6H, Me 2.05(s) 9H, CH_2 2.92(s) 2H, Cp 4.40(s) 4H, arene 5.50(s) 3H.

1'-Acyl monophosphaferrocenes

All acyl derivatives were synthesised by one general procedure as given for 1'-acetyl-3,4-dimethylphosphaferrocene described below. The yields of phosphaferrocenes are based on phosphole added. % Yields and physical properties are given in Table I, NMR spectroscopic data are given in Table II.

1'-Acetyl-3,4-dimethylphosphaferrocene

3,4-Dimethyl-1-phenylphosphole (1.9 g, 0.01 mol) was stirred in dry THF (~75 cm^3) for 5 h with lithium metal (0.15 g, 0.021 g ats). The resulting deep red solution was transferred by syringe to a clean flask and η^6-benzene η^5-acetylcyclopentadienyl iron hexafluorophosphate (7.72 g, 0.02 mol) added. The mix was heated at reflux for 0.75 h. After cooling an equal volume of benzene was added and the solution filtered through Celite or anhydrous Na_2SO_4. The solvent was evaporated *in vacuo* and the residue chromatographed on alumina with benzene/CH_2Cl_2 dichloromethane (70:30 *v/v*). The title compound was the first red band eluted followed by 1,1'-diacetylferrocene (with dichloromethane as eluent). The product was rechromatographed on silica with CH_2Cl_2. Yield 0.93 g.

An identical process using the η^6-mesitylene η^5-acetyl-cyclopentadienyl iron PF_6^- gave a 13% yield of the title compound.

Further compounds were obtained using the corresponding η^6-benzene η^5-1'-acyl cyclopentadienyl iron hexafluorophosphates.

1'-Benzoyl-3,4-dimethylphosphaferrocene

3,4-Dimethyl-1-phenylphosphole (1.9 g, 0.01 mol) gave the title compound as a deep red oil 1.45 g.

1'-t-Butanoyl-3,4-dimethylphosphaferrocene

3,4-Dimethyl-1-phenylphosphole (1.2 g, 6.4 mmol) gave the title compound as a red oil 1.0 g. Initial chromatography was run with hexane/benzene (70:30 *v/v*) as eluent.

1'-Benzoylphosphaferrocene

1-Phenylphosphole (1 g, 6.3 mmol) gave the title compound as a red oil 0.19 g.

1'-(N,N-Dimethylaminomethyl)-3,4-dimethylphosphaferrocene

In an identical process to that described for the 1'-acyl derivatives, the lithio derivative of 3,4-dimethyl-1-phenylphosphole (1.9 g, 0.01 mol) was reacted with the required arene complex (9.0 g, 0.02 mol). Reaction time 2 h at 67 °C. Chromatography on alumina using ethyl acetate/CH_2Cl_2 (75:25 *v/v*). Evaporation of the solvent gave the title compound as an orange–brown oil. Yield 1.3 g. Owing to the ease of oxidation of alkyl monophosphaferrocenes the product was further characterised as the methiodide.

The above amine (0.45 g, 1.5 mmol) in benzene/CH_2Cl_2 (90: 10 *v/v* ~ 20 cm^3) was treated with excess methyl iodide (~3 cm^3). After 10 min complete precipitation of the product had occurred. The solvent was decanted and the yellow solid triturated with ether and isolated by filtration. Yield 0.62 g.

1'-Methyl-2,3,4,5-tetraphenylphosphaferrocene

Pentaphenylphosphole (2 g, 4.3 mmol) and potassium (0.34 g, 0.0086 g ats) were refluxed in dry DME (~75 cm^3) for 3 h. After cooling the solution was transferred to a clean flask via syringe and η^6-mesitylene η^5-methylcyclopentadienyl iron hexafluorophosphate (1.72 g, 4.3 mmol) added (only one equivalent of arene complex is used in this case as C_6H_5K is removed by reaction with the solvent) [27].

The mixture was refluxed for 2 h, cooled and tBuOH ~10 cm^3 added and stirred at room temperature for 1½ h. Benzene was added and the product isolated as previously described and recrystallised from CH_2Cl_2/MeOH. Yield 1.4 g.

3,4-Dimethylphosphaferrocene-1'-carboxylic acid

3,4-Dimethyl-1-phenylphosphole (3.8 g, 0.02 mol) was lithiated as previously described and reacted with η^6-benzene η^5-cyclopentadienyl carboxylic acid iron hexafluorophosphate (7.76 g, 0.02 mol) with a 2 h reflux. After cooling, the reaction mixture was quenched with aqueous hydrochloric acid (200 cm^3, 2 N). The aqueous phase was extracted with ether (2 × 150 cm^3), the organic phase was washed with water (100 cm^3) and extracted with aqueous potassium hydroxide (100 cm^3, 10% *w/v*) (a coloured impurity remains in the organic phase). The aqueous phase was washed with ether (100 cm^3) then made strongly acidic with concentrated hydrochloric acid. The product was extracted into CH_2Cl_2 (100 cm^3) and the organic phase washed with water (100 cm^3). After drying over anhydrous sodium sulphate the volume was adjusted to ~50 cm^3, hexane added (50 cm^3) and filtered. The filtrate was evaporated *in vacuo* and the residue chromatographed on silica with ethyl acetate. The product was recrystallised from CH_2Cl_2/hexane. Yield 1.4 g.

3-Methylphosphaferrocene-1'-carboxylic acid

The above was produced by an identical method starting from 3-methyl-1-phenylphosphole.

1(2,5-Diphenylphospholyl)η^6-benzene η^5-cyclopentadienyl iron hexafluorophosphate

1,2,5-Triphenylphosphole (4 g, 13 mmol) and lithium (0.18 g, 0.026 g ats) was refluxed in dry DME (~50 cm^3) for 3 h. The solution was cooled to 0 °C and η^6-chlorobenzene η^5-cyclopentadienyl iron hexafluorophosphate (4.9 g, 13 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 1 h during which the colour changed from deep purple to pale yellow. Excess ether was added (~200 cm^3) and a yellow solid filtered off. The solid was dissolved in acetone and reprecipitated with aqueous hexafluorophosphate acid (5% *w/v*). The product was filtered, washed with water and dried. Recrystallisation from dichloromethane/ether gave the title compound. Yield 6 g (81%). The compound contained slight traces of the starting chlorobenzene complex which could be removed by washing with CH_2Cl_2/ether (80:20) and precipitating the title compound from the filtrate with ether. M.p. 170–174 °C.*

^1H NMR (acetone d_6)

Cp 4.20(s) 5H, 1-phenyl 5.65(s) 5H, others broad multiplet = 7.0 ppm 12H, $\delta^{31}P$ (acetone d_6) + 1.06 ppm (CF_3SO_3H) + 5.24 $^1J_{PH}$ 510 Hz.

The compound was analysed as the P oxide. 0.25 g (0.43 mmol) was dissolved in acetone (5 cm^3) and hydrogen peroxide added (~5 cm^3 6% *w/v*). After 4 h yellow crystals were filtered off and washed with cold acetone. Yield 0.15 g (58%) m.p. >250 °C decomp. *Anal.* Calc. for $C_{27}H_{22}F_6FeOP_2$: C, 54.6; H, 3.7. Found: C, 54.4; H, 3.8%.

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*The complex appears to undergo a phase change at 125 °C and changes from yellow to orange and remains orange on cooling.

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