A New Synthetic Route to Monophosphaferrocenes

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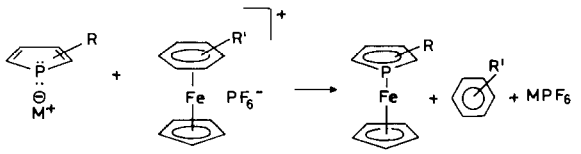
Abstract

Phosphacyclopentadienyl anions (**A**) derived from 1 phenylphospholes cleave the η^6-bonded arene from η^6-arene-η^5-cyclopentadienyliron(II) cations (**B**) via nucleophilic attack at iron to yield η^5-cyclopentadienyl-η^5-phosphacyclopentadienyliron(II) sandwich compounds (**C**).

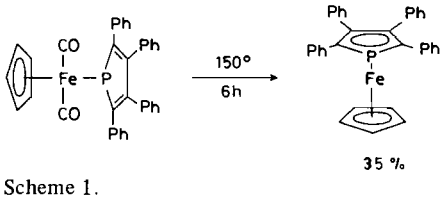


A **B** **C**

The reaction provides a versatile synthetic route to phosphaferrocenes with one general reaction giving a pathway to phosphaferrocenes with greatly varying degrees of ring substitution.

Introduction

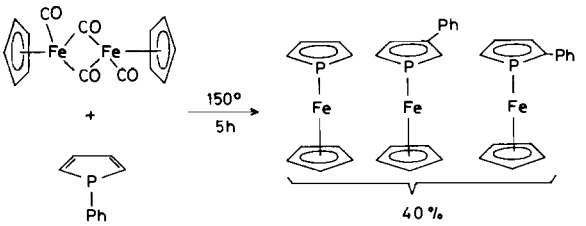
To date, two synthetic routes to mono phosphaferrocenes have appeared in the literature.



Scheme 1.

Scheme 1 was reported by Abel *et al.* [1], but we have found this route of no general applicability. It does appear to produce some of the corresponding 2,5-diphenyl derivative in low yield [2] but fails with alkyl substituted derivatives. Earlier Braye and Joshi [3] failed to effect the transformation in Scheme 1 because of too short a reaction time [1].

The second and more general route (Scheme 2) first published by Mathey [4] has several drawbacks although subsequent improvements have been made [6, 7].



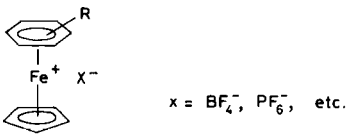
Scheme 2.

Generally low yields of mixed products are obtained and ring phenyl products result via phenyl group migration at high temperature [5].

The use of 1-t-butylphospholes results in no phenylated products being producted [6], whilst route 2 under CO pressure results in pure 2-phenyl derivatives [7].

We considered a general synthetic route to these interesting ferrocene analogues to be highly desirable, particularly with respect to controlled ring substitution. Accordingly we have studied the reaction of phosphacyclopentadienyl anions with η^6-arene-η^5-cyclopentadienyliron(II) cations.

These cations of general formula:



are well known and their extensive chemistry especially as synthetic precursors has recently been comprehensively reviewed by Astruc [8].

As the η^6-arene ring is uncharged the complex bears a positive charge and thus, in contrast to ferrocene, which undergoes electrophilic substitution, η^6-arene complexes show a wide range of nucleophilic reactions.

These can be complex and follow many paths [8] but certain oxygen and nitrogen nucleophiles cause decomposition via initial nucleophilic attack at iron with such η^6-arene complexes.

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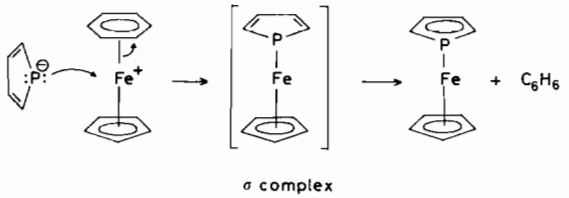
Phosphacyclopentadienyl (phospholyl) anions, apart from being facile $\eta^5\pi$-bonding ligands, are strong nucleophiles [9] and as such should attack the iron centre of η^6-arene complexes and displace the arene forming the $\eta^5\pi$-bonded monophosphaferrocene, Scheme 3.



Scheme 3.

With this reaction pathway in mind we investigated the reaction between η^6-arene complexes and phospholyl anions as possible new route to phosphaferrocenes.

Although other reactions compete, once conditions are optimised, the major reaction between the two species is as described in Scheme 3 and provides an excellent general route, rendering accessible a wide range of monophosphaferrocenes with greatly varied degrees of ring substitution.

Discussion

A vast range of η^6-arene-η^5-cyclopentadienyliron(II) cations can be easily produced, making them very attractive substrates for further modification. However, their susceptibility towards alkyl and aryl metals [8] had to be considered at the start of this work.

Phospholyl anions are produced via the reductive cleavage of 1-phenylphospholes by group I alkali metals [9].

Generally phenyl metal systems (Ph^-M^+) are very undesirable byproducts in the synthesis of mono and diphosphaferrocenes since they rapidly react with the product once formed via nucleophilic attack at phosphorus [10]. In the present context Ph^-M^+ are even more undesirable since phenyllithium has been reported to react with a range of η^6-arene-η^5-cyclopentadienyliron(II) complexes [11].

When the phospholyl anion is phenyl-substituted, the use of refluxing DME (1,2-dimethoxyethane) destroys Ph^-M^+ by reaction with the solvent, the resulting phenyl substituted phospholyl anion being stable [12].

Usually the cleavage of alkyl substituted phenylphospholes is performed in THF at room temperature [13, 14], Ph^-M^+ being removed by addition of t-butyl bromide sometimes at the expense of some of the phospholyl anion [13].

Initially we conducted the cleavage of alkyl substituted 1-phenylphospholes in refluxing DME. However, erratic yields of the final products seemed to indicate that the stability of the resulting phospholyl anion in this medium was questionable and we discontinued this approach.

The problem of removal of Ph^-M^+ in the synthesis of diphosphaferrocenes has been recently solved by Mathey [15, 16].

$$C_6H_5Li + 1/3AlCl_3 \longrightarrow 1/3Al(C_6H_5)_3 + LiCl$$

Scheme 4.

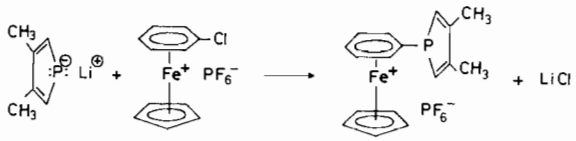
Unfortunately the addition of aluminium chloride to a solution of phospholyl anion and Ph^-M^+ before the η^6-arene complex resulted in low yields. Although this was not investigated in full, several factors indicate why this should be so. Monophosphaferrocenes seem to be unstable in contact with Lewis acids [4], which also catalyse the reverse reaction, *i.e.* the formation of the η^6-arene complex from ferrocenes and free arene. Azaferrocene makes a better substrate than ferrocene for such reactions [17].

Eventually the method chosen for alkyl phospholyl metals was to use a two molar excess of the arene complex.

The Ph^-M^+ reacting with the excess η^6-arene cation, thus prevented the attack of this species on the phosphaferrocene once formed.

The substitution pattern on the arene was also considered and some preliminary investigations were made using the reaction of 3,4-dimethylphospholyllithium with various arenes.

The η^6-chlorobenzene complex proved to be a very poor substrate giving less than a 1% yield of 3,4-dimethylphosphaferrocene the major product being a new η^6-arene cation where the chlorine was replaced by the 3,4-dimethylphospholyl moiety (Scheme 5).



Scheme 5.

The complex was characterised by ^{13}C, ^{31}P and ^1H NMR spectroscopy.

This result was not entirely unexpected as the iron cyclopentadienyl unit is as activating as two nitro substituents in nucleophilic displacement on the arene [8].

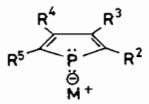
The η^6-toluene complex proved to be a much better substrate, the major side reactions being addition of the phospholyl anion to the η^6-arene to form the neutral iron(II) cyclohexadienyl deriva-

tive. The arene complex giving the best overall yields was that of 1,3,5-trimethylbenzene (mesitylene) which, whilst not completely eliminating nucleophilic addition, discourages such reactions since nucleophilic attack is not favoured at quaternary carbons and *ortho* to alkyl groups [8].

However, whilst the toluene and mesitylene complexes gave good yields of phosphaferrocenes, the hexamethylbenzene complex proved to be very inert towards even the most nucleophilic phospholyl metal.

This indicated that too heavy alkyl substitution on the arene ring sterically inhibits the attack of the phosphorus nucleophile on the iron centre. In addition alkylation stabilises the arene complex.

Having established that the mesitylene complex contained the best overall substitution pattern, we examined the reaction of this arene complex with six phospholyl metals with varying degrees of substitution.



I: $R^2 = R^3 = R^4 = R^5 = C_6H_5$.
II: $R^2 = R^5 = C_6H_5$; $R^3 = R^4 = H$.
III: $R^2 = R^5 = H$; $R^3 = R^4 = CH_3$.
IV: $R^2 = R^4 = R^5 = H$; $R^3 = CH_3$.
V: $R^3 = R^4 = R^5 = H$; $R^2 = CH_3$.
VI: $R^2 = R^3 = R^4 = R^5 = H$.

The phospholyl metals* were produced from the corresponding 1-phenylphospholes of **I** and **II** using K and refluxing DME followed by addition of the arene complex. The phospholyl metals (**III** → **VI**) were produced in THF at room temperature and two equivalents of the arene were used to remove the Ph^-M^+.

After addition of the arene complex, the reaction mixture was refluxed for 2 h. On quenching, the resulting phosphaferrocene could be isolated in good yield. The preparation of **Ia** → **Va** were performed on several occasions and gave reproducible yields. Traces of ferrocene were sometimes detected in crude products but contamination was very small and could usually be eliminated by careful chromatography and recrystallisation.

NMR investigation of byproducts indicated as expected, that it was always the neutral η^6-arene which was displaced, *i.e.* no cationic products of the type η^6-arene-η^5-phospholyliron(II) cation were found.

The reaction was greatly facilitated by refluxing: a comparable synthesis of **IVa** performed at room temperature produced negligible amounts of 3-methylphosphaferrocene.

*The corresponding monophosphaferrocenes derived from the phospholyl metals (**I** → **VI**) are subsequently denoted as follows, **Ia** → **VIa**.

Results

All the products were unambiguously characterised by NMR spectroscopy and molecular weight determination (molecular ion, mass spectra at 70 eV). Compounds **Ia**, **IIa**, **IIIa** and **VIa** have been previously reported [1, 2, 4].

The ^1H NMR and ^{31}P NMR results reported here are in agreement with those already published where available. **IVa** and **Va** are new compounds but no elemental analysis was performed as these phosphaferrocenes undergo facile atmospheric oxidation [4]. Compounds **IVa** and **Va** seemed much more unstable than other monophosphaferrocenes presumably because as oils at room temperature they are more susceptible to oxygen uptake. Compound **IVa** was a solid at −20 °C and crystallizes from methanol or light petroleum ether at −78 °C. It melted on warming to room temperature and underwent rapid oxidation but could be kept at −20 °C under N_2 for short periods.

Table I lists the results obtained together with the spectroscopic data.

In all cases the yields are comparable or better than published routes to date and are obtained under much milder conditions.

The overall results obtained do not parallel the nucleophilicity of the phospholyl anion or its final π-bonding capacity for several reasons:

(i) Phenyl derivatives were used as potassium rather than lithium derivatives. Generally organopotassium derivatives are much more reactive than their lithium analogues, although the electron withdrawing phenyl substitution may counter this to some extent. The first step in the reaction is probably the removal of the counter ion associated with the phospholyl metal by the PF_6 anion thus creating a 'super' nucleophile.

(ii) The yields of the methyl derivatives show that the most electron donating, *i.e.* 3,4-dimethyl gives slightly lower yields, than the methyl compound, the more nucleophilic anion tending to be more prone to side reactions.

Thus the cleavage of η^6-arenes from cationic cyclopentadienyliron(II) complex appears to be an excellent route to monophosphaferrocenes. The process is rapid, and does not lead to mixed ring substituted products. Thus one general method can be used to synthesise many derivatives with a wide range of ring substitution.

Although the results reported here are the best found to date, the range of η^6-arene complexes known is vast and reactions of these complexes with nucleophiles and bases can be solvent and tempera-

TABLE I. Yields and ^{1}H, ^{31}P NMR Data for Monophosphaferrocenes

Compound	Yield (%)	Literature yield (%)	Molecular weight (found)	$\delta\,^{31}P$[a] (ppm)	$\delta^{1}H$[b] (ppm)
Ia	58	35 [1]	508	−60.23 ($CDCl_3$)	arene 7.15(s) 20H Cp 4.37(s) 5H
IIa	61	50 [2][c]	356	−66.20 ($CDCl_3$)	arene 7.33(s) 10H Cp 4.20(s) 5H, βH 5.80 (d) 2H
IIIa	51	21 [4][d]	232	−82.35 ($CDCl_3$)	Cp 4.18(s) 5H, αH 3.73 (d) 2H, Me 2.18(s) 6H
IVa	64		218[e]	−59.42 (CS_2)	Cp 4.30(s) 5H, αH 3.81 (m) 2H βH 5.10 (m) 1H, Me 2.40(s) 3H
Va	65		218[e]	−57.30 (CS_2)	Cp 4.40(s) 5H, αH 3.79 (m) 1H βH 5.18(m) 2H, Me 2.08(d) 3H
VIa	23[f]	27 [4][d]	204	−66.95 ($CDCl_3$)	Cp 4.40(s) 5H, αH 4.05 (m) 2H βH 5.30(m) 2H

[a] $\delta\,^{31}P$ reference 85% H_3PO_4 external. CS_2 samples run with external D_2O lock. [b] ^{1}H NMR reference external TMS. (s) = singlet, (d) = doublet, (m) = multiplet. (All $^{2}J_{P-H}$ Hα ~38 Hz, $^{3}J_{P-H}$ H_β ~5 Hz. **V** $^{3}J_{P-H}$ CH_3 ~10 Hz. [c] We have found this reaction to give unreliable yields, often much lower than 50%. [d] Also produces phenyl substituted products (Scheme 2). [e] Other ions in mass spectrum. **IVa**: m/e 152 $(C_6H_5PFe)^+$, 121 $(C_5H_5Fe)^+$, 56 $(Fe)^+$, M^+ **I** = 100%. **Va** gave identical fragmentation patterns; the fragmentation patterns of **IVa** and **Va** are comparable to those reported for **IIIa** and **VIa** [4]. [f] This reaction was only performed once with impure 1-phenyl phosphole owing to difficulties in reproducing literature yields.

ture dependent [8]; thus the scope for optimisation of such a synthetic route is considerable. We believe that there is a wide applicability for such reactions in the synthesis of other η^5-ferrocene analogues. We are at present undertaking a more detailed study of the system to determine its overall general utility.

The reaction between phospholyl metals and η^6-arene cations was tailored towards the synthesis of phosphaferrocenes; however some other potentially very interesting byproducts can arise, the most notable being that via displacement of chloride (Route 5).

This regenerates the 1-phenylphosphole with a η^6-coordinated iron cyclopentadienyl unit. We hope to characterise such products more fully and examine their reactivity compared to uncomplexed 1-phenylphospholes.

Experimental

All preparations were carried out under dry argon. As far as possible all manipulations involving phosphaferrocenes were carried out under N_2 or Ar to avoid atmospheric oxidation [4].

Unless otherwise stated, all reagents were supplied commercially and used as such without further purification.

Ethereal solvents were dried over anhydrous $CaCl_2$ and passed through an active alumina column before fractionation from excess CaH_2 into the flask used for the cleavage reaction.

Preliminary chromatography was performed on acidic or neutral Al_2O_3 (Aldrich Chemical Co.) freshly deactivated with 5% H_2O (wt/wt).

Products were then rechromatographed on silica gel (Silica Gel 60, 70–230 mesh/Merck).

1-Phenylphospholes

1-Phenylphospholes were prepared by literature methods: 1,2,3,4,5-pentaphenylphosphole [18]; 1,2,5-triphenylphosphole [2]; 3,4-dimethyl-1-phenylphosphole, 3-methyl-1-phenylphosphole, and 1-phenylphosphole [19].

2-Methyl-1-phenylphosphole was prepared by a procedure analogous to the above using $C_6H_5PBr_2$ and piperylene. Bases used for dehydrohalogenation gave the following yields (not optimised): 2-Picoline, 8%; N-methyl pyrrolidine, 15%; triethylamine, 15%. $\delta(^{31}P)$ was +14.18 ppm (C_6H_6).

η^6-Arene-η^5-cyclopentadienyl Arene Complexes

The known η^6-arene complexes were prepared by standard literature methods [8].

2,3,4,5-Tetraphenylphosphaferrocene

1,2,3,4,5-Pentaphenylphosphole (3.0 g, 6.5 mmol) was stirred with freshly cut potassium (0.51 g, 13 mmol) for 3 h in dry DME (*ca.* 100 ml). After cooling to room temperature the purple solution was transferred by syringe into another flask containing

η^6-mesitylene-η^5-cyclopentadienyliron(II) hexafluorophosphate [20] (2.51 g, 6.5 mmol). The mixture was heated at reflux with stirring for 2 h, during which time the colour changed to red/orange. Upon cooling t-butyl alcohol* (*ca.* 20 ml) was added and the mixture then stirred for 30 min. The reaction was quenched with an excess of cold water and the mixture extracted with ethyl acetate until the organic solvent was colourless; the aqueous phase and insoluble byproducts were discarded. The organic phase was dried over anhydrous sodium or magnesium sulphate and evaporated *in vacuo*. Chromatography on alumina with benzene/dichloromethane (90:10 v/v) eluted the title compound first as a red orange band which was rechromatographed on silica (benzene).

The product was recrystallized from dichloromethane/methanol. Yield: 1.90 g. (58%). Melting point (decomposition) >210 °C. Literature 227–9 °C [1].

2,5-Diphenylphosphaferrocene (II)

The above was prepared in a similar manner using 1,2,5-triphenyl phosphole (3 g, 9.6 mmol), potassium (0.75 g, 19.2 mmol) and arene complex (3.71 g, 9.6 mmol). Upon quenching with water extraction was carried out with benzene and chromatography was performed with the same solvent. The product was recrystallized from methanol at –20 °C. Yield 2.09 g (61%). Melting point 113 °C. 3,4-Dimethyl, 3-methyl and 2-methyl phosphaferrocenes together with the parent compound were all synthesised by a similar procedure, giving yields of 51, 64, 65, 23%. As mentioned in the text, the procedure was modified using Li in THF to prepare the phospholyl metal which was subsequently reacted with *two* equivalents of the arene complex. After reaction, the solution was cooled and diluted with an equal volume of hexane. After filtration through celite, the eluent was chromatographed as described above.

The aqueous extraction is omitted for the alkyl derivatives owing to their more facile ease of atmospheric oxidation. Phenylated derivatives may be isolated by a similar procedure using benzene as the initial diluent.

Instrumentation

^{1}H NMR spectra were obtained on a Varian EM360 spectrometer and ^{31}P spectra on a Bruker Spectrospin WP80 spectrometer.

*The addition of t-butyl alcohol is to destroy any trace of remaining potassium.

Acknowledgement

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