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Aluminium Chloride Induced Cleavage of Diphosphaferrocenes in Aromatic Hydrocarbons; the Synthesis of η^6-Arene η^5-Phosphacyclopentadienyl Iron(II) Cations

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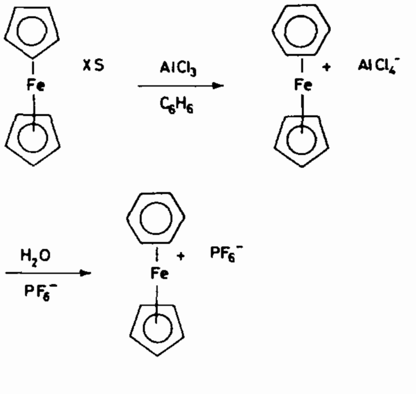
Abstract

The reactivity of a number of diphosphaferrocenes towards aluminium chloride in aromatic solvents has been investigated. Where the substrate contains a 2-acyl substituent, the ligand is cleaved and a η^6-arene η^5-phosphacyclopentadienyl iron(II) cation formed by reaction with the solvent. Two such novel cations have been isolated as their hexafluorophosphate salts and the π-bonded nature of both ligands demonstrated using NMR spectroscopy.

Introduction

Ferrocene is cleaved by aluminium trichloride in the presence of arenes to produce η^6-arene η^5-cyclopentadienyl iron(II) cations, e.g.



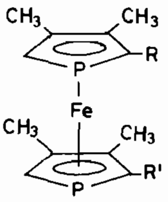
After hydrolysis, the cations are usually isolated as PF_6^- salts. Such reactions have been studied with many substituted ferrocenes and arenes, and have been the subject of several extensive review articles [1, 2]. To date, no η^6, η^5 Fe(II) cations containing a group V hetero-atom in the η^6-arene* or η^5-Cp ring have been reported. Some pyridines can act as η^6 ligands for $Cr(CO)_3$ [3] or $Cr(PF_3)_3$ [4, 5], and several neutral bis η^6-phosphabenzene iron(II) derivatives have been reported [6]. The $AlCl_3$ catalysed cleavage of ferrocene by nitrogen-containing aromatics fails even in the cases of quinoline and isoquinoline [1], where a benzenoid ring is available for coordination.

η^5-Cyclopentadienyl η^5-thiophen iron(II) cations are known [7, 8] but here the thiophen ligand is uncharged and thus replaces the η^6-arene ligand. The use of azaferrocene in the ligand exchange reaction has been reported to produce only η^5-cyclopentadienyl products [9]. Diazaferrocene itself has not yet been synthesised. Much more accessible are diphosphaferrocenes largely due to the work of Mathey and co-workers [10–12].

We report here the synthesis of a new series of η^6-arene η^5-phosphacyclopentadienyl iron(II) derivatives from $AlCl_3$ catalysed cleavage of diphosphaferrocenes in the presence of aromatic hydrocarbons as a part of our study of the interaction of diphosphaferrocenes with Lewis and Brønsted acids.

Discussion and Results

We have investigated the $AlCl_3$ cleavage of the readily available 3,3′4,4′-tetramethyldiphosphaferrocene [11, 12] and its acyl derivatives [9].



R = R′ = H = I; R = $COCH_3$, R′ = H = II; R = COC_6H_5, R′ = H = III; R = R′ = $COCH_3$ = IV; R = R′ = COC_6H_5 = V

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*During the preparation of this paper the synthesis of a η^6-phosphabenzene complex has been reported [23].

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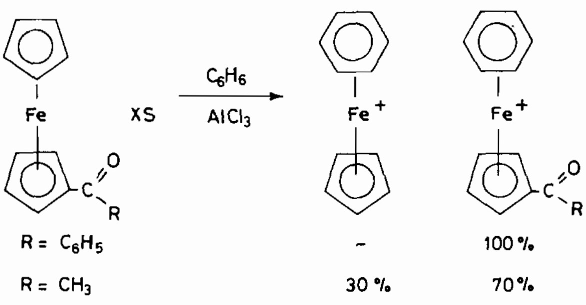
Initially we attempted to cleave the parent diphosphaferrocene (I) using the standard reaction conditions employed for ferrocene [1] [**I**, 1 equivalent (eq): Al powder: 1 eq: $AlCl_3$ 2 eq: benzene excess] however all attempts failed. **I** was rapidly and quantitatively removed from solution but regenerated after hydrolysis in >50% yield. The only ionic product obtained was a small amount of a pale purple paramagnetic compound which was assigned as the diphosphaferricinium hexafluorophosphate derivative of **I** on the basis of its IR spectrum. The compound proved to be too unstable to obtain satisfactory analytical data (the instability of phosphaferricinium cations has been demonstrated by cyclic voltammetry [13]). The exclusion of the Al powder did not alter the course of the reactions. The presence of a stoichiometric amount of water has been shown to catalyse the $AlCl_3$ cleavage of ferrocene [14] (yields increase from ~15 to 85%) but similar modifications did not produce any of the η^6-arene cleavage product of **I**. For ferrocene derivatives, the reaction can be inhibited by polyalkyl substitution. Thus octa- and decamethyl ferrocene fail to react, whereas 1,1′3,3′-tetraethylferrocene gives comparable yields to those using ferrocene [15] hence the four β methyl groups in **I** should not completely inhibit the reaction.

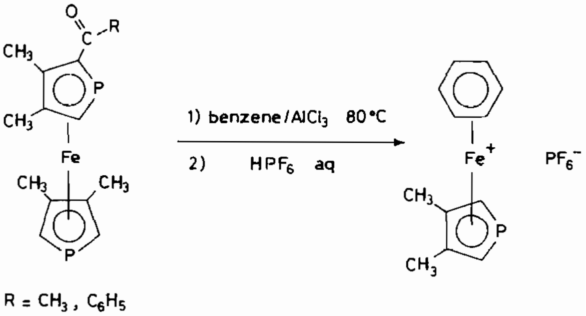
With ferrocene, the mechanism is believed to be the formation of a π complex with the $AlCl_3$ which results in the removal of a Cp^- ligand, the resulting $CpFe^+$ unit reacting with the solvent to produce the η^6-arene cation. The reaction is inhibited by the formation of an Fe bonded $AlCl_3$ adduct. We therefore suspect that **I** does not form the required π complex necessary for reaction but, instead, the metal bonded adduct, hydrolysis of which regenerates **I**.

Reactivity of Mono-acyl Derivatives II and III

Mono-acyl ferrocenes are cleaved by $AlCl_3$ in benzene to give products containing mainly the Cp-substituted ligand [16, 17];



Such reactions give better yields than ferrocene in the absence of catalytic amounts of H_2O. The initial reaction is coordination of the $AlCl_3$ to the keto function. This inhibits the removal of the substituted ring and lowers electron density on the iron atom preventing the formation of metal–metal bonded adducts [17]. In contrast to **I**, the mono-acyl derivatives **II** and **III** did react to give the desired products, but the distribution of products were quite different to those of acylferrocenes:



In both cases no η^6-arene cations were detected where the PCp ligand carried a 2-acyl substituent. **III** produced the product shown in 25% yield. **II** gave a much lower yield ~5% which was contaminated with a polymeric material and difficult to purify. The different product distribution reflects the weaker π PCp–metal bond compared to π Cp–metal [18]. With **II** and **III** coordination of $AlCl_3$ at the keto oxygen sufficiently weakens the ligand–metal bond for the acyl-substituted ligand to be thermally cleaved in preference to the unsubstituted ligand. An identical reaction of **III** in toluene produced the η^6-toluene analogue in 22% yield.

Reactivity of Diacyl Derivatives IV and V

The reactivity of **IV** paralleled that of diacetylferrocene. The latter is inert to $AlCl_3$ in refluxing benzene. At higher temperatures, no η^6/η^5-cations are produced, but decomposition occurs liberating Fe(II) ions which produce bis η^6-arene Fe(II) dications [17]. **IV** could be recovered in >80% yield from $AlCl_3$/benzene (4 h, 80 ℃). No ionic products could be detected. With $AlCl_3$/mesitylene (4 h/180 ℃) **IV** produced only 10 → 20% yield of bis mesitylene iron(II) hexafluorophosphate. Rather than use $AlCl_3$, we chose trifluoromethanesulphonic acid (CF_3SO_3H) as a catalyst. **I** → **V** can be protonated at the keto oxygen in acids of suitable strength [19]. However, refluxing **V** or 1,1′-dibenzoylferrocene in benzene produced no ionic products.

$^{13}C/^{31}P$ NMR of η^6-Benzene η^5-(3,4-Dimethyl)phospholyl Iron(II) Hexafluorophosphate

The π-bonded nature of both arene and PCp ligands is apparent from ^{13}C and ^{31}P NMR spectroscopy. δ ^{31}P occurs at –49.0 ppm, a region characteristic of π-bonded PCp anions [20]. δ ^{31}P occurs at ~35 ppm downfield from 3,4-dimethylmonophosphaferrocene [21] due to deshielding by the positive charge on the iron atom. ^2J(PH) values of 36 Hz are identical to those found in mono- and diphosphaferrocenes [11, 21]. For η^6-benzene η^5-cyclopentadienyl iron(II) hexafluorophosphate δ ^{13}C for the Cp ring occurs at 75.63 ppm [22], ~10 ppm downfield from ferrocene. Similar downfield shifts are found here for C_α and C_β carbons of the PCp ligand, compared to 3,4-dimethylmonophosphaferrocene [21], 9.8 ppm for C_α and 13.12 ppm for C_β. ^1J *and* ^2J(PC) values of 64 and 7 Hz respectively are also highly characteristic of η^5-PCp anions [20]. In the Cp analogue δ ^{13}C arene occurs at 87.27 ppm [22], an upfield shift of ~41 ppm from uncomplexed benzene. Here the arene shift occurs at 90.87 ppm confirming that the benzene is acting as a η^6-ligand. Similar comments apply to the η^6 toluene analogue, the only noteworthy difference is that $C_{2,6}$ and $C_{3,5}$ of the arene ring have identical shifts in the ^{13}C NMR spectrum, whereas both are distinct in the Cp analogue [22].

The similarity of the chemical shifts and coupling constants to other η^5-PCp systems shows that the geometry of the η^5-PCp ligand in these novel cations must be very close to that found in other η^5-PCp derivatives [20].

Relevant to this work is the recent publication by Nief and Fischer [23] on the synthesis of η^6-2,4,6 triphenylphosphabenzene η^5-cyclopentadienyl iron(II) hexafluorophosphate. The desired η^6/η^5 cation was not isolated directly from the reaction of the phosphabenzene, ferrocene and $AlCl_3$. Hydrolysis occurred during work up to give a P(O)H species with the arene being bonded to Fe only via the five ring carbons in a η^5-cyclohexadienyl configuration. The desired η^6/η^5 cation was produced via reduction with $HSiCl_3$ followed by hydride abstraction with trityl PF_6.

A major difference resulting from the P atom being in the η^5 ring is that no hydrolysis is found on work up. The reason for this is that it is much less favourable to form a six electron π system over four carbons than five.

Experimental

Diphosphaferrocenes **I** → **IV** were produced by literature methods [9, 10]. Aromatic solvents were dried over sodium wire, aluminium chloride (99%) was purchased from Aldrich Chemical Company. ^{1}H NMR spectra were obtained on a Varian EM 360, reference external TMS, ^{13}C and ^{31}P spectra were obtained on a Bruker WP80 [reference TMS and 85% H_3PO_4 respectively]. Microanalysis was done by the Analytical Department, University of Manchester.

η^6-Benzene-η^5-3,4-dimethylphosphacyclopentadienyl Iron(II) Hexafluorophosphate

III (2 g, 5.2 mmol) and $AlCl_3$ (2.9 g, 20.8 mmol) were refluxed in dry benzene (275 ml) for 2 h. After cooling, the mixture was quenched with ice water (~75 ml) and the organic phase discarded. The yellow aqueous phase was filtered and washed with ether (2 × 75 ml) and refiltered. Aqueous HPF_6 (~5 mol, 65% *w*/*v*) was added. The product was extracted into CH_2Cl_2 (2 × 50 ml) which was dried and reduced in volume. The product was precipitated as a pale orange powder by the addition of ether. Yield, 0.5 g (25%). *Anal.* Found: C, 37.6; H, 3.6; Calc. for $C_{12}H_{14}FeP_2F_6$: C, 36.9; H, 3.7%. ^{1}H NMR* 1.80(s) (6H) βMe, 3.95(d) (2H**), 5.85(s) (6H) C_6H_6. δ ^{31}P* −49.0(c)**, −141.5, ^1J(PF) = 708. ^{13}C NMR* 13.53 βMe, 88.00 C_d, ^1J(PC) = 64, 90.87 arene, 107.29 C_β ^2J(PC) = 7.

η^6-Toluene Analogue

The toluene analogue was produced by an identical procedure except that the reaction time was 0.5 h. Yield, 0.48 g (22%). *Anal.* Found: C, 40.1; H, 4.0; Calc. for $C_{13}H_{16}FeP_2F_6$; C, 39.6, H, 4.0%. ^{1}H NMR* 1.90(s) (6H) βMe, 2.08(s) (3H) Me, 4.40(d) (2H) αH, 6.00(s) (5H) arene. δ ^{31}P* −43.9(t)**, −137.8, ^1J(PF) = 708. ^{13}C NMR* 14.41 βMe, 20.20 Me, 88.16 C_α ^1J(PC) = 64.0, 89.52 C_4 arene, 90.24 $C_{2,3,5,6}$ arene, 105.27 C_1 arene, 106.33 C_β ^2J(PC) = 7.

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*Solvent acetone d_6.

** ^2J(PH) ~ 37, δ in ppm J in Hz. Both cations show no defined MP and darken above 200 °C.

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