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Synthesis of (η^6-arene)(η^5-cyclopentadienyl) iron (II) complexes with heteroatom and carbonyl substituents. Part I: Oxygen and carbonyl substituents

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Abstract

A series of reactions have been used to introduce oxygen substituents into (η-arene)(η-cyclopentadienyl) iron (II) complexes. Photochemical ligand exchange led to the formation of the first recorded trioxygenated complex as well as mono- and di-oxygenated species. Using microwave techniques, reaction times for S_NAr displacement reactions of halobenzene complexes by phenols were reduced from several hours to a few minutes. Phenols protected by either *t*-butylation or trimethylsilylation were found to give modest yields of the corresponding phenol complexes, using conventional thermal ligand exchange reactions. Without such protection, yields were extremely low. The above method led to the synthesis of the first example of a dihydroxybenzene complex. Some miscellaneous syntheses are also reported.

The Nef reaction has been adapted to convert (η^6-α-nitroalkylarene)(η^5-Cp) iron (II) salts to corresponding aldehyde and ketone complexes. The α-nitroalkyl arene complexes were synthesised in good yields from (η^6-halobenzene)(η^5-Cp) iron (II) complexes using NaO*t*Bu in DMSO. H/D exchange reactions with $^2[H]_6$-DMSO in the presence of K_2CO_3 showed partial D incorporation in the methyl group for the unreacted α-nitroethylbenzene complex and complete exchange for the carbanion generated by deprotonation. Conversion of the α-nitroalkylarene complexes to the corresponding aldehyde and ketone complexes was accomplished in moderate yields using three methods:

(A) H_2O_2 and NaO*t*Bu in DMSO followed by reaction with CF_3CO_2H.
(B) $SnCl_{32}$/aq. HCl.
(C) K_2CO_3 in DMF using microwave-mediated reactions.

In addition, two one-pot syntheses are reported using methods B and C.

Keywords: Microwave; Photochemical; Synthesis; Iron; Nef reaction

1. Introduction

(η^6-Arene)(η^5cyclopentedienyl) iron (II) complexes, ArFeCp, have found many uses in organic synthesis [1]. New microwave methods [2] have resulted in their rapid and efficient preparation [3] and this, together with facile decomplexation techniques [3,4], allows convenient routes to aromatic compounds which may otherwise be difficult to obtain. The following papers deal with the synthesis of ArFeCp complexes containing oxygen, nitrogen and carbonyl substituents.

The first part (A) of the work described here deals with the preparation of hydroxyl-, alkoxy- and

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aryloxy-substituted complexes using a range of synthetic routes including microwave-mediated techniques. Part (B) reports on the use of the Nef reaction in the synthesis of ArFeCp complexes containing carbonyl substituents.

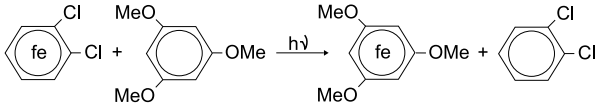
No attempt has been made to optimise yields, since the purpose of the work was to investigate the range and applicability of these diverse routes.

2. Results and discussion

2.1. Part A – oxygen-substituted complexes

2.1.1. Photochemical ligand exchange

This synthetic method was devised by Gill and Mann [5–7]. Using this technique, the 1,3,5-trimethoxybenzene complex has been prepared in 46% yield from the 1,2-dichlorobenzene complex using a 300 W tungsten lamp as the radiation source.



(1)*

*ArFeCp complexes represented as 

This complex cannot be obtained by the usual S_NAr displacements [8] since the precursor 1,3,5-trichlorobenzene complex cannot be prepared by conventional thermal ligand exchange owing to the strong electron withdrawal by three chlorine substituents. The advent of a simple method of heterolytic C–O bond cleavage in arylether complexes to give π phenate complexes [9] should prove useful in the case of the 1,3,5-trimethoxybenzene complex and would result in the formation of an important template for the synthesis of polymeric ArFeCp compounds [10]. The corresponding methoxy- and 1,2-dimethoxybenzene complexes were obtained in 35% and 32% yields, respectively. Both the phenol and 1,3-dihydroxybenzene complexes were likewise obtained in 20% yields. Use of the naphthalene complex in these photolytic ligand exchange reactions generally led to lower yields. Inter alia, it is worth noting that the phenylsilatrane complex can be synthesized in 46% yield using this method, whereas no product is formed in thermal ligand exchange reactions due to deactivation of $AlCl_3$ by strong complexation with the oxygen atoms in the silatrane moiety. The ^{13}C NMR spectrum of the phenylsilatrane complex shows strong deshielding at the C2, C6 positions in the aromatic ring indicating powerful electron withdrawal by the silatrane substituent even when the phenyl ring has the strongly electron withdrawing $[FeCp]^+$ group attached.

2.1.2. Microwave-mediated synthesis

Synthesis of the starter complexes [ArXFeCp][PF_6] by thermal ligand exchange reactions using ferrocene (FcH) has been known for many years [1] and has been improved with the advent of microwave-mediated methods [3].

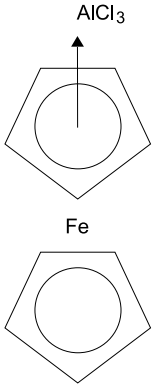
$$\mathrm{FcH} + \mathrm{ArX} \xrightarrow[\text{(ii) } \mathrm{HPF_6}]{\text{(i) } \mathrm{AlCl_3},\ \mathrm{Al}} [(\mathrm{ArX})\mathrm{Fe}(\mathrm{Cp})][\mathrm{PF_6}] \qquad (2)$$

The success of the latter depends on the absorption of microwave energy by dipolar species in the reaction medium. In this connection, a series of semi-quantitative experiments have been performed to determine the key microwave absorbers in the system. The following results were obtained using 1,2,4-trichlorobenzene (TCB) as solvent, and recording the temperature of components of the mixture immediately after an irradiation time of 4 min on a medium microwave oven setting.

(Components followed by temperatures in parentheses)

TCB (50); TCB/FcH(60); TCB/Al (80); TCB/$AlCl_3$ (96); TCB/FcH/Al (78); TCB/FcH/$ALCl_3$ (170); TCB/Al/$AlCl_3$ (90); TCB/FcH/Al/$AlCl_3$ (180).

It is clear from these results that the combination of ferrocene and $AlCl_3$ has by far the greatest absorption of microwave radiation. This is strong evidence of a highly dipolar complex intermediate, probably of the type



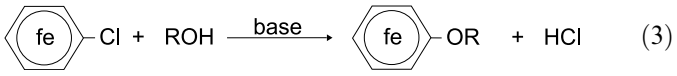
2.1.2.1. Synthesis of (ArOH)FeCp complexes. Application of the microwave-assisted ligand exchange reactions to the synthesis of phenolic complexes gave very low yields, e.g., <1% for phenol itself. This is probably due to strong complexation or reaction with $AlCl_3$, thus destroying the latter's Lewis acid strength. Improved yields were obtained when the phenolic OH group was protected. Thus, phenyl *t*-butylether gave a mixture of the phenyl *t*-butylether complex (5%) and the phenol complex (45%) after a 4 min reaction time. Electron withdrawing substituents led to a marked inhibition of reaction, exemplified by a 5% yield for the 4-chlorophenol complex from 4-chlorophenyl-t-butylether.

The readily available *O*-trimethylsilyphenols [11] also show promise in these reactions. The reaction of *O*-trimethylsilyphenol gave a 44% yield of the phenol complex in 4 min. As before, electron withdrawing substituents cause a lowering of yield. Thus, *O*-trimethylsilyl 4-fluor-

ophenol gave a 16% yield of the corresponding phenol complex. Both OH groups in catechol can be trimethylsilylated in 72% yield, and the resultant bis-silyl ether gave 9% of the corresponding catechol complex. This is the first report of an ArFeCp complex containing two OH groups. However, no product was obtained from resorcinol using this procedure. Silylated 2-phenylphenol gave a 30% yield of the 2-phenylphenol complex with the FeCp group bound to the monosubstituted phenyl ring. $AlCl_3$ complexes with the oxygen atom in the phenol moiety thus deactivating this ring to complexation by the FeCp group. 4-Aminophenol can be silylated at both oxygen [12] and nitrogen atoms (69%), and the resultant silylated material gave a 7% yield of the 4-aminophenol complex.

Clearly, both *t*Bu and Me_3Si groups afford some protection in these ligand exchange reactions, presumably by steric inhibition of complexation by $AlCl_3$. There is, however, a balance between this protection and the ease of removal of the protecting group. The Me_3Si group is much more labile than the *t*-butyl group in this reaction, but silylation is much easier to achieve than *t*-butylation particularly for adjacent OH groups. There are, of course, more sophisticated OH protecting groups which could well improve on the yields obtained here. The above reactions, however, do allow extra scope in synthetic strategy for oxygen containing ArFeCp complexes.

2.1.2.2. Synthesis of (ArOR)FeCp complexes. Hitherto, these complexes have been prepared by S_NAr displacements of halogen substituents in the sandwich complexes by the appropriate alcohol in the presence of base.



(3)

These reactions generally require long reaction times [8] (12–15 h). Using microwave irradiation, the diphenylether complex can be obtained in 25% yields in 5 min from the reaction of the chlorobenzene complex with phenol in the presence of Et_3N in solvent DMF. During the period of microwave irradiation, the temperature of the reaction mixture rose to near the boiling point of solvent DMF. To verify the effectiveness of microwave assistance, a control experiment was performed in refluxing DMF (5 min). This resulted in only a yield of 8% of the diphenylether complex, thus demonstrating the effectiveness of the microwave method. Interestingly, when flaked graphite (an excellent microwave absorber) is used, the *phenol* complex is formed in 20% yield. This is probably due to dephenylation of the diphenylether complex at the surface of the graphite where high local temperatures are generated.

2.1.3. Miscellaneous reactions

Deprotonation of dimethylphosphite with NaH, followed by reaction with the fluorobenzene complex gave a 30% yield of the anisole complex. The mechanism of this reaction is uncertain.

The microwave-mediated reaction of 4-phenylazophenol with ferrocene, $AlCl_3$, and Al in 1,2,4-trichlorobenzene resulted in a 53% yield of the aniline complex (after 4 min reaction time) instead of the hoped-for-4-aminophenol complex.

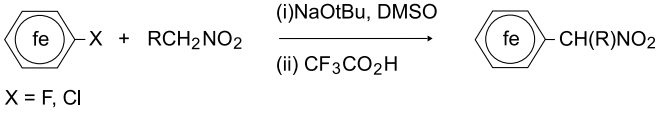
2.2. Part B – complexes with carbonyl substituent

The Nef reaction [13,14] converts primary or secondary nitroalkanes into the corresponding carbonyl compounds and is thus an important tool for the synthetic organic chemist. ArFeCp complexes containing carbonyl substituents have been reported. Those complexes bearing methylene substituents can be converted into oximes which can then be hydrolysed by aqueous HF [15]. However, only keto-complexes are formed by this method. The Nef reaction has been used for ArFeCp complexes, though again only for the synthesis of keto complexes. The precursor nitroalkane derivatives can be prepared in good yields by reaction of nitromethane or nitroethane with halo-arene complexes in the presence of K_2CO_3 [16,17].

Other methods for ArFeCp complexes include direct thermal ligand exchange using fluorene and related species with ferrocene and $AlCl_3$ followed by permanganate oxidation to form the keto complexes [18]. The purpose of this paper is to further investigate the Nef reaction with a view to the synthesis of aldehyde-containing ArFeCp complexes.

2.2.1. α-Nitroarene complexes (see Table 1 for ^{13}C NMR data)

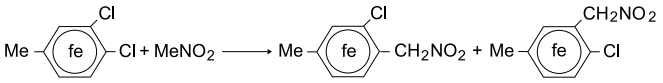
The precursor α-nitroarene complexes for the Nef reaction can be readily synthesised in good yields from S_NAr displacements in the corresponding haloarene complexes by nitroalkanes in strongly basic media.



(4)

NaO*t*Bu was chosen as the base rather than the K salt since the latter causes significant decomplexation even at room temp. The fluoroarene complexes were more reactive than the chloro analogues. Thus, the α-nitroethylbenzene complex (**III**) was obtained in 52% yield from the fluorobenzene complex whereas little reaction was observed for the chlorobenzene complex.

A doubling of signals was observed for C2,6 and C3,5 in the ^{13}C NMR spectrum for **III**. This is due to the chiral nature of the substituent which renders these ring carbons diastereotopic. The reaction of the 3,4-dichlorobenzene complex with nitromethane shows some regiospecificity, there being a preponderance of one regio-isomer over the other (60:40) though it is not possible to identify each from NMR data.



(5)

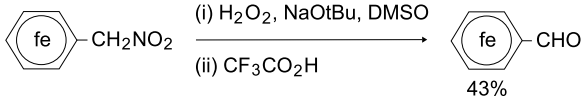
In addition, there are two pairs of Cp signals, each pair separated by approximately 0.1 ppm in the ^{13}C NMR spectrum. This suggests restricted rotation about the C–CH_2NO_2 bond which would generate two different configurations.

In an NMR study, the formation of the carbanion by deprotonation of the α-nitroethylbenzene complex (**III**) using K_2CO_3 in $[^2H]_6$-DMSO showed a 77% conversion after 5 min. The ^1H NMR spectrum of the carbanion showed no signal for the methyl group, indicating complex H/D exchange. There was no evidence of any exchange of arene or cyclopentadienyl hydrogens but integration of the methyl group of the unreacted parent complex showed 27% H/D exchange. The ^{13}C NMR spectrum of the carbanion showed no methyl resonance due to C–D coupling making the resulting low intensity septet undetectable. The Cp signal appeared some 4 ppm upfield from the parent α-nitroethylbenzene complex reflecting the electron-rich nature of the carbanion.

2.2.2. (η^6-ArCOR)(η^5-Cp) iron (II) complexes (see Table 2 for ^{13}C NMR and CH analyses)

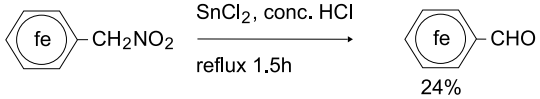
Attempts to prepare these complexes by the usual thermal ligand exchange reactions always resulted in the formation of the corresponding ArCH(OH)RFeCp complexes due to reduction during the exchange process. Oxidation of the alcohol complexes to the carbonyl complexes has proved very difficult.

Hydrogen peroxide has been used to convert nitroalkanes into aldehydes and ketones in weakly basic media [19]. This method (Method A) was modified for the ArFeCp complexes by using a much more strongly basic medium and led to a moderate yield of the benzaldehyde complex (**IIA**).



(6)

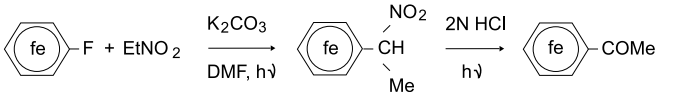
This is the first example of an ArFeCp complex containing an aldehydic substituent. A second route to aldehyde derivatives was devised (Method B) based on the Nef reaction. The usual acid-catalysed Nef reactions [20] for (η^6-α-nitroalkylarene)(η^5-Cp) iron (II) complexes is accompanied by further oxidation to the carboxylic acid complex for primary α-nitroalkyl complexes. To circumvent this, reactions were carried out in the presence of $SnCl_2$ to give moderate yields of the corresponding aldehyde complexes.



(7)

The following aldehyde and ketone complexes were prepared by this method: acetophenone (**IIIA**) 43%, *o*-tolualdehyde (**IVA**), 35%, *m*-tolualdehyde (**VA**), 22%, *p*-tolualdehyde (**IA**), 26%. The above method was developed into a one-pot procedure. Thus, reaction of (η^6-fluorobenzene)(η^5-Cp) iron (II) PF_6 with nitromethane and NaO*t*Bu in dry DMSO, followed by $SnCl_2$/HCl treatment gave a 33% yield of the benzaldehyde complex.

A microwave-mediated one-pot reaction has also been developed (Method C). Reaction of the fluorobenzene complex with nitroethane and K_2CO_3 in dry DMF gave the α-nitroethylbenzene complex after 1 min irradiation, and the acetophenone complex (55% yield) after a further 1 min irradiation in the presence of 2 N HCl.



(8)

Finally, it is worth noting that the $SnCl_2$/HCl Nef reaction did not occur when argon was passed through the reaction medium. This indicates a radical-dependent mechanism for the ArFeCp complexes.

3. Experimental

Microwave-mediated syntheses were conducted using a conventional unmodified domestic microwave oven [Sharp Easy Chef, Model R5A53, 850 W], using solid CO_2 as coolant in an apparatus described in Ref. [3].

^1H and ^{13}C NMR were recorded on a Jeol EX 270 spectrophotometer, using $[^2H_6]$-acetone as the solvent unless otherwise stated. Chemical shifts (δ) are in ppm relative to TMS [s, singlet; d, doublet; tr, triplet; m, mulitplet]. For the BPh_4 salts, the signals for the BPh_4 group are not reported in the interest of brevity. Mass spectra were obtained in-house, using a Kratos MS 50 double focusing instrument with a FAB source and employing a matrix of 3-nitrobenzyl alcohol. The masses of the cations of the complexes, M^+, reported were accurate to within ±0.5 mass numbers.

CHN analyses were performed at the Analytical Laboratory of the University of Manchester.

4. Syntheses

4.1. Part A – oxygen-substituted complexes

4.1.1. Photochemical ligand exchange

4.1.1.1. Synthesis of (η^6-1,3,5-trimethoxybenzene)(η^5-cyclopentadienyl) iron (II) hexafluorophosphate. (η^6-1,2-Dichlorobenzene)(η^5)-cyclopentadienyl iron (II) hexafluorophosphate (0.82 g, 2.0 mmol) was dissolved in CH_2Cl_2 (25 ml) in a 100 ml RB flask equipped with a condenser, and 1,3,5-trimethoxybenzene (1.00 g, 5.9 mmol) added. The mixture was irradiated with stirring for $3\frac{1}{2}$ h using a 300 W tungsten lamp held close to the reaction vessel. The cooled mixture was filtered into Et_2O (100 ml) and

the resultant dark green precipitate. Filtered off, washed with Et_2O, then air dried to give 0.50 g crude product. This was purified by recrystallisation from CH_2Cl_2/Et_2O to give 0.40 g pure product in 46% yield. ^1H NMR: δ_H, 4.08 (OMe), 5.10 (Cp), 6.28 (H2,4,6). ^{13}C NMR: δ_C, 57.90 (C2,4,6), 59.98 (OMe), 76.58 (Cp), 133.72 (C1,3,5).

Anal. Found: C, 38.76; H,3.94%. Calc. for $C_{14}H_{17}F_6FeO_3P$: C, 38.71; H, 3.92. Similarly, the methoxybenzene and 1,2-dimethoxybenzene complexes were prepared in 35% and 32% yields, respectively.

Phenol gave a 21% yield of the corresponding complex and a similar yield was obtained for the 1,3-dihydroxybenzene complex. ^{13}C NMR: δ_C, 66.30 (C2), 71.05 (C4,6), 76.61 Cp, 84.27 (C5), 130.04 (C1,3).

Anal. Found: C, 35.32; H 3.00%. Calc. for $C_{11}H_{11}F_6FeO_2P$: C, 35.14; H, 2.95.

The phenylsilatrane complex can also be obtained in 46% yield. ^1H NMR: δ_H, 3.21 t, $J = 5.9$ Hz, (N–CH_2); 3.99t, $J = 5.9$ Hz (O–CH_2); 5.01s, (Cp); 6.2–6.3m (Ph). ^{13}C NMR: δ_C, 51.60 (N–CH_2) 58.21 (O–CH_2), 76.94 (Cp), 87.20 (C4), 88.14 (C3,C5), 93.59 (C2,C6).

4.1.2. Microwave syntheses

4.1.2.1. Synthesis of (η^6-diphenylether)(η^5-cyclopentadienyl) iron (II) hexaflurophosphate. (η^6-Chlorobenzene)(η^5-cyclopentadienyl) iron (II) hexafluorophosphate (1.1 g, 2.9 mmol), phenol (0.6 g 6.4 mmol) and Et_3N (1.0 g, 10 mmol) were dissolved in dry DMF (10 ml) and the solution irradiated in microwave oven for 5 min at a medium setting in the apparatus described in Ref. [3]. The mixture was filtered into Et_2O (200 ml) to give a brown oil. The supernatant Et_2O was decanted off, and the residue dissolved in acetone (15 ml) and filtered slowly into 0.08 M NH_4PF_6 (50 ml).

The mixture was allowed to stand at 0 °C for 3 days whereupon a yellow crystalline solid was obtained. Yield: 0.31 g, 25%. ^1H and ^{13}C NMR agreed with the literature values [21]. The experiment was repeated in the presence of flaked graphite (2 g) and led to the formation of the phenol complex in 25% yield.

4.1.3. Syntheses using –OH group protection

4.1.3.1. Protection by t-butylation. Phenol was *t*-butylated by reaction with *t*BuBr in dry pyridine for 2 h at 30 °C [22] to give a 65% yield of pure product. Phenyl-t butylether (1.5 g, 0.01 mol), ferrocene (5.6 g, 0.03 mol) Al powder (3 g, 0.111 mol) and $AlCl_3$ powder (8.1 g, 0.06 mol) were mixed with 1,2,4-trichlorobenzene (TCB) (10.8 g) and microwaved for 4 min on a medium setting. The excess $AlCl_3$ was carefully decomposed by the addition of small portions of ice (50 g). The aqueous mixture was filtered, and the filtrate treated with 1 M, NH_4PF_6 (10 ml), then extracted with CH_2Cl_2 (2×150 ml). After drying the combined CH_2Cl_2 extracts with anhydrous $MgSO_4$, the CH_2Cl_2 was removed by rotary evaporation to give an oily solid. This was dissolved in acetone (10 ml) and added dropwise to a cold aqeous solution of 0.5 M $NaBPh_4$ (10 ml). The resultant flocculent yellow precipitate was stirred well for a few minutes then filtered off and washed with a little cold distilled H_2O to give a yellow solid (1.7 g) which comprised the phenol and the phenyl-t butylether complex in a ratio of 9:1 as shown by NMR in [$^2H_6$]-DMSO. ^{13}C NMR for the phenol complex, δ_C 74.85 (C2,6), 75.57 (Cp), 82.36 (C4), 86.22 (C3,5), 134.62 (C1); for the *o-t*-butyl complex, 30.24 (Me), 73.50 (C2,6), 74.98 (Cp), 81.67 (C4), 86.22 (C3,5), 133.64 (C1). (Quaternary carbon for *t*-butyl group not observed.)

Using the above method, the 4-chlorophenol complex was formed in 5% yield. ^{13}C NMR: δ_C, 74.28 (3,5) 78.16 (Cp) 87.82 (2,4), 101.59 (C1), 133.27 (C4).

4.1.3.2. Protection by trimethylsilylation. Catechol (5.5 g, 0.05 mol) in trimethylchlorosilane (20 ml) was refluxed overnight excluding moisture. The reaction mixture was treated with a little decolourising charcoal and 40:60 pet.ether added. Filtration and evaporation gave 9.1 g (72%) of the bis-silylated product.

^{13}C NMR: δ_C, 0.41 (Me), 121.99 (C2,6), 122.75 (C4,5), 147.43 (C1,2). The product (2.5 g 0.01 mol), ferrocene (5.6 g, 0.03 mol), Al powder (3.0 g, 0.11 mol) and $AlCl_3$ powder (4.0 g, 0.03 mol) were mixed with TCB (11 g) and microwaved for 4 min on a medium setting. After decomposition with ice, followed by filtration, a deep green solution was obtained which gave no precipitate with NH_4PF_6. This solution was evaporated to dryness and the residue taken up into hot acetone (100 ml), filtered, and evaporated. After washing well with Et_2O, a dark oil was obtained. This was redissolved in acetone and added dropwise to aq. 0.15 M $NaBPh_4$ (10 ml). The resultant pale green solid was filtered off, washed with a little ice-water, then air dried to give 0.5 g (9%) product.

^1H NMR: δ_H, 4.73 (Cp), 5.54 (H3,6), 5.97 (H4,5). ^{13}C NMR: δ_C, 74.73 (C3,6), 75.64 (Cp), 80.20 (C4,5), 121.48 (C1,2). M^+: Found: 230.9; calcd. 231.

Similarly prepared were the phenol complex (44%), the 4-fluorophenol complex (16%). M^+: Found: 232.8; calcd. 233, the 4-aminophenol complex (7%) [NB: no complex was formed with the unsilylated phenol] ^{13}C NMR: δ_C, 67.06 (C3,5), 72.33 (2,6), 75.79 (Cp), 121.71 (C4), 127.38 (C1) and the 4-chloro-2-methylphenol complex (12%) ^{13}C NMR: δ_C, 15.39 (Me), 76.05 (C6), 78.41 (Cp), 84.71 (C5), 88.16 (C3), 89.90 (C2), 100.87 (C4), 131.31 (C1).

No reaction was observed for resorcinol. Reaction using 2-phenyphenol gave mainly complexation at the mono-substituted ring (30%). Reaction 2,2′-biphenol gave a 5% yield of the mono-complexed product. M^+: Found: 307.1, calcd. 307.

4.1.4. Miscellaneous reactions

Deprotonation of dimethylphosphite with 60% NaH, followed by reaction with (η^6-fluorobenzene)(η^5-cyclopentadienyl) iron (II) hexafluorophosphate in dry THF (RT, 24 h) yielded the methoxybenzene complex (30%). The

microwave-mediated reaction of 4-phenylazophenol with ferrocene, Al, $AlCl_3$ in TCB (4 min MED) yielded the aniline complex in 53% yield instead of the hoped-for-4-aminophenol complex.

4.2. Part B – complexes with carbonyl substituents

4.2.1. α-Nitroarene complexes

4.2.1.1. Synthesis of (η^6-α-nitro-p-xylene)(η^5-cyclopentadienyl) iron (II) PF_6(I). To a solution of nitromethane (1.2 g, 16 mmol) in dry DMSO (10 ml) was added sodium t-butoxide (0.8 g, 8 mmol) and the whole stirred at RT for 0.5 h to form a slurry of the nitronate. (η^6-4-fluorotoluene) (η^5-C_p) iron (II) PF_6 (1.0 g, 2.6 mmol) was added and the mixture stirred for 5 min to give a deep red colour. CF_3CO_2H (1.4 g, 12 mmol) was added and the mixture shaken to give a clear brown solution which was added dropwise to 0.05 M NH_4PF_6 (75 ml). The resultant yellow precipitate. was filtered off, washed with distilled H_2O and dried at 100 °C for 2 h.

Yield: 0.79 g, 70%. ^{1}H NMR: $[^2H]_6$-acetone, δ, 2.62s (Me); 5.26s (Cp); 6.04s (CH_2); 6.59d × 2, $J = 6.6$ Hz, (H2,3,5,6).

The following α-nitroalkyl complexes were prepared by the above method (yields in parentheses): α-nitrotoluene, **II**, (71%): ^{1}H NMR, δ, 5.28, 5.31s (Cp); 6.06s (CH_2); 6.64s, 6.68s (H3,4,5,6).

α-Nitroethyl benzene, **III**, (52%): ^{1}H NMR, δ, 2.03d, $J = 6.9$ Hz (Me); 5.19s (Cp); 6.17q, $J = 6.9$ Hz (CH); 6.50m (H2,3,5,6); 6.59m (H4).

α-Nitro-*o*-xylene, **IV**, (70%), α-nitro-*m*-xylene, **V**, 90%: ^{1}H NMR, δ, 2.61s (Me); 5.26s (Cp); 6.04s, 6.01s (H2, CH_2); 6.60m (H4,5,6). α-nitro-2-chlorotoluene, **VI**, (54%).

α-Nitro-2-chloro-*p*-xylene, **VII** (70%), α-nitro-4-methylacetanilide, **VIII** (91%).

The α-nitro-*o*-toluidine complex, **IX**, was prepared in 50% yield by treatment of **VI** with $(Me_3Si)_2NH$ as described the following paper [23]. ^{13}C NMR data appear in Table 1.

4.2.1.2. H/D exchange reactions. A slurry of dry K_2CO_3 (0.15 g, 1.1 mmol) in $[^2H]_6$-DMSO (1.0 ml) was treated with **III** (0.15 g, 0.35 mmol). The mixture shaken for 5 min then filtered directly into an NMR tube and ^{1}H and ^{13}C NMR obtained on the deep red solution. The ^{1}H spectrum showed a 77% conversion to the corresponding carbanion whose δ values were: 4.86_s (Cp), 6.00 br.s (H4), 6.14 br.s.(H2,6), 6.85 br.s (H3,5). No signal was observed for the Me group. From integration, the Me group of the unreacted parent complex a 27% H/D exchange had occurred. ^{13}C NMR of the carbanion gave 75.16 (Cp), 77.85 (carbanionic C) 82.60 br (C2,4,6) 86.05 (C3,5). No signal was observed for the Me group.

4.2.2. Syntheses of arylaldehyde and arylketone complexes

4.2.2.1. Method A

4.2.2.1.1. Hydrogen peroxide. (η^6-α-Nitrotoluene)(η^5-Cp) iron (II) PF_6 (1.0 g, 2.4 mmol) was dissolved in dry DMSO (20 ml) and NaO*t*Bu (0.3 g, 3.1 mmol) added. The mixture was stirred for 10 min then 30% H_2O_2 (5 ml) added and was accompanied by an exotherm and considerable frothing. On cooling, CF_3CO_2H (1.5 g, 13 mmol) was added dropwise to give a clear brown-red solution. This was added slowly to cold aqueous 0.02 M $NaBPh_4$ (75 ml) to give a pale yellow precipitate. which was filtered off, washed with distilled H_2O then air dried to give 0.71 g A (η^6-benzaldehyde)(η^5-Cp) iron (II) BPh_4, **IIA**, (43%).

4.2.2.2. Method B

4.2.2.2.1. Acidic tin (II) dichloride. (η^6-α-Nitrotoluene)(η^5-Cp) iron (II) PF_6 (1.0 g 2.6 mmol) was added to $SnCl_2$ (2.2 g, 12 mmol) in conc. HCl (100 ml) and the whole refluxed for 1.5 h with stirring. The mixture was cooled to 0 °C then filtered and the filtrate treated dropwise with aq 0.3 M $NaBPh_4$ (10 ml) to give a flocculent yellow precipitate. This was filtered and air dried, then extracted with acetone (80 ml) and chromatographed on neutral alumina (10 g) eluting with acetone to give 0.32 g **IIA**, (24%) product. The following complexes were obtained by this method:

Table 1
^{13}C chemical shifts for (η^6-α-nitroalkylarene)(η^5-Cp) iron (II) complexes

Complex	C1	C2	C3	C4	C5	C6	Cp	Others
I	92.48	90.41	89.79	105.69	89.79	90.41	78.94	20.59, Me; 77.50, CH_2
II	93.97	90.95	89.40	89.60	89.40	90.95	78.62	77.72, CH_2
III	98.63	87.60	88.05	83.55	88.05	87.60	77.45	17.55, Me; 85.85, CH
		88.55	88.28		88.28	88.55		
IV[a]	91.25	104.16	89.31	87.92	86.79	89.88	77.45	17.50, Me; 75.40, CH_2
V	93.56	91.43	105.33	90.03	89.22	88.84	78.96	20.55, Me; 77.84, CH_2
VI[a,b]	88.34	108.62	90.80	90.17	88.59	89.04	79.48	75.18, CH_2
VII[a,b]	90.05	107.24	88.84	103.38	88.01	89.31	78.74	19.29, 19.49, Me
	90.28		88.95		88.25	89.52	78.82	74.95, 75.27, CH_2
							79.82	
							79.93	
IX	79.39	126.10	69.30	85.56	79.32	87.85	75.18	77.25, CH_2

[a] Solvent $[^2H]_6$-DMSO.
[b] BPh_4 salt.

Table 2
^{13}C NMR[a] and analytical data[b] for aldehyde and ketone ArFeCp complexes[c]

Complex	C1	C2	C3	C4	C5	C6	Cp	CH_2	CO	CH analysis	
										C	H
IA	89.27	86.99	89.27	105.88	89.27	86.99	77.90	20.24	193.22	79.43 (79.31)	5.78 (5.94)
IIA	90.82	87.60	88.95	90.01	88.95	87.60	77.64	–	193.29	79.0 (79.15)	5.89 (5.72)
IIIA	92.31	87.17	88.61	89.58	88.61	87.17	77.70	27.00	198.13	–	–
IVA	90.32	104.36	89.07	89.52	87.60	86.27	77.86	17.56	193.18	–	–
VA	90.37	87.38	104.59	90.44	88.32	86.10	77.97	19.96	193.41	–	–

[a] Solvent $[^2H]_6$-DMSO.
[b] Calculated values in parentheses.
[c] BPh_4 salts.

acetophenone, **IIIA**, (43%), *o*-tolualdehyde, **IVA**, (35%), *m*-tolualdehyde, **VA**, (22%), *p*-tolualdehyde, **IA**, (26%).

The α-nitro-4-methylacetanilide complex gave an inseparable mixture of starting material and product. Reaction of the α-nitrotoluene complex in the absence of $SnCl_2$ gave a mixture of the corresponding aldehyde and carboxylic acid complexes.

The same reaction with $SnCl_2$ was performed whilst bubbling argon through the reaction mixture. No product was formed under these conditions. ^{13}C NMR data and CH analyses appear in Table 2.

4.2.2.2.2. One-pot reaction. The intermediate α-nitrotoluene complex was prepared as above, using (η^6-fluorobenzene)(η^5-Cp) iron (II) PF_6 (0.5 g, 1.38 mmol), nitromethane (1.2 g 16 mmol), and NaO*t*Bu (0.8 g 8.2 mmol) in dry DMSO (10 ml) with a total reaction time of 45 min. A solution of $SnCl_2$ (1.1 g, 5.8 mmol) in 6 N HCl (50 ml) was added to the reaction mixture to give a yellow-orange precipitate. The mixture was refluxed for 4 h and the resultant clear light brown solution cooled in ice then filtered. The filtrate was extracted with CH_2Cl_2 (6×75 ml). This extract was dried (anhydrous $MgSO_4$) and evaporated to give a yellow-orange oil which was added dropwise to 0.06 M aq. $NaBPh_4$ (20 ml). The resultant precipitate was filtered off, washed with distilled H_2O and dried at 80 °C overnight to give 0.27 g product (33%).

4.2.2.3. Method C. (η^6-Fluorobenzene)(η^5-Cp) iron (II) PF_6 (1.0 g, 2.8 mmol) was dissolved in a mixture of dry DMF (10 ml) and nitroethane (5 ml) and dry, finely ground K_2CO_3 (1.2 g, 8.7 mmol) added. The whole was microwaved for 60 s on a high setting in the apparatus described in Ref. [3]. The resulting deep red reaction mixture was treated with 2 N HCl (25 ml), and the whole microwaved on a medium setting for a further 60 s. The clear brown solution was cooled to 0 °C then extracted with CH_2Cl_2 (3×50 ml). After drying and evaporation, a brown solution was obtained which was washed well with Et_2O to remove residual DMF. The resultant oil was taken up in acetone (10 ml) and added dropwise to a cold aq. 0.17 M solution of $NaBPh_4$ (10 ml). The resultant precipitate was filtered off, washed well with distilled H_2O then dried at 70 °C to give a pale yellow solid (0.86 g, 55%) shown by ^{13}C NMR to be the acetophenone complex.

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