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Synthesis of (η^6-arene)(η^5-cyclopentadienyl) iron (II) complexes with heteroatom and carbonyl substituents Part II, Amino substituents ☆

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Abstract

A variety of methods have been used in the synthesis of amino-substituted (η^6-arene)(η^5-cyclopentadienyl) iron(II) complexes. Conventional thermal ligand exchange of 2-fluoroaniline with ferrocene in the presence of Devarda's alloy gave an Ullmann coupling product, 2,2′ diaminobiphenyl complex, whereas omitting metal powder gave the 2-fluorobenzene complex. Double S_NAr substitution of the 1,2-dichlorobenzene complex by dimethylamine is reported. Microwave-assisted S_NAr reactions have led to the development of a one-pot synthesis of *N*-arylaminoacids. Acetylation of amino-complexes is described and the product anilide complexes used in S_NAr displacements to form aminoanilide analogues. Hexamethyldisilazane was found to be an efficient aminating agent in the presence of alcohols or phenols in DMSO, leading to the synthesis of the (η^6-1,2-diaminobenzene)(η^5-Cp) iron(II) complex, the first $(ArFeCp)^+$ species reported containing two primary amino groups.

Keywords: Amino; Iron; Cyclopentadienyl; Synthesis

1. Introduction

Synthesis of (η^6-arylamino)(η^5-cyclopentadienyl) iron-(II) complexes $(ArFeCp)^+$ is usually accomplished by either direct ligand exchange [1] or by S_NAr displacements, using halobenzene complexes as the substrate and amines as nucleophilic reagents [2]. Microwave-mediated ligand exchange reactions have led to great reductions in reaction times and in some cases increased yields [3]. S_NAr reactions by oxygen nucleophiles can result in double displacements in dihalobenzene complexes [4]. For primary amines as nucleophiles, however, only mono-substitution is observed for 1,2-dichlorobenzene complexes [4], whereas disubstitution occurs for 1,4 analogues using piperazines as nucleophiles [5]. Recent work has shown that amino complexes can be synthesized using water as a solvent under mild conditions [6]. This paper reports new synthetic routes to amino-substituted $(ArFeCp)^+$ complexes[1] and includes the preparation of 1,2-disubstituted species. No attempt has been made to optimize yields in these reactions.

2. Results and discussion

2.1. Thermal ligand exchange reactions

These reactions proceed readily for most arylamines according to

[1] For structural formulae, these complexes are represented by

☆ Part 1.

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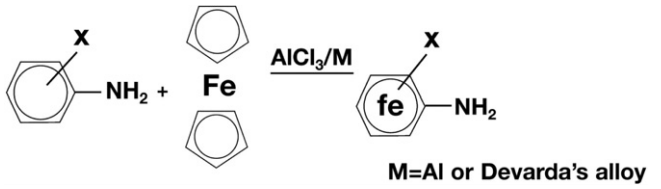
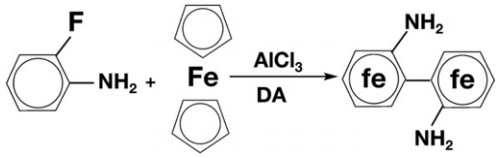


(1)

However, a difficulty arises where X = F, particularly where the fluorine is in the *ortho* position to the amino group. Using Devarda's alloy (DA) (50%Cu, 45%Al, and 5%Zn) 2-fluoroaniline, and 1,2,4-trichlorobenzene (TCB) as solvent, Ullmann coupling reactions [7] dominate giving a yield of 28% of the 2,2-diaminobiphenyl complex



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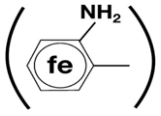
The product exists as two diastereomeric forms due to the enantiomeric nature of the moiety

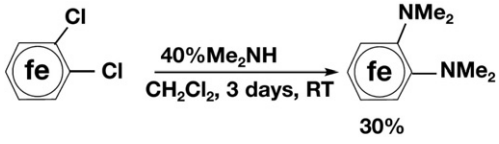


and biphenyl isomerism. These isomers occur in a 3:1 ratio though it is difficult to assign structure to them from ^{13}C NMR data. Normal Ullmann reactions are activated by electron withdrawing substituents such as NO_2 groups [7]. The [$CpFe^+$] unit is equivalent to approximately two NO_2 groups in its electron withdrawing power and activates even fluorine substituents which are normally unreactive. The fact that no coupling was observed for 2-fluoroaniline itself under the above conditions for (2) testifies to this strong activation.

The use of Al powder instead of DA resulted in mainly the desired 2-fluoroaniline complex with ~10% of the coupling product. Omitting metal powder altogether, and using a lower boiling solvent (80–100° pet. ether), the 2-fluoroaniline complex alone was formed in 42% yield. 4-Fluoroaniline gave much less coupling when metal powders were used – a 3.5:1 mixture of the 4-fluoroaniline and 4,4-diaminobiphenyl complex was obtained with DA.

2.2. S_NAr displacements

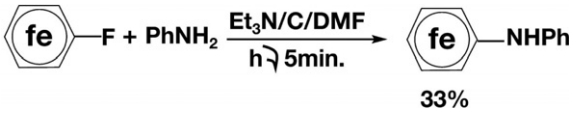
Mono-substitution is usually observed in S_NAr reactions of dichlorobenzene complexes with primary amines [4]. However, for dimethylamine, it is possible to doubly substitute the 1,2-dichlorobenzene complex under mild conditions using a very large excess of 40% aq. Me_2NH.



(3)

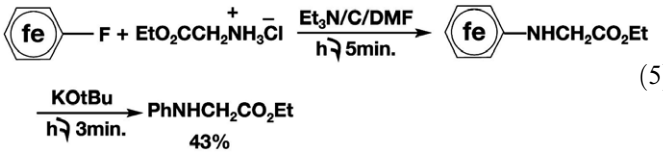
This complex has been previously reported but with no experimental details [8]. The reason for disubstitution in this case is the lack of an acidic hydrogen on the N atom in the intermediate mono substituted complex. Such a hydrogen is present when primary amines are used as nucleophiles and is easily removed in basic media to form an electron rich conjugate base which inhibits further nucleophilic substitution [4].

S_NAr reactions of $(ArFeCp)^+$ complexes take place over several hours and in some cases days. The use of microwave radiation greatly accelerates the rates of these reactions leading to S_NAr displacements which do not occur using conventional methods. Thus the diphenylamine complex can be made in moderate yields by reaction of the fluorobenzene complex with aniline



(4)

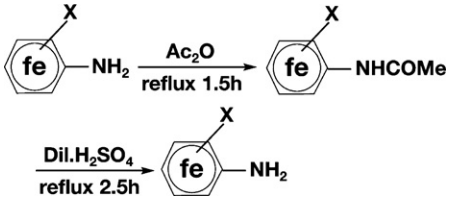
The above technique was used to devise a one-pot synthesis [9] of an arylated aminoacid in moderate yield



(5)

2.3. Activation of halo-aniline complexes to S_NAr substitution

Halo-aniline complexes do not normally undergo S_NAr displacements by nitrogen nucleophiles (vide supra). Acetylation of the halo amino complexes provides an alternative route for delocalisation of the incipient lone pair of the deprotonated complex, thus reducing electron donation to the complexed arene thus lessening inhibition to nucleophilic substitution. The acetanilide complexes are readily prepared and easily hydrolysed.



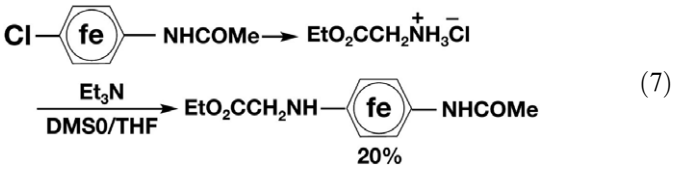
(6)

This strategy enables S_NAr reactions to be performed on the intermediate anilide complex and the NH_2 group to be regenerated. Trifluoroacetylation should, of course, be a much stronger electron attracting N-substituent, but unfortunately is extremely sensitive to hydrolysis which now dominates over the S_NAr process. In passing, it is worth noting that acetylation reactions can be monitored easily from the Cp signals in ^{13}C NMR spectra. For aniline

complexes these signals lie in the range 75.3–76.6 ppm; for haloaniline complexes, 78.0–79.4 ppm and for anilide complexes, 79.9–80.4 ppm.

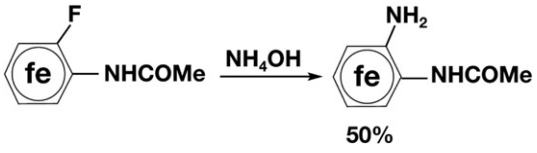
The effect of acetylation in S_NAr reactions is shown by the fact that substitution occurs for the chloroacetanilde complexes but not for the chloroaniline complexes themselves.

The S_NAr product in Eq. (7) shows a doubling of some signals in the ^{13}C NMR spectrum indicating the existence of two isomeric species. From signal intensities, these isomers are present in a 1:1 ratio and could occur due to restricted rotation about both C–N bonds resulting in *cis*/*trans* isomerism.



(7)

Using ammonia as a nucleophile, S_NAr substitution was observed in the case of the 2-fluoroacetanilide complex yielding the 2-aminoacetanilide analogue



(8)

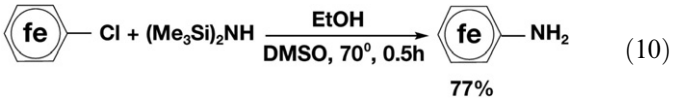
Interestingly, the 2-fluoroaniline complex gave a 40% yield (as estimated from ^{13}C NMR) of the 1,2-phenylenediamine complex but was contaminated with starting material which proved difficult to remove. A 6% yield of the 2-chloroaniline complex was obtained from reaction with the 1,2-dichlorobenzene complex. The 1,3- and 1,4-dichlorobenzene complexes did not react which suggests activation by an *ortho* inductive effect. A 40% yield of the 4-aminoacetanilide complex was obtained by this method. Hydrolysis of the 2-aminoacetanilide complex formed above resulted in an inseparable mixture of the 1,2-phenylenediamine and aniline complexes in a 3:1 ratio. The cause of the de-amination is unclear but appears to be due to the ortho nature of the substitution since the 1,4-phenylenediamine complex can be prepared in 30% yield without this complication.

2.4. Hexamethyldisilazane (HMDS) as an aminating agent

Treatment of HMDS with alcohols or phenols produces ammonia in accordance with

$$(Me_3Si)_2NH + 2ROH \rightarrow NH_3 + 2Me_3SiOR \quad (9)$$

This reaction can be used to generate NH_3 in situ as a nucleophile for S_NAr displacements. Thus reaction of the chlorobenzene complex with HMDS gives an excellent yield of the aniline complex.



(10)

This reaction can be used (phenol replacing ethanol as the ammonia forming reagent) to give a 14% yield of the 1,2-phenylenediamine complex, isolated as a monohydrate. This is the first example of an $(ArFeCp)^+$ complex containing two primary amino groups. Thermal and photochemical ligand exchange involving 1,2-phenylenediamine itself gave no product.

3. Conclusion

The reactions described here offer some alternative routes to the synthesis of (η^6-arylamine)(η^6-Cp) iron(II) complexes and hence by decomplexation [3,10] to new arylamines, though decomplexation is more difficult for arylamine complexes due to the dominant contribution of the iminocyclohexadienyl mesomeric form to the structure which strengthens iron-ligand bonding [6].

4. Experimental

^1H and ^{13}C NMR were obtained using a JEOL EX270 spectrometer; chemical shifts, δ, are in ppm relative to TMS [s, single; d, doublet; tr, triplet for ^1H NMR]. J_{CF} coupling constants are in Hz. Solvents used were $[^2H]_6$-acetone for PF_6 salts and $[^2H]_6$-DMSO for BPh_4 salts. For the latter, the BPh_4 signals are omitted in the interest of brevity. CHN analyses were obtained from the Microanalytical Laboratory, University of Manchester. Mass Spectra were recorded using a Kratos MS 50 Double Focusing mass spectrometer with an FAB source. Synthesis of $(ArFeCp)^+$ complexes as starting materials followed microwave-mediated techniques described in Ref. [1].

4.1. Synthesis of (η^6-2-fluoroaniline) (η^5-cyclopentadienyl) iron(II) hexafluorophosphate

Ferrocene (5.6 g, 0.030 mol) and $AlCl_3$ (4.8 g, 0.036 mol) were ground together and added to 80–100 °C pet.ether (10 ml). Flaked graphite (1.0 g) and 2-fluoroaniline (1.1 g, 0.010 mol) were added to the mixture. [NB: Al powder or Devarda's alloy were not used, see below]. After thorough stirring, the mixture was microwaved for 4 min on a MEDIUM setting in the apparatus described in Ref. [1]. After careful quenching with ice, followed by the usual work-up, 1.6 g (42%) of the desired product was obtained. ^{13}CMR, δ, 71.82, $^3J_{CF}$ 3.5 (C6); 76.54, $^2J_{CF}$ 17.6 (C3); 79.01, $^3J_{CF}$ 5.6 (C4); 84.83, (C5); 117.63, $^2J_{CF}$ 13.3 (C1); 124.84, $^1J_{CF}$ 272.9 (C2).

The synthesis of (η^6-2,2^1-diaminobiphenyl)bis-[η^5-cyclopentadienyl iron(II) hexafluorophosphate] followed the above procedure, except that Devarda's alloy (12.4 g) was added and TCB used as the solvent. The product was obtained in 28% yield.

CHN analysis: Found, C, 36.8; H, 3.1; N, 3.9%. Calcd. for $C_{22}H_{22}F_{12}Fe_2N_2P_2$: C, 36.90; H, 3.10; N, 3.91. Using Al powder (3.0 g 0.111 mol), a mixture of the 2-fluoraniline complex and the above biphenyl complex was obtained in a ratio of 10:1.

The ^{13}C NMR of the biphenyl complex showed a doubling of signals suggesting two isomeric species. The shifts for the main isomer (74%) only are reported, using conventional numbering for the biphenyl system. ^{13}C NMR, δ, 71.17(C3), 81.17 (C5), 86.70 (C1), 86.84 (C4,C6), 126.14 (C2).

The corresponding reaction using 4-fluoroaniline and Devarda's alloy resulted in the formation of the 4-fluoroaniline complex and the 4,4[1]-diaminobiphenyl complex in a ratio of 3.5:1 ^{13}C NMR of the latter: δ, 71.21(C3,5), 86.90 (C2,6), 89.74 (C1) 125.33 (C4).

5. S_NAr reactions

5.1. Synthesis of (η^6-1,2-N-dimethylaminobenzene) (η^5-cyclopentadienyl) iron(II) PF_6

(η^6-1,2-Dichlorobenzene)(η^5-Cp) iron(II)PF_6 (1.0 g, 2.4 mmol) in CH_2Cl_2 (30 ml) was stirred at RT for three days with 40% Me_2NH(50 ml) in a stoppered flask. The two layers were then separated and the aqueous phase extracted with CH_2Cl_2 (3×25 ml). The combined CH_2Cl_2 extracts were dried (anhyd $MgSO_4$), filtered and evaporated to give 1.0 g orange-red oil. This was redissolved in CH_2Cl_2 and chromatographed on neutral alumina to give 0.32 g (30%) red-orange solid whose ^{13}C NMR [δ_c, 40.66(Me), 74.77 (Cp), 75.80 (C3,6), 81.70 (C4,5) 117.12 (C1)] agreed well with calculated and literature values [8].

6. Microwave-mediated S_NAr reactions

6.1. Synthesis of (η^6-diphenylamine)(η^5-cyclopentadienyl) iron(II) PF_6

A mixture of (η^6-fluorobenzene)(η^5-Cp) iron(II) PF_6 (1.0 g 2.8 mmol), aniline (0.6 g, 6.4 mmol). Et_3N (1.0, 10 mmol), and flaked graphite (2 g) in dry DMF (10 ml) was microwaved for 5 min. on a MEDIUM setting. The mixture was filtered into Et_2O (200 ml) and the residue leached with MeOH into the Et_2O. The whole was cooled to 0 °C overnight. The supernatant Et_2O was then decanted off and the residue triturated with a further portion of ether then extracted with CH_2Cl_2 (50 ml). After filtration, the filtrate was washed with 5% aq. NaOH, separated, dried ($MgSO_4$), filtered and evaporated to give 0.52 g orange-brown solid whose IR spectrum was identical to the desired product. Yield: 33%.

The above method was used to devise a one-pot synthesis of an N-arylated aminoacid.

[(PhF)FeCp] PF_6 (1 g, 2.8 mmol), glycine hydrochloride ethylester (0.8 g 5.7 mmol) Et_3N (1.0 g, 10 mmol), and flaked graphite (2 g) in DMF (10 mls) were microwaved for 5 min on a MEDIUM setting. *t*-BuOK (1.0 g, 8.9 mmol) was added, and the whole microwaved for a further 3 min, then filtered into Et_2O (200 ml) to give a ppt. This was filtered off and the residue washed with MeOH and leached into the ethereal filtrate. After further filtration, the Et_2O extract was warmed with a little decolourising charcoal and filtered. The Et_2O and DMF were removed by rotary evaporation at 40 °C and 95 °C, respectively. The brown residue was extracted with CH_2Cl_2 (100 ml) and washed with dist. H_2O to remove residual DMF. Evaporation gave an oil (0.20 g) whose ^{13}C NMR showed it to be *N*-phenylglycine of ~95% purity. Yield: 43%.

6.2. Acetylation of aniline complexes

The following procedure was adopted for all acetylations. A solution of (η^6-aniline)(η^5-Cp) iron(II) PF_6 (0.70 g 1.95 mmol) in acetic anhydride (5 g) was refluxed for 0.5 h. After cooling, the mixture was poured into ether (100 ml) to give yellow ppt. This was filtered off, washed with ether and air dried to give 0.60 g product (77%). ^1H NMR: δ, 1.18s (CH_3), 5.14 s (Cp), 6.26 tr (H4), 6.41d (H2,6), 6.87 tr(H3,5). ^{13}C: δ, 24.40 (Me), 77.81 (Cp), 78.99 (C2,6), 85.71 (C4), 87.62 (C3,5), 111.60 (C1), 171.44 (CO). CHN analysis: Found: C, 38.62; H,3.50; N, 3.74%. Calcd. For $C_{13}H_{14}F_6Fe$ NOP: C, 38.93; H, 3.51; N, 3.49. Mass spectrum Found 256.0: Calcd. 256.1 (loss of H^+).

The following acetylated aniline complexes were also prepared (yields in parentheses) 4-chloroacetanilide (84%): ^{13}C NMR, δ, 24.39 (Me), 78.33 (C2,4), 80.20 (Cp), 87.96 (C3,5), 104.69 (C4), 111.33 (C1), 171.47 (CO). 2-Methyl-3-chloroacetanilide (44%): ^{13}C 18.80 (aryl Me), 24.37 (acetyl Me), 77.29, 77.36 (C6), 79.01, 79.09 (C2), 80.41 (Cp), 87.93 (C5), 99.99 (C4), 107.13 (C3), 110.83, 110.92 (C1), 171.49 (CO). 2-Fluoroacetanilide (75%): ^{13}C, 24.36 (Me), 77.48, $^3J_{CF}$ 19.9 (C3), 77.87 (C6), 79.23 (Cp) 84.02, $^3J_{CF}$ 6.0 (C4), 85.77 (C5), 102.64, $^2J_{CF}$ 11.9 (C1), 129.37, $^1J_{CF}$271.3 (C2), 171.68 (CO). 4-Fluoroacetanilide: CHN analysis: Found: C, 36.6; H, 3.2; N, 3.0%. Calcd. For $C_{13}H_{13}F_7FeNOP$: C, 37.32; H, 3.13; N, 3.34.

6.3. Hydrolysis of anilide complexes

(η^6-Acetanilide)(η^5-Cp) iron(II) PF_6 (1.0 g 2.5 mmol) was added to 0.18 M H_2SO_4 (20 ml) and the whole refluxed for 2.5 h. The mixture was filtered, cooled in ice, and 10% NaOH (15 ml) added dropwise. After filtration, an aq. solution of 0.26 M $NaBPh_4$ (10 ml) was added and the resultant ppt. filtered off, washed with dist. H_2O and dried at 85 °C for 2 h to give the aniline complex (0.89 g 67%).

7. S_NAr displacements in halo-acetanilide complexes

7.1. [η^6-4-(Ethylglycinylacetanilide)](η^5-cyclopentadienyl) iron(II) BPh_4

Glycine hydrochloride ethylester (4.2 g, 30.0 mmol) was dissolved in dry DMSO (10 ml.) and Et_3N (4.0 g, 39.6 mmol) added. The resultant ppt. of Et_3N. HCl was filtered off and dry THF (10 ml) added to the filtrate followed by further filtration. (η^6-4-Chloroacetanilide)(η^5-Cp) iron-(II) PF_6 (0.9 g 2.0 mmol) was added and the mixture refluxed overnight, excluding moisture. On cooling, CH_2Cl_2 (25 ml) was added and the whole filtered. The filtrate was rotary evaporated at 55 °C to remove CH_2Cl_2 and THF and the resulting brown red solution was washed with Et_2O (3×50 ml). The brown residue was extracted with CH_2Cl_2 filtered and re ppted. with Et_2O. The oily sludge was taken up in MeOH (20 ml) and added dropwise to aq. 0.15 M $NaBPh_4$ (20 ml). The MeOH was removed by rotary evaporation and the resultant mixture extracted with CH_2Cl_2, dried, and evaporated to give a brown oil (1.4 g) This was chromatographed on neutral alumina eluting with acetone to give a yellow-orange solid (0.25 g, 20%). ^{13}C NMR, δ, 14.45 (CH_3CH_2–), 24.23, 24.26 (CH_3CO–), 44.86, 44.97 (–$NHCH_2$–), 62.00 (–CH_2OCO–), 66.85 (C3), 76.67, 76.76 (C2), 77.33 (Cp), 105.59, 105.68 (C1), 123.79, 123.85 (C4) 170.30 (–CO_2–), 170.86, 170.92 (CH_3CO–)

Mass spectrum; found 357.1: Calcd 357.2

A similar reaction using the 2-chloroacetanilide complex gave a mixture of the 2-[ethylglycinyl] aniline (47%) and 2-[ethylglycinyl] acetanilide (17%) complexes. The 2-chloroaniline complex gave no reaction.

7.2. (η^6-2-Aminoacetanilide)(η^5-cyclopentadienyl) iron(II) tetraphenylborate

A slurry of (η^6-2-fluoroacetanilide)(η^5-Cp) iron(II) PF_6 (0.5 g, 1.2 mmol) in conc. [NH_4][OH] (40 ml) was refluxed for 1.5 h with stirring, then filtered and the orange filtrate evaporated to dryness. The yellow residue was extracted with acetone (15 ml) and filtered into ice-cold aq. 0.04 M $NaBPh_4$ (25 ml). The flocculent yellow ppt. was filtered off, washed with a little dist. H_2O then dried at 60 °C to give 0.35 g yellow solid. (50%) whose IR showed the presence of H_2O.

^{13}C, 23.86 (Me), 71.95, (C3), 76.35, 76.52 (C6), 77.15, 77.59 (Cp) 79.84, 80.09 (C5), 83.94, 84.57 (C4), 91.43 (C1), 119.35 (C2), 171.06, 171.15 (CO). CHN analysis: Found: C, 73.0; H, 5.9; N, 4.2%. Calcd. for $C_{37}H_{37}BFeN_2O_2$: C, 73.00; H, 6.12; N, 4.60. Using the 2-fluoroaniline complex, partial substitution occurred giving a 40% yield of the 1,2-phenylenediamine complex admixed with starting material. However, it was not possible to separate the two materials by column chromatography.

The 1,2-dichlorobenzene complex gave a 6% yield of the 2-chloroaniline complex, but the 1,3- and 1,4-dichlorobenzene complexes did not react. The 4-fluoroacetanilide complex gave a 40% yield of the 4-aminoacetanilide complex. Hydrolysis of the 2-aminoacetanilide complex by 0.2 M H_2SO_4 gave an inseparable mixture of the 1,2-phenylenediamine and aniline complexes in a 3:1 ratio. Similar hydrolysis of the 4-aminoacetanilide complex gave a 30% yield of the 1,4-phenylenediamine complex.

^1H NMR: 4.60 (Cp), 5.43 (H2,3,4,6), 5.56 (NH_2). ^{13}C NMR 67.33 (C2,3,5,6), 75.56 (Cp), 119.56 (C1,4).

CHN analysis: Found C, 76.10; H, 6.08; N, 4.83%. Calcd. for $C_{35}H_{33}BFeN_2$: C, 76.67; H, 6.07; N, 5.11.

7.3. Hexamethyldisilazane (HMDS) as an arninating reagent

A solution of (η^6-chlorobenzene)(η^5-cyclopentadienyl) iron(II) PF_6(0.5 g, 1.3 mmol) ethanol (0.6 ml, 10 mmol), and HMDS (1.0 ml. 4.7 mmol) in dry DMSO (3 ml) was heated at 70 °C for 0.5 h using a condenser. After cooling to RT, the mixture was added to aq. 0.05 M NH_4PF_6 (50 ml). The orange-yellow ppt. was filtered off, washed with cold dist H_2O and Et_2O then air dried to give 0.29 g product. Extraction of the aqueous layer with CH_2Cl_2 (100 ml) gave a further 0.07 g. Total yield 77%.

A cognate synthesis using (η^6-2-fluoroaniline)(η^5-cyclopentadienyl) iron(II) PF_6 but replacing ethanol with phenol, gave a 14% yield of the 1,2-phenylenediamine complex as a monohydrate ^{13}C NMR 70.74 (C3,6), 75.22 (Cp), 77.65 (C4,5), 109.00 (C1,2).

CHN analysis: Found C, 74.9; H, 6.1; N, 4.7%. Calcd. for $C_{35}H_{35}BFeN_2O$: C, 74.23; H, 6.23; N, 4.95.

Acknowledgements

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