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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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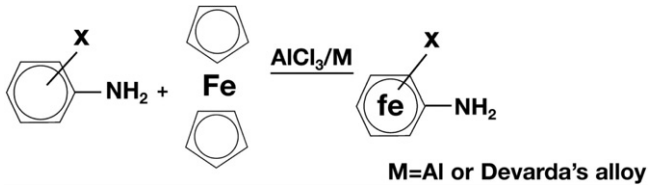
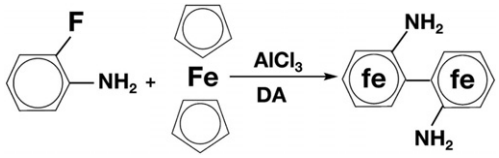


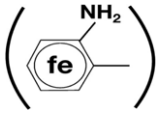
(1)

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



(2)

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

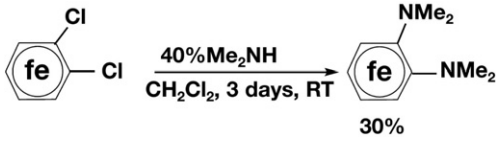


and biphenyl isomerism. These isomers occur in a 3:1 ratio though it is difficult to assign structure to them from ^{13}C NMR data. Normal Ullmann reactions are activated by electron withdrawing substituents such as NO_2 groups [7]. The [$CpFe^+$] unit is equivalent to approximately two NO_2 groups in 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

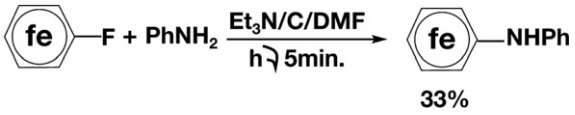
Mono-substitution is usually observed in S_NAr reactions of dichlorobenzene complexes with primary amines [4]. However, for dimethylamine, it is possible to doubly substitute the 1,2-dichlorobenzene complex under mild conditions using a very large excess of 40% aq. Me_2NH.



(3)

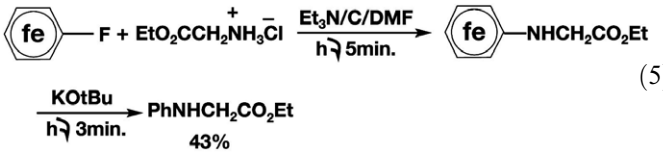
This complex has been previously reported but with no experimental details [8]. The reason for disubstitution in this case is the lack of an acidic hydrogen on the N atom in the intermediate mono substituted complex. Such a hydrogen is present when primary amines are used as nucleophiles and is easily 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)

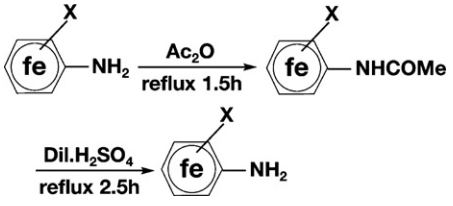
The above technique was used to devise a one-pot synthesis [9] of an arylated aminoacid in moderate yield



(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