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Synthesis of chiral (η^6-arene)(η^5-cyclopentadienyl)iron(II) complexes and their characterisation by ^{13}C NMR spectroscopy

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Abstract

Displacement of halogen substituents in (η^6-haloarene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphates [ArFeCp]$^+$ by a chiral amine, α-methylbenzylamine, yields diastereomeric mixtures. The diastereomers have been identified by $\{^1H\}^{13}C$ NMR and ^1H NMR spectroscopy and their ratios determined. No stereoselectivity was observed for the 2-methylchlorotoluene and 3-methylchlorotoluene [ArFeCp]$^+$ complexes. However, for the 1,2-dichlorobenzene complex one diastereomer was formed preferentially. For the 3,4-dichlorotoluene complex, positional isomers and their diastereomeric components were identified and the relative ratios determined from ^{13}C spectra.

In the case of the 1,2-difluorobenzene complex, both fluorines can be displaced to give a product with two chiral side chains.

Introduction

(η^6-arene)(η^5-cyclopentadienyl)iron(II) salts [ArFeCp]$^+$ were first synthesised by Coffield et al. in 1957 [1] and interest in these complexes has continued to grow particularly since the advent of a simple preparative method involving $AlCl_3$-catalysed ring exchange pioneered by Nesmeyanov's group [2]. Two reviews have appeared covering the literature up to late 1983 [3,4].

Amongst the most interesting chemical properties of these complexes is the ease with which halogen substituents on both arene and Cp rings are displaced by nucleophiles [5]. This reaction has since been exploited by Sutherland's group [4] and a wide range of substituted derivatives have been prepared. More recently it has been demonstrated that even nitro substituents [6] can be displaced which opens up new preparative routes to substituent patterns which are difficult to obtain by conventional electrophilic substitution reactions on the uncomplexed arenes. Knipe [7] has offered evidence of rate determining nucleophilic attack at the halogen-bearing carbon atom to form what is effectively an iron complex of a Meisenheimer intermediate [8]. The most commonly used leaving group is chloride which can be displaced by a wide variety of nucleophiles [3,4] and even double S_N2 Ar reactions have been reported [9]. We have been interested in these systems for some time and

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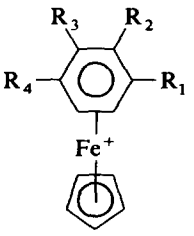
have reported the synthesis of a novel aryltin derivative [10] together with detailed Mössbauer studies on a series of $[ArFeCp]^+$ complexes [11] which included some new biphenyl derivatives [12]. Although there are numerous examples of halogen displacement by amines, there are no reports of reactions using chiral amines. The two chlorine atoms in (η^6-1,2-dichlorobenzene)(η^5-cyclopentadienyl)iron(II) salts are enantiotopic and thus using a chiral nucleophile, diastereoisomers can be produced. This paper reports on the synthesis of such chiral complexes and their characterisation by ^1H and ^{13}C NMR spectroscopy.

Results and discussion

The chiral amine chosen for this work was α-methyl benzylamine (α-methylbenzenemethanamine, MBA) because of its commercial availability in *R*, *S*, and *RS* forms. The substrates used were:



	R_1	R_2	R_3	R_4
1A	Cl	H	H	H
2A	Cl	CH_3	H	H
3A	Cl	H	CH_3	H
4A	Cl	Cl	H	H
5A	F	F	H	H
6A	Cl	Cl	H	CH_3

1A reacted with an excess of (*R*)-(+)-MBA on warming to give a 55% yield of [η^6-(*R*)-(+)-*N*-(1-phenylethyl)aniline](η^5-cyclopentadienyl)iron(II) hexafluorophosphate (**1B**). The product was optically active with values of $[\alpha]_D^{22}$ and $[M]_D^{22}$ of 41°

Table 1

^{13}C Chemical shifts [a] for products of halogen displacements by α-methylbenzylamine

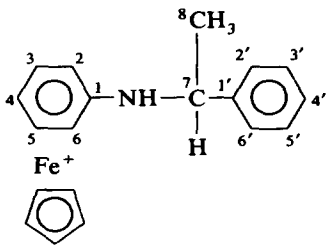
Compound [b]		C1	C2	C3	C4	C5	C6	Cp
(±)-**1B**		126.54	67.92	86.33	81.17	86.70	69.36	76.02
(+)-**2B**	I	125.68	82.50	88.96	80.53	84.88	65.73	76.77
	II	124.15	79.38	88.86	80.39	85.62	68.43	76.03
(±)-**3B**	I	125.99	70.72	101.90	81.53	85.52	66.26	76.32
	II	125.99	69.48	101.77	81.53	85.78	67.74	76.32
(−)-**4B**	I	123.01	90.09	87.13	80.87	85.49	68.75	78.49
	II	124.30	88.94	87.13	80.76	85.27	66.43	77.69
(−)-**5B**		111.64	106.71	71.89	78.09	77.88	67.30	75.17
(±)-**6B**	I	122.22	89.97	86.47	96.88	85.89	65.84	79.27
	II	122.22	89.97	86.47	96.88	85.60	67.78	78.48
(±)-**6C**	I	122.22	89.07	87.75	81.32	101.59	68.27	79.27
	II	122.22	89.07	87.75	81.15	101.68	70.30	78.37

[a] ppm from TMS (for numbering, see text). [b] The chirality of the amine used is indicated in parentheses

and 190° respectively. This compares with values of 47° and 57° respectively for MBA itself. Complexation thus greatly enhances the molar rotation of the amine. Other displacement products were obtained by a similar procedure and in comparable yields. The exception was the reaction with substrate **2A** which required a higher temperature and longer reaction time, presumably due to a sterically hindered reaction site.

Analysis of products by ^{1}H and $\{^{1}H\}$ ^{13}C NMR spectroscopy

For the purposes of the ensuing discussion, the following numbering scheme has been adopted.



The ^{13}C data appear in Table 1. Assignments for **1B** were made by reference to (η^6-$C_6H_5NHCH_3$)(η^5-Cp)iron(II) hexafluorophosphate and MBA. These models were then used to analyse the ^{13}C spectra of the other products employing the substituent additivity principle.

Table 1 (continued)

C1′	C2′	C3′	C4′	C5′	C6′	C7′	C8′	Others
144.38	127.29	129.90	128.67	129.9	127.29	53.45	24.34	–
144.54	127.75	130.12	128.86	130.12	127.75	53.91	24.53	Me(C2) 17.96
144.42	126.67	129.58	128.12	129.58	126.67		24.30	17.81
144.41	127.25	129.81	128.56	129.81	127.25	53.36	24.35	Me(C3) 20.80 20.63
143.49	126.53	129.49	128.18	129.49	126.53	53.94	23.99	–
143.24	127.58	129.98	128.96	129.98	127.58		23.83	
144.72	127.66	129.92	128.78	129.92	127.66	54.37	25.07	
144.72	126.57	129.57	128.05	129.57	126.57	54.04	24.68	–
143.88	126.79	129.72	128.41	129.72	126.79	53.95	24.04	Me(C4)
143.66	127.82	130.23	129.19	130.23	127.82			19.04
143.88	126.79	129.72	128.41	129.72	126.79	54.27	24.28	Me(C5)
143.66	127.82	130.23	129.19	130.23	127.82			19.04

[$R \equiv (+)$, $S \equiv (-)$].

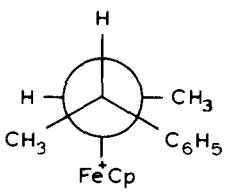
Table 2

Calculated and observed ^{13}C chemical shifts for diastereomers formed by reaction of **3A** with (*S*)-(−)-MBA

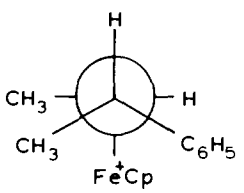
	C1	C2	C3	C4	C5	C6
Diastereomer I						
Calc.	125.9	69.8	102.5	81.0	85.7	66.0
Found	126.0	70.7	101.9	81.5	85.5	66.3
Diastereomer II						
Calc.	125.9	68.3	102.1	81.0	86.1	67.5
Found	126.0	69.5	101.8	81.5	85.8	67.7

For **1B**, C2 and C6 were magnetically non equivalent as were C3 and C5. This is unlikely to be due to restricted rotation about the C1–N bond since no such effect was noted for the *N*-methylaniline complex. Thus, although there is evidence of a strong +M mesomeric effect of the NHMe group viz; the marked reduction in basicity [13] of the NH_2 group of the aniline complex relative to that of aniline itself (pK_a −1.07 and 4.5 respectively), this is not enough to create a significant barrier to rotation. The observed non-equivalences in **1B** must therefore be due to the chiral centre in the side chain. In theory, the carbon pairs C′2,C′6 and C′3,C′5 should also show magnetic nonequivalence due to the proximate chiral centre. However only single lines were found for **1B**.

The presence of a substituent on either C2 or C3 creates an enantiomeric substrate, and hence halogen displacement by a chiral reagent will generate diastereomers This is illustrated by the Newman projection of the product of reaction of **2A** with (*S*)-(−)-MBA. (The linking NH group is omitted for clarity.)



Diastereomer I



Diastereomer II

^{13}C NMR has proved to be very useful in identifying these diastereomers. Using the magnetic non-equivalences observed for **1B**, chemical shifts (δ) can be calculated for the two orientations of the $[ArFeCp]^+$ moiety (I and II). The results for **3B** appear in Table 2 and show excellent agreement with observed values. The assignments * enable estimation of the composition of the diastereomeric mixture. This is most accurately done from analysis of the C2 and C6 signals which appear in the range 66–71 ppm which is free of other resonances. The almost equal intensities of the four lines observed indicates at 50% mixture of I and II i.e. no stereoselective diastereomer formation. This is confirmed from the equal intensities of the C5 signals of I and II at 85.52 and 85.78 ppm respectively. In this case the free Cp signals of the diastereomers are identical. By contrast, separate ^1H signals were

* Because of uncertainty as to the absolute assignment of the pairs of signals (C2 or C6 and C3 and C5) absolute assignments of I and II are not possible at this stage.

Table 3

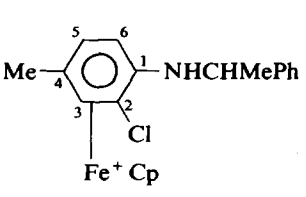
Yields and ^{1}H NMR [a,b] data for products of halogen displacements

Compound	Yield (%)	Uncomplexed arene	Complexed arene	Cp	CH_3-Ar	CH_3-CH
(±)-**1B**	55	7.40–6.80(m,5H)	5.80–5.10(m,5H)	4.19(s,5H)	–	1.28,1.16(3,H)
(+)-**2B**	58	7.80–6.90(m,5H)	6.17–5.25(m,4H)	4.72s,4.08s(5H)	2.33s,2.23(3H)	1.50d,1.38d(3H)
(±)-**3B**	58	7.44–6.96(M,5H)	5.88–5.18(m,4H)	4.32s,4.26s(5H)	2.38s,212s(3H)	12.3,1.13(d,3H)
(−)-**4B**	62	7.58–6.72(m,5H)	6.24–5.38(m,4H)	4.64s,4.00s(5H)	–	1.36d,1.25d(3H)
(−)-**5b**	40	7.42–6.80(m,10H)	5.64–5.00(m,4H)	3.90(5H)	–	1.36,1.26(d,6H)
(±)-**6B**/**6C**	58	7.44–6.80(m,5H)	6.24–5.38(m,3H)	4.62s,4.01s(5H)	2.02s,1.96s(3H)	1.38,1.26(d,3H)

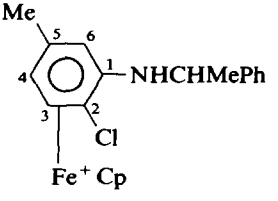
[a] ppm from external TMS; s = singlet, d = doublet, m = multiplet. [b] The methine, signal of the side chain was partially masked by the Cp signals in all cases.

observed for the Cp resonances of I and II (4.32, 4.26 ppm see Table 3). A similar approach was used in analysing the ^{13}C data for **2B** where the methyl substituent is adjacent to the amino substituent. As anticipated, the additivity principle worked less well due to the *ortho* nature of the groups. Nevertheless, assignments could be made with reasonable certainty. Analysis of the diastereomeric mixture was made easier by the observation that in this case the Cp signals of each isomer were noticeably different (76.77, 76.03 ppm) giving an diastereomer ratio of 53 : 47. The signals at 65.73 and 68.43 ppm can be unambiguously assigned to the C6 signals of diastereomer I and II respectively (using the same notation as for the Newman projections of **2B**). These signals were of equal intensity again indicating that, in spite of the closer approach of the ring methyl to the seat of substitution (cf. **3B**), little or no stereoselectivity occurs. One consequence of this change in position of the methyl substituent is apparent in the ^{13}C shifts of the uncomplexed benzene ring of the side chain. The arene carbons of I and II are now no longer equivalent, resulting in two sets of signals. This must be due to different shifts of the free phenyl groups in I and II and not simply due to magnetic non-equivalence of the carbon pairs C2′,C6′; C3′,C5′ since two signals are found for the C4′ carbons. The slight but systematic differences in the integrals also support this. Clearly this phenomenon is due to the greater proximity (to the side chain chiral centre) of the methyl group causing the chirality in the $[ArFeCp]^+$ moiety. Another result of this is seen in the ^1H NMR of **2B** where a large difference in shift ($\Delta\delta = 0.64$ ppm) of the Cp resonances occurs relative to **3B** ($\Delta\delta = 0.06$ ppm). The free arene also appears as a more complex multiplet than in **1B**.

The *ortho* chloro-substituted product (**4B**) was analysed in the same way and displayed general features similar to those of **2B**. Thus separate Cp signals were found for diastereomers I and II from which it was calculated that II was present in significant excess (61 : 39). An identical composition was found from an examination of the C6 signals for the diastereomers. In this case, therefore, there is strong evidence for stereoselectivity favouring one diastereomer. This is confirmed by the spectrum where the Cp signals are now widely separated (4,64, 4.00 ppm) with relative integrals of 62 : 38. Another feature of the diastereomeric mixture is that the methyl groups on C7 in the side chain have significantly different ^1H shifts for I and II, the signals appearing as overlapping doublets (this was also observed for **2B** but not for **3B**). The reaction products from the (η^6-3,4-dichlorotoluene)(η^5-cyclopentadienyl)iron(II) substrate were more complex due to the possibility of positional isomers as well as diastereomer formation. The two positional isomers are represented below:



(6B)

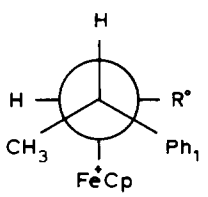


(6C)

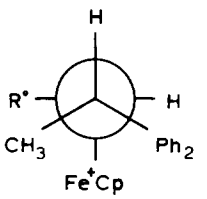
The ^{13}C spectrum is best analysed by reference to the signals for C4 in **6B** and C5 in **6C** (i.e. the methyl bearing carbons of the complexed ring) which appear in an

uncluttered region of the spectrum. C4 appears as a single peak at 96.88 ppm whereas there are two signals for C5 at 101.59 and 101.68 ppm. This confirms the assignment since C4 should be the same for each diastereomer I and II of **6B** whereas C5 in **6C** should have different resonances for the two diatereomers. Since the relaxation times of these two carbons are likely to be very similar, the ratio of the positional isomers can be assessed. This reveals that **6B** and **6C** are formed in the ratio 40:60 which indicates a degree of positional selectivity. This result is confirmed by examination signals which appear at 79.27, 78.48 and 78.37 ppm with integral ratios 1:0.53:0.62. The corresponding resonances for diastereomers I and II of **4B** lie at 78.49 and 77.69 ppm respectively. It is thus probable that the downfield signal in the **6B/6C** spectrum is due to the I diastereomer of both positional isomers and that the two upfields signals are due to diastereomers **6B**-II and **6C**-II. The integral ratios suggest that the upfield signal of the latter pair is due to the **6C**-II isomer. Further confirmatory evidence comes from and analysis of the C6 signals in the region 66–71 ppm.

Finally, for substrate **5A**, it was possible to displace both fluorine substituents by (*S*)-(−)-MBA to give a product with two chiral side chains ((−)-**5B**). The interesting feature of the ^{13}C spectrum of **5B** is the doubling of all carbon signals in the side chain with the exception of C1′. This is due to the different configuration of the $[ArFeCp]^+$ moiety relative to the chiral groups (R°).



view along C1–C4 axis



view along C2–C5 axis

Thus Ph_1 will always be in a magnetically different environment from Ph_2.

Experimental

^1H NMR were run on a JEOL PMX60SI spectrometer and ^{13}C NMR spectra on a Bruker WP80 instrument. Polarimetry was performed using an Optical Activity Ltd Polarimeter Type AA-10. Analyses were obtained from the Analytical Department of Manchester University. All the (η^6-halobenzene)(η^5cyclopentadienyl)iron(II) hexafluorophosphates were prepared by standard methods based on Nesmeyanov's original procedure [5].

Preparation of [η^6-N-(1-phenylethyl)aniline](η^5-cyclopentadienyl)iron(II) hexafluorophosphate (1B)

A mixture of (η^6-chlorobenzene)(η^5-cyclopentadienyl)iron(II) hexafluorophosphate (1 g, 2.64 mmol) and (*R*)-(+)-α-methylbenzylamine (2 g, 16.5 mmol) was heated for 5 min on a steam bath then allowed to cool overnight. The resultant red oil was shaken with a solution of NH_4PF_6 (0.50 g, 3.1 mmol) in distilled water (5 ml) and extracted with CH_2Cl_2 (30 ml). The mixture was filtered through phase separation paper into ether (70 ml) whereupon a red oil was thrown out of solution. This was triturated several times with ether to remove any remaining amine then

Table 4

Elemental analyses [a] of halogen displacement products

Compound	C (%)	H (%)	N (%)
(±)-**1B**	49.1 (49.3)	4.8 (4.4)	3.1 (3.0)
(+)-**2B**	50.0 (50.3)	4.8 (4.6)	3.0 (3.0)
(±)-**3B**	50.1 (50.3)	4.7 (4.6)	3.0 (2.9)
(−)-**4B**	45.9 (45.9)	4.0 (3.8)	2.4 (2.8)
(+)-**6B**	46.4 (46.9)	4.2 (4.1)	2.5 (2.7)

[a] Calculated values in parentheses.

redissolved in CH_2Cl_2 and reprecipitated with ether to give 0.67 g of a red oil. The ^1H spectrum of the product in acetone-d_6 showed that the desired compound had been made in 55% yield.

The other MBA derivatives were synthesised using the same procedure except that for **2B** the reaction was carried out at 100 °C for 5 h (Table 3). Also the CH_2Cl_2 extract was washed well with water to remove MBA · HCl formed. Analytical data appear in Table 4.

Preparation of η^6*-(N-methylaniline)(*η^5*-cyclopentadienyl)iron(II) hexafluorophosphate*

(η^6-Chlorobenzene)(η^5-cyclopentadienyl)iron(II) . hexafluorophosphate (2.40 g, 6.35 mmol) was dissolved in CH_2Cl_2 (20 ml) and 40% $MeNH_2$ in H_2O (7 g, 90 mmol) added with vigorous shaking. The mixture was left for 2h then filtered through phase separation paper. The filtrate was shaken with NH_4PF_6 solution (0.9 g in 4 ml H_2O) refiltered and the product precipitated with Et_2O to give an orange-brown solid (2.2 g, 92%)

^1H NMR (acetone-d_6): δ (ppm) 2.44s (3H), 4.44s (5H), 5.1–5.9 m (5H). $\{^1H\}^{13}C$ (acetone-d_6): δ (ppm) 29.60 (NH*Me*), 68.30 (C2), 75.82 (Cp), 81.05 (C4), 86.27 (C3), 127.47 (C1).

Acknowledgement

The authors thank Mrs J.F. Warmsley for running the ^1H and ^{13}C NMR spectra.

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