Synthesis of some heterocyclic derivatives of (η-arene)-(η-cyclopentadienyl)iron(II) hexafluorophosphates including estimation of dihedral angles in both free and complexed ligands

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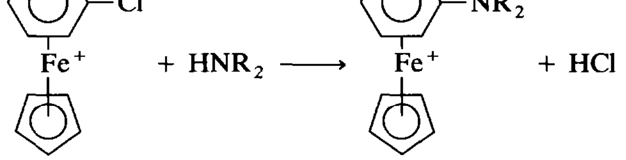
Abstract

The preparations are described of a series of mono and disubstituted derivatives of [(η-arene)(η-cyclopentadienyl)Fe][PF_6] complexes in which a range of indole-related substituents is bonded to the arene moiety via nitrogen. The preparations involved the S_NAr displacement of chlorine from the corresponding chlorobenzene iron sandwich complex by nitrogen-centred anions derived by reaction of the heterocycle with ^{t}BuOK in DMSO or 80% DMSO-^{t}BuOH. The ^{1}H and ^{13}C NMR data are presented and discussed. Analysis of the ^{13}C data using substituent chemical shifts of the *ortho* and *meta* carbons of the arene moiety has allowed estimation of the dihedral angle between the arene and the heterocyclic components in both the free and complexed N-phenyl heterocyclic systems.

Key words: Iron; Arene; Cyclopentadienyl; Indole

1. Introduction

One of us (RMGR) recently reported the synthesis of new N-substituted imidazolyl and triazolyl derivatives of [(η-arene)(η-cyclopentadienyl)iron(II)] hexafluorophosphates ([ArCpFe][PF_6]) [1]. The objective is to develop a simple method of arylation at oxygen, nitrogen and sulphur sites in organic molecules using these iron sandwich complexes as arylating agents. The results of studies of the arylation reactions will be published separately in due course. We felt it important first to extend the range of the intermediate iron sandwich complexes that can be made by the well known chloride displacement reactions [2,3], *e.g.*



(1)

Very few preparations of complexes based on indole and related heterocycles have appeared in iron group chemistry. Moriarty and Gill [4,5] have reported the synthesis of [(η-indole)(η-Cp)Ru][PF_6] and have studied displacement reactions of 4- and 5-chloroindole derivatives. For the cobalt group, the rhodium and iridium analogues have also been prepared [6]. Because of our interest in N-arylation mediated by [ArCpFe] complexes, we decided to investigate the complexes of indole and a range of related heterocyclic systems, and we report our findings here.

2. Results and discussion

The anions of indole-based heterocycles are readily generated *in situ* by deprotonation by a strong base such as potassium t-butoxide. The usual solvent for KO^{t}Bu is DMSO, but the resulting solution is very strongly basic and can cause unwanted side reactions. The basicity can be reduced by using ^{t}BuOH as a cosolvent since it solvates the O^{t}Bu anion [7] and thus increases its selectivity. An added advantage is that the liberated KCl is only very slightly soluble in such me-

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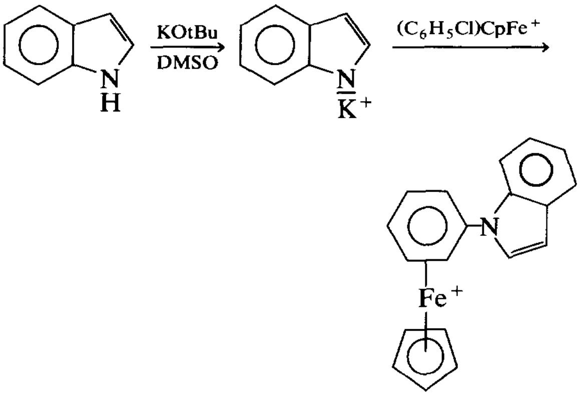
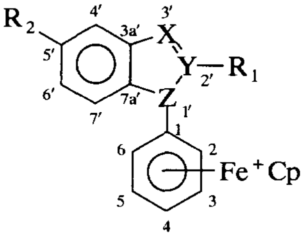
dia. We have used both solvents in this work; DMSO alone has been extensively used in S_NAr reactions of the Meisenheimer type [8], of which reaction (1) is an example.

Thus, treating potassium indolate with [(η-C_6H_5Cl)(η-Cp)Fe][PF_6] gave a 47% yield of the desired complex, as shown in eqn. (2).

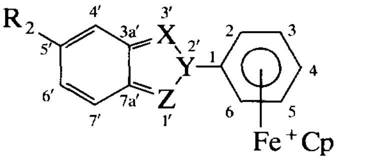


(2)

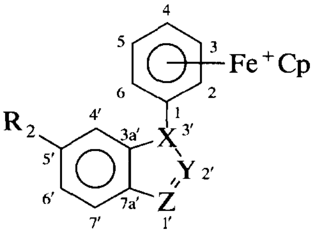
By use of the above procedure, the following [ArCpFe][PF_6] complexes have been prepared:



X	Y	Z	R_1	R_2	
CH	C	N	H	H	**1**
CH	C	N	C_6H_5	H	**2**
CH	N	N	–	H	**3**
N	C	N	H	H	**4**
N	C	N	2-pyridyl	H	**5**
N	N	N	–	H	**6**
N	N	N	–	CH_3	**7**
N	N	N	–	Cl	**8**
NH	C	N	=O	–	**9**

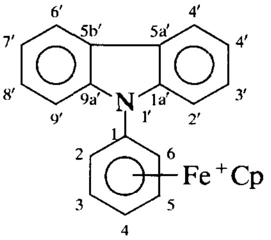


X	Y	Z	R_2	
CH	N	N	H	**10**
N	N	N	H	**11**
N	N	N	CH_3	**12**
N	N	N	Cl	**13**



X	Y	Z	R_2	
N	N	N	CH_3	**14**
N	N	N	Cl	**15**

and additionally



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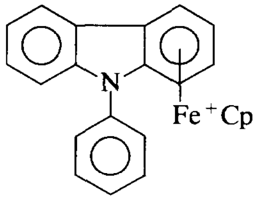

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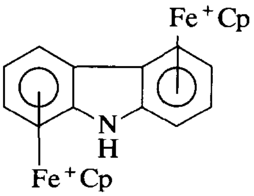

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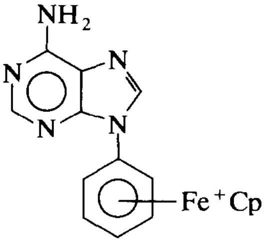

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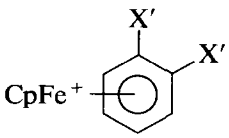
The numbering system used for NMR analysis is not strictly conventional but has the advantage of making correlations easier to identify.

The following disubstituted complexes have also been made:



X′	
indazolyl	**20**
benzimidazolyl	**21**
benzotriazolyl	**22**
adeninyl	**23**

TABLE 1. ^{1}H NMR data [a] for [ArCpFe][PF$_6$] complexes of some heterocyclic derivatives in acetone-d_6

Complex	H2	H3	H4	H5	H2′	H3′	H4′	H5′	H6′	H7′	Cp
1	7.06d	6.74t	6.53t	6.74t	8.01d	6.89d	7.88d	7.24t	7.33t	7.71d	5.30s
	(5.9)	(5.9)	(5.3)	(5.9)	(3.3)	(3.3)	(7.5)	(7.5)	(7.3)	(7.2)	–
3 [b]	7.13d	6.58t	6.40t	6.58t	–	8.61s	8.11d	7.39t	7.39t	7.97d	5.11s
	(6.7)	(6.1)	(5.9)	(6.1)	–	–	(8.8)	(7.1)	(7.1)	(8.0)	–
10 [b]	7.17d	6.64t	6.46t	6.64t	–	9.31s	7.74d	7.64t	7.64t	7.81d	5.09s
	– [c]	(6.3)	– [c]	(6.3)	–	–	(8.7)	(7.7)	(7.7)	(8.7)	–
19	7.43d	6.76t	6.56t	6.76t	8.35s	–	–	–	8.65s	–	5.31s
	(6.3)	(6.4)	(6.2)	(6.4)	–	–	–	–	–	–	–
6	7.38d	6.89t	6.71t	6.89t	–	–	7.79t	8.21t	8.21t	7.63d	5.37s
	(6.4)	(6.3)	(6.2)	(6.3)	–	–	(7.3)	(9.3)	(9.3)	(7.3)	–
11	7.38d	6.89t	6.71t	6.89t	–	–	8.03dd	7.72d	7.72d	8.03dd	5.26s
	(6.4)	(6.3)	(6.2)	(6.3)	–	–	(6.6,2.8)	(6.6)	(6.6)	(6.6,2.8)	–
16	7.15d	6.85t	6.66t	6.85t	8.13d	7.61t	7.44t	8.28d	8.28d	7.44t	5.39s
	(5.7)	(6.5)	(6.2)	(6.5)	(8.4)	(7.3)	(7.3)	(7.5)	(7.5)	(7.3)	–
24	7.24s	–	6.81brs	6.81brs	7.29d	6.42d	7.53d	7.00t	7.06t	7.42d	5.36s
	–	–	–	–	(2.6)	(2.6)	(7.9)	(7.5)	(7.5)	(8.3)	–
29	7.59brs	7.59brs	–	7.59brs	8.37s	–	–	–	8.91s	–	5.26s
	–	–	–	–	–	–	–	–	–	–	–

[a] ppm from ext. TMS, coupling constants in parentheses (Hz), s = singlet, d = doublet, dd = doublet of doublets, t = triplet, br = broad.
[b] Solvent DMSO-d_6.
[c] Signal partially masked by that of 1H isomer.

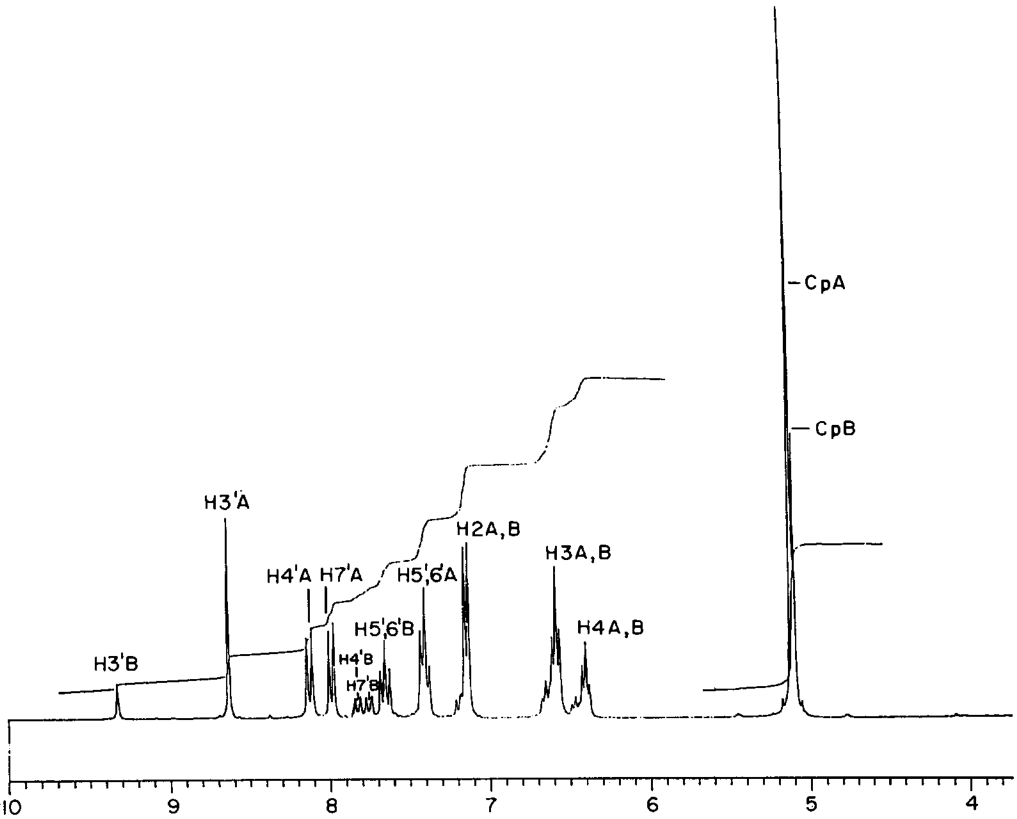
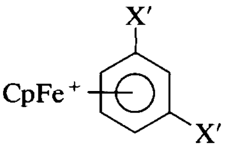


Fig. 1. ^{1}H NMR spectrum (DMSO-d_6) of a mixture of 1H- and 2H-indazolyl complexes (**3**) (**10**). Signals labelled A and B refer to (**3**) and (**10**) respectively.

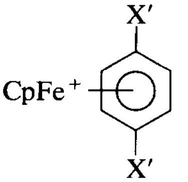
TABLE 2. ^{13}C NMR data [a-d] for N-phenylderivatives of indole, indazole, benzimidazole, benzotriazole and adenine and their [η-arene)(η-cyclopentadienyl)Fe][PF$_6$] analogue complexes

Heterocycle	C1	C2	C3	C4	Cp	C2′	C3′	C3a′	C4′	C5′	C6′	C7′	C7a′
N-phenylindole [b,e]	140.4	124.8	130.5	127.2	–	128.8	104.3	130.4	121.8	121.0	123.0	111.0	136.4
Complex **1** [b,e]	102.2	82.3	88.5	87.4	78.7	128.4	108.3	131.3	122.6	122.9	124.6	111.8	136.7
N-phenylbenzimidazole [c,f]	139.7	122.0	129.5	126.4	–	–	135.6	125.0	121.5	121.5	127.3	110.3	138.0
Complex **3** [d,e]	108.2	80.4	87.4	86.6	77.6	–	139.1	125.9	122.3	123.2	128.8	111.2	138.9
2H-N-phenylindazole [c,f]	140.0	120.2	129.6	127.8	–	–	121.4	122.5	122.1	120.9	126.8	117.5	149.0
Complex **10** [d,e]	108.3	80.4	87.4	86.6	78.1	–	117.7	123.4	124.4	121.3	128.5	110.3	– [g]
N-phenylbenzimidazole [c,f]	135.9	123.5	130.0	127.6	–	142.3	–	143.7	119.9	122.3	122.5	110.7	133.0
Complex **4** [d,e]	106.5	81.9	87.6	87.3	78.0	143.8	–	144.1	120.6	123.7	124.5	111.5	132.7
1H-N-phenylbenzotriazole [c,e]	– [g]	122.8	129.7	128.6	–	–	–	146.4	120.2	124.3	128.1	110.3	131.7
Complex **6** [b,e]	105.8	82.1	87.8	88.3	78.8	–	–	146.1	120.3	125.6	129.8	111.3	132.2
2H-N-phenylbenzotriazole [c,e]	– [g]	120.6	129.4	128.9	–	–	–	145.0	118.3	127.1	127.1	118.3	145.0
Complex **11** [b,e]	106.7	82.1	87.8	88.3	78.6	–	–	145.3	118.5	129.1	129.1	118.5	145.3
1-N-phenyladenine [b,e]	– [g]	123.0	129.6	127.5	–	139.7	–	119.5	156.5	–	153.3	–	149.3
Complex **19** [d,e]	105.3	81.3	87.2	86.8	78.0	139.7	–	119.6	156.6	–	153.6	–	149.7

[a] ppm from TMS; [b] solvent acetone-d_6; [c] solvent $CDCl_3$; [d] solvent DMSO-d_6; [e] this work; [f] ref. 13; [g] not observed.



indolyl **24**
benzotriazolyl **25**
adeninyl **26**



indolyl **27**
benzotriazolyl **28**
adeninyl **29**

2.1. ^{1}H NMR spectroscopy

^{1}H NMR data for a selection of the compounds prepared appear in Table 1. Assignments of the indole complexes were made by reference to Elvidge's data [9], whilst those containing indazole and benzotriazole groups were based on analysis by Palmer *et al.* [10]. The assignments for the carbazole complexes were based on earlier work by Heffernan [11,12]. ^{1}H NMR spectroscopy is a very effective tool for analysing the [ArCpFe][PF$_6$] complexes reported here. This is particularly true for distinguishing between the 1H and 2H isomers of the indazolyl and benzotriazolyl complexes, as illustrated by the spectrum of a mixture of **3** and **10** reproduced in Fig. 1. The signals for H3′, H4′, H5′, H6′ and H7′ are clearly separated for the two isomers and a full analysis is possible. Integration of the Cp signals reveals an isomer ratio 1H/2H of 4/1. One interesting feature of the spectrum is the large chemical shift difference between the H3′ signals for the 1H and 2H isomers. The latter appears downfield from the former by 1.70 ppm. Both signals are significantly downfield from those in 1- and 2-methylindazole [10], reflecting electron withdrawal by the ArCpFe$^+$ moiety. The downfield shift of H3′ in **10** (2H) is much greater than that in **3** (1H), suggesting that inductive effects of the iron sandwich substituent dominate over resonance effects at this ring position. This is in keeping with evidence from ^{13}C NMR data of relatively weak delocalisation of the nitrogen lone pairs around the attached phenyl group.

2.2. ^{13}C NMR spectroscopy

^{13}C NMR data for the complexes and their free ligand analogues appear in Tables 2–7. The assignments for the heterocyclic moieties were made by reference to the free ligands, using data appearing in the review by Begtrup and Elguero [13] on azoles, whilst those for the complexed arene ring were based on the data obtained by Sutherland *et al.* [14] for [ArCpFe][PF$_6$] salts. Additional chemical shift data for

TABLE 3. ^{13}C NMR data for carbazole N-substituted [(η-arene)(η-Cp)Fe][PF$_6$] complexes in acetone-d_6

Compound	C1	C2	C3	C4	Cp	C1a′	C2′	C3′	C4′	C5′	C5a′	C5b′	C6′	C7′	C8′	C9′	C9a′
N-Phenylcarbazole	138.3	127.8	130.9	128.4	–	141.6	110.4	126.9	120.8	121.1	124.1	124.1	121.1	120.8	126.9	110.4	141.6
16	111.7	83.4	88.6	87.8	78.4	140.2	112.0	127.8	121.6	123.1	125.8	125.8	123.1	121.6	127.8	112.0	140.2
17 [a]	134.4	126.6	130.6	129.9	75.6	112.8	70.1	82.9	78.7	81.3	85.0	– [b]	122.7	122.1	129.0	111.1	144.5
18	–	–	–	–	78.9	118.8	74.9	86.5	82.0	84.2	88.1	88.1	84.2	82.0	86.5	74.9	118.8

[a] Solvent DMSO-d_6; [b] quaternary signal masked by C6′.

TABLE 4. ^{13}C NMR [a] data for various [(η-arene)(η-Cp)Fe][PF_6] salts with arene substituents based on the indane carbon skeleton

Complex	C1	C2	C3	C4	Cp	C2′	C3′	C3a′	C4′	C5′	C6′	C7′	C7a′	Others	
2	109.7	84.5	86.5	86.3	77.1	131.1	108.1	137.4	122.5	122.5	123.6	112.3	141.1	2-phenylsubstituent	C1 128.3, C2 128.7 C3 129.3, C4 129.1
5 [b]	110.2	85.4	87.5	88.6	78.3	150.2	–	144.2	121.5	125.8	125.8	112.9	136.3	2-(2-pyridyl)-substituent	C1 152.7 C3 149.2, C4 126.1 C5 138.5, C6 125.2
9 [b]	– [c]	83.7	88.3	87.5	79.1	153.5	–	129.5	110.2	122.5	124.2	110.8	– [c]		
7 [b]	– [c]	82.8	88.8	89.0	79.4	–	–	–	120.7	– [c]	128.3	110.8	– [c]	CH_3 21.8	
12 [b]	– [c]	81.4	88.8	88.8	79.4	–	–	–	118.7	– [c]	132.5	117.2	– [c]	CH_3 21.0	
14 [b]	– [c]	82.6	88.8	88.8	79.4	–	–	–	111.2	– [c]	132.9	120.3	– [c]	CH_3 22.0	
8	– [c]	81.0	86.1	86.5	76.9	–	–	–	124.8	– [c]	128.5	109.8	– [c]		
13	– [c]	80.9	86.1	84.3	76.9	–	–	–	120.4	– [c]	131.6	120.2	– [c]		
15	– [c]	81.0	86.1	86.1	76.9	–	–	–	111.4	– [c]	133.4	120.2	– [c]		

[a] ppm from TMS in solvent DMSO-d_6; [b] acetone-d_6; [c] not observed.

TABLE 5. ^{13}C NMR data for [(η-1,2-$C_6H_4X_2$)(η-Cp)Fe][PF_6] complexes

X	C1	C2	C3	C4	Cp	C2′	C3′	C3a′	C4′	C5′	C6′	C7′	C7a′
1H-N-Indazolyl [a] 1H-**20**	109.7	109.7	85.7	87.3	79.9	–	138.0	127.4	122.5	122.8	128.2	104.8	138.4
2H-N-Indazolyl [a] 2H-**20**	117.4	117.4	85.7	87.3	80.3	–	121.8	121.9	124.8	121.2	128.0	109.4	– [b]
1H-N-Benzimidazolyl [c] **21**	103.9	103.9	88.9	90.6	82.6	–	–	146.6	122.8	126.1	126.8	112.7	136.2
1H-N-Benzotriazolyl [a] **22**	103.0	103.0	88.0	89.8	82.3	–	–	146.6	121.0	126.1	130.3	110.2	134.7
1H-N-Adeninyl [c] **23**	99.6	99.6	85.8	87.6	80.1	140.5	–	118.4	156.1	–	153.1	–	149.9

[a] Solvent acetone-d_6; [b] not observed; [c] solvent DMSO-d_6.

TABLE 6. ^{13}C NMR data for [(η-1,3-$C_6H_4X_2$)(η-Cp)Fe][PF_6] complexes

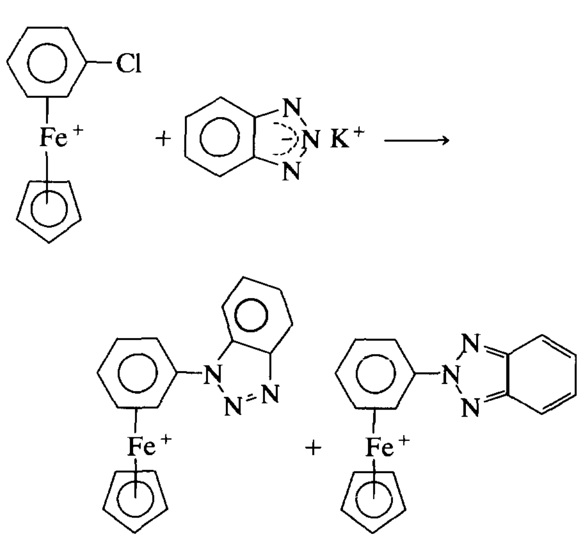
X	C1	C2	C3	C4	C5	Cp	C2′	C3′	C3a′	C4′	C5′	C6′	C7′	C7a′
1H-N-Indazolyl [a] **24**	102.1	88.7	102.1	88.8	90.0	82.1	125.5	107.8	128.9	119.7	120.9	121.9	112.1	137.2
1H-N-Benzotriazolyl [b] 1H-**25**	105.5	77.0	105.5	82.4	87.1	80.4	–	–	146.1	120.4	125.7	130.0	111.3	132.7
2H-N-Benzotriazolyl [b] 2H-**25**	106.0	77.0	106.0	82.4	87.1	80.4	–	–	145.2	118.6	129.8	129.8	118.6	– [c]
1H-N-Adeninyl **26**	104.6	75.0	104.6	79.7	86.0	79.4	139.7	–	119.9	156.4	–	153.4	–	149.7

[a] Solvent acetone-d_6; [b] solvent DMSO-d_6; [c] not observed.

TABLE 7. ^{13}C NMR data for [(η-1,4-$C_6H_4X_2$)(η-Cp)Fe][PF_6] complexes

X	C1	C2	Cp	C2′	C3a′	C4′	C5′	C6′	C7′	C7a′
1H-N-Benzimidazolyl **27**	105.7	80.9	79.6	143.7	144.0	120.6	123.8	124.5	111.4	132.8
1H-N-Benzotriazolyl 1H-**28**	105.6	81.6	80.3	–	146.1	120.4	125.7	129.9	111.2	132.4
2H-N-Benzotriazolyl 2H-**28**	106.0	81.6	81.6	–	145.6	118.6	129.4	129.4	118.6	130.2
1H-N-Adeninyl **29**	104.0	80.0	79.5	139.6	119.5	156.5	–	153.6	–	149.7

indoles [15] were also used. The ^{13}C spectra of both the indazole and benzotriazole complexes also revealed the presence of 1H and 2H-isomers resulting from attack by the ambident nitrogen nucleophiles in each case, as *e.g.*, in eqn. (3).



(3)

1H 2H

For reaction (3), the isomer ratio 1H/2H was found to be 2/1 from signal intensities, indicating a statistical product distribution. The product distribution is dependent on the cation used. Thus for sodium and potassium benzotriazolates, the above almost statistical distribution was observed (70% and 68% of 1H isomer respectively). For the smaller lithium cation a much greater preponderance (95%) of the 1H isomer was found. This reflects the much tighter ion pairing in the lithium salt, which localises the negative charge on N1, resulting in dominant attack at this position. For the 5-substituted benzotriazole complexes, three isomers were observed (1H, 2H, and 3H) again with a statistical isomer distribution that was independent of the nature of the 5-substituent (H, Cl, CH_3). For the imidazole reaction, the ^{13}C NMR data also reveal a preponderance (4/1) of the 1H isomer, which suggests some selectivity by the ambident anion. There was no evidence of any C-substitution in the indole, indazole and benzimidazole complexes.

One of the most important structural features of the N-phenylated heterocyclic compounds is the value of the dihedral angle, Θ, between the phenyl plane and that of the heterocycle. Extended Hückel Theory (EHT) calculations [13,16] for N-phenylated heterocycles suggest values of (a) 0° for 2H-1,2,3-triazole, 2H-1,2,3,4-tetrazole and 2H-benzotriazole; (b) 32° for pyrazole, 2H-1,2,4-triazole, 1H-1,2,3-triazole, 1H-1,2,3,4-tetrazole and 2H-indazole; (c) 50° for pyrrole, imidazole and 1H-1,2,4-triazole; (d) 58° for 1H-indazole and 1H-benzotriazole; (e) 64° for indole and benzimidazole; and (f) 90° for carbazole.

These theoretical values of Θ are at variance with those calculated by Fong [17] from ^{13}C NMR substituent chemical shifts (SCS, Δ) for the *meta* and *para* carbons of the N-phenyl substituent. This leads, for example, to an estimated value of 0° for N-phenylpyrrole. The use of Δ values for *para* carbons in the estimation of θ is highly questionable in this particular case. For such analysis the following relationship is commonly used [18,19];

$$\cos^2\Theta = \frac{\Delta_p - \Delta_p^{90}}{\Delta_p^0 - \Delta_p^{90}} \qquad (4)$$

where Δ_p^0 and Δ_p^{90} represent the SCS for the *para* position for θ values of 0° and 90° respectively. Usually model compounds are used to assess these parameters. For the heterocyclic systems in question, a suitable model for $\theta = 0$ would be 2H-N-phenyl-1,2,3-triazole(I) and for $\Theta = 90$, N-phenyl-2,5-dimethylpyrrole(II). However, Δ_p values for these two heterocycles are almost identical (-1.3 [13] and -0.9 [20] ppm respectively). Clearly there is an insufficient range of shifts for this method to be accurate enough for the prediction of Θ values.

An alternative approach to the problem of Θ evaluation is to use the *ortho* and *meta* SCS as a measure of steric inhibition of resonance. Thus Δ_{23} ($= \delta C2 - \delta C3$) values have been used to quantify such steric inhibition although values of Θ were not calculated [21]. The use of *ortho* SCS in such analyses has been criticised since they are influenced by proximity effects [22]. However, the most important of these in the case of the heterocyclic systems used in this work is the change in anisotropy of the heterocyclic moiety with dihedral angle. Such changes in anisotropic deshielding, however, should also show a dependence on $\cos^2\Theta$ [23].

With the appearance [20] of ^{13}C data for II, we are now in a position to quantify the parameters in eqn. (4). I ($\Theta = 0$) has a value of Δ_{23} of -10.2 ppm [13] whereas that of II ($\Theta = 90°$) is -0.9 ppm. This leads to eqn. (5).

$$\cos^2\Theta = \frac{\Delta_{23} + 0.9}{-9.3} \qquad (5)$$

Using this relationship, we have calculated values for a range of N-phenylated heterocyclic compounds (Table 8). The results are very consistent with what one would predict from simple molecular modelling. The Δ_{23} values are subject to errors of certainly not more than ± 0.1 ppm, and Θ values should be accurate to within $\pm 2°$ if eqn. (5) holds. The method predicts $\Theta = 0 \sim 25°$ for the monocyclic heterocycles. Annelation causes a

TABLE 8. Estimated values of the dihedral angle Θ for some N-phenyl heterocycles using eqn. (5)

Heterocycle	Δ_{23}	$\cos^2\Theta$	Θ
Pyrrole	−8.9	0.860	22
Imidazole	−8.4	0.806	26
1H-Pyrazole	−10.3	1.000	0
1H-1,2,4 Triazole	−10.3	1.000	0
4H-1,2,4 Triazole	−8.8	0.849	23
1H-1,2,3 Triazole	−9.0	0.870	21
1H-Tetrazole	−9.0	0.870	21
2H-Tetrazole	−9.8	0.957	12
1H-Indole	−6.0	0.548	42
1H-Benzimidazole	−6.5	0.602	39
1H-Adenine	−6.6	0.613	38
1H-Indazole	−7.5	0.710	33
2H-Indazole	−9.4	0.914	17
1H-Benzotriazole	−7.4	0.699	33
2H-Benzotriazole	−9.8	0.957	12
9H-Carbazole	−4.0	0.333	55

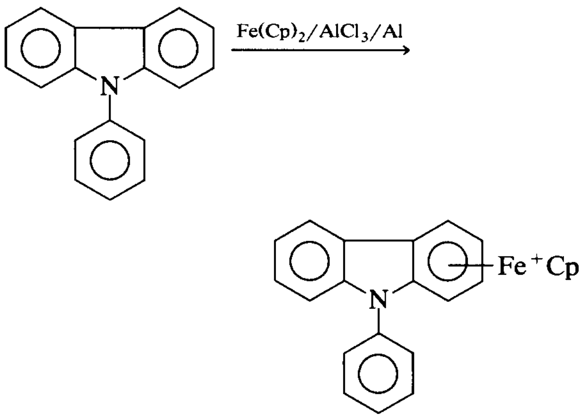
marked increases of Θ to 30°–45°. The exceptions are the 2H-indazole (17°) and 2H-benzotriazole (12°) derivatives, in which steric hindrance to rotation is likely to be much reduced. The calculated Θ for N-phenylcarbazole is 55°, which is considerably lower than that predicted by EHT calculations (90°) [13]. It is instructive in this context to compare our value of Θ with that of 67° obtained from molecular polarisability studies [24] for 9-phenylanthracene in CCl_4. This molecule has a similar geometry to that of N-phenylcarbazole except that the central ring is six-membered. A value of 55° for the latter would therefore seem to be reasonable, given that the *peri* hydrogens are directed more away from the C2, C6 hydrogens of the phenyl substituent than in 9-phenylanthracene.

Turning to the ArCpFe complexes, the evaluation of Θ is more problematical since a model for the case of $\Theta = 90°$ does not and cannot exist. We have chosen the N-phenyl-1H-1,2,4-triazole complex [1] as a model for $\Theta = 0°$ and have assumed that Δ_{23}^{90} is zero. This leads to the expression

$$\cos^2\Theta = \frac{\Delta_{23}}{-7.6} \qquad (6)$$

The Δ values thus calculated appear in Table 9. The values are generally lower than those for the free ligand, which is to be expected since the barrier to rotation comprises interactions with the Cp ring as well as the *peri–ortho* interactions described above. The angle for the N-phenylcarbazole complex is some 20° lower than that in the free ligand. This change in angle is manifested in the ^{1}H NOE difference spectrum of the complex. Irradiation of H2,6 (7.15 ppm) causes the disappearance of all signals except those for H3,5 (6.85 ppm), H4 (6.66 ppm) and H2′ (8.13 ppm), signifying that H2′ and H2,6 are fairly close in the complex.

Evidence that the nitrogen lone pair is delocalised mainly around the heterocyclic moiety comes from the finding that reaction of N-phenylcarbazole by the ligand exchange reaction (7)



(7)

17

results in specific complexation of one of the carbazole benzenoid rings. Such complexation is easily determined from the characteristic upfield shifts (30–35 ppm) of the 1a′–5a′ carbons and by reference to the known bis complex **18** [25].

2.3. *Disubstituted complexes*

These were prepared by chloride displacement from the corresponding [(η-dichlorobenzene)(η-Cp)Fe][PF_6] salts. As expected, the 1,2-disubstituted derivatives were rather more difficult to prepare than the 1,3 or 1,4-analogues. We were, not surprisingly, unable to prepare the 1,2-bis carbazole complex. However, we also failed to prepare the 1,2-bis indole complex, which

TABLE 9. Estimated values of the dihedral angle Θ for [ArCpFe][PF_6] complexes of some indole-related heterocycles using eqn. (6)

Heterocycle	Complex	Δ_{23}	$\cos^2\Theta$	Θ
Indole	**1**	−6.2	0.816	25
1H-Indazole	**3**	−7.0	0.921	16
Benzimidazole	**4**	−5.7	0.750	30
1H-Benzotriazole	**6**	−5.7	0.750	30
1H-Adenine	**19**	−5.9	0.776	28
Carbazole	**16**	−5.2	0.684	34
2-Phenylindole	**2**	−2.0	0.263	59
2(2-Pyridyl)benzimidazole	**5**	−2.0	0.263	59
1H-5-Methylbenzotriazole	**7**	−6.0	0.789	27
1H-5-Chlorobenzotriazole	**8**	−5.1	0.671	35
Imidazole [a]		−7.5	0.987	7
Benzimidazolin-2-one	**9**	−4.6	0.605	39

[a] See Ref. 1.

is rather puzzling since the benzimidazole and adenine analogues presented no real difficulty. The ^{13}C data appear in Tables 5–7. The ^{13}C chemical shifts of the heterocyclic moieties for the 1,3 and 1,4-complexes were almost identical with those for the corresponding monosubstituted complexes. More variation appears generally for the 1,2-species, though curiously in the case of adeninyl substituents all the complexes had almost identical shifts to those for the free ligand. For the 1,2-series it is impossible for the heterocyclic substituents to adopt either coplanar (because of *peri–ortho* interactions) or orthogonal conformations (because of steric hindrance by the cyclopentadienyl ring). A crude estimate of the dihedral angle Θ can be made using eqn. (6) and Δ_{34} values after allowing for the presence of the second heterocyclic substituent (using additivity factors obtained from the corresponding monosubstituted complexes). This results in the following estimates of θ for the 1,2 complexes: 1H-indazolyl, 56°; benzimidazolyl, 59°; 1H-benzotriazolyl, 66°; and 1H-adeninyl, 57°. These values seem quite reasonable. The heterocyclic substituents inclined at ~ 60° to the complexed arene ring are likely to adopt a parallel disposition to alleviate any steric strain between the two substituents, the five-membered ring being in the *endo* position of the iron sandwich in each case. For the 1,3-bis(benzotriazolyl) system, we were able to characterise both 1H and 2H isomers by ^{13}C NMR spectroscopy. There was no evidence of any mixed species.

3. Experimental section

The chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene and 1,4-dichlorobenzene [ArCpFe][PF$_6$] complexes were prepared by standard methods [26]. The following procedures are typical of the synthesis of the mono- and disubstituted complexes described in this work. The yields of the other complexes appear in Table 10.

3.1. Preparation of [(η-N-phenylindole)(η-Cp)Fe(II)]-[PF$_6$] (1)

Potassium t-butoxide (0.58 g, 5.2 mmol) was stirred with DMSO (10 ml) at room temperature for 5 min. Indole (0.40 g, 2.6 mmol) was added and the resulting yellow solution was stirred for 45 min. [(η-Chlorobenzene)(η-Cp)Fe][PF$_6$] (1.00 g, 2.6 mmol) was added to give a red-brown solution, which was stirred for a further 10 min and then added to an aqueous solution of NH_4PF_6 (0.5 g/100 ml). The resulting light-brown precipitate was filtered off, washed well with distilled water, and air dried. The crude material was recrystallised from aqueous methanol to give 0.60 g (47%) of pure product.

Analysis Found: C, 49.75; H, 3.50; N, 3.05. $C_{19}H_{16}F_6FeNP$ requires C, 49.70; H, 3.51; 3.05%. The ^1H and ^{13}C NMR data appear in Tables 1 and 2 respectively.

3.2. Preparation of the 1,2-bis adenine complex (23)

Potassium t-butoxide (0.88 g, 8.0 mmol) and adenine (1.1 g, 8.0 mmol) were stirred in DMSO (10 ml) at 50° for 2 h. [(η-1,2-dichlorobenzene)(η-Cp)Fe][PF$_6$] (1.64 g, 4 mmol) was added and the dark brown mixture was stirred at 50° for a further 2 h, then left overnight at room temperature. The mixture was worked up as in the preceding experiment to give 0.8 g (33%) of a brown solid. Analysis Found: C, 41.50; H, 3.00; N, 22.60. $C_{21}H_{17}F_6FeN_{10}P$ requires C, 41.33; H, 2.81; N, 22.95%. The ^{13}C NMR data appear in Table 5.

3.3. NMR and analytical data

The ^1H and ^{13}C NMR spectra were run on the JEOL EX270 spectrometer. Microanalyses were performed by the Analytical Department of the University of Manchester (Mr. Maurice Hart).

TABLE 10. Yields (%) and reaction times [a] (h) of [(η-arene)(η-Cp)Fe][PF$_6$] complexes

COMPLEX	**1**	**2**	**3(10)**	**4**	**5**	**6(11)**	**7(12,14)**	
Reaction time	1.0	2.0	0.5	1.0	1.0 [b]	4.0	17	
Yield	47	72	100 [c]	89	37	53 [c]	80 [c]	
COMPLEX	**8(13,15)**	**9**	**16**	**17**	**19**	**20**	**21**	**22**
Reaction time	17	1.0 [d]	0.05	–	2.0	2.5	17	2.5
Yield	48 [c]	76	62	11 [e]	72	14 [c]	43	73
COMPLEX	**23**	**24**	**25**	**26**	**26**	**28**	**29**	
Reaction time	24	0.6	2.0	0.25	17	0.6	0.6	
Yield	33	76	91 [c]	68	29	78 [c]	52	

[a] Reaction time of heterocyclic anion with chloroarene complex in DMSO at room temperature.
[b] 50° in 80% DMSO: ^{t}BuOH.
[c] Total yield of all isomers.
[d] Solvent 80% DMSO: ^{t}BuOH.
[e] Complex prepared via eqn. (7) using 4 h reflux in octane.

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