

## SYNTHESIS AND STRUCTURE OF $\eta^6$ -(BIPHENYL)- $\eta^5$ - (CYCLOPENTADIENYL)IRON(II) HEXAFLUOROPHOSPHATES

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### Summary

A series of  $\eta^6$ -(biphenyl)- $\eta^5$ -(cyclopentadienyl)iron(II) hexafluorophosphates have been prepared. Demethylation occurred during the synthesis of the 2'-OMe derivative to yield the corresponding 2'-OH product. The mechanism of this process is discussed. In all cases the complexation involved the unsubstituted phenyl ring. From  $^{13}\text{C}$  NMR data, values of Hammett resonance parameters,  $\sigma_{\text{R}}$ , were calculated which show that the  $[\text{CpFeC}_6\text{H}_5]^+$  group behaves as an electron-withdrawing substituent comparable in strength to the cyano group. Approximate values of the biphenyl interplanar angle ( $\theta$ ) were obtained.  $\theta$  appeared to be significantly lower when electron-releasing substituents were present.  $^{57}\text{Fe}$  Mössbauer data support the strong electron acceptor properties of the  $[\text{CpFe}^+\text{C}_6\text{H}_5]$  moiety. In particular the quadrupole splitting ( $QS$ ) shows a marked increase for the 4-OMe derivative relative to the unsubstituted complex. This is in direct contrast to the aryl ferrocenes. Here, the ferrocenyl and OMe substituents are electronically non-complementary, and so there is no  $QS$  enhancement.

### Introduction

Arene complexes of iron  $[\text{ArFeCp}]^+\text{X}^-$  have elicited much interest during the last decade particularly since the chemical properties of the arene are markedly different when complexed [1]. We have recently completed a Mössbauer investigation of some simple  $\text{ArFe}^+\text{Cp}$  derivatives [2] and have shown that the arene ligand causes marked attenuation in the range of quadrupole splittings ( $QS$ ). This is attributed to the dominance of back-bonding from the iron  $e_{2g}$  orbitals to  $\pi^*$  orbitals on the arene ligand. We have, in a parallel study examined aspects of the

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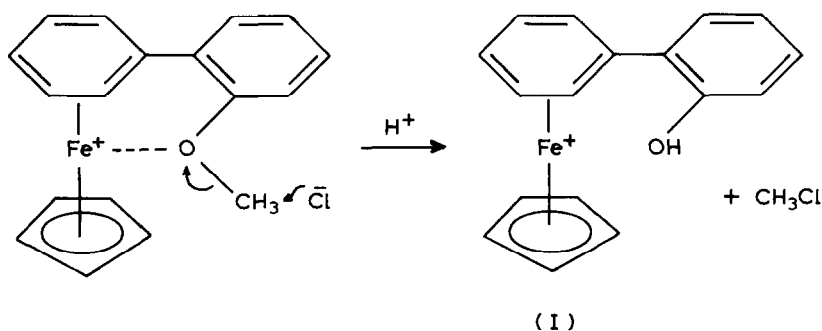
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electronic structure of novel biphenyl derivatives using Mössbauer and  $^{13}\text{C}$  spectroscopy. These complexes show some interesting features which are reported here.

### Discussion and results

$\eta^6$ -(Biphenyl)- $\eta^5$ -(cyclopentadienyl)iron(II) hexafluorophosphate [bph  $\text{Fe}^+\text{Cp}$ ]- $\text{PF}_6^-$  has been previously reported [3–6] together with its  $^{57}\text{Fe}$  Mössbauer spectrum [7]. The dication has also been synthesised [5] and its electronic structure investigated using polarography, electronic absorption and Mössbauer spectroscopy [6].

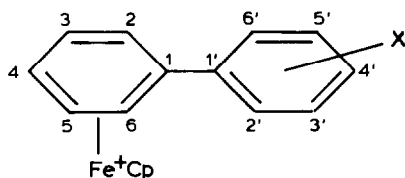
The syntheses of the complexes reported here  $[\text{C}_2\text{H}_5\text{Fe}^+\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{X}]\text{PF}_6^-$ , were accomplished by the literature method [8] using the reactant ratio biphenyl/ $\text{AlCl}_3$ / $\text{Al}$ /ferrocene of 1/2/1/1. The recommended addition of a stoichiometric quantity of water [8] did not appreciably enhance the yields. In all cases complexation was found to occur on the unsubstituted ring. This can be readily deduced from the  $^{13}\text{C}$  NMR chemical shifts of the complexed ring which decrease by about 40 ppm relative to the uncomplexed ring. This effect has been explained by back-donation of the  $e_{2g}$  metal based electron density into vacant  $\pi^*$  orbitals on the arene [9]. The regioselectivity shown in the complexation occurs even for strongly electron-releasing substituents such as OMe and  $\text{NH}_2$ . This behaviour is clearly the result of complexation of the substituent with  $\text{AlCl}_3$  which strongly deactivates the ring to attack by the  $\text{Fe}^+\text{Cp}$  moiety. Another interesting feature of these reactions is that whereas *p*-methoxybiphenyl complexes behave normally, the *O*-methoxy analogue undergoes demethylation during the reaction. This was confirmed by the lack of signals at 56 and 3.4 ppm in the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra respectively ( $\text{OCH}_3$ ), the calculated shifts (vide infra) and elemental analysis. The above observation indicates that the  $\text{ArFe}^+\text{Cp}$  moiety catalyses the demethylation process since no such reaction occurs in the synthesis of the *p*-methoxy derivative where the substituent unable to undergo such complexation. The demethylation probably involves nucleophilic attack by chloride ion. Such a displacement would not normally occur without a catalyst. The obvious candidate for such a catalytic role would be  $\text{AlCl}_3$ , but this apparently is not the case here. We therefore conclude that the  $\text{ArFe}^+\text{Cp}$  group itself acts as the catalyst as depicted below.



The 2'-OH product was readily soluble in water. The  $^{13}\text{C}$  NMR spectrum in  $\text{D}_2\text{O}$  showed a marked downfield shift of the  $\text{C}(2')$  signal from 155.3 (in acetone- $d_6$ ) to 163.2 ppm. This behaviour is typical of phenols. In view of the interaction described above, I should have an unusually low  $\text{p}K_a$ . Interestingly no dephenylation was

observed during the preparation of the 2'-Oph derivative. Two factors would mitigate against the above mechanism in this case. Firstly,  $S_N2$  reactions in benzene derivatives require very strong activation equivalent to two  $\text{NO}_2$  substituents, which is absent here. Secondly the *endo* conformation necessary for catalysis would be very unfavourable for the large OPh substituent.  $^{13}\text{C}$  data suggests a rather large interplanar angle for the biphenyl system for the OPh derivative (*vide infra*). It is thus likely that an *exo* conformation is preferred which would place the OPh group on the side of the sandwich remote from the iron atom.

We have been particularly interested in the transmission of resonance effects in such structures, both from the viewpoint of effects on  $^{57}\text{Fe}$  Mössbauer and  $^{13}\text{C}$  NMR spectroscopy [10,11]. This interest is reflected in the range of biphenyl complexes used here which include several *ortho*-substituted derivatives. The  $^{13}\text{C}$  NMR data listed in Tables 1 and 2 using the following numbering system.



We have very recently [2] shown that C(4) chemical shifts correlate well with Hammett substituent parameters  $\sigma_{\text{R}}^0$ ,  $\sigma_{\text{R}}^+$  and  $\sigma_{\text{R}}^-$ . Using the equations developed, values of these constants for the  $\text{C}_5\text{H}_5\text{Fe}^+\text{C}_6\text{H}_5$  group are calculated as 0.08, 0.04 and 0.18, respectively. As a comparison, the corresponding values for a cyano substituent are 0.08, 0.08 and 0.26 [12] and those calculated for a ferrocenyl substituent  $-0.26$ ,  $-0.11$  and  $-0.24$ , respectively. This shows the  $\text{ArFe}^+\text{Cp}$  group to be a strong electron-withdrawing substituent. From the unsubstituted biphenyl complex itself, additivity factors [ $C_{\text{ipso}} + 6.8$ ,  $C_{\text{ortho}} - 0.6$ ,  $C_{\text{meta}} + 1.1$  and  $C_{\text{para}} + 1.8$  ppm] can be used to compute shifts and thus aid assignments. For the most part the agreement between the observed and calculated values is good, the exceptions being those carbons close to the interannular link in the 2' derivatives. A rough assessment of  $\theta$ , the interplanar dihedral angle, may be made using the method of Dhimi and Stothers [13] which was modified in these laboratories for biphenyls [14]. The following relationship was found

$$\cos^2\theta = \frac{\Delta^x - \Delta^{90}}{\Delta^0 - \Delta^{90}} = \frac{\Delta^x - 10.9}{3.6} \quad (1)$$

where  $\Delta^x$ ,  $\Delta^0$  and  $\Delta^{90}$  are the values of  $\delta(\text{C}(1)) - \delta(\text{C}(4))$  for the compound under consideration, and model system where  $\theta = 0^\circ$  and  $90^\circ$  respectively. Unfortunately, model systems for the  $\theta = 90^\circ$  case are not at present available for the biphenyl complexes. However, an indirect method can be used to gain a crude estimate of  $\theta$ .

The following correlations were found between the chemical shifts in the complexed ring  $\delta^{\text{C}}(\text{fe})$  and the corresponding ring in the biphenyl precursor (BP), and also between the uncomplexed ring  $\delta^{\text{UC}}(\text{fe})$  and that of the parent system


$$\delta^{\text{C}}(\text{fe}) = 1.24 \delta(\text{BP}) - 70.0 \quad [N = 30, r = 0.970] \quad (2)$$

$$\delta^{\text{UC}}(\text{fe}) = 0.94 \delta(\text{BP}) + 7.6 \quad [N = 32, r = 0.952] \quad (3)$$

(Continued on p. 252)

TABLE 1

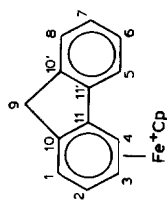
 $^{13}\text{C}$  CHEMICAL SHIFTS <sup>a</sup> FOR BIPHENYLCYCLOPENTADIENYLIRON(II) (feBP) COMPLEXES AND THEIR UNCOMPLEXED PRECURSORS (BP)



Compound	C(1)	C(2),C(6) <sup>b</sup>	C(3),C(5) <sup>b</sup>	C(4)	C(1')	C(2')	C(3')	C(4')	C(5')	C(6')	Cp	others
feBP	104.1	86.5	88.5	87.6	135.3	127.9	129.6	130.6	129.6	127.9	77.9	-
BP	141.4	127.3	129.3	127.7	141.4	127.3	129.3	127.7	129.3	127.3	-	-
2'-OH-feBP	103.3	87.9	88.1	87.1	121.2	155.3	117.0	131.1	120.9	131.6	77.5	-
2'-OH-BP	139.5	128.8	130.0	127.5	(122.6)	(154.8)	(116.9)	(131.7)	(122.3)	(129.3)	-	-
4'-OMe-feBP	104.9	86.3	89.1	87.7	(120.9) <sup>c</sup>	(159.3) <sup>c</sup>	(115.1) <sup>c</sup>	(131.3) <sup>c</sup>	(121.9) <sup>c</sup>	(128.5) <sup>c</sup>	-	-
4'-OMe-BP	141.4	127.1	129.5	127.3	127.6	130.0	115.8	162.3	115.8	130.0	78.5	56.0 Me
2'-OPh-feBP	104.8	90.7	91.2	90.3	(127.6)	(128.9)	(115.2)	(161.7)	(115.2)	(128.9)	-	-
2'-OPh-BP	138.1	128.4	130.0	124.6	134.1	128.6	115.1	160.2	115.1	128.6	-	55.7 Me
2'-NH <sub>2</sub> -feBP	104.9	88.5	89.5	88.0	128.6	157.9	127.0	134.4	127.1	134.5	80.4	- <sup>d</sup>
2'-NH <sub>2</sub> -BP	140.8	129.5	129.6	130.9	(125.9)	(157.1)	(120.2)	(131.9)	(124.5)	(129.5)	-	-
2'-Br-feBP	106.8	88.1	90.5	88.8	134.1	147.3	117.8	129.2	123.0	131.5	-	-
2'-Br-BP	141.4	128.3	129.6	129.3	121.8	(145.9)	(116.3)	(131.2)	(120.6)	(128.8)	81.9	-
					(122.0)	145.4	115.6	128.2	119.1	128.3	-	-
					136.6	123.4	134.5	133.0	129.7	132.1	78.7	-
					(138.7)	(122.4)	(133.0)	(132.0)	(128.0)	(129.6)	-	-
					142.8	122.5	133.4	128.0	131.7	128.0	-	-

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> Where values differ by less than 1 ppm, assignments must be regarded as arbitrary. <sup>c</sup> Calculated for methoxy substituent. <sup>d</sup> 158.8, 133.0, 121.0, 121.1 Ph. <sup>e</sup> 158.2, 129.4, 120.6, 118.1 Ph.

TABLE 2  
 $^{13}\text{C}$  CHEMICAL SHIFTS FOR  $\eta^6$ -(FLUORENYL)- $\eta^5$ -(CYCLOPENTADIENYL)IRON(II) HEXAFLUOROPHOSPHATE (I) <sup>a</sup> AND FLUORENE (II) <sup>b</sup>



Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(10')	C(11')	Cp
I	86.0	86.3	86.7	81.0	122.9	130.8	128.3	126.5	37.8	107.5	105.5	144.7	138.1	78.4
II	124.5	126.6	126.6	119.8	119.8	126.6	126.6	126.0	36.8	143.1	141.6	143.1	141.6	-

<sup>a</sup> Data from Ref. 16. <sup>b</sup> Data from Ref. 15.

The data also includes the results from the planar fluorenyl system [15,16] (Table 2). The correlation of the complexed ring data is much better than that of the free ring and has a significantly greater slope. This indicates that the range of  $^{13}\text{C}$  shifts is about 24% greater than in the free biphenyl. Accordingly, eq. 1 can be modified to account for this increase

$$\cos^2\theta = \frac{\Delta^x - 13.5}{4.5} \quad (4)$$

Using the data in Table 1 the following angles are calculated for the various substituted complexes H 35, 4-OMe 25, 2-OH 39, 2-NH<sub>2</sub>, 30, 2 OPh 62, 2-Br 0 and fluorenyl 0°. These values are of necessity crude, and probably overestimate  $\theta$ . Nevertheless the order appears realistic with the exception of the 2-Br derivative which has an anomalously high value for  $\delta(\text{C}(1))$  due probably to direct field effects. In particular, the 4-OMe derivative shows a lower  $\theta$  than that of the parent biphenyl complex. In view of the strong electron-withdrawing capacity of the  $\text{ArFe}^+\text{Cp}$  substituent, this is quite understandable, and is further supported by Mössbauer data (vide infra).

The complimentary nature of the  $\text{ArFe}^+\text{Cp}$  and OMe substituents is illustrated in the  $^1\text{H}$  NMR spectra (Table 4). For the uncomplexed biphenyl, the protons in the OMe substituted ring appear as an AB doublet ( $J$  8 Hz) with a shift separation ( $\Delta\delta$ ) of 0.56 ppm. On complexation  $\Delta\delta$  increases to 0.84 ppm.

For 2' substituents, a compromise is reached between resonance and steric effects. The NH<sub>2</sub> group is a considerably stronger +M donor than OH as judged by the relative  $\sigma_{\text{R}}^+$  values of -1.10 and -0.64. Interestingly, the 2'-NH<sub>2</sub> derivative shows a lower value of  $\theta$  than the 2'-OH analogue which is in keeping with the stronger resonance effects. For the much bulkier OPh group ( $\sigma_{\text{R}}^+ = -0.48$ ) a much larger angle is apparent.

### Mössbauer results

The  $^{57}\text{Fe}$  Mössbauer parameters appear in Table 3. Only one value [7] has previously appeared, that for the biphenyl complex itself and this as the  $\text{BF}_4^-$  rather than the  $\text{PF}_6^-$  salts listed here. Our own values are self-consistent and reproducible

TABLE 3

$^{57}\text{Fe}$  MÖSSBAUER PARAMETERS: ISOMER SHIFT ( $IS$ ), QUADRUPOLE SPLITTING ( $QS$ ) AND LINEWIDTH AT HALF-HEIGHT  $\tau_{\frac{1}{2}}$  (all in  $\text{mm s}^{-1}$ ) FOR  $[\text{C}_5\text{H}_5\text{Fe}^+\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_4\text{X}]\text{PF}_6^-$  COMPLEXES AT 80 K

X	IS	QS	$\tau_{\frac{1}{2}}$
H	0.53(1) 0.52 <sup>a</sup>	1.63(1) 1.45 <sup>a</sup>	0.18(1)
<i>p</i> -Ph	0.53(1)	1.67(1)	0.17(1)
<i>p</i> -OMe	0.54(1) 0.52(1)	1.73(1) 1.71(1)	0.17(1) 0.16(1)
<i>o</i> -OH	0.52(1)	1.67	0.17(1)
<i>o</i> -Br	0.51(1)	1.62(1)	0.25(1)
<i>o</i> -OPh	0.54(1)	1.69(1)	0.16(1)
<i>o</i> -NH <sub>2</sub>	0.53(1)	1.67(1)	0.14(1)

<sup>a</sup>  $\text{BF}_4^-$  salt Ref. 7.

TABLE 4

REACTION CONDITIONS <sup>a</sup>, YIELDS AND <sup>1</sup>H NMR SPECTRA FOR THE SYNTHESIS OF [C<sub>5</sub>H<sub>5</sub>Fe<sup>+</sup>C<sub>6</sub>H<sub>5</sub>·C<sub>6</sub>H<sub>4</sub>X] PF<sub>6</sub><sup>-</sup> COMPLEXES

X	Solvent	T (°C)	Reaction time (h)	Yield (%)	<sup>1</sup> H NMR <sup>b</sup>
H	decalin	100	3	11	<sup>c</sup>
4'-OMe	cyclohexane	80	3	8	7.51 (d, 2H, <i>J</i> 8 Hz, H(2',5')), 6.67 (d, 2H, <i>J</i> 8 Hz, H(3',5')), 6.1 (m, 5H, H(2-5)), 4.58 (s, 5H, Cp), 3.45 (s, 3H, OCH <sub>3</sub> )
2'-OH	methylcyclohexane	100	5.5	3	5.8-7.2 (m, 9H, H(2-6) and H(3'-6')), 4.55 (s, 5H, Cp)
2'-OPh	cyclohexane	80	4	18	5.7-7.2 (m, 14H), 4.65 (s, 5H, Cp)
2'-NH <sub>2</sub>	cyclohexane	80	4	12	6.8-7.0 (s, 4H, H(3'-6')), 6.1 (br s, 5H, H(2-6)) 4.60 (s, 5H, Cp)
2'-Br	cyclohexane	80	4	8	7.0-8.0 (m, 4H, H(3'-6')), 6.20 (s, 5H, H(2-6)) 4.81 (s, 5H, Cp)

<sup>a</sup> Ratio arene/AlCl<sub>3</sub>/Al/ferrocene was 1/2/1/1. <sup>b</sup> Shifts (δ) in ppm from external TMS. s = singlet, d = doublet, m = multiplet. <sup>c</sup> See Ref. 3.

and even allowing for small anion effects noted previously [17] considerable doubt must attach to the reported quadrupole splitting (*QS*) of 1.45 mm s<sup>-1</sup>.

For aryl ferrocenes with electron withdrawing groups (e.g. NO<sub>2</sub>) in the *para* position of the phenyl ring, the Cp and arene rings are coplanar in the solid state [18]. This is a result of minimum steric factors and the complimentary nature of the ferrocenyl group (+M) and the nitro substituent (-M) which results in strong resonance interaction which is maximised at  $\theta = 0$ . The situation is reversed with the CpFe<sup>+</sup>C<sub>6</sub>H<sub>5</sub> group which is a strong -M substituent. Consequently a low value of  $\theta$  is expected for a *para*-methoxy group (+M). This effect is nicely demonstrated in the Mössbauer data by comparing the effect of a *p*-OMe on the aryl ferrocenes with that on the (biphenyl)Fe<sup>+</sup>Cp system. For the phenyl ferrocenes, the unsubstituted complex has a *QS* of 2.30 mm s<sup>-1</sup> and this is unchanged (within experimental error) when a *p*-OMe group is present. A *p*-NO<sub>2</sub> group, however, causes a significant reduction in *QS* as expected [19]. For CpFe<sup>+</sup>C<sub>6</sub>H<sub>5</sub>·C<sub>6</sub>H<sub>5</sub> a *QS* of 1.63 mm s<sup>-1</sup> is observed whereas for CpFe<sup>+</sup>C<sub>6</sub>H<sub>5</sub>·C<sub>6</sub>H<sub>4</sub>-*p*-OMe a marked increase occurs (1.72 mm s<sup>-1</sup>). As expected, *ortho*-substituted oxygen and nitrogen substituents show intermediate behaviour in keeping with an increased value of  $\theta$ . The *ortho* bromo substituent has no real effect on the *QS* though it is not possible in the case to assess  $\theta$ . The Br substituent has a  $\sigma_R^+$  of -0.19 thus even if a coplanar conformation were possible, the electronic effect would be considerably smaller than that of an OH group. The *QS* value for the *p*-terphenyl complex suggests that there is some resonance contribution from the remote phenyl ring.

### Experimental

The  $\eta^6$ -(biphenyl)- $\eta^5$ -(cyclopentadienyl)iron(II) hexafluorophosphates were synthesised by standard procedures [3]. Yields, reaction conditions, and <sup>1</sup>H NMR

data appear in Table 4. In view of the demethylation of the 2'-OMe derivative, an elemental analysis was obtained (Analytical Dept. University of Manchester). Found: C, 45.9; H, 3.2. 2'-OMe substituent calc. C, 48.0; H, 3.8%. 2'-OH substituent calc: C, 46.8; H, 3.5%. <sup>1</sup>H NMR were run on a Varian EM 360 instrument and <sup>13</sup>C spectra obtained using a Bruker WP 80 FT spectrometer. Mössbauer spectra were obtained and fitted as described previously [20,21].

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