Synthesis and Characterisation of Pentaphenylcyclopentadienyliron Arene Sandwich Complex Cations $[Fe(\eta^5-C_5Ph_5)(arene)]^+$ and the X-Ray Crystal Structure of the $[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6H_5Me)]^+$ Cation†

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A series of $[Fe(\eta^5-C_5Ph_5)(\eta^6-arene)]^+$ complex cations [arene = benzene, toluene, *o*-, *m*- and *p*-xylene, mesitylene, durene (1,2,4,5-tetramethylbenzene) or hexamethylbenzene] is reported. The structure of the cation of the toluene derivative was determined by single-crystal X-ray diffraction [refined to R 0.034, R' 0.038 with 4328 data having $I \geqslant 2.5\sigma(I)$]. It crystallises from acetone as discrete molecules in the monoclinic space group $P2_1/n$, with $a = 10.016(2)$, $b = 21.568(6)$, $c = 16.920(4)$ Å, $\beta = 92.17(2)°$ and $Z = 4$. The cyclopentadienyl ring binds in an η^5 fashion and the Fe–C (C_5 ring) bond distances average 2.093(3) Å; the Fe–C (C_6 ring) bond distances average 2.113(4) Å. The Fe–C (C_5 ring plane) and Fe–C (C_6 ring plane) distances are 1.702(5) and 1.588(5) Å, respectively. All complexes exhibit two reversible reductions.

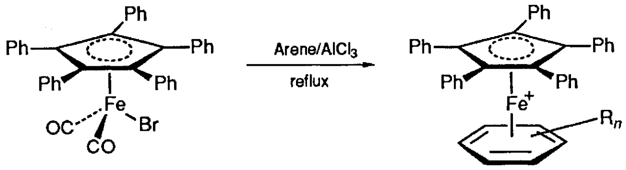
Over the past two decades there has been considerable interest in transition-metal complexes containing substituted cyclopentadienyl ligands. Most work has utilised the pentamethylcyclopentadienyl group, and much important new chemistry has been made possible using this modified ligand. Comparatively little use has been made of the related pentaphenylcyclopentadienyl group, which is expected to exert considerably different steric and electronic effects than either C_5Me_5 or C_5H_5 on the metals to which it binds.

Metal complexes of C_5Ph_5 are relatively rare: among the complexes of Fe,[1–4] the open sandwich $[Fe(\eta^5-C_5Ph_5)(CO)_2Br]$ is the only structurally characterised derivative.[2] The cation $[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6H_6)]^+$ was reported briefly by McVey and Pauson.[1] Neutral cyclopentadienyliron arene complexes[5] which have nineteen valence electrons have been used previously as electron-transfer reagents[6,7] but these complexes are often thermally unstable. The C_5Me_5 ligand confers stability on 19-electron metal centres[8] and the C_5Ph_5 ligand is expected considerably to modify the electronic states of these species.

We report here the synthesis and characterisation of a series of related arene complexes $[Fe(\eta^5-C_5Ph_5)(\eta^6-arene)]X$ [arene = benzene, toluene, *o*-, *m*- and *p*-xylene, mesitylene, durene (1,2,4,5-tetramethylbenzene) and hexamethylbenzene] and the structural characterisation of $[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6H_5Me)]^+$ with a mixed tetrahalogenoferrate anion.

Results and Discussion

Syntheses of Complexes.—The $[Fe(\eta^5-C_5Ph_5)(\eta^6-arene)]X$ complexes **1**–**6** were prepared in yields of 20–50% by reaction of the open sandwich complex $[Fe(\eta^5-C_5Ph_5)(CO)_2Br]$ with aluminium chloride and the appropriate arene as solvent under an inert atmosphere. For the durene and hexamethylbenzene derivatives, **7** and **8**, chlorobenzene was employed as a reaction solvent and the arene was present in excess (Scheme 1).



	R_n
1	H
2	Me
3	Me_2-1,2
4	Me_2-1,4
5	Me_2-1,3
6	Me_3-1,3,5
7	Me_4-1,2,4,5
8	Me_6

Scheme 1

Reaction mixtures were decomposed with water and the products were recrystallised in air from methanol. In the absence of other counter ions, the complexes crystallised as salts with mixed $[FeBr_xCl_{4-x}]^-$ anions which presumably arise from partial decomposition of the starting material with regeneration of C_5Ph_5. When solutions of $[Fe(\eta^5-C_5Ph_5)(\eta^6-arene)][FeX_4]$ were treated with methanol solutions of sodium tetrafluoroborate, metathesis readily afforded the corresponding tetrafluoroborate salts. In a similar fashion, tetraphenylborate salts could be isolated by treating methanol solutions of the $[Fe(\eta^5-C_5Ph_5)(\eta^6-arene)][FeX_4]$ salts with sodium tetraphenylborate, followed by recrystallisation from acetone.

In the ^{13}C NMR spectra of each of complexes **1**–**8** four resonances due to the monosubstituted phenyl rings of C_5Ph_5 are observed at low field (δ 120–145) and the carbons of the C_5 ring are observed to higher field (approximately 95 ppm). The ^{13}C NMR resonances of the η^6-C_6 rings appear in the region δ 80–100. At room temperature there is no evidence for any restricted rotation about the C–Ph bonds in the C_5Ph_5 group. Similarly, in those complexes containing η^6-arene ligands with one, two, three or four methyl substituents, rotation about the $Fe-C_5Ph_5$ and/or iron–arene bonds is rapid on the NMR timescale. Proton NMR spectra show the expected chemical shifts

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Positional parameters (× 10^4) for $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5Me)][FeX_4]$

Atom	*x*	*y*	*z*	Occupancy
Fe(1)	6 296(1)	4 418(1)	2 833(1)	
C(1)	4 611(3)	3 934(1)	2 371(2)	
C(2)	4 688(3)	3 899(1)	3 222(2)	
C(3)	5 925(3)	3 606(1)	3 453(2)	
C(4)	6 607(3)	3 463(1)	2 751(2)	
C(5)	5 809(3)	3 672(1)	2 084(2)	
C(6)	3 406(3)	4 104(2)	1 879(2)	
C(7)	3 587(3)	4 063(2)	3 756(2)	
C(8)	6 323(3)	3 394(2)	4 262(2)	
C(9)	7 843(3)	3 088(2)	2 714(2)	
C(10)	6 075(3)	3 552(2)	1 244(2)	
C(11)	3 462(4)	4 476(2)	1 220(2)	
C(12)	2 323(5)	4 585(2)	751(2)	
C(13)	1 129(4)	4 313(2)	930(3)	
C(14)	1 061(4)	3 927(2)	1 576(3)	
C(15)	2 190(3)	3 831(2)	2 051(2)	
C(16)	2 874(4)	4 611(2)	3 672(2)	
C(17)	1 780(4)	4 728(2)	4 121(2)	
C(18)	1 381(4)	4 295(2)	4 663(2)	
C(19)	2 081(4)	3 750(2)	4 759(2)	
C(20)	3 179(3)	3 630(2)	4 306(2)	
C(21)	6 386(4)	3 788(2)	4 917(2)	
C(22)	6 709(5)	3 551(2)	5 654(2)	
C(23)	6 936(4)	2 928(3)	5 764(2)	
C(24)	6 843(4)	2 537(2)	5 127(2)	
C(25)	6 549(3)	2 768(2)	4 375(2)	
C(26)	7 841(4)	2 584(2)	2 198(2)	
C(27)	8 948(4)	2 203(2)	2 175(3)	
C(28)	10 053(4)	2 318(2)	2 656(3)	
C(29)	10 062(3)	2 807(2)	3 173(2)	
C(30)	8 963(3)	3 192(2)	3 205(2)	
C(31)	5 154(3)	3 217(2)	785(2)	
C(32)	5 394(4)	3 067(2)	12(2)	
C(33)	6 562(5)	3 245(2)	−312(2)	
C(34)	7 484(5)	3 564(3)	133(3)	
C(35)	7 256(4)	3 720(2)	901(2)	
C(36)	6 477(4)	5 302(2)	2 216(3)	
C(37)	5 871(5)	5 369(2)	2 942(3)	
C(38)	6 459(5)	5 143(2)	3 646(3)	
C(39)	7 669(4)	4 832(2)	3 622(3)	
C(40)	8 285(4)	4 737(2)	2 905(3)	
C(41)	7 682(4)	4 966(2)	2 224(3)	
C(42)	5 909(6)	5 601(3)	1 484(3)	
Fe(2)	4 423(1)	1 408(1)	2 761(1)	
Cl(1)	3 848(1)	2 398(1)	2 847(1)	0.8070(30)
Br(1)	3 848(1)	2 398(1)	2 847(1)	0.1930(30)
Cl(2)	5 705(1)	1 129(1)	3 820(1)	0.6850(32)
Br(2)	5 705(1)	1 129(1)	3 820(1)	0.3150(32)
Cl(3)	0(1)	5 458(1)	1 258(1)	0.6449(33)
Br(3)	0(1)	5 458(1)	1 258(1)	0.3551(33)
Cl(4)	1 624(1)	2 576(1)	856(1)	0.9244(30)
Br(4)	1 624(1)	2 576(1)	856(1)	0.0756(30)

Table 2 Selected bond lengths (Å) for $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5Me)][FeX_4]$

C(1)–Fe(1)	2.109(3)	C(2)–Fe(1)	2.089(3)
C(3)–Fe(1)	2.083(3)	C(4)–Fe(1)	2.088(3)
C(5)–Fe(1)	2.094(3)	C(36)–Fe(1)	2.184(4)
C(37)–Fe(1)	2.104(4)	C(38)–Fe(1)	2.085(4)
C(39)–Fe(1)	2.081(4)	C(1)–C(2)	1.440(4)
C(2)–C(3)	1.432(4)	C(3)–C(4)	1.426(4)
C(4)–C(5)	1.430(4)	C(5)–C(1)	1.429(4)
C(36)–C(37)	1.399(7)	C(37)–C(38)	1.398(7)
C(38)–C(39)	1.387(6)	C(39)–C(40)	1.397(7)
C(40)–C(41)	1.373(6)	C(41)–C(36)	1.408(5)

Table 3 Selected bond angles (°) for $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5Me)][FeX_4]$

C(2)–Fe(1)–C(1)	40.1(1)	C(3)–Fe(1)–C(1)	67.3(1)
C(3)–Fe(1)–C(2)	40.2(1)	C(4)–Fe(1)–C(1)	66.8(1)
C(4)–Fe(1)–C(2)	67.1(1)	C(4)–Fe(1)–C(3)	40.0(1)
C(5)–Fe(1)–C(1)	39.7(1)	C(5)–Fe(1)–C(2)	67.3(1)
C(5)–Fe(1)–C(3)	67.4(1)	C(5)–Fe(1)–C(4)	40.0(1)
C(36)–Fe(1)–C(1)	109.6(1)	C(36)–Fe(1)–C(2)	134.2(1)
C(36)–Fe(1)–C(3)	174.0(1)	C(36)–Fe(1)–C(4)	144.5(1)
C(36)–Fe(1)–C(5)	113.8(1)	C(37)–Fe(1)–C(1)	110.7(2)
C(37)–Fe(1)–C(2)	109.5(2)	C(37)–Fe(1)–C(3)	137.3(2)
C(37)–Fe(1)–C(4)	176.6(2)	C(37)–Fe(1)–C(5)	139.4(2)
C(37)–Fe(1)–C(36)	38.0(2)	C(38)–Fe(1)–C(1)	131.1(2)
C(38)–Fe(1)–C(2)	103.6(2)	C(38)–Fe(1)–C(3)	108.0(1)
C(38)–Fe(1)–C(4)	140.7(1)	C(38)–Fe(1)–C(5)	170.4(2)
C(38)–Fe(1)–C(36)	69.9(2)	C(38)–Fe(1)–C(37)	39.0(2)
C(39)–Fe(1)–C(1)	161.8(2)	C(39)–Fe(1)–C(2)	121.8(2)
C(39)–Fe(1)–C(3)	99.4(1)	C(39)–Fe(1)–C(4)	111.6(1)
C(39)–Fe(1)–C(5)	148.3(1)	C(39)–Fe(1)–C(36)	82.4(2)
C(39)–Fe(1)–C(37)	69.9(2)	C(39)–Fe(1)–C(38)	38.9(2)

and H–H coupling patterns with the protons of the coordinated arenes shifted to slightly higher field (to δ *ca.* 6.5) with respect to the normal aromatic region.

Crystal Structure of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5Me)][FeX_4]$.—Positional parameters, selected interatomic bond distances and angles derived from the refinement of the structure of complex **2** are given in Tables 1, 2 and 3. The atomic nomenclature is defined in Fig. 1. Figs. 1 and 2 depict the molecular geometry viewed down the C_5 axis of the C_5Ph_5 ligand, and approximately perpendicular to it, respectively. The crystal structure confirms that in the solid state the C_5Ph_5 ligand is bound in an η^5 fashion *via* the five-membered ring and not in an η^6 fashion *via* a phenyl substituent.

Surprisingly few crystal structures have been reported for alkyl-substituted $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})]^{n+}$ complexes in either the 18- or 19-electron configuration. Although analytically pure samples of the $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-arene})]$ complexes could be obtained as the BF_4^- and BPh_4^- salts, only the mixed $[FeBr_xCl_{4-x}]^-$ salt afforded crystals suitable for structural analysis.

(*i*) *The iron centre of the cation.* The iron atom is sandwiched between the planar and near-parallel C_5 and C_6 rings at distances of 1.70 and 1.59 Å, respectively, from the planes of each. The analogous iron–ring distances in the neutral complexes $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ **12**[7] and $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_6Me_5CH_2)]$ **11**[9] are 1.79(1) (C_5H_5), 1.58(1) (arene) and 1.66(1) (C_5H_5), 1.54(1) Å (arene), respectively. For both of the cations $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Et_6)]^+$ [10] and $[Fe(\eta^5\text{-}C_5Me_5)(\eta^6\text{-}C_6Et_5H)]^+$ [11] the corresponding distances are 1.68 Å (C_5H_5), 1.55 Å (arene). In contrast to the cationic complexes **9** and **10**, $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5Me)][FeX_4]$ exhibits significantly longer iron–arene bond distances, despite the greater bulk of the ethyl groups in **9** and **10** compared to the lone methyl in **2**. Similarly, the Fe–C_5 and iron–arene distances of **2** are greater than those of the formally 18-electron species $[Fe(\eta^5\text{-}C_6Me_5CH_2)]$ **11**.[9] The 19-electron species $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6Me_6)]$ however has a longer Fe–C_5 bond distance, consistent with the presence of the extra electron in an antibonding e^*_{1g} orbital. The Fe–C_5Ph_5 distance in $[Fe(\eta^5\text{-}C_5Ph_5)(CO)_2Br]$ **13** is 1.74 Å.[2] The Fe–C_5H_5 distances of derivatives fall into two broad categories: essentially undistorted $Fe(\eta^5\text{-}C_5H_5)_2$ derivatives and $[Fe(\eta^5\text{-}C_5H_5)L^1L^2L^3]$ derivatives,[12] being shorter in the former than in the latter. The complex $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5Me)][FeX_4]$ exhibits an iron–ring distance which is intermediate between those of the two groups.

The iron centre is approximately coincident with the projection of the centroid of the C_5 ring but is displaced

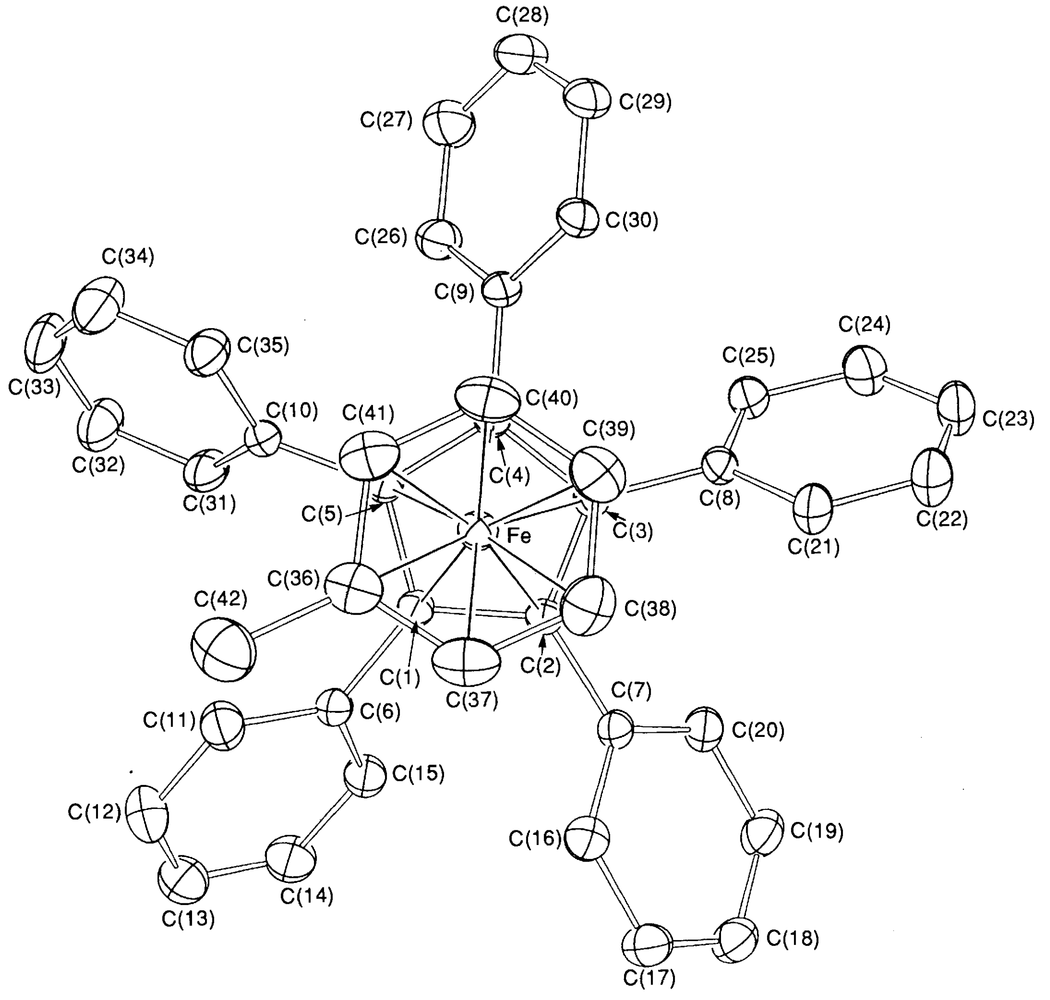

Fig. 1 ORTEP (30% probability) plot of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5Me)]^+$ **2**, viewed along the normal to the C_5Ph_5 plane

Table 4 Oxidation and reduction potentials for $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-arene})][BPh_4]$ complexes in tetrahydrofuran

		First reduction			Second reduction			Ferrocenium–ferrocene standard	
Compound	Arene	$\Delta E_p{}^a$	$E_{\frac{1}{2}}{}^b$	$(i_p)_{rev}/(i_p)_{for}$	$\Delta E_p{}^a$	$E_{\frac{1}{2}}{}^b$	$(i_p)_{rev}/(i_p)_{for}$	$\Delta E_p{}^a$	$(i_p)_{rev}/(i_p)_{for}$
1	Benzene	74	−1446	0.9	93	−2408	0.6	78	1.0
2	Toluene	67	−1443	0.8	69	−2422	0.5	51	1.0
3	*o*-Xylene	70	−1462	0.9	72	−2444	0.5	74	1.0
4	*o*-Xylene	75	−1441	1.0	92^c	−2449	0.6	79	1.0
5	*m*-Xylene	68	−1476	0.8	81	−2462	0.5	74	0.9
6	Mesitylene	87	−1506	0.9	105^c	−2474	~0.6	86	1.0
7	Durene	70	−1502	0.8	89	−2471	0.7	73	0.9
8	C_6Me_6	113	−1470	0.8	82	−2507	1.0	73	1.0

[a] In mV, scan rate 100 mV s^{-1}, 100% *iR* compensation. [b] In mV *vs.* ferrocenium–ferrocene. [c] Scan rate 1000 mV s^{-1}, 100% *iR* compensation, irreversible at 100 mV s^{-1}.

significantly from the projection of the centroid of the toluene ligand, *i.e.* the toluene moiety is 'slipped' relative to the $[Fe(\eta^5\text{-}C_5Ph_5)]^+$ fragment. The Fe–C(36) (toluene *ipso*-C) distance in **2** (2.184 Å) is significantly longer than the distances between the iron atom and other arene carbon atoms (average 2.099 Å), indicative of the strong steric influence of the lone methyl group. Atom C(36) is also displaced significantly out of the plane of the arene carbon atoms and away from the iron centre. The C_5-ring carbons nearest to the toluene methyl group also exhibit the longest Fe–C bond lengths. The *ipso* carbons on the substituent phenyl rings are all bent away from the iron and hence away from the η^6-co-ordinated toluene ligand. This effect is most dramatic for the phenyl rings closest to the methyl group.

(*ii*) *The ligand structure.* The C_5 ring, the phenyl substituents of the C_5Ph_5 ligand and the aromatic ring of the toluene group are planar to within 0.014, 0.020 and 0.031 Å, respectively. The C–C–C angles in the C_5 ring are equal within experimental error and are typical for a C_5 ring. The C–C bond lengths in the C_5 ring average 1.431(4) Å, similar to that observed for $[Fe(\eta^5\text{-}C_5Ph_5)(CO)_2Br]$,[2] but significantly longer than those of ferrocene.[13–16] The *ipso* carbon atoms of each of the phenyl rings are located out of the C_5 plane by 0.14–0.24 Å (average 0.18 Å)

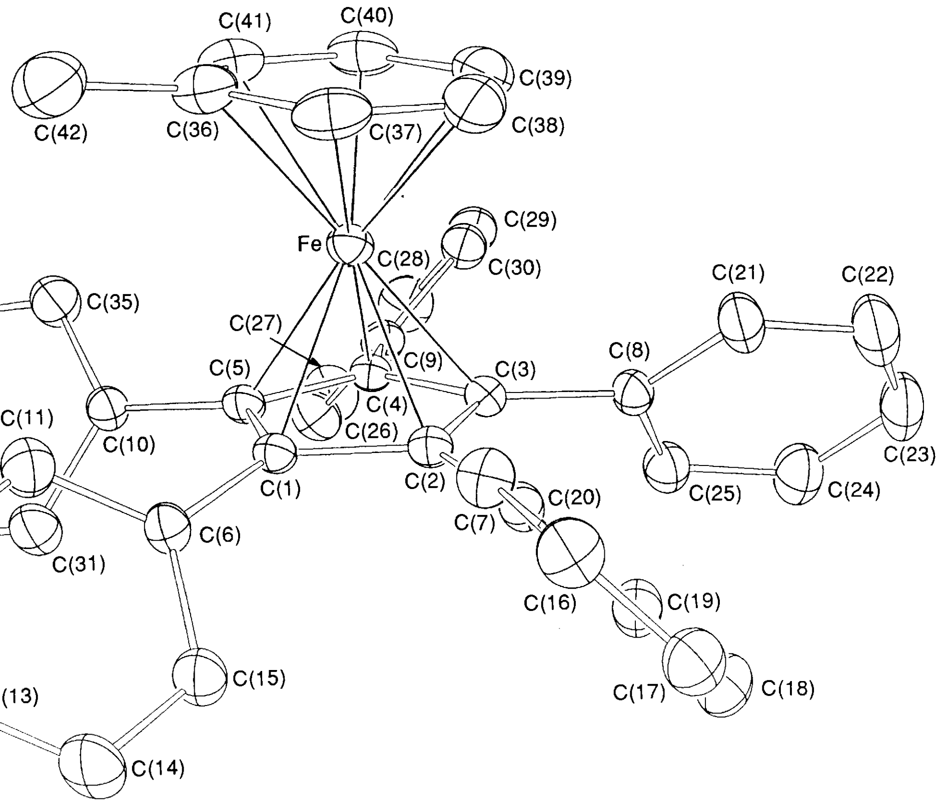

Fig. 2 ORTEP (30% probability) plot of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5Me)]^+$ **2** viewed parallel to the C_5Ph_5 plane

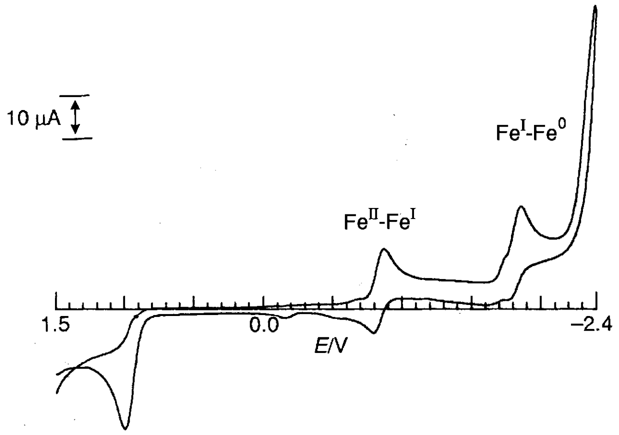

Fig. 3 Cyclic voltammogram of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_4Me_2\text{-}1,2)]$-$[BPh_4]$ **3** in tetrahydrofuran solution (glassy carbon working electrode, potential range −2400 to 1500 mV *vs.* ferrocenium–ferrocene, scan rate 50 mV s^{-1})

away from the iron atom. The phenyl rings are canted at angles of 51.4, 48.0, 56.3, 48.0 and 55.4° (average 51.4°) with respect to the C_5 ring. These values compare with those observed[2] in $[Fe(\eta^5\text{-}C_5Ph_5)(CO)_2Br]$ of 59.7, 37.2, 59.3, 87.4 and 49.1° (average 58.7°). The significantly increased coplanarity of the phenyl rings and C_5 ring in $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5Me)]$-$[FeX_4]$ suggest that the toluene is more sterically demanding than the two carbonyls and bromine ligands in the open-sandwich complex $[Fe(\eta^5\text{-}C_5Ph_5)(CO)_2Br]$. In **2** the toluene and C_5Ph_5 ligands are tilted with respect to each other at an angle of 6.0(5)°, consistent with steric repulsion by the methyl group.

Electrochemistry.—Complexes **1**–**8** (as their tetraphenylborate salts) were examined by cyclic voltammetry in tetrahydrofuran solution (with 0.1 mol dm^{-3} tetrabutylammonium tetrafluoroborate as electrolyte) using a glassy carbon electrode. Each complex exhibited two reduction processes in the ranges −1440 to −1510 and −2400 to −2510 mV *vs.* ferrocenium–ferrocene[17] with equal cathodic currents (Fig. 3, Table 4).

Controlled-potential coulometry on complex **1** in tetrahydrofuran at −1050 mV *vs.* saturated calomel electrode (SCE) using a mercury-pool working electrode confirmed that the first reduction was a one-electron process on the coulometric time-scale. The resulting solution was deep green, typical of nineteen-electron cyclopentadienyliron arene complexes.[6–8] However, if the potential was applied for long periods of time the measured charge gradually increased and the colour of the solution changed to yellow-brown. By comparison of the peak heights observed with cyclic voltammetry, it can be concluded that the second reduction is also a one-electron process. The peak potentials for both (first and second) reductions tended to more negative potentials with increased methylation on the co-ordinated arene ligand although not in a regular progession (Table 4). This trend is consistent with the methyl groups on the arene acting as electron donors and this type of substituent effect has been noted previously[8] in Fe–C_5H_5-arene complexes. The non-regular progression may be due, in part, to steric factors.

In general, the first reduction process ($Fe^{II} \longrightarrow Fe^I$) for all complexes is close to being electrochemically reversible at a scan rate of 100 mV s^{-1} with a peak-to-peak separation in the range 60–80 mV for most of the complexes, characteristic of a one-electron couple (Table 4). The two exceptions are the mesitylene and hexamethylbenzene derivatives where the ΔE_p values are 87 and 113 mV, respectively. In all instances, the ratios of the anodic and cathodic peak currents is unity within experimental error, showing that the processes are chemically reversible.

Cyclic voltammetry shows that the second reduction processes are not completely chemically reversible at slow scan rates. This was evidenced by the current ratio $(i_p)_{rev}/(i_p)_{for}$ being significantly less than 1.0:1 at a scan rate of 100 mV s^{-1}. In addition, for the toluene and *o*-xylene derivatives, **2** and **3**, respectively, a small irreversible reduction peak was observed at potentials more positive than that of the second reduction. The other derivatives exhibited small irreversible reduction peaks on the negative edge of the second reduction. At faster scan rates, the second reductions become more chemically reversible, as evidenced by the ratio $(i_p)_{rev}/(i_p)_{for}$ becoming closer to unity and the disappearance of the irreversible pre- and post-waves. Therefore, these products are attributed to the decomposition products of the iron(0) complex.

The peak-to-peak separations for the $Fe^I \longrightarrow Fe^0$ reductions were greater than those of the Fe^{II}–Fe^I couples and of the standard ferrocenium–ferrocene couple under identical conditions, indicating quasireversibility of the $Fe^I \longrightarrow Fe^0$ reductions, even at low scan rates.

Few[18–21] of the electrochemical studies on cyclopentadienyliron arene complexes have reported a Fe^I–Fe^0 couple despite the variety of complexes with substituted arenes and cyclopentadienyls that have been examined in a range of solvents.[8,22–24] There are a number of possible structural changes which could occur upon reduction (*e.g.* η^6-co-ordination of one of the phenyl groups of the co-ordinated C_5Ph_5, dimerisation through an arene ligand and/or cyclohexadienyl type co-ordination) leading to secondary reactions. Dimerisation through the co-ordinated arene ligand would be less likely for highly substituted arenes.[7,8,25–27] A change in the co-ordination mode of C_5Ph_5 to an η^6 configuration may be favoured in reduced (19e) species and this mode of co-ordination to iron has been observed previously.[3]

A multielectron reduction was observed at very negative potentials (in the range −2100 to −2300 mV) close to the solvent limit, for all complexes, but only at slow scan rates (<100 mV s^{-1} for arene = benzene, toluene, *p*-xylene, mesitylene or hexamethylbenzene; <50 mV s^{-1} for arene = *o*-xylene, *m*-xylene or durene). It was independent of the counter ion in the complex and the nature of the process is currently under investigation.

All of the $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-arene})][BPh_4]$ complexes exhibit an irreversible oxidation in the range 300–500 mV (relative to the ferrocenium–ferrocene couple) which is probably due to oxidation of the tetraphenylborate counter ion.[28]

Experimental

Unless otherwise stated, all reactions were performed under an argon atmosphere using conventional Schlenk techniques. Arene solvents (Merck, A.R.) were distilled from sodium wire under argon and degassed before use. Methanol was distilled from magnesium methoxide. Aluminium chloride (Fluka) was sublimed before use. The complex $[Fe(\eta^5\text{-}C_5Ph_5)(CO)_2Br]$ was prepared using the procedure of McVey and Pauson.[1] Arene solids (Fluka), sodium tetraphenylborate (Merck) and sodium tetrafluoroborate (Aldrich) were used without further purification.

Elemental analyses were performed by the Australian Microanalytical Service. Infrared spectra were recorded on a Digilab 20/80 FTS spectrophotometer, ^1H and ^{13}C NMR spectra on Bruker WM-400 and AC-200 spectrometers. NMR spectra were referenced internally to residual solvent absorbances. Visible spectra were recorded on a Cary model 17D spectrometer interfaced to a Commodore PET microcomputer. Melting points were obtained in air and are uncorrected.

Electrochemistry.—Electrochemical experiments were performed using a three-electrode system with a BAS-100 electrochemical analyser. The working electrode was a BAS glassy carbon disc (diameter 3 mm) electrode. The auxiliary electrode was a platinum wire (diameter 0.5 mm). The reference was a BAS Ag–AgCl–KCl(saturated) electrode. All measurements were performed with approximately 1 mmol dm^{-3} solutions of the complex at room temperature and atmospheric pressure. The supporting electrolyte used in all experiments was tetrabutylammonium tetrafluoroborate (0.1 mol dm^{-3}). This was prepared from tetrafluoroboric acid (35% v/v, Merck, extra pure grade) and aqueous 40% (w/w) tetrabutylammonium hydroxide (Aldrich). It was recrystallised four times from ethyl acetate–diethyl ether in air and dried under high vacuum. Full (100%) *iR* compensation was employed using BAS software. The solvent used was tetrahydrofuran which was distilled from sodium wire–benzophenone immediately prior to use. All solutions were degassed with high-purity argon, prebubbled through a Cr^{2+} solution (0.2 mol dm^{-3} Cr^{2+}, 0.5 mol dm^{-3} $HClO_4$) and a sulphuric acid bubbler tower (18 mol dm^{-3}, reagent grade) to remove traces of oxygen and water, respectively. Peak potentials were referenced to the ferrocenium–ferrocene redox couple[17] which was observed at +641 mV with respect to a Ag–AgCl–KCl(saturated) reference electrode in our cell configuration. Controlled-potential coulometry was performed using a Princeton Applied Research model-173 (PAR-173) potentiostat/galvanostat, in conjunction with a PAR model-179 digital coulometer. The reference electrode was the saturated calomel electrode (SCE), the auxiliary electrode was a platinum mesh, and the working electrode was a mercury pool (Matthey Garrett Pty Ltd, vacuum distilled).

Crystallography.—*Crystal data.* $C_{42}H_{33}BrCl_3Fe_2$, $M = 835.8$, monoclinic, space group, $P2_1/n$, $a = 10.016(2)$, $b = 21.568(6)$, $c = 16.920(4)$ Å, $\beta = 92.17(2)^\circ$, $U = 3652$ Å^3, D_c $(Z = 4) = 1.519$ g cm^{-3}, $F(000) = 1740$, μ(Mo-Kα) = 19.02 cm^{-1}. Specimen: red-brown prisms, 0.17 × 0.19 × 0.13 mm, $A^*_{min,max}$ 0.66, 0.53, $N = 6839$, $N_o = 4328$ $[I \geqslant 2.5\sigma(I)]$, range of *hkl* 0–22, 0–23, 0–19, merging $R = 0.01$, $R = 0.034$, $R' = 0.038$ $\{w = 1.48/[\sigma^2(F_o) + 0.00051\ F_o^2]\}$, residual extrema ± 0.4 e Å^{-3}.

Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf-Nonius CAD4-F diffractometer within the limit $2\theta_{max} = 50^\circ$, with Mo-Kα radiation, $\lambda = 0.710\,69$ Å, graphite monochromator, and operating in the ω–1.33θ mode. Data were reduced and Lorentz, polarisation, decomposition and absorption corrections were applied using the Enraf–Nonius Structure Determination Package (SDP).[29] The structure was solved by Patterson and Fourier synthesis techniques, and was refined by full-matrix least-squares analysis with SHELX 76.[30] The $[FeX_4]^-$ anion was found to be disordered. It was not possible to distinguish between rotational and constitutional disorder; all halide sites were occupied by both Cl and Br. The disorder was modelled by refining both Cl and Br at each site with complementary occupancies. Each site refined to a different occupancy and gave an average Cl : Br ratio of 3.26 : 1. As a result, the Fe–X distances in the anion are not physically meaningful, being averages of Fe–Cl and Fe–Br distances. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined with isotropic thermal parameters. Scattering factors and anomalous dispersion corrections for Fe were taken from ref. 31 and for all others the values supplied in SHELX 76 were used. The atomic nomenclature is defined in Fig. 1. Figures were drawn using the program ORTEP.[32]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Preparation of $[Fe(\eta^5\text{-}C_5Ph_5)(arene)]X$ (*arene = benzene, toluene,* o-, m-, p-*xylene, or mesitylene*).—*General procedure.* A solution of bromodicarbonyl(pentaphenylcyclopentadienyl)iron(II) (1.0 g, 1.6 mmol) and aluminium chloride (0.2 g, 1.6 mmol) was heated under reflux for 2 h in the arene (*ca.* 40 cm^3), with vigorous stirring. The reaction mixture was poured onto degassed water (20 cm^3) and stirred for 30 min. The crude product was isolated by filtration (as a tetrahalogenoferrate salt) and recrystallised from methanol in air to yield orange-red needles. Tetraphenylborate salts were obtained by adding 1 equivalent of sodium tetraphenylborate to an acetone solution of the tetrahalogenoferrate salt in air. The crude product precipitated immediately, and was recrystallised from acetone in air to yield pink-orange solids. Yields are given below. All complexes gave satisfactory microanalyses.

Preparation of $[Fe(\eta^5-C_5Ph_5)(arene)]X$ (*arene = durene or hexamethylbenzene*).—*General procedure.* A solution of bromodicarbonyl(pentaphenylcyclopentadienyl)iron(II) (1.0 g, 1.6 mmol), aluminium chloride (0.4 g, 3.2 mmol) and the solid arene (6.4 mmol) in chlorobenzene (*ca.* 30 cm^3) was refluxed for 12 h with vigorous stirring. The reaction mixture was poured onto degassed water (20 cm^3), and stirred for 30 min. The solvent was removed *in vacuo* and any unreacted arene removed by extraction with hexane. The crude product was recrystallised from methanol in air. Tetraphenylborate salts were obtained following the procedure outlined above.

$[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6H_6)][BPh_4]$ **1**. Yield 40%, m.p. 276–277 °C (decomp.) (from acetone) (Found: C, 86.6; H, 5.8. $C_{65}H_{51}BFe$ requires C, 86.9; H, 5.7%). NMR (CD_3OD): ^1H, δ 6.77 (s, 6 H, $\eta^6-C_6H_6$), 7.32–7.57 (m, 45 H, 5 C_6H_5, 4 BPh_4^-); ^{13}C, δ 94.0 ($\eta^6-C_6H_6$ ring, 6 CH), 95.5 (η^5-C_5 ring, 5 C), 129.6, 133.6 (C_6H_5 rings, 10 *o*/*m*-CH), 130.3 (C_6H_5 rings, 5 *p*-CH), 131.4 (C_6H_5 rings, 5 *ipso*-C), 122.4, 126.3, 136.5 and 166.0 (BPh_4^-, 24 C). IR (KBr)/cm^{-1} 3056m, 1501w, 1444m, 1408w, 1078w, 1025w, 801w, 784w, 740m, 709s and 700s; λ_{max}/nm(CH_2Cl_2): 490 (ε 3.63 × 10^2) and 326 (1.04 × 10^4 dm^3 mol^{-1} cm^{-1}).

$[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6H_5Me)][BPh_4]$ **2**. Yield 20%, m.p. 265–267 °C (decomp.) (from acetone) (Found: C, 86.6; H, 6.0. $C_{66}H_{53}BFe$ requires C, 86.8; H, 6.0%). NMR (CD_2Cl_2): ^1H, δ 2.13 (s, 3 H, CH_3), 5.81–6.00 (m, 5 H, $\eta^6-C_6H_5$) and 6.78–7.40 (m, 45 H, 5 C_6H_5, 1 BPh_4^-); ^{13}C, δ 30.1 (CH_3), 92.8 (η^5-C_5 ring, 5 C), 106.3, 107.0, 107.6 ($\eta^6-C_6H_5Me$ ring, 5 CH), 110.0 ($\eta^6-C_6H_5Me$ ring, *C*Me), 127.6 (C_6H_5 rings, 5 *ipso*-C), 129.9 (C_6H_5 rings, 5 *p*-CH), 131.6, 135.2 (C_6H_5 rings, 10 *o*/*m*-CH), 122.5, 126.4 and 136.7 (BPh_4^-, 24 C). IR(KBr)/cm^{-1} 3106s, 3088s, 3059s, 3030s, 1500w, 1465w, 1444m, 1411m, 1027w, 747m, 741m, 710s and 699s; λ_{max}/nm(CH_2Cl_2): 498 (ε 3.06 × 10^2) and 324 (1.29 × 10^4 dm^3 mol^{-1} cm^{-1}).

$[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6H_4Me_2-1,2)][BPh_4]$ **3**. Yield 50%, m.p. 253–255 °C (decomp.) (from acetone) (Found: C, 86.7; H, 5.9. $C_{67}H_{55}BFe$ requires C, 86.8; H, 6.0%). NMR (CD_2Cl_2): ^1H, δ 2.07 (s, 6 H, 2 CH_3), 5.78–5.91 (m, 4 H, $\eta^6-C_6H_4$) and 6.75–7.43 (m, 45 H, 5 C_6H_5, 1 BPh_4^-); ^{13}C, δ 16.3 (2 CH_3), 92.1, 92.6 ($\eta^6-C_6H_4Me_2$ ring, 4 CH), 93.1 (η^5-C_5 ring, 5 C), 103.9 ($\eta^6-C_6H_4Me_2$ ring, 2 *C*Me), 130.0 (C_6H_5 rings, 5 *ipso*-C), 129.6 (C_6H_5 rings, 5 *p*-CH), 129.0, 132.6 (C_6H_5 rings, 10 *o*/*m*-CH), 122.5, 126.3, 136.6 and 165.2 (BPh_4^-, 24 C). IR (KBr)/cm^{-1} 3049w, 1600w, 1501m, 1468w, 1442m, 1403m, 1313w, 1177w, 1157w, 1074m, 1023m, 1001w, 872w, 798m, 781m, 743m, 712m, 702s and 612m; λ_{max}/nm(CH_2Cl_2): 505 (ε 3.63 × 10^2) and 325 (1.45 × 10^4 dm^3 mol^{-1} cm^{-1}).

$[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6H_4Me_2-1,4)][BPh_4]$ **4**. Yield 20%, m.p. 232–234 °C (decomp.) (from acetone) (Found: C, 86.5; H, 6.0. $C_{67}H_{55}BFe$ requires C, 86.8; H, 6.0%). NMR (CD_2Cl_2): ^1H, δ 2.06 (s, 6 H, 2 CH_3), 5.80 (s, 4 H, $\eta^6-C_6H_4$) and 6.72–7.41 (m, 45 H, 5 C_6H_5, 1 BPh_4^-); ^{13}C, δ 19.9 (2 CH_3), 91.1 ($\eta^6-C_6H_4Me_2$ ring, 4 CH), 93.2 (η^5-C_5 ring, 5 C), 105.6 ($\eta^6-C_6H_4Me_2$ ring, 2 *C*Me), 129.6 (C_6H_5 rings, 5 *p*-CH), 130.0 (C_6H_5 rings, 5 *ipso*-C), 129.0, 132.7 (C_6H_5 rings, 10 *o*/*m*-CH), 122.5, 126.4, 136.7 and 165.2 (BPh_4^-, 24 C). IR (KBr)/cm^{-1} 3050w, 3023w, 1598w, 1487m, 1442m, 1406m, 1378w, 1179w, 1069w, 1027m, 797w, 783w, 767w, 745s, 710s, 708s, 699s and 609w cm^{-1}; λ_{max}/nm(CH_2Cl_2): 506 (ε 3.48 × 10^2) and 325 (1.26 × 10^4 dm^3 mol^{-1} cm^{-1}).

$[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6H_4Me_2-1,3)][BPh_4]$ **5**. Yield 30%, m.p. 263–265 °C (decomp.) (from acetone) (Found: C, 86.6; H, 6.1. $C_{67}H_{55}BFe$ requires C, 86.8; H, 6.0%). NMR (CD_2Cl_2): ^1H δ 2.12 (s, 6 H, 2 CH_3), 5.76–6.07 (m, 4 H, $\eta^6-C_6H_4$) and 6.78–7.42 (m, 45 H, 5 C_6H_5, 1 BPh_4^-); ^{13}C, δ 20.0 (2 CH_3), 93.2 (η^5-C_5 ring, 5 C), 90.2, 91.0, 92.9 ($\eta^6-C_6H_4$ ring, 4 CH), 106.0 ($\eta^6-C_6H_4Me_2$ ring, 2 *C*Me), 129.6 (C_6H_5 rings, *ipso*-C), 129.8 (C_6H_5 rings, *p*-CH), 128.9, 132.4 (C_6H_5 rings, *o*/*m*-CH), 122.3, 126.2, 136.5 and 166.0 (BPh_4^-, 24 C). IR (KBr)/cm^{-1} 3050w, 1598w, 1544w, 1497m, 1440m, 1407m, 1374m, 1179w, 1076w, 1026m, 802m, 784m, 770w, 736s, 706s, 697s and 609m; λ_{max}/nm(CH_2Cl_2): 503.5 (ε 3.20 × 10^2) and 324 (1.43 × 10^4 dm^3 mol^{-1} cm^{-1}).

$[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6H_3Me_3-1,3,5)][BPh_4]$ **6**. Yield 30%, m.p. 241–243 °C (decomp.) (from acetone) (Found: C, 86.4; H, 6.1. $C_{68}H_{57}BFe$ requires C, 86.8; H, 6.1%). NMR (CD_2Cl_2): ^1H, δ 2.11 (s, 9 H, 3 CH_3), 5.60 (s, 2 H, $\eta^6-C_6H_3$) and 6.76–7.39 (m, 45 H, 5 C_6H_5, 1 BPh_4^-); ^{13}C, δ 20.4 (3 CH_3), 92.7 ($\eta^6-C_6H_3Me_3$ ring, 3 CH), 93.3 (η^5-C_5 ring, 5 C), 106.3 ($\eta^6-C_6H_3Me_3$ ring, 3 *C*Me), 129.6 (C_6H_5 rings, 5 *ipso*-C), 129.9 (C_6H_5 rings, 5 *p*-CH), 129.0, 132.6 (C_6H_5 rings, 10 *o*/*m*-CH), 122.4, 126.3, 136.6 and 165.3 (BPh_4^-, 24 C). IR (KBr)/cm^{-1} 3051w, 2954w, 2921w, 1601w, 1548w, 1502w, 1448w, 1409w, 1375w, 1185w, 1072w, 1026w, 738m, 697m and 612m; λ_{max}/nm(MeCN): 507 (ε 3.63 × 10^2), 459 (3.07 × 10^2) and 317 (1.74 × 10^4 dm^3 mol^{-1} cm^{-1}).

$[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6H_2Me_4-1,2,4,5)][BPh_4]$ **7**. Yield 15%, m.p. 229–231 °C (decomp.) (from acetone) (Found: C, 86.8; H, 6.3. $C_{69}H_{59}BFe$ requires C, 86.7; H, 6.2%). NMR (CD_2Cl_2): ^1H, δ 1.96–2.18 (m, 12 H, 4 CH_3), 5.89 (s, 2 H, $\eta^6-C_6H_2$) and 6.78–7.35 (m, 45 H, 5 C_6H_5, 1 BPh_4^-); ^{13}C, δ 16.7, 18.6, 19.6 (4 CH_3), 91.8, 92.0, 92.3, 95.5 (η^5-C_5 ring, 5 C), 92.3 ($\eta^6-C_6H_2Me_4$ ring, 2 CH), 101.4, 103.4, 103.7 ($\eta^6-C_6H_2Me_4$ ring, 4 *C*Me), 129.9 (C_6H_5 rings, 5 *p*-CH), 130.3 (C_6H_5 rings, 5 *ipso*-C), 129.0, 132.7, (C_6H_5 rings, 10 *o*/*m*-CH), 122.4, 126.3, 136.6 and 165.3 (BPh_4^-, 24 C). IR (KBr)/cm^{-1} 3055w, 3026w, 2998w, 1581m, 1499w, 1478w, 1445m, 1424w, 1407w, 1182w, 1081w, 1026w, 746m, 735m, 705s, 615m and 560m; λ_{max}/nm(MeCN): 518 (ε 2.62 × 10^2) and 309 (9.12 × 10^3 dm^3 mol^{-1} cm^{-1}).

$[Fe(\eta^5-C_5Ph_5)(\eta^6-C_6Me_6)][BPh_4]$ **8**. Yield 20%, m.p. 224–227 °C (decomp.) (from acetone (Found: C, 86.8; H, 6.8. $C_{71}H_{63}BFe$ requires C, 86.7; H, 6.5%). NMR (CD_2Cl_2): ^1H, δ 2.10 (s, 18 H, 6 CH_3) and 6.78–7.39 (m, 45 H, 5 C_6H_5, 1 BPh_4^-); ^{13}C, δ 14.4 (6 CH_3), 91.1 (η^5-C_5 ring, 5 C), 94.7 ($\eta^6-C_6Me_6$ ring, 6 CH_3), 128.9, 132.4 (C_6H_5 rings, 10 *o*/*m*-CH), 129.5, 129.6 (C_6H_5 rings, 5 *ipso*-C and 5 *p*-CH), 122.3, 126.1 and 136.4 (BPh_4^-, 24 C). IR (KBr)/cm^{-1} 3057w, 1628m, 1499m, 1445m, 1443m, 1409m, 1096m, 1079m, 1029m, 804m, 785m, 747s, 739s, 709s and 698s; λ_{max}/nm(MeCN): 501 (ε 4.36 × 10^2) and 316 (8.48 × 10^3 dm^3 mol^{-1} cm^{-1}).

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