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Organometallic synthesis in ambient temperature chloroaluminate(III) ionic liquids. Ligand exchange reactions of ferrocene

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The ambient temperature ionic liquid system [bmim]Cl–$AlCl_3$ (where $[bmim]^+$ = 1-butyl-3-methylimidazolium cation) has been used to prepare a number of arene(cyclopentadienyl)iron(II) complexes of the type $[Fe(C_5H_5)(arene)]^+$ from ferrocene. The ionic liquid acts as both solvent and Lewis acid source ($[Al_2Cl_7]^-$). The products were only formed on addition of a proton source, $[bmim][HCl_2]$, confirming mechanistic formulations involving a combination of Lewis and Brønsted acid activity. The X-ray crystal structure analysis of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_5C_6H_4Br)][PF_6]$ is also reported. The structure clearly shows both π–π stacking interactions between neighbouring cations and hydrogen bonds between the cations and anions.

From the initial elucidation of the structure of ferrocene, transition-metal cyclopentadienyl complexes have constituted a key area of activity in the development of modern organometallic chemistry.[1] Benzene and other arene complexes, while studied to a lesser extent, also occupy an important position in the development of organometallic chemistry.[2] Complexes containing both cyclopentadienyl and arene ligands are rarer still. Salts of the benzene(cyclopentadienyl)iron(II) cation $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)]^+$, were first prepared from the reaction between $[FeCp(CO)_2Cl]$ (Cp = $\eta^5\text{-}C_5H_5$) and benzene in the presence of aluminium(III) chloride at high temperatures.[3] Subsequently, it was found that the same product could be obtained from the reaction of ferrocene with benzene in the presence of aluminium powder and aluminium(III) chloride.[4] Using this method, it was also possible to replace one of the cyclopentadienyl groups in ferrocene with a variety of arene ligands.[5–8] It has also been found that electron donating groups on the arene encourage the ring substitution reaction, whereas electron-withdrawing substituents inhibit the exchange process.[6] With polyaromatics, such as biphenyl and naphthalene both of the rings may take part in the exchange with ferrocene.[4,9]

Although the ambient temperature ionic liquids have now been known for some time, little synthetic chemistry has been reported in them. Notable exceptions to this are the use of acidic ionic liquids as a combination of catalyst and solvent for a number of Friedel–Crafts reactions and the polymerization of ethene using titanocene dichloride derived catalysts.[10–12]

In this paper, we report a direct synthetic approach using the acidic [bmim]Cl–$AlCl_3$ ionic liquid (where $[bmim]^+$ = 1-butyl-3-methylimidazolium cation) to the following monocations: $[Fe^{II}Cp(R)]^+$ (where R = benzene, toluene, biphenyl, 4-bromobiphenyl or naphthalene). These reactions are ideally suited to this medium which acts as both solvent and Lewis acid source.

Results and Discussion

The room temperature chloroaluminate(III) ionic liquids are formed by the direct combination of substituted imidazolium chloride salts and aluminium(III) chloride.[13] There are a number of ways in which the precise composition of the ionic liquid can be described, in this paper we use a [bmim]Cl–$AlCl_3$ ionic liquid with an apparent mol fraction of $AlCl_3$ of 0.65 which we refer to simply as the 'acidic' ionic liquid. In fact, the ionic liquids contained no free $AlCl_3$; the acidic ionic liquids contain significant concentrations of the $[Al_2Cl_7]^-$ ion, which is the active Lewis acid species.[14] Hence, the room temperature chloroaluminate(III) ionic liquids offer an ideal potential environment for the investigation of Lewis acid catalysed reactions.

We have found that arene-exchange reactions of ferrocene using the methods described in the literature often result in lower yields than those reported especially when the arene is solid at the reaction temperature and a solvent is required to homogenize the reaction. By using the acidic [bmim]Cl–$AlCl_3$ ionic liquid as a combination of both catalyst and solvent, these problems are largely avoided.

In a typical reaction, ferrocene is first dissolved in the acidic ionic liquid and aluminium powder, $[bmim][HCl_2]$ and the appropriate arene are added. The mixture is then heated to *ca.* 80 °C for several hours. The arenes employed in this study together with the reaction time and yield of the arene(cyclopentadienyl)iron(II) products are listed in Table 1 (fuller details are given in the Experimental section).

The need to add a Brønsted acid to the reaction mixture in these reactions has been known for some time.[15] This has often been achieved adventitiously by using wet starting materials which produce HCl on contact with aluminium(III) chloride. The mixture of HCl and aluminium(III) chloride is highly Brønsted acidic and will protonate the ferrocene. In the absence of a suitable reducing agent, aluminium powder in this case, this is followed by oxidation of the metal and the formation of the ferrocenium ion. However, under the conditions used here the proton is transferred to one of the cyclopentadienyl rings which then becomes a good leaving group, *viz*. cyclopentadiene. Finally, the cyclopentadiene ring is displaced by the arene, yielding the product.

Great care is always taken to exclude moisture during the preparation of the ionic liquids. Hence a proton source must be specifically added. Although in early experiments both water

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Table 1 Products and yields obtained from the arene exchange reactions of ferrocene in the acidic ionic liquid

Arene	Reaction t/h	Product	Yield (%)
Benzene	8	$[Fe(C_5H_5)(C_6H_6)][PF_6]$	53
Toluene	8	$[Fe(C_5H_5)(C_6H_5Me)][PF_6]$	64
Biphenyl	18	$[Fe(C_5H_5)(C_6H_5Ph)][PF_6]$	46
4-Bromobiphenyl	18	$[Fe(C_5H_5)(C_6H_5C_6H_4Br)][PF_6]$	47
Naphthalene	18	$[Fe(C_5H_5)(C_{10}H_8)][PF_6]$	53

Table 2 Selected bond lengths (Å) for the $[Fe(C_5H_5)(C_6H_5C_6H_4Br)]^+$ cation

Fe–C(2)	2.033(6)	Fe–C(2)	2.035(6)
Fe–C(3)	2.034(6)	Fe–C(1)	2.045(7)
Fe–C(4)	2.054(6)	Fe–C(10)	2.066(6)
Fe–C(9)	2.070(6)	Fe–C(8)	2.077(6)
Fe–C(7)	2.083(6)	Fe–C(6)	2.087(5)
Fe–C(11)	2.099(5)		

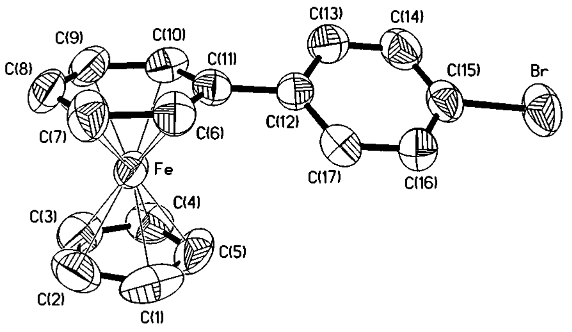

Fig. 1 Molecular structure of the cation $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_5C_6H_4Br)]^+$

and concentrated aqueous HCl were used as the proton source, we prefer the use of $[HCl_2]^-$ salts which were first used by Trulove and Osteryoung.[16] These allow the ionic liquid to be made Brønsted acidic without also adding oxide (from water) which reduces the Lewis acidity of the system. They can also be used with much greater ease than anhydrous HCl.

The solid state structure of 4-bromobiphenyl(cyclopentadienyl)-iron(II) hexafluorophosphate

Single crystals of 4-bromobiphenyl(cyclopentadienyl)iron(II) hexafluorophosphate suitable for X-ray analysis were grown from an acetone–water solution at 5 °C. Selected bond lengths for the 4-bromobiphenyl(cyclopentadienyl)iron(II) cation are presented in Table 2. A view of the cation, with atom numbering, is shown in Fig. 1. The iron atom is co-ordinated to the cyclopentadienyl ring at a ring centroid–iron distance of 1.666(6) Å and to the unsubstituted ring of the 4-bromobiphenyl moiety at a ring centroid–iron distance of 1.530(6) Å, these values being typical of η^5–Fe–η^6 co-ordination.[17] The two co-ordinated rings are essentially parallel, with the ring centroid–iron–ring centroid vectors collinear to within 2°. The iron is only very slightly offset from the ring centroids. The C(5) atom of the cyclopentadienyl ring is 'eclipsed' relative to C(11) of the co-ordinated phenyl ring. The plane of the bromophenyl ring is rotated by *ca.* 26° out of the co-ordinated phenyl ring plane (see below). In addition to this rotation, the bromophenyl ring is folded out of the plane of the co-ordinated phenyl ring, the C(11) ··· C(15) vector being 5° out of this plane in the direction of the Fe atom.

Inspection of the crystal packing reveals the absence of any single dominant anion–cation interaction. Of note, however, is a coulombic interaction involving the approach of the bromine atom to one of the faces of the $[PF_6]^-$ anion, the shortest Br ··· F separation being 3.20 Å. Centrosymmetrically related pairs of cations pack back-to-back, the bromophenyl ring of one ring overlaying that of another, with a mean interplanar separation of 3.78 Å and a ring centroid–ring centroid distance of 4.14 Å, indicative of a weak π–π stacking interaction (Fig. 2). This arrangement results in the directing of one of the co-ordinated phenyl ring hydrogen atoms towards one of the fluorine atoms of the anion, the H ··· F distance of 2.74 Å suggesting a possible weak C–H ··· F hydrogen bond supplementing the electrostatic anion–cation interaction (see above). The ordered arrangement of the $[PF_6]^-$ anion, which is relatively unusual in crystal structures, led us to analyse possible stabilizing interactions involving the fluorine atoms on the opposite face to that approached by the bromine atom. This search revealed additional C–H ··· F approaches from symmetry related cations involving both C(3) and C(6) of the co-ordinated cyclopentadienyl and aryl ring systems with associated C ··· F and H ··· F distances (Å) with C–H ··· F angles (°) of 3.46, 2.69 and 141, and 3.30, 2.63 and 129 respectively.

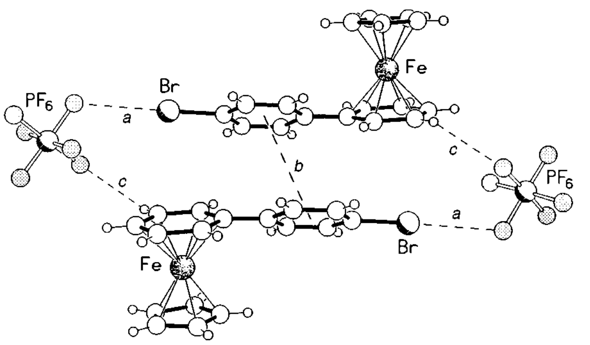

Fig. 2 Back-to-back packing of pairs of $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_5C_6H_4Br)]^+$ cations and their associated $[PF_6]^-$ anions. The interaction geometries are (*a*) Br ··· F 3.20 Å, C–Br ··· F 178°; (*b*) centroid ring–centroid ring distance 4.14 Å with a mean interplanar separation of 3.78 Å and (*c*) C ··· F 3.43, H ··· F 2.74 Å and C–H ··· F 132°

There has been some discussion of the degree of rotation of the unco-ordinated ring of iron-co-ordinated biphenyls in the literature and Roberts *et al.*[18] have developed a technique for estimating this angle, based on ^{13}C NMR spectroscopic data. Our NMR spectroscopic data (see Experimental section) would predict the angle to be 38.5°, somewhat larger than found in the solid state structure (*ca.* 26°). This may, to some degree, be explained by the geometry of the weak π–π stacking between neighbouring bromophenyl rings which places a limit on the degree of rotation possible between the co-ordinated and unco-ordinated ring systems before unfavourable steric interactions occur between the η^6 ring of one molecule and the bromine atom of the other.

Experimental

Proton and ^{13}C NMR spectra were recorded on a JEOL JNM-EX270 Fourier-transfer spectrometer, elemental analyses and fast atom bombardment (FAB) mass spectra were recorded by the microanalytical and mass spectrometry laboratories of the Department of Chemistry at Imperial College, London.

Solvents and starting materials

Acetonitrile, benzene, toluene, 1-chlorobutane, light petroleum (b.p. 60–80 °C) and diethyl ether were distilled from the appropriate drying agent, under dry nitrogen, immediately prior to use; 1-methylimidazole was distilled from KOH, again immediately prior to use. The preparation of the ionic liquids, by addition of aluminium(III) chloride to 1-butyl-3-methylimidazolium chloride, followed previously described methods in a dry nitrogen atmosphere glove box.[19,20] All other starting materials were used as supplied.

1-Butyl-3-methylimidazolium chloride[21]

Under N_2, freshly dried 1-methylimidazole (40 cm^3, 0.50 mol) and 1-chlorobutane (90 cm^3, 0.86 mol) were added to dry toluene (50 cm^3) in a round-bottomed Schlenk flask. The mixture was heated under reflux under N_2 for 24 h, upon which two layers had formed. The flask was allowed to cool to room temperature and was then cooled to -10 °C overnight, during which time a white solid was formed. The excess toluene was decanted, while N_2 was being passed over the product layer. The white product was recrystallized from the minimum amount of dry acetonitrile (30 cm^3) by addition of dry diethyl ether (10 cm^3). The resulting white precipitate was isolated by filtration and then dried *in vacuo* for 24 h. Yield: 56 g (64%) (Found: C, 54.23; H, 8.96; N, 16.12. Calc. for $C_8H_{15}ClN_2$: C, 54.31; H, 9.62; N, 15.84%). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 11.0 (s, H^2), 7.3 (d, H^4), 7.2 (d, H^5), 4.4 (t, NCH_2), 4.1 (s, NCH_3), 1.9 (m, NCH_2CH_2), 1.4 (m, $NCH_2CH_2CH_2$) and 1.0 (t, CH_3); FAB mass spectrum: *m*/*z* 139 $[bmim]^+$, 313 $\{[bmim]_2Cl\}^+$ and 487 $\{[bmim]_3Cl_2\}^+$.

1-Butyl-3-methylimidazolium hydrogen dichloride

The compound [bmim]Cl was placed in a three-necked flask, containing a magnetic stirrer bar, immersed in a solid CO_2–acetone slush bath. Hydrogen chloride gas was passed (*via* a Dreschel bottle containing concentrated sulfuric acid, in order to remove any water) into the flask containing the solid, while it was immersed in the solid CO_2–acetone slush bath. The mixture was stirred while the hydrogen chloride was being condensed onto the solid. Once approximately 3 cm^3 of liquid was present in the flask and all of the solid had dissolved, the reaction was stopped. The flask was removed from the slush bath, and allowed to reach room temperature with a stream of N_2 passing over the product. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 12.11 (s, HCl_2^-), 9.55 (s, H^2), 7.68 (d, H^4), 7.65 (d, H^5), 4.34 (t, NCH_2), 4.09 (s, NCH_3), 1.92 (m, NCH_2CH_2), 1.39 (m, $NCH_2CH_2CH_2$) and 0.98 (t, $NCH_2CH_2CH_2CH_3$).

Benzene(cyclopentadienyl)iron(II) hexafluorophosphate

In an inert atmosphere glove box, ferrocene (1.00 g, 0.0054 mol) was dissolved in an acidic [bmim]Cl–$AlCl_3$ ionic liquid (5.00 cm^3). The resulting solution was transferred to a Schlenk flask, which was then sealed and removed from the glove box. Under N_2, aluminium powder (0.12 g), [bmim]-[HCl_2] (2 drops) and freshly distilled benzene (1 cm^3) were added to the ferrocene solution. The reaction mixture was then heated at approximately 80 °C for 8 h, maintaining a N_2 atmosphere.

The reaction mixture was allowed to cool to room temperature and was finally placed in an ice-bath. Ice–water (200 cm^3) was slowly added to the cold reaction mixture. The aqueous solution was filtered and washed with light petroleum (60–80 °C, 5 × 20 cm^3). The washed aqueous layer was collected and filtered directly into a concentrated aqueous solution of ammonium hexafluorophosphate (2.00 g in 10 cm^3). A green precipitate formed immediately. The green salt was isolated by filtration and recrystallized from acetone and characterized as $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_6)][PF_6]$. Yield: 0.99 g (53%) (Found: C, 38.40; H, 3.29. Calc. for $C_{11}H_{11}F_6FeP$: C, 38.50; H, 3.21%). ^{1}H NMR [$(CD_3)_2CO$, 270 MHz]: δ 6.49 (s, C_6H_6), 5.23 (s, C_5H_5); FAB mass spectrum: *m*/*z* 199, $[FeC_{11}H_9]^+$ and 543, $\{[FeC_{11}H_9]_2[PF_6]\}^+$.

Toluene(cyclopentadienyl)iron(II) hexafluorophosphate

In an inert atmosphere glove box, ferrocene (1.00 g, 0.0054 mol) was dissolved in an acidic [bmim]Cl–$AlCl_3$ ionic liquid (5.00 cm^3). The solution that resulted was transferred to a Schlenk flask, which was then sealed and removed from the glove box. Under N_2, aluminium powder (0.12 g), [bmim]-[HCl_2] (two drops) and freshly distilled toluene (1 cm^3) were added to the ferrocene solution. The reaction mixture was then heated at approximately 80 °C for 8 h, maintaining a N_2 atmosphere.

The reaction mixture was allowed to cool to room temperature and was finally placed in an ice-bath. Ice–water (200 cm^3) was slowly added to the cold reaction mixture. The aqueous solution was filtered and washed with light petroleum (60–80 °C, 5 × 20 cm^3). The washed aqueous layer was collected and filtered directly into a concentrated aqueous solution of ammonium hexafluorophosphate (2.00 g in 10 cm^3). A pale green precipitate formed immediately. The pale green salt was isolated by filtration and recrystallized from acetone and characterized as $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_5Me)][PF_6]$. Yield: 0.60 g (64%) (Found: C, 39.99; H, 3.59. Calc. for $C_{12}H_{13}F_6FeP$: C, 40.46; H, 3.09%). ^{1}H NMR [$(CD_3)_2CO$, 270 MHz]: δ 7.20 (s, C_6H_5), 5.95 (s, C_5H_5), 3.35 (s, CH_3); FAB mass spectrum: *m*/*z* 213, $[FeC_{12}H_{13}]^+$ and 571, $\{[FeC_{12}H_{13}]_2[PF_6]\}^+$.

Biphenyl(cyclopentadienyl)iron(II) hexafluorophosphate

In an inert atmosphere glove box, ferrocene (5.58 g, 0.03 mol) was dissolved in an acidic [bmim]Cl–$AlCl_3$ ionic liquid (25.00 cm^3). Biphenyl (4.62 g, 0.03 mol) was also dissolved in an acidic [bmim]Cl–$AlCl_3$ ionic liquid (10.00 g) in another beaker. The two solutions were combined and then transferred to a Schlenk flask, which was sealed and removed from the glove box. Under N_2, aluminium powder (1.35 g) and two drops of [bmim][HCl_2] were added to the ferrocene solution. The reaction mixture was then heated at approximately 85 °C for 18 h, maintaining a N_2 atmosphere.

The reaction mixture was allowed to cool to room temperature and was then placed in an ice-bath. Ice–water (200 cm^3) was slowly added to the cold reaction mixture. The aqueous solution was filtered and washed with light petroleum (60–80 °C, 5 × 20 cm^3). The washed aqueous layer was collected and filtered directly into a concentrated aqueous solution of ammonium hexafluorophosphate (2.00 g in 10 cm^3). An orange precipitate formed immediately. After standing for 1 h, the orange salt was isolated by filtration and recrystallized from a warm acetone–water mixture. The resulting orange-yellow solid was isolated by filtration and dried *in vacuo* for 24 h and then over phosphorus(V) oxide for another 24 h. The solid was characterized as $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_5Ph)][PF_6]$ Yield: 5.78 g (46%) (Found: C, 48.87; H, 3.58. Calc. for $C_{17}H_{15}F_6FeP$: C, 48.57; H, 3.57%). ^{1}H NMR [$(CD_3)_2CO$, 270 MHz]: δ 7.76 (m, aromatic), 4.81 (s, C_5H_5); FAB mass spectrum: *m*/*z* 275, $[FeC_{17}H_{15}]^+$ and 695, $\{[FeC_{17}H_{15}]_2[PF_6]\}^+$.

4-Bromobiphenyl(cyclopentadienyl)iron(II) hexafluorophosphate

In an inert atmosphere glove box, ferrocene (5.58 g, 0.03 mol) was dissolved in an acidic [bmim]Cl–$AlCl_3$ ionic liquid (25.00 cm^3). 4-Bromobiphenyl (6.99 g, 0.03 mol) was also dissolved in an acidic [bmim]Cl–$AlCl_3$ ionic liquid (10.00 g). The two solutions were combined and then transferred to a Schlenk flask, which was then sealed and removed from the glove box. Under N_2, aluminium powder (1.35 g) and [bmim][HCl_2] (two drops) were added to the solution. The reaction mixture was

Table 3 Crystal data, data collection and refinement parameters[a]

Formula	$C_{17}H_{14}BrFe\cdot PF_6$
M	499.0
Colour, habit	Orange-yellow, blocks
Crystal size/mm	0.70 × 0.57 × 0.20
Lattice type	Triclinic
Space group	$P\bar{1}$ (no. 2)
T/K	293
a/Å	7.498(1)
b/Å	8.863(1)
c/Å	13.957(2)
α/°	83.67(1)
β/°	77.46(1)
γ/°	79.08(1)
U/Å^3	886.7(2)
Z	2
D_c/g cm^{-3}	1.87
F(000)	492
Radiation used	Mo-Kα
μ/mm^{-1}	3.25
θ Range/°	2.4–25.0
No. unique reflections measured	3092
observed, $\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$	2251
Absorption correction	Semiempirical
Maximum, minimum transmission	0.48, 0.27
No. variables	235
$R1$[b]	0.053
$wR2$[c]	0.133
Weighting factors a, b[d]	0.077, 0.826
Largest difference peak, hole/e Å^{-3}	0.89, −0.48

[a] Graphite-monochromated radiation, ω scans, Siemens P4 diffractometer, refinement based on F^2. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{\frac{1}{2}}$. [d] $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$; $P = (F_o^2 + 2F_c^2)/3$.

then heated at approximately 85 °C for 18 h, maintaining a N_2 atmosphere.

The reaction mixture was allowed to cool to room temperature and was finally placed in an ice-bath. Ice–water (200 cm^3) was slowly added to the cold reaction mixture. The aqueous solution was filtered and washed with light petroleum (60–80 °C, 5 × 20 cm^3). The washed aqueous layer was collected and filtered directly into a concentrated aqueous solution of ammonium hexafluorophosphate (2.00 g in 10 cm^3). A yellow-green precipitate formed immediately. After standing for 1 h, the yellow-green salt was isolated by filtration and recrystallized from a warm acetone–water mixture. The resulting yellow-green solid was filtered and first dried *in vacuo* for 24 h then over phosphorus(v) oxide for another 24 h. The yellow-green solid was characterized as $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_5C_6H_4Br)][PF_6]$ Yield: 5.91 g (47%) (Found: C, 40.64; H, 2.80. Calc. for $C_{17}H_{14}BrF_6FeP$: C, 40.88; H, 2.81%). ^{1}H NMR [$(CD_3)_2CO$, 270 MHz]: δ 8.095 (m, aromatic), 6.95 (s, C_5H_5); ^{13}C NMR [$(CD_3)_2CO$, 90.55 MHz]: δ 87.27 (C^8), 88.51 ($C^{6,10}$), 89.30 ($C^{7,9}$), 103.52 (C^{11}), 130.67 ($C^{13,17}$), 124.98 ($C^{14,16}$), 133.34 (C^{12}) and 135.43 (C^{15}); FAB mass spectrum: m/z 353, $[FeC_{17}H_{14}Br]^+$.

η^6-Naphthalene(cyclopentadienyl)iron(II) hexafluorophosphate

In an inert atmosphere glove box, ferrocene (5.58 g, 0.03 mol) was dissolved in an acidic [bmim]Cl–$AlCl_3$ ionic liquid (25.00 cm^3). Naphthalene (3.84 g, 0.03 mol) was dissolved in an acidic [bmim]Cl–$AlCl_3$ ionic liquid (10.00 g) in another beaker. The two solutions were combined and then transferred to a Schlenk flask, which was then sealed and removed from the glove box. Under N_2, aluminium powder (1.35 g) and [bmim][HCl_2] (two drops) were added to the ferrocene solution. The reaction mixture was then heated at approximately 85 °C for 18 h, maintaining a N_2 atmosphere.

The reaction mixture was allowed to cool to room temperature and was finally placed in an ice-bath. Ice–water (200 cm^3) was slowly added to the cold reaction mixture. The aqueous solution was filtered and washed with light petroleum (60–80 °C, 5 × 20 cm^3). The washed aqueous layer was collected and filtered directly into a concentrated aqueous solution of ammonium hexafluorophosphate (2.00 g in 10 cm^3). A red precipitate formed immediately. After standing for 1 h, the red salt was isolated by filtration and recrystallized from a warm acetone–water mixture. The resulting red solid was filtered and first dried *in vacuo* for 24 h and then over phosphorus(v) oxide for another 24 h. The red solid was characterized as $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_{10}H_8)][PF_6]$ Yield: 6.25 g (53%) (Found: C, 45.15; H, 3.43. Calc. for $C_{15}H_{13}F_6FeP$: C, 45.69; H, 3.30%). ^{1}H NMR [$(CD_3)_2CO$, 270 MHz]: δ 7.86 (m, aromatic), 4.80 (s, C_6H_5); FAB mass spectrum: m/z 249, $[FeC_{15}H_{13}]^+$ and 643, $\{[FeC_{15}H_{13}]_2[PF_6]\}^+$.

Crystal data for 4-bromobiphenyl(cyclopentadienyl)iron(II) hexafluorophosphate

Table 3 provides a summary of the crystal data, data collection and refinement parameters for $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-}C_6H_5C_6H_4Br)][PF_6]$. The structure was solved by direct methods and all of the non-hydrogen atoms were refined anisotropically using full-matrix least squares based on F^2. The positions of the hydrogen atoms were idealized, assigned isotropic thermal parameters, $U(H) = 1.2U_{eq}(C)$, and allowed to ride on their parent carbon atoms. Computations were carried out using the SHELXTL PC program system.[22]

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