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Chloroaluminate(III) ionic liquid mediated synthesis of transition metal–cyclophane; complexes: their role as solvent and Lewis acid catalyst[1]

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Abstract

The preparation of transition metal–cyclophane complexes using the ionic liquid system [bmim]Cl–$AlCl_3$ ($[bmim]^+$ = 1-butyl-3-methylimidazolium cation) as both the solvent and Lewis acid catalyst is described. Both known and novel complexes are prepared. Simple arene complexes of manganese have also been prepared in order to demonstrate the chemistry and these reactions are compared with the literature preparations conducted in conventional organic solvents. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ionic liquid; Aluminium chloride; Cyclophane; Metal–arene complexes

1. Introduction

Room-temperature ionic liquids are a novel class of solvents with highly unusual properties which may promote a different reactivity to that seen in conventional molecular solvents [1,2]. Still the most widely investigated of these solvents are the chloroaluminates(III), which may be exemplified by [bmim]Cl–$AlCl_3$ (where $[bmim]^+$ = 1-butyl-3-methylimidazolium cation) [1]. Thus far, the synthetic chemistry reported in these ionic liquids has mostly focused on organic reactions [3,4], and very little synthetic organometallic chemistry has been reported to date. In fact, the acylation of ferrocene [5] and arene exchange reactions of ferrocene [6] represent the only examples, with only the latter involving metal–carbon bond formation. However, aluminium halide mediated synthesis is a widely used type of reaction in organometallic chemistry, in particular, in the preparation of metal–arene complexes and the synthesis of these complexes is covered in several prominent review articles [7–13]. Two main types of reaction are generally used; firstly, when aluminium(III) chloride, functioning as a dehalogenating agent, is reacted with a suitable metal halide precursor in the presence of an arene, and secondly, when aluminium metal is also added, acting as a reducing agent, affording metal–arene compounds in lower oxidation states.

With their high concentrations of chloroaluminate(III) species, room-temperature chloroaluminate(III) ionic liquids offer a potential environment for these reactions. The composition of a particular chloroaluminate(III) ionic liquid, and hence its chemistry, is determined by the ratio in which the aluminium(III) chloride and the organic chloride salt are mixed. This is best described by the apparent mole fraction of $AlCl_3$ present $\{X(AlCl_3)\}$. When aluminium(III) chloride is in excess $\{X(AlCl_3) > 0.5\}$ the melt is described

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as acidic and the formation of the Lewis acid $[Al_2Cl_7]^-$ is strongly favoured. When the concentration of aluminium(III) chloride is < 0.5 the melt is described as basic. The reactions described in this paper all use acidic [bmim]Cl–$AlCl_3$ ionic liquids.

In a previous paper we showed that the same ionic liquid can be used as the solvent for arene-exchange reactions of ferrocene [6]. In this paper this work is extended to the preparation of both known and novel, iron–cyclophane complexes. We also report that, using similar reaction conditions, a number of manganese(arene)tricarbonyl complexes can be prepared.

2. Results and discussion

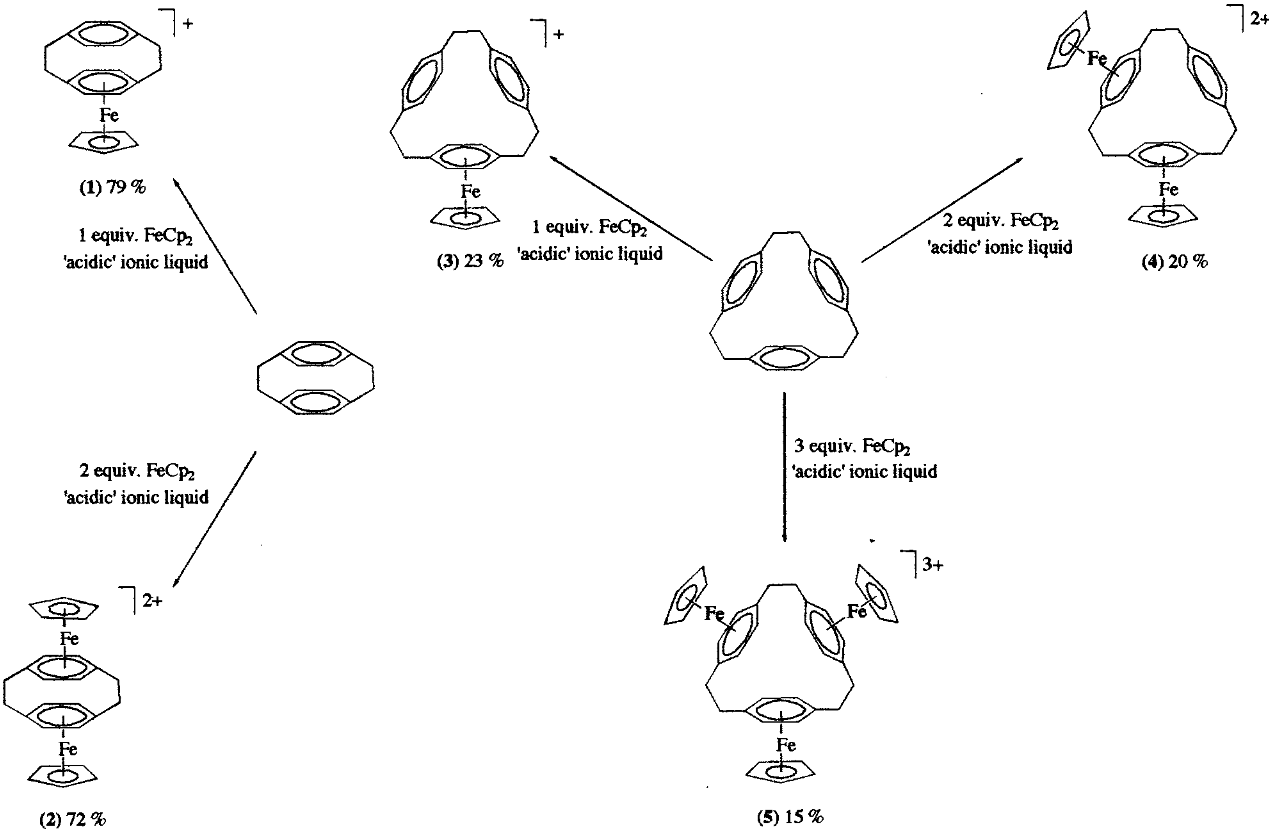
The reactions described in this paper are illustrated in Schemes 1–3 and full details are given in the experimental section.

2.1. Iron complexes

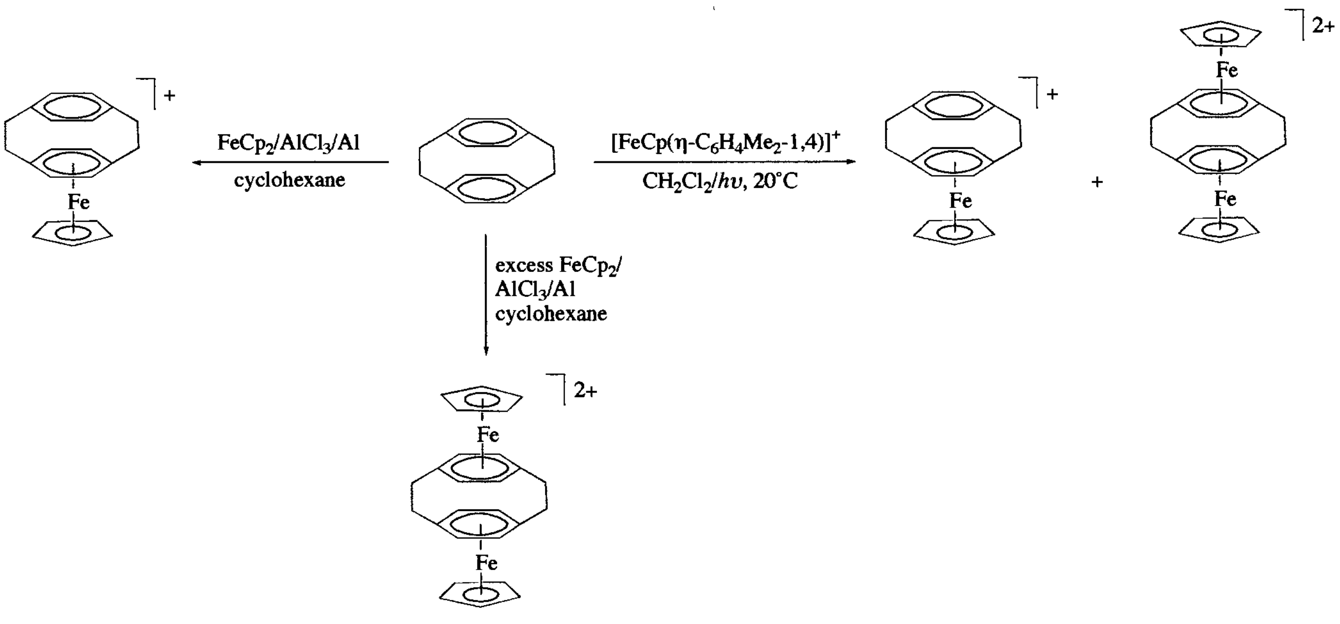
In our previous paper [6] we showed that it was possible to prepare iron(arene)cyclopentadienyl complexes (for a range of simple arene ligands and biphenyls) in the [bmim]Cl–$AlCl_3$ $\{X(AlCl_3) = 0.65\}$ ionic liquid. This has now been extended to the synthesis of $[Fe(\eta\text{-}C_5H_5)]^+$ complexes of [2.2]paracyclophane $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_{16}H_{16})][PF_6]$ **1** and $[\{Fe(\eta\text{-}C_5H_5)\}_2(\eta\text{-}C_{16}H_{16})][PF_6]_2$ **2** and of the novel compounds $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_{24}H_{24})][PF_6]$ **3** and $[\{Fe(\eta\text{-}C_5H_5)\}_2(\eta\text{-}C_{24}H_{24})][PF_6]_2$ **4** and $[\{Fe(\eta\text{-}C_5H_5)\}_3(\eta\text{-}C_{24}H_{24})][PF_6]_3$ **5** (Scheme 1).

The positive ion FAB mass spectrum of **3** contains a parent peak at 433 Th together with fragment ions which correspond to loss of either the [2.2.2] paracyclophane or cyclopentadienyl ligands. The mass spectra of **4** and **5** are somewhat more complicated given that they are multiply charged. Compound **4** shows a strong peak at 699 Th which corresponds to the sum of the dictation and one anion, namely $\{[\{Fe(\eta\text{-}C_5H_5)\}_2(\eta\text{-}C_{24}H_{24})][PF_6]\}^+$, together with a number of fragments of this ion. Similarly, the highest mass peak of **5** occurs at 965 Th and corresponds to the ion $\{[\{Fe(\eta\text{-}C_5H_5)\}_3(\eta\text{-}C_{24}H_{24})][PF_6]_2\}^+$.

The ^{1}H-NMR spectra of **3**–**5** were recorded in acetone-d_6. The ^{1}H-NMR spectrum of **3** contains four peaks centred at 6.77, 5.93, 5.01 and 3.1 ppm. The peak at 6.77 ppm is a multiplet and corresponds to the protons of uncoordinated rings. The peaks at 5.93 and 5.01 are both singlet resonances and correspond to the protons of the coordinated cyclophane and cyclopentadienyl rings, respectively. The peak centred at approximately 3.1 ppm is a complicated multiplet resonance,



Scheme 1. The synthesis of **1**–**5** from ferrocene.



Scheme 2.

partially obscured by impurities in the solvent and is attributed to the CH$_2$ protons in the [2.2.2]paracyclophane ligand. Compound **4** gives rise to four signals at 6.78, 6.05, 5.00 and 3.1 ppm in the ^{1}H-NMR spectrum. The peaks at 6.78, 6.05 and 5.00 are singlet resonances corresponding to the free cyclophane ring, coordinated cyclophane rings and cyclopentadienyl rings, respectively. The multiplet resonance centred at approximately 3.1 ppm corresponds to the cyclophane CH$_2$ protons. The ^{1}H-NMR spectrum of **5** is very simple. Three broad singlet resonances are observed at 5.0, 4.1 and 3.2 ppm which correspond to the [2.2]paracyclophane ring, cyclopentadienyl and [2.2]paracyclophane aliphatic protons, respectively.

Compounds **1** and **2** have been prepared previously, using two different routes [14,15]. The first involves the exchange of a cyclopentadienyl ring in ferrocene for the [2.2]paracyclophane ligand using the Fischer-Hafner method [14]. However, it has been found that [2.2]paracyclophane can isomerise in the presence of traces of HAlCl$_4$ [16], which is ubiquitously present in all but the purest aluminium(III) chloride. The arene rings are easily protonated and the resulting carbocation can then rearrange to [2.2]metaparacyclophane. Although we did not investigate this, we assumed that [2.2]paracyclophane will undergo similar isomerisation reactions. To avoid this problem the other route to **1** and **2** involves the arene exchange reaction with the *p*-xylene complex [Fe(η-C$_5$H$_5$)(η-C$_6$H$_4$Me$_2$-1,4)]$^+$ [15]. The xylene-complex is still prepared from ferrocene using Al/AlCl$_3$ and is subsequently replaced by the [2.2]paracyclophane in a photochemical process, thereby preventing isomerisation of the [2.2]paracyclophane ring. These reactions are illustrated in Scheme 2.

The room-temperature ionic liquid [bmim]Cl–AlCl$_3$ is ideally suited to these reactions as it can easily be prepared proton-free [17]. Indeed, because of its aprotic nature, the addition of [bmim][HCl$_2$] as a proton source is required to complete the arene exchange reactions of ferrocene [6]. This is because one of the cyclopentadienyl rings must first be protonated before it can be replaced by the arene. In order to minimise the risk of isomerisation of the cyclophanes, the [bmim][HCl$_2$] was only added after all of the other starting materials were well mixed. This strategy proved successful and at no time did we see evidence for the isomerisation of either of the cyclophanes used.

The original preparation of compounds **1** and **2** [14], led to the formation of a mixture of the products which could only be separated by preparative scale TLC. An important synthetic advantage of our reaction conditions is that it allows us to prepare pure products without the need for chromatography. We found that the pure products could be prepared by careful stoichiometric addition of the starting materials, combined with control of the reaction times.

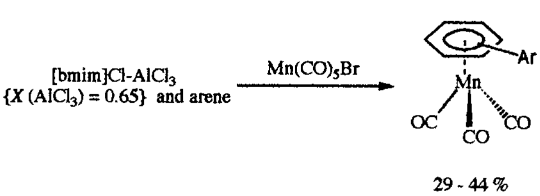
2.2. Manganese carbonyl complexes

In order to investigate the possibility of forming manganese(arene)tricarbonyl complexes in the chloroaluminate ionic liquids, we first attempted the reaction with a number of simple arenes. Initially, reaction of Mn(CO)$_5$Br with these arenes in the acidic ionic liquid, followed by extraction into a number of common counter anions, afforded yellow oils which could not be fully characterised, although their IR spectra in dichloromethane were characteristic of complexes with the formula $[Mn(CO)_3(\eta\text{-arene})]^+$ [18]. However, when $Mn(CO)_5Br$ was reacted with arenes in a stoichiometric amount of acidic [bmim]Cl–$AlCl_3$ ionic liquid, i.e. 1:1 ratio of $Mn(CO)_5Br$:$[Al_2Cl_7]^-$, the tricarbonyl cationic compounds of formula $[Mn(CO)_3(\eta\text{-arene})]^+$ (arene = C_6H_6 **6**, C_6H_5Me **7**, $C_6H_4Me_2$-1,3 **8**, $C_6H_3Me_3$-1,3,5 **9**, C_6H_4Ph **10**, $C_{16}H_{16}$ **11**, $C_{24}H_{24}$ **12**) are obtained as yellow solids (Scheme 3). A similar phenomenon has been noted previously when excess $AlCl_3$ is used in a conventional Fischer-Hafner reaction in the preparation of palladium complexes [19].

Unlike the reactions of ferrocene, it is unnecessary to add aluminium metal to the reaction mixture. This is because the manganese is less susceptible to oxidation under the reaction conditions and consequently no reducing agent is required to return it to the original oxidation state. Similarly, there is no need for a proton source, which serves to make the cyclopentadienyl ligand into the better leaving group cyclopentadiene in the arene exchange reactions of ferrocene, as the two carbonyl ligands which need to be lost from the $[Mn(CO)_5]^+$ fragment are thermally labile.

Compounds **6**–**10** have been prepared previously in conventional molecular solvents using $AlCl_3$ as a halide abstractor [20,21]. Alternative routes to these compounds, as well as other arene derivatives, include the use of silver(I) salts as the dehalogenating agent for $Mn(CO)_5Br$ [22], oxidation of $Mn_2(CO)_{10}$ with trifluoroacetic anhydride [23], and arene exchange methods [24].

Compounds **11** and **12** are new and of particularly interest as potential precursors to mixed valence bimetallic complexes with transannular communication between the metal sites. The mass spectra of **11** and **12** exhibit peaks at 347 and 451 Th, respectively, which correspond to the intact parent ions $[Mn(CO)_3(\eta\text{-}C_{16}H_{16})]^+$ and $[Mn(Co)_3(\eta\text{-}C_{24}H_{24})]^+$. The ^{1}H-NMR spectrum of **11** contains four peaks at 7.07, 6.21, 3.46 and 3.32 ppm with equal relative intensities. The peaks at 7.07 and 6.21 ppm are both singlet resonances and may be assigned to the C–H protons of the uncoordinated and coordinated rings, respectively. The peaks at 3.46 and 3.32 ppm are both multiplets and may be assigned to the CH_2 group protons, the former signal being due to those further from the $[Mn(CO)_3]^+$ fragment and the latter signal being due to those nearest to the $[Mn(CO)_3]^+$ fragment. The ^{1}H-NMR spectrum of **12** contains three peaks at 7.24, 6.62 and 3.04 ppm with relative intensities of 1:2:3, respectively. The peaks at 7.24 and 6.62 ppm are singlet resonances and correspond to the coordinated and two uncoordinated rings whereas the peak centred at 3.04 is a multiplet which can be assigned to the CH_2 protons in the aliphatic bridges.



Scheme 3. The synthesis of **6**–**12** from $Mn(CO)_5Br$ {arene = benzene (**6**), toluene (**7**) mxylene (**8**), mesitylene (**9**) biphenyl (**10**), [2.2]paracyclophane (**11**) or [2.2.2]paracyclophane (**12**)}.

Other related reactions are currently in progress as the acidic [bmim]Cl–$AlCl_3$ ionic liquids are well suited to Fischer-Hafner synthesis. We are also investigating the potential use of these systems for the generation of in situ catalysts for organic transformations, as a number of transition metal–arene complexes have been found to be active catalysts.

3. Experimental

3.1. General comments

Room temperature ionic liquids are formed by the direct combination of substituted imidazolium chloride salts and aluminium(III) chloride. There are a number of ways in which the precise composition of the ionic liquid can be described and in this paper we use an ionic liquid with an apparent mole fraction of $AlCl_3$ $\{X(AlCl_3)\} = 0.65$ and refer to this as the acidic ionic liquid. In fact, the ionic liquids contain no free $AlCl_3$ but have significant concentrations of the $[Al_2Cl_7]^-$ ion, which is the active Lewis acid species. All reagents were used as received expect for the following; $AlCl_3$ was repeatedly sublimed, [bmim]Cl and [bmim]$[HCl_2]$ were made using the literature procedures [6]. The preparation of the ionic liquids, by addition of $AlCl_3$ to 1-butyl-3-methylimidazolium chloride, followed previously described methods in a dry nitrogen atmosphere glove box [25]. Reactions were conducted under an atmosphere of nitrogen gas using a combination of glove box and Schlenk techniques. IR spectra were recorded using a Matson Research Series FTIR instrument, mass spectra were recorded in positive mode using fast atom bombardment on a VG AutoSpec Q instrument using 3-nitrobenzyl alcohol as the matrix and ^{1}H-NMR spectra were recorded on an Jeol JNM-EX270 FT instrument.

3.2. Synthesis of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_{16}H_{16})][PF_6]$ 1

In an inert atmosphere glove box, ferrocene (0.89 g, 4.81 mmol) and [2.2]paracyclophane (1.00 g, 4.81 mmol) were dissolved in [bmim]Cl–$AlCl_3$ $\{X(AlCl_3) = 0.65\}$ ionic liquid (8 g) in a Schlenk flask. Aluminium powder (0.13 g) was added, the flask was sealed and transferred to a Schlenk line. Finally, under an atmosphere of N_2, [bmim][HCl_2] (0.1 cm^3) was added to the reaction mixture. The reaction mixture was heated at 80°C for 40 h. The reaction mixture was cooled to r.t. and ice water (200 cm^3) was added slowly. The aqueous solution was filtered and washed with petroleum ether (5×20 cm^3). The aqueous layer was collected and filtered directly into an aqueous solution of [NH_4][PF_6] (2 g in 10 cm^3). An orange precipitate formed immediately. After standing for 1 h, the product was filtered and dried in vacuo for 24 h and characterised as **1** (orange, 1.8 g, 79%). Analytical data, C, 53.04; H, 4.30; $C_{21}H_{22}F_6FeP$ requires C, 53.16; H, 4.43%. ^1H-NMR (($(CD_3)_2CO$, 270 MHz): δ (ppm) 6.71 (s, uncomplexed ring), 5.78 (s, complexed ring), 4.84 (s, cyclopentadienyl ring) and 3.07 (s, CH_2); FAB-MS; *m/z* 329 $[C_{21}H_{21}Fe]^+$.

3.3. Synthesis of $[\{Fe(\eta\text{-}C_5H_5)\}_2(\eta\text{-}C_{16}H_{16})][PF_6]_2$ 2

In an inert atmosphere glove box, ferrocene (0.89 g, 4.81 mmol) and [2.2]paracyclophane (0.50 g, 2.42 mmol) were dissolved in [bmim]Cl–$AlCl_3$ $\{X(AlCl_3) = 0.65\}$ ionic liquid (8 g) in a Schlenk flask. Aluminium powder (0.13 g) was added, the flask was sealed and transferred to a Schlenk line. Finally, under an atmosphere of N_2, [bmim][HCl_2] (0.1 cm^3) was added to the reaction mixture. The reaction mixture was heated at 80°C for 65 h. After cooling to r.t., ice water (200 cm^3) was added slowly to the mixture. The aqueous solution was filtered and washed with petroleum ether (5×20 cm^3). The aqueous layer was collected and filtered directly into an aqueous solution of [NH_4][PF_6] (2 g in 10 cm^3). An orange precipitate formed immediately. After standing for an hour, the product was filtered and dried in vacuo for 24 h, and characterised by spectroscopy as **2** (orange, 1.6 g, 72%). Analytical data, C, 58.19; H, 5.94; $C_{26}H_{26}F_6FeP$ requires C, 57.91; H, 4.86%. ^1H-NMR ($(CD_3)_2CO$, 270 MHz): δ (ppm) 5.96 (s, complexed ring), 4.91 (s, cyclopentadienyl ring), and 3.23 (s, CH_2); FAB-MS; *m/z* 595 $\{[C_{26}H_{26}Fe][PF_6]\}^+$, 450 $[C_{26}H_{26}Fe]^+$and 329 $[C_{21}H_{21}Fe]^+$, 242 $[(C_5H_5)Fe_2]^+$, 121 $[C_5H_5Fe]^+$.

3.4. Synthesis of $[Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_{24}H_{24})][PF_6]$ 3

In an inert atmosphere glove box, ferrocene (0.029 g, 0.160 mmol), aluminium powder (0.5 g) and [2.2.2]paracyclophane (0.05 g, 0.160 mmol) were dissolved in [bmim]Cl–$AlCl_3$ $\{X(AlCl_3) = 0.65\}$ ionic liquid (10 g) in a Schlenk tube. Under dry N_2 [bmim][HCl_2] (2 drops) was added and the reaction mixture was heated at 80°C for 40 h with rapid stirring.

After this time, the mixture was allowed to cool to r.t. and ice water (200 cm^3) was added. The aqueous solution formed was filtered to remove solid impurities, washed with light petroleum (60–80°C, 5×20 cm^3) and then filtered into a concentrated aqueous solution of ammonium hexafluorophosphate (1.00 g in 5 cm^3) upon which, precipitation of a yellow solid occurred. The product was collected by filtration and recrystallized from an acetone/water mixture. The resulting yellow crystalline salt was dried over phosphorus pentoxide and then dried in vacuo for 24 h, and was characterized as **3** (orange, 0.02 g, 23%). Analytical data, C, 59.47; H, 4.57; $C_{29}H_{29}F_6FeP$ requires C, 60.23; H, 5.05%. ^1H-NMR ($(CD_3)_2CO$, 270 MHz): δ (ppm) 6.77 (m, uncomplexed rings), 5.93 (s, complexed ring), 5.01 (s, cyclopentadienyl ring) 3.1 (m, CH_2); FAB-MS; 433 $[C_{29}H_{29}Fe]^+$, 368 $[C_{24}H_{24}Fe]^+$, 121 $[C_5H_5Fe]^+$.

3.5. Synthesis of $[\{Fe(\eta\text{-}C_5H_5)\}_2(\eta\text{-}C_{24}H_{24})][PF_6]_2$ 4

In an inert atmosphere glove box, ferrocene (0.058 g, 0.315 mmol), aluminium powder (0.05 g) and [2.2.2]paracyclophane (0.05 g, 0.160 mmol) were dissolved in [bmim]Cl–$AlCl_3$ $\{X(AlCl_3) = 0.65\}$ ionic liquid (10 g) in a Schlenk tube. Under dry N_2 [bmim][HCl_2] (2 drops) was added and the reaction mixture was heated at 80°C for 65 h with rapid stirring.

After this time, the reaction mixture was allowed to cool to r.t. ice water (100 cm^3) was added. The mixture was filtered to remove solid impurities, washed with light petroleum (60–80°C, 5×10 cm^3) and then filtered into a concentrated aqueous solution of ammonium hexafluorophosphate (1.00 g in 5 cm^3) upon which, precipitation of a yellow solid occurred. The product was collected by filtration and washed with ether. The resulting yellow salt was dried over phosphorus pentoxide and then dried in vacuo for 24 h, and characterized as **4** (orange, 0.053 g, 20%). Analytical data, C, 48.28; H, 4.19; $C_{34}H_{34}F_6FeP$ requires C, 48.37; H, 4.06%. ^1H-NMR ($(CD_3)_2CO$, 270 MHz): δ (ppm) 6.78 (s, uncomplexed ring), 6.05 (s, complexed rings), 5.00 (s, cyclopentadienyl rings) 3.1 (m, CH_2); FAB-MS; *m/z* 699 $\{[C_{34}H_{34}Fe_2][PF_6]\}^+$, 554 $[C_{34}H_{34}Fe_2]^+$, 433 $[C_{29}H_{29}Fe]^+$, 368 $[C_{24}H_{24}Fe]^+$, 121 $[C_5H_5Fe]^+$.

3.6. Synthesis of $[\{Fe(\eta\text{-}C_5H_5)\}_3(\eta\text{-}C_{24}H_{24})][PF_6]_3$ 5

In an inert atmosphere glove box, ferrocene (0.087 g, 0.471 mmol), aluminium powder (0.05 g) and [2.2.2]paracyclophane (0.05 g, 0.160 mmol) were dissolved in [bmim]Cl–$AlCl_3$ $\{X(AlCl_3) = 0.65\}$ ionic liquid (10 g) in a Schlenk tube. Under dry N_2 [bmim][HCl_2] (2 drops) was added and the reaction mixture was heated at 80°C for 85 h with rapid stirring.

After this time, the reaction mixture was allowed to cool to r.t. and ice water (100 cm^3) was added. The mixture was filtered to remove solid impurities, washed with light petroleum (60–80°C, 5×10 cm^3) and then filtered into a concentrated aqueous solution of ammonium hexafluorophosphate (1.6 g in 20 cm^3) upon which precipitation of a yellow solid occurred. The product was collected by filtration and washed with ether. The resulting yellow crystalline salt was dried over phosphorus pentoxide and then dried in vacuo for 24 h, and characterized as **5** (orange, 0.078 g 15%) Analytical data, C, 42.06; H, 3.70; $C_{39}H_{39}F_6FeP$ requires C, 42.16; H, 3.51%. ^{1}H-NMR ($(CD_3)_2CO$, 270 MHz): δ (ppm) 5.0 (s, complexed rings), 4.1 (s, cyclopentadienyl rings) 3.2 (m, CH_2); FAB-MS; 965 $\{[C_{39}H_{39}Fe_3][PF_6]_2\}^+$, 820 $\{[C_{39}H_{39}Fe_3][PF_6]\}^+$, 699 $\{[C_{34}H_{34}Fe_2][PF_6]\}^+$, 433 $[C_{29}H_{29}Fe]^+$, 368 $[C_{24}H_{24}Fe]^+$.

3.7. Synthesis of $[Mn(CO)_3(\eta\text{-}C_6H_6)][PF_6]$ 6

In an inert atmosphere glove box, $Mn(CO)_5Br$ (0.10 g, 0.36 mol) and $\{X(AlCl_3) = 0.65\}$ [bmim]Cl–$AlCl_3$ ionic liquid (0.073 cm^3, 0.36 mmol) were placed in a Schlenk flask. The sealed flask was removed from the glove box and transferred to a Schlenk line. Under a nitrogen atmosphere benzene (1 cm^3) was added to the reaction mixture which was then heated at 60°C for 15 h with rapid stirring. The reaction mixture was cooled and ice water (50 cm^3) added slowly. The mixture was filtered and the yellow solution washed with diethyl ether (5 × 10 cm^3). The aqueous layer was then filtered into a concentrated solution of $[NH_4][PF_6]$ (0.06 g in 5 cm^3 of water) which gave a yellow solid which was filtered and dried under vacuum and characterised as **6** (yellow, 0.055 g, 42%). Analytical data, C, 30.08; H, 1.74; $C_9H_6F_6MnO_3P$ requires C, 29.86; H, 1.67%. ν_{CO}(Nujol, cm^{-1}) 2082, 2017; ^{1}H-NMR ($(CD_3)_2CO$, 270 MHz): δ (ppm); 7.03 (s, C_6H_6); FAB-MS; m/z 217 $[C_9H_6MnO_3]^+$.

3.8. Synthesis of $[Mn(CO)_3(\eta\text{-}C_6H_5Me)][PF_6]$ 7

In an inert atmosphere glove box, $Mn(CO)_5Br$ (0.5009 g, 1.84 mmol), and [bmim]Cl–$AlCl_3$ ($X(AlCl_3) = 0.65$) ionic liquid (0.36 cm^3, 1.84 mmol) were placed in a Schlenk flask. The sealed flask was removed from the glove box and transferred to a Schlenk line. Under N_2, dry toluene (0.23 cm^3, 1.84 mmol) was added to the reaction mixture. Maintaining a N_2 atmosphere, the reaction mixture was heated at 80°C for 15 h with rapid stirring. Ice water (50 cm^3) was added to the reaction mixture. The yellow aqueous solution was filtered to remove solid impurities, and then washed with diethyl ether (5 × 10 cm^3) in order to remove any unreacted $Mn(CO)_5Br$. The aqueous layer was then filtered into a concentrated solution of $[NH_4][PF_6]$ (0.4 g in 5 cm^3 of water) upon which precipitation of a yellow solid occurred. The salt was collected by filtration and dried in vacuo for 24 h, and characterized as **7** (yellow, 0.206 g, 30%). Analytical data, C, 30.52; H, 1.76. $C_7H_8O_3MnPF_6$ requires C, 31.94; H, 2.14%. $\nu_{CO}(CH_2Cl_2, cm^{-1})$: 2082, 2024; ^{1}H-NMR (CD_3COCD_3, 270 MHz) δ (ppm) 6.92 (s, aromatic), 6.66 (s, aromatic), 2.58 (s, CH3); FAB-MS: m/z 231 $[C_7H_8Mn(CO)_3]^+$, 203 $[C_7H_8Mn(CO)_2]^+$, 175 $[C_7H_8Mn(CO)]^+$.

3.9. Synthesis of $[Mn(CO)_3(\eta\text{-}C_6H_4Me_2\text{-}1,3)][PF_6]$ 8

In an inert atmosphere glove box, $Mn(CO)_5Br$ (0.10 g, 0.36 mol) and [bmim]Cl–$AlCl_3$ $\{X(AlCl_3) = 0.65\}$ ionic liquid (0.073 cm^3, 0.36 mmol) were placed in a Schlenk flask. The sealed flask was removed from the glove box and transferred to a Schlenk line. Under a nitrogen atmosphere, *m*-xylene (1 cm^3) was added to the reaction mixture which was then heated at 110°C for 15 h. The reaction mixture was cooled and ice water (50 cm^3) added slowly. The mixture was filtered and the yellow solution washed with diethyl ether (5 × 10 cm^3). The aqueous layer was then filtered into a concentrated solution of $[NH_4][PF_6]$ (0.06 g in 5 cm^3 of water) which gave a yellow solid which was removed by filtration and dried under vacuum and characterised as **8** (yellow, 0.52 g, 37%). Analytical data, C, 33.73; H, 2.55; $C_{11}H_{10}F_6MnO_3P$ requires C, 33.87; H, 2.58%. ν_{CO}(Nujol, cm^{-1}) 2075, 2001; ^{1}H-NMR ($(CD_3)_2CO$, 270 MHz): δ (ppm) 6.7 (s, aromatic), 2.3 (s, CH3); FAB-MS; m/z 245 $[C_{11}H_{10}MnO_3]^+$, 189 $[C_9H_{10}MnO]^+$, 161 $[C_8H_{10}Mn]^+$.

3.10. Synthesis of $[Mn(CO)_3(\eta\text{-}C_6H_3Me_3\text{-}1,3,5)][PF_6]$ 9

In an inert atmosphere glove box, $Mn(CO)_5Br$ (0.107 g, 0.40 mmol) and [bmim]Cl–$AlCl_3$ $\{X(AlC_3) = 0.65\}$ ionic liquid (0.075 cm^3, 0.40 mmol) were placed in a Schlenk flask. The sealed flask was removed from the glove box and transferred to a Schlenk line. Under N_2, dry mesitylene (0.5 cm^3) was added to the reaction mixture. Maintaining a N_2 atmosphere, the reaction mixture was heated at 80°C for 15 h. Ice water (50 cm^3) was added to the reaction mixture. The yellow aqueous solution was filtered to remove solid impurities, and then washed with diethyl ether (5 × 10 cm^3) in order to remove any unreacted $Mn(CO)_5Br$. The aqueous layer was then filtered into a concentrated solution of $[NH_4][PF_6]$ (0.3 g in 5 cm^3 of water) upon which precipitation of a yellow solid occurred. The salt was collected by filtration and dried in vacuo for 24 h and characterized as **9** (yellow, 0.07 g, 42%) Analytical data, C, 34.88; H, 2.27; $C_{12}H_{12}O_3MnPF_6$ requires C, 35.67; H, 2.99%. $\nu_{CO}(CH_2Cl_2, cm^{-1})$: 2015, 2075; ^{1}H-NMR (CD_3COCD_3, 270 MHz) δ (ppm) 6.40 (s, aromatic), 2.59 (s, CH_3); FAB-MS; m/z 259 $[C_9H_{12}Mn(CO)_3]^+$, 203 $[C_9H_{12}Mn(CO)]^+$.

3.11. Synthesis of [Mn(CO)$_3$(η-C_6H_5Ph)][PF$_6$] **10**

In an inert atmosphere glove box, Mn(CO)$_5$Br (0.10 g, 0.36 mol) and $\{X(\mathrm{AlCl_3}) = 0.65\}$ [bmim]Cl–AlCl$_3$ ionic liquid (0.073 cm^3, 0.36 mmol) were placed in a Schlenk flask. The sealed flask was removed from the glove box and transferred to a Schlenk line. Under a nitrogen atmosphere biphenyl (0.055 g, 0.36 mmol) was added to the reaction mixture which was then heated at 80°C for 15 h. The reaction mixture was cooled and ice water (50 cm^3) added slowly. The mixture was filtered and the yellow solution washed with diethyl ether (5 × 10 cm^3). The aqueous layer was then filtered into a concentrated solution of [NH$_4$][PF$_6$] (0.06 g in 5 cm^3 of water) which gave a yellow solid which was filtered and dried under vacuum and characterised as **10** (yellow, 0.047 g, 29%). Analytical data, C, 40.98; H, 2.33; $C_{15}H_{10}F_6MnO_3$ P requires C, 41.12; H, 2.30%. ν_{CO}(Nujol, cm^{-1}) 2075, 2013; ^{1}H NMR ((CD$_3$)$_2$CO, 270 MHz): δ (ppm) 7.8 (s, uncoordinated ring), 7.3 (s, coordinated ring); FAB-MS; *m/z* 293 [$C_{15}H_{12}MnO_3$]$^+$, 237 [$C_{12}H_{11}MnO$]$^+$, 209 [$C_{12}H_{10}Mn$]$^+$.

3.12. Synthesis of [Mn(CO)$_3$(η-$C_{16}H_{16}$)][PF$_6$] **11**

Mn(CO)$_5$Br (0.491 g, 1.80 mmol), [2.2]paracyclophane (0.376 g, 1.81 mmol) and $\{X(\mathrm{AlCl_3}) = 0.65\}$ [bmim]Cl–AlCl$_3$ ionic liquid (0.375 cm^3, 1.81 mmol) were placed in a Schlenk tube. The mixture was stirred 70°C for 41 h. After allowing the mixture to cool, ice water (35 cm^3) was added to afford a red-brown aqueous mixture. After filtration this gave a yellow solution which was washed with diethyl ether (2 × 5 cm^3). The aqueous extracts were filtered into a solution of [NH$_4$][PF$_6$] (0.4 g in 5 cm^3 water) and a yellow precipitate formed. After standing for an hour, the product was filtered and dried in vacuo for 24 h and characterised by spectroscopy as **11** (yellow, 0.39 g, 44%). Analytical data, C, 46. 12; H, 3.52; $C_{19}H_{16}F_6MnO_3P$ requires C, 46.36; H, 3.28%. ν_{CO}(CH$_2$Cl$_2$, cm^{-1}) 2017, 2073; ^{1}H-NMR ((CD$_3$)$_2$CO, 270 MHz): δ (ppm) 7.07 (s, coordinated ring), 6.21 (s, uncoordinated ring), 3.46 (multiplet, CH$_2$), 3.32 (multiplet, CH$_2$); FAB-MS; *m/z* 347 [$C_{19}H_{16}$MnO3]$^+$.

3.13. Synthesis of [Mn(CO)$_3$(η-$C_{24}H_{24}$)][PF$_6$] **12**

In an inert atmosphere glove box, Mn(CO)$_5$Br (0.10 g, 3.6 mmol), [2.2.2]paracyclophane (1.28 g, 3.6 mol) and $\{X(\mathrm{AlCl_3}) = 0.65\}$ [bmim]Cl–AlCl$_3$ ionic liquid (0.073 cm^3) were placed in a Schlenk flask. The sealed flask was removed from the glove box and transferred to a Schlenk line. Maintaining a N$_2$ atmosphere, the reaction mixture was heated at 80°C for 15 h with rapid stirring. Ice water (50 cm^3) was added and the yellow aqueous solution was filtered to remove solid impurities, and then washed with diethyl ether (5 × 10 cm^3) in order to remove any unreacted Mn(CO)$_5$Br. The aqueous layer was then filtered into a concentrated solution of [NH$_4$][PF$_6$] (0.059 g in 5 cm^3 of water) upon which precipitation of a yellow solid occurred. The salt was collected by filtration and dried in vacuo for 24 h, and characterized as **12** (yellow, 0.76g, 35%). Analytical data, C, 54.22; H, 4.10; $C_{27}H_{24}F_6MnO_3P$ requires C, 54.38; H, 4.06%. IR: ν_{CO}(Nujol, cm^{-1}) 2017, 2076; ^{1}H-NMR ((CD$_3$)$_2$CO, 270 MHz): δ (ppm) 7.24 (s, coordinated ring), 6.62 (s, uncoordinated rings) 3.04 (multiplet, CH$_2$); FAB-MS: *m/z* 451 [$C_{27}H_{24}MnO_3$]$^+$, 367 [$C_{24}H_{24}Mn$]$^+$, 111 [C_2MnO_2]$^+$, 93 [CMnO]$^+$.

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