Polymethylated $[\text{Fe}(\eta^6\text{-arene})_2]^{2+}$ dications: methyl-group rearrangements and application of the EINS mechanism†‡

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Reactions between the methylated arenes $\text{ArMe}_n$ [where $\text{ArMe}_n = \text{C}_n\text{Me}_n\text{H}_{12-6n}$, and $n = 1-6$] and $\text{FeCl}_3$ in heptane at $90^\circ\text{C}$ in the presence of anhydrous $\text{AlCl}_3$ give, for the arenes with $n = 1-5$, extensive isomerisations and disproportionations involving the methyl groups on the arene rings, and the formation of mixtures of $[\text{Fe}(\text{ArMe}_n)]^{2+}$ dications that defy separation into pure species. GC-MS studies of $\text{AlCl}_3$/mesitylene and $\text{AlCl}_3$/durene reactions in the absence of $\text{FeCl}_2$ (90 °C; 2 h) allow quantitative assessments of the rearrangements, and the EINS mechanism (electrophile-induced nucleophilic substitution) is applied to rationalise the phenomena. By contrast, $\text{ArMe}_n / \text{FeCl}_2 / \text{AlCl}_3$ reactions in heptane for 24–36 h at room-temperature proceed with no rearrangements, allowing the synthesis of the complete series of pure $[\text{Fe}(\text{ArMen})]^{2+}$ cations in yields of 48–71%. The pure compounds are characterised by $^1\text{H}$ NMR spectroscopy and electrospray-ionization mass-spectrometry (ESI-MS), and the structures of $[\text{Fe}(\text{m-xylene})]^{2+}$ and $[\text{Fe}(\text{durene})]^{2+}$ are established by single-crystal X-ray diffraction analyses.

Introduction

We have become interested in the preparation and properties of compounds resulting from the incorporation of $\{\text{Fe}(\eta^6-\text{ArMe}_n)\}$ units [where $\text{ArMe}_n = \text{C}_n\text{Me}_n\text{H}_{12-6n}$, and $n = 1-6$] into carboraboranes, and have recently reported preliminary results on some polymethylated complexes $[3-(\eta^6-\text{ArMe}_n)-\text{closo}-3,1,2-\text{FeC}_n\text{B}_2\text{H}_8]$. The synthetic route to these metallacarboraboranes requires the use of salts of the $[\text{Fe}(\eta^6-\text{ArMe}_n)]^{2+}$ dications, and our preliminary work highlighted the known problems, exemplified by the work of Helling and Braitsch in 1972, in the preparation of pure samples of these fundamental dications. The preparative route is based on that of Fischer et al., who, in 1956, reported the isolation of the $[\text{Fe}(\text{mes})]^{2+}$ dication [where mes = mesitylene, $\text{C}_9\text{H}_5\text{H}_{1-3,5-6}$] from the $\text{AlCl}_3$-promoted reaction between $\text{FeBr}_2$ and mesitylene. The work of Helling and Braitsch, and of others, subsequently reported improved procedures based on the use of either $\text{FeCl}_2$ or $\text{FeCl}_3$ as a starting compound, and the use of either neat arenes, or their solutions in an inert solvent at ambient or higher temperatures; for example in cyclohexane at reflux. The stoichiometry of the $\text{FeCl}_2$ reaction is that given in eqn (1).

$$2 \text{ArMe}_n + \text{FeCl}_2 + 2 \text{AlCl}_3 \rightarrow [\text{Fe}(\text{ArMen})]_2[\text{AlCl}_4] \quad (1)$$

However, this route, as we have also found more recently, for example in heptane at reflux, generates mixtures of methylated $[\text{Fe}(\eta^6-\text{ArMe}_n)]^{2+}$ dications, ascribed by the original authors to result from isomerisations. There is a clear need for pure syntheses of these classic organometallic species. This present communication examines the origins of the $\text{ArMe}_n$ rearrangements in more detail, and establishes optimum conditions for the syntheses of the isomerically pure $[\text{Fe}(\eta^6-\text{ArMe}_n)]^{2+}$ salts.

Results and discussion

Syntheses

We have recently communicated† that the reaction of eqn (1) with the two selected polymethylated arenes mesitylene and durene [dur; $\text{C}_9\text{H}_{1-1.2,4,5-6}$] in heptane for 6 h proceeds with extensive rearrangement of the arene ligand. Now we report in more detail the results of electrospray-ionization mass-spectrometric (ESI-MS) and NMR spectroscopic examination of this process. The ESI-MS studies have clearly shown that the main reaction mode is consistent with that outlined in Scheme 1. However, the product of the mesitylene reaction was mostly a mixture of at least three dication types, while durene provided two dominant dication
Scheme 1  The principal products from the reaction of eqn (1) with mesitylene (mes) and durene (dur) at 90 °C (heptane, reflux, 2 h), as assessed by ESI-MS. The prefix I is used to indicate that the individual dication formulations consist of mixtures of essentially all the possible isomers of the given methylated arene formulation. The positional isomers are not recognised by ESI-MS, but are detectable and elucidated by 1H NMR spectroscopy.

types. Both reactions also showed significant smaller quantities of other [Fe(η6-ArMe2n)2]2+ dication types. In both cases, not only do all these dications differ in the number of methyl groups (resulting from disproportion, D) but also in their positioning on the arene ring (resulting from isomerisation, I), overall indicating that processes other than simple aryl-for-chloride exchange about the iron atom are also occurring.

The results led us to the supposition that the observed D-mode and I-mode rearrangements of the arene ligands stem from interactions between the free arenes and AlCl3 at higher temperatures. The relevant reaction systems, i.e. the same as for the [Fe(η6-ArMe2n)2]2+ preparations, but with no FeCl2 present, were therefore investigated by GC-MS analysis under the following standard conditions: equimolar AlCl3:ArMe2n (where ArMe2n is mes or dur), 90 °C, 6 h. The results are represented in Fig.1.

It is apparent from the results that two processes, consisting of disproportionations D and isomerisations I, are confirmed.

For mesitylene, it is readily seen that the main reaction mode is one of disproportionation D into the meta and ortho isomers of xylene (m-xyl and o-xyl), three isomers of tetramethylbenzene, viz. durene, isodurene (i-dur, Me4C6H2-1,2,3,5) and 1,2,3,4-tetramethyl-benzene (1,2,3,4-tmb), and also pentamethyl-benzene (pmb). A little less pronounced is the isomerisation mode I, yielding pseudocumene (pcm, 1,2,4-trimethylbenzene) and hemimellitene (hmt, 1,2,3-trimethylbenzene). The overall I/D ratio is 0.8.

In contrast to the mesitylene situation, the dominant mode of the durene conversion is isomerisation I, with an I / D ratio 1.7. The isomerisation I gives isodurene and, to a lesser extent, 1,2,3,4-tetramethyl-benzene. The less pronounced D-mode then yields all three trimethylbenzene isomers along with pentamethylbenzene.

As exemplified in Scheme 2 for the mesitylene substrate, the AlCl3-induced conversions (retro Friedel–Crafts reactions) can be explained on the basis of our previously proposed EINS concept. According to this approach, electrophilic AlCl3 can abstract either Me or H of from the mesitylene substrate to generate either of the two anionic nucleophilic particles [HAlCl3]− and [MeAlCl3]−, together with either of two carbenium cations that have the positive charge dissipated over all non-substituted positions. The anionic nucleophiles would then immediately combine with either cation as in Scheme 2 to give the observed disproportionation and isomerisation products.

Scheme 2 Possible steps of an EINS mechanism for the mesitylene reaction, leading to isodurene and meta-xylene (D-mode) and two isomers of trimethylbenzene (I-mode).

In attempts to avoid these rearrangement complications in the preparation of the iron dications, we essayed the reaction of eqn (1) in heptane for 24–36 h, but now at room temperature rather than under reflux. Under these conditions we found that arene rearrangement was suppressed to a minimum and that all of the dications of constitution I (Table 1) were isolatable in pure state as their [PF6]− salts. The yields ranged from 48 to 71%, depending on the nature of the arene (see Scheme 3). Although all the methylated species are stable in the solid state and in solution in the absence of AlCl3, it is of interest to note that the
The structures confirm the expected constitution in which the Fe numbers of methyl groups. These are shown in Fig. 2 and Fig. 3.

The formation and yields of the [Fe(\(\eta^1\)-pentamethylbenzene)]\([PF_6]_2\) salts, [1a–g][PF_6]], as prepared at room temperature; bz = benzene, tol = toluene, m-xyl = \textit{meta}-xylene, mes = mesitylene, dur = durene, pmb = pentamethylbenzene and hmb = hexamethylbenzene.

The \(^1\)H NMR chemical-shift data for all the individual dications 1 are given in Table 1 (for comparison of the measured shifts with those already published see references 2–5), together with the measured and calculated ESI-MS molecular-ion highest-mass cut-offs.

Structural studies

As far as we are aware, the only crystallographic study that has been published on this type of compound is for [Fe(mesityl)][PF_6]], [1e][PF_6]], which has an odd number (three) of methyl groups per ring, and which shows a severe disorder of the Fe atom position.\(^7\)

In this work we now report the molecular structures (as determined by single-crystal X-ray diffraction analyses on their [PF_6]²⁻ salts) of the \textit{meta}-xylene and durene dications 1e and 1f that contain even numbers of methyl groups. These are shown in Fig. 2 and Fig. 3. The structures confirm the expected constitution in which the Fe

![Scheme 3](image312x585to547x721)

![Fig. 2](image48x355to283x514)

![Fig. 3](image548x732)
of the aromatic rings in 1e is 2.706(3) Å with the Fe atom in the middle of the parallel, while the more sterically crowded durene dication If reveals significant elongation of the same distance to 3.176(3) Å, together with a slightly unsymmetrical location of the Fe atom. The mean Fe-(ring centroid) distance in If, viz. 1.588(3) Å, is 0.105 Å longer than the equivalent distance in the mixed-ligand carborane complex [1-(η4-dur)-closo-1,2,3-FeC₂B₉H₁₁],¹ threshes the Fe–C(Ar) and the C–C(Ar) distances are comparable.

Conclusions

We have shown that all the methylated [Fe(η⁴-arene)]²⁺ dications can be readily prepared in essentially pure form according to reaction 1, if carried out at room temperature. Yields are moderate to good, and there is no significant rearrangement of the arene methyl groups. On the other hand, we have also shown that high-temperature reactions are associated with extensive isomerisation and disproportionation of the methyl substituents on the arene rings, which is caused by the action of anhydrous AlCl₃ on the arenes themselves, as assessed by GC-MS analysis of the rearrangement products of the mesitylene and durene reactions. A mechanistic approach invoking the EINS mechanism to account for the products is consistent with the generation of carbenium cations which immediately interact with methanion- and hydride-containing nucleophiles to give either isomerisation or disproportionation products. The two single-crystal X-ray diffraction studies on dications 1e and and If are, as far as we are aware, the first reliable structural studies in the whole area of iron bis(arene) dications. Further work in this field, namely addition reactions with nucleophilic boron-containing cluster compounds, is underway in our laboratories.

Experimental

Materials and Methods

All reactions were carried out with use of standard vacuum or inert-atmosphere techniques as described by Shriver;⁸ although some subsequent operations were carried out in air. The starting methylated arenes, FeCl₂, NH₄PF₆, and AlCl₃ were purchased from Sigma–Aldrich and used as received. Dichloromethane and AlCl₃ on the arenes themselves, as assessed by GC-MS analysis of the rearrangement products of the mesitylene and durene reactions. A mechanistic approach invoking the EINS mechanism to account for the products is consistent with the generation of carbenium cations which immediately interact with methanion- and hydride-containing nucleophiles to give either isomerisation or disproportionation products. The two single-crystal X-ray diffraction studies on dications 1e and and If are, as far as we are aware, the first reliable structural studies in the whole area of iron bis(arene) dications. Further work in this field, namely addition reactions with nucleophilic boron-containing cluster compounds, is underway in our laboratories.

Room temperature synthesis of the [Fe(η⁴-Ar)][PF₆]⁺ compounds, [1a–1g][PF₆]⁺. In a typical experiment, arene (30 mmol), FeCl₂ (10 mmol), AlCl₃ powder (30 mmol), and heptane (10 ml) were stirred vigorously under nitrogen at ambient temperature for 36 h. The mixture was then treated with water (50 ml) and ice (50 g) under shaking and the aqueous layer then separated and precipitated with a concentrated aq. solution of NH₄PF₆ (3.3 g, 20 mmol). In each case, the orange precipitate was crystallized by addition of ether to a solution of the crude salt in 95% aqueous acetone. Yields of individual dications 1a–1g are in Scheme 3, while Table 1 summarizes the results of the ¹H NMR and ESI-MS experiments.

X-ray crystallography. The X-ray diffraction data for orange crystals of [1e][PF₆]⁺ and [If][PF₆]⁺ were obtained at 150 K, on a Nonius KappaCCD diffractometer using an Oxford Cryostream low-temperature device, and with Mo-Kα radiation (λ = 0.71073 Å), a graphite monochromator, and the φ and χ scan mode. Data reductions were performed with DENZO-SMN.¹⁰ The absorption was corrected by integration methods.¹¹ Structures were solved by direct methods (SIR92)¹² and refined by full-matrix least-squares based on F² (SHELXL97).¹³ Hydrogen atoms were mostly localized on a difference Fourier map, but to ensure uniformity of

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crystal treatment, all hydrogen-atom positions were recalculated into idealized positions (riding model) and assigned temperature factors \(U_{eq}\) (pivot atom), and of 1.5 \(U_{eq}\) for the methyl moieties, with C–H = 0.96 Å, and 0.93 Å for methyl hydrogen atoms and ring hydrogen atoms, respectively.

Crystallographic data for [1e][PF₆]₂: C₉₀H₄₄F₈₀P₂Fe, M = 558.11, monoclinic, \(C₂/c\), \(a = 15.5808(7), b = 9.7552(13), c = 13.2471(12) Å, \(β = 107.37(3)°, Z = 4, V = 1921.6(3) Å³, \(Dₐ = 1.929 \text{ g cm}⁻³, \mu = 0.8 \text{ mm}⁻¹, T_{\text{min}} = 0.768, T_{\text{max}} = 0.867; 7139 reflections measured (\(θ_{\text{max}} = 27.5°\)), 2192 independent (\(R_{\text{int}} = 0.0353\), 1833 with \(I > 2\sigma(I)\)), 141 parameters, \(S = 1.103, R_(\text{obs. data}) = 0.0334, W_R\) (all data) = 0.0682; max., min. residual electron density = 0.344, –0.462 e Å⁻³. \(R_{\text{int}} = \sum F_o^2 - F_c^2 / \sum F_o^2, GOF = [\sum w(F_o^2 - F_c^2)^2 / (N_{\text{param}} - N_{\text{obs}})]^{1/2}\) for all data, \(R(F) = \sum F_o - |F_c| / \sum F_o\) for observed data, \(w_R(F) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2))]^{1/2}\) for all data.

Crystallographic data for [1f][PF₆]₂: C₁₀₀H₅₆F₆₄P₂Fe, M = 614.21, chiral orthorhombic space group \(P₂\_2\_2\_1\), \(a = 9.9241(7), b = 13.4542(8), c = 17.7747(15) Å, Z = 4, V = 2373.3(3) Å³, \(Dₐ = 1.719 \text{ g cm}⁻³, \mu = 0.8 \text{ mm}⁻¹, T_{\text{min}} = 0.875, T_{\text{max}} = 0.928; 19066 reflections measured (\(θ_{\text{max}} = 27.5°\)), 5398 independent (\(R_{\text{int}} = 0.0415\), 4628 with \(I > 2\sigma(I)\)), 316 parameters, \(S = 1.120, R_(\text{obs. data}) = 0.0472, W_R\) (all data) = 0.1001; max., min. residual electron density = 0.549, –0.485 e Å⁻³.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference numbers 782984 and 782983 for [1e][PF₆]₂ and [1f][PF₆]₂, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk

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