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Bis-arene iron dications: synthetic problems and reactions with nucleophiles

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Abstract

The synthesis of the complexes $[Fe(\eta^6\text{-arene})_2]^{2+}(PF_6^-)_2$ (arene = benzene (**1a**), toluene (**1b**), *p*-xylene (**1c**), mesitylene (**1d**) and hexamethylbenzene (**1e**)) has been reexamined. Isomerization occurs, especially in the case of toluene. Reactions of **1a–e** with 1 eq. $NaBH_4$ give $[Fe(\eta^5\text{-cyclohexadienyl})(\eta^6\text{-arene})]^+$ cations **2a–e**. Reactions of **1a** and **1e** with C and O nucleophiles give mainly electron transfer, which inhibits the formation of C–C or C–O bonds. The labile complexes $[Fe(\eta^4\text{-}C_6H_8)(\eta^6\text{-}C_6Me_6)]$ (**3**) and $[Fe(\eta^4\text{-}exo\text{-}(C_6H_5)_2-C_6H_4Me_2)(\eta^6\text{-}p\text{-}C_6H_4Me_2)]$ (**5**) have, however, been synthesized, but in low yields.

There is considerable interest in the reaction of nucleophiles with aromatic compounds which are activated by a transition metal moiety [1–7]. The bis-arene iron series is of special interest because reaction of two different nucleophiles could in principle lead to heterobifunctional cyclohexadienes [6,8–11]. The complexes $[Fe(C_6H_{6-n}Me_n)_2]^{2+}(PF_6^-)_2$ were discovered by Fischer et al. [12] shortly after ferrocene, but detailed procedures are not available. In reinvestigating these syntheses, with the aim of using the dicationic iron complexes as precursors for further activation procedures, we have found significant isomerization, which we report here. We have also prospected the possibilities of nucleophilic attack on these dications and have found that most of the carbanion reactions failed. These attempts are also reported in this article. Previous work had been carried out by Helling et al. [13] on the mesitylene complex $[Fe(\text{mesitylene})_2]^{2+}(PF_6^-)_2$, but it turns out that this aromatic is not at all representative [8]. Finally we also report the

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reactions with $NaBH_4$, which open the routes to further functionalization. The first step of the $NaBH_4$ reduction of **1a** was briefly reported by Nesmeyanov et al. [14] and the addition of phosphites to **1a** is also known [15].

Results

Fischer–Haffner syntheses of $[Fe(arene)_2]^{2+}(PF_6^-)_2$ and isomerization

The preparations were based on the Fischer–Haffner syntheses using $FeCl_2$ and $AlCl_3$ for the C_6Me_6 complex and $FeCl_3$, instead of $FeCl_2$, for the other complexes.

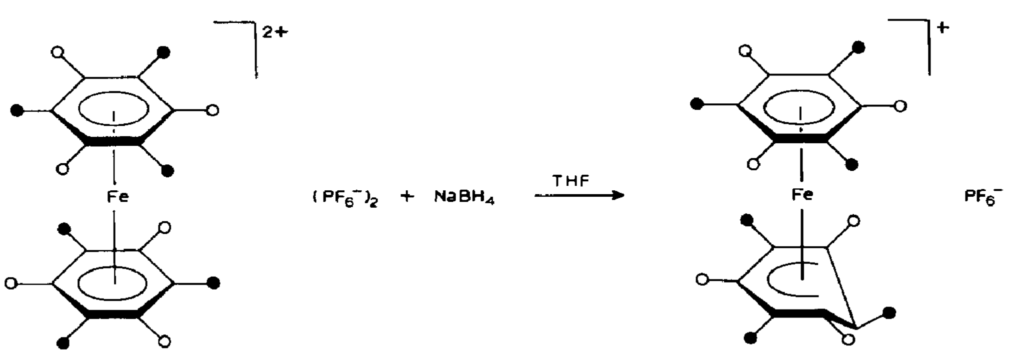
$$FeCl_n + 2\ \text{arene} \xrightarrow{AlCl_3} [Fe(\text{arene})_2]^{2+}(AlCl_4^-)_2 \qquad (1)$$

$$[Fe(\text{arene})_2]^{2+}(AlCl_4^-)_2 \xrightarrow[\text{2) aq. } NH_4^+PF_6^-]{\text{1) hydrolysis}} [Fe(\text{arene})_2]^{2+}(PF_6^-)_2 \qquad (2)$$

The reactions were performed for the arenes, $C_6H_{6-n}Me_n$ ($n = 0, 1, 2, 3, 6$). The hydrolyses (eq. 2) were carried out at 0 °C with the methylated arenes and, more carefully, at −50 °C for the synthesis of **1a** (arene = C_6H_6). Yields of **1a** were much improved by the use of trisublimed aluminium chloride and a PF_6 salt, instead of aqueous $H^+PF_6^-$. The quality of aluminium chloride was also crucial in the isomerization process. When commercial aluminium chloride was used, isomerization of all the aromatic (except C_6Me_6) occurred in the course of the reaction. With trisublimed aluminium chloride, mesitylene and hexamethylbenzene were not isomerized before complexation. The isomerization of *p*-xylene was limited to ca. 5%, but the isomerization of toluene was not reduced. Thus, the synthesis of $[Fe(toluene)_2]^{2+}(PF_6^-)_2$ cannot be considered as satisfactory, given the mixture indicated by the ^1H NMR spectra. When *p*-xylene was heated for 1 h in the presence of aluminium chloride (but in the absence of $FeCl_3$) isomerization was extensive, as shown by chromatography. Thus isomerization and complexation occur at similar rates. When isomerization is as fast or faster than complexation, mixtures of complexes of isomerized arenes are found. Since isomerization occurs by a retro Friedel–Crafts reaction, it can only occur before complexation. After complexation, the arene ligands are deactivated towards electrophilic reactions and thus cannot isomerize. It is probable that the use of an $AlCl_3/AlMe_3$ mixture would inhibit isomerization, as has been reported for bis-cyclophane iron complexes [16]. Isomerization becomes less important as the number of methyl substituents on the arene is increased, presumably because the increase of rate due to the presence of methyl groups is larger for complexation than for isomerization. Isomerization by aluminium chloride in the course of Fischer–Haffner type syntheses of sandwich compounds also depends very much on the nature of the transition metal moiety complexed to the arene [17].

Hydride transfer by reaction of $NaBH_4$ with 1

The light orange complexes **1a**, **1c**, **1d** and **1e**, when reacted with 1 equivalent of $NaBH_4$ in THF, gave the clean red hydride transfer products **2** with the structure $[Fe(\eta^5\text{-cyclohexadienyl})(\eta^6\text{-arene})]^+PF_6^-$ (eq. 3). The yields were quantitative and the complexes **2** were obtained as stable microcrystals. They were characterized by ^1H and ^{13}C NMR and infrared spectroscopy and by elemental analysis (**2d**).



(1a : —○ = —● = H ;
1d : —○ = Me , —● = H ;
1e : —○ = —● = Me ;
1c : arene = *p*-xylene)

(2a : —○ = —● = H ;
2d : —○ = Me , —● = H ;
2e : —○ = —● = Me ;
2c : arene = *p*-xylene)

Electron-transfer by reaction of C and O nucleophiles with 1

Reaction of $PhCH_2MgBr$, CH_3Li or KCN with **1a** at −90 °C, followed by a slow increase of the temperature to 20 °C, gave metallic iron and benzene but no organometallic complex. With **1e**, the addition of KCN or $PhCH_2MgBr$ in THF gave no reaction even at 20 °C, and the starting material was recovered. Decomposition was noted in refluxing THF. The addition of MeLi to **1e** gave a colour change from light orange to brown at −20 °C; after work up, only decomposition products (metal and ligands) were obtained.

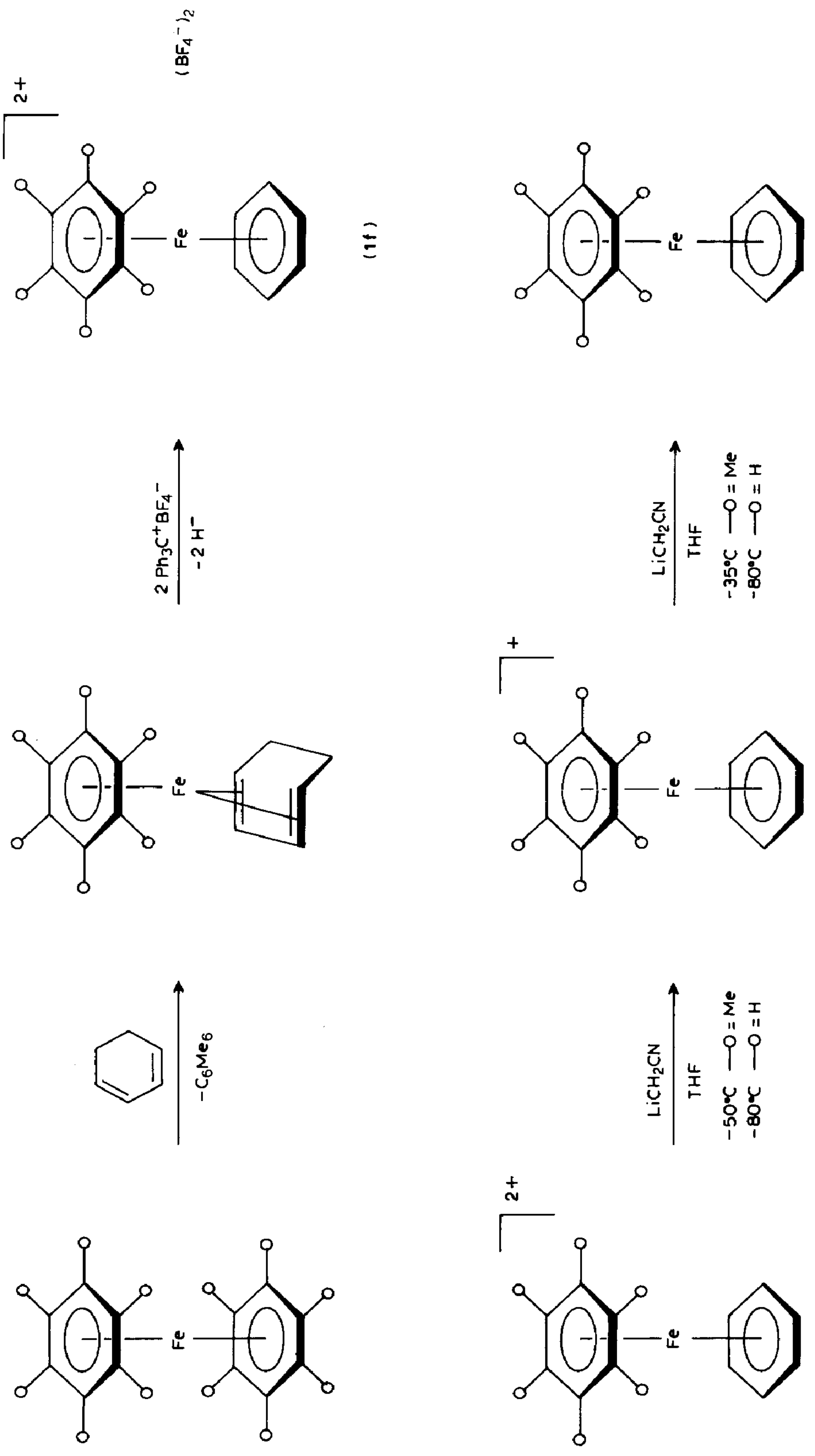
Reaction of **1e** with NaOMe in THF at −50 °C gave the purple 19e complex $[Fe(C_6Me_6)_2]^+PF_6^-$, which was characterized by Mössbauer spectroscopy [18].

The mixed complex $[Fe(C_6Me_6)(C_6H_6)]^{2+}(BF_4^-)_2$ (**1f**) was synthesized by double hydride abstraction from the known complex $[Fe(\eta^6\text{-}C_6Me_6)(\eta^4\text{-}C_6H_8)]$ [6a]. It was reacted, as for **1a**, with $LiCH_2CN$ in THF. A smooth colour change occurred from light orange (suspension) to deep purple (−80 °C for **1a**, −50 °C for **1f**), the characteristic colour of the electron transfer product $[Fe^I(arene)_2]^+PF_6^-$. (The electron transfer product was characterized in the C_6Me_6 series by its Mössbauer spectra [7b].) The reaction medium then turned brown-black (−80 °C for **1a**, −35 °C for **1f**), the colour of the unstable 20e neutral complexes $Fe^0(arene)_2$ (Scheme 1 [7b]). Decomposition to metallic iron and ligands ensued.

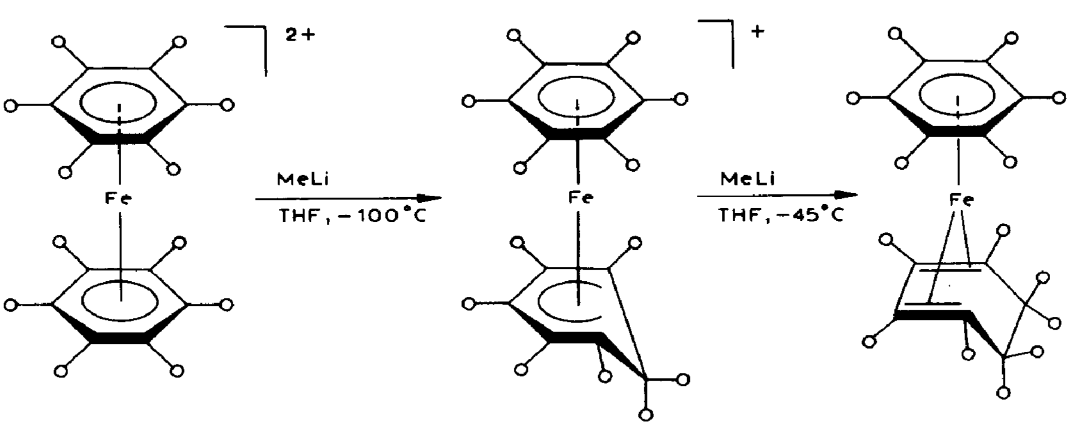
In the reaction between dithiamyllithium and **1e**, the same colour changes occurred (light orange → deep purple → brown black), followed by decomposition to metallic iron and C_6Me_6.

Double C–C bond formation by reaction of carbanions with 1c and 1e

The complex **1e** reacted immediately with MeLi at −100 °C, to give the first methide transfer, and further at −45 °C to give the second methide transfer. Thus, depending on the stoichiometry, the cation $[Fe(C_6Me_6)(\eta^5\text{-}C_6Me_7)]^+PF_6^-$ (**3**) or the neutral complex $[Fe(C_6Me_6)(\eta^4\text{-}C_6Me_8)]$ (**4**) were isolated in modest yields. The $[^1H]$ ^{13}C spectrum showed that **4** was the only neutral product of the reaction. Thus, in spite of steric factors, both methides add on to the same ring to give a cyclohexadiene complex.


Fe
−C6Me6
Fe
2 Ph3C+BF4−
−2 H−
Fe
2+
(BF4−)2
(1f)
2+
Fe
LiCH2CN
THF
−50°C —O = Me
−80°C —O = H
+
Fe
LiCH2CN
THF
−35°C —O = Me
−80°C —O = H
Fe

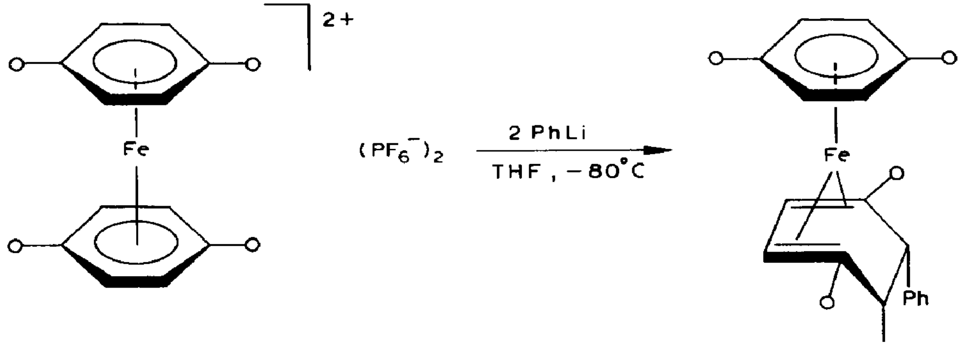
Scheme 1



(3) (4)

Scheme 2

The reaction of two equivalents of PhLi with **1c** in THF at −80 °C gave a brown solution from which a pentane-soluble, thermally unstable cyclohexadiene complex **5** was characterized by ^{1}H NMR.



(4)

(1c) (5)

Discussion

The isomerization disclosed in the syntheses of iron sandwiches using aluminium chloride illustrates that caution must be exercised when using this method. The reaction of carbanions and other bases is clearly not a suitable route to cyclohexadiene derivatives, although there is a limited number of cases in which some reaction products can be obtained with a cyclohexadiene ligand. The results of this study emphasize the peculiarity of the chemistry of the mesitylene complex **1d**. Helling has shown that many carbanions can attack **1d** to give good yields of C–C bond formation [13], and we have been able to reproduce Helling's reactions. The 1,3,5-methyl substitution does bring a perfect stereoelectronic situation for the attack of a carbanion between two methyl-substituted arene carbons, but these optimal conditions are not found for other arenes. The cationic cyclohexadienyl-arene complexes obtained by Helling from **1d** react with non-stabilized carbanions to give bis-cyclohexadienyl complexes. We find, on the other hand, that this second nucleophilic attack generally occurs on the same ring as the first (with non-mesitylene aromatics). We have also reported that this second nucleophilic attack was essentially under orbital control, not under charge control [8]. Indeed, attack on the same ring occurs even when cyclohexadienes are disubstituted in the *exo*-position by two neighbouring groups. This is confirmed here by the formation of **3**, **4**, and **5**, and other cases are known [11].

Contrary to the reactions with carbanions and bases, quantitative hydride transfer occurred in the reaction of all of the complexes **1a–d** with $NaBH_4$ and the hydride-transfer product formed always proved suitable for C–C bond formation with a variety of carbanions (K, Na, Li, Grignard reagents). Since we now know how to remove the hydride first introduced [10,11], the route to heterobifunctional cyclohexadienes is available, starting from **1a** and **1e**. The hydride protection–deprotection is thus an efficient means of extending the scope for aromatic transformations by temporary complexation to Fe^{2+}. The contrast between the extremely varied reactivity of arene-cyclohexadienyl iron cations and the failure of the complexes **1** to react with a variety of carbanions can only be explained as resulting from a very unfavorable orbital overlap between the HOMO of the carbanion and the LUMO of the dicationic sandwich complex. In contrast, the overlap with the $NaBH_4$ HOMO is very favorable with the dication (no side electron-transfer) and unfavorable with the arene-cyclohexadienyl iron cations (which are subjected to electron-transfer pathway in the hydride attack) [19].

Experimental

Reagent-grade tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl under argon immediately before use. Benzene and toluene were distilled and stored under argon. Reagent-grade pentane was degased with argon before use. All other chemicals were used as received, unless stated otherwise. All manipulations were carried out by Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere drylab. Infrared spectra were recorded with a Pye-Unicam SP 1100 IR spectrometer, which was calibrated with polystyrene. Samples were examined in solution (0.1 mm cells with KBr windows) or in KBr pellets. ^1H NMR spectra were recorded using Varian FM 360 (60 MHz) and Bruker WP 80 (80 MHz) spectrometers. ^{13}C NMR spectra were obtained at 20.115 MHz with a Bruker WP 80 spectrometer. All chemical shifts are reported in parts per million (δ, ppm) with reference to tetramethylsilane (Me_4Si) and were measured relative to the solvent or Me_4Si. Mass spectra were recorded using a Varian MAT 311 spectrometer. Mössbauer spectra were recorded in the laboratory of Professeur F. Varret at the Université du Maine in Le Mans with a 25-mLi ^{57}Co source on Rh, using a symmetric triangular sweep mode and fitted by Dr J.-P. Mariot. Elemental analyses were performed by the Centre of micro-analyses of the CNRS at Lyon-Villeurbane.

Preparation of $[Fe(C_6H_6)_2]^{2+}(PF_6^-)_2$ (1a)

Anhydrous $FeCl_3$ (10 g, 61.5 mmol), white trisublimed $AlCl_3$ (24 g, 184.5 mmol), distilled benzene (10 ml) and bidistilled hexane (150 ml) were introduced into a deaerated 500 ml three-necked flask. The mixture was refluxed for 12 h under an inert atmosphere, and then cooled to −50 °C before the cautious addition of 200 ml of a $H_2O/MeOH$ mixture at −50 °C. After hydrolysis, the reaction mixture was filtered and the solution was washed with 2 × 50 ml ether. Saturated aqueous NH_4PF_6 was then progressively added, to give the precipitation of 16 g of **1a**, as orange microcrystals (crude yield: 52%). The thermally stable complex **1a** decomposed in solution. The use of commercial $AlCl_3$ led to yields of **1a** of between 12 and 30%.

Preparation of $[Fe(p\text{-}Me_2C_6H_4)_2]^{2+}(PF_6^-)_2$ *(1c)*

Anhydrous $FeCl_2$ (4.5 g, 35 mmol), white trisublimed $AlCl_3$ (9.5 g, 70 mmol), *p*-$Me_2C_6H_4$ (8.6 ml, 70 mmol) and bidistilled hexane (150 ml) were introduced into a deaerated 500 ml three-necked flask. The mixture was refluxed for 4 h under an inert atmosphere, and then cooled to 0 °C before the cautious addition of 200 ml of ice water with vigourous stirring. After hydrolysis and decantation, the aqueous phase was washed with 2 × 50 ml ether. An aqueous solution of HPF_6 was progessively added with stirring, to give a precipitate of **1b** (10 g, 51% crude yield). ^1H NMR (CD_3CN): 2.57 (s, 12H, CH_3); 6.68 (s, 8H, arene); ^{13}C NMR (CD_3CN); 20.0 (CH_3); 112.4 (CH, arene); 116.2 (C-CH_3, arene). The same reaction when carried out in the absence of $FeCl_2$, led to the isomerization of *p*-xylene and to the scrambling of methyl groups to form heavier aromatic compounds. The bication **1d** was prepared according to ref. 12b. (with no scrambling of the methyl groups).

Preparation of $[Fe(C_6Me_6)_2]^{2+}(PF_6^-)_2$ *(1e)*

Anhydrous $FeCl_2$ (9 g, 70 mmol), commercial $AlCl_3$ (30 g, excess), C_6Me_6 (23 g, 140 mmol) and bidistilled heptane (150 ml) were introduced into a deaerated 500 ml three-necked flask. The mixture was refluxed for 12 h under an inert atmosphere, and then cooled down to 0 °C before 200 ml of ice water were cautiously added with vigourous stirring. After hydrolysis and decantation, the aqueous phase was washed with ether. Aqueous HPF_6 was then progressively added, leading to the precipitation of **1e**, which was washed with ethanol/ether, dried in vacuo (31 g, 65% crude yield) and recrystallized from acetone. ^1H NMR (CD_3CN): 2.50 (CH_3).

Preparation of $[Fe(C_6Me_6)(C_6H_6)]^{2+}(BF_4^-)_2$ *(1f)*

The complex $Fe(C_6Me_6)(C_6H_8)$ (864 mg, 3 mmol), prepared according to the method of Brintzinger et al. [6a], was dissolved in CH_2Cl_2 and $Ph_3C^+BF_4^-$ (1.98 g, 6 mmol) was added at 20 °C. The reaction was instantaneous. Ether (60 ml) was added to ensure precipitation of the complex **1f** (580 mg, 40% crude yield). It is sparingly soluble in acetone and acetonitrile. Thus it could not be recrystallized and was used in its crude form for the attempted reactions with carbanions. ^1H NMR (CD_3CN): 6.66 (s, 6H, C_6H_6), 2.20 (s, 18H, C_6Me_6)

Attempts to synthesize $[Fe(C_6H_5Me)_2]^{2+}(PF_6^-)_2$ *(1b)*

The reaction was carried out with toluene, as described above for *p*-xylene. The ^1H NMR spectra showed many low and high field absorptions, indicating a complicated mixture; the mixture of complexes obtained showed little stability in solution.

Reaction of $[Fe(p\text{-}Me_2C_6H_4)_2]^{2+}(PF_6^-)_2$ (1c) with 1 eq. $NaBH_4$

To a Schlenk tube were added **1c** (2.79 g, 5 mmol) and $NaBH_4$ (190 mg, 5 mmol), and then 15 ml THF under argon at 0 ° C. The mixture was stirred for 1.5 h at 0 ° C, and the THF was removed in vacuo. The red complex **2c** was crystallized by dissolution in CH_2Cl_2, filtration and the addition of ether (1.75 g, 84% yield). ^1H NMR (CD_3CN): 1.94, 2.38, 2.66 (CH_3); 2.95, 4.50 (H dienyl); 5.74, 6.66 (H arene); 1.35 (CH_2 *ipso*).

Reaction of $[Fe(1,3,5\text{-}C_6H_6Me_3)_2]^{2+}(PF_6^-)_2$ (1d) with 1 eq. $NaBH_4$

To a Schlenk tube were added **1d** (1.46 g, 2.5 mmol) and $NaBH_4$ (100 mg, 2.6 mmol), and then 15 ml THF under argon at 0 ° C. The mixture was stirred for 1.5 h at 0 ° C, and THF was removed in vacuo. The red complex **2d** was crystallized by dissolution in CH_2Cl_2, filtration and the addition of ether (0.97 g, 88% yield). ^1H NMR (CD_3CN): 1.46 (m, 8H, *o,o'*-CH_3, CH_2 *ipso*); 2.33 (s, 9H, -CH_3 arene); 2.70 (s, 3H, *p*-CH_3); 4.16 (s, 2H, H dienyl), 5.51 (s, 3H, H arene). ^{13}C NMR (CD_3CN): 19.0 (-CH_3 arene); 20,2 (*p*-CH_3); 24.1 (*o,o'*-CH_3); 37.8 (C *ipso*); 59.1 (*o,o'*-C-dienyl); 86.6 (*m,m'*-C-dienyl); 93.5 (C–H arene); 96.1 (*p*-C-dienyl); 103.1 (*C*-CH_3 arene). Anal. Found: C, 48.6; H, 5.6. $C_{18}H_{25}FePF_6$ calc: C, 48.9; H, 5.6%.

Reaction of $[Fe(C_6Me_6)_2]^{2+}(PF_6^-)_2$ (1e), with 1 eq. $NaBH_4$

A similar reaction with **1e** (3 g, 4.48 mmol), carried out at 20 ° C for 1 h with $NaBH_4$ (255 mg, 6.72 mmol) in THF (30 ml), gave the dark-red complex $[Fe(C_6Me_6)(\eta^5\text{-}exo\text{-}C_6Me_6H)]^+PF_6^-$ (**2e**) in 98% yield (2.3 g) after hydrolysis with acetone-water: 9/1, addition of 100 ml ethanol and the removal of THF and acetone under reduced pressure. ^1H NMR (CD_3CN): 1.5 (m, 10H, *o,o'*-CH_3, CH *ipso*, Me *ipso*); 2.30 (m, 24H, -CH_3 arene, *m,m'*-CH_3), 2.70 (s, 3H, *p*-CH_3). ^{13}C NMR (CD_3CN): 100.8 (C_6Me_6); 95.1 (*m*-C); 92.3 (*p*-C); 50.6 (*o*-C); 39.1 (*C*H-CH_3); 16.6 (*endo* Me); 15.1 (*p*-Me); 15.6 (*m*-Me); 14 (*o*-Me); 16.1 (Me). Anal. Found: C, 54.64; H, 6.90; Fe, 10.66. $C_{24}H_{37}FePF_6$ calc: C, 54.75; H, 7.03; Fe, 10.64%.

*Reaction of **1a–e** with Li, Na, K and Grignard reagents*

Two mmol of complex **1a** or **1c** (1 to 1.1 g) in a THF suspension (30 ml) were treated under argon with 2.5 mmol (2.5 ml, ether solution) of MeLi at −100 ° C (dropwise addition). The solution became purple (**1a**: immediately; **1c**: −90 ° C), then brown-black (**1a**: −95 ° C, **1c**: −90 ° C). During the work up, iron powder was found to the magnetic stirbar and the free arenes were characterized by ^1H NMR. Reaction of **1e** with $LiCH_2CN$ proceeded similarly (purple: −50 ° C, brown-black: −20 ° C, free ligand observed by ^1H NMR at 20 ° C). When the same procedure was applied to the reaction of dithiamyllithium with **1d**, the purple colour developed immediately at −100 ° C and the solution also turned brown-black at −90 ° C when two equivalents of the lithium reagent were used. The stable purple 19e complex $[Fe(C_6Me_6)_2]^+PF_6^-$ was characterized by Mössbauer spectroscopy [19] in the reaction of 1 eq. of dithiamyllithium as was the brown 20e electron complex $Fe(C_6Me_6)_2$ in the reaction of 2 eq. of dithiamyllithium. In the reaction of **1d** with 1 equivalent of NaOMe by a similar procedure the purple colour appeared at −30 ° C. The 19e complex $[Fe(C_6Me_6)_2]^+PF_6^-$ was characterized as above. The compound **1d** did not react with 1 equivalent of $PhCH_2MgBr$ in THF at +20 ° C. In refluxing THF, decomposition was characterized by ^1H NMR of C_6Me_6. The reactions of KCN with **1a**, **1c** and **1d** were carried out in acetone at 20 ° C. No purple colour was noted, and the reactions were very slow (**1a**, **1c**) or did not occur (**1d**). In the case of **1a** and **1c**, the free arenes were characterized by ^{1}H NMR and in the case of **1d**, only the starting complex was characterized by ^{1}H NMR.

Reaction of two eq. PhLi with 1c

To a THF suspension (20 ml) of **1c** (1.116 g, 2 mmol) under argon was added dropwise a molar ether solution of PhLi (4 ml, 4 mmol) at −80 ° C. The reaction mixture became dark brown. After warming to 20 ° C and removal of the solvent in vacuo, the residue was dissolved in pentane and, when the solution was concentrated, $[Fe(p\text{-}C_6H_4Me_2)(\eta^4\text{-}C_6H_4Me_2Ph_2)]$ (**5**) separated as an oil (50 mg). The ^{1}H NMR spectrum was recorded quickly at 20 ° C and the solution decomposed under argon. ^{1}H NMR (C_6D_6): 1.47, 1.53, 1.60 (4H, H *endo*, CH_3); 3.76, 4.15, 4.33 (2H diene); 6.90 (4H, arene), 7.15, 7.41 (10H, phenyl).

Reaction of one or two eq. MeLi with 1d

To a THF suspension (30 ml) of **1d** (1.34 g, 2 mmol) under argon was added dropwise a 1.16 *M* ether solution of CH_3Li (1.72 ml, 2 mmol) at −100 ° C. The colour change to dark-red was instantaneous. After the mixture has warmed up to 20 ° C, the THF was removed in vacuo, the residue was dissolved in 20 ml acetone and the solution was filtered into 100 ml ethanol. Evaporation of the solvents under reduced pressure gave $[Fe(C_6Me_6)(\eta^5\text{-}C_6Me_7)]^+PF_6^-$ (**3**) as dark red crystals (44 mg, 37% yield). ^{1}H NMR (CD_3COCD_3); 2.56 (s, 3H, $p\text{-}CH_3$); 2.40 (s, 18H, CH_3); 1.96 (s, 6H, $m\text{-}CH_3$); 1.56 (s, 3H, *o* and *endo* CH_3).

In an analogous reaction, MeLi (5.2 ml, 6 mmol) was added to **1d** (2.01 g, 3 mmol) in THF at −100 ° C. After an immediate colour change to dark-red, the reaction mixture was slowly warmed and became dark-red at around −45 ° C. At 20 ° C, the THF was removed in vacuo and the residue was extracted with pentane under argon. After the addition of charcoal, filtration and concentration, crystallization at −80 ° C gave $[Fe(C_6Me_6)(\eta^4\text{-}C_6Me_8)]$ (**4**) (300 mg, 24% yield). ^{1}H NMR (C_6D_6): 2.17 (s, 6H, $\beta\text{-}CH_3$); 2.05 (s, 18H, CH_3 arene); 1.81 (s, 6H, $\alpha\text{-}CH_3$); 0.97 (s, 6H, *endo* CH_3); 0.43 (s, 6H, *exo* CH_3). ^{13}C NMR (C_6D_6): 91.3 (C_6Me_6); 90.5 (β-C); 71.3 (α-C); 30.3 (CMe_2); 15.9 ($C_6(CH_3)_6$): 20.7, 19.3, 17.4, 14.7 (CH_3).

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