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Syntheses of deuterated sandwich- and piano-stool organo-iron complexes and polyalkylbenzenes *

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Abstract

Deuteration of cationic iron sandwich complexes of the $FeCp(arene)^+$ family has been achieved by use of 1 *M* NaOD in D_2O. The deuterated complexes are the starting point for the syntheses of various organo-iron and aromatic compounds.

Introduction

The complexation of aromatics by transition metal moieties has powerful effects on the reactivity of the arene [1–3]. Exploitation of this effect has led to significant advances in transition metal mediated aromatic chemistry. One major feature is the enhancement of the acidity of the benzylic protons when the transition metal moiety is electron-withdrawing, as is the case for $Cr(CO)_3$ [1d,2b–d], $FeCp^+$ [1,3] and $Mn(CO)_3^+$ [2e,f], the most used transition metal groups in arene activation. This property was first demonstrated by Trahanovsky and Card for H^+/D^+ exchange in indane $Cr(CO)_3$ complexes [4]. However, although the enhanced acidity of benzylic protons has been exploited for the synthesis of C–C bonds, little work has subsequently been carried out on the use of H^+/D^+ exchange, though Helling and Cash have deuterated $[Fe(C_6Me_6)_2]^{2+}(PF_6^-)_2$ using D_2O and a strong base [5]. We now report a detailed study of the deuteration of the family of robust complexes $[FeCp(arene)]^+PF_6^-$, which has led to the synthesis of a number of aromatic and organo-iron compounds. The metallocenes-d_{10} have been reported [6]; the acidity of cyclopentadiene, which permits facile H^+/D^+ exchange in such species, has long been known to allow perdeuteration followed by complexation to transition metals

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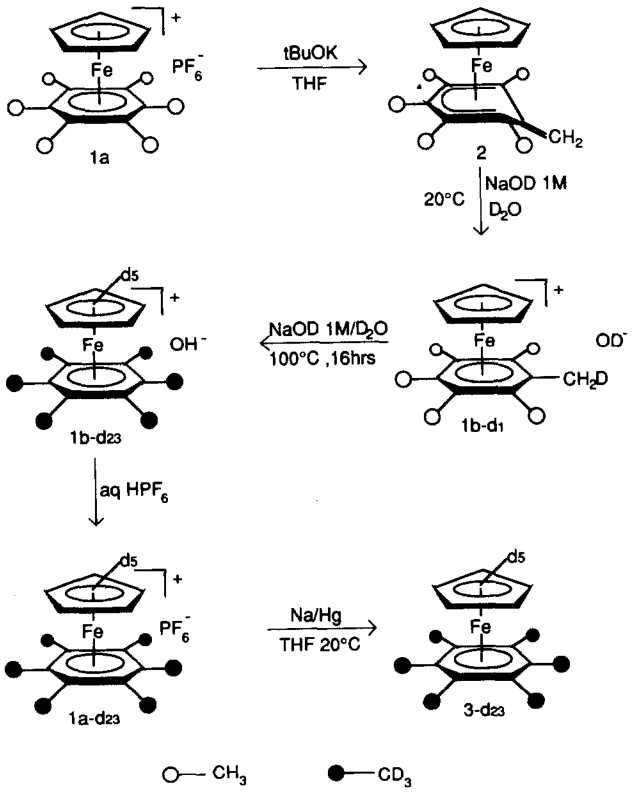
* Dedicated to Professor Peter L. Pauson on the occasion of his retirement

[6]. The compounds C_6Me_6-d_{18} and $FeCp_2$-d_{10} have been the subject of numerous spectroscopic and other physical studies [7].

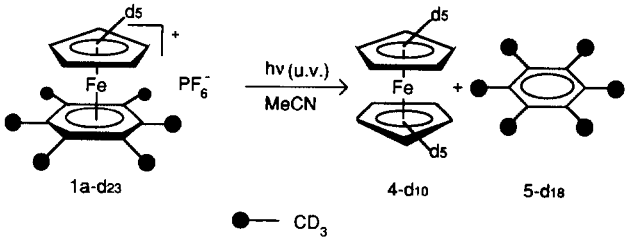
Results

1. Perdeuteration of [FeCp(C$_6$Me$_6$)]$^+$PF$_6^-$, 1a

The deprotonation of **1** to **2** is very facile and has been reported. A convenient medium for the deprotonation/deuteration procedure is commercial 1 *M* NaOD in D_2O. However, the PF_6^- salt, **1a**, is not soluble in this medium, and it was first deprotonated by use of ^{t}BuOK in THF. The neutral red deprotonated complex **2** reacts rapidly with 1 *M* NaOD in D_2O at 20 °C to give the yellow soluble monodeuterated cationic arene complex **1b**-d_1, as the hydroxide. Complete deuteration is achieved by heating this solution for 16 hours at 100 °C and repeating these operations a second time. The PF_6 salt **1a**-d_{23} is isolated as usual by addition of aq. $H^+PF_6^-$. The yield is around 75% for each operation, e.g. 56% overall. The extent of deuteration was determined by ^1H NMR spectroscopic monitoring of the $NaOD/D_2O$ solution of the hydroxide **1b**-d_x. The perdeuterated complex was characterized by its ^2D and ^{13}C NMR spectra and by the high-resolution mass spectrum of the neutral monoreduced Fe^I complex **3**-d_{23}, previously well known under its undeuterated form. All these methods showed that under the conditions



Scheme 1.

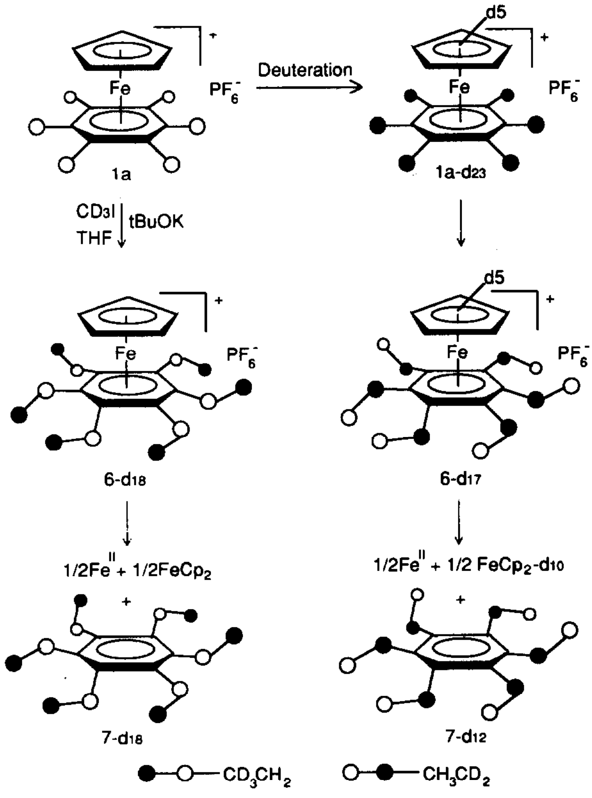


Scheme 2.

necessary to achieve a complete deuteration of the C_6Me_6 ligand the Cp ligand is also fully deuterated.

2. *Synthesis of ferrocene-*d_{10} *and of hexamethylbenzene-*d_{18}

The UV photolysis of **1a** has been reported previously [9]. (Unlike $FeCp(arene)^+$ salts with one or two methyl substituents [10], **1a** is stable to visible light irradiation.) Thus UV photolysis of **1a**-d_{23} in MeCN gave ferrocene-d_{10}, **4**-d_{10} and C_6Me_6-d_{18}, **5**-d_{18}. Addition of $FeCl_3$ in ether to the solid mixture resulted in the oxidation of **4**-d_{10} to purple ferricinium-d_{10} chloride, which was separated from **5**-d_{18} in this way, and then reduced to **4**-d_{10} using $Na_2S_2O_4$ in a water-diethyl ether mixture. Such work-up gave reasonable yields given the 1-mmol scale (Scheme 2).



Scheme 3.

3. *Syntheses of regiospecifically deuterated hexaethylbenzenes*

The synthesis of $[FeCp(C_6Et_6)]^+PF_6^-$, **6**, can be achieved either by direct complexation of C_6Et_6 using the classical complexation procedure with ferrocene and $AlCl_3/Al$ at 100°C [9] (use of higher temperature brings about loss of Et substituents [11]) or by permethylation of **1a** using $^tBuOK/CH_3I$ in THF [12]. We used the second route in the present study, because, in particular, either position can be deuterated in this way (Scheme 3).

(a) $C_6(CD_2CH_3)_6$. The reaction of ^tBuOK and MeI with **1a**-d_{23} in THF gave a 77% yield of recrystallized complex **6**-d_{17} on a 1-mmol scale. The complex **6**-d_{17} was characterized by ^1H, ^2D, and ^{13}C NMR spectroscopy, which showed that there had been specific deuteration of the Cp ring and the benzylic positions. The free arene was readily obtained as in the case of **5**-d_{18} by photolysis in MeCN, which gave a 84% yield of the white $C_6(CD_2CH_3)_6$, **7**-d_{12}.

(b) $C_6(CH_2CD_3)_6$. Similarly, the reaction involving **1a**, ^tBuOK and CD_3I in THF gave a 76% yield of **6**-d_{23} after recrystallization from ethanol (5.5 mmol-scale), and photolysis of the latter in MeCN gave the free arene $C_6(CH_2CD_3)_6$, **7**-d_{18} in 77% yield.

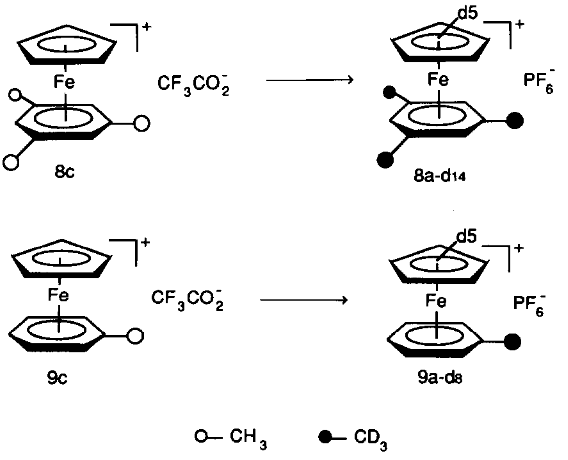
4. *Perdeuteration of the mesitylene and toluene complexes*

The perdeuteration reaction described above for **1a** was extended to the complexes $[FeCp(mesitylene)]^+PF_6^-$, **8a** and $[FeCp(toluene)]^+PF_6^-$, **9a** [3a]. For this purpose, the water-soluble trifluoroacetate salts **8c** and **9c** were prepared.

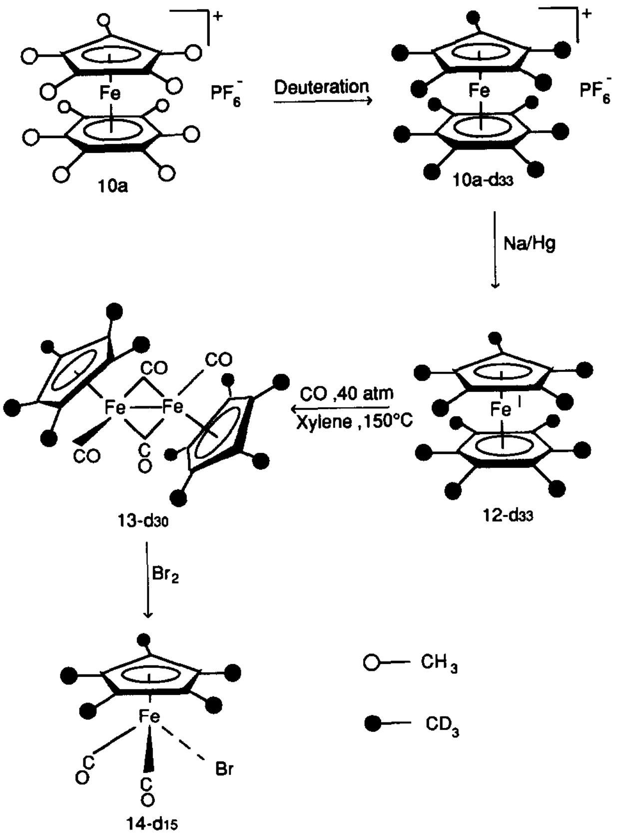
The perdeuteration of **8c** proceeds as well as that of **1a** and a 75% yield is obtained by extraction of each reaction mixture on a 4-mmol scale. The complex **8a**-d_{14} was characterized by ^1H and ^{13}C NMR spectroscopy. On the other hand, the perdeuteration of **9c** also proceeds under these conditions. **9c**-d_8 was similarly characterized (Scheme 4). However, the yield is low (8%) owing to the side reaction of the deprotonated intermediate.

5. *Synthesis of perdeuterated pentamethylcyclopentadienyl iron complexes*

The permethylated complex $[Fe(C_5Me_5)(C_6Me_6)]^+PF_6^-$, **10a**, was synthesized by



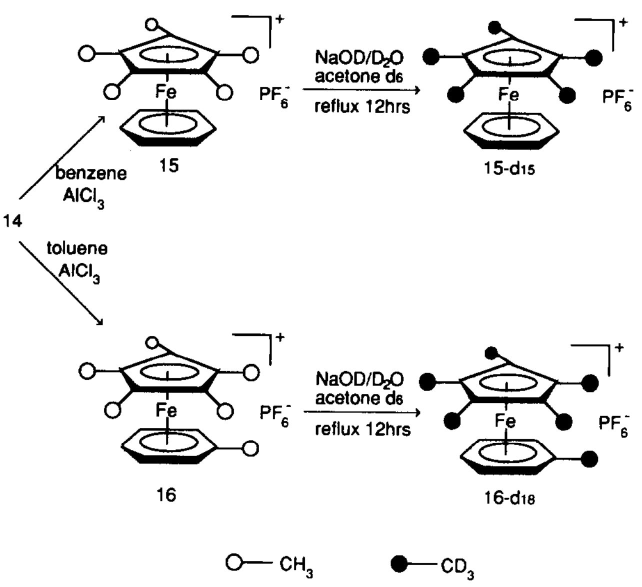
Scheme 4.



Scheme 5.

the previously reported procedure [9] and deprotonated in the same way as **1a** with ^{t}BuOK in THF to give **11** [8d]. Complex **11**, $Fe(C_5Me_5)(CH_2C_6Me_5)$, was perdeuterated in 1 *M* NaOD in D_2O at 100 °C under the conditions used for **2** to give a 76% yield of **10a**-d_{33}, which was identified from its ^1H, ^2D and ^{13}C NMR spectra and the mass spectrum of the monoreduced 19-electron complex $Fe^I[C_5(CD_3)_5]$, $[C_6(CD_3)_6]$, **12**-d_{33}. The complex **12**-d_{33} was treated with CO (40 atm) at 150 °C to give $[Fe[C_5(CD_3)_5](CO)_2]_2$, **13**-$d_{30}$. The undeuterated compounds **12** and **13** were known [9], but the route **12** → **13** was not known for the permethylated series. This carbonylation occurs under milder conditions for the non-methylated series [13]. The dimer **13**-d_{30} was treated with Br_2 by a procedure known for the non-deuterated series [9] to give the bromo complex **14**-d_{15} (Scheme 5).

We investigated the possibility of perdeuterating some cationic Cp* sandwich complexes without isolating the deprotonated complex (i.e. **2** or **11**). This was especially useful in the case of complexes bearing no methyl group on the arene ligand. Thus the known complex $[FeCp^*(C_6H_6)]^+PF_6^-$, **15** [9], was treated directly with 1 *M* NaOD in D_2O. For this purpose **15** was first dissolved in acetone-d_6, then the biphasic mixture was refluxed for 12 h to give $Fe^{II}[C_5(CD_3)_5](C_6H_6)^+PF_6^-$, **15**-$d_{15}$ in 72% yield. By the same procedure $Fe^{II}Cp^*(C_6H_5CH_3)^+PF_6^-$, **16**, was perdeuterated to give $Fe^{II}[C_5(CD_3)_5](C_6H_5CD_3)^+PF_6^-$, **16**-$d_{18}$. The ^1H NMR spec-



Scheme 6.

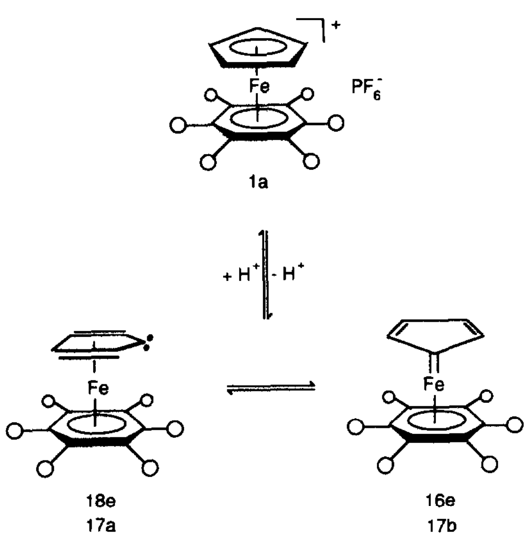
trum of **16**-d_{18} showed that only the methyl groups of the Cp* and toluene ligands were deuterated, with the five phenyl protons unaffected (Scheme 6).

In order to ascertain whether the deuteration of the Cp* ligand in the complexes bearing methyl groups on both the Cp* and arene ligand was intra- or inter-molecular, we carried out a cross-over experiment in which the deprotonated complexes **11** and its perdeuterated analogue **11**-d_{32} were mixed in equal amounts in C_6D_6. The ^{1}H NMR spectra of this solution were recorded at intervals and the equilibrium, arising from the scrambling, was found to be reached after one week. The experiment revealed that the protonated form **10**-d_x (present in traces) serves as a relay for the intermolecular proton exchange, though this does not exclude the concurrence of intramolecular proton exchange.

Discussion

1. Deuteration

The acidity of the methyl hydrogens of arene ligands in cationic complexes is well known [1g,3,5,8]. It allows a facile deuteration using the cheap deuterating reagent 1 *M* NaOD in D_2O, but we found that it was essential to use a homogeneous medium. Attempts to use suspensions of the organo-iron PF_6^- salt failed. The stability of the deprotonated form (i.e. **2**) is thus important in the procedure, as shown by the relative yields for the deuteration of **1** (75%) and **9** (8%). Not only the arene methyl groups but also the Cp* methyl groups are deuterated. The latter are less acidic than the former because the arene is an even ligand whereas Cp* is an odd one [14]. Thus the positive charge is more shifted towards an arene than towards a Cp ligand as emphasized by Green et al. [14]. In the case of **15**, complete deprotonation is thus much more difficult than that of **1**, and was not achieved. Thus it was necessary to find another method for solubilization of both NaOD and **15**. The biphasic system



Scheme 7.

acetone-d_6/NaOD–D$_2$O worked well. Presumably, the deprotonation and deuteration reactions occur at the interface of the layers.

The deuteration of the unsubstituted Cp ligand is more surprising. It could be attributed to stabilization of the deprotonated species **17a** by a 16e cyclopentadienylidene structure **17b** (Scheme 7).

2. Recovery of the deuterated compounds

Since the UV photolysis of **1a**-d_{23} in MeCN gives ferrocene-d_{10} as the only organo-iron compound, the method provides a convenient way of making this compound from a cheap deuterated reagent. The formation of ferrocene results from the decomposition of the known unstable intermediate FeCp(NCMe)$_3^+$ [10b] formed in the photolytic replacement of the arene of **1a** by three MeCN ligands. Note that the photolysis of **1a** in other solvents is not clean and does not lead to ferrocene, but to polymers derived from cyclopentadiene, whose separation is tedious. Ferrocene and the aromatic are not easily separated, but ferrocene is readily oxidized to a ferricinium salt which is easily separated. This way of recovering the arenes and ferricinium salts by photolysis of various FeCp(arene)$^+$PF$_6^-$ salts in MeCN was described in 1981 [15].

The hexaethylbenzenes-d_{12} and -d_{18} were recovered in this way in the present study. The permethylation of **1a** with ^{t}BuOK–MeI is also known to give **6**, as a result of the acidity of the methyl groups of **1a**, in a one-pot series of deprotonation–alkylation reactions [12]. In principle, **6**-d_{12} could also probably be made by benzylic perdeuteration of **6** but since the procedure requires prolonged heating at 100 °C and **6** would not be as robust as **1** under these conditions, the yield might be low.

Decomposition of the Cp* complexes is much more difficult than that of the parent Cp complexes. Photolysis did not bring it about. Reduction of the Fe$^{\mathrm{I}}$ complex provided a good opportunity to replace the arene ligand by CO ligands at 150 °C, opening up the route to deuterated piano-stool FeCp* complexes. However, attempts to perform the same reaction with **15** failed because the Fe$^{\mathrm{I}}$ complex dimerized through the benzene ligand (as was previously known [9]). This reaction is faster than arene exchange with CO, and so **10** has to be used.

Conclusions

1. Deuteration of the methyl substituents in the complexes $FeCp(arene)^+$ or $FeCp^\star(arene)^+$ can be easily carried out by using 1 *M* NaOD in D_2O under reflux. The complex must be solubilized by prior deprotonation or by using acetone.

2. The Cp ligand of the $FeCp(arene)^+$ salts is also deuterated under these conditions, but the phenyl hydrogens are not.

3. These deuteration reactions have been used to synthesize ferrocene-d_{10}, hexamethylbenzene-d_{18}, hexaethylbenzene-d_{12} and -d_{18} in good yields. The synthesis of other polymethylbenzenes specifically deuterated in the methyl groups has also been carried out. Six sandwich- or piano-stool $FeCp^\star$ complexes containing a fully deuterated $Cp^\star$ ligand have been synthesized, including $[FeCp^\star(CO)_2]_2$-d_{30}.

Experimental section

General data

All manipulations were carried out under argon or nitrogen by Schlenk techniques or in a BS 531 Jacomex dry box filled with nitrogen. Reagent grade 1,2-dimethoxyethane (DME), diethyl ether and pentane were predried and distilled over sodium benzophenone ketyl prior to use. Other chemicals were used as received. For reactions performed in sealed tubes the glassware was flamed under vacuum immediately before its introduction into the glove bag so as to minimize absorbed moisture. Photolyses were performed with a Hanovia lamp (250 nm, 450 W) at room temperature under a stream of argon. ^1H NMR spectra were recorded with a Bruker WP80 or AM 300WB * and ^{13}C NMR spectra with Bruker WP80 FT * (20.115 MHz) or AM 300WB * (75.469 MHz) spectrometers. ^2D NMR spectra were recorded with a Bruker AM 300WB * (46.072 MHz) spectrometer. Chemical shifts are reported in parts per million (δ, ppm) relative to tetramethylsilane as an internal standard. Infrared spectra were recorded with a Pye-SP1100 Unicam spectrophotometer and calibrated with a polystyrene film. Samples were examined as Nujol mulls on KBr plates or as pentane solutions in 0.10 mm KBr cells. Mass spectra were obtained with a Double Focussing Mass Spectrometer Varian MAT 311*. The proportions of deuterated species were determined from mass spectra recorded at 12 eV. Elemental analyses were carried out by the "Centre de Microanalyses du CNRS" at Lyon-Villeurbanne.

Pentamethylcyclopentadiene was prepared by the standard procedure [16].

1. Deuteration of $[FeCp(\eta^6\text{-}C_6Me_6)]^+[PF_6]^-$, 1a

In a 25 mL flask equipped with a reflux condenser, 0.484 g (2 mmol) of $[FeCp(\eta^5\text{-}C_6Me_5CH_2)]$ was dissolved in 5 mL of a 1 *M* NaOD/D_2O solution under argon. The mixture was stirred at 100 °C for 16 h then the solvent was removed under vacuum and the flask refilled with 5 mL of D_2O. Stirring and heating were carried on for a further 12 h at 100 °C. The mixture was then cooled to room temperature and 1.5 mL (10 mmol) of HPF_6 added to precipitate a yellow solid. The solid was filtered off, washed with water, and dissolved in acetone and the solution

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was dried over $MgSO_4$ then concentrated. Addition of an excess of diethyl ether gave 0.69 g (77%) of $[FeCp(\eta^6\text{-}C_6Me_6\text{-}d)]^+[PF_6]^-$ as a yellow powder. ^2D NMR: (CH_3CN/CD_3CN; $CDCl_3$ as internal standard): 4.57 (s, Cp, 3.8D); 2.43 (s, CD_3, 16.8D).

The dark-red complex corresponding to the partially deuterated compound described above was prepared, and treated with 5 mL of 1 *M* $NaOD/D_2O$ solution for 12 h at 100 °C. Work-up described as above gave 0.50 g (73%) of **1a**-d_{23} as a yellow powder. ^2D NMR (CH_3CN/CD_3CN; $CDCl_3$ as internal standard): 4.57 (s, Cp, 3.8 D); 2.43 (s, CD_3, 16.8 D). ^{13}C NMR (CD_3CN): 99.7 (C_6 ring); 78.7 (D, Cp, *J*(CD) 28 Hz); 17.8 (sept., CD_3, *J*(CD) 20 Hz).

Reduction of **1a**-d_{23} with Na/Hg in DME followed by extraction with and recrystallization from pentane gave $[Fe^I(C_5D_5)C_6(CD_3)_6]$, **3**-$d_{23}$. M.S. calcd. for $C_{17}D_{23}Fe$: 306.2592; found: 306.258 (d_{22}, major labeled species: 27%). Total deuterium incorporation calculated for the d_{18} to d_{23} species: 91%.

A solution of 0.451 g (1 mmol) of **1a**-d_{23} in 10 mL of acetonitrile contained in a Schlenk tube under argon was irradiated for 30 min, during which the color changed from yellow to dark orange. The solvent was removed under vacuum and the brown residue extracted with 2 × 10 mL of diethyl ether. Addition of an etheral solution of $FeCl_3$ (0.6 mmol) gave a precipitate of $[FeCp_2\text{-}d_{10}]^+Cl^-$ as a deep purple powder. The solid was filtered off and washed with diethyl ether. The filtrate was purified chromatographically after evaporation of the solvent to dryness; yield 0.12 g (66%) of hexamethylbenzene, **5**-d_{18}.

^{13}C NMR ($CDCl_3$): 132.1 (C_6 ring); 16.2 (m, CD_3, ^1J(CD) 20 Hz). M.S. calcd. for $C_{12}D_{18}$: 180.2538; found: 180.253. d_{18} major labeled species: 62%. Total deuterium incorporation calculated for d_{16} to d_{17} species: 97.4%.

The ferricinium salt obtained above was stirred for 3 min with 0.174 g (1 mmol) of $Na_2S_2O_4$ in 10 mL of a water/diethyl ether mixture. The etheral layer became immediately orange, and it was separated from the aqueous layer, dried over $MgSO_4$, filtered, and evaporated to dryness, to give 0.063 g (64%) of deuterated ferrocene **4**-d_{10}. M.S. calcd. for $C_{10}D_{10}Fe$: 196.0759; found: 196.076. d_{10} major labelled species: 71%. Total deuterium incorporation calculated for d_8 to d_{10}: 96.2%.

2. *Syntheses of* $[FeCp(\eta^6\text{-}C_6(CD_2CH_3)_6)]^+[PF_6]^-$, **6**-$d_{17}$ *and* $C_6(CD_2CH_3)_6$, 7-d_{12}

By the general peralkylation procedure 0.5 g (1.17 mmol) of **1a**-d_{23} was treated with 3.26 g (29 mmol) of ^{t}BuOK and 2 mL (35 mmol) of CH_3I in THF at 20 °C to give 0.47 g (77%) of **6**-d_{17} as yellow microcrystals after work up. ^1H NMR (CD_3COCD_3): 4.83 (s, Cp, 5H); 3.02 (m, CD_2, 1H); 1.40 (bs, CH_3, 18H). ^{13}C NMR (CD_3CN): 104.6 (C_6 ring); 77.2 (d, Cp, *J*(CD) 5 Hz); 22.7 (m, CD_2, *J*(CD) 20 Hz); 15.2 (CH_3). ^2D NMR (CH_3COCH_3): 4.82 (C_5D_5), 2.98 (CD_2).

The free deuterated arene was easily recovered by photolyzing 0.40 g (0.78 mmol) of **6**-d_{17} in CH_3CN. Work up gave 0.162 g (84%) of $C_6(CD_2CH_3)_6$, **7**-d_{12} as a white powder sample, m.p. 129–131 °C. ^1H NMR ($CDCl_3$, $[FeCp_2]$ as internal standard): 2.58 (m, CD_2, < 1H); 1.20 (bs, CH_3, 18H).

3. *Syntheses of* $[FeCp(C_6(CH_2CD_3)_6)]^+[PF_6]^-$, **6**-$d_{18}$ *and* $C_6(CH_2CD_3)_6$, 7-d_{18}

As described under 2, 2.354 g (5.5 mmol) of $[FeCp(\eta^6\text{-}C_6Me_6)]^+[PF_6]^-$, **1a**, was treated with 12.32 g (110 mmol) of ^{t}BuOK and 20 g (138 mmol) of CD_3I in THF at room temperature, to give, after extraction and recrystallization, from hot ethanol, 2.15 g (76%) of canary-yellow microcrystals of **6**-d_{18}. ^{1}H NMR (CD_3COCD_3): 4.90 (s, Cp, 5H); 3.02 (bs, CH_2, 10 H). Photolysis of 2.0 g (3.91 mmol) of **6**-d_{18} in CH_3CN for 3 min gave 0.74 g (77%) of white crystals of $C_6(CH_2CD_3)_6$, **7**-d_{18}, m.p. 129–131°C. ^{1}H NMR ($CDCl_3$, [$FeCp_2$] as internal standard): 3.02 (bs, CH_2, 10H).

4. Deuteration of $[FeCp(\eta^6\text{-}1,3,5\text{-}C_6Me_3H_3)]^+[PF_6]^-$, **8a**

(a) Syntheses of $FeCp[C_6H_3(CH_3)_3]^+CF_3CO_2^-$, **8c** and $FeCp(C_6H_5CH_3)^+CF_3CO_2^-$, **9c**. A mixture of 1.86 g (10 mmol) of ferrocene, 0.27 g (10 mmol) of aluminum powder and 5.33 g (40 mmol) of $AlCl_3$ in 50 mL of arene (toluene or mesitylene) contained in a three-necked flask under argon was refluxed for 12 h then cooled to 0°C and treated with 100 mL of ice water. The mixture was filtered and the yellow filtrate treated with aqueous NH_4OH until pH 9 to precipitate Al^{3+} ions. The suspension was filtered and the filtrate acidified with an excess of CF_3CO_2H. Extraction with CH_2Cl_2 followed by drying of the extract over $MgSO_4$, reduction of the volume of solvent and addition of an excess of diethyl ether gave, as a yellow oil, $FeCp(C_6H_5CH_3)^+CF_3CO_2^-$, **9c**, (3.06 g, 95%) or $FeCp[C_6H_3(CH_3)_3]^+CF_3CO_2^-$, **8c**, (2.12 g, 60%) identified by comparison of their ^{1}H NMR parameters with those of authentic samples.

(b) By the procedure described under 1 above 5 mL of a 1 *M* NaOD/D_2O solution was added to 0.960 g (4 mmol) of $[FeCp(1,3,5\text{-}C_6Me_3H_3]^+[CF_3CO_2]^-$, **8c**. The yellow solution was refluxed for 16 h. The solvent was removed under vacuum and 5 mL of D_2O added to the residue. The mixture was stirred and heated for 12 h at 100°C then cooled to 20°C. Work up as in 1 gave 1.19 g (75%) of $[FeCp(1,3,5\text{-}C_6(CD_3)_3H_3)]^+[PF_6]^-$, **8a**-$d_{14}$ as yellow microcrystals after recrystallization from acetone/ether. ^{1}H NMR (CD_3COCD_3): 6.21 (s, C_6H_3, 3H); 4.99 (s, Cp, 5H). ^{13}C NMR (CD_3CN): 103.3 ($C_6(CD_3)$); 88.6 (C_6H); 78.3 (Cp); 19.8 (m, CD_3, *J*(CD) 19 Hz).

The neutral complex $[Fe^{II}Cp(\eta^5\text{-}2,4,6,\text{-}C_6(CD_3)_3H_4)]$ was prepared by the usual method to allow for isotopic analysis by mass spectrometry. Calcd. for $C_{14}H_9D_9Fe$: 251.1323; found: 251.133 (d_9 major labeled species: 36%). Total deuterium incorporation calculated from d_7 to d_{12} species: 67.7%.

5. Preparation of $[FeCp(\eta^6\text{-}C_6H_5CD_3)]^+[PF_6]^-$, **9a**-$d_8$

The procedure described under 4 above was applied to 0.646 g (2 mmol) of $[FeCp(C_6H_5CH_3)]^+[CF_3CO_2]^-$, **9c** dissolved in 5 mL of D_2O and 0.115 g (5 mmol) of Na was added. The mixture was refluxed for 2 h and work up as described under 1 followed by recrystallisation from acetone/ether gave 0.06 g (8%) of yellow microcrystals of $[FeCp(C_6H_5CD_3)]^+[PF_6]^-$, **9a**-$d_8$. ^{1}H NMR ($CD_3COCD_3$): 6.37 (s, C_6H, 5H); 5.14 (s, Cp, 5H). ^{13}C NMR (CD_3CN): 89.7, 88.6, 87.4 (*m*, *o*, *p*-C_6); 104.8 (C *ipso*); 77.7 (Cp); 21.0 (m, CD_3, *J*(CD) 20 Hz).

6. Synthesis of $[Fe(C_5(CD_3)_5)(\eta^6\text{-}C_6(CD_3)_6)]^+[PF_6]^-$, **10**-$d_{33}$

In a Schlenk tube equipped with a reflux condenser, 1.154 g (4.1 mmol) of $[Fe^{II}(C_5Me_5)(\eta^5\text{-}C_6Me_5CH_2)]$, **11**, were dissolved in 5 mL of 1 *M* NaOD/D_2O solution. The mixture was stirred at 100°C for 16 h. The solvent was removed under vacuum and the residue treated with 5 mL of D_2O. The solution was refluxed for 16 h and work-up as under 1 gave 1.60 g (74%) of **10a**-d_{33} as a yellow powder.

^{1}H NMR (CD_3COCD_3, [$FeCp_2$] as internal standard) 2.30 (m, C_6CD_3, 2H); 1.70 (m, C_5CD_3, 3H). ^{2}D NMR (CH_3COCH_3): 2.22 (s, $C_6(CD_3)$); 1.71 (s, $C_5(CD_3)$). ^{13}C NMR (CD_3CN): 98.5 (C_6 ring); 87.1 (C_5 ring); 14.8 (m, $C_6(CD_3)$, ^1J(CD) 20 Hz); 7.9 (m, $C_5(CD_3)$, ^1J(CD) 20 Hz).

Na/Hg reduction of (3.1 mmol) of **10a**-d_{33} in DME gave 1.10 g (88%) of $Fe^I[C_5(CD_3)_5][C_6(CD_3)_6]$, **12**-$d_{33}$ as olive-green needles. M.S. calcd. for $C_{22}H_5D_{28}Fe$ 381.3689; found: 381.367 (d_{28} major labelled species: 16%). Total deuterium incorporation calculated from d_{22} to d_{32} species: 85%.

7. Synthesis of deuterated (Fe[C$_5$(CD$_3$)$_5$](CO)$_2$)$_2$, 13-d$_{30}$

The neutral Fe^I complex prepared as immediately above (1.10 g, 2.73 mmol) was dissolved in 150 mL of xylene and the solution transferred under argon by canula into an autoclave. The temperature was raised to 150 °C and the CO pressure to 40 bars and the autoclave mechanically shaken for 12 h. The solvent was removed by rotary evaporation and the residue extracted with hexane. The purple extract was concentrated and cooled to − 80 °C, and the solid rapidly filtered off and dried under vacuum, yielding 0.965 g (67%) of violet crystals of **13**-d_{30} identified from its infrared spectrum by comparison with that of an authentic undeuterated sample.

Chromatography of the filtrate on an alumina column with hexane as eluant gave 0.408 g (92%) of deuterated hexamethylbenzene, **5**-d_{18}. ^{1}H NMR ($CDCl_3$, [$FeCp_2$] as internal standard): 2.12 (m, CD_3, 2H). ^{13}C NMR ($CDCl_3$): 132.1 (C_6 ring); 16.2 (m, CD_3, J(CD) 20 Hz).

8. Synthesis of deuterated Fe[C$_5$(CD$_3$)$_5$](CO)$_2$Br, 14-d$_{15}$

Following the usual procedure, 0.965 g (1.95 mmol) of **13**-d_{30} was treated with 0.07 mL (1.95 mmol) of Br_2 at 0 °C in CH_2Cl_2 to give, after extraction and crystallization, 0.92 g (75%) of dark red microcrystals of **14**-d_{15}, characterized by comparison of its infrared spectrum with that of an authentic undeuterated sample [9]. M.S. calcd. for $C_{12}H_2D_{13}O_2Fe^{79}Br$ 339.0421; found: 339.042 (d_{12} major labeled species: 23.5%). Total deuterium incorporation calculated for d_7–d_{15} species: 79%.

9. Intermolecular H/D exchange

In a Schlenk tube an equimolar mixture of $[Fe(C_5Me_5)(C_6Me_6)]^+[PF_6]^-$, **10a** and **10a**-$d_{33}$ was stirred under argon with 1 eq. of ^{t}BuOK in THF at 20 °C for 1 h. Removal of the solvent, extraction of the dark-red residue with pentane, and evaporation of the extract gave a dark-red powder **11**-d_x. A ^{1}H NMR sample of **11**-d_x in C_6D_6 was prepared in the dry-Lab and the tube sealed under N_2. NMR spectra were periodically recorded until equilibrium, as indicated by the integration ratios, was reached (8 days). ^{1}H NMR (C_6D_6): 3.46 (m, < 1H); 2.05 (m, 1H); 1.76 (m, 3H); 1.44 (m, 3H); 1.27 (m, 8H). Protonation of the dark red C_6D_6 solution of **11**-d_x with CF_3CO_2H immediately precipitated the yellow acid $[Fe(C_5Me_5)(C_6Me_6)]$-$d_{16}{}^+[CF_3CO_2]^-$. ^{1}H NMR (CD_3COCD_3): 2.29 (m, C_6Me_5, 9H); 1.68 (m, C_5Me_5, 8H).

10. Synthesis of Fe[C$_5$(CD$_3$)$_5$](C$_6$H$_6$)PF$_6$, 15-d$_{15}$

In a Schlenk tube under argon 0.41 g (1 mmol) of $Fe(C_5Me_5)(C_6H_6)PF_6$, **15** [9], was dissolved in 2 mL of CD_3COCD_3 to give a yellow solution and 5 mL of 1 *M* NaOD/D_2O solution were added. The biphasic mixture was refluxed for 12 h and cooled to room temperature and the yellow solid was filtered off and dissolved in acetone. The solution was dried over $MgSO_4$ and the solute precipitated with an excess of diethyl ether. Recrystallization from acetone/ether mixture gave 0.3 g (72%) of $Fe[C_5(CD_3)_5](C_6H_6)PF_6$, **15-$d_{15}$** as yellow microcrystals. ^1H NMR (CD_3COCD_3): 6.10 (s, C_6H_6). ^2D NMR (CH_3COCH_3): 1.97 (s, CD_3). ^{13}C NMR (CD_3CN); 92.1 (C_6 ring); 90.5 (C_5 ring); 9.4 (m, CD_3, J(CD) 20 Hz). M.S. calcd. for $C_{16}H_6D_{15}Fe$: 284.1934; found: 284.192. (d_{15} major labeled species: 31%). Total deuterium incorporation calculated from d_{11} to d_{18} species: 82.5%.

11. Synthesis of $Fe[(C_5(CD_3)_5](C_6H_5CD_3)^+PF_6^-$, *16-$d_{18}$*

In a Schlenk tube equipped with a reflux condenser 0.40 g (0.93 mmol) of $Fe(C_5Me_5)(C_6H_5CH_3)^+PF_6^-$, **16** was dissolved in CD_3COCD_3 to give a yellow solution and 5 mL of a 1 *M* $NaOD/D_2O$ solution were added. The biphasic mixture was refluxed for 12 h, cooled to room temperature, and the solvent removed under vacuum. The residue was extracted as in 10 and the extract treated with diethyl ether. The solid obtained was recrystallized from CH_3COCH_3/diethyl ether to give 0.21 g (50%) of microcrystalline $Fe[C_5(CD_3)_5](C_6H_5CD_3)^+PF_6^-$, **16-$d_{18}$**. ^1H NMR (CD_3COCD_3): 5.92 (m, C_6H_5, 5H); 1.91 (m, C_5CD_3, 7.5H).

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