Bull Soc Chim Fr (1996) 133, 101-107
© Elsevier, Paris

FeCp$^+$-induced polybenzylation of polymethylbenzenes: double and triple branching

Christine Valério, Bruno Gloaguen, Jean-Luc Fillaut, Didier Astruc*

Laboratoire de chimie organique et organométallique, URA CNRS 35,
Université Bordeaux I, 351, cours de la Libération, 33405 Talence Cedex, France

(Received 16 October 1995; accepted 28 November 1995)

Summary – The clean polybenzylation reactions of polymethylaromatics using excess *t*-BuOK or KOH and $PhCH_2Br$ are induced by the temporary complexation by FeCp$^+$ (Cp = η^5-C_5H_5) under mild conditions. The toluene complex yields di- or tribenzylation; the *p*-xylene and hexamethylbenzene complexes yield hexabenzylation; and the durene complex yields octabenzylation. The mesitylene complex does not give nonabenzylation. The free ligands are routinely obtained in high yields by decomplexation using visible light.

iron polymethylbenzene complex / polybenzylation / arene activation

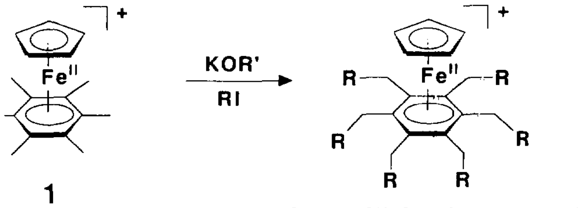
Résumé – **Polybenzylations des polyméthylbenzène induites par le greffon FeCp$^+$: double et triple branchage.** *Les réactions de polybenzylation efficaces des aromatiques utilisant un excès de* t-*BuOK ou KOH et* $PhCH_2Br$ *sont réalisées à l'aide de la complexation temporaire par le greffon* FeCp$^+$ (Cp = η^5-C_5H_5) *dans des conditions douces. Le complexe du toluène donne lieu à la di- ou à la tribenzylation, ceux du* p-*xylène et de l'hexaméthylbenzène conduisent à l'hexabenzylation et celui du durène subit l'octabenzylation. Le complexe du mésitylène ne donne pas de nonabenzylation. Les aromatiques décomplexés sont facilement obtenus avec des rendements élevés lors de l'irradiation des complexes du fer par la lumière visible.*

complexe polyméthylbenzène-fer / polybenzylation / activation aromatique

Introduction

Although activation of ligands by transition metals is a central property in transition-metal chemistry, multiple activation of the same ligand by iteration is much more rare [1-3]. We have developed this principle by suitable molecular engineering of polymethylaromatics in one-pot reactions [4]. The [FeCp(arene)]$^+$ salt serves as a proton reservoir complex. The prototype reaction is the FeCp$^+$-induced hexamethylation of $[FeCp(C_6Me_6)]^+PF_6^-$ **1** [5], which has been extended to hexaalkylation [6], hexaallylation [7], hexabenzylation [5b] and hexaalkoxybenzylation [8] (scheme 1). Thus, hexafunctional aromatics and their FeCp$^+$ complexes [8, 9] are now available by this method. Recently, this method was used to place ferrocene [10, 11] and [FeCp(arene)]$^+$ redox centers on the branches [10]. This reaction proved very useful for synthesizing molecular architectures used in molecular electronics and multi-electron catalysis [4c, 12].

Besides hexamethylbenzene, other methylaromatics were examined for the reaction in eq 1. In the permethylation reaction, it was found that, if a methyl substituent on the arene ligand had no neighbor, it could undergo the replacement of its three hydrogens by three methyl groups, and that, if it had one neighbor, two of its hydrogens could be replaced by methyl groups. In the hexamethylbenzene complex above, each methyl substituent has two methyl neighbors and only one of its hydrogens can be replaced by a methyl group. In order to perfunctionalize polymethylaromatics using this reaction, we examined whether this rule also applies to other groups. We already know that the rule holds true for allyl bromide, except that $[Fe(Cp)(C_6Me_6)]^+PF_6^-$ gives a double branching instead of the single branching obtained with methyl iodide [13, 14] (eq 2).



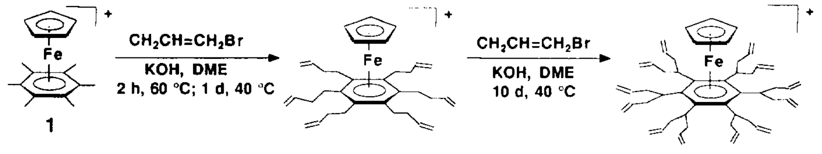
1

R = CH_3, CD_3, $CH_2CH{=}CH_2$, C_nH_{2n+1} (n = 2-5)
CH_2Ph, CH_2PhOR'' (R'' = alkyl),
CH_2Fc (Fc = ferrocenyl)

(eq 1)

---

* Correspondence and reprints; e-mail: astruc@cribx1.u-bordeaux.fr



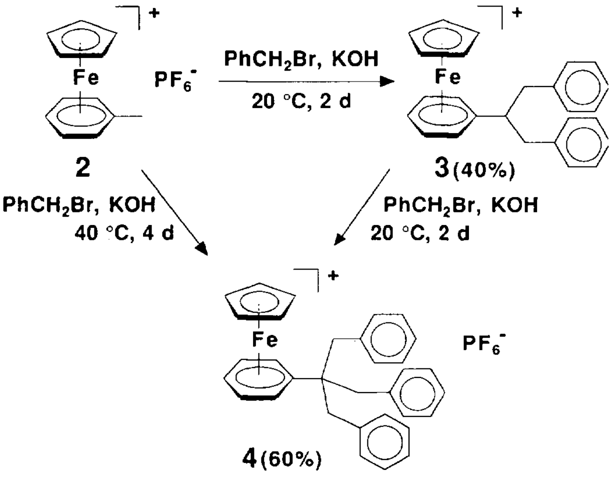
(eq 2)

In a preliminary communication, we demonstrated that double branching is possible using benzyl bromide for durene to give octabenzylation compounds [13] whose X-ray crystal structure have been reported [15]. This octabenzylation is routinely used in our laboratory as a starting point to design large molecular architectures [16]. We report here details of these reactions together with those of the trend governing the perbenzylation of the toluene, *p*-xylene and mesitylene ligands in $[Fe^{II}Cp(arene)]^+$ complexes. In the case of pentamethylcobalticinium, decaalkylation and decabenzylation have also been achieved via the double branching of each methyl group of the C_5-ring ligand [17, 18].

Results

[FeCp(toluene)]$^+$PF$_6^-$ 2

The reaction of **2** with excess KOH and $PhCH_2Br$ (neat) at 20 °C for 2 days provides the complex $[Fe^{II}Cp\{\eta^6\text{-}PhCH(CH_2Ph)_2\}]^+PF_6^-$ **3** in 40% yield after chromatography and recrystallization. This double benzylation reaction was carried out on a 5 mmol scale. The ^1H NMR spectrum shows an ABX pattern in the region δ 2.85–3.60 ppm for the $CH(CH_2Ph)_2$ alkyl protons due to the diastereotopic methylene groups. The ^{13}C NMR spectrum shows a single resonance for the CH_2 carbons at δ 41.25 ppm in addition to the CH resonance at δ 47.20 ppm (CD_3CN). When compound **3** was allowed to react under analogous conditions at 20 °C for 2 days, the third benzylation occurred completely, giving pure $[Fe^{II}Cp\{\eta^6\text{-}PhCH(CH_2Ph)_3\}]^+PF_6^-$ **4** as yellow microcrystals in 60% yield after chromatography and recrystallization (eq 3).



(eq 3)

[Fe^{II}Cp(p-xylene)]$^+$PF$_6^-$ 5

The reaction of **5** was carried out with excess KOH and $PhCH_2Br$ (neat) at 20 °C for 2 days. Under these conditions, the hexabenzylation was complete, giving **6** in 60% yield after chromatography and recrystallization (eq 4).

[Fe^{II}Cp(mesitylene)]$^+$PF$_6^-$ 7

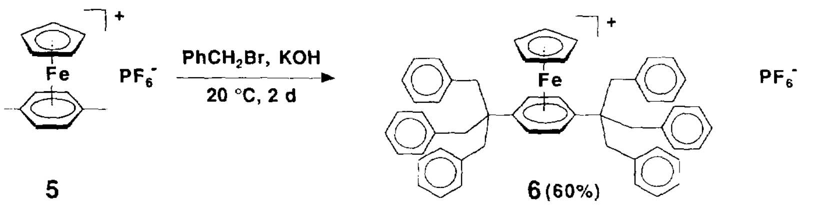
The reaction of **7** was carried out under forcing conditions either neat or using tetrahydrofuran (THF) or 1,2-dimethoxyethane (DME) as the solvent. Various temperatures and ultrasound were probed as reaction conditions. The reaction products were also a mixture of polybenzylation complexes. These reaction mixtures were reacted again under the most drastic conditions of temperature, excess reagent and sonification. Extensive decomplexation was a seriously limiting factor. The largest number of benzyl groups that could be introduced in the polybenzylation of the $FeCp^+$ complex as well as in the decomplexed aromatic was between seven and eight, leaving between one and two hydrogens in the benzyl position of the ligand. Thus, the nonabenzylated aromatic could never be obtained (eq 5).

[Fe^{II}Cp(durene)]$^+$PF$_6^-$ 8

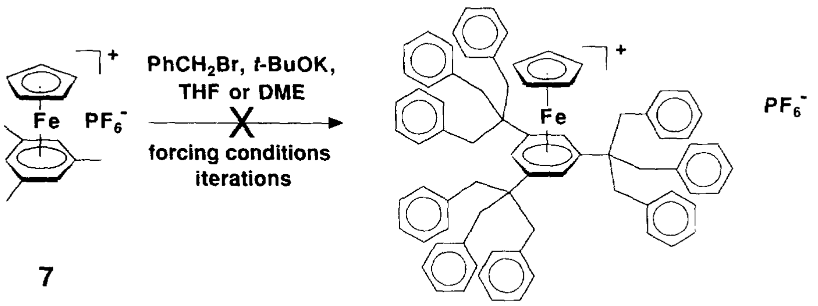
The best procedure, which was optimized after a large number of reactions of **8**, used KOH, $PhCH_2Br$ and DME (48 °C, 2 days). Octabenzylation was selectively obtained, giving **9** in 45% yield on a 5 mmol scale after chromatography and recrystallization. Another procedure used excess KOH and $PhCH_2Br$ in DME for 6 days at 40 °C and gave a 60% yield after the same purification. This procedure involved a heterogeneous reaction mixture (eq 6).

The ^1H and ^{13}C NMR spectra clearly distinguished two sets of benzyl signals corresponding to the *exo* and *endo* benzyl groups. In addition, the CH_2 region of the ^1H NMR spectrum showed four distinct multiplets, each representing one methylene proton, which indicates the diastereotopy of these methylene groups. The *exo* and *endo* phenyl signals were also clearly separated.

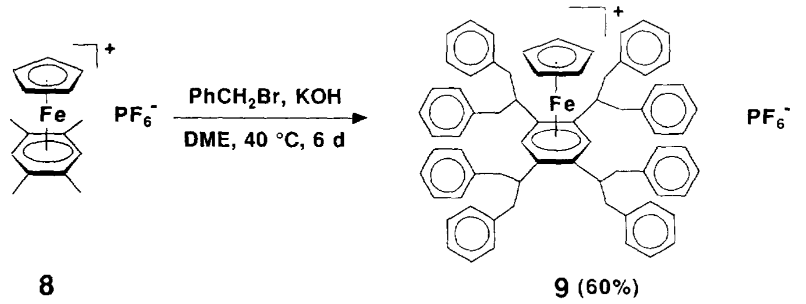
Heating to 130 °C in $1,2\text{-}Cl_2C_6H_4$ and cooling to −90 °C did not significantly change the spectra. Thus, the rotation is believed to be slow on the NMR timescale even at high temperatures. Given the large size of the $CH(CH_2Ph)_2$ group, rotation can only occur in a gearing process for two adjacent groups, but this process is either slowed down or sterically inhibited by the FeCp group. The gearing behavior (if any) of the other set of two groups must be independent. A complete description of the molecular dynamics must take into



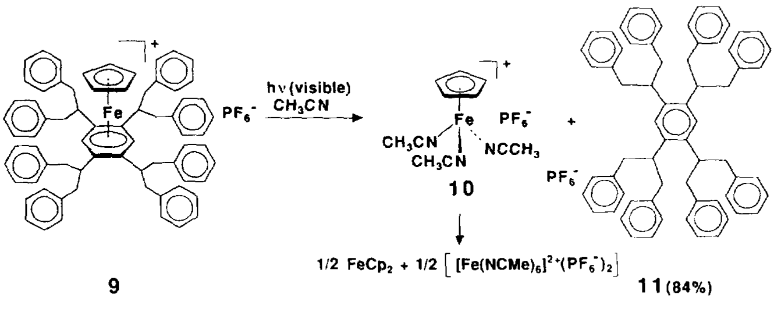
(eq 4)



(eq 5)



(eq 6)

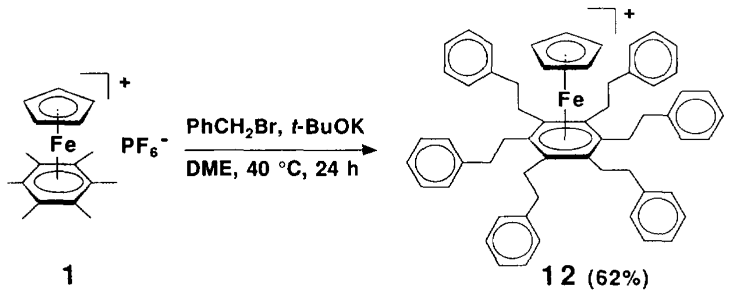


(eq 7)

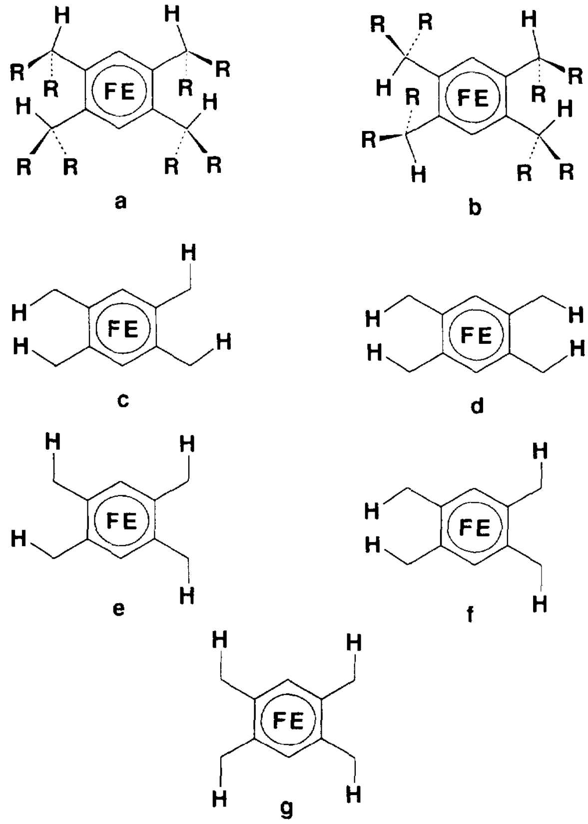
account the two energetically equivalent forms a and b (scheme 1), which cannot be distinguished by NMR. It is not possible to distinguish between the R group that faces the adjacent CHR_2 group and the R group (on the same side of the molecule) that does not (note that the right form with a single directionality is chiral, whereas the left form with the two opposite benzylic C–H directionalities is not) [19]. Because of the gearing effect due to the large size of the $CH(CH_2Ph)_2$ groups, the forms in which the CH bonds face each other (**c**, **d** and **f**) and those in which the benzyl groups do so (**e**, **f** and **g**) are believed to be too high in energy to be considered (see the X-ray structures in fig 1).

Decomplexation of 9

The decomplexation of **9** is best carried out by visible photolysis in CH_3CN [5b] (eq 7). The resulting tris-acetonitrile complex **10** is unstable below −40 °C and affords ferrocene (which is separated by oxidation to ferricinium using concentrated sulfuric acid) and $[Fe(NCMe)_6]^{2+}$ (which is insoluble in ether).



(eq 8)



The benzyl groups are omitted for clarity.

Scheme 1. Various conformations of **9**.

The organic residue is chromatographed to give a 84% yield of **11** as a white microcrystalline powder. The ^1H and ^{13}C NMR spectra show only one type of benzyl signal indicating equivalence of the eight benzyl groups. The gearing rotation of the $CH(CH_2Ph)_2$ groups must now be fast even at low temperature (see fig 1).

$[Fe^{II}Cp(C_6Me_6)]^+PF_6^-$ **1**

In our original work [5], we found that the perbenzylation of the C_6Me_6 ligand led to single branching, ie, to the formation of $[Fe^{II}Cp\{C_6(CH_2CH_2Ph)_6\}]^+PF_6^-$. The reinvestigation of this reaction confirms the original reports. The reaction is best carried out in DME rather than THF, which immediately gives a homogeneous solution, and the results are routinely reproducible. After 24 h at 40 °C, a 62% yield is obtained. The photolytic decomplexation was carried out as in the original report using visible light in CH_3CN (eq 8).

Discussion

The perbenzylation of polymethyl aromatics, induced by the activating $FeCp^+$ group, proceeds best in the system t-BuOK/$PhCH_2Br$ in DME. This system was compared to the KOH/$PhCH_2Br$ (no solvent) in the case of **9** which gave lower yields. However, this system allowed the isolation of the bisbenzyl complex **3** in the case of **2**. Given the homogeneity of the solution with t-BuOK in DME, the results are routinely reproducible. The new perbenzylation could be achieved for the $FeCp^+$ complexes of toluene, *p*-xylene and durene using either reaction system. In the two first cases, triple branching is obtained. The bisbenzylation of **2** is peculiar. We believe this is due to the low rate of the third benzylation due to steric bulk together with the deactivation of KOH with time once it is hydrated. Solubility may also be involved, since, surprisingly, this selectivity was not encountered in the case of the xylene and durene complexes **5** and **8**.

The largest number of benzyl groups that could be introduced is eight in the case of the durene complex **8** giving **9**. The double branching proceeds well but the complex formed is very bulky as indicated by the X-ray crystal structure [15] (fig 1).

This explains why the gearing rotation of the $CH(CH_2Ph)_2$ is either very slow or inhibited. In addition, attempts to introduce nine benzyl groups into the mesitylene complex failed, obviously for steric reasons due to the $FeCp^+$ group. On the other hand, nine methyl groups could be introduced with CH_3I giving the 1,3,5-tris-*tert*-butylbenzene complex from mesitylene [5]. Since the hexabenzylation of the hexamethylbenzene complex **1** is confirmed and routinely reproduced, the initial rule indicating the number of groups introduced as a function of the number of methyl neighbors on the arene ligand still holds [5b]. It now shows one more exception, however, with the bulk problem of the mesitylene complex. Given the difference in the success of permethylation between decamethylcobalticinium and decamethylrhodocenium (only the latter gives the decaisopropylmetallocenium [18]), we will have to attempt the nonabenzylation using $[RuCp(mesitylene)]^+$ in the future. Thus benzyl bromide is about as reactive as

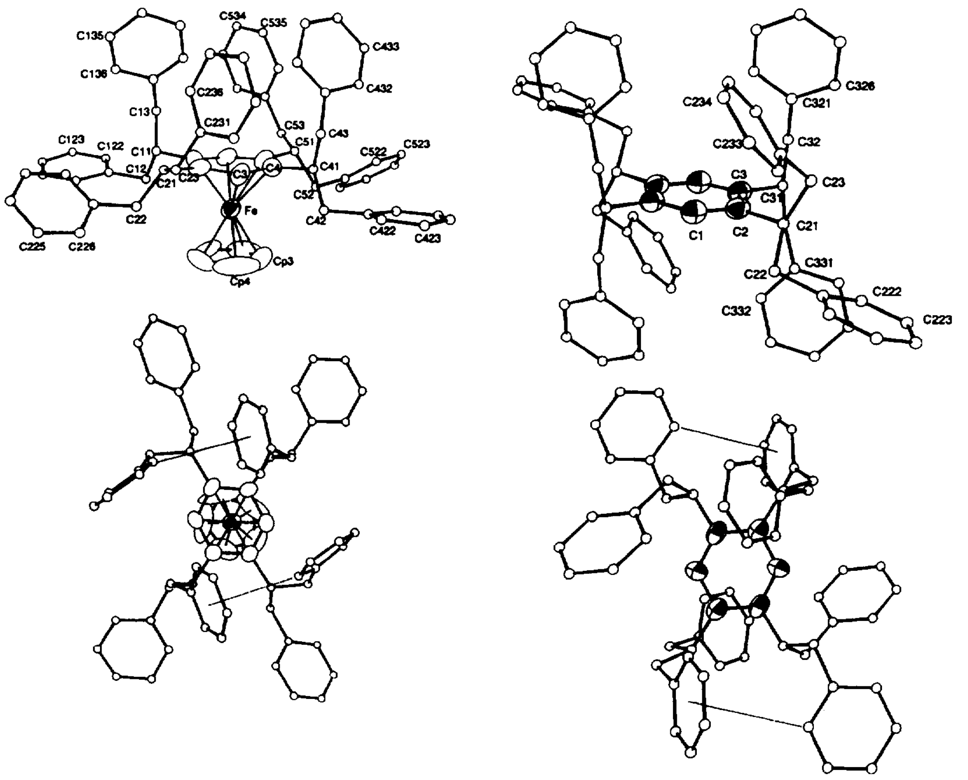


Fig 1. Perspective (top) and overhead (bottom) views of cation **9** (left) and the free ligand **11** (right). Reproduced with permission from ref 15.

Table I. Maximum number of groups cleanly introduced in a [FeCp(polymethylbenzene)]$^+$ complex as a function of the electrophile.

Electrophile	$CH_2{=}CHCH_2Br$	CH_3I	$PhCH_2Br$	$Fc(CH_2)_4I^a$
Maximum number of groups introduced	12 (double branching of **1**)	9 (triple branching of **7**)	8 (double branching of **9**)	6 (single branching of **1**) [11]

Note that in [Co(C$_5$Me$_5$)Cp]$^+$, the first three electrophiles all give the decabranched compounds [Co{C$_5$(CHR$_2$)$_5$}Cp]$^+$ but with decreasing yields as a function of bulk [17, 18]. [a] Fc(CH$_2$)$_4$I = (η^5-C$_5$H$_5$)Fe(η^5-C$_5$H$_4$-{CH$_2$}$_4$I).

methyl iodide as long as there is no bulk problem. Both benzyl bromide and methyl iodide give single branching only of the hexamethylbenzene complex **1**, whereas allyl bromide can lead either to single or double branching depending on the reaction time. The order of reactivity deduced from the maximum number of groups introduced in [FeCp(arene)]$^+$ complexes is as follows (table I).

Polybenzylation of polymethylbenzene complexes is very useful as a starting point for further functionalization of the phenyl rings leading, for instance, to star-shaped living polymers [20] and other giant architectures [10, 16]. Thus, it was important to define the detailed behavior of most polymethylaromatic ligands towards the perbenzylation reaction.

Conclusion

The FeCp$^+$-induced polybenzylation of polymethylbenzene ligands has been achieved in [FeCp(arene)]$^+$PF$_6^-$ complexes. Good and reproducible results have been obtained using the system *t*-BuOK/PhCH$_2$Br complex in DME (40 °C, 3 h), which is homogeneous. In the case of the FeCp$^+$-induced octabenzylation of durene, the system KOH/PhCH$_2$Br was also found to be very convenient and routinely used.

The toluene and *p*-xylene ligands give triple branching leading to the tri- and hexabenzylation respectively. However, with toluene, the reaction in THF can stop at the bibranching level to give [FeCp{PhCH(CH$_2$Ph)$_2$}]$^+$PF$_6^-$.

Nonabenzylation of the mesitylene complex cannot be completed because of the steric hindrance. Eight is the maximum number of benzyl groups which can be introduced into a [FeCp(polybenzene)]$^+$ complex. No rotation of the CH(CH$_2$Ph)$_2$ groups can be observed by NMR due to the bulk of the octabenzylation product **9**.

The free octabenzylated aromatic is easily obtained in high yield by visible photolysis of the [FeCp(arene)]$^+$ complex in CH$_3$CN in the presence of 1 equiv PPh$_3$. Geared rotation of the two sets of two CH(CH$_2$Ph)$_2$

groups is now fast at the NMR time-scale at all observable temperatures.

The initially reported hexabenzylation of [FeCp(C_6Me_6)]$^+$ has been confirmed and is now routinely and reproducibly performed with *t*-BuOK in DME (rather than THF). These hexa- and octabenzyl complexes **12** and **9** and the corresponding free aromatics are important starting cores for further syntheses of more elaborate giant molecules.

Experimental section

General data

All manipulations of air-sensitive materials were conducted in a VAC argon drylab or under argon in Schlenk apparatus connected to a double manifold. Reagent grade THF, DME, pentane and toluene were predried over Na foil and distilled from sodium benzophenone ketyl under argon (*caution*: DME and THF are not distilled to dryness). All other chemicals were used as received. ^{1}H NMR spectra were obtained with Bruker AC 200 (200 MHz) or AC 250 (250 MHz) spectrometers, and ^{13}C NMR spectra were recorded with Bruker AC 200 (50.3 MHz) or a Bruker AC 250 (67.9 MHz) spectrometers. NMR spectra were referenced to Me_4Si (^{1}H) or the appropriate deuterated solvent (^{13}C). Cyclic voltammetry studies were performed with a Princeton Applied Research 273 potentiostat. Elemental analyses were performed by the CNRS Center of Microanalyses at Lyon-Villeurbanne.

[FeCp{(dibenzylmethyl)benzene}]$^+$PF$_6^-$ **3**

In a Schlenk tube, 2 g of [FeCp(toluene)]$^+$PF$_6^-$ **2** [21-23] (5.58 mmol) and 12.54 g (223 mmol) of finely ground KOH were dried for 2 h under vacuum at 40 °C, and then 36.7 g of (223 mmol) $PhCH_2Br$ was added under argon. The reaction mixture turned orange; it was stirred for 2 days at 20 °C in the dark under argon. The solvent was then removed under vacuum. KOH dissolved in 100 mL distilled water was added. The yellow solid was filtered, dissolved in 100 mL CH_2Cl_2, and this solution was shaken with an aqueous H$^+$PF$_6^-$ solution, decanted, and dried over Na_2SO_4. After filtration, the solvent was removed under vacuum, and the solid residue was washed with pentane and ether, and chromatographed on a 10 cm alumina column using CH_2Cl_2 as the eluent. After removing CH_2Cl_2 under vacuum, the yellow powder was recrystallized in an acetone/alcohol 1:1 mixture at -20 °C to give 1.20 g (40% yield) of yellow-brown microcrystals of **3**.

^{1}H NMR (250 MHz, CD_3CN, TMS), δ ppm: 7.26 and 7.11 (m, 10H, free phenyls), 6.15 (d, 2H), 6.08 (t, 1H) and 5.84 (d, 2H) (CH of the coordinated arene), 4.85 (s, 5H, Cp), 3.34 (q, 1H, CH), 3.00 and 2.93 (m, 4H, CH_2).

^{13}C NMR (62.38 MHz, CD_3CN), δ ppm: 138.79 (quaternary carbons of the free phenyls), 130.54, 129.58 and 127.68 (CH of free phenyls), 112.15 (quaternary carbons of the coordinated arene), 88.08, 87.81 and 87.34 (CH of the coordinated arene), 77.5 (Cp), 47.20 (*C*H-CH_2) and 41.25 (CH-*C*H_2).

Anal calc for $C_{26}H_{25}FePF_6$: C 57.98, H 4.68, Fe 10.39; found C 58.05, H 4.71, Fe 10.44.

[FeCp{(tribenzylmethyl)benzene}]$^+$PF$_6^-$ **4**

The same procedure as in **1** was applied to 2 g (3.71 mmol) of **3**, 8.34 g (148 mmol) of KOH and 24.35 g (148 mmol) of $PhCH_2Br$ and gave 1.39 g (60% yield) of yellow-brown microcrystals of **4**.

^{1}H NMR (250 MHz, CD_3CN, TMS), δ ppm: 7.30 and 7.28 (m, 15H, free phenyls), 6.09 (m, 5H, CH of the coordinated arene), 4.58 (s, 5H, Cp) 3.27 (s, 6H, CH_2).

^{13}C NMR (62.38 MHz, CD_3CN, TMS), δ ppm: 137.93 (quaternary carbons of the free phenyls), 132.46, 129.39 and 127.99 (CH of the free phenyls), 118.46 (quaternary carbons of the coordinated arene), 87.97, 87.79 and 87.10 (CH of the coordinated arene), 77.14 (Cp), 46.86 (aliphatic quaternary carbon), 44.44 (CH_2).

Anal calc for $C_{33}H_{31}FePF_6$: C 63.04, H 4.97, Fe 8.90; found C 63.13, H 5.04, Fe 8.95.

[FeCp{1,4-bis{(tribenzylmethyl)benzene}]$^+$PF$_6^-$ **6**

The same procedure as in **1** applied to 2 g (5.37 mmol) of [FeCp(*p*-xylene)]$^+$PF$_6^-$ [20-22] **5**, 12.06 g (215 mmol) of KOH and 36.7 (215 mmol) of $PhCH_2Br$ gave 2.93 g (60% yield) of yellow microcrystals of **6**.

^{1}H NMR (250 MHz, CD_3CN, TMS), δ ppm: 7.29 and 7.22 (m, 30H, free phenyls), 6.14 (s, 4H, aromatic CH of the coordinated arene), 4.36 (s, 5H, Cp), 3.31 (s, 12H, CH_2).

^{13}C NMR (62.38 MHz, CD_3CN, TMS), δ ppm: 138.09 (quaternary carbons of the free phenyls), 132.42, 129.54 and 128.09 (aromatic CH of the free phenyls), 115.18 (quaternary carbons of the coordinated arene), 86.43 (aromatic CH of the coordinated arene), 77.37 (Cp), 46.66 (aliphatic quaternary carbon), 44.82 (CH_2).

Anal calc for $C_{55}H_{51}FePF_6$: C 72.34, H 5.63, Fe 6.13; found C 72.41, H 5.74, Fe 6.21.

[FeCp{1,2,4,5-tetrakis(dibenzylmethyl)benzene}]$^+$PF$_6^-$ **9**

- *Method A*

The same procedure as in **1** applied to 2 g (5 mmol) of [FeCp(durene)]$^+$PF$_6^-$ **8** [23], 11.22 g (200 mmol) of KOH and 34.2 g (200 mmol) of $PhCH_2Br$ in 30 mL DME at 48 °C for 2 days gave 2.52 g (45% yield) of **9** as yellow-brown crystals.

- *Method B*

The same procedure as in **1** was applied to 2 g (5 mmol) of [FeCp(durene)]$^+$PF$_6^-$ **8** [23], 6.73 g (120 mmol) of KOH and 20.52 g (120 mmol) of $PhCH_2Br$ in 20 mL of DME at 40 °C for 2 days. Portions of KOH (6.73 g, 120 mmol) were then added after 2 and 4 days. The solvent was removed under vacuum and the residue was extracted with dichloromethane. The organic phase was washed with an aqueous H$^+$PF$_6^-$ solution and then with water. It was dried over Na_2SO_4 and the solvent was removed under vacuum. The residue was extracted with pentane and ether, and then chromatographed on an alumina column using dichloromethane. After removing the solvent under vacuum, 3.36 g (60% yield) of **9** were obtained as yellow-brown crystals.

^{1}H NMR (250 MHz, CD_3COCD_3, TMS), δ ppm: 7.45 and 6.31 (m, 20H, *exo* phenyls), 7.14 and 6.68 (m, 20H, *endo* phenyls), 6.49 (s, 2H, coordinated arene), 5.32 (s, 5H, Cp), 3.79 (septet, 4H, aliphatic CH), 3.62 and 3.43 (m, 8H, *exo* CH_2), 2.80 and 2.70 (m, 8H, *endo* CH_2).

^{13}C NMR (62.38 MHz, CD_3COCD_3, TMS), δ ppm: 140.4 and 139.3 (quaternary carbons of the *endo* and *exo* phenyls), 129.8 and 127.5 (*endo* and *exo* phenyls), 110.38 (quaternary $C_6H_2R_4$), 83.54 (CH of coordinated arene), 77.63 (Cp), 42.28 (aliphatic CH), 42.65 and 41.16 (*endo* and *exo* CH_2).

Anal calc for $C_{71}H_{67}FePF_6$: C 76.06, H 6.02, Fe 4.98; found C 76.11, H 6.11, Fe 5.13.

Cyclic voltammetry (Pt, -30 °C, DMF 0.1 M *n*-Bu_4NBF_4, 0.4 V s^{-1}): Fe^{II}/Fe^{I}, $E^\circ = -1.26$ V vs SCE, $i_a/i_c = 1$,

$n = 1$) (for comparison: [FeCp(1,2,4,5-tetraisopropylbenzene)]$^+$PF$_6^-$ [5b], $E° = -1.44$ V vs SCE).

1,2,4,5-Tetrakis(dibenzylmethyl)benzene **11**

Compound **9** (3 g) was photolyzed with the intense visible light of a xenon lamp in acetonitrile for 12 h. The solvent was evaporated and the crude product was treated with concentrated sulfuric acid to oxidize ferrocene to ferricinium. After extraction using ether, the organic layer was washed using water, and then dried over Na_2SO_4 and evaporated. After chromatography on alumina with ether as the eluent, 1.9 g of **11** (84% yield) was obtained as a white microcrystalline powder.

^{1}H NMR (250 MHz, $CDCl_3$, TMS), δ ppm: 7.17 (m, 40H, C_6H_5), 3.38 (m, 8H, CH), 2.46–2.68 (m, 16H, CH_2).

^{13}C NMR (62.96 MHz, $CDCl_3$, TMS), δ ppm: 140.77 (quaternary C, C_6H_5), 129.61, 128.28 and 126.08 (C_6H_5), 125.81 ($C_6H_2R_4$), 42.93 (CH), 41.89 (CH_2).

Anal calc for $C_{66}H_{62}$: C 92.68, H 7.32; found C 92.69, H 7.31.

Attempts to synthesize [FeCp{1,3,5-tris(tribenzylmethyl)benzene})$^+$*PF*$_6^-$ **8**

The same procedure as in **1** applied to 2 g (5.16 mmol) of [FeCp(mesitylene)]$^+$PF$_6^-$ **7** [21-23], 11.6 g (207 mmol) of KOH and 35.3 g (207 mmol) of $PhCH_2Br$ gave a yellow powder whose ^{1}H NMR spectrum showed a mixture corresponding to the introduction of between six and seven benzyl groups into the molecule. Similar reaction of the same mixture was repeated under more drastic conditions, up to several days at 120 °C using KOH or *t*-BuOK, and under ultrasound. The maximum number of branches obtained was between seven and eight and a high percentage of decomplexed arene was obtained with a similar number of benzyl substituents.

[FeCp{hexakis((2-phenylethyl)benzene)}]$^+$*PF*$_6^-$ **12**

The synthesis of **12** from **1** [23, 24], *t*-BuOK and $PhCH_2Br$ in THF was reported previously. An alternative procedure which is routinely carried out in our laboratory now uses *t*-BuOK in DME as follows.

[FeCp(C_6Me_6)]$^+$PF$_6^-$ **1** (1.3 g, 3 mmol) and *t*-BuOK were stirred together under vacuum at 40 °C for 3 h, and then an inert atmosphere was maintained. A solution of 54 mmol of $PhCH_2Br$ in 75 mL of freshly distilled DME was introduced by cannula. This mixture was stirred at 40 °C for 24 h in the dark. The solvent was removed under vacuum and the residue was extracted with dichloromethane. This solution was washed with H_2O, dried over Na_2SO_4 and washed with ether to give a tan powder. Recrystallization yielded 2 g (70%) of **12** as a microcrystalline powder. See the analytical and spectroscopic data in ref [5b].

Acknowledgments

We thank JR Hamon (Rennes) for helpful discussions and the CNRS, the University Bordeaux I and the Région Aquitaine for financial support.

References

1 Mathey F, Sevin A, *Introduction à la Chimie Moléculaire des Eléments de Transition*, Ellipses, Paris, 1991, Chap 4

2 Elschenbroich Ch, Salzer A, *Organometallics*, 2nd ed, VCH, 1991, Weinheim, Chap 15

3 Crabtree RH, *The Organometallic Chemistry of the Transition Metals*, 2nd ed, Wiley, New York, 1994, Chap 5

4 a) Astruc D, *Acc Chem Res* (1986) 19, 377
b) *Top Curr Chem* (1991) 160, 47
c) *New J Chem* (1992) 16, 305

5 a) Astruc D, Hamon JR, Althoff G, Román E, Batail P, Michaud P, Mariot JP, Varret F, Cozak D, *J Am Chem Soc* (1979) 101, 5445
b) Hamon JR, Saillard JY, Le Beuze A, McGlinchey, Astruc D, *J Am Chem Soc* (1982) 104, 7549
c) Desbois MH, Astruc D, *Organometallics* (1989) 8, 1841

6 Moulines F, Astruc D, *J Chem Soc, Chem Commun* (1989) 614

7 Moulines F, Astruc D, *Angew Chem Int Ed Engl* (1988) 27, 1347

8 Fillaut JL, Boese R, Astruc D, *Synlett* (1992) 55

9 Moulines F, Djakovitch L, Fillaut JL, Astruc D, *Synlett* (1992) 57

10 Fillaut JL, Astruc D, *J Chem Soc, Chem Commun* (1993) 1320

11 Fillaut JL, Linares J, Astruc D, *Angew Chem Int Ed Engl* (1994) 33, 2460

12 Astruc D, *Electron-Transfer and Radical Processes in Transition-Metal Processes*, VCH, New York, 1995, Chaps 2, 4 and 5

13 Moulines F, Gloaguen B, Astruc D, *Angew Chem Int Ed Engl* (1992) 28, 458

14 Moulines F, Djakovitch L, Boese R, Gloaguen B, Thiel W, Fillaut JL, Delville MH, Astruc D, *Angew Chem Int Ed Engl* (1993) 32, 1075

15 Subramanian S, Wang L, Zaworotko MJ, *Organometallics* (1993) 12, 310

16 Valerio C, Thesis, Univ Bordeaux I, 1996

17 Gloaguen B, Astruc D, *J Am Chem Soc* (1990) 112, 4607

18 a) Buchholz D, Gloaguen B, Fillaut JL, Cotrait M, Astruc D, *Chem Eur J* (1995) 374
b) Buchholz D, Astruc D, *Angew Chem Int Ed Engl* (1994) 106, 1721

19 For chirality in organotransition-metal chemistry, see: Brunner H, *Adv Organomet Chem* (1980) 18, 151

20 Cloutet E, Fillaut JL, Gnanou Y, Astruc D, *J Chem Soc, Chem Commun* (1994) 2433

21 Coffield TH, Sandel V, Closson RD, *J Am Chem Soc* (1957) 79, 5826

22 Nesmeyanov AN, Vol'kenau NA, Bolesova IN, *Dokl Akad Nauk SSSR* (1966) 166, 607

23 Khand IU, Pauson PL, Watts WE, *J Chem Soc C* (1968) 2257

24 Astruc D, Hamon JR, Lacoste M, Desbois MH, Madonik AM, Román E, *Organometallic Synthesis*, King RB Ed, Vol IV, 1988, 172