Rings Cages and Polymers

A Fast Organometallic Route from *p*-Xylene, Mesitylene, and *p*-Diisopropylbenzene to Organoiron and Polycyclic Aromatic Cyclophanes, Capsules and Polymers

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Para-xylene and mesitylene are among the most common and cheapest organic compounds.[1,2] They form well-known robust sandwich complexes of the type $[\mathrm{Fe}(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})]^+$,[3] by high-yield, large-scale reactions with ferrocene in the presence of aluminum chloride.[4] Herein we report that these sandwich complexes and the *p*-diisopropylbenzene iron complex lead to new cyclophanes,[5] organoiron cyclo-

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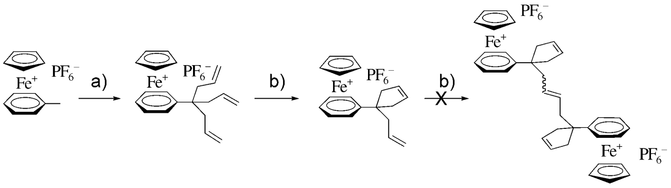
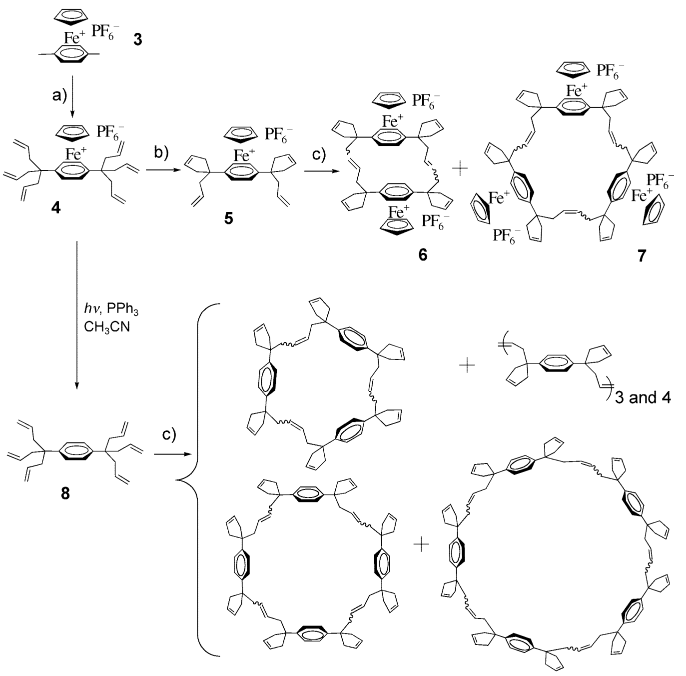
phanes,[6] polyring derivatives, capsules, and polymers in two steps (three steps for the iron-free compounds). The electron-withdrawing character of the cationic 12-electron group FeCp$^+$ lowers the pK_a value of polymethylaromatics from 43 to 28 in DMSO,[7a,b] and the subsequent convenient deprotonation reaction can be exploited for facile and multiple C–C bond formation under ambient conditions.[7b,c] For instance, FeCp$^+$-induced triallylation of toluene can be followed by ring-closing metathesis (RCM) to give a derivative containing a five-membered ring in 5 min at room temperature[7c] using the Grubbs metathesis catalyst [Ru(PCy$_3$)$_2$Cl$_2$(=CHPh)], **1**.[8] On the other hand, dimerization of the iron complex by cross metathesis (CM) under these conditions does not occur, even after several days (Scheme 1).

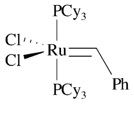


Scheme 1. a) Allyl bromide, KOH, DME; b) [Ru(PCy$_3$)$_2$Cl$_2$(=CHPh)], **1**, CH$_2$Cl$_2$, room temperature.

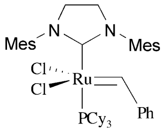


Scheme 2. a) Allyl bromide, KOH, DME; b) [Ru(PCy$_3$)$_2$Cl$_2$(=CHPh)], **1**, CH$_2$Cl$_2$; c) [Ru(PCy$_3$){C(N(mesityl)CH)$_2$}Cl$_2$(=CHPh)], **2**, C$_2$H$_4$Cl$_2$, 60 °C.

We have now explored the two-step polyallylation/cross-coupling-metathesis sequence with the complexes [Fe(η^5-C$_5$H$_5$)(η^6-arene)][PF$_6$] towards the more challenging construction of cyclophanes by using **1** and the more efficient second-generation Grubbs commercial catalyst, [Ru(PCy$_3$){C(N(mesityl)CH)$_2$}Cl$_2$(=CHPh)], **2**.[8]



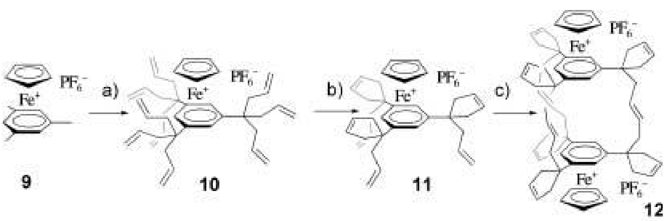
1



2

The *p*-xylene iron complex **3** leads to CpFe$^+$-induced hexaallylation giving **4**. When **4** is heated at 60 °C for 6 days in the presence of the catalyst **2**, a mixture of [6,6] and [6,6,6] paracyclophanes **6** and **7** (in comparable amounts, from the MALDI-TOF mass spectrum) is obtained in 45 % yield. A small amount of [6,6,6,6] tetranuclear compound is also detected. Under these conditions, the iron-free compound **8** gives a mixture of three paracyclophanes and linear open trisarene and tetra-arene (Scheme 2) that were identified by their molecular peaks in the MALDI-TOF mass spectra.

The same sequence was investigated with the mesitylene complex **9**. After CpFe$^+$-induced nonaallylation of **9** at room temperature giving the nonaallyl complex **10**, metathesis of **10** catalyzed by **1** gives **11**, resulting from RCM. However, metathesis catalyzed by **2** at reflux for 4 h gives a mixture whose MALDI-TOF mass spectrum shows the nonselective formation of singly, doubly, or triply linked dimers corresponding to the loss of one, two, or three ethylene units respectively, and singly and doubly linked trimers, tetramers, and pentamers. As the metathesis reaction is thermodynamically controlled,[8,9] we heated the reaction mixture further for 2 days at 60 °C to approach or reach equilibrium. Indeed, the major products observed in the MALDI-TOF mass spectrum then became dimers, with almost equal amounts of doubly and triply bridged compounds. The oligomers were in lower amounts. Finally, the reaction mixture was heated for a week to give almost exclusively the triply bridged organoiron [6$_3$](1,3,5) cyclophane **12**, a molecular capsule, and only trace amounts of the other compounds (Scheme 3).[6] This sequence of MALDI-TOF mass spectra can be seen in Figure 1. The outcome of this reaction is strongly concentration dependent as required by the thermodynamic control. Under more concentrated conditions, the amounts of oligomers obtained are larger, and the final equilibrium may even lie in favor of these oligomers under very concentrated conditions. The



Scheme 3. a) Allyl bromide, KOH, DME; b) [Ru(PCy$_3$)$_2$Cl$_2$(=CHPh)], **1**, CH$_2$Cl$_2$, RT; c) [Ru(PCy$_3$){C(N(mesityl)CH)$_2$}Cl$_2$(=CHPh)], **2**, C$_2$H$_4$Cl$_2$, 60 °C.

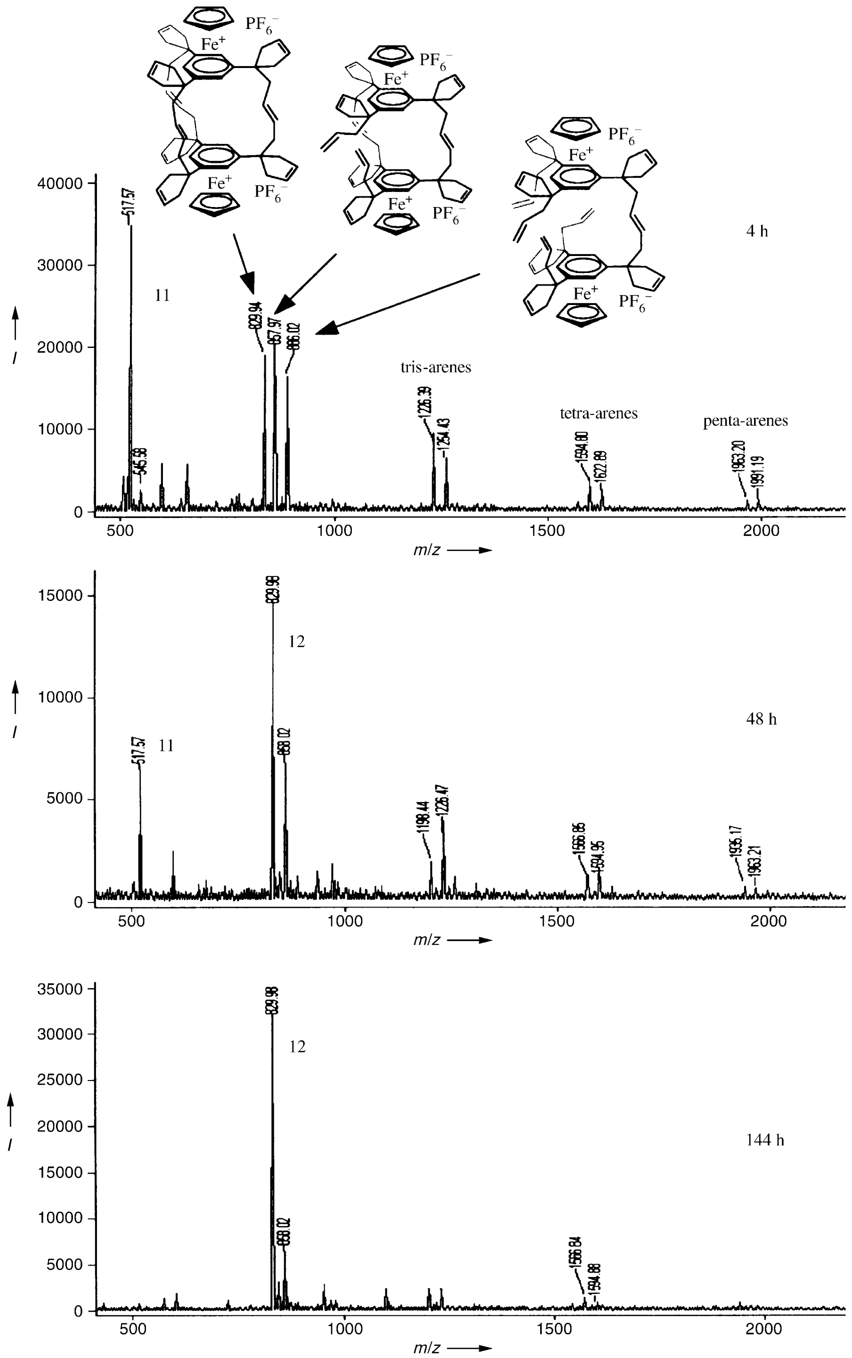


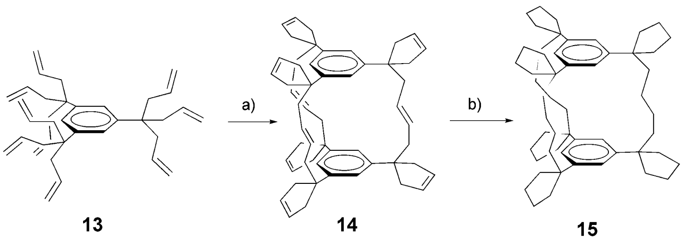
Figure 1. MALDI-TOF mass spectra during the metathesis reaction of **10** catalyzed by **2**.

$CpFe^+$ group has a negative effect on the metathesis rate presumably for steric reasons, and the low yield of **12** also arises from decomplexation during the reaction. When the metathesis reaction is carried out on the metal-free nonaallylated arene **13** obtained by the decomplexation of **10**, it proceeds more readily and selectively to form the triply bridged CM product **14**. The triply-bridged capsule **14** is isolated as a mixture of isomers whose hydrogenation with H_2/Pd/C in CH_2Cl_2 yields the single product **15** (Scheme 4).

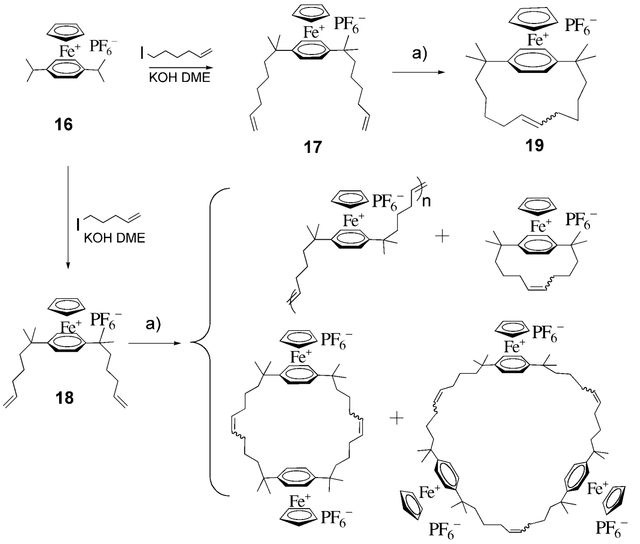
Because of the well-known magnetic anisotropy of the arene ring in the cyclophane alkyl hydrogens,[5a] the ^{1}H NMR signals of the β-hydrogens are shifted upfield at 0.64 ppm (see the Supporting Information).

To investigate the feasibility of the synthesis of organometallic [n] paracyclophanes using the same type of strategy, we first synthesized the new *p*-diisopropylbenzene complex $[FeCp(\eta^6\text{-}p\text{-}i\text{Pr}_2\text{-}C_6H_4)][PF_6]$, **16**, by using the classic Nesmeyanov ligand-substitution reaction.[3] Dialkenylation was carried out in one pot with complex **16**, KOH, and longer-chain *ω*-alkenyl iodides in THF. The reactions were carried out in refluxing THF, because alkyl iodides are much less reactive electrophiles than allyl bromide. Thus, dialkenylation of **16** with ω-iodoalkenes allows the preparation of a variety of paradisubstituted arenes bearing terminal double bonds such as the new complexes **17** and **18**. Potentially, RCM may lead to the desired paracyclophanes iron complexes and eventually the metal-free cyclophanes by using the classic decomplexation procedure (i.e. photolysis by using visible light in MeCN in the presence of one equiv PPh_3, followed by extraction with ether). Complex **17** indeed selectively gives **19** in CH_3Cl at room temperature by using the catalyst **1**. In the ^{1}H NMR spectra of **19**, the signals of the β-hydrogens of the cyclophanes are shifted to 0.51 ppm because of aromatic anisotropy.[5a] On the other hand, metathesis with **1** of the complex **18**, containing alkenyl chains that are one methylene unit shorter than in **17**, leads to a mixture of linear oligomers (2 to 6 units) and mono-, bi- and trimetallic paracyclophanes (Scheme 5) that are identified by their molecular peaks in the MALDI-TOF mass spectrum.

In summary, a variety of cyclophanes, metallocyclophanes polyring



Scheme 4. a) $[Ru(PCy_3)\{C(N(\text{mesityl})CH)_2\}Cl_2(=CHPh)]$, **2**, $C_2H_4Cl_2$, 60 °C; b) H_2 Pd/C CH_2Cl_2.



Scheme 5. a) $[Ru(PCy_3)_2Cl_2(=CHPh)]$, **1**, CH_3Cl, RT.

derivatives and capsules are quickly formed from *p*-xylene, mesitylene and *p*-diisopropylbenzene, which are activated by $FeCp^+$ followed by ring closing- and cross metathesis catalyzed by the Grubbs commercial catalysts **1** or **2**. These results illustrate the potential of this synthetic strategy combining these two spectacular and remarkably efficient modes of C–C coupling. This work is also an example of the use of MALDI-TOF mass spectrometry as a remarkably powerful tool for the investigation of complex structures in a nonbiological area.

Experimental Section

Compounds **3** and **9**: see ref. [2] and [3]. Compounds **4**, **10**, **17** and **18**: see ref. [7c]. The perallylation reaction was carried out at room temperature until completion monitored by ^1H NMR, whereas the peralkenylation was conducted at reflux. Product **10** was purified on an Al_2O_3 gel column eluting with CH_2Cl_2. Compounds **5**, **11** and **19:** Catalyst **1** (5–10 % mol) was added to a stirred solution of complex **4** (0.5 mmol) in CH_2Cl_2 (20 mL). After completion of the reaction, the solvent was removed in vacuo, and the residue was washed repeatedly with ether. Recrystallization of the product in a CH_2Cl_2/ether mixture and slow-diffusion crystallization with a CH_2Cl_2/ether mixture gave yellow crystals. Compounds **6**, **7**, **12** and **14**: A stirred solution of **5** (0.5 mmol) and **2** (10 % mol) in dichloroethane (5 mL) was heated to reflux over seven days under nitrogen, and **2** (10 % mol) was added every other day (i.e., the total amount of **2** used was 30 %). The solvent was removed in vacuo and the solid residue was washed with 3x10 mL ether (except **14**) and purified by column chromatography over silica. Compound **15**: Pd/C (10 mg) was added to a solution of compound **14** (70 mg; 0.14 mmol) in CH_2Cl_2 and this mixture was flushed with dihydrogen and kept under atmospheric pressure for 10 h. The mixture was filtered over celite and the solvent was removed in vacuo (yield: 100 %). See the Supporting Information for the other experimental procedures and the analytical and spectroscopy data confirming the proposed structures.

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Keywords: cage compounds · C–C coupling · cyclophanes · iron · metathesis

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