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General Route from Simple Methyl, Alkyl, and Cycloalkyl Arenes to Polycyclic Cyclopentenyl Aryl Derivatives. The CpFe$^+$ Group as an Activator and Tag

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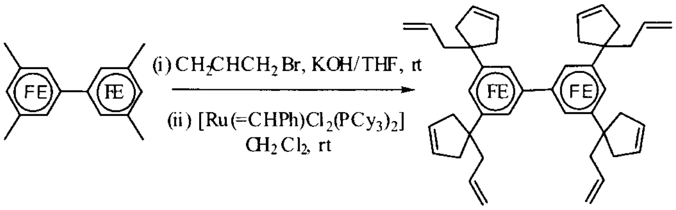
ABSTRACT



The CpFe$^+$ group activates the perallylation of the benzylic groups of arenes using KOH and allylbromide under ambient conditions. This reaction can be followed by ruthenium-catalyzed RCM metathesis using Grubbs' catalyst at room temperature to give polycyclic aromatic derivatives in high yields, and these products are easily separated from the catalyst by extraction using ether. Alternatively, the RCM metathesis can be best carried out in ionic liquids at 80 °C, and extraction using ether is then facile.

Sequential, multistep, and tandem reactions mediated by transition metals are becoming a major goal in synthetic chemistry in order to minimize costs and waste.[1] Arenes and olefins are obvious candidates for such a strategy because they are abundant at low cost. The transition-metal-catalyzed polymerization of olefins[2] and tandem reactions including olefin metathesis[3] are remarkable examples along this line. Cyclopentene derivatives are easily functionalized[4] and heterobifunctionalized[5] and are precursors of unnatural and natural compounds. We now report a two-step, high-yield route at room temperature from simple alkyl aromatics to cyclopentenyl aryl derivatives in their sandwich complexes

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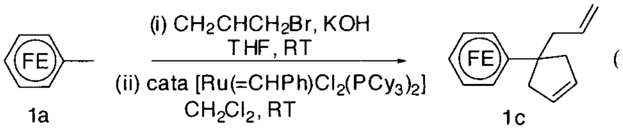
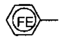
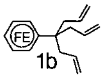
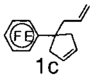
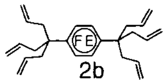
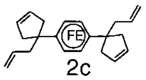
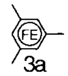
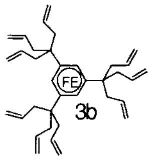
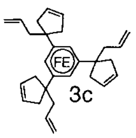
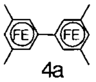
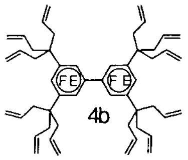
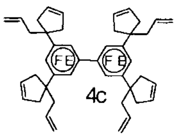
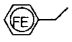
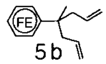
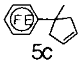
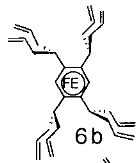
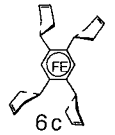
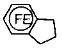
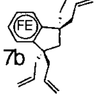
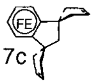
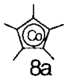
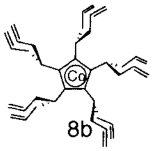
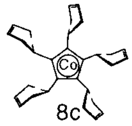
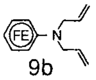
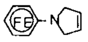
[FeCp(η^6-arene)]$^+$ [7] (Cp = η^5-C_5H_5), as exemplified in eq 1 (FE = [η^5-CpFe]$^+PF_6^-$).



(1)

Temporary π complexation of the arenes[6,7] as well as their decomplexation[7b] after the CpFe$^+$-induced transformation also proceeds in high yields, so that new families of sophisticated organo-iron complexes in Table 1 and the free aromatic derivatives become available.

Table 1. Perallylation (in THF) and RCM (in CH_2Cl_2) Products[a]

substrate	perallylation product	metathesis product	t (h)	yield (%)
 1a	 1b	 1c	1b: 72 1c: 4	77 65
 2a	 2b	 2c	2b: 72 2c: 6	72 60
 3a	 3b	 3c	3b: 96 3c: 8	65 74
 4a	 4b	 4c	4b: 72 4c: 8	59 70
 5a	 5b	 5c	5b: 72 5c: 4	85 65
 6a	 6b	 6c	6b: 48 6c: 4	72 70
 7a	 7b	 7c	7b: 96 7c: 4	67 76
 8a	 8b	 8c	8b: 24 8c: 4	15 81
 9a	 9b	 9c	9b: 15 9c: 20	61 65

[a] t (h) = reaction times (rt); yield % = yields of isolated and purified products.

The first step is the CpFe$^+$-induced perallylation **1a**→**1b**, etc. (Table 1) in the benzylic position of alkyl arenes, which has been known for some time in the case of polymethylarenes.[8] We now find that this reaction can be carried out under more simple conditions at ambient temperature using KOH, allyl bromide, and THF, and that it can be extended to the iron complexes **2a**, **4a**, **5a**, **7a**, and **9a**. The first example using a binuclear biaryl complex, **4a**, leads to the remarkable diiron dodecaallyl dendritic core **4b** and its iron-free dodecaallyl organic analogue. A perfect selectivity is observed in all the cases, and high yields are obtained for most compounds.

The second reaction is the ring-closing metathesis (RCM) using Grubbs' commercial catalyst [Ru(=CHPh)$Cl_2(PCy_3)_2$],[9,10] which readily proceeds at room temperature in NMR tubes using $CDCl_3$ as well as in CH_2Cl_2 in Schlenk tubes yielding **1c**−**9c** (Table 1). This reaction can be carried out on the metal complexes. Alternatively, the perallylated iron derivatives can be decomplexed in MeCN by photolysis using visible light in the presence of PPh_3,[7b] providing excellent yields of the metal-free perallylated arenes **1d**−**7d**. The role of the CpFe$^+$ group is also important for solubility and selectivity reasons in the metathesis reactions, however. Indeed, the RCM reaction can then be successfully applied with a good selectivity to iron-free organic compounds for the syntheses of **3e** and **6e**, but not **1e** or **2e** (vide supra and Figure 1).

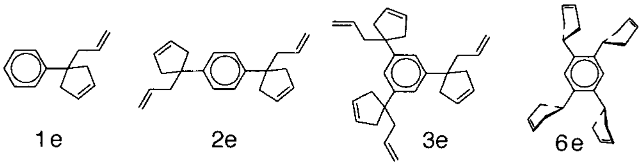


Figure 1.

In all the cases of RCM metathesis, it is much more convenient to use the former method with the iron complex,

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(6) The alkyl arene complexes are synthesized in high yields and large scale by reaction between ferrocene and the arene in the presence of Al_2Cl_6 overnight around 100 °C or at reflux of the arene.[7] Decomplexation of the arene after activation is usually carried out by photolysis using visible light in MeCN in the presence of PPh_3, or in the case of arylamine complexes **9b** and **9c**, by exergonic single-electron reduction using 1 equiv [Fe^{I}Cp-(η^6-C_6Me_6)].[7b]

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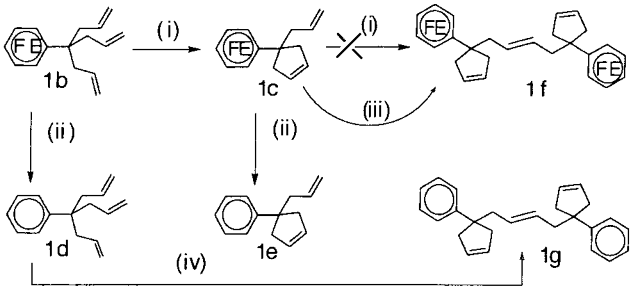
however, because the ruthenium catalyst can be very easily separated from the cationic iron complex after the metathesis reaction. The catalyst is extracted using ether in which the iron complexes are not soluble. The separation of the catalyst has appeared as a non-trivial problem in the myriad of publications dealing with the RCM of organic substrates[10] and has been the special subject of very recent papers.[11] After metathesis of the iron complexes, separation of the ruthenium catalyst is followed by the easy observation of its methylene signal at 19 ppm vs SiMe$_4$ in ^{1}H NMR, as reported by Grubbs for the less active complex [Ru(=CH$_2$)Cl$_2$(PCy$_3$)$_2$] in which the benzylidene ligand has been replaced by the methylene group coming from the terminal olefin.[12] An excellent green alternative is to carry out the RCM reaction of the neutral, iron-free aromatic compound **3d** in the ionic liquid 1-butyl-3-imidazolium hexafluorophosphate ([bmin]PF$_6$) at 80 °C, which gives a 75% yield of **3e** after extraction of the neutral methathesis product using ether.[13]

The case of toluene, *p*-xylene, mesitylene, and tetramethylbiphenyl leading to triple allylation at each benzylic carbon is distinct from the others for which only two allyl groups are found in the benzylic position (Table 1). The RCM reaction rapidly forms a cyclopentene ring in benzylic position, and the third allyl group is left, which is not the case when only two allyl groups are present. Thus, the third allyl group can potentially give rise to cross metathesis (CM) in the case of the mono- and polymethylaromatics except when methyl groups are adjacent (**6a**→**6b**[8a] and **8a**→**8b**[8c] in which Co = η^5-CpCo$^+$, PF$_6^-$). This possibility has been scrutinized in the example of toluene. Its iron-free, triallylated derivative **1d** gives competitive RCM and CM reaction, and no selectivity is observed. It is only possible to isolate the organic bis-arene product **1g** resulting from concomitant RCM and CM of **1d**. On the other hand, CM is considerably slowed in the CpFe$^+$ complex **1b**, probably for steric reasons, whereas RCM proceeds readily. Thus, the RCM product **1c** is selectively obtained with the iron complex **1b** at 20 °C; the corresponding free arene **1e** can be obtained by photolytic decomplexation of **1c**, whereas it is not available in pure form by metathesis of the iron-free derivative **1d** (Scheme 1). The same situation arises in the *p*-xylene series **2a**−**g**.

Scheme 1. Selectivity Effected by the CpFe$^+$ Moiety in the Metathesis Reactions[a]



[a] (i) 5% [Ru(=CH$_2$)Cl$_2$(PCy$_3$)$_2$], CH$_2$Cl$_2$, rt, 1 h; (ii) $h\nu$ (vis), MeCN, 1 equiv PPh$_3$; (iii) 10% [Ru(=CH$_2$)Cl$_2$(PCy$_3$)$_2$], C$_2$H$_4$Cl$_2$, 80 °C, 3 days; (iv) 5% [Ru(=CH$_2$)Cl$_2$(PCy$_3$)$_2$], rt, 3 days.

Interestingly, the iron-free arene **3d** resulting from CpFe$^+$-mediated nonallylation of mesitylene in **3a**[8b] gives the RCM reaction selectively since its CM reaction is slow, again probably for steric reasons. Both the RCM and RCM + CM products are of interest. The RCM products are heterobifunctional. For instance, the RCM products provided from **3b** and **4b** are heterobifunctional dendritic cores. The RCM + CM products will have potential in materials chemistry since linear polymers should be available from *p*-xylene by ADMET and dendritic polymers should be accessible from mesitylene.[14] This aspect of the research line is under study.

In conclusion, we have provided, from very simple arenes, a general and facile method of synthesis of a new class of organometallic and organic polycyclic cyclopentenyl aryl derivatives. The CpFe$^+$ moiety not only provides a straightforward polyallylation method under routine conditions, providing new, remarkable topologies, but also plays a key, useful role in the metathesis process for the separation of the products and the selectivity.[15]

Acknowledgment. We thank Dr. J. Ruiz for samples of **2a** and **8a** and Drs. J. Juiz and S. Nlate (Bordeaux) for fruitful discussions.

Supporting Information Available: Experimental procedures and spectroscopic data (^{1}H and ^{13}C NMR spectra and MALDI TOF mass spectra) for all the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) All the new complexes have been suitably characterized by ^{1}H and ^{13}C NMR (including the distinct endo and exo positions of the new complexes **6c** and **8c** in which the directionality is expected[8c]) and by their molecular peak in the MALDI TOF mass spectrum. Spectroscopic and analytical data are provided in Supporting Information.