Coupling Multiple Benzylic Activation of Simple Arenes by $CpFe^+$ with Multiple Alkene Metathesis Using Grubbs Catalysts: An Efficient Carbon−Carbon Bond Formation Strategy Leading to Polycycles, Cyclophanes, Capsules, and Polymeric Compounds and Their $CpFe^+$ Complexes

Victor Martinez,[†] Jean-Claude Blais,[‡] George Bravic,[§] and Didier Astruc*[,†]

Molecular Nanosciences and Catalysis Group, LCOO, UMR CNRS No. 5802, Université Bordeaux I, 33405 Talence Cedex, France, LCSOB, UMR CNRS No. 7613, Université Paris VI, 75252 Paris, France, and ICMCB Université Bordeaux I, 33405 Talence Cedex, France

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The $CpFe^+$-induced perallylation of arenes containing benzylic hydrogens in the complexes $[FeCp(\eta^6\text{-arene})][PF_6]$ using a base and allyl bromide has been improved by using room-temperature conditions and KOH as a base, which simplifies the procedure and brings the selectivity when some benzylic hydrogens remain. This reaction has been combined with RCM metathesis of two allyl groups borne by the same benzylic carbon using the Grubbs catalyst $[Ru(=CHPh)(PCy_3)_2Cl_2]$ (**1**) in a few minutes at room temperature and with cross-metathesis (CM) in refluxing dichloroethane using the more efficient second-generation Grubbs catalyst $[Ru(=CHPh)(PCy_3)_2\{C(NMesCH_2)_2Cl_2\}]$ (**2**). The $FeCp^+$ tag allows an easy separation of the product from the catalyst and slows down the CM reaction for steric reasons, providing selectivity for the RCM reaction. The iron-free polyallyl arenes undergo both RCM and CM metathesis, and catalysis can also be carried out in the ionic liquid 1-butyl-3-imidazolium hexafluorophosphate as the solvent at 80 °C. CM metathesis of the perallylated arenes gives organoiron and organic macrocycles, cyclophanes, capsules, and polymers, all these compounds being conveniently detected by MALDI-TOF mass spectroscopy, which also gives useful information concerning the advancement of the metathesis reaction and the purity or mixture of the metathesis products.

Introduction

Efficient metathesis of olefins by air-stable commercial ruthenium has been conveniently used by organic chemists for the construction of sophisticated molecules.[1] In some cases, this reaction has been successfully coupled with another useful reaction in tandem reactions producing highly efficient processes.[2] Organotransition-metal activation of arenes is another area that has been the subject of considerable interest for three decades,[3−7] and some activation processes have also led to the synthesis of biologically important compounds.[5] We have developed various one-pot reactions involving a base such as *t*-BuOK or KOH and an electrophile using the powerful activation of arene by the 12-electron $CpFe^+$ fragment[7a] that increases the acidity of benzylic protons in DMSO from $pK_a = 43$ in free arenes to $pK_a = 28$ in the robust complexes $[FeCp(\eta^6\text{-arene})][PF_6]$.[7b,c] Deprotonated complexes are pentane-soluble Fe^{II} deep red cyclohexadienylidene intermediate complexes bearing a nucleophilic exocyclic methylene group that undergo nucleophilic substitution of the halide in various alkyl halides. In the presence

* To whom correspondence should be addressed. E-mail: d.astruc@lcoo.u-bordeaux1.fr.
[†] UMR CNRS No. 5802, Université Bordeaux I.
[‡] UMR CNRS No. 7613, Université Paris VI.
[§] ICMCB Université Bordeaux I.

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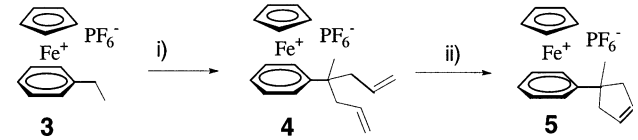
of excess base and alkyl halide electrophile, iterative reactions occur, leading to the multiple formations of C−C bonds that result from a number of sequences consisting of deprotonation followed by nucleophilic substitution. In particular, star-shaped molecules resulting from one-pot formation of six C−C bonds are synthesized from [FeCp(η^6-C_6Me_6)][PF_6],[7d] whereas, for instance, dendritic cores resulting from one-pot formation of nine C−C bonds are formed from [FeCp(η^6-$C_6H_3Me_3$)][PF_6][7e] and are the starting point for the construction of giant dendrimers.[7f] Following preliminary communications,[7i,j] we now report in detail a set of reactions, using allyl bromide as the electrophile, in which the arene activation in various [FeCp(η^6-arene)]$^+$ complexes is coupled with subsequent metathesis using Grubbs commercial ruthenium catalysts.

Results and Discussion

$CpFe^+$-Induced Diallylation at Benzylic Positions Followed by Ru-Catalyzed Metathesis. First, we have reinvestigated the $CpFe^+$-induced perallylation of polymethylbenzene derivatives induced by the $CpFe^+$ group in the complexes [FeCp(η^6-arene)][PF_6]. In doing so, we wished to improve the simplicity and eventually the selectivity of the one-pot perallylation reactions, which have previously been reported at 60 °C using *t*-BuOK as a base. Therefore, we have carried out the reactions at room temperature using KOH in THF or DME. The reactions do work under ambient conditions, but they are slow, requiring several days to reach completion. The room-temperature conditions do not present a significant advantage over the 60 °C conditions for the toluene, *p*-xylene, and mesitylene complexes, because in these cases it is necessary to make sure that all the benzylic hydrogen atoms are replaced by the allyl groups. Indeed, the third proton substitution on each benzylic carbon is slow for steric reasons. On the other hand, for the hexamethylbenzene and durene complexes, mono- and disubstitution at each methyl group have been reported.[7e] It has also been found that forcing reaction conditions led to further substitution. In these cases, the room-temperature conditions are especially useful, because these side reactions are avoided.

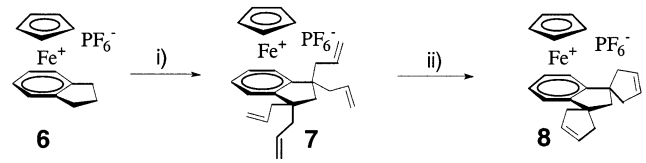
We have also investigated the perallylation reactions with other arene complexes having arene substituents different from methyl groups. Thus, with the ethylbenzene complex [FeCp(η^6-C_6H_5Et)][PF_6] (**3**)[7k,8] both benzylic hydrogens are replaced by allyl groups, giving [FeCp(η^6-PhC($CH_2CH{=}CH_2$)$_2$Me)][PF_6] (**4**) (Scheme 1).

Scheme 1[a]



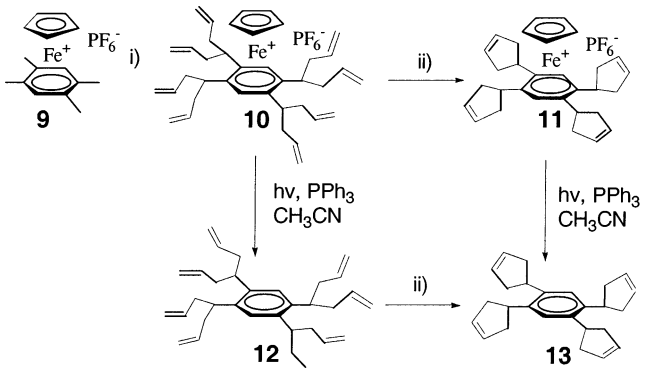
[a] Legend: (i) allyl bromide, KOH, DME; (ii) [Ru(PCy_3)$_2$$Cl_2$(=CHPh)] (**1**), CH_2Cl_2, room temperature.

Scheme 2[a]



[a] Legend: (i) allyl bromide, KOH, DME; (ii) [Ru(PCy_3)$_2$$Cl_2$(=CHPh)] (**1**), CH_2Cl_2, room temperature.

Scheme 3[a]



[a] Legend: (i) allyl bromide, KOH, THF; (ii) [Ru(PCy_3)$_2$$Cl_2$(=CHPh)] (**1**), CH_2Cl_2, room temperature.

The same result is obtained with the indane complex [FeCp(η^6-indane)][PF_6] (**6**),[7k] for which the perallylation leads to the introduction of four allyl groups, yielding [FeCp(η^6-indane($CH_2CH{=}CH_2$)$_4$)][PF_6] (**7**) (Scheme 2).

In the durene complex [FeCp(η^6-Ph(CH_3)$_4$)][PF_6] (**9**),[7k] the situation is more complicated. Former studies have shown that perallylation of **9** leads to the replacement of two allyl groups on each benzylic carbon, the third benzylic hydrogen being not replaced for steric reasons.[7e] We have noticed, however, that the third perallylation is also partially obtained, although it is much slower. In particular, this is observed in the MALDI-TOF mass spectra of crude reaction products obtained by perallylation at 60 °C. At this point, our finding that the perallylation could be carried out at room temperature in THF is crucial, because under these conditions the octaallylation of the durene complex is completely selective, giving [FeCp(η^6-1,2,4,5-Ph(CH($CH_2CH{=}CH_2$)$_2$)$_4$]-[PF_6] (**10**) (Scheme 3). When the room-temperature reaction is over, no trace of heptaallylated or nonaallylated derivative is found by MALDI-TOF mass spectroscopy, the octaallylated compound **10** being the only organoiron reaction product. It is also important to note that no decomplexation occurs during the reaction time, whereas, in reactions carried out at 60 °C, minute amounts of iron-free arene product resulting from metal loss in unfinished perallylation derivatives are obtained and recognized by the MALDI-TOF mass spectrum of

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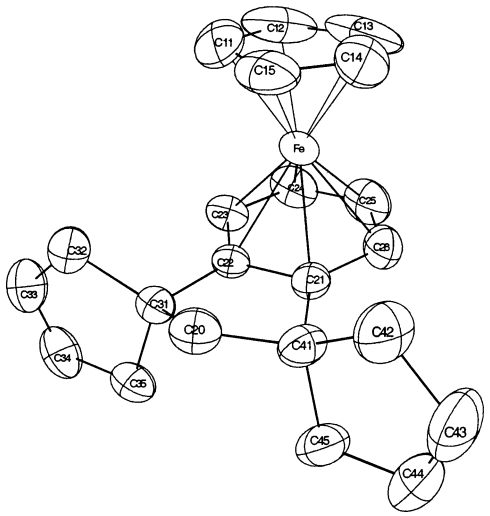

Figure 1. ORTEP diagram for complex **8**, in which the ellipsoids are represented at the 50% probability level. The PF_6^- group is omitted.

Table 1. Crystallographic Data for 8

λ(Mo Kα), Å	0.710 73
a, Å	19.8904(3)
b, Å	10.9561(1)
c, Å	9.3234(1)
α, deg	90
β, deg	90.0555(5)
γ, deg	90
V, Å^3	2031.77(7)
Z	4
cryst syst	monoclinic
space group	$P2_1/n$
formula	$H_{17}C_{22}F_6PFe$
M_r	482.2
no. of molecules	4
D_{exptl}, g cm^{-3}	1.576
F(000)	976
μ, mm^{-1}	0.840
no. of rflns total	8820
no. of obsd rflns ($I > 3\sigma$)	4751
index limits	$-31 < h < 31$
	$0 < k < 17$
	$0 < l < 15$
diffraction limits, deg	$6.2 < \theta < 35.0$

this organic fraction. With the arene complexes of ethylbenzene, indane, and durene, for which the perallylation reaction allows us to introduce two allyl groups on each benzylic carbon, the metathesis reaction catalyzed by [Ru(=CHPh)$(PCy_3)_2Cl_2$] (**1**) quantitatively leads to ring closure (RCM) in a few minutes at room temperature in dichloromethane, giving the cyclopentenyl derivatives [FeCp(η^6-PhC(CH_2CH=$CHCH_2$)Me)][PF_6] (**5**), [FeCp(η^6-indane(CH_2CH=$CHCH_2$)$_2$)][PF_6] (**8**), and [FeCp(η^6-Ph($CHCH_2CH$=$CHCH_2$)$_4$)][PF_6] (**11**), respectively.

The X-ray crystal structure of **8** was recorded and is represented in Figure 1, showing that the two faces of each cyclopentene ring are differentiated by the $CpFe^+$ group (see the data in Tables 1 and 2). The bond distances and angles in the iron-sandwich group are as in other recorded X-ray crystal structures containing this group.[7l]

The workup of the metathesis reactions is easier, since the complexes are cationic, allowing us to remove the catalyst by washing the reaction product with ether, the organoiron cation being insoluble in this solvent.

Table 2. Interatomic Distances for 8

Fe−C(11)	2.07(2)	C(21)−C(22)	1.415(2)
Fe−C(12)	2.02(2)	C(21)−C(26)	1.409(3)
Fe−C(13)	2.00(3)	C(21)−C(41)	1.516(3)
Fe−C(14)	2.02(2)	C(22)−C(23)	1.411(3)
Fe−C(15)	1.98(2)	C(22)−C(31)	1.510(2)
Fe−C(21)	2.114(2)	C(23)−C(24)	1.404(3)
Fe−C(22)	2.116(2)	C(24)−C(25)	1.399(4)
Fe−C(23)	2.097(2)	C(25)−C(26)	1.412(4)
Fe−C(24)	2.068(2)	C(31)−C(32)	1.544(3)
Fe−C(25)	2.061(3)	C(31)−C(35)	1.568(3)
Fe−C(26)	2.085(2)	C(32)−C(33)	1.485(3)
C(11)−C(12)	1.39(3)	C(33)−C(34)	1.309(4)
C(11)−C(15)	1.34(3)	C(34)−C(35)	1.499(3)
C(12)−C(13)	1.39(4)	C(41)−C(42)	1.545(3)
C(13)−C(14)	1.41(3)	C(41)−C(45)	1.570(3)
C(14)−C(15)	1.36(3)	C(42)−C(43)	1.482(4)
C(20)−C(31)	1.531(3)	C(43)−C(44)	1.299(5)
C(20)−C(41)	1.535(3)	C(44)−C(45)	1.475(4)

Thus, the cationic $CpFe^+$ group is used as a tag for separating the catalyst from the product, whereas separation of the ruthenium metathesis catalyst from neutral organic products is usually tedious. This advantage is a general one for all the $CpFe^+$ perallylated products throughout this article. It is not at all trivial and, among the rich literature on metathesis,[9] the problem of catalyst separation has been specifically addressed.[10] In fact, ^{1}H NMR analysis of the ruthenium catalyst easily recovered from **1** shows the methylene signal at δ 19 ppm vs TMS in $CDCl_3$ characteristic of [Ru(CH_2)$(PCy_3)_2Cl_2$], as shown by Grubbs.[11] Nevertheless, it was also of interest to examine the metathesis reaction with the iron-free perallylated arenes and the influence of the $CpFe^+$ group on the metathesis reaction. The removal of the $CpFe^+$ group from [FeCp(η^6-arene)][PF_6] is routinely carried out in our laboratory by photolyzing the complex in acetonitrile using visible light in the presence of 1 equiv of triphenylphosphine. This reaction leads to the quantitative formation of [FeCp(η^1-PPh_3)$(MeCN)_2$][PF_6] and the iron-free arene, which is again separated from the organoiron cation by extraction with pentane or ether.[7] Thus, the cationic organoiron group was removed from **10** using photolysis, giving Ph[$CH(CH_2CH$=$CH_2)_2]_4$ (**12**), whose metathesis catalyzed by **1** in a few minutes gave Ph[$CH(CH_2CH$=$CHCH_2)]_4$ (**13**), which was separated from **1** or its decomposition products using column chromatography. The compound **13** could also be more conveniently obtained by decomplexation of the metathesized organoiron complex **11**, avoiding chromatographic separation (Scheme 3). Finally, catalysis of RCM of organic polyallylated arenes can also be carried out in the ionic liquid 1-butyl-3-imidazolium hexafluorophosphate as the solvent at 80 °C (vide infra).

$CpFe^+$-Induced Triallylation of Toluene in [FeCp(η^6-toluene)][PF_6] Followed by Ru-Catalyzed Metathesis. The $CpFe^+$-induced perallylation of toluene

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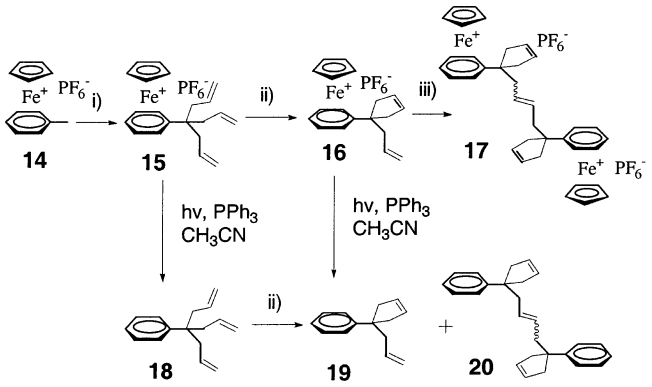
Scheme 4[a]



[a] Legend: (i) allyl bromide, KOH, DME; (ii) $[Ru(PCy_3)_2Cl_2(=CHPh)]$ (**1**), CH_2Cl_2, room temperature; (iii) $[Ru(PCy_3)\{C(N(mesityl)CH)_2\}Cl_2(=CHPh)]$ (**2**), $C_2H_4Cl_2$, 60 °C.

in $[FeCp(\eta^6\text{-toluene})][PF_6]$ (**14**) using KOH and allyl bromide in DME at room temperature now leads to the triallylation of **14**, giving $[FeCp\{\eta^6\text{-}PhC(CH_2CH{=}CH_2)_3\}][PF_6]$ (**15**). Subsequently, metathesis of **15** in dichloromethane catalyzed by **1** at room temperature selectively yields $[FeCp\{\eta^6\text{-}PhC(CH_2CH{=}CH_2)(CH_2CH{=}CHCH_2)\}][PF_6]$ (**16**), the simple RCM product. Further metathesis reaction can only be catalyzed by **1** at 60 °C, a temperature at which cross-metathesis (CM) proceeds, giving the bimetallic complex **17**. On the other hand, if the organoiron group is removed by photolysis of **14**, giving the metal-free arene $PhC(CH_2CH{=}CH_2)_3$ (**18**), catalysis of metathesis of **18** by **1** now proceeds at room temperature, giving a mixture of the organic RCM product $PhC(CH_2CH{=}CH_2)(CH_2CH{=}CHCH_2)$ (**19**) and CM product **20**. We believe that the steric bulk of the $CpFe^+$ group in the complex **16** is responsible for slowing down the CM metathesis reaction, which is more difficult than the RCM reaction (Scheme 4). To easily isolate compound **19** alone and avoid the formation of the dimeric compound **20**, we removed the $CpFe^+$ group from the organometallic RCM product **16** using photolysis.

$CpFe^+$-Induced Hexallylation of *p*-Xylene in $[FeCp(\eta^6\text{-}p\text{-}C_6H_4Me_2)][PF_6]$ Followed by Ru-Catalyzed Metathesis: Access to Cyclophanes. The reaction of $[FeCp(\eta^6\text{-}p\text{-}C_6H_4Me_2)][PF_6]$ (**21**) with allyl bromide and KOH in THF at room temperature gives the hexaallyl complex $[FeCp(\eta^6\text{-}p\text{-}C_6H_4\{C(CH_2CH{=}CH_2)_3\}_2)][PF_6]$ (**22**). The metathesis of **22** catalyzed by **1** at room temperature selectively gives the RCM product $[FeCp(\eta^6\text{-}p\text{-}C_6H_4\{C(CH_2CH{=}CH_2)(CH_2CH{=}CHCH_2)\}_2)][PF_6]$ (**23**), in which two allyl groups remain unreacted on the para substituents. These two terminal double bonds are located too far away from each other to react together in a cross-metathesis reaction. On the other hand, upon heating **22** or **23** at 60 °C with **2** as metathesis catalyst, CM of these two olefinic groups occurs, leading to the formation of oligomers. Due to the reversibility of the metathesis reaction that is thermodynamically controlled, the final CM products are the cyclic dimer and trimer **24** and **25**, respectively. These two compounds could not be easily separated from their mixture and only gave a common set of NMR signals, but their structure is easily deduced from the MALDI-TOF mass spectrum, also showing that they are formed in comparable amounts. The organoiron group was removed from **22**, giving the organic derivative $p\text{-}C_6H_4\{C(CH_2CH{=}CH_2)_3\}_2$ (**26**), and metathesis of **26** catalyzed by **1** at room temperature gives the RCM product $p\text{-}C_6H_4\{C(CH_2CH{=}CH_2)(CH_2CH{=}CHCH_2)\}_2$ (**27**) and a mixture of cyclic and linear oligomers resulting from cross-metathesis. To obtain pure **27**, however, it is necessary to use the organometallic route involving metathesis of **22** followed by decomplexation of **23**, which is free of oligomers (Scheme 5).

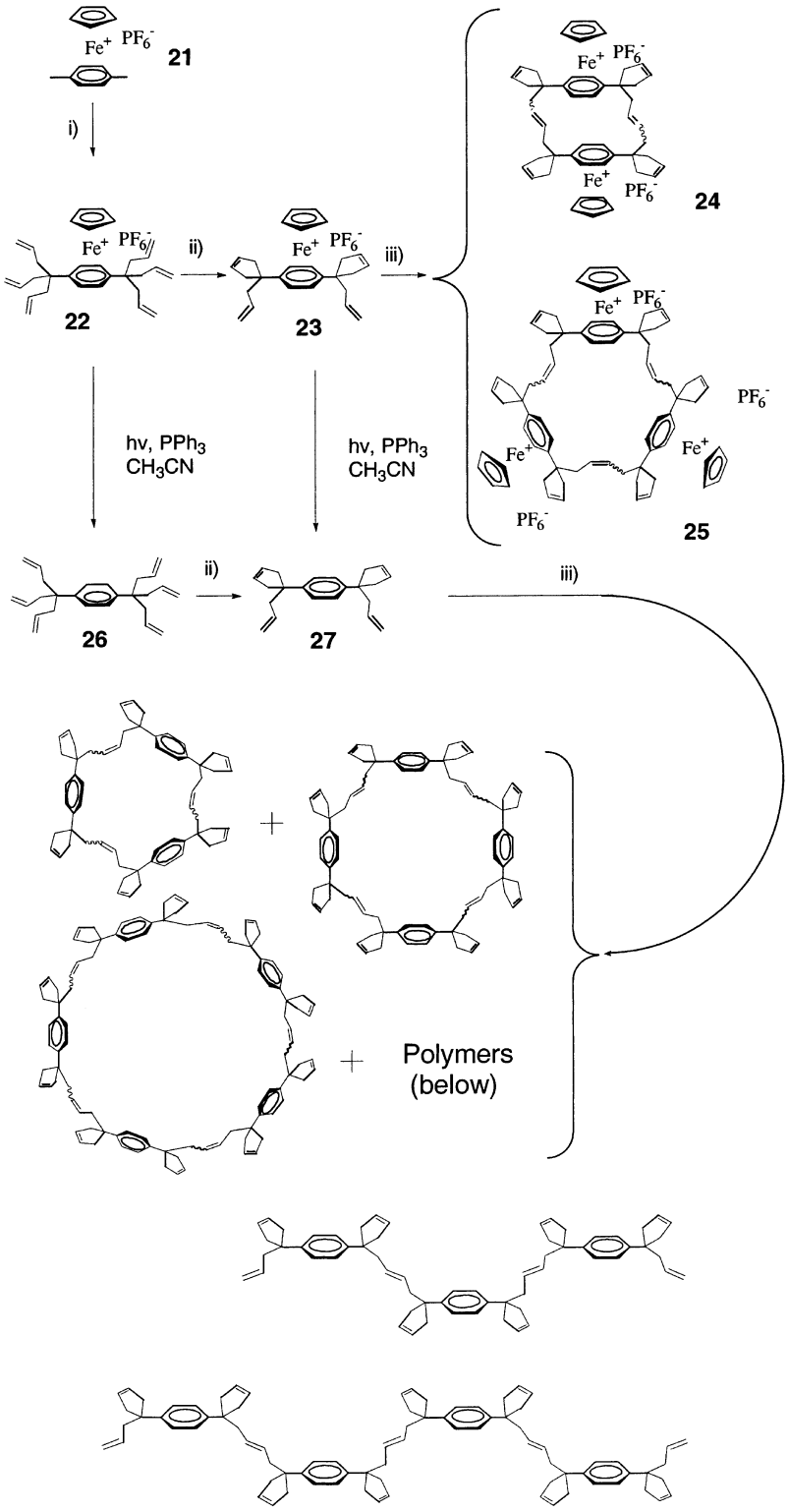
$CpFe^+$-Induced Nonaallylation of Mesitylene in $[FeCp(\eta^6\text{-mesitylene})][PF_6]$ Followed by Ru-Catalyzed Metathesis: Access to Capsules. The one-pot reaction of $[FeCp(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)][PF_6]$ (**28**) with KOH and allyl bromide in THF at room temperature yields the nonaallylated complex $[FeCp(\eta^6\text{-}1,3,5\text{-}C_6H_3\{C(CH_2CH{=}CH_2)_3\}_3)][PF_6]$ (**29**). Metathesis of **29** catalyzed by **1** at room temperature gives the triple-RCM product $[FeCp(\eta^6\text{-}1,3,5\text{-}C_6H_3\{C(CH_2CH{=}CH_2)(CH_2CH{=}CHCH_2)\}_3)][PF_6]$ (**30**) after a few minutes. More intriguing is the continuation of this metathesis at higher temperature using the more active catalyst **2**. In principle, this reaction could give rise to dendrimers or dendritic polymers.[12] When the metathesis reaction is carried out at reflux of dichloroethane for 4 h and catalyzed by the more active ruthenium complex **2**, the mass spectrum shows a complex mixture of many cross-metathesized compounds (Figure 2). Two families of products are detected, besides the RCM product **30**. At high masses, oligomers containing up to seven coupled units are obtained. The largest peaks in the spectrum, however, were a series of three peaks of comparable intensities corresponding to the loss of one, two, or three ethylene units expected from cross-metathesis. This shows the formation of singly, doubly, and triply bridged cyclophane compounds. After 60 h, the peak corresponding to three bridges became the major one in the MALDI-TOF mass spectrum. Finally, after 1 week, this peak corresponding to the cage compound **31** was found almost alone with only minute amounts of the other compounds. Under more concentrated conditions, however, the reaction was less selective and more oligomers were obtained.

To also investigate the metathesis reaction of the metal-free nonaallylated arene, the $CpFe^+$ group was removed from **29** using photolysis, providing $1,3,5\text{-}C_6H_3[C(CH_2CH{=}CH_2)_3]_3$ (**32**). Metathesis of **32** catalyzed by $[Ru(=CHPh)(PCy_3)_2\{C(NMesCH_2)_2Cl_2\}]$ (**2**) first rapidly gives the triple-RCM product **33** under ambient conditions. Catalysis of RCM can also be effected by **1** and a reaction carried out in the ionic liquid 1-butyl-3-imidazolium hexafluorophosphate[13] as the solvent at 80 °C, for instance in the case of **32**, giving $1,3,5\text{-}C_6H_3[C(CH_2CH{=}CHCH_2)(CH_2CH{=}CH_2)]_3$ (**33**) in 75% yield. Then, cross-metathesis in refluxing dichloroethane proved to be more facile than that of **29**, and the reaction was selective, giving good yields of the organic capsule **34** using 5% of the Grubbs catalyst **2**. After hydrogenation with H_2/Pd/C in CH_2Cl_2 of this triply bridged cage **34**, which is a mixture of isomers, the single product **35** is isolated. The ^1H NMR signals of the β-hydrogens are shifted upfield at 0.64 ppm in

(12) Buijsman, R. C.; Van Vuuren, E.; Sterrenburg, J. G. *Org. Lett.* **2001**, *3*, 3785.

(13) Morrison, W. H.; Ho, E. Y.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1974**, *96*, 3603.

Scheme 5[a]



[a] Legend: (i) allyl bromide, KOH, DME; (ii) $[Ru(PCy_3)_2Cl_2(=CHPh)]$ (**1**), CH_2Cl_2, room temperature; (iii) $[Ru(PCy_3)\{C(N(mesityl)\text{-}CH)_2\}Cl_2(=CHPh)]$ (**2**), $C_2H_4Cl_2$, 60 °C.

35, as expected, due to their location somewhat above the arene plane (Scheme 6).

The molecular model of compound **35**, obtained by a MOPAC modelization program (Figure 3), shows a three-bar cage molecule. Arene groups at the top and bottom of the cage are joined by three alkyl chains. The inside cavity is 6.51 Å high between aryls, and the smallest distance from one alkyl chain to another is 2.93 Å. The distances between an inserted electron-poor arene charge transfer (CT) forming aromatic compounds and the two arene groups is on the order of 3 Å, and experiments are in progress along this line.[14]

Dodecaallylation with Bimetallic Activation and Metathesis of Dodecaallylated Compounds. Bime-

(14) Hubig, S. M.; Kochi, J. K. In *Modern Arene Chemistry*; Astruc, D., Ed.; Wiley-VCH: Weinheim, Germany, 2002; pp 435−478.

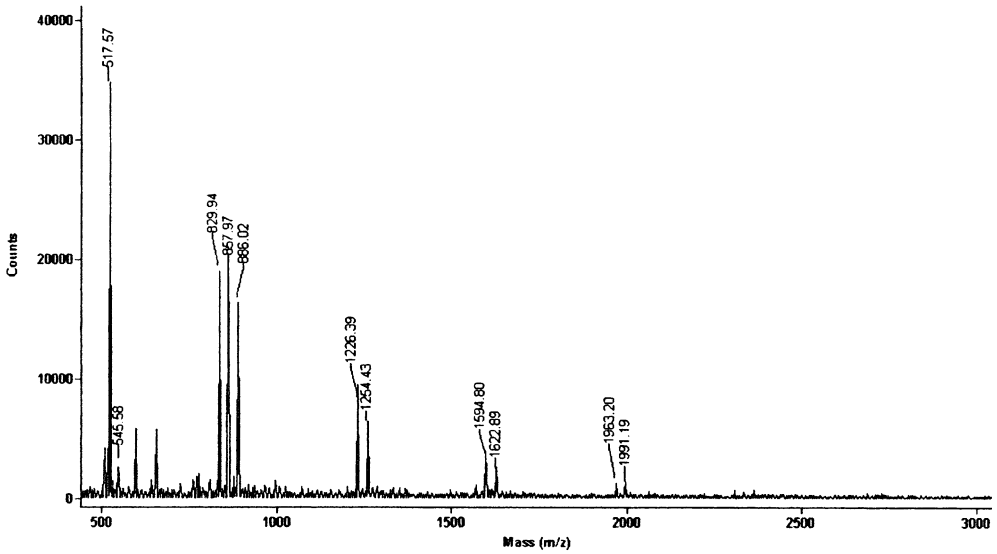
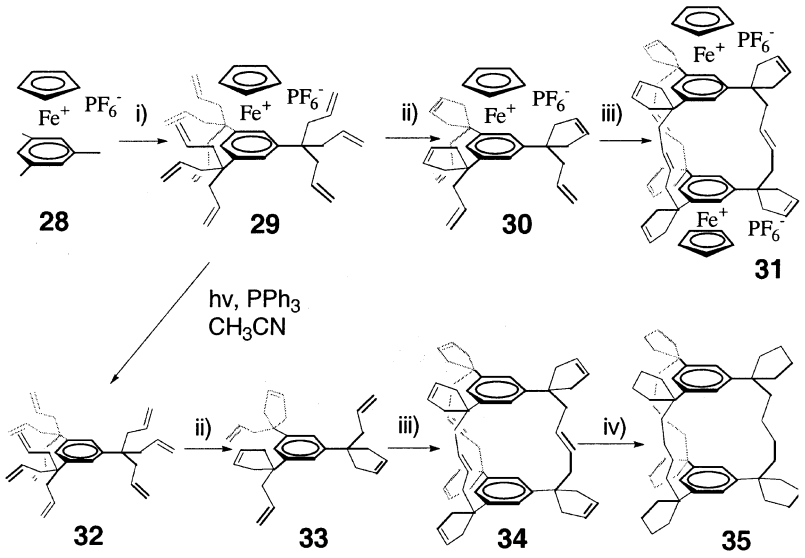


Figure 2. MALDI-TOF mass spectrum of the products of metathesis of **29** after 4 h at 60 °C.

Scheme 6[a]



[a] Legend: (i) allyl bromide, KOH, DME; (ii) [Ru(PCy$_3$)$_2$Cl$_2$(=CHPh)] (**1**), CH_2Cl_2, room temperature; (iii) [Ru(PCy$_3$)-{C(N(mesityl)CH)$_2$}Cl$_2$(=CHPh)] (**2**), $C_2H_4Cl_2$, 60 °C; (iv) H_2, Pd/C, CH_2Cl_2.

tallic complexation of 3,3′,5,5′-tetramethylbiphenyl[13] by two $CpFe^+$ groups, leading to [(FeCp)$_2$(η^6,μ_2-3,3′,5,5′-tetramethylbiphenyl)][PF_6]$_2$ (**36**), brings about a situation in which the methyl groups, in meta positions, are free of steric constraint, as in the mesitylene complex **28**. Thus, full substitution of the 12 benzylic hydrogen atoms is possible in 12 deprotonation−allylation sequences, providing the tether-rich bimetallic dendritic[15] core **37** (Scheme 7). Facile quadruple-RCM metathesis of **37** catalyzed by **1** at room temperature leads to the octacyclic diiron complex **38**. Compound **38** still contains four unreacted terminal double bonds, which are too far apart from one another to react intramolecularly.

Quintuple RCM of a Decaallylated Cobaltocenium Derivative. The decaallylation of 1,2,3,4,5-pentamethylcobaltocenium hexafluorophosphate (**39**) was reported to give the decaallylated cobaltocenium **40**.[16] This synthesis has been reproduced; metathesis of **40** catalyzed by **1** in dichloromethane at room temperature now gives quintuple RCM leading to [CpCo(η^5-C$_5${CH(CH$_2$CH=CHCH$_2$)}$_5$)][PF_6] (**41**) (Scheme 8).

Transformation of an Aniline Complex into a Bicyclic Heterocycle. The complex [CpFe(η^6-C$_6$H$_5$-NH$_2$)][PF_6] (**42**) is synthesized by direct ligand exchange from ferrocene and aniline, although the yield is reproducibly low, i.e., 10%[7k,8] (alternatively, it is possible to complex chlorobenzene in [CpFe(η^6-PhCl)][PF_6], followed by reaction with ammonia in dichloromethane[7k,8] or even in water[17]). The reaction of **42** with KOH and allyl bromide in THF at room temperature yields the diallylated product [CpFe(η^6-C$_6$H$_5$N(CH$_2$CH=CH$_2$)$_2$)]-

(15) (a) For dendrimers, see: Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic and Dendrons: Concepts, Synthesis and Applications*, Wiley-VCH: Weinheim, Germany, 2001. *Dendrimers and other Dendritic Polymers*; Tomalia, D., Fréchet, J. M. J., Eds.; Wiley-VCH: New York, 2002. (b) For dendritic polymers, see: Sunder, A.; Heinemann, J.; Frey, H. *Chem. Eur. J.* **2000**, *6*, 2499.

(16) Buchholz, D.; Gloaguen, B.; Fillaut, J.-L.; Cotrait, M.; Astruc, D. *Chem. Eur. J.* **1995**, *1*, 374.

(17) Moulines, F.; Kalam-Alami, M.; Martinez, V.; Astruc, D. *J. Organomet. Chem.* **2002**, *125*, 643.

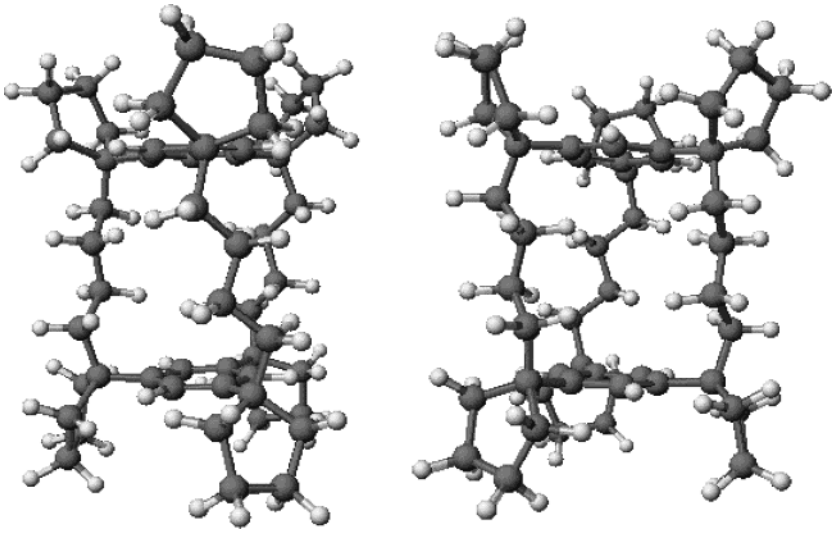
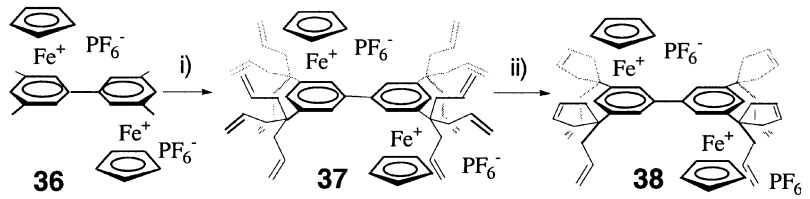


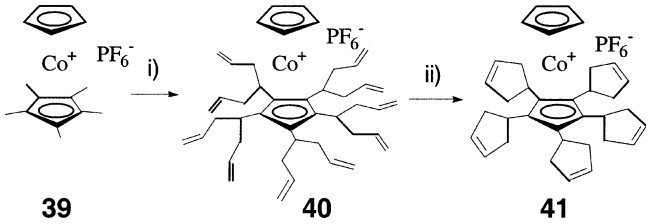
Figure 3. Molecular modelization of compound **35** calculated under vacuum by MOPAC ab initio program (carbon atoms as black balls and hydrogen atoms as white balls).

Scheme 7[a]



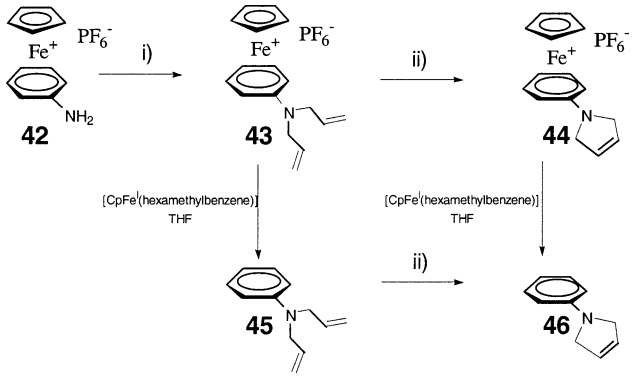
[a] Legend: (i) allyl bromide, KOH, DME; (ii) [Ru(PCy_3)$_2$$Cl_2$(=CHPh)] (**1**), CH_2Cl_2, room temperature.

Scheme 8[a]



[a] Legend: (i) allyl bromide, KOH, DME; (ii) [Ru(PCy_3)$_2$$Cl_2$-(=CHPh)] (**1**), CH_2Cl_2, room temperature.

Scheme 9[a]



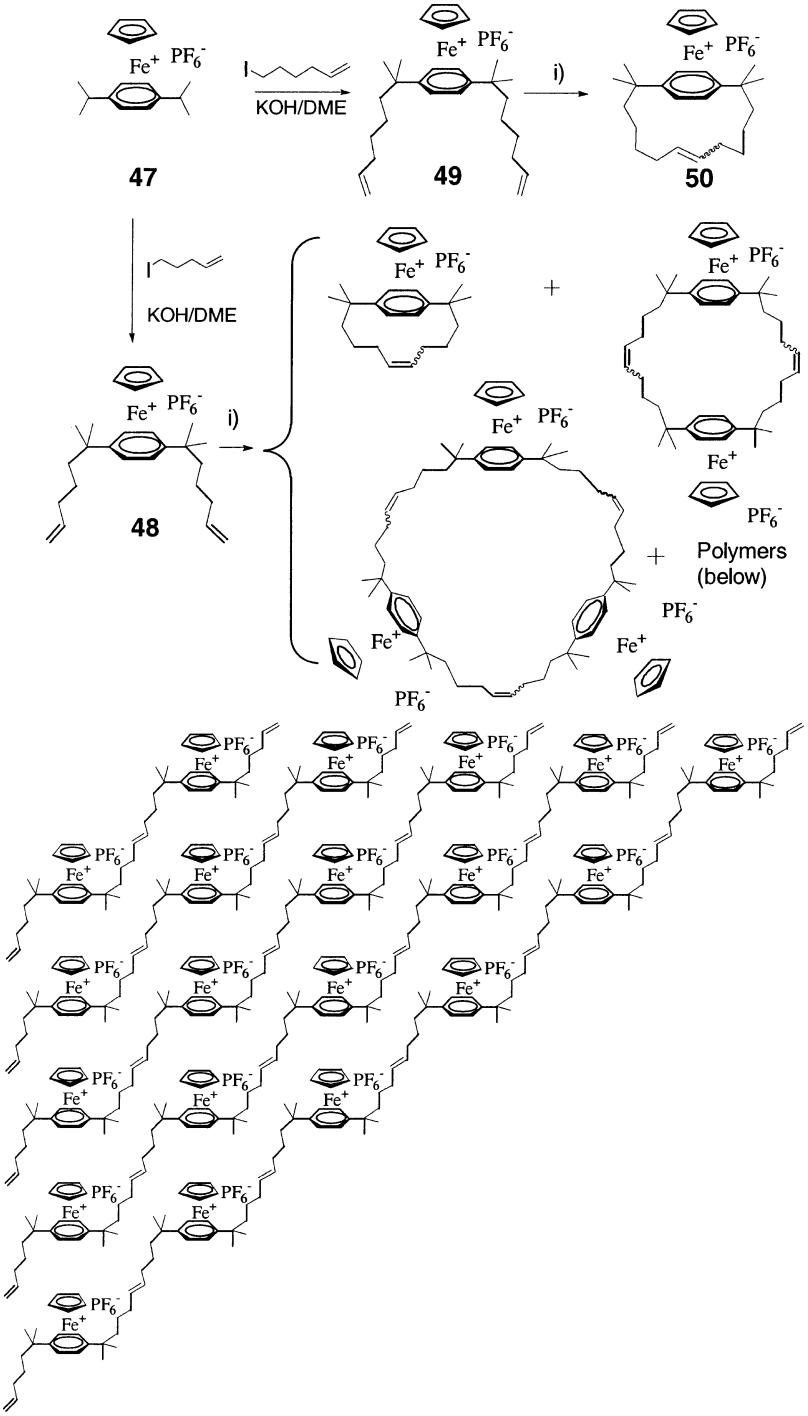
[a] Legend: (i) allyl bromide, KOH, DME; (ii) [Ru(PCy_3)$_2$$Cl_2$-(=CHPh)] (**1**), CH_2Cl_2, room temperature.

[PF_6] (**43**). Metathesis of **43** catalyzed by **1** yields the *N*-cyclopentenylaniline iron complex [CpFe(η^6-$C_6H_5N(CH_2CH{=}CHCH_2)$)][PF_6] (**44**). Decomplexation of **42**, **43**, or **44** is not possible by photolysis, probably because of the cyclohexadienyliminium character of the ligand that shifts to the UV region the absorption of **42**−**44**, leading to decomplexation. It is possible to remove the metal, however, via the unstable 19-electron Fe^I complex. Thus, exergonic and clean single-electron reduction of the cationic 18-electron Fe^{II} complexes **43** and **44** using 1 equiv of the electron-reservoir complex [$Fe^ICp(\eta^6$-$C_6Me_6)$][18] followed by extraction using ether gives the iron-free arenes $C_6H_5N(CH_2CH{=}CH_2)_2$ (**45**) and $C_6H_5N(CH_2CH{=}CHCH_2)$ (**46**), respectively. Metathesis of the iron-free diallylaniline **45** catalyzed by **1** at room temperature yields the *N*-phenylpyrroline derivative **46** (Scheme 9).

Synthesis of Organoiron Cyclophane Macrocycles. Here, we are applying the possibility of activation of tertiary benzylic hydrogen atoms in the complexes [FeCp(η^6-arene)]$^+$ to selectively introduce alkenyl chains in the two para positions and further study the intra- vs intermolecular metathesis reaction as a function of chain length. We chose the complex [FeCp(η^6-*p*-*i*-$Pr_2C_6H_4$)][PF_6] (**47**) (Scheme 10) as the starting point for the difunctionalization in the para substituents. To target organoiron [*n*]paracyclophanes,[19,20] dialkenyl-substituted complexes were synthesized with sufficiently long chains. Dialkenylation of the *p*-diisopropylbenzene ligand upon reaction with KOH and an ω-alkenyl halogen via the organoiron complex **47** allows the preparation of a variety of para-disubstituted substrates whose intramolecular metathesis may lead to the desired paracyclophanes. Thus, dialkenylation of **47** was

(18) (a) Astruc, D. *Electron-Transfer and Radical Processes in Transition-Metal Chemistry*; VCH: New York, 1995; Chapters 3 and 6. (b) Astruc, D. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Mattay, P., Astruc, D., Vol. Eds.; Wiley-VCH: Weinheim, Germany, 2001; Vol. 2, Chapter 8, pp 714−803.

Scheme 10[a]



[a] Legend: (i) $[Ru(PCy_3)_2Cl_2(=CHPh)]$ (**1**), $CHCl_3$, room temperature.

carried out in refluxing dimethoxyethane with KOH and 5-bromopentene or 6-bromohexene, which yielded $[FeCp(\eta^6\text{-}p\text{-}C_6H_4(C(CH_2CH_2CH_2CH{=}CH_2)Me_2)_2)][PF_6]$ (**48**) and $[FeCp(\eta^6\text{-}p\text{-}C_6H_4(C(CH_2CH_2CH_2CH_2CH{=}CH_2)Me_2)_2)][PF_6]$ (**49**), respectively. Using **1** as catalyst in chloroform at room temperature, the organoiron complex **48** leads to a mixture of linear oligomers (2−6 units) and mono-, bi-, and trimetallic paracyclophanes identified by their molecular peaks in the MALDI-TOF mass spectrum. On the other hand, **49**, containing alkenyl chains that are one methylene unit longer than in **48,** selectively gives the intramolecular metathesis product **50** (see Figure 4), a macrocyclic cyclophane**.** In the ^1H NMR spectra of **50**, the signals of the β-hydrogens of the cyclophane are shifted to 0.51 ppm because of aromatic anisotropy.[19]

Metathesis of the Hexabutenylbenzene Complex. The preparation of the hexabutenyl complex $[FeCp(\eta^6\text{-}C_6(CH_2CH_2CH{=}CH_2)_6)][PF_6]$ (**52**) is also improved by carrying out the selective hexaallylation of $[FeCp(\eta^6\text{-}C_6Me_6)][PF_6]$ (**53**), using KOH and allyl bromide in THF at room temperature. The metathesis of the terminal double bonds of **52** catalyzed by **1** in dichloromethane gives a yellow precipitate insoluble in various solvents. The MALDI-TOF spectrum of the soluble intermediates during the reaction shows the

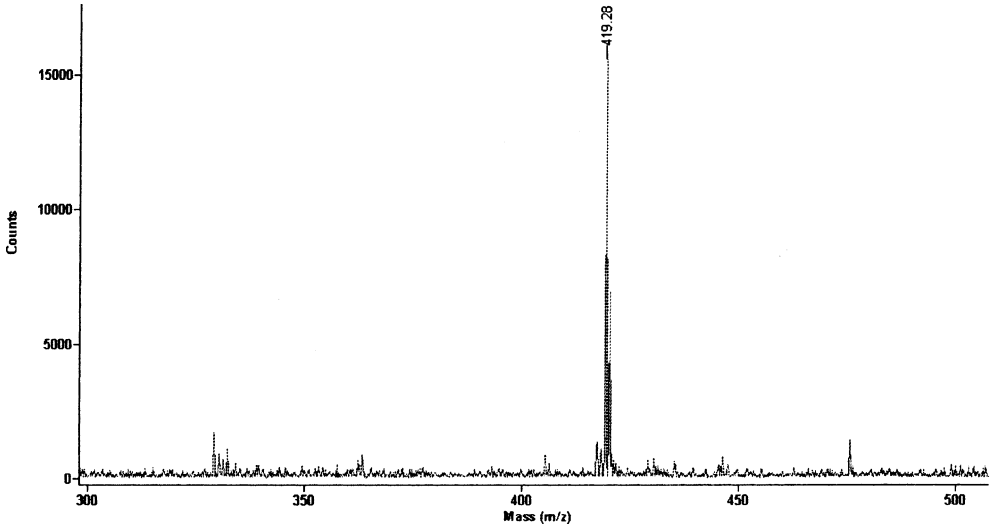


Figure 4. MALDI-TOF mass spectrum of **50** (calcd for $C_{27}H_{39}Fe^+$ 419.2).

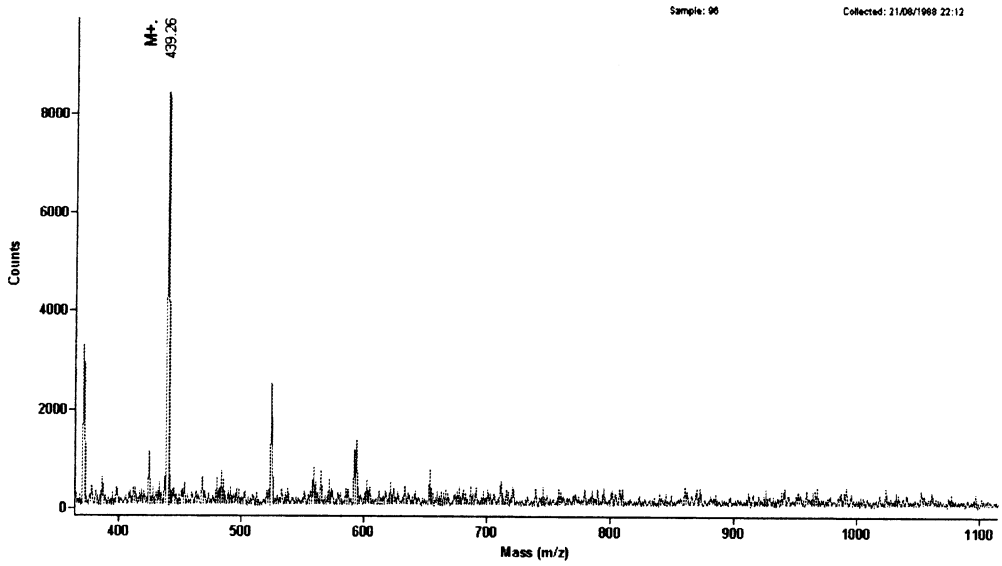
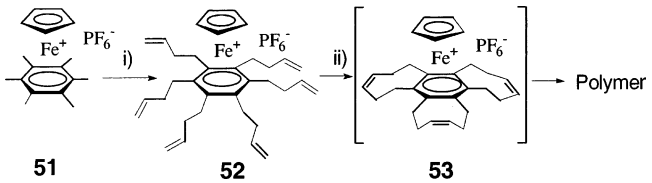


Figure 5. MALDI-TOF mass spectrum of **53** (calcd for $C_{29}H_{35}Fe^+$ 439.26).

Scheme 11[a]



[a] Legend: (i) allyl bromide, KOH, THF; (ii) $[Ru(PCy_3)_2Cl_2(=CHPh)]$ (**1**), $CHCl_3$, room temperature.

formation of the intermediate complex **53** (Figure 5). Nevertheless, its concentration is low and the equilibrium is always displaced toward the formation of insoluble products. CM of **52** as well as ROMP of **53** may form a reticulated polymer (Scheme 11).

Concluding Remarks

1. The $CpFe^+$-induced benzylic perallylation of arenes in the complexes $[FeCp(\eta^6\text{-arene})]^+$ has been improved by performing these reactions at room temperature using KOH in THF or DME, which brings about selectivity that was sometimes missing in the former higher temperature procedure. The perallylation of new complexes such as these of indane and 3,3′,5,5′-tetramethylbiphenyl have been carried out, and the first bimetallic activation in the latter case leads to the one-pot formation of 12 C−C bonds at room temperature with introduction of 12 double bonds at the periphery of the tether-rich dendritic core synthesized in this way.

2. This powerful method of one-pot multiple C−C bond formation with introduction of terminal double C=C bonds has been combined with another useful C=C bond formation, alkene metathesis using Grubbs commercial catalyst. This leads to quick RCM of the complexes $[FeCp(\eta^6\text{-arene})]^+$ bearing at least two allyl

(19) (a) Vögtle, F. *Cyclophane Chemistry*; Wiley: New York, 1993. (b) Gleiter, R.; Kratz, D. *Acc. Chem. Res.* **1993**, *26*, 311. (c) Boekelheide, V. *Acc. Chem. Res.* **1980**, *13*, 65. (d) König, B.; Knieriem, B.; de Mejere, A. *Chem. Ber.* **1993**, *126*, 1643. (e) Reuter, C.; Schmieder, R.; Vögtle, F. *Pure Appl. Chem.* **2000**, *72*, 2233. (f) For a recent updated account on synthetic methods of cyclophanes, see: Hopf, H. *Classic in Hydrocarbon Chemistry*; Wiley-VCH: Weinheim, Germany, 2000; Chapter 12.3, pp 337−378. (g) For the synthesis of organic cyclophanes using metathesis, see: Tae, J.; Yang, Y. K. *Org. Lett.* **2003**, *5*, 741. Tsuji, T.; Ohkita, M.; Kawai, H. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 415. Layton, M. E.; Morales, C. A.; Shair, M. D. *J. Am. Chem. Soc.* **2002**, *124*, 773. Smith, A. B., III; Adams, C. M.; Kozmin, S. A.; Paone, D. V. *J. Am. Chem. Soc.* **2001**, *123*, 5592. Smith, A. B., III; Adams, C. M.; Kozmin, S. A. *J. Am. Chem. Soc.* **2001**, *123*, 990. Smith, A. B., III; Kozmin, S. A.; Adams, C. M.; Paone, D. V. *J. Am. Chem. Soc.* **2000**, *122*, 3391.

groups on benzylic carbons catalyzed by [Ru(=CHPh)-$(PCy_3)_2Cl_2$] at room temperature. Up to quintuple RCM with formation of cyclopentenyl rings can be achieved starting from pentamethylcobaltocenium via decaallylation. On the other hand, cross-metathesis is accessible only by reflux in 1,2-dichloroethane using the second-generation Grubbs catalyst [Ru(=CHPh)$(PCy_3)_2${C-$(NMesCH_2)_2Cl_2$}] (**2**).

3. The $CpFe^+$ moiety is a useful tag that allows us to easily separate the ether-soluble catalyst from the ether-insoluble organoiron metathesis products. The $CpFe^+$ moiety also influences the selectivity, because it slows down the cross-metathesis for steric reasons, rendering the fast RCM completely selective at ambient temperature in the presence of this moiety.

4. After removal of the $CpFe^+$ moiety by simple photolysis using visible light, RCM of this type of polyallyl derivative can also be catalyzed by **1** in good yields, even in the ionic liquid 1-butyl-3-imidazolium hexafluorophosphate as the solvent at 80 °C.

5. A variety of new organoiron and organic structures, including macrocycles, cyclophanes, capsules, and polymers, can be synthesized shortly from these simple arenes by this combination of the perallylation reaction with cross-coupling metathesis catalyzed by **2**. These results illustrate the potential of this synthetic strategy combining these two spectacular and remarkably efficient modes of C−C coupling.

6. MALDI-TOF mass spectroscopy turns out be to be an invaluable tool for the analysis of complex reaction mixtures involving these compounds as well as selective metathesis reactions and for following the progress of the metathesis product mixture toward the product awaited at the concentration-dependent thermodynamic equilibrium.

Experimental Section

General Considerations. All air-sensitive manipulations were performed using standard Schlenk techniques under an atmosphere of nitrogen. Tetrahydrofuran, dichloromethane, and dichloroethane were dried on Na foil and distilled from benzophenone under nitrogen. Grubbs catalysts **1** and **2** were supplied by Strem and stored and transferred under a nitrogen-filled Vacuum Atmospheres drybox or under an atmosphere of nitrogen. The complexes **3**, **9**, **14**, **21**, **28**, **45**, and **54** of the [FeCp(η^6-arene)][PF_6] type were synthesized in high yields by reactions between ferrocene and the arene (neat or in cyclohexane or Decalin) in the presence of 2 equiv of Al_2Cl_6 and 1 equiv of water overnight around 100 °C or at reflux of the arene.[7k,8,21] For some examples, including the new complexes and their spectroscopic and analytical data, see the Supporting Information.

Compound 4. A mixture of [FeCp(η^6-C_6H_5Et)][PF_6] (**3**; 7.2 g, 20 mmol) and KOH (11.2 g, 200 mmol) was dissolved in a degassed DME (40 mL) solution of allyl bromide (17.5 mL, 200 mmol). The mixture was stirred under nitrogen at room temperature for 72 h. The solvent was removed in vacuo, the solid residue was dissolved in 60 mL of CH_2Cl_2, and the solution was filtered off, washed with an aqueous HPF_6 solution, and dried over Na_2SO_4. Then, the solvent was removed in vacuo. A brown oil was obtained; it was washed repeatedly with pentane and ether, giving a yellow powder (7.4 g, 85% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 6.35 and 6.19 (m, 5H, CH aromatic), 5.62 (m, 2H, CH allylic), 5.04 (s, 5H, cyclopentadienyl), 5.04 (m, 4H, CH_2 allylic), 2.45 and 2.43 (d, J = 7 Hz, 4H, CH_2 aliphatic), 1.56 (s, 3H, CH_3 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 132.4 (CH allylic), 120.1 (CH_2 allylic), 118.3 (C aromatic), 87.2 and 84.8 (CH aromatic), 76.4 (CH Cp), 44.9 (CH_2 aliphatic), 40 (C aliphatic), 25 (CH_3 aliphatic). MALDI-TOF: calcd for $C_{19}H_{23}Fe^+$, 307.11; found, 307.20.

Compound 5. [$Ru(PCy_3)Cl_2$(=CHPh)] (**1**; 0.017 g, 5 mol %) was added to a stirred solution of [FeCp(η^6-$C_6H_5C(C_3H_5)_2Me$)]-[PF_6] (**4**; 0.180 g, 0.4 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 4 h at room temperature. The solvent was removed in vacuo, leaving a brown solid residue. After the residue was washed repeatedly with ether, recrystallization in a CH_2Cl_2/ether mixture and slow diffusion crystallization from a CH_2Cl_2/ether mixture gave pure products as yellow crystals (127 mg; 75% yield). ^{1}H NMR (250 MHz, acetone-d_6; δ, ppm): 6.47 and 6.38 (m, 5H, CH aromatic), 5.84 (s, 2H, CH allylic), 5.20 (s, 5H, CH Cp), 3.00 and 2.70 (d, J = 14.5 Hz, 4H, CH_2 aliphatic), 1.48 (s, 3H, CH_3 aliphatic). ^{13}C NMR (50 MHz, acetone-d_6; δ, ppm): 129.5 (CH allylic), 88.7, 88.0 and 86.6 (CH aromatic), 77.3 (CH Cp), 47.8 (CH_2 aliphatic), 46.0 (CH_3 aliphatic). MALDI-TOF: calcd for $C_{17}H_{19}Fe^+$, 279.08; found, 279.15. Anal. Calcd for $C_{17}H_{19}FePF_6$: H, 4.51; C, 48.14. Found: H, 4.61; C, 48.24.

Compound 7. The same procedure as for **4** was applied to 3.48 g of [CpFe(η^6-1,2,4,5-$Me_2C_6H_2$)][PF_6] (**6**; 10 mmol), leading to [CpFe(η^6-tetraallylindane)][PF_6] (**7**) as a yellow powder (3.4 g, yield 67%). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 6.37 and 6.19 (d, 4H, CH aromatic), 5.97 and 5.73 (m, 4H, CH allylic exo and endo), 5.04 (s, 5H, Cp) 5.20 and 4.86 (m, 8H, CH_2 allylic exo and endo), 2.93, 2.42 and 2.20 (m, 10H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 132.4 and 132.0 (CH allylic exo and endo), 120.6 and 120.0 (CH_2 allylic exo and endo), 118.3 (C aromatic), 85.7 and 82.4 (CH aromatic), 76.3 (CH Cp), 47.9, 45.6, and 43.7 (CH_2 aliphatic exo, endo and cycle), 49 (C aliphatic). MALDI-TOF: calcd for $C_{26}H_{31}Fe^+$, 399.18; found, 399.32. Anal. Calcd for $C_{26}H_{31}FePF_6$: H, 5.74; C, 57.34. Found: H, 5.72; C, 56.99.

Compound 8. The same procedure as for **5** was applied to 0.213 g of **6** (0.4 mmol), leading to the complex **8** (0.160 g, 76% yield). Slow crystallization from CH_2Cl_2/Et_2O at room temperature gave needle-shaped crystals (monoclinic system). ^{1}H NMR (200 MHz, acetone-d_6; δ, ppm): 6.41 (m, 4H, CH aromatic), 5.93 and 5.70 (m, 4H, CH allylic exo and endo), 5.27 (s, 5H, CH Cp), 3.30, 2.93, and 2.38 (m, 10H, CH_2 aliphatic). ^{13}C NMR (63 MHz, acetone-d_6; δ, ppm): 130.5 and 129.2 (CH allylic exo and endo), 117.2 (C aromatic), 87.2 and 81.6 (CH aromatic), 77.4 (CH Cp), 54.9, 49.4, and 46.3 (CH_2 aliphatic exo, endo, and cycle), 52.1 (C aliphatic). MALDI-TOF: calcd for $C_{22}H_{23}Fe^+$, 343.11; found, 343.23**.** Anal. Calcd for $C_{22}H_{23}FePF_6$: H, 4.75; C, 54.12. Found: H, 5.18; C, 54.34.

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X-ray Structural Analysis of 8. Yellow prismatic monocrystals with approximate dimensions of 0.35 × 0.28 × 0.08 mm were grown by slow diffusion of gaseous ether into a dichloromethane solution (needle crystals; monoclinic system; space group $P2_1/n$; a = 19.8904(3) Å, b = 10.9561(1) Å, c = 9.3234(1) Å, β = 90.0555(5)°, V = 2031.77(7) Å^3, μ = 0.840 mm^{-1}). Data were collected on a Kappa-CCD Enraf-Nonius diffractometer equipped with a bidimensional CCD detector and analyzed by Mo Kα (λ = 0.7073 Å) radiation (graphite monochromator). A total of 17 548 reflections were collected with 4° ≤ θ ≤ 35°. The structure was solved by direct methods using the SIR97[22] program and refined by full-matrix least-squares techniques. Hydrogen atoms were located from their theorically calculated positions and included with isotropic temperature parameters. Refinement of the model led to convergence with $R(F)$ = 0.037 and $R_w(F^2)$ = 0.141. Scattering factors were obtained from ref 23.[23−25] A final difference Fourier map yielded the largest residual density at 0.343 e Å^{-3}.

Compound 10. A mixture of [FeCp(η^6-1,2,4,5-$Me_4C_6H_2$)][PF_6] (**9**; 2 g, 5 mmol) and KOH (11.2 g, 200 mmol) was dissolved in a degassed THF solution (40 mL) of allyl bromide (17.5 mL; 200 mmol). The mixture was stirred under nitrogen at room temperature for 48 h, and then the solvent was removed in vacuo. The solid residue was dissolved in 60 mL of CH_2Cl_2, the solution was filtered off, washed with an aqueous HPF_6 solution, and dried over Na_2SO_4, and then the solvent was removed in vacuo. The brown oily residue was repeatedly washed with pentane and ether, which gave a yellow powder (2.6 g, 72% yield). ^{1}H NMR (250 MHz, acetone-d_6; δ, ppm): 6.15 (s, 2H, CH aromatic), 6.10 and 5.15 (m, 8H, CH allylic exo and endo), 5.34 (s, 5H, cyclopentadienyl), 5.33 and 5.00 (m, 16H, CH_2 allylic exo and endo), 3.45 (m, 4H, CH aliphatic), 2.87 and 2.52 (m, 16H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 135.2 and 133.4 (CH allylic exo and endo), 118.8 and 118.4 (CH_2 allylic exo and endo), 108.3 (C aromatic), 81.3 (CH aromatic), 76.3 (CH Cp), 38.2 and 38.0 (CH_2 aliphatic exo and endo), 37.3 (CH aliphatic). MALDI-TOF: calcd for $C_{39}H_{51}Fe^+$, 575.33; found, 575.48. Anal. Calcd for $C_{39}H_{51}FePF_6$: H, 7.14; C, 64.97. Found: H, 7.11; C, 64.87.

Compound 11. The same procedure as for **5** was applied to 0.216 g of **10** (0.3 mmol), leading to **11** as a yellow powder (0.120 g, 70% yield). ^{1}H NMR (250 MHz, acetone-d_6; δ, ppm): 6.06 (s, 2H, CH aromatic), 5.88 and 5.70 (m, 8H, CH allylic exo and endo), 5.16 (s, 5H, CH Cp), 4.13 (m, 4H, CH aliphatic), 3.08 (m, 16H, CH_2 aliphatic). ^{13}C NMR (63 MHz, acetone-d_6; δ, ppm): 130.6 and 129.7 (CH allylic exo and endo), 108.8 (C aromatic), 82.0 (CH aromatic), 77.4 (CH Cp), 39.7 and 38.1 (CH_2 aliphatic exo and endo), 43.8 (CH aliphatic). MALDI-TOF: calcd for $C_{31}H_{35}Fe^+$, 463.45; found, 463.25. Anal. Calcd for $C_{31}H_{35}FePF_6$: H, 8.80; C, 61.20. Found: H, 5.92; C, 61.12.

Compound 12. A degassed acetonitrile solution (50 mL) of **10** (1.5 g, 4.14 mmol) and triphenylphosphine (0.519 g, 3.93 mmol) was irradiated using visible light for 12 h, while the system was kept below 25 °C. The volatiles were removed in vacuo, and the product was extracted from the violet residue using pentane (3 × 100 mL). The pentane solution was filtered over Al_2O_3 and evaporated to yield a brown oil that could be purified by passing through a silica gel column, leaving an off-white oil (0.450 g, 48% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 6.93 (s, 2H, CH aromatic), 5.62 (m, 8H, CH allylic), 4.94 (m, 16H, CH_2 allylic), 3.05 (q, 4H, CH aliphatic), 2.35 (m, 16H, CH_2 aliphatic).

Compound 13. This white compound was obtained by photolysis of **11** or RCM of **12**. ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 7.18 (s, 2H, CH aromatic), 5.78 (m, 8H, CH allylic), 3.72 (tt J = 8 Hz, 4H, CH aliphatic), 2.77 and 2.46 (ddd, J = 8 Hz, 16H, CH_2 aliphatic). MALDI-TOF: calcd for $C_{26}H_{30}Ag^+$, 449.53 and 451.53; found, 449.32 and 451.32.

Compound 15. A mixture of [CpFe(η^6-$C_6H_5CH_3$)][PF_6] (**14**; 1.79 g, 5 mmol) and KOH (4.2 g, 75 mmol) was dissolved in a degassed DME solution (30 mL) of allyl bromide (6.5 mL, 75 mmol). The mixture was stirred under nitrogen at room temperature for 48 h, and the solvent was removed in vacuo. The solid residue was dissolved in 60 mL of CH_2Cl_2, and the solution was filtered off, washed with an aqueous HPF_6 solution, and dried over Na_2SO_4. Then, the solvent was removed in vacuo. The brown oily residue was repeatedly washed with pentane and ether, which gave a yellow powder (1.85 g, 77% yield). ^{1}H NMR (250 MHz, CD_3CN; δ, ppm): 6.24 and 6.17 (m, 5H, CH aromatic), 5.8 (m, 3H, CH allylic), 4.98 (s, 5H, CH Cp), 5.19 (m, 6H, CH_2 allylic), 2.55 (d, J = 7.3 Hz, 6H, CH_2 aliphatic). ^{13}C NMR (63 MHz, acetone-d_6; δ, ppm): 134.3 (CH allylic), 120.0 (CH_2 allylic), 115.5 (C aromatic), 88.3, 88.0, and 86.2 (CH aromatic), 77.6 (CH Cp), 44.1 (C aliphatic), 42.9 (CH_2 aliphatic).

Compound 16. The Grubbs catalyst [Ru(PCy_3)Cl_2(=CHPh)] (**1**; 0.025 g, 5 mol %) was added to a stirred solution of [CpFe(η^6-$C_6H_5C(C_3H_5)_3$)][PF_6] (**15**; 0.270 g, 0.6 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred for 4 h at room temperature. The solvent was removed in vacuo, leaving a brown oily residue. After the residue was washed repeatedly with ether, recrystallization in a CH_2Cl_2/ether mixture and slow diffusion crystallization from a CH_2Cl_2/ether mixture gave the product as yellow crystals found pure by NMR (0.120 g, 65% yield). ^{1}H NMR (250 MHz, CD_3CN; δ, ppm): 6.46 and 6.27 (m, 5H, CH aromatic), 5.88 (s, 2H, CH cycloallylic), 5.60 (m, 1H, CH allylic), 5.18 (s, 5H, CH Cp), 4.9 (m, 2H, CH_2 allylic), 3.10 and 2.81 (d, J = 14.95 Hz, 4H, CH_2 cycloaliphatic), 2.37 (d, J = 7 Hz, 2H, CH_2 aliphatic). ^{13}C NMR (63 MHz, acetone-d_6; δ, ppm): 134.2 (CH allylic), 129.6 (CH cycloallylic), 119.6 (CH_2 allylic), 115.7 (C aromatic), 88.7, 88.1, and 87.6 (CH aromatic), 77.3 (CH Cp), 49.7 (C benzylic), 49.3 (CH_2 aliphatic), 44.3 (CH_2 cycloaliphatic). MALDI-TOF: calcd for $C_{19}H_{21}Fe^+$, 305.09; found, 305.21. Anal. Calcd for $C_{19}H_{21}FePF_6$: H, 4.70; C, 50.69; found: H, 4.87; C, 49.29.

Compound 17. A stirred solution of **16** (0.239 g, 0.5 mmol) and [Ru(PCy_3)Cl_2(=CHPh)] (**1**; 5 mol %) in 1,2-dichloroethane (5 mL) was refluxed for 3 days under nitrogen, and **1** (5 mol %) was added every 12 h (five times). The solvent was removed in vacuo, and the solid residue was washed repeatedly with ether and THF. The product **17** was obtained as a brown powder after recrystallization in a CH_2Cl_2/ether mixture and slow diffusion crystallization from a CH_2Cl_2/ether mixture (40% yield). ^{1}H NMR (250 MHz, CD_3CN; δ, ppm): 6.47 and 6.17 (m, 10H, CH aromatic), 5.85 (s, 4H, CH cycloallylic), 5.18 (s, 10H, CH Cp and 2H, CH allylic), 3.05 and 2.72 (d, J = 14.9 Hz, 8H, CH_2 cycloaliphatic), 2.26 (d, 2H, CH_2 aliphatic). MALDI-TOF: calcd for $C_{31}H_{33}Fe^+$, 461.22; found, 461.13. Anal. Calcd for $C_{31}H_{37}FePF_6$: H, 4.39; C, 49.57. Found: H, 4.76; C, 49.85.

Compound 18. A degassed acetonitrile solution (50 mL) of [FeCp(η^6-$C_6H_5C(C_3H_5)_3$)][PF_6] (**15**; 1.79 g, 5 mol) and triphenylphosphine (1.18 g, 4.5 mmol) was irradiated using visible light for 12 h, while the system was kept below 25 °C. The volatiles were removed in vacuo, and the product was extracted from the violet residue using pentane (3 × 100 mL). The pentane solution was filtered over Al_2O_3 and evaporated, yielding a light brown oil that could be purified through a silica gel column, giving a colorless oil (0.253 g, 55% yield). ^{1}H NMR (250 MHz, CD_3Cl; δ, ppm): 6.33 (m, 5H, CH aromatic), 5.58 (m, 3H, CH allylic), 5.05 (m, 6H, CH_2 allylic), 2.49 (d, J = 7 Hz, 6H, CH_2 aliphatic). ^{13}C NMR (63 MHz, acetone-d_6; δ, ppm): 146 (C aromatic), 135.6 (CH allylic), 118.6 (CH_2 allylic),

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129.1, 127.7 and 126.8 (CH aromatic), 44.1 (C aliphatic), 42.9 (CH_2 aliphatic).

Compound 19. Using the procedure described above for **16** (0.231 g, 0.5 mmol) and PPh_3 (0.127 g, 0.49 mmol), **19** was obtained free of dimer as a white solid (0,053 g, 48% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 7.25 (m, 5H, CH aromatic), 5.76 (s, 2H, CH cycloallylic), 5.5 (m, 1H, CH allylic), 4.96 (m, 2H, CH_2 allylic), 2.69 (m, 4H, CH_2 alicyclic), 2.39 (d, $J = 7.1$ Hz, 2H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 135.5 (CH allylic), 129.3 (CH cycloallylic), 117.0 (CH_2 allylic), 128.0, 126.9 and 125.5 (CH aromatic), 47.7 and 44.4 (CH_2 aliphatic). Anal. Calcd for $C_{14}H_{16}$: H, 8.75; C, 91.25. Found: H, 8.39; C, 90.83.

Compound 20. A mixture of **1** (0.012 g, 10 mmol %) and **18** (0.150 g, 0.71 mmol) was stirred in vacuo for 12 h at room temperature. The brown residue was chromatographed on a silica gel column using pentane as eluent. A white solid was obtained after evaporation under reduced pressure and purified by sublimation (0.075 g, 62% yield). ^{1}H NMR (250 MHz, CD_3CN; δ, ppm): 7.7−7.5 (m, 10H, CH aromatic), 6.08 (s, 4H, CH cycloallylic), 5.41 (s, 2H, CH allylic), 3.03 and 2.90 (d, $J =$ 14.6 Hz, 8H, CH_2 cycloaliphatic), 2.61 (d, $J = 5.2$ Hz, 2H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 149.6 (C aromatic) 129.7 (CH allylic), 129.4 (CH cycloallylic), 128.0, 127.0, and 125.4 (CH aromatic), 49.9 (C aliphatic), 46.7 (CH_2 aliphatic), 44.4 (CH_2 cycloaliphatic). MALDI-TOF: calcd for $C_{26}H_{28}Cu^+$, 403.16; found, 403.33. Anal. Calcd for $C_{26}H_{28}$: H, 8.29; C, 91.71. Found: H, 8.32; C, 91.69.

Compound 22. The same procedure as for **4** was applied to 2.5 g of **21** (6.7 mmol), leading to **22** as a yellow powder (3.0 g, 72% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 6.21 (s, 4H, CH aromatic), 5.72 (m, 6H, CH allylic), 4.97 (s, 5H, CH Cp), 5.19 (m, 12H, CH_2 allylic), 2.55 (d, $J = 6.7$ Hz, 12H, CH_2 aliphatic). MALDI-TOF: calcd for $C_{31}H_{39}Fe^+$, 467.24; found, 467.40. Anal. Calcd for $C_{31}H_{39}FePF_6$: H, 6.42; C, 60.79. Found: H, 6.31; C, 60.06.

Compound 23. The same procedure as for **5** was applied to 0.200 g of **22** (0.3 mmol), leading to complex **23** as a yellow powder (0.100 g, 60% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 6.03 (s, 4H, CH aromatic), 5.86 (s, 4H, CH cycloallylic), 5.46 (m, 2H, CH allylic), 4.90 (s, 5H, CH Cp), 4.95 and 4.75 (m, 4H, CH_2 allylic), 3.00 and 2.76 (d, $J = 16$ Hz, 8H, CH_2 alicyclic), 2.29 (d, $J = 6.4$ Hz, 4H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 132.4 (CH allylic), 128.9 (CH cycloallylic), 119.9 (CH_2 allylic), 113.9 (C aromatic), 85.8 (CH aromatic), 76.0 (CH Cp), 49.2 (C benzylic), 48.9 (CH_2 aliphatic), 43.6 (CH_2 cycloaliphatic). MALDI-TOF: calcd for $C_{27}H_{31}Fe^+$, 411.18; found, 411.35. Anal. Calcd for $C_{27}H_{31}FePF_6$: H, 5.62; C, 58.29. Found: H, 5.58; C, 57.06.

Compounds 24 and 25. A stirred solution of **22** (0.180 g, 0.3 mmol) and **2** (5 mol %) in 1,2-dichloroethane (5 mL) was refluxed over 7 days under nitrogen, and **2** (5 mol %) was added every other day (twice overall). The solvent was removed in vacuo, and the solid residue was repeatedly washed with ether and THF. The product was obtained as a brown oil after recrystallization from a CH_2Cl_2/ether mixture and slow diffusion crystallization using a CH_2Cl_2/ether mixture. Dimeric and trimeric cyclic products were obtained. ^{1}H NMR (250 MHz, acetone-d_6; δ, ppm): 6.17 (s, 4H, CH aromatic), 5.86 (s, 4H, CH cyclovinylic), 5.06 (s, 7H, CH Cp and CH vinyl), 3.00 and 2.76 (8H, CH_2 cyclopentene), 2.26 (4H, CH_2 aliphatic). MALDI-TOF: calcd for $C_{45}H_{49}Fe^+$, 645.72; found, 645.05; calcd for $C_{65}H_{69}Fe^+$, 905.47; found, 907.10.

Compound 26. This white compound was prepared by photolysis of **22** (1.9 g, 3.16 mmol) in the presence of PPh_3 (786 mg, 3 mmol) in 100 mL of acetonitrile (0.750 g, 68% yield). ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.26 (m, 4H, CH aromatic), 5.5 (m, 6H, CH allylic), 5.1 (s, 12H, CH_2), 2.45 (d, $J = 7.5$ Hz, 12H, CH_2 aliphatic). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 142.4 (C aromatic), 134.2 (CH allylic), 125.7 (CH_2 allylic), 116.9 (CH aromatic), 42.5 (C aliphatic), 41.3 (CH_2 aliphatic).

Compound 27. This compound was obtained as a white solid by photolysis of **23** using the same procedure as above. ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 7.17 (s, 4H, CH aromatic), 5.75 (s, 4H, CH cycloallylic), 5.5 (m, 2H, CH allylic), 4.95 (m, 4H, CH_2 allylic), 2.68 (m, 8H, CH_2 alicyclic) 2.39 (d, 4H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 146.4 (C aromatic), 135.8 (CH allylic), 129.3 (CH cycloallylic), 126.5 (CH aromatic), 117.0 (CH_2 allylic), 49.2 (C benzylic), 47.8 (CH_2 aliphatic), 44.4 (CH_2 cycloaliphatic). MALDI-TOF: calcd for $C_{22}H_{26}Ag^+$, 397.11; found, 397.12. Anal. Calcd for $C_{22}H_{26}$: H, 9.02; C, 90.98. Found: H, 9.72; C, 90.48.

Cross-Metathesis of 27. ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 7.1 (m, 4H, CH aromatic), 5.7 (4H, CH cyclovinylic), 5.1 (s, 2H, CH vinyl), 2.6 and 2.5 (d, $J = 16.2$ Hz, 8H, CH_2 cycloaliphatic), 2.21 (2H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 145 (C aromatic), 129 (CH cyclovinylic), 125 (CH vinyl), 115 (CH aromatic), 48, 45 and 42 (aliphatic). MALDI-TOF: calcd for $(C_{20}H_{22})_nAg^+$, 843.42 1155.59, 1417.76, and 1679.9; calcd for $(C_{20}H_{22})_nC_2H_4Ag^+$, 921.42 and 1183.59; found, 893.59, 921.51, 1155.76, 1183.87, 1417.88, and 1680.03.

Compound 29. A mixture of $[FeCp(\eta^6\text{-}1,3,5\text{-}Me\text{-}C_6H_3)][PF_6]$ (**14**; 5 g, 13 mmol) and KOH (33 g, 590 mmol) was dissolved in a degassed DME (100 mL) solution of allyl bromide (51 mL, 590 mmol), and the mixture was stirred under nitrogen at room temperature for 2 days. KOH (33 g, 590 mmol) and allyl bromide (51 mL, 590 mmol) were added, the mixture was stirred for 2 days, the solvent was removed in vacuo, the solid residue was dissolved in 60 mL of CH_2Cl_2, and the solution was filtered off, washed with an aqueous HPF_6 solution, and dried over Na_2SO_4. Then, the solvent was removed in vacuo, leaving a brown oil that was washed repeatedly with pentane and ether, which gave a yellow powder (7.4 g, 65% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 6.02 (s, 3H, CH aromatic), 5.7 (m, 9H, CH allylic), 4.94 (s, 5H, CH Cp), 5.19 (m, 18H, CH_2 allylic), 2.54 (d $J = 5.5$ Hz, 18H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 132.4 (CH allylic), 120.4 (CH_2 allylic), 113 (C aromatic), 80.6 (CH aromatic), 76.9 (CH Cp), 43.5 (C aliphatic), 42.9 (CH_2 aliphatic).

Compound 30. The same procedure as for **5** was applied to 0.200 g of **29** (0.35 mmol), leading to the yellow complex **30** (0.171 g, 74% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 5.58 (s, 3H, CH aromatic), 5.87 (s, 6H, CH cycloallylic), 5.48 (m, 3H, CH allylic), 4.79 (s, 5H, CH Cp), 5.00 and 4.73 (d, $J = 8.2$ Hz, 6H, CH_2 allylic), 2.92 and 2.78 (d, $J = 15$ Hz, 12H, CH_2 cycloaliphatic), 2.30 (d, $J = 7.0$ Hz, 6H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 132.9 (CH allylic), 129.2 (CH cycloallylic), 120.3 (CH_2 allylic), 114.2 (C aromatic), 83.7 (CH aromatic), 76.1 (CH Cp), 49.4 (C benzylic), 49.5 (CH_2 cycloaliphatic), 44.3 (CH_2 aliphatic). MALDI-TOF: calcd for $C_{35}H_{41}Fe^+$, 517.26; found, 517.24. Anal. Calcd for $C_{35}H_{41}FePF_6$: H, 6.24; C, 63.45. Found: H, 6.10; C, 62.53.

Compound 31. A stirred solution of **30** (0.200 g, 0.3 mmol) and **2** (5 mol %) in 1,2-dichloroethane (5 mL) was refluxed for 7 days under nitrogen, and **2** (5 mol %) was added every other day (twice overall). The solvent was removed in vacuo, and the solid residue was washed repeatedly with ether and THF. The product was obtained as a brown oil after recrystallization in a CH_2Cl_2/ether mixture and slow diffusion crystallization using a CH_2Cl_2/ether mixture. MALDI-TOF: calcd for $C_{59}H_{65}Fe^+$, 829.44; found, 829.94.

Compound 32. The same procedure as for **12** was applied to 6.3 g of **29** (8.4 mmol), leading to **32** as a white powder (3.0 g, 75% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 7.04 (s, 3H, CH aromatic), 5.5 (m, 9H, CH allylic), 4.98 (m, 18H, CH_2 allylic), 2.42 (d, $J = 7$ Hz, 18H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 144.4 (C aromatic), 134.7 (CH allylic), 122.6 (CH aromatic), 117.5 (CH_2 allylic), 43.7 (C benzylic), 42.0 (CH_2 aliphatic).

Compound 33. A stirred solution of **32** (0.240 g, 0.5 mmol) and **1** (5 mol %) in 1,2-dichloroethane (5 mL) was stirred for 4 h. The solvent was removed in vacuo, and the solid residue

was purified by chromatography, yielding a white solid (0.189 g, 75%). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 6.83 (s, 3H, CH aromatic), 5.74 (s, 6H, CH cycloallylic), 5.45 (m, 3H, CH allylic), 4.90 (m, 6H, CH_2 allylic), 2.68 and 2.63 (d, 12H, CH_2 cycloaliphatic), 2.33 (d, 6H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 148.4 (C aromatic), 135.8 (CH allylic), 129.3 (CH cycloallylic), 122.9 (CH aromatic), 116.8 (CH_2 allylic), 49.9 (C benzylic), 48.2 (CH_2 aliphatic), 44.4 (CH_2 cycloaliphatic). Anal. Calcd for $C_{30}H_{36}$: H, 9.15; C, 90.85. Found: H, 9.41; C, 90.95.

Compound 34. A stirred solution of **33** (0.200 g, 0.3 mmol) and **2** (5 mol %) in dichloroethane (5 mL) was refluxed for 7 days under nitrogen, and **2** (1.67 mol %) was added every other day (twice overall). The solvent was removed in vacuo, and the solid residue was purified by chromatography, yielding a white solid (100 mg, 56% yield). ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 6.85 (s, 6H, CH aromatic), 6.09 (s, 12H, CH cyclovinylic), 5.04 (m, 6H, CH vinyl), 2.90 (m, 24H, CH_2 cycloaliphatic), 2.1 (m, 12H, CH_2 aliphatic). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 147.3 (C aromatic), 129.6 (CH vinyl), 129.3 (CH cyclovinylic), 123.8 (CH aromatic), 50.9 (CH_2 cycloaliphatic); 46.3 (CH_2 aliphatic), 44.4 (C aliphatic). MALDI-TOF: calcd for $C_{54}H_{60}Ag^+$, 815.37; found: 815.50. Anal. Calcd for $C_{54}H_{60}$: H, 8.53; C, 91.47. Found: H, 8.51; C, 91.53.

Compound 35. A solution of **34** (0,070 g, 0.14 mmol) and Pd/C (0.010 g) in CH_2Cl_2 was flushed with hydrogen and kept under atmospheric pressure for 10 h. The mixture was filtered over Celite, and the solvent was removed in vacuo to leave a white powder (100% yield). ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm): 6.76 (s, 6H, CH aromatic), 1.88, 1.73, and 1.64 (m, 48H, CH_2 cycloaliphatic), 1.25 and 0.64 (m, 24H, CH_2 aliphatic). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm): 147.8 (C aromatic), 123.2 (CH aromatic), 51.9 (C aliphatic), 42.5 and 24.9 (CH_2 aliphatic), 36.0 and 22.8 (CH_2 cycloaliphatic).

Compound 37. A mixture of **36** (0.371 g, 0.5 mmol) and *t*-BuOK (2 g, 18 mmol) was dissolved at −40 °C in a degassed THF (30 mL) solution of allyl bromide (3.0 mL, 18 mmol). The mixture was stirred under nitrogen at room temperature over 1 day. Then, *t*-BuOK (2 g, 18 mmol) and allyl bromide (3.0 mL, 18 mmol) were added at −40 °C. The mixture was stirred at room temperature for 1 day. Again, *t*-BuOK (2 g, 18 mmol) and allyl bromide (3.0 mL, 18 mmol) were added at −40 °C, and the mixture was stirred at room temperature for 1 day more. The solvent was then removed in vacuo, the solid residue was dissolved in 60 mL of CH_2Cl_2, and the solution was filtered off, washed with an aqueous HPF_6 solution, and dried over Na_2SO_4. Then, the solvent was removed in vacuo, leaving a brown oily residue that was repeatedly washed with pentane and ether, which yielded a red powder. This product was purified on an alumina gel column with CH_2Cl_2 as eluent, which gave an off-white solid (59% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 6.47 and 6.10 (s, 6H, CH aromatic), 5.84 and 5.60 (m, 12H, CH allylic), 4.81 (s, 10H, CH Cp), 5.3 and 5.1 (m, 24H, CH_2 allylic), 2.64 and 2.55 (d, 24H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 133.7 and 132.6 (CH allylic), 120.4 and 118.6 (CH_2 allylic), 76.5 (CH Cp), 44.3 and 43.8 (C aliphatic), 42.6 and 41.9 (CH_2 aliphatic). MALDI-TOF: calcd for $C_{57}H_{71}Fe^+$, 811.49; found, 811.71. Anal. Calcd for $C_{62}H_{76}Fe_2P_2F_{12}$: H, 6.26; C, 60.89. Found: H, 6.45; C, 60.25.

Compound 38. The same procedure as for **5** was applied to 0.216 g of **37** (0.3 mmol), leading to **38** as a brown solid (70% yield). ^{1}H NMR (200 MHz, $CDCl_3$; δ, ppm): 6.68 and 6.32 (s, 6H, CH aromatic), 5.8 (s, 8H, CH cycloallylic), 6.8 (m, 4H, CH allylic), 4.86 (s, 10H, CH Cp), 4.9 (d, 8H, CH_2 allylic), 2.77 and 2.57 (m, 24H, CH_2 aliphatic). ^{13}C NMR (63 MHz, CD_3CN; δ, ppm): 134.5, 130.3, and 129.7 (CH allylic), 118.9 and 118.8 (CH_2 allylic), 79.9 (CH Cp), 51.1, 50.1, and 42.2 (aliphatic). MALDI-TOF: calcd for $C_{49}H_{55}Fe^+$, 699.81; found, 699.57.

Synthesis[20] and Decallallylation[15] of 39, Giving 40. See the Supporting Information.

Compound 41. The same procedure as for **5** was applied to 0.200 g of **40** (0.25 mmol), leading to complex **41** as a brown powder (0.135 g, 81% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 5.70 (10H, CH allylic), 4.9 (5H, CH Cp), 2 (5H, CH aliphatic; 20H, CH_2 aliphatic). MALDI-TOF: calcd for $C_{35}H_{40}Co^+$, 519.62; found, 519.28.

Compound 42. See the Supporting Information.

Compound 43. The same procedure as for **4** was applied to 3.48 g of **42** (538 mg, 1.5 mmol) leading to the brown [CpFe(η^6-$C_6H_5N(C_3H_5)_2$)][PF_6] (61% yield). ^{1}H NMR (250 MHz, acetone-d_6; δ, ppm): 6.21, 6.06, and 5.85 (t, t, and d, J = 6, 5.6, and 6.4 Hz, 5H, CH aromatic), 5.4 (m, 2H, CH), 4.98 (s, 5H, cyclopentadienyl), 5.1 (m, 4H, CH_2 allylic), 4.17 (d, J = 4.8 Hz, 4H, CH_2 aliphatic). ^{13}C NMR (63 MHz, acetone-d_6; δ, ppm): 133.0 (CH allylic), 118.4 (CH_2 allylic), 86.6, 81.4, 77.9, and 68.1 (aromatic), 76.4 (CH Cp), 53.5 (CH_2 aliphatic). MALDI-TOF: calcd for $C_{17}H_{20}Fe^+N$, 294.19; found, 294.12.

Compound 44. The same procedure as for **5** was applied to 0.216 g of **43** (0.3 mmol), leading to **43** as a brown solid (65% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 5.99 (m, 5H, CH aromatic), 5.55 (s, 2H, CH allylic), 4.88 (s, 5H, CH Cp), 4.22 (s, 4H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 126.4 (CH allylic), 86.4, 80.8, 78.7, and 68.2 (CH aromatic), 75.7 (CH Cp), 55.4 (CH_2 aliphatic). MALDI-TOF: calcd for $C_{15}H_{16}Fe^+N$, 266.14; found, 266.13.

Compound 45. A THF (30 mL) solution of [$Fe^ICp(\eta^6$-$C_6Me_6)$][17] (0.170 g, 0.6 mmol) was added to **43** (0,250 g, 0.6 mmol). Filtration over Celite and evaporation of the solvent left a solid residue, whose extraction with pentane gave **45** (0.050 g, 60% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 7.26, 7.04, and 6.74 (m, 5H, CH aromatic), 5.9 (m, 2H, CH), 5.28 (m, 4H, CH_2 allylic), 3.97 (d, J = 4.6 Hz, 4H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 147.1 (C aromatic), 135.8 (CH allylic), 125.6, 119.4, and 110.5 (CH aromatic), 115.7 (CH_2 allylic), 34.3 (CH_2 aliphatic). For a former synthesis, see ref 21.

Compound 46. The same procedure as for **12** was applied to 0.246 g of **45** (0.6 mmol), leading to **46** (65% yield). ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 7.3, 7.0, and 6.6 (m, 5H, CH aromatic), 6.01 (s, 2H, CH allylic), 4.16 (s, 4H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 147.1 (C aromatic), 129.4 (CH allylic), 129.4, 120.6, and 111.2 (CH aromatic), 54.5 (CH_2 aliphatic). For a former synthesis, see ref 22.

Compound 48. A mixture of complex **47** (0.856 g, 2 mmol), NaI (3 g, 20 mmol), and KOH (1.1 g, 20 mmol) was dissolved in a degassed DME (10 mL) solution of 5-bromo-1-pentene (2.9 g, 20 mmol). The mixture was stirred under nitrogen at 80 °C for 72 h, and then the solvent was removed in vacuo. The solid residue was dissolved in 60 mL of CH_2Cl_2, and the solution was filtered off, washed with an aqueous HPF_6 solution, and dried over Na_2SO_4. Then, the solvent was removed in vacuo, leaving a brown oil, which was repeatedly washed with pentane and ether, giving a yellow powder. ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 6.23 (s, 4H, CH aromatic), 5.61 (m, 2H, CH allylic), 4.98 (s, 5H, CH Cp), 4.88 (m, 4H, CH_2 allylic), 1.92, 1.50, and 1.13 (m, 22H, CH_3 and CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 137.9 (CH allylic), 116.7 (C aromatic), 115.1 (CH_2 allylic), 83.4 (CH aromatic), 75.7 (CH Cp), 44.9, 37.0, 33.2, 26.8, and 23.7 (CH_3 and CH_2 aliphatic). MALDI-TOF: calcd for $C_{27}H_{39}Fe^+$, 419.24; found, 419.27.

Cross-Metathesis of 48. 1 (0.017 g, 5 mol %) was added to a stirred solution of **48** (0.4 mmol) in $CHCl_3$ (20 mL), and the mixture was stirred for 24 h at room temperature. The solvent was then removed in vacuo, giving a brown residue. ^{1}H NMR (250 MHz, acetone-d_6; δ, ppm): 6.12 (s, 4H, CH aromatic), 4.96 (m, 7H, CH Cp and CH vinyl), 1.80, 1.44, and 1.05 (m, 24H, CH_3 and CH_2 aliphatic). MALDI-TOF: calcd for [$FeCp(C_{20}H_{30})_n(C_2H_4)$]$^+$ and [$FeCp\,(C_{20}H_{30})_n$]$^+$, 391.21, 661.44, 689.44, 931.77, 959.67, 1229.90, 1500.13, and 1770.36; found, 391.33, 661.53, 689.75, 931.77, 960.02, 1230.3, 1500.34, and 1770.68.

Compound 49. The same procedure as for **48**, using 6-bromo-1-hexene (3.7 g, 20 mmol), gave **49** as a yellow powder. ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 6.21 (s, 4H, CH aromatic), 5.68 (m, 2H, CH allylic), 4.98 (s, 5H, CH Cp), 4.88 (m, 4H, CH_2 allylic), 1.95, 1.59, 1.37, and 1.05 (m, 26H, CH_3 and CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 138.3 (CH allylic), 116.4 (C aromatic), 114.7 (CH_2 allylic), 83.3 (CH aromatic), 75.7 (CH Cp), 45.6, 37.3, 33.4, 28.9, 26.9, and 23.7 (CH_3 and CH_2 aliphatic). MALDI-TOF: calcd for $C_{29}H_{43}Fe^+$, 447.27; found, 447.30.

Compound 50. The same procedure as that used for the cross-metathesis of **48** was applied to **49** and selectively gave the cyclophane **50** as a yellow powder (56% yield). ^{1}H NMR (250 MHz, acetone-d_6; δ, ppm): 6.33 (s, 4H, CH aromatic), 5.17 (s, 5H, CH Cp), 4.88 (s, 2H, CH vinyl), 1.79, 1.59, 1.10, and 0.51 (m, 26H, CH_3 and CH_2 aliphatic). MALDI-TOF: calcd for $C_{27}H_{39}Fe^+$, 419.24; found, 419.28. Anal. Calcd for $C_{27}H_{39}FePF_6$: H, 6.96; C, 57.46. Found: H, 6.93; C, 57.02.

Compound 52. The conditions described above for the synthesis of **10** were used (reaction time 2 days) in order to selectively obtain **52** from **51**. ^{1}H NMR (250 MHz, $CDCl_3$; δ, ppm): 5.7 (m, 6H, CH allylic), 5.19 (m, 12H, CH_2 allylic), 4.65 (s, 5H, CH Cp), 2.96 and 2.37 (m, 24H, CH_2 aliphatic). ^{13}C NMR (63 MHz, $CDCl_3$; δ, ppm): 135.4 (CH allylic), 116.6 (CH_2 allylic), 102.9 (C aromatic), 78.2 (CH Cp), 35.4 and 30.2 (CH_2 aliphatic). MALDI-TOF: calcd for $C_{35}H_{47}Fe^+$, 523.3; found, 523.35.

Compound 53. The above procedure used for the cross-metathesis of **48** was applied to **52**, which produced a yellow precipitate of **53** in 95% yield. The yellow solution was filtered off, and the resulting product structure was explored using the MALDI-TOF mass spectrum. MALDI-TOF: calcd for $C_{29}H_{35}Fe^+$, 439.21; found, 439.26.

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Supporting Information Available: Synthetic procedures for compounds **3**, **36**, **39**, and **44**, MALDI TOF mass spectra of compounds **8**, **11**, **16**, **22**, **23**−**25**, **30**, **31**, **34**, **35**, **38**, **41**, **50**, and **53** and of the metathesis products of compounds **26** and **48**, and complete crystallographic data for complex **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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