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Zirconium-catalyzed and zirconium-promoted cyclization reactions of non-conjugated dienes with alkylmagnesium halides to give cycloalkylmethylmagnesium derivatives [1]

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This paper is dedicated to the memory of Professor Mark Vol'pin

Abstract

The stoichiometric reaction of certain non-conjugated dienes with n-Bu_2ZrCp_2 provides the corresponding zirconabicycles, such as *trans*-3 bis(cyclopentadienyl)zirconabicyclo[3.3.0]octane, that can be fully characterized by spectroscopic means. Their treatment with EtMgBr or n-BuMgCl in THF gives the corresponding monocyclic monomagnesium derivatives along with the corresponding alkene–$ZrCp_2$ derivatives in high yields. In cases where the Grignard reagent is either sterically hindered or lacking β-H, little or no reaction may occur, although some, e.g., *s*-BuMgCl, react, albeit slowly, to give the expected products in high yields. In cases where either a Grignard reagent in diethyl ether or a dialkylmagnesium (irrespective of solvent) is used, the major product is the corresponding dimagnesio derivative. A couple of intramolecular transmetallation paths are proposed for these cases. The Cp_2ZrCl_2-catalyzed reaction of 1,6-heptadiene with EtMgBr fails to induce the desired bicyclization–ring opening sequence to give the corresponding monocyclic monomagnesium derivatives. On the other hand, the corresponding reaction with n-BuMgBr does proceed as desired to give the monocyclic monomagnesium product which contains a minor amount of the corresponding *exo*-methylene derivative. Only traces, if any, of the corresponding dimagnesium derivatives reported to be the major products in Et_2O are formed. This procedure has been applied to catalytically convert several other dienes, i.e., (*E*)-1-phenyl-1,6-heptadiene, 2,4,4-trimethyl-1,6-heptadiene, diallyl(benzyl)amine, 1,7-octadiene and 1,2-diallylbenzene, into the corresponding monocyclized compounds in moderate to excellent combined yields.

Keywords: Zirconium-catalyzed; Cyclization reactions; Non-conjugated dienes

1. Introduction

In contrast to the Zr-catalyzed methylalumination of alkynes [2], for which a four-centered addition mechanism has been proposed [2c,d], the Zr-catalyzed reaction of alkylmagnesium derivatives with alkenes to give the corresponding alkylmagnesiation products [3] has been shown to involve zirconacyclopentane intermediates [4,5]. One of the keys to the mechanistic clarification in our study is our discovery that preformed zirconacyclopentanes react with the stoichiometric amount of ethylmagnesium derivatives in THF to give the observed ethylmagnesiation product and ethylene–$ZrCp_2$, which in turn reacts stoichiometrically with 1-alkenes in a 'pair-' and regioselective manner to regenerate the zirconacyclopentanes [4]. These findings have supported our notion that both ethylene–$ZrCp_2$ and zirconacyclopentanes must serve as catalytic intermediates. Another key finding is that alkyl groups containing β-Me, such as Et, can serve as better β-H donors than those containing β-methylene or β-methine [6], which explains the unique role of Et relative to higher alkyl groups.

The results observed with simple alkenes suggested to us that dienes [7] and perhaps even enynes and diynes [8,9] might undergo related Zr-catalyzed reactions [10]. Indeed, the reaction of 1,6-heptadiene and 1,7-octadiene with Bu_2Mg or BuMgCl to give 1,2-bis(magnesiomethyl)cyclopentane and -cyclohexane, respectively, has been reported [5b,11]. In this paper, we report our results with dienes, which display

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[1] This work is based in part on a Ph.D. Dissertation by C.J. Rousset [11].

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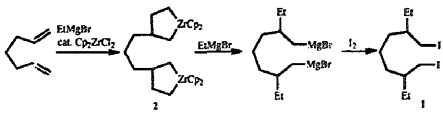
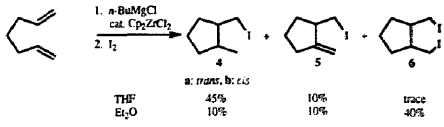
some features distinct from those that have been previously reported. Most strikingly, the major products can be monomagnesiomethylcycloalkanes in sharp contrast with the results reported recently [5b,11].

2. Results and discussion

In view of the favorable results observed in the reaction of simple 1-alkenes with EtMgBr in the presence of a catalytic amount of Cp_2ZrCl_2 [3,4], 1,6-heptadiene was initially treated with EtMgBr (6 molar equiv.) in the presence of 0.2 molar equiv. of Cp_2ZrCl_2 in THF at 25°C for 24 h. Treatment of the reaction mixture with I_2 (9 molar equiv.) gave an essentially 1:1 diasteriomeric mixture of 3,7-bis(iodomethyl)nonane (**1**) in 51% isolated yields without producing a significant amount of any cyclization products. Similar results involving diethylmagnesiation have previously been obtained using Et_2Mg and Cl_2ZrCp_2 [3b]. The formation of **1** is consistent with the intermediacy of **2**, suggesting that ethylene is not readily detached from Zr via displacement with dienes. Thus, the two alkene groups of a diene molecule must independently react with two molecules of ethylene–$ZrCp_2$ generated in situ (Eq. (1)). Since we had earlier found that 1-butene–$ZrCp_2$ generated in situ via n-Bu_2ZrCp_2 would react with 1,6-heptadiene to give the corresponding zirconabicycle **3** [7], we replaced EtMgBr used above with n-BuMgCl (3 molar equiv.) and carried out its reaction with 1,6-heptadiene in the presence of 0.1 molar equiv. of Cp_2ZrCl_2 at 55°C for 24 h. Iodinolysis with 4 molar equiv. of I_2 afforded a 4:1:1 mixture of **4a**, **4b** and **5** in 55% combined yield (Eq. (2)). Noteworthy is the virtual absence of the diiodide **6** which was recently reported to be the major product when the reaction was carried out in Et_2O [5b]. We reasoned that the contrasting results shown in Eq. (2) might be attributable to accelerated rates of transmetallation steps in Et_2O relative to those in THF and/or accelerated rates of β-H abstraction in THF relative to those in Et_2O. To probe the first factor as simply as possible, $Cp_2Zr(CD_3)_2$, prepared by treatment of Cl_2ZrCp_2 with CD_3MgI, was allowed to undergo CH_3–CD_3 exchange with 1 equiv. of CH_3MgBr in THF in one case and in Et_2O in another. Analysis of these two reaction mixtures by ^1H NMR spectroscopy has revealed that there is no significant difference between them. Specifically, for example, the extents of CH_3 incorporation into $ZrCp_2$ derivatives, i.e., formation of $Cp_2Zr(CD_3)(CH_3)$ and $Cp_2Zr(CH_3)_2$ were 20% in THF and 18% in Et_2O after 60 min at 20°C. To compare the rates of β-H abstraction in THF and in Et_2O, n-Bu_2ZrCp_2 was allowed to decompose at 0°C in the presence of 10 equiv. of n-BuMgCl. The use of the latter reagent was to simulate the initial catalytic conditions. Under these conditions the rates of decomposition via β-H abstraction were indistinguishable in the two solvents. Thus, the extents of decomposition over 24 min in THF and in Et_2O were 60 and 59%, respectively.



(1)



(2)

The unsuccessful efforts with simple dialkylzirconocenes discussed above prompted us to probe this matter using 1,6-heptadiene itself and organometallic compounds derived from it, such as a putative intermediate **3**. Accordingly, both catalytic and stoichiometric reactions of 1,6-heptadiene were carried out using n-BuMgCl or n-Bu_2Mg and Cl_2ZrCp_2 in THF or in Et_2O. In the stoichiometric reaction, **3** was generated in situ in nearly quantitative yield and then treated with either n-BuMgCl or n-Bu_2Mg. These reactions were monitored by NMR spectroscopy, and the final products were analyzed after their conversion to the corresponding iodides. The results summarized in Table 1 indicate the following. First, the agreement between the results of the stoichiometric reactions and those of the corresponding catalytic reactions is excellent, suggesting that the stoichiometric reactions are reasonable models for the catalytic reactions and that **3** is a likely intermediate in the catalytic reations of 1,6-heptadiene. Second, the formation of a monomagnesio derivative yielding **4** upon iodinolysis as the major product was observed only with n-BuMgCl and THF. When the other three combinations, i.e., n-BuMgCl in Et_2O and n-Bu_2Mg in either Et_2O or THF, were used, the major product was a dimagnesio derivative, which most likely is **7**, although **8** or its polymeric analogues cannot be ruled out in cases where X is n-Bu. As previously reported, Grignard reagents, i.e., RMgX where X

Table 1
The stoichiometric reaction of 3-bis(η^5-cyclopentadienyl)zirconabicyclo[3.3.0]octane with n-BuMgCl or n-Bu_2Mg and the reaction of 1,6-heptadiene with n-BuMgCl or n-Bu_2Mg catalyzed in Cl_2ZrCp_2 in THF or diethyl ether

Magnesium reagent	Solvent	Stoichiometric or catalytic	Product yield (%)		
			4	5	6
n-BuMgCl	THF	stoichiometric	56	trace	trace
n-BuMgCl	THF	catalytic	45	10	trace
n-BuMgCl	Et_2O	stoichiometric	17	trace	49
n-BuMgCl	Et_2O	catalytic	10	10	40
n-Bu_2Mg	THF	stoichiometric	32	3	52
n-Bu_2Mg	THF	catalytic	28	6	26
n-Bu_2Mg	Et_2O	stoichiometric	30	trace	48
n-Bu_2Mg	Et_2O	catalytic	17	trace	75

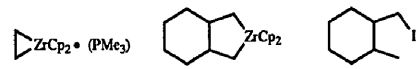
is a halogen, tend to be monomeric in THF but dimeric in Et_2O [12]. With either bridged dimers of Grignard reagents or dialkylmagnesiums, the transfer of the second alkyl group from Mg to Zr can be intramolecular, whereas no such intramolecular delivery is feasible with monomeric Grignard reagents in THF, as illustrated in Scheme 1. With R_2Mg, intramolecular delivery of the second R group may involve either a 1:1 or 1:2 complex of **3** with R_2Mg.

To further probe the presumed intermediacy of the zirconabicycle **3**, it was prepared as reported previously [7] by the stoichiometric reaction of 1,6-heptadiene with n-Bu_2ZrCp_2 generated in situ by treatment of Cp_2ZrCl_2 with 2 equiv. of n-BuLi [8b]. We have previously characterized **3** mainly through chemical transformations [7]. It has now been spectroscopically identified by ^1H and ^{13}C NMR as well as high resolution mass spectroscopies. The *trans* to *cis* stereoisomeric ratio was >95% by ^1H and ^{13}C NMR spectroscopies. Several other bicyclic zirconacyclopentane derivatives have also been similarly identified. The zirconabicycle **3** was then treated at 23°C in THF with 3–5 molar equiv. of a series of Grignard reagents containing Me, Et, i-Bu, *s*-Bu, t-Bu and Ph in addition to n-BuMgCl used above either in the absence or in the presence of PMe_3 (1.3 molar equiv.). We have previously established that there is no detectable interaction between dialkylzirconocenes and PMe_3 and that PMe_3 will merely stabilize alkene–$ZrCp_2$ without affecting the rate of β-H abstraction reaction of dialkylzirconocenes [6]. The amounts of **3** and alkene–$ZrCp_2$–PMe_3 complexes were determined by ^1H NMR analysis of the Cp signals using a suitable internal standard. The reaction mixtures were then treated with I_2. The organic products thus obtained were analyzed by GLC and NMR spectroscopy. The experimental results are summarized in Table 2. As expected, the reaction of **3** with EtMgBr was fast and complete within 2 h at 23°C. In the presence of PMe_3, ethylene–$ZrCp_2$–PMe_3 (**9**) [13] was formed in 91% yield. After iodinolysis, a 92:8 mixture of the *trans* and *cis* isomers of **4** was obtained in >90% yield. Notably, neither **5** nor **6** were present in more than trace quantities. Similarly, the reaction of preformed 8-bis(cyclopentadienyl)zirconabicyclo[4.3.0]nonane (**10**), which was ~80% *cis*, with EtMgBr (3 equiv.) was complete in 19 h, providing **9** in nearly quantitative yield and a 1:6 mixture of the *trans* and *cis* isomers of **11**, after iodinolysis.

Table 2
Stoichiometric reaction of Grignard reagents with 3-bis(cyclopentadienyl)zirconabicyclo[3.3.0]octane (**3**) in THF at 23°C

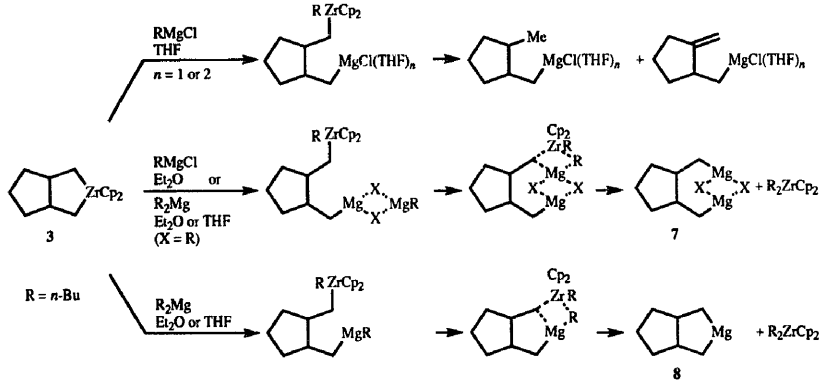
RMgX (equiv.)	Time (h)	3 [a] (%)	Product yield (%)		
			4 [b] (*trans*/*cis*)	5 [b]	6 [b]
EtMgBr (3)	2	0	>90 (92/8)	trace	trace
n-BuMgCl (5)	24	trace	56 (91/9)	trace	trace
i-BuMgCl (3)	17	90	7 (50/50)	trace	93 [c]
s-BuMgCl (3)	48	3	75 (50/50)	trace	6 [c]
t-BuMgCl (3) [d]	24	91			
MeMgBr (3) [d]	17	97			
PhMgBr (3) [d]	17	97			

[a] By ^1H NMR spectroscopy.
[b] By GLC.
[c] This figure includes **6** derived from **3**.
[d] No iodinolysis was performed.



9 **10** **11**

The reaction of **3** with n-BuMgCl was considerably slower than the corresponding reaction with EtMgBr. It thus required 48 h to produce a 91:9 mixture of **4a** and **4b** in 56% combined yield after iodinolysis. With i-BuMgCl and t-BuMgCl, the reaction was slower still with ≥90% of **3** remaining after 24 h. These results may, in part, be explained in terms of the differences in the steric requirements of the Grignard reagents

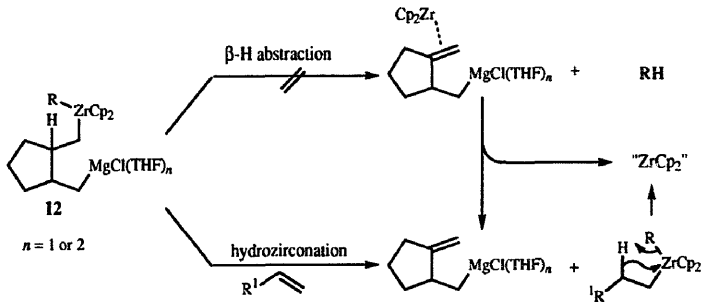


Scheme 1.

used. However, the reaction of *s*-BuMgCl with **3** was not only faster than that with i-BuMgCl but also produced **4** in 75% yield after iodinolysis. The major difference between *s*-BuMgCl and i-BuMgCl is attributable to the fact that *s*-Bu contains a β-methyl group while the only β group in i-Bu is β-methine. The observed trend is in agreement with the relative ability of these alkyl groups to act as a β-H donor in the β-H abstraction process, i.e., β-methyl > β-methylene > β-methine [6]. We have observed that i-Bu_2ZrCp_2 lacking β-methyl or β-methylene is indeed thermally very stable [6,13f]. Despite the low steric requirements, MeMgBr lacking a β-H did not react with **3** to give **4**. The lack of formation of **5** in this case strongly supports a notion that the 2-magnesiomethylcyclopentylmethyl moiety in putative intermediates shown in Scheme 1, which contains a β-methine group cannot serve as an effective β-H donor. This, in turn, rules out β-H abstraction as a major route to **5**.

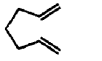
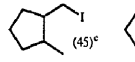
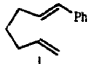
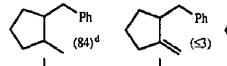
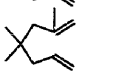
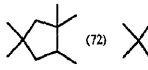
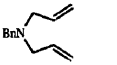
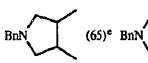
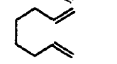
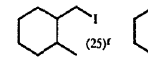
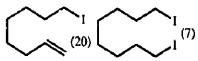
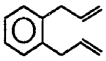
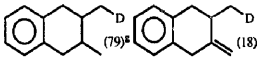
In search for an alternate and plausible explanation for the formation of **5** under only catalytic conditions, we noted that, whereas the stoichiometric reaction of **3** with a Grignard reagent was carried out in the absence of free 1,6-heptadiene, the same reaction must take place in the presence of this diene under the catalytic conditions. We have previously reported that i-$BuZrCp_2Cl$ generated in situ from t-BuMgCl and Cp_2ZrCp_2 is a convenient substitute for $HZrCp_2Cl$ in the hydrozirconation of alkenes [14a] and alkynes [14b]. It is therefore possible and likely that **5** is formed via the putative intermediate **12** not by β-H abstraction but by hydrozirconation (Scheme 2). Our attempts to distinguish the two processes using **12** or simpler dialkylzirconcenes were not practical because the Zr-containing byproducts of hydrozirconation in such cases were dialkylzirconocenes which, in turn, could undergo β-H abstraction to give products that were not readily distinguishable from those of direct β-H abstraction (Scheme 2). To support a notion that, in contrast with β-H abstraction, the relative rates of hydrozirconation with $RZrCp_2Cl$ would be: R = β-methine > R = β-methylene > R = β-methyl, two such reagents, i.e., i-$BuZrCp_2Cl$ and n-dodecyl$ZrCp_2Cl$, were generated in situ via treatment of Cl_2ZrCp_2 with t-BuMgCl and hydrozirconation of 1-dodecene with i-$BuZrCp_2Cl$ [14], respectively, in >90% yields and identified by ^1H NMR spectroscopy and analysis of n-dodecyl iodide in the latter case. Their relative reactivity was probed by reacting them with 1-octyne at 22°C in benzene. The courses of the reactions were monitored by ^1H NMR spectroscopy and analysis of (*E*)-1-iodo-1-octene obtained via iodinolysis. Whereas the yields of (*E*)-1-octenyl-zirconocene chloride observed with i-$BuZrCp_2Cl$ were 38, 55 and 77% after 18, 45 and 68 h, the corresponding yields observed with n-dodecyl$ZrCp_2Cl$ were only 9, 13 and 15%. These results support the above-mentioned assumption that $RZrCp_2Cl$ complexes containing an isoalkyl group are more effective hydrozirconating agents than those containing an n-alkyl group. Although yet to be established, it is likely that **5** can arise mainly via hydrozirconation of **12** with alkenes. Another point to be noted in Table 2 is that the *trans*/*cis* ratio of the cyclic organic products is widely variable. While no satisfactory explanation can be offered at this point, it must be linked to the facile cleavage of the C_β–C_β· bonds of zirconacyclopentanes [13g,h].

To explore the scope of the $ZrCp_2$-catalyzed reaction of non-conjugated dienes with n-BuMgCl, 1,7-octadiene, 1,2-diallylbenzene [7a], (*E*)-1-phenyl-1,6-heptadiene, 2,4,4-trimethyl-1,6-heptadiene and diallyl(benzyl)amine [7a] were chosen as test substrates. (*E*)-1-phenyl-1,6-heptadiene was prepared by the Pd-catalyzed reaction of 4-pentenylmagnesium bromide with (*E*)-β-bromostyrene [15], while the reaction of 4,4-dimethyl-6-hepten-2-one [16] with the Wittig reagent derived from Ph_3PMeBr and n-BuLi provided 2,4,4-trimethyl-1,6-heptadiene. The results of their reactions with 3–6 equiv. of n-BuMgCl in the presence of 5–20 mol% of Cp_2ZrCl_2 in THF are summarized in Table 3. In all cases monocyclization products were the major products obtained after protonolysis. Specifically, the reaction of 1,2-diallybenzene with 3 equiv. of n-BuMgCl in the presence of 15 mol% of Cp_2ZrCl_2 at 55°C for 16 h gave, after deuterolysis with DCl–D_2O, **13** (92% *cis*) and **14** in 79 and 18% yields, respectively (Eq. (3)), while quenching the reaction mixture with



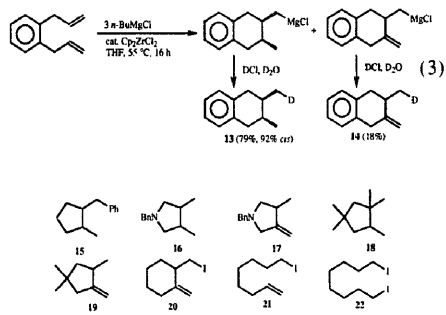
Scheme 2.

Table 3
Reaction of non-conjugated diens with n-BuMgCl catalyzed by Cp_2ZrCl_2 in THF

Diene	Equiv. of *n*-BuMgCl	mol.% of Cp_2ZrCl_2	Reaction conditions Temp. (°C)	Time (h)	Workup [a]	Cyclization products (yield [b] %), others (yield [b] %)
	3	10	55	24	I	 (45)[c] (10)
	3	20	23	24	II	 (84)[d] (≤3) (≤3) starting diene (5)
	3	5	55	24	II	 (72) (13) starting diene (≤2)
	6	20	50	3	II	 (65)[e] (15)
	3	5	55	24	I	 (25)[f] (28)  (20) (7)
	3	15	55	16	III	 (79)[g] (18)

[a] I = iodinolysis with I_2 in THF; II = protonolysis with aqueous HCl; III = deuterolysis with DCl in D_2O.
[b] By GLC.
[c] 80% *trans*.
[d] 65% *trans*.
[e] 62% *trans*.
[f] 50% *trans*.
[g] 92% *cis*.

I_2 provided the corresponding monoiodides in 55 and 14% yields, respectively. However, the other reactions were less clean. Although the combined yields of the monocyclic protonolysis products **15** and **16** derived from (*E*)-1-phenyl-1,6-heptadiene and diallyl(benzyl)amine were 84 and 65%, respectively, these compounds were only 65 and 62% *trans*, respectively. In the latter reaction, the corresponding *exo*-methylene derivative **17** was also formed in 15% yield. Curiously, the reaction of (*E*)-1-phenyl-1,6-heptadiene did not produce exocyclic alkene products in more than trace quantities ($\leq 3\%$), if any. The reaction of 2,4,4-trimethyl-1,6-heptadiene gave, after protonolysis, a 72% yield of **18** along with a 13% yield of **19**. The ^1H NMR spectrum of the stoichiometric reaction of this diene with n-Bu_2ZrCp_2 revealed that the zirconabicyclic product was a roughly 1:1 mixture of the *trans* and *cis* isomers exhibiting four Cp signals of comparable integrations between δ 6.0–6.15 ppm (THF, *p*-xylene). The lowest cyclization yield was observed with 1,7-octadiene. After iodinolysis, **11** ($\sim 50\%$ *trans*) and **20** were obtained in 25 and 28% yields, respectively. Interestingly, two acyclic products **21** and **22** were formed in 20 and 7% yields, respectively. Although the exact courses of their formation are unclear at this time, these compounds correspond to mono- and dihydrozirconation of 1,7-octadiene. It is likely that a competitive hydrozirconation involving cyclohexylmethyl–zirconium derivatives similar to that discussed above operates.



(3)

3. Conclusions

(i) The reaction of 1,6-heptadiene with EtMgBr catalyzed by Cp_2ZrCl_2 does not proceed via the expected bicyclization. The two double bonds of the diene independently react with EtMgBr in the presence of Cp_2ZrCl_2 to give, after iodinolysis, the acyclic diiodide **1**.

(ii) On the other hand, the preformed zirconabicycle **3** reacts stoichiometrically with EtMgBr to give the corresponding monocyclic monomagnesium derivative convertible to **4** via iodinolysis and ethylene–$ZrCp_2$ that can be

trapped with PMe_3 to give **9** in high yields. The corresponding reaction of **10** gives **9** and **11**.

(iii) Investigation of the stoichiometric reaction of the zirconabicycle **3** with a series of Grignard reagents has revealed that, although less reactive and less satisfactory, n-BuMgCl induces a similar transformation, providing a 91:9 mixture of the *trans* and *cis* isomers of **4** in 56% yield. Sterically more hindered Grignard reagents, such as those containing i-Bu and t-Bu react with **3** very slowly. Although slow, *s*-BuMgCl does induce the desired reaction. Those Grignard reagents lacking β-hydrogen, e.g., MeMgBr and PhMgBr, do not readily react with **3**.

(iv) Either the use of n-Bu_2Mg in place of n-BuMgCl or the use of Et_2O in place of THF radically changes the course of the reaction, producing 1,2-bis(iodomethyl)cyclopentane (**6**) rather than **4** as the major product, as recently reported [5b,10]. Neither the transmetallation reaction of $Cp_2Zr(CD_3)_2$ with CH_3MgBr nor the β-H abstraction reaction of n-Bu_2ZrCp_2 in the presence of a ten-fold excess of n-BuMgCl is affected by the choice between THF and Et_2O. It is likely, however, that the formation of bis(magnesiomethyl)cyclopentane derivatives is facile in cases where the second transmetallation step can be intramolecular.

(v) Several non-conjugated dienes have been shown to react with n-BuMgCl (3–6 equiv.) in the presence of 5–20 mol% of Cp_2ZrCl_2 in THF to give, after protonolysis, deuterolysis or iodinolysis, the corresponding monocyclization compounds as the major products which contain varying amounts of exocyclic alkenes as unexpected byproducts. Significantly, these compounds predominantly correspond to monomagnesium derivatives. The extent of formation of the corresponding dimagnesium derivatives are generally < 5%. These results sharply contrast themselves with those observed with n-Bu_2Mg and/or Et_2O.

(vi) The *exo*-methylenecycloalkane derivatives formed as byproducts likely arise not via competitive β-H abstraction but via hydrozirconation involving cycloalkylmethylzirconium derivatives. Significantly, the observed order of reactivity of alkylzirconocene chlorides as hydrozirconating agents, i.e., isobutyl > n-dodecyl, is exactly the opposite to the order of their ability to donate a β-H in β-H abstraction, clearly indicating that the two processes giving the same elimination products are discrete.

4. Experimental

4.1. General

Manipulations involving organometallics were carried out under an atmosphere of N_2 or Ar using standard techniques. Organolithium and organomagnesium halides were titrated before use [17]. Tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl; pentane, hexane, benzene and toluene from $LiAlH_4$; acetone from CaH_2; and HMPA from triphenylmethyllithium. The other starting materials were purchased from commercial sources and used as received. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini-200, GE QE-300, and JEOL EX-270 FT NMR spectrometers.

4.2. Preparation of dienes

4.2.1. (E)-1-phenyl-1,6-heptadiene

This compound was prepared by Pd-catalyzed cross coupling [15]. To a mixture of (*E*)-β-bromostyrene [18] (1.83 g, 10 mmol) and $Pd(PPh_3)_4$ (350 mg, 0.3 mmol) in 30 ml of benzene was added at 23°C a solution of 4-pentenylmagnesium bromide in Et_2O, prepared from 294 mg of magnesium turnings and 1.79 g (12 mmol) of 5-bromo-1-pentene. The reaction mixture was stirred for 15 h at 23°C, quenched with H_2O, extracted with Et_2O, washed with H_2O and dried over $MgSO_4$. After filtration and concentration, Kugelrohr distillation provided 1.1 g (64%) of the title compound (≥97% isomeric purity). IR (neat): 964s, 910m, 740m, 692s cm^{-1}. ^1H NMR ($CDCl_3$, Me_4Si): δ 1.56 (tt, *J* = 7 and 7 Hz, 2H), 2.10 (dt, *J* = 7 and 7 Hz, 2H), 2.22 (dt, *J* = 7 and 7 Hz, 2H), 4.95–5.05 (m, 2H), 5.75–5.9 (m, 1H), 6.20 (dt, *J* = 16 and 7 Hz, 1H), 6.38 (d, *J* = 16 Hz, 1H), 7.15–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 28.54, 32.41, 33.23, 114.62, 125.89, 126.79, 128.44, 130.05, 130.62, 137.80, 138.61. High resolution MS calc. for $C_{13}H_{16}$: 172.1252; found: 172.1252.

4.2.2. Diallyl(benzyl)amine

To a solution of diallylamine (3 ml, 24.3 mmol) in THF (50 ml) was added at −78°C n-BuLi (1.66 M in hexane, 15 ml, 24.9 mmol). After warming the reaction mixture to 0°C, benzyl chloride (2.8 ml, 24.3 mmol) was added. The reaction mixture was stirred at 23°C for 15 h, quenched with water, extracted with diethyl ether, washed with brine and dried over $MgSO_4$. After filtration and concentration, silica gel chromatography (pentane/diethyl ether = 95/5) afforded 2.7 g (59%) of the title compound [19]. ^1H NMR ($CDCl_3$, Me_4Si): δ 3.06 (d, *J* = 6 Hz, 4H), 3.56 (s, 2H), 5.1–5.25 (m, 4H), 5.8–5.95 (m, 2H), 7.15–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 56.37, 57.50, 117.27, 126.73, 128.10, 128.81, 135.84, 139.38.

4.2.3. 2,4,4-Trimethyl-1,6-heptadiene

To a solution of methyltriphenylphosphonium bromide (3.04 g, 8.51 mmol) in THF (10 ml) at −78°C was added n-BuLi (3.23 ml, 8.51 mmol, 2.63 M solution of n-hexane). The reaction mixture was warmed to 25°C and stirred for 1 h, cooled to −78°C, and treated with 4,4-dimethyl-6-hepten-2-one prepared by the Ti-catalyzed reaction of allyltrimethylsilane with 4-methyl-3-penten-2-one [16].

4.2.4. 1,2-Diallylbenzene

The following is a modification of a literature procedure [20]. Copper cyanide (8.06 g, 90 mmol) was azeotropically dried with toluene (20 ml) under reduced pressure at room

temperature. After addition of THF (90 ml), vinylmagnesium bromide (1 M in THF, 180 ml, 180 mmol) was added dropwise. The reaction mixture was warmed to 0°C and recooled to −78°C. α,α′-Dibromo-*o*-xylene (7.2 g, 30 mmol) in 30 ml of THF was added and the mixture was warmed to 0°C, stirred for 3 h and quenched with NH_4Cl. The usual extractive workup, and distillation provided 3.89 g (82%) of the title compound [21]. B.p. 85–90°C (5 mm Hg). IR (neat): 1638s, 994s, 912s, 752s cm^{-1}. ^1H NMR ($CDCl_3$, Me_4Si): δ 3.38 (dt, J=6 and 1.5 Hz, 4H), 4.9–5.1 (m, 4H), 5.8–6.1 (m, 2H), 7.15 (s, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 37.12, 115.98, 126.80, 129.90, 137.41, 138.27.

4.3. Preparation of bis(cyclopentadienyl)zirconabicyclo-[n.3.0]alkanes by the $ZrCp_2$-promoted bicyclization of non-conjugated dienes [7]

4.3.1. Trans-3-bis(cyclopentadienyl)zirconabicyclo-[3.3.0]octane

Representative procedure. To a mixture of Cp_2ZrCl_2 (292 mg, 1 mmol) in THF (3 ml) was added at −78°C n-BuLi (2.57 M in hexane, 0.78 ml, 2 mmol). After 1 h, 1,6-heptadiene (135 μl, 1 mmol) was added, and the reaction mixture was warmed to 23°C over 1 h. Analysis of the ^1H NMR Cp signals (δ 5.99 ppm) using mesitylene as an internal standard indicated the formation of the title compound [7a] in 99% yield. After removal of the solvents, standard and inorganics, the crude product yielded the following data. Stereoisomeric purity ≥97%. ^1H NMR (C_6D_6, Me_4Si): δ 0.8–0.85 (m, 2H), 1.15–1.4 (m, 8H), 2.05–2.15 (m, 2H), 5.74 (s, 10H). ^{13}C NMR (C_6D_6, Me_4Si): δ 17.96, 35.86, 42.73, 43.07, 109.61. High resolution MS calc. for $C_{17}H_{22}Zr$ (^{90}Zr isotopomer): 316.0765; found: 316.0759.

*4.3.2. (1R,*2R,*5R*)-2-phenyl-3-bis(cyclopentadienyl)-zirconabicyclo[3.3.0]octane*

The title compound was obtained in 85% yield from Cp_2ZrCl_2 (292 mg, 1 mmol), n-BuLi (1.66 M in hexane, 1.2 ml, 2 mmol), and (*E*)-1-phenyl-1,6-heptadiene (172 mg, 1 mmol). Stereoisomeric purity ≥96%. ^1H NMR (C_6D_6, Me_4Si): δ 0.8–1.7 (m, 8H), 2.0–2.15 (m, 1H), 2.3–2.45 (m, 1H), 3.24 (d, J=12 Hz, 1H), 5.44 (s, 5H), 5.76 (s, 5H), 6.65–7.35 (m, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 18.11, 34.88, 37.60, 38.35, 42.28, 45.32, 64.03, 110.37, 111.85, 120.09, 123.77, 128.41, 154.47.

4.3.3. 3-Benzyl-7-bis(cyclopentadienyl)-3-aza-7-zirconabicyclo[3.3.0]octane

The title compound [7a] was obtained in quantitative yield from Cp_2ZrCl_2 (292 mg, 1 mmol), n-BuLi (2.57 M in hexane, 0.78 ml, 2 mmol) and diallyl(benzyl)amine (187 mg, 1 mmol), as a 1:1 stereoisomeric mixture which underwent a slow stereoisomerization to give a 4:1 mixture of the *trans* and *cis* isomers after 40 h at 23°C. ^1H NMR (C_6D_6, Me_4Si): *trans* δ 1.00 (dd, J=11 and 4 Hz, 2H), 1.21 (dd, J=11 and 11 Hz, 2H), 1.25-1.4 (m, 2H), 2.46 (dd, J=9 and 9 Hz, 2H), 3.03 (dd, J=9 and 6 Hz, 2H), 3.70 (d, J=13 Hz, 1H), 3.79 (d, J=13 Hz, 1H), 5.69 (s, 10H), 7.1–7.55 (m, 5H); *cis* δ 0.06 (dd, J=13 and 7 Hz, 2H), 1.56 (dd, J=13 and 10 Hz, 2H), 1.83 (dd, J=8 and 8 Hz, 2H), 2.8–2.95 (m, 2H), 3.13 (dd, J=9 and 7 Hz, 2H), 3.59 (s, 2H), 5.79 (s, 5H), 5.87 (s, 5H), 7.1–7.55 (m, 5H). ^{13}C NMR (C_6D_6, Me_4Si): *trans* δ 34.07, 38.90, 61.53, 68.52, 109.76, 126.82, 128.41, 128.86, 141.58; *cis* δ 39.97, 47.72, 60.88, 69.70, 110.17, 111.32, 128.38, 129.00, 141.06 (one of the phenyl carbon signals is not discernible).

4.3.4. Cis-8-bis(cyclopentadienyl)zirconabicyclo-[4.3.0]nonane

The title compound [7a] was prepared in >90% yield as a 5:1 mixture of the *cis* and *trans* isomers from Cp_2ZrCl_2 (0.31 g, 1.06 mmol), 1,7-octadiene (0.14 ml, 0.95 mmol) and n-BuLi (3.13 M solution in hexane, 0.68 ml, 2.13 mmol). ^1H NMR (C_6D_6, Me_4Si): δ 0.6-0.8 (m, 1H), 0.8–1.1 (m, 2H), 1.2–1.8 (m, 11H), 5.91 (s, 5H), 5.97 (s, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 24.46, 34.87, 41.89, 42.86, 111.51, 111.61. The following signals for the *trans* isomer were also discernible. ^1H NMR (C_6D_6, Me_4Si): δ 5.92 (s, 10H). ^{13}C NMR (C_6D_6, Me_4Si): δ 27.19, 41.28, 45.74, 49.11, 111.18.

4.3.5. Cis-2-bis(cyclopentadienyl)zircona-2,3,3a,4,9,9a-hexahydrobenz[f]indene

The title compound [7a] was prepared in >90% yield (95% *cis*) from Cp_2ZrCl_2 (0.33 g, 1.14 mmol), 1,2-diallylbenzene (0.19 g, 1.13 mmol) and n-BuLi (3.12 M solution in hexane, 0.73 ml, 2.28 mmol). ^1H NMR (C_6D_6, Me_4Si): δ 0.5–0.7 (m, 2H), 0.8–1.1 (m, 2H), 1.2–1.4 (m, 2H), 2.7–3.0 (m, 4H), 5.84 (s, 5H), 5.87 (s, 5H), 7.1–7.3 (m, 4H). ^{13}C NMR (C_6D_6, Me_4Si): δ 39.23, 39.37, 44.78, 111.63, 111.61, 125.57, 128.94, 137.71.

4.4. Protonolysis of zirconabicycles

Either reaction mixtures containing zirconabicycles or isolated zirconabicyles dissolved in THF were treated with 3 N HCl to give the following protonolysis products after the standard extractive workup and chromatographic purification (silica gel).

*4.4.1. Trans-1-benzyl-2-methylcyclopentane (**15**)*

Yield: 67% based on (*E*)-1-phenyl-1,6-heptadiene; ≥96% *trans*. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.97 (d, J=6 Hz, 3H), 1.1–1.3 (m, 3H), 1.45–1.75 (m, 4H), 1.75–1.9 (m, 1H), 2.36 (dd, J=9 and 13.5 Hz, 1H), 2.83 (dd, J=4 and 13.5 Hz, 1H), 7.1–7.3 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 19.40, 23.20, 32.26, 34.60, 40.29, 40.86, 49.42, 125.51, 128.10, 128.89, 142.23. High resolution MS calc. for $C_{13}H_{18}$: 174.1409; found: 174.1405.

*4.4.2. 1,1,3,3,4-Pentamethylcyclopentane (**18**)*

The reaction of 2,4,4-trimethyl-1,6-heptediene (138 mg, 1 mmol) with n-Bu_2ZrCp_2 generated in situ by the treatment

of Cp_2ZrCl_2 (292 mg, 1 mmol) with n-BuLi (2.0 M in hexane, 2 ml, 2 mmol) in 2 ml of THF followed by quenching with 3 N HCl and standard extractive workup provided, after concentration, an 80% yield of the title compound [22] which was ≥95% pure by GLC and ^{13}C NMR spectroscopy. $n^{20}D$ 1.4211 (lit.[22] $n^{20}D$ 1.4212). ^1H NMR ($CDCl_3$, Me_4Si): δ 0.78 (s, 3H), 0.81 (d, J=6.7 Hz, 3H), 0.94 (s, 3H), 0.96 (s, 3H), 0.98 (s, 3H), 1.26 (dd, J=8 and 12.5 Hz, 1H), 1.37 (s, 2H), 1.50 (dd, J=6 and 12.5 Hz, 1H), 1.65–1.85 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.48, 23.17, 29.37, 32.15, 32.62, 35.50, 41.63, 43.73, 49.47, 57.44.

4.4.3. N-benzyl-3,4-dimethylpyrrolidines (16) [7a]

An essentially 1:1 stereoisomeric mixture of 3-benzyl-7-bis(cyclopentadienyl)-3-aza-7-zirconabicyclo[3.3.0]octanes was treated with 3 N HCl. After neutralization with 3 N NaOH and extraction with diethyl ether, the organic layer was washed with water and dried over $MgSO_4$. Purification by column chromatography (hexane/ethyl acetate = 5/1), the *trans* and *cis* isomers yielded the following data. *Trans* isomer: ^1H NMR ($CDCl_3$, Me_4Si): δ 0.99 (d, J=6.6 Hz, 6H), 1.7 (m, 2H), 2.24 (dd, J=9 and 7 Hz, 2H), 2.75 (dd, J=9 and 7 Hz, 2H), 3.53 (d, J=13 Hz, 1H), 3.62 (d, J=13 Hz, 1H), 7.2–7.3 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 18.44, 40.75, 60.92, 62.16, 126.72, 128.75, 139.46. High resolution MS calc. for $C_{13}H_{19}N$: 189.1518; found: 189.1536. *Cis* isomer: ^1H NMR ($CDCl_3$, Me_4Si): δ 0.88 (d, J=6.6 Hz, 6H), 1.96 (dd, J=9 and 7.5 Hz, 2H), 2.28 (m, 2H), 3.00 (dd, J=9 and 7 Hz, 2H), 3.57 (s, 2H), 7.2–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.41, 34.43, 61.04, 62.25, 126.79, 128.16, 128.82, 139.46. High resolution MS calc. for $C_{13}H_{19}N$: 189.1518; found: 189.1502.

4.4.4. 1,2-Dimethylcyclohexanes [7a]

A 5:1 mixture of the *cis* and *trans* isomers of the title compound was prepared from Cp_2ZrCl_2 (1.46 g, 5 mmol), 4.30 ml (2.33 M in hexane, 10 mmol) of n-BuLi and 1,7-octadiene (0.73 ml, 5 mmol). Due to its low boiling point the compound was not readily separated from the solvents. Instead, it was obtained in solution as a 5:1 mixture of the *cis* and *trans* isomers [23]. ^{13}C NMR ($CDCl_3$, Me_4Si): *cis* δ 15.86, 23.54, 31.34, 34.36; *trans* δ 20.26, 27.03, 35.93, 39.43.

4.4.5. Cis-2,3-dimethyltetralin

95% *cis*. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.91 (d, J=7 Hz, 6H), 1.95–2.05 (m, 2H), 2.55 (dd, J=16 and 7 Hz, 2H), 2.85 (dd, J=16 and 5 Hz, 2H), 7.0–7.1 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 15.70, 31.93, 35.41, 125.35, 129.19, 135.82; IR (neat): 2900s, 1640w, 1580w, 1500m, 910m, 470s cm^{-1}.

4.5. Preparation of 1,2-bis(iodomethyl)cycloalkanes via iodinolysis of the corresponding zirconacycles

4.5.1. 1,2-Bis(iodomethyl)cyclopentane (6) [7a]

Representative procedure. To a solution of Cp_2ZrCl_2 (0.876 g, 3 mmol) in THF (6 ml) at −78°C was added 2.60 ml (2.3 M in hexane, 6 mmol) of n-BuLi. After stirring for 1 h at −78°C, 1,6-heptadiene (0.4 ml, 3 mmol) was added dropwise. The mixture was allowed to warm to 0°C and stirred overnight. Iodine (2.28 g, 9 mmol) in THF (9 ml) was then added. After stirring for 16 h at room temperature, the reaction mixture was quenched with 3 N HCl, extracted with pentane/diethyl ether, washed with $Na_2S_2O_3$, brine and dried over $MgSO_4$. Concentration followed by purification by flash chromatography (hexane) provided 0.64 g (60%) of the title compound as a 3:1 mixture of the *trans* and *cis* isomers [24]. IR (neat): 1185s cm^{-1}. ^1H NMR ($CDCl_3$, Me_4Si): δ 1.4–2.05 (m, 7H), 2.35–2.5 (m, 1H), 3.0–3.4 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): *trans* δ 13.01, 22.81, 33.79, 46.93; *cis* δ 7.56, 22.13, 31.39, 45.76.

4.5.2. 1,2-Bis(iodomethyl)cyclohexane [7a]

This compound was prepared in an analogous manner from 0.58 g (2 mmol) of $ZrCp_2Cl_2$, 1.74 ml (2.3 M in hexane, 4 mmol) of n-BuLi, 0.3 ml (2 mmol) of 1,7-octadiene and 1.52 g (6 mmol) of iodine. Concentration and purification by flash chromatography (hexane) provided 0.38 g (52%) of the title compound as a 4:1 diasteromeric mixture of the *cis* and *trans* isomers [25]. IR (neat): 1185s cm^{-1}. ^1H NMR ($CDCl_3$, Me_4Si): δ 1.2–1.7 (m, 8H), 2.0–2.2 (m, 2H), 3.1–3.4 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): *cis* δ 8.33, 22.52, 28.82, 41.75; *trans* δ 15.67, 25.22, 32.00, 40.82.

4.5.3. Cis-2,3-bis(iodomethyl)tetralin [7c]

This compound was prepared from Cp_2ZrCl_2 (0.58 g, 2.0 mmol), 2.33 M n-BuLi in hexane (1.72 ml, 4.0 mmol), 1,2-diallylbenzene (0.32 g, 2.0 mmol) and iodine (1.52 g, 6 mmol) in 71% yield (0.59 g). IR (neat): 1582s, 1494s, 746s, 642s cm^{-1}. ^1H NMR ($CDCl_3$, Me_4Si): δ 2.3–3.3 (m, 10H), 7.07 (s, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.67, 33.26, 40.48, 126.27, 129.32, 133.54.

4.6. Reaction of 3-bis(cyclopentadienyl)zirconabicyclo-[3.3.0]octane with various organomagnesium reagents

4.6.1. Ethylmagnesium bromide

Representative procedure. To a solution of 3-bis(cyclopentadienyl)zirconabicyclo[3.3.0]octane (3) (1 mmol) in THF were added at 0°C PMe_3 (135 μl, 1.3 mmol) and EtMgBr (1.0 M in THF, 3 ml, 3 mmol). The reaction mixture was warmed to 25°C. After 2 h, mesitylene (139 μl, 1 mmol) was added to the reaction mixture as an internal standard and an aliquot (0.5 ml) was transferred to a 5 mm NMR tube containing C_6D_6 (0.2 ml). Analysis by ^1H NMR spectroscopy indicated the clean formation of $Cp_2Zr(CH_2{=}CH_2)$-PMe_3 [13] in 91% yield (δ Cp 5.10 ppm, d, J=2 Hz). The reaction mixture was treated with I_2 (1.52 g, 6 mmol) in THF (6 ml) at 0°C, stirred for 12 h at 23°C, quenched with 3 N HCl, extracted with Et_2O, washed with $NaHCO_3$ and $Na_2S_2O_3$, dried over $MgSO_4$, filtered and concentrated. 1-Iodomethyl-2-methylcyclopentane (4) was obtained in >90% GLC yield, using nonane as a standard, as a 92:8

mixture of the *trans* and *cis* isomers. Purification by column chromatography (silica gel, hexane) provided 0.16 g (71%) of 1-iodomethyl-2-methylcyclopentane. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.82 (*cis*) and 0.99 (*trans*) (2d, J = 7 and 6 Hz, 3H), 1.2–2.0 (m, 8H), 3.1–3.45 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): *trans* δ 13.90, 19.07, 22.94, 33.66, 35.25, 40.73, 49.42; *cis* δ 9.58, 14.07, 22.78, 30.75, 33.31, 36.73, 46.74; IR (neat): 1180 cm^{-1}. No other compounds, such as **3**, **5** and **6**, were present in more than trace quantities.

4.6.2. n-Butylmagnesium chloride

A similar reaction using n-BuMgCl (2.0 M in THF, 2.5 ml, 5 mmol) in the absence of PMe_3 for 24 h led to the formation of **4** in 56% yield as a 91:9 mixture of the *trans* and *cis* isomers. The amounts of **3**, **5** and **6** were $\leq$2–3%, if any. The corresponding reaction run in Et_2O led, after iodinolysis, to the formation of **4** in 17% yield as an 85:15 mixture of the *trans* and *cis* isomer and **6** in 49% yield as a 99:1 mixture of the *trans* and *cis* isomers. The ^{1}H NMR spectrum of the reaction mixture prior to iodinolysis indicated that 97% of **3** had been consumed.

4.6.3. Di(n-butyl)magnesium

The reaction of **3** (0.5 mmol) with n-Bu_2Mg (1.5 mmol) in THF led after 12 h at 23°C and after iodinolysis to the formation of **4** in 32% yield (*trans*:*cis* = 79:21) and **6** in 52% yield (*trans*:*cis* = 55:45). Analysis of the reaction mixture by ^{1}H NMR spectroscopy prior to iodinolysis indicated that 90% of **3** had been consumed. The corresponding reaction in Et_2O gave after iodinolysis a 30% yield of **4** (*trans*:*cis* = 68:32) along with 48% of **6** (*trans*:*cis* = 84:16). Again, the ^{1}H NMR spectrum of the reaction mixture before iodinolysis indicated that at least 97% of **3** had been consumed.

4.6.4. i-Butylmagnesium chloride

When 1 mmol of **3** in THF was treated with PMe_3 (135 μl, 1.3 mmol) and i-BuMgCl (2.0 M in Et_2O, 1.3 ml, 3 mmol), analysis of the ^{1}H NMR spectrum of the reaction mixture after 17 h at 23°C indicated that 90% of the starting material (δ Cp 5.98 ppm) was remaining unreacted. Iodinolysis of the mixture provided a 93% GLC yield of **6** along with a 7% GLC yield of **4** as a 1:1 mixture of the *trans* and *cis* isomers.

4.6.5. s-Butylmagnesium chloride

The reaction of **3** (1 mmol) with *s*-BuMgCl (2.0 M in Et_2O, 1.5 ml, 3 mmol) and PMe_3 (135 μl, 1.3 mmol) in THF at 23°C required 48 h for 97% completion, with 3% of **3** still remaining unreacted. The yield of $Cp_2Zr(CH_2{=}CHEt)PMe_3$ [8f] was 97% by ^{1}H NMR spectroscopy (δ 5.08 (d, J = 2 Hz) and 5.09 (d, J = 2 Hz)). Treatment with I_2 (1.52 g, 6 mmol) produced **4** in 75% yield as a 1:1 stereoisomeric mixture along with a 6% yield of **6**.

4.6.6. t-Butylmagnesium chloride

In the reaction of **3** with t-BuMgCl (2.0 M in Et_2O, 1.5 ml, 3 mmol) in the presence of PMe_3 (1.3 mmol), 91% of **3** remained unreacted after 24 h at 23°C.

4.6.7. Methylmagnesium bromide

The use of MeMgBr (3.2 M in Et_2O, 0.94 ml, 3 mmol) in place of t-BuMgCl did not induce any noticeable reaction, with 97% of **3** remaining unreacted after 17 h at 23°C.

4.6.8. Phenylmagnesium bromide

The use of PhMgBr (4.0 M in Et_2O, 0.75 ml, 3 mmol) did not induce any noticeable reaction, with 97% of **3** remaining unreacted after 17 h at 23°C. In the experiments, Sections 4.6.6–4.6.8, heating the mixture at 55°C induced a slow decomposition of **3** by an unspecified reaction.

These results are summarized in Tables 1 and 2.

*4.7. Reaction of 8-bis(cyclopentadienyl)zirconabicyclo-[4.3.0]nonane (**10**) with ethylmagnesium bromide*

The zirconabicycle **10** was prepared as described above from Cp_2ZrCl_2 (292 mg, 1 mmol) and 1,7-octadiene (148 μl, 1 mmol) in 100% yield as a 5:1 mixture of the *cis* and *trans* isomers (δ Cp_{cis} 6.15 and 6.19 ppm, δ Cp_{trans} 6.14 ppm). To this were added sequentially at 0°C PMe_3 (1.35 μl, 1.3 mmol) and EtMgBr (1.0 M in THF, 3 ml, 3 mmol). The reaction mixture was warmed to 23°C and analysis by ^{1}H NMR spectroscopy after 19 h indicated the formation of $Cp_2Zr(CH_2{=}CH_2)PMe_3$ [13] in 100% yield. The reaction mixture was treated with I_2 (1.52 g, 6 mmol), quenched with 3 N HCl, extracted with Et_2O, washed with $NaHCO_3$ and $Na_2S_2O_3$, and dried over $MgSO_4$. After filtration and concentration 1-iodomethyl-2-methylcyclohexane (**11**) was obtained in 90% GLC yield, using nonane as an internal standard, as a 6:1 mixture of the *cis* and *trans* isomers. The spectral data for the *cis* isomer are as follows. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.82 (d, J = 7 Hz, 3H), 1.1–1.7 (m, 8H), 1.7–1.9 (m, 1H), 1.9–2.1 (m, 1H), 3.11 (d, J = 7.5 Hz, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 12.53, 12.86, 21.51, 25.12, 27.93, 32.49, 32.61, 43.14.

*4.8. Zirconium-catalyzed reaction of 1,6-heptadiene with ethylmagnesium bromide to produce 3,7-bis(iodomethyl)-nonane (**1**)*

To 1,6-heptadiene (135 μl, 1 mmol) in 2 ml of THF were added at 0°C Cp_2ZrCl_2 (58.4 mg, 0.2 mmol) and EtMgBr (1.0 M in THF, 6 ml, 6 mmol). After stirring the mixture at 25°C for 24 h, I_2 (2.28 g, 9 mmol) was added. The mixture was stirred overnight at 25°C, quenched with H_2O, extracted with pentane–diethyl ether, washed with $Na_2S_2O_3$ and dried over $MgSO_4$. Concentration followed by flash chromatography (hexane) provided 0.21 g (51% yield) of **1**. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.8–0.9 (m, 6H), 1.0–1.15 (m, 2H), 1.15–1.45 (m, 10H), 3.2–3.35 (m, 4H). ^{13}C NMR ($CDCl_3$,

Me_4Si): δ 10.89, 15.91 (16.04), 23.29 (23.41), 26.89 (27.10), 34.03, 39.92 (40.03). IR (neat): 1190m cm^{-1}. High resolution MS calc. for $C_{11}H_{22}I_2$: 407.9811; found: 407.9807. Judging from the ^{13}C NMR spectrum the product consisted of an essentially 1:1 diastereomeric mixture.

4.9. Zirconium-catalyzed cyclization reaction of non-conjugated dienes with n-butylmagnesium chloride or di(n-butyl)magnesium

The results of the following experiments, Sections 4.9.1–4.9.6 are summarized in Tables 1 and 3.

4.9.1. Reaction of 1,2-diallylbenzene

4.9.1.1. Zirconium catalyzed carbomagnesiation

To a solution of Cp_2ZrCl_2 (29 mg, 0.1 mmol) in 2 ml of THF were added sequentially n-BuMgCl (2.0 M in THF, 1.5 ml, 3 mmol) and 1,2-diallylbenzene (158 mg, 1 mmol) at −78°C. After 1 h, the reaction mixture was allowed to warm and then heated at 55°C for 24 h.

4.9.1.2. Protonolysis

In one run, the reaction mixture was quenched with 3 N HCl, extracted with hexane, washed with $NaHCO_3$ and brine, and dried over $MgSO_4$. Concentration provided 150 mg (94% combined yield) of 2,3-dimethyltetralin (92% *cis*) and 2-methylene-3-methyltetralin as an 85:15 mixture. The latter compound has been characterized as its monodeuterio derivative as described below.

4.9.1.3. Deuterolysis

In another run using 3 equiv. of n-BuMgCl, 15 mol% of Cp_2ZrCl_2 at 55°C and for 16 h, the mixture was quenched with 3 N DCl in D_2O to give the expected monodeuterio derivatives **13** (92% *cis*) and **14** in 79 and 18% yields, respectively.

13: ^{13}C NMR ($CDCl_3$, Me_4Si): δ 15.45 (t, J = 19.3 Hz), 15.76, 32.01, 35.55, 125.78, 129.61, 136.22.

14: ^{13}C NMR ($CDCl_3$, Me_4Si): δ 18.35 (t, J = 19.4 Hz), 34.80, 37.70, 39.62, 106.50, 126.29, 127.99, 128.44, 128.90, 136.68, 136.82, 150.18.

4.9.1.4. Iodinolysis

In the third run, the mixture was quenched with I_2 (1.01 g, 4 mmol). Concentration provided 2-iodomethyl-3-methyltetralin (~90% *cis*), 2-methylene-3-iodomethyltetralin and 2,3-bis(iodomethyl)tetralin in a 8:2:1 molar ratio and in 75% overall yield. Purification by column chromatography (silica gel) readily separated the diiodide, but the two monoiodides were not separated. They were characterized as a mixture.

2-Iodomethyl-3-methyltetralin: ^1H NMR (partial, $CDCl_3$, Me_4Si): δ 0.88 (*cis*, d, J = 7 Hz), 1.08 (*trans*, d, J = 7 Hz). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 10.64, 13.94, 31.47, 32.76, 36.50, 41.03, 125.85, 126.06, 129.31, 129.48, 134.58, 135.02. IR (neat): 1180m cm^{-1}. High resolution MS calc. for $C_{12}H_{15}I$: 286.0219; found: 286.0216.

2-Methylene-3-iodomethyltetralin: ^1H NMR (partial, $CDCl_3$, Me_4Si): δ 3.5 (bs, 2H), 4.9 (bs, 1H), 5.0 (bs, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 10.77, 36.29, 36.95, 43.48, 110.33, 126.19, 126.53, 127.99, 128.99, 134.86, 136.20, 137.76. IR (neat): 890s cm^{-1}. High resolution MS calc. for $C_{12}H_{13}I$: 284.0062; found: 284.0059.

4.9.2. Reaction of 1,6-heptadiene

The reaction of 1,6-heptadiene (134 μl, 1 mmol) with n-BuMgCl (2.0 M in THF, 1.5 ml, 3 mmol) in the presence of Cp_2ZrCl_2 (29 mg, 0.1 mmol) was carried out as above. Iodinolysis with I_2 (1.01 g, 4 mmol) produced 1-iodomethyl-2-methylcyclopentane (**4**) (80% *trans*) and 1-methylene-2-iodomethylcyclopentane (**5**) in 45 and 10% yields, respectively. These compounds were separated by chromatography (silica gel, hexane).

5: ^1H NMR ($CDCl_3$, Me_4Si): δ 1.2–2.8 (m, 7H), 3.1–3.45 (m, 2H), 4.85–4.9 (m, 1H), 5.0–5.05 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 12.44, 23.68, 33.78, 34.45, 46.08, 106.82, 154.06. IR (neat): 890s cm^{-1}. High resolution MS calc. for $C_7H_{11}I$: 222.9984; found: 222.9980.

The same reaction run with n-Bu_2Mg (1.5 mmol) gave after 24 h at 23°C and after iodinolysis, a 28% yield of **4** (*trans*:*cis* = 82:18), along with a 26% yield of **6** (*trans*:*cis* = 77:23), and a 6% yield of **5**.

When the reaction of 1,6-heptadiene with n-BuMgCl catalyzed by Cp_2ZrCl_2 was carried out in Et_2O [5b], the major product was 1,2-bis(iodomethyl)cyclopentane which was produced in 40% yield along with a 10% yield each of **4** and **5**. The corresponding reaction run with n-Bu_2Mg gave **6** in 75% yield (*trans*:*cis* = 86:14) and **4** in 17% yield (*trans*:*cis* = 81:19). Only a trace amount (<2%) of **5** was observed.

4.9.3. Reaction of (E)-1-phenyl-1,6-heptadiene

This reaction was carried out as above at 23°C for 24 h using (*E*)-1-phenyl-1,6-heptadiene (172 mg, 1 mmol), 1.5 ml of n-BuMgCl (2.0 M in THF, 3 mmol) and Cp_2ZrCl_2 (58 mg, 0.2 mmol). Protonolysis provided, after column chromatography (silica gel, pentane), 114 mg (65%, 84% by GLC) of 1-benzyl-2-methylcyclopentane as a 2:1 mixture of the *trans* and *cis* isomers. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.89 (*cis*) and 0.96 (*trans*) (2 d, J_{cis} = 7 Hz, J_{trans} = 6 Hz, 3H), 1.1–2.15 (m, 8H), 2.35 (*trans*) and 2.39 (*cis*) (2 dd, J = 9 and 13.5 Hz, 1H), 2.70 (*cis*) and 2.82 (*trans*) (2 dd, J_{cis} = 6 and 13.5 Hz, J_{trans} = 4 and 13.5 Hz, 1H), 7.1–7.3 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): *cis* δ 15.15, 22.37, 29.40, 33.33, 36.28, 36.60, 45.12, 125.42, 128.11, 128.71, 142.53. Analysis of the ^1H and ^{13}C NMR spectra of the crude mixture indicated that the two possible exocyclic alkenes are obtained in ≤3% each, if any.

4.9.4. Reaction of 2,4,4-trimethyl-1,6-heptadiene

This reaction was carried out as above at 55°C for 24 h using 2,4,4-trimethyl-1,6-heptadiene (138 mg, 1 mmol), n-BuMgCl (2.0 M in THF, 1.5 ml, 3 mmol) and Cp_2ZrCl_2 (15 mg, 0.05 mmol). Protonolysis provided 1,1,3,3,4-pentamethylcyclopentane (**18**) [22] and 2,2,4,4-tetramethyl-1-methylenecyclopentane (**19**) in 72 and 13% yields, respectively. The minor product **19** was hydroborated with BH_3 in THF and treated with I_2 and NaOH in MeOH [26] to produce, after purification by column chromatography (silica gel 230–400, pentane), 2-iodomethyl-1,1,4,4-tetramethylcyclopentane. Yield: 36%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.81 (s, 3H), 1.00 (s, 3H), 1.02 (s, 3H), 1.04 (s, 3H), 1.38 (dd, J = 12.6 and 12.6 Hz, 1H), 1.51 (s, 2H), 1.92 (dd, J = 12.6 and 6.3 Hz, 1H), 2.0–2.2 (m, 1H), 2.94 (dd, J = 11.0 and 9.3 Hz, 1H), 3.27 (dd, J = 9.3 and 4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.84, 23.18, 29.68, 31.92, 32.17, 34.55, 42.53, 48.60, 52.81, 58.83. High resolution MS calc. for $C_{10}H_{19}I$: 266.0532; found: 266.0529.

4.9.5. Reaction of diallyl(benzyl)amine

This reaction was carried out at 50°C for 3 h using diallyl(benzyl)amine (375 mg, 2 mmol), n-BuMgCl (1.05 M in THF, 11.4 ml, 12 mmol) and Cp_2ZrCl_2 (117 mg, 0.4 mmol). Protonolysis provided *N*-benzyl-3,4-dimethylpyrrolidine (**16**) (62% *trans*) and *N*-benzyl-3-methylene-4-methylpyrrolidine (**17**) in 65 and 15% yields, respectively.

17: ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.10 (d, J = 6.6 Hz, 3H), 2.08 (dd, J = 8.6 and 8.6 Hz, 1H), 2.71 (m, 1H), 2.95–3.05 (m, 2H), 3.42 (d, J = 13.5 Hz, 1H), 3.57 (s, J = 12.9 Hz, 1H), 3.63 (d, J = 12.9 Hz, 1H), 4.81 (d, J = 2 Hz, 1H), 4.87 (d, J = 2 Hz, 1H), 7.2–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 17.70, 37.54, 59.51, 60.70, 62.34, 103.79, 126.95, 128.23, 128.82, 138.96, 154.09. High resolution MS calc. for $C_{13}H_{17}N$: 187.1361; found 187.1367.

4.9.6. Reaction of 1,7-octadiene

This reaction was carried out at 55°C for 24 h using 1,7-octadiene (331 mg, 3.0 mmol), n-BuMgCl (2.0 M in THF, 4.5 ml, 9.0 mmol) and Cp_2ZrCl_2 (58 mg, 0.2 mmol). Iodinolysis provided a mixture of the following iodides, identified by ^{13}C NMR ($CDCl_3$, Me_4Si) spectroscopy, in the yields shown in parentheses.

1-Iodomethyl-2-methylcyclohexane (**11**) (1:1 diastereomeric mixture) (25%) (δ_{trans} 10.36, 24.27, 28.63, 34.35, 34.90, 45.66, 107.53, 150.66; δ_{cis} 12.54, 12.86, 21.51, 25.13, 27.93, 32.61, 32.63, 43.15).

1-Methylene-2-iodomethylcyclohexane (**20**) (28%) (δ 10.50, 24.22, 28.57, 34.30, 34.85, 45.59, 107.49, 150.67).

8-Iodo-1-octene (**21**) [27] (20%) (δ 7.26, 28.08, 28.75, 30.43, 33.59, 33.75, 114.74, 139.30).

1,8-Diiodooctane (**22**) (7%) (δ 7.23, 28.36, 30.42, 33.50).

4.10. 1-Iodomethyl-2-methylcyclohexane (11)

An authentic sample of (94% *cis*) was prepared by the treatment of 8-bis(cyclopentadienyl)zirconabicyclo[4.3.0]-nonane with 1 equiv. of I_2 in THF first at −30°C and then at 25°C for 30 min, followed by quenching with 3 N HCl, extraction with Et_2O, washing with $Na_2S_2O_3$ and $NaHCO_3$. Its NMR spectra were indistinguishable from those of the sample obtained by the reaction of **10** with EtMgBr.

4.11. Reaction of $Cp_2Zr(CD_3)_2$ with CH_3MgBr

Zirconocene dichloride dissolved in Et_2O or THF was treated with 2 equiv. of CD_3MgI to give $Cp_2Zr(CD_3)_2$ in quantitative yield. To this was added 1 equiv. of CH_3MgBr. The course of the reaction was monitored at 20°C by ^{1}H NMR spectroscopy. After 1 h 18 and 20% of the CH_3 group was incorporated in $Cp_2Zr(CD_3)(CH_3)$ and/or $Cp_2Zr(CH_3)_2$ in Et_2O and THF, respectively.

4.12. Decomposition of n-Bu_2ZrCp_2 in the presence of n-BuMgCl

Treatment of Cp_2ZrCl_2 with 2 equiv. of n-BuLi [8b,f] in Et_2O or THF produced n-Bu_2ZrCp_2 in quantitative yield. After addition of 10 equiv. of n-BuMgCl at −78°C, an aliquot was transferred to an NMR tube, and the course of the reaction was monitored at 20°C by ^{1}H NMR spectroscopy. After 24 min 59 and 60% of n-Bu_2ZrCp_2 had decomposed in Et_2O and THF, respectively.

4.13. Hydrozirconation of 1-octyne with chloro(isobutyl)-zirconocene [14b]

The preparation of i-BuZrCp$_2$Cl was carried out in the following manner as previously reported [14b]. To a suspension of Cl_2ZrCp_2 (585 mg, 2 mmol) in dry benzene (5 ml) was added at 22°C t-BuMgCl (2.0 M in Et_2O, 1 ml, 2 mmol). The mixture was heated with stirring at 50°C for 1 h. Analysis of the reaction mixture by ^{1}H NMR spectroscopy using mesitylene as an internal standard (240 mg, 278 μl, 2 mmol) indicated the formation of i-BuZrCp$_2$Cl (δ_{Cp} 5.81 ppm) in 90% yield. To this mixture was added 1-octyne (220 mg, 295 μl, 2 mmol). An aliquot (0.5 ml) was transferred to a 5 mm NMR tube containing C_6D_6 (0.2 ml), and the reaction was monitored by ^{1}H NMR spectroscopy at 22°C. The extent of the formation of chloro(1-octenyl)zirconocene (δ_{Cp} 5.88 ppm) was 38, 55 and 77%, after 18, 45 and 68 h, respectively. Analysis after 68 h of an iodinated aliquot by GLC using n-undecane as an internal standard indicated the formation in 70% yield of (*E*)-1-iodo-1-octene. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.85–1.95 (m, 3H), 1.2–1.4 (m, 8H), 2.03 (dt, J = 7 and 7 Hz, 2H), 5.95 (d, J = 14 Hz, 1H), 6.50 (dt, J = 7 and 14 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.07, 22.49, 28.25, 28.53, 31.50, 35.98, 74.27, 146.62.

4.14. Hydrozirconation of 1-octyne with chloro-(n-dodecyl)zirconocene

The preparation of chloro(n-dodecyl)zirconocene was carried out as reported previously [14a] by adding at 22°C t-BuMgCl (2.0 M in Et_2O, 1.1 ml, 2.2 mmol) to a mixture of Cl_2ZrCp_2 (585 mg, 2 mmol) and 1-dodecene (337 mg, 444 μl, 2 mmol) in dry benzene (5 ml) and stirring the resulting mixture for 24 h. Analysis of the mixture by ^1H NMR spectroscopy using mesitylene as an internal standard (240 mg, 278 μl, 2 mmol) indicated the formation of chloro(n-dodecyl)zirconocene ($\delta_{C_5H_5}$ 5.82 ppm) in 100% yield. Analysis of an iodinated aliquot by GLC using n-undecane as an internal standard indicated the formation of 1-iodododecane in 100% yield. To this mixture was added 1-octyne (220 mg, 295 μl, 2 mmol) and an aliquot (0.5 ml) was transferred to a 5 mm NMR tube containing C_6D_6 (0.2 ml). The formation of chloro(1-octenyl)zirconocene was monitored by ^1H NMR spectroscopy at 22°C, and its yields were 9, 13 and 15%, after 18, 45 and 68 h, respectively. Analysis after 68 h of an iodinated aliquot by GLC indicated the formation of 1-iodododecane in 82% yield, indicating that 82% of chloro(n-dodecyl)zirconocene had remained unreacted.

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