

# Adjusting the Features of Active Metallocene Ziegler Systems for Their Potential Use as Carbon–Carbon Coupling Catalysts in Organic Synthesis

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A variety of bent metallocene dichloride/methylalumoxane catalysts, derived from the zirconocene complexes **10**, **12–18**, have been employed in intramolecular olefin-coupling reactions yielding monomeric or dimeric products. This was achieved by using optimized reaction conditions employing low substrate concentrations (1.0–1.8 M) and rather long reaction times. Under these particular conditions, 1,5-hexadiene was cyclodimerized to give 1-methylene-3-(cyclopentylmethyl)cyclopentane (**11**). 1,6-Heptadiene was cleanly

converted to methylenecyclohexane, and *cis*-1,2-divinylcyclopentane (**19**) and *cis*-1,2-divinylcyclohexane (**22**) were cyclized to yield 2-methylenebicyclo[3.3.0]octane (**20**) and 7-methylenebicyclo[4.3.0]nonane (**23**), respectively. In many cases, the cyclization products were accompanied by isomers originating from double-bond shift reactions that often occur rapidly at these catalyst systems under the specific reaction conditions chosen to keep the products in the monomeric regime.

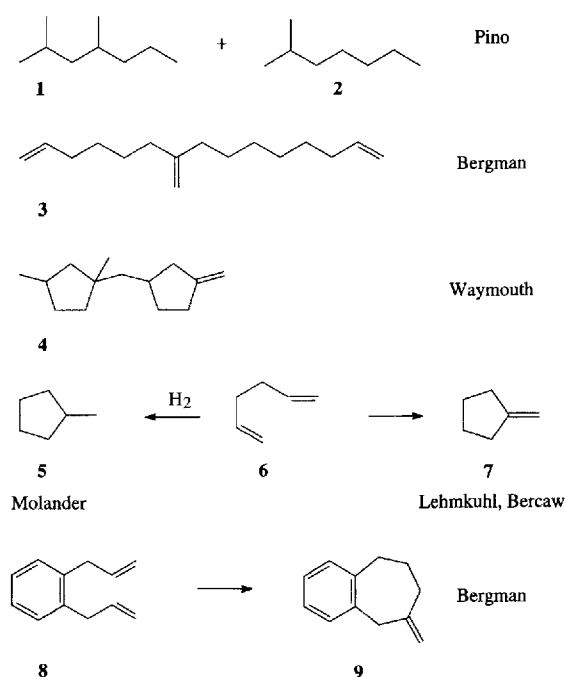
Homogeneous Ziegler catalysts based on group-4 bent metallocenes have become of enormous importance in  $\alpha$ -olefin polymerization<sup>[1]</sup>. Over the past decade, a great variety of such catalyst systems have been developed which are capable of performing the repetitive  $\alpha$ -olefin carbon–carbon coupling process with an extremely high reaction rate, often accompanied with remarkably high diastereoselectivity<sup>[2]</sup>. Some of these specifically developed  $\alpha$ -olefin polymerization catalyst systems come close, or even surpass, enzymatic catalysts with regard to some of their reactivity/selectivity characteristics.

It would, of course, be highly desirable to use these fascinating features of the bent metallocene Ziegler catalysts in organic synthesis. For such applications it would be necessary to find a means of drastically reducing the  $k_{\text{prop(agation)}}/k_{\text{term(ination)}}$  ratio of rate constants. If that could be achieved, then the preferred carbon–carbon coupling process at these catalyst systems could ultimately be diverted from a rapid polymerization process to e.g. a synthetically useful dimerization of olefins<sup>[3]</sup>.

There have been a few attempts at bringing about the required, significant decrease in the  $k_{\text{prop}}/k_{\text{term}}$  ratio<sup>[4–7]</sup>. One obvious way is to introduce an additional terminating reaction. Hydrogenation has been used (see Scheme 1; formation of the products **1** or **5**), but this has the disadvantage of yielding unfunctionalized, low molecular mass products<sup>[4]</sup>. In a few cases, hydrosilylation or carbometallation reactions have successfully been employed to terminate the catalytic C–C coupling sequence after forming a single new carbon–carbon bond<sup>[5]</sup>.

Alternatively, one might search for specific metallocene catalysts that inherently favour the formation of low mo-

Scheme 1. Selected examples of nonpolymeric products obtained by carbon–carbon coupling processes at various metallocene Ziegler-type catalyst systems (for details see text)



lecular mass products. Scandocene and ytrocene catalyst systems have been shown to favour low  $k_{\text{prop}}/k_{\text{term}}$  ratios and have consequently been used for various  $\alpha,\omega$ -diolefin cyclizations<sup>[6]</sup>. It has also been argued that the classical zirconocene/methylalumoxane Ziegler catalysts may favour the formation of low molecular mass products at very low Al:Zr ratios (e.g. ca. 1:1). Under such conditions, the non-

polymeric C–C coupling products **3** (from 1,7-octadiene) and **9** (from *o*-diallylbenzene) were indeed obtained<sup>[7]</sup>.

In recent years in our laboratory we have investigated potential ways of using the group-4 bent metallocene/MAO Ziegler-type catalyst systems for inducing ring-closure reactions of  $\alpha,\omega$ -diolefins to yield preferentially monomeric or at least low molecular mass carbon–carbon coupling products<sup>[8]</sup>. In view of the increased general interest in such reactions we describe a variety of typical examples in this article.

## Results and Discussion

Typically, the zirconocene/MAO Ziegler catalyst systems operate at rather high Al:Zr ratios<sup>[1,2]</sup>. Nevertheless, the molecular mass of e.g. polypropylene formed at such catalyst systems is dramatically dependent on a variety of easily adjustable parameters. First, there is the nature of the bent metallocene and the substitution pattern at e.g. the cyclopentadienyl or indenyl ligands. In particular, some open (e.g. non-*ansa*) metallocenes exhibit a high tendency of forming rather low molecular mass products<sup>[9]</sup>. Opening the Cp–M–Cp angle in *ansa*-metallocenes has a similar effect<sup>[10]</sup>. Secondly, many metallocene/MAO catalyst systems show a pronounced temperature dependence, sometimes exhibiting a drastic decrease in the  $k_{\text{prop}}/k_{\text{term}}$  ratio with increasing temperature. Dilution of the system also seems to lead to decreased molecular masses. In view of these commonly observed characteristics of the zirconocene-derived homogeneous Ziegler catalyst systems, it should be possible to shift the favoured product formation of the  $\alpha,\omega$ -diolefin C–C coupling process into the monomeric (or low molecular mass) regime by very carefully adjusting the specific reaction conditions and by selecting the appropriate bent metallocene backbone. This we have done for a number of selected examples and have indeed found that some such systems can be adjusted in such a way that the reactions turn into catalytic processes that may become useful in the synthesis of some monomeric target molecules.

In the initial phase of this study we briefly investigated the cyclization reactions of 1,5-hexadiene. It was known from the work of Waymouth et al. that many metallocene Ziegler catalysts can be used for the cyclopolymerization of this  $\alpha,\omega$ -diolefin<sup>[11]</sup>. We employed the  $\text{Cp}_2\text{ZrCl}_2$  (**10a**)/MAO catalyst system which is known to give generally rather low molecular mass  $\alpha$ -olefin C–C coupling products. Also, a short series of Cp-substituted derivatives of the metallocene component was employed [ $(\text{RCp})_2\text{ZrCl}_2$ , R =  $\text{CH}_3$  (**10b**), R = isopropyl (**10c**), R = *tert*-butyl (**10d**)]. We used rather high [Al]:[Zr] ratios for generating these catalysts (see e.g. Table 1). All these simple catalyst systems converted 1,5-hexadiene to cyclopolymer when high  $\alpha,\omega$ -diolefin concentrations were used or the neat nonconjugated diene was employed.

However, the situation changed upon dilution of the system. Using a 1 M solution of 1,5-hexadiene in toluene, dimers, trimers and tetramers were found to be the principal products. In the temperature range between ambient and 70 °C, the dimeric reaction product **11** was predominantly

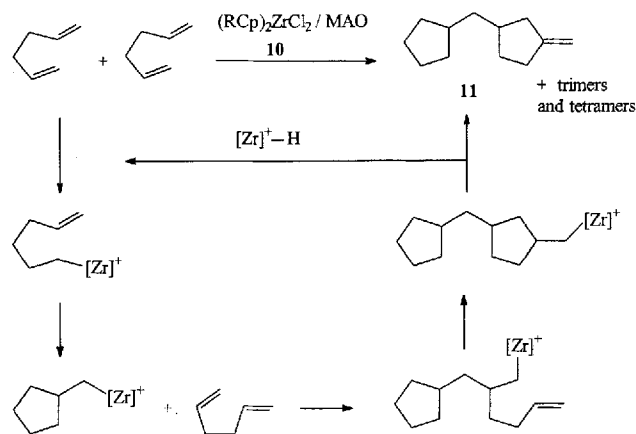
formed, albeit in a rather slow carbon–carbon coupling reaction. Reaction times of about a day at room temperature were required in order to obtain sufficient quantities of the cyclodimerization product **11** to allow its isolation by distillation. The formation of the cyclodimer **11** can be rationalized by a mechanistic scheme (see Scheme 2) involving a sequence of individual steps similar to those proposed by Waymouth et al. for the cyclopolymerization reaction of 1,5-hexadiene or the catalytic formation of oligomers starting from 2-methyl-1,5-hexadiene<sup>[12]</sup>. We did not obtain any monomeric cyclization products under the conditions used in this study. The differently substituted **10a**–**10d**/MAO catalysts all behaved similarly (see Table 1).

Table 1. Catalytic cyclization of 1,5-hexadiene using various substituted  $(\text{RC}_5\text{H}_4)_2\text{ZrCl}_2$ /methylalumoxane catalysts (in toluene solution)

$(\text{RCp})_2\text{ZrCl}_2$ (R = )	<b>10a</b> (H)	<b>10b</b> (Me)	<b>10c</b> (iPr)	<b>10d</b> (tBu)	<b>10d</b> (tBu)
[Hexadiene]:[Zr]	2400	2400	2400	1900	2400
[Al]:[Zr]	360	360	360	360	360
Hexadiene conc. [M]	1.3	1.3	1.3	1.0	1.3
Temp [°C]	70	70	70	50	50
React. time [h]	5	5	5	5	5
Hexadiene consumed (%)	63	36	44	29	35
Product composition (%) <sup>[a]</sup>					
Monomers	–	–	1 <sup>[b]</sup>	–	–
Dimers	58	51	46	40	36
Trimers	30	36	33	33	35
Tetramers	12	13	20	27	29

[a] Determined by GLC. – [b] Potentially isomerized starting material.

Scheme 2

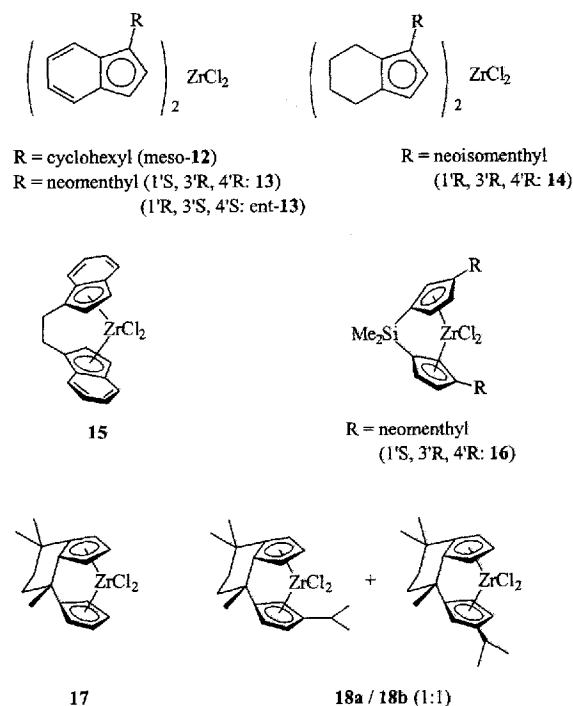


It occurred to us that the successful diolefin cyclization process might be facilitated by choosing substrates that had the two reacting olefinic units in a favourable spatial arrangement. Therefore, *cis*-1,2-divinylcyclopentane was the starting material of choice for our next series of experiments. The diolefin **19** was prepared according to a synthetic sequence published some years ago in the literature<sup>[13]</sup>. Dibromocarbene was added to 1,5-cyclooctadiene and the resulting bicyclic dibromocyclopropane system was then treated with methyllithium in ether. Cyclopropylidene  $\rightarrow$  allene rearrangement led to the formation of 1,2-*cis*-6-

cyclononatriene, which was subsequently reduced by treatment with sodium in liquid ammonia to yield *cis,cis*-1,5-cyclononadiene. The thermally induced Cope rearrangement (at 230 °C) eventually produced the desired *cis*-1,2-divinylcyclopentane product **19** in good yield.

We used the zirconocene dichlorides **10a**, and **12–18a/b** (see Scheme 3 and Table 2) to generate metallocene/methylalumoxane Ziegler catalysts for the conversion of **19**. The catalytic reactions were all carried out in dilute benzene solution (1.0–1.9 M) in a temperature range of 20–60 °C. The reactions were all rather slow, requiring total reaction times ranging from a few hours to almost one week to go to completion. The product distribution was monitored directly by <sup>1</sup>H NMR (in [D<sub>6</sub>]benzene) and indirectly by GLC analysis. In addition, by a combination of chromatographic work-up and distillation, the major products were isolated from several representative catalytic reaction mixtures and characterized. Representative results of the respective series of experiments are listed in Table 2.

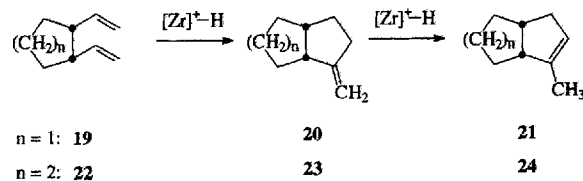
Scheme 3



For the Ziegler catalyst generation we selected zirconocene dichloride components, most of which are known to favour rather low molecular mass  $\alpha$ -olefin polymer formation. By selecting the reaction conditions indicated in Table 2, in many of the cases investigated the simple cyclization reaction of *cis*-1,2-divinylcyclopentane (**19**) to yield monomeric products exhibiting the bicyclo[3.3.0]octane framework could be achieved.

We started this series of experiments with the parent Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO catalyst. This catalyst system cleanly converts the diolefin **19** at 20 °C in dilute benzene solution (1.6 M) to yield non-polymeric products. Under these conditions the reaction went to completion within a period of six days and the majority of the products were monomeric. The

overall major product was 2-methylenebicyclo[3.3.0]octane (**20**). After work-up and fractionating distillation, this product was isolated in 67% yield (ca. 3 g). In addition to the monomers (total 77%, probably including a small amount of unreactive double-bond shift isomers of the starting material, as estimated by the GLC analysis) ca. 23% of dimeric coupling products (mixture of as yet unidentified structures) were also formed with this particular catalyst system.



The amount of dimeric products diminished when the bis(*tert*-butylcyclopentadienyl)ZrCl<sub>2</sub>/MAO system was employed. Two representative examples are listed in Table 2. At 60 °C (1 M solution of **19** in benzene) the reaction was complete within a period of 9 h. Only 12% of the products were dimeric. However, the primary product **20** amounted to only 41% of the product mixture. A fraction of 31% was identified as its double-bond shift isomer 2-methylbicyclo[3.3.0]octene **21**. The remaining 15% of the monomer product fraction probably consisted of products that were derived from **19** by double-bond isomerizations. The resulting internal olefins (the individual components of the resulting complicated mixture were not separated) appear to show a very low cyclization tendency since they would require multiple catalytic double bond isomerization steps before cyclization could occur.

Extending the reaction time at the **10d**/MAO catalyst to 30 h under otherwise unchanged reaction conditions (see entry 3 of Table 2) clearly supports the interpretation that **20** undergoes a subsequent double-bond shift at the bent metallocene Ziegler catalyst to yield the thermodynamically favoured product **21**. After a total reaction time of 30 h, only 8% of **20** remained, whereas the isomerized product **21** amounted to 64%. As expected, the amount of dimers and isomerized starting material was not affected.

The catalyst systems derived from the open, nonbridged bis(indenyl)- and bis(tetrahydroindenyl)ZrCl<sub>2</sub> complexes **12–14**<sup>[9]</sup> showed very similar features when they were exposed to a large excess of **19** (Table 2, entries 4–7). Dimer and higher oligomer formation was even less favourable at these systems. The overall transformation of **19** to cyclized monomeric products was good, but extensive subsequent isomerization of the primary product **20** to **21** was again observed. Also, the fraction of isomerized starting material became larger at these catalyst systems.

We also investigated the potential use of *ansa*-metallocene catalysts for the formation of monomeric cyclization products from **19**. The parent "Brintzinger *ansa*-metallocene" **15** (*rac* diastereomer)<sup>[14]</sup> led to the formation of 55% of **20** (Table 2, entry 8) without concomitant formation of **21**. However, this system exhibited a rather high tendency to form dimers and oligomers (18% dimers, 6% trimers

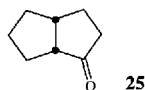
Table 2. Selected examples of selective intramolecular cyclization of *cis*-1,2-divinylcyclopentane (**19**) catalyzed by various group-4 metallocene/methylalumoxane catalyst systems (in benzene solution)<sup>[a]</sup>

Metallocene dichloride component	10a	10d	10d	12	13	ent-13	14	15	16	17	17	18a/b
[19]:[Zr]	90	110	110	120	200	250	250	90	205	130	130	110
[Al]:[Zr]	67	330	330	260	93	324	204	23	1740	1070	1070	740
Conc. [19] [M]	1.6	1.0	1.0	1.9	1.7	1.6	1.6	1.7	1.5	1.5	1.5	1.5
Temp. [°C]	20	60	60	60	60	60	60	60	35	20	20	20
React. time	6 d	9 h	30 h	27 h	76 h	3 d	3.5 d	49 h	24 h	24 h	11 d	4 d
Product composition (%)												
<b>20</b>	73	41	8	49	35	36	32	55	21	62	30	39
<b>21</b>	—	31	64	23	31	44	29	—	24	20	40	21
Total monomers <sup>[b]</sup>	77	87	86	97	95	96	98	76	99	98	77	99
Dimers <sup>[c]</sup>	23	12	12	3	4	4	1	18 <sup>[d]</sup>	1	2	23	1

<sup>[a]</sup> Product composition determined by GLC; under the chosen conditions quantitative consumption of the starting material **19** was achieved. — <sup>[b]</sup> Contains in some cases a complicated mixture of doublebond isomerized starting material and product. — <sup>[c]</sup> Of as yet unidentified structures. — <sup>[d]</sup> Plus 6% of trimeric products.

found) suggesting that the **15**/MAO catalyst is probably less well-suited for such synthetic organic applications. However, it is well-known that a variety of more strained *ansa*-metallocene complexes, such as **16**–**18**<sup>[15,16]</sup>, have a tendency to form rather low molecular mass  $\alpha$ -olefin polymers and oligomers, respectively<sup>[10,16]</sup>. As expected, some of the catalyst systems derived from these *ansa*-metallocene dichlorides gave high conversions of **19** to **20** under suitable reaction conditions. However, all these systems exhibited a pronounced tendency to additionally serve as double-bond isomerization catalysts and thus varying amounts of **21** were invariably found.

The terphenyl-substituted metallocene complexes **13** and **14** were each employed as pure diastereoisomers. Each of these diastereoisomers was, of course, enantiomerically pure since they were prepared starting from the respective terpine derivatives originating from the natural chiral pool<sup>[9b]</sup>. Consequently, the products derived from the catalytic cyclization reactions (Table 2, entries 5–7) of **19** with these optically active catalyst systems were checked for asymmetric induction. For this purpose the **20** + **21** product mixtures of the respective experiments (Table 2, entries 5–7) were isolated and their optical rotations were measured. The product mixtures were then subjected to ozonolysis<sup>[17]</sup> and the optical rotation of the isolated resulting product, bicyclo[3.3.0]octan-2-one (**25**), was also determined.



The catalytic ring closure reaction of **19** at the (+)-**14**/MAO catalyst system did not produce optically active products. However, the mixture of **20** + **21** obtained at the (–)-**13**/MAO catalyst system had an optical rotation of  $[\alpha]_D^{20} = -8.9 \pm 1^\circ$  ( $c = 0.5$  in benzene). The bicyclo[3.3.0]octan-2-one (–)-**25** derived from this product mixture had an  $[\alpha]_D^{20} =$  value of  $-9.9 \pm 0.6^\circ$  ( $c = 1$  in benzene). The corresponding experiment was carried out with the enantiomeric catalyst system (+)-**13**/MAO and, as expected, yielded a **20** + **21** product mixture exhibiting an opposite optical rotation of  $[\alpha]_D^{20} = +6.3 \pm 0.7^\circ$  ( $c = 1$  in benzene). The ketone (+)-

**25** derived from oxidative degradation of this mixture gave  $[\alpha]_D^{20} = +8.3 \pm 0.6^\circ$  ( $c = 1$  in benzene). The literature value of the optical rotation of enantiomerically pure (–)-**25** is  $[\alpha]_D^{25} = -105^\circ$  ( $c = 3.0$  in  $\text{CHCl}_3$ )<sup>[18]</sup>. We conclude that the catalytic intramolecular cyclization reaction of **19** at the **13**/MAO and at *ent*-**13**/MAO catalyst systems, respectively, occurs with some degree of asymmetric induction. However, the optical induction at these catalyst systems is as yet rather low (between 5 and 10% ee) and must be considerably improved (e.g. by the proper design of suitable optically active bent metallocene catalyst components) to become synthetically useful.

The cyclization of *cis*-1,2-divinylcyclohexane (**22**)<sup>[19]</sup> at the zirconocene/MAO catalyst systems worked equally well. With the parent  $\text{Cp}_2\text{ZrCl}_2$ /MAO system, 7-methylenebicyclo[4.3.0]nonane (**23**) amounted to 72% of the total product. Dimers and higher oligomers were practically absent. An equally favourable result was obtained with the *ansa*-metallocene **16**/MAO catalyst. Predominant formation of **23** was observed, accompanied by a small amount of unreactive double-bond isomers of the starting material. As expected, the **13**/MAO catalyst system was slightly less favourable for the **22** → **23** transformation under the experimental conditions, since this system showed a pronounced tendency to induce the subsequent **23** → **24** isomerization reaction (see Table 3).

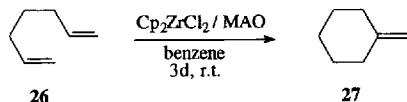
Table 3. Cyclization of *cis*-1,2-divinylcyclohexane (**22**) catalyzed by selected group-4 metallocene/methylalumoxane Ziegler catalysts (in benzene solution)

Metallocene dichloride component	10a	13	16
[22]:[Zr]	290	175	310
[Al]:[Zr]	250	220	360
Conc. [22] [M]	1.6	1.4	1.6
Temp. [°C]	41	60	45
Product composition (%)			
<b>23</b>	72	36	58
<b>24</b>	1	22	1
Total monomers <sup>[b]</sup>	98	86 <sup>[d]</sup>	98 <sup>[e]</sup>
Dimers <sup>[c]</sup>	2	11	1

<sup>[a–c]</sup> See Table 2. — <sup>[d]</sup> Contains 19% of the starting material **22**. — <sup>[e]</sup> Contains 23% of **22**.

We conclude that there is reason to believe that a variety of group-4 metallocene derived Ziegler catalyst systems are becoming useful for inducing selective intramolecular diolefin coupling reactions to form organic reaction products in a monomeric regime. It appears that the metallocene components must be selected, employing specifically those systems which exhibit an inherent tendency of favouring rather low  $k_{\text{prop}}/k_{\text{term}}$  ratios, and furthermore that the reaction conditions (dilution, temperature) must be optimized accordingly. Then, intramolecular cyclization reactions can be made very favourable at these catalysts at the expense of the otherwise observed oligomerization or polymerization reactions. Of course, there is a price to be paid in some cases: increasing the value of  $k_{\text{term}}$ , the relative termination rate, usually facilitates the  $\beta$ -hydride elimination/addition pair of reactions, a consequence of which is more pronounced alkene double-bond positional shifting. This has been frequently observed as a subsequent reaction to ring closure (see Tables 2 and 3) but may also occur at the stage of the noncyclized starting material, where it may result in the formation of unreactive internal alkenes.

We feel that the examples selected for detailed investigation in the course of this study, which have all involved five-membered ring formation, are especially critical and perhaps problematic examples, which have been useful to study as they serve to illustrate the limitations and potential difficulties encountered in this chemistry. The catalytic formation of six-membered ring systems may turn out to be much easier, as may be exemplified by the rapid intramolecular ring closure of 1,6-heptadiene (**26**) to give a high yield of methylenecyclohexane (**27**) at the parent  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  catalyst under the typical reaction conditions  $\{[\textbf{26}]:[\text{Zr}] \text{ ratio } 20, [\text{Al}]:[\text{Zr}]:10, \text{ benzene solution, } 3 \text{ d at room temperature, } 1.37 \text{ g (68.5\% of } \textbf{27} \text{ isolated)}\}$ .



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## Experimental Section

The reactions involving organometallic compounds were carried out under argon using Schlenk-type glassware. Solvents (including deuterated solvents) were dried and distilled under argon prior to use. Complexes **10**, **12**–**18** were prepared according to literature procedures<sup>[9,14,15,16,20]</sup>. The organic substrates **19** and **22** were prepared as described in the literature<sup>[13,19]</sup>. – NMR: Bruker AC 200 P and ARX 300 NMR spectrometers. – IR: Nicolet 5 DXC FT IR spectrometer. – Optical rotation: Perkin-Elmer polarimeter 241 MC (sodium line, 589 nm, conc. in g/100 ml): – GLC: Hewlett-Packard gas chromatograph HP-5097 [GLC columns HP1 (100% dimethylpolysiloxane) and HP5 (5% diphenyl and 95% dimethylpolysiloxane)]: – GC-MS: Gas chromatograph Varian 3400 (HP5 column)/Finnigan MAT 8200. – HRMS: Finnigan 312.

*Cyclization of  $\alpha,\omega$ -Dienes. – General Procedure:* A 20-ml Schlenk flask was charged with a commercial solution of methylal-

umoxane in toluene (up to 10 ml). The solvent was then removed in vacuo to yield a sample (0.5–1.5 g) of solid methylalumoxane (10–30 mmol).  $[\text{D}_6]\text{benzene}$  (ca. 2 ml) was added and then the appropriate  $\alpha,\omega$ -diene (2–5 mmol). The mixture was then brought to the chosen reaction temperature, and the respective zirconocene dichloride complex (0.007–0.05 mmol) was added. The mixture usually turned yellow to red, and samples were taken at various intervals. The samples were analyzed by  $^1\text{H}$  NMR (diluted with additional  $[\text{D}_6]\text{benzene}$ ) and by GLC. For the GLC analysis, the sample was hydrolyzed with a small amount of water, filtered through a small silica gel column (0.4  $\times$  1 cm) to remove the organometallic components, and dried with magnesium sulfate. In this way, the optimized reaction conditions (see Tables 1–3) were determined.

*1-Methylene-3-(cyclopentylmethyl)cyclopentane (11):* 0.30 g (10.4 mmol) of methylalumoxane was dissolved in 15 ml of benzene and 1,5-hexadiene (1.7 g, 0.7 mmol) was added. After 30 min, 220 mg (0.75 mmol) of zirconocene dichloride (**10a**) was added and the reaction mixture was stirred for 24 h at room temperature. It was then hydrolyzed by the addition of 4 ml of water and stirred for a further 2 h. The mixture was filtered through a short silica gel column to remove the metal-containing components. The resulting organic solution was washed with water and dried with magnesium sulfate. GLC analysis revealed that the mixture contained 70.3% dimers (53.6% **11**), 26.7% trimers and 3.0% tetramers. Fractionating distillation (using a “Fischer Spaltrohr” column) furnished 0.9 g of **11** (52% yield) with a purity of 76% (as determined by GLC). Repeated fractionating distillation (55°C/0.01 Torr) eventually yielded 0.3 g (18%) of **11** with a purity of >92% (GLC).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta$  = 4.90 (m, 2H, =CH<sub>2</sub>), 0.8–2.5 (m, 18H). –  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta$  = 152.6 (C-1), 105.4 (=CH<sub>2</sub>), 42.4, 40.5 (CH<sub>2</sub>), 40.0, 39.5 (CH), 33.6, 33.4, 33.3, 32.6, 25.5 (double intensity) (CH<sub>2</sub>). – IR (film):  $\tilde{\nu}$  = 3070 cm<sup>−1</sup>, 2948, 2921, 2867, 2857, 1657, 1451, 1438, 1433, 874. – MS (70 eV);  $m/z$  (%): 164 (6) [ $\text{M}^+$ ], 149 (5), 135 (7), 97 (5), 95 (31), 83 (11), 81 (100), 69 (10), 67 (41).

*Methylenecyclohexane (27) by Cyclization of 1,6-Heptadiene:* A Schlenk flask was charged with 0.3 g (10.4 mmol) of methylalumoxane, 15 ml of benzene, 2 g (20.8 mmol) of 1,6-heptadiene and 290 mg (1.0 mmol) of zirconocene dichloride (**10a**). The mixture was stirred for 3 d at ambient temperature and then hydrolyzed by the addition of 10 ml of water. After stirring for a further 2 h, the organic phase was washed three times with water (3 ml each) and dried with magnesium sulfate. GLC analysis revealed the presence of 85.4% monomers (78.8% **27**), 8.0% dimers, 5.7% trimers and 0.8% tetramers in the mixture. Methylenecyclohexane (**27**) was separated from the solvent and the other components of the mixture by fractionating distillation (“Fischer Spaltrohr” column) to yield 1.37 g (68%) of **27**, identified by comparison with published spectroscopic data<sup>[21]</sup>.

*2-Methylenebicyclo[3.3.0]octane (20):* A 50-ml Schlenk flask was charged with 0.8 g (27.8 mmol) of methylalumoxane, 30 ml of benzene, 4.5 g (37.8 mmol) of *cis*-1,2-divinylcyclopentane and then 0.12 g (0.4 mmol) of bis( $\eta^5$ -cyclopentadienyl)zirconium dichloride (**10a**). The mixture was stirred for 6 d at room temperature and then hydrolyzed by the addition of 10 ml of water. The resulting mixture was passed through a short silica gel column, then washed with water (3  $\times$  5 ml) and dried with magnesium sulfate. GLC analysis revealed the presence of 73.1% of **20** (plus 23% of unidentified dimers). Distillation (“Fischer-Spaltrohr” column) yielded 3 g (67%) of **20** (b.p. 70–80°C/20 Torr)<sup>[22]</sup>. –  $^1\text{H}$  NMR ( $[\text{D}_6]\text{benzene}$ ):  $\delta$  = 4.88 (m, 1H) and 4.79 (m, 1H, =CH<sub>2</sub>), 2.76 (m, 1H, 1-H), 2.29–2.49 (m, 1H, 5-H), 2.04–2.29 (m, 2H, 3-H),

0.85–1.85 (m, 8H, CH<sub>2</sub>). – <sup>13</sup>C NMR ([D<sub>6</sub>]benzene): δ = 158.4 (C-2), 104.7 (=CH<sub>2</sub>), 48.3 (C-1), 44.3 (C-5), 34.7, 34.0, 32.3, 26.7 (double intensity) (CH<sub>2</sub>). – IR (film): ν̄ = 3070 cm<sup>-1</sup>, 2938, 2863, 1655, 1466, 878. – C<sub>9</sub>H<sub>14</sub>: calcd. 122.1095, found 122.1093 (HRMS).

**2-Methylbicyclo[3.3.0]oct-2-ene (21):** A 10-ml Schlenk flask was charged with 0.63 g (21.9 mmol) of methylalumoxane, 3 ml of benzene, 0.4 g (3.3 mmol) of *cis*-1,2-divinylcyclopentane (**19**) and then 9 mg (0.013 mmol) of (–)-(p-S,p-S)-bis[η<sup>5</sup>-1-(neomenthyl)indenyl]-zirconium dichloride (1'S,3'R,4'R-**13**). After two weeks at room temperature the reaction was complete and the mixture contained (GLC analysis) 55.4% of **21** and 4.6% of **20**. The major monomeric reaction product **21** was recovered by fractionating distillation ("Fischer Spaltrohr" column) to yield 0.2 g (50%) (b.p. 153 °C)<sup>[23]</sup>. – <sup>1</sup>H NMR ([D<sub>6</sub>]benzene): δ = 5.15 (br. s, 1H, 3-H), 0.85–2.90 (m, 13H). – <sup>13</sup>C NMR ([D<sub>6</sub>]benzene): δ = 141.9 (C-2), 123.8 (C-3), 54.1 (C-1), 41.7 (C-5), 40.6 (C-4), 36.2, 30.9 (C-6, C-8), 26.0 (C-7), 15.2 (CH<sub>3</sub>). – IR (film): ν̄ = 3004 cm<sup>-1</sup>, 2918, 2825, 1655, 1452, 1032, 790. – MS: (70 eV); *m/z* (%): 122 (30) [M<sup>+</sup>], 93 (100).

**Cyclization Reactions of *cis*-1,2-Divinylcyclopentane (19) with Optically Active Metallocene Catalyst Systems:** The catalytic cyclization reactions were carried out analogously to those described above. The mixtures were hydrolyzed and the respective **20** + **21** product mixtures isolated by filtration. The corresponding optical rotations [α]<sub>D</sub><sup>20</sup> of the mixtures were measured in benzene solution. Each of the mixtures was then subjected to olefinic cleavage with ozone according to a literature procedure<sup>[24]</sup>. In each case the corresponding ketone **25** was isolated in 50–70% yield and its optical rotation measured. Using the (+)-(p-R,p-R)-bis[η<sup>5</sup>-1-(neoisomenthyl)-4,5,6,7-tetrahydroindenyl]ZrCl<sub>2</sub> derived catalyst, 2.1 g (47%) of the **20/21** mixture was isolated, no optical rotation could be measured. With the (–)-(p-S,p-S)-bis[η<sup>5</sup>-1-(neomenthyl)indenyl]ZrCl<sub>2</sub> (**13**)/MAO catalyst, 2.3 g (51%) of **20/21** was formed with an optical rotation of [α]<sub>D</sub><sup>20</sup> = –8.9 ± 1° (*c* = 0.5 in benzene); the actual measured optical rotation was α = –0.045 ± 0.005°. Ozonolysis of the mixture gave 62% of **25**, [α]<sub>D</sub><sup>20</sup> = –9.9 ± 0.6° (*c* = 1.01 in benzene; α = –0.100 ± 0.005°). The corresponding ring-closure reaction of **19** at the *ent*-**13**/MAO catalyst systems (for detailed conditions see Table 2) gave 2.7 g (53%) of the **20/21** mixture, [α]<sub>D</sub><sup>20</sup> = +6.3 ± 0.7 (*c* = 1.0 in benzene), α = +0.065 ± 0.005°. Subsequent ozonolysis furnished the ketone (+)-**25**<sup>[18]</sup> in 67% yield, [α]<sub>D</sub><sup>20</sup> = +8.3 ± 0.6 (*c* = 1.0 in benzene), α = +0.084 ± 0.005°.

**7-Methylenebicyclo[4.3.0]nonane (23):** A 50-ml Schlenk flask was charged with 0.75 g (25.9 mmol) of methylalumoxane, 25 ml of benzene, 4.0 g (29.4 mmol) of *cis*-1,2-divinylcyclohexane and then 30 mg (0.102 mmol) of Cp<sub>2</sub>ZrCl<sub>2</sub> (**10a**). The mixture was stirred for 1 week at 40 °C and then hydrolyzed by the addition of 10 ml of H<sub>2</sub>O. The resulting mixture was passed through a short silica gel column, washed with water (3 × 5 ml) and dried with magnesium sulfate. The crude product contained ca. 72% of **23** (analyzed by GLC). Distillation (40 °C/10 Torr) gave 2.7 g (67%) of **23**<sup>[22]</sup>. – <sup>1</sup>H NMR ([D<sub>6</sub>]benzene): δ = 4.98 (m, 1H), 4.90 (m, 1H, =CH<sub>2</sub>), 2.60–0.80 (m, 14H, CH and CH<sub>2</sub>). – <sup>13</sup>C NMR ([D<sub>6</sub>]benzene): δ = 154.3 (C-7), 104.8 (=CH<sub>2</sub>), 44.5, 39.9 (CH), 30.4, 28.9, 27.9, 26.7, 24.7, 22.6 (CH<sub>2</sub>). – IR (film): ν̄ = 3070 cm<sup>-1</sup>, 2981, 2924, 2851, 1654, 1448, 1032, 911, 876, 861, 710. – MS (70 eV); *m/z* (%): 136 (74) [M<sup>+</sup>], 57 (100). – C<sub>10</sub>H<sub>16</sub>: calcd. 136.1252, found 136.1249 (HRMS).

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