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Invited review

Some novelties in the chemistry of organomagnesium compounds with zirconium complexes

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Abstract

The unusual results of the present authors' research work obtained for the last 3 years in the field of synthesis and transformation of organomagnesium compounds with metal complex catalysts are considered in this review. Special attention has been paid to catalytic cyclometallation of linear and cyclic olefins with n-R_2Mg, synthesis of alkenyl organomagnesium compounds from α-olefins and R_2Mg, and catalytic transformation of cyclopentanes in the presence of Cp_2ZrCl_2. The reaction mechanism implying the formation of zircona–cyclopentane complexes as intermediate species are discussed.

Keywords: Catalysis; Cyclometallation; Alkene; Magnesium; Zirconium

1. Introduction

In the last 10–15 years, the research chemists showed their increasing interest to the problems of application of non-transition organometallics to the regioselective and stereoselective synthesis of new organometallic and natural compounds.

There is no doubt about it; the significant progress in this field was made owing to the application of metal complex catalysts in the chemistry of organometallic compounds of non-transition metals that led to a development of atypical methods to synthesize organomagnesium compound (OMC) of various structures.

From the series of research paper on the topic, the most practical importance may be attributed to the Ti- and Zr-complex-catalyzed hydrometallation and carbometallation of olefins, conjugated dienes and acetylenes with hydride and alkyl magnesium derivatives [1–4].

The present authors contributed much to this scientific field. They established many new organometallic reagents, promising catalytic methods of selective hydromagnesiation, carbomagnesiation and cyclomagnesiation of olefins, which manifested their high potentials for the synthesis of complex natural species of the desired structure.

From among the promising developments made by the present authors, we would stress the procedures of catalytic hydromagnesiation of unsaturated compounds with such reagents as $^iBu_2Mg$ [5] and $HMgNR_2$ [6], and catalytic carbomagnesiation of olefins with R_2Mg [7,8]. Similarly to the reaction of cycloalumination described elsewhere [9], we succeeded in conducting some reactions of catalytic cyclometallation of olefins with alkyl magnesium derivatives in the presence of Cp_2ZrCl_2, which resulted in cyclic OMCs.

As opposed to cyclometallation, cyclomagnesiation was found to be less selective to afford a mixture of 2,4- and 2,5-disubstituted magnesia-cyclopentanes (MCPs). Threshold limits of application of the reactions are discussed in this review.

2. Results and discussion

Low valent zirconium complexes are known to give easily five-membered metal cycles in reactions with unsaturated hydrocarbons [10,11]. The resultant compounds were used as convenient syntones in the synthesis of various heterocycles [12]. Also, the zirconacyclopentanes (ZCPs) are the key intermediates in cat-

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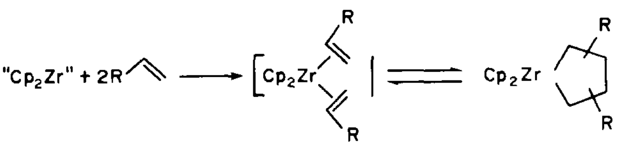
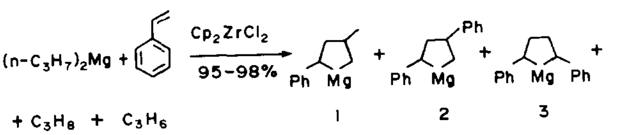
alytic carbomagnesiation [7], dimerization and codimerization [13,14], and β-alkylation of α-olefins [15]:



Accounting for the unique reactivity of the zirconium–carbon bond in ZCPs of various substitution, we managed to synthesize OMCs via several different catalytic reactions. Thus, substituted MCPs were synthesized via cyclometallation of styrene with $(n\text{-}C_3H_7)_2Mg$ in the presence of catalytic amounts of Cp_2ZrCl_2 [16]. This reaction proceeded in a solution of diethyl ether (20 °C; 30–40 h), affording disubstituted MCPs **1**–**3**:



During the reaction, a gas was liberated as a mixture of propane and propylene (10 : 1). Reactions $(n\text{-}C_3H_7)_2Mg$, $(n\text{-}C_4H_9)_2Mg$, $(n\text{-}C_6H_{13})_2Mg$ with styrene, its derivatives and hexene-1, catalyzed by Cp_2ZrCl_2, were studied in order to enlarge the range of application of the approach, to find optimal conditions for the preparation of MCPs and also to consider all possible routes for the involvement of different OMCs and olefins into the reaction.

The reaction of styrene with $(n\text{-}C_3H_7)_2Mg$ was investigated in detail in order to establish the effects of the ratio of starting reagents, temperature, reaction time, catalyst concentration and solvent type on the yield of the target products **1**–**3**.

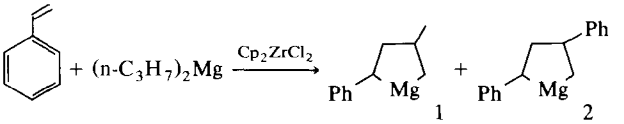
Table 1 shows the results of the reaction of styrene with $(n\text{-}C_3H_7)_2Mg$ in dependence on their molar ratio in an ether–tetrahydrofuran (THF) mixture:

In diethyl ether, the total yield 98% of **1**–**3** is reached in 40 h, while a mixture of diethyl ether with THF (1 : 1) promotes an increased reaction rate, and the same yield can be obtained in as little time as 7 h. Note that the OMC **3** cannot be formed in the mixture of the solvents. Our attempts to carry out the cyclometallation of styrene in a solution of THF failed.

In reactions conducted at with a styrene: $(n\text{-}C_3H_7)_2Mg$ ratio of 3 : 1 or 2 : 1, the styrene conversion is always below 54%, although the selectivity for the product **2** reaches 90–95%, and the share of **1** is only 10%. The yield of 2-phenyl-4-methylmagnesacyclopentane **1** increases essentially with a higher amount of the OMC in the reaction mixture. Therefore our further experimental work on the synthesis of MCPs was implemented with the complex Cp_2ZrCl_2 (2–3 wt.%) at a $(n\text{-}C_3H_7)_2Mg$: styrene rate of 1 : 1 under the found optimal conditions.

Table 1

The effect of the ratio of starting reagents on the yield and composition of the products of cyclometallation of styrene with $(n\text{-}C_3H_7)_2Mg$ [a]



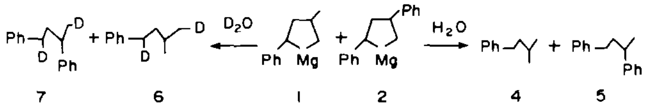
Styrene:$(n\text{-}C_3H_7)_2Mg$	Yield of 1 + 2 [b] (%)	Product ratio (%)	
		1	2
3:1	40	5	95
2:1	54	10	90
1:1	98	25	75
1:1.5	97	44	56
1:3	98	52	48

[a] Reaction conditions: Cp_2ZrCl_2:$(n\text{-}C_3H_7)_2Mg$, 2.5, 100; ether–THF (1:1) as a solvent; 20°C; 7 h; $C_{OMC} = 0.7$ mmol ml^{-1}. The yields for **1** and **2** were calculated from the reaction mixture hydrolysis products.

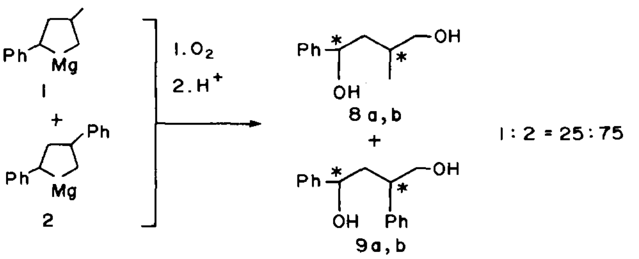
[b] In the presence of THF, **3** was not formed.

To gain some more reliable evidence for the structures of **1** and **2**, we studied some of their chemical transformations.

Thus hydrolysis of **1** and **2** (**1**:**2**, 25 : 75) results in 2-methyl-4-phenyl–butane (**4**) and 1,3-diphenylbutane (**5**), while their deuterolysis leads to 1,4-dideutero-2-methyl-4-phenylbutane (**6**) and 1,4-dideutero-2,4-diphenylbutane (**7**):



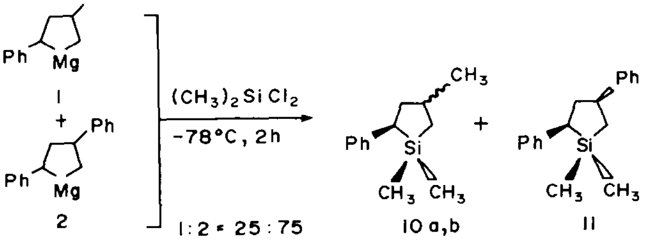
After complete oxidation of the MCP **1** and **2** with oxygen, and further hydrolysis of the oxidation products, the diols **8a** and **8b** and the diols **9a** and **9b** respectively were obtained:



^{13}C NMR spectroscopy was used to identify **8a**,**8b** and **9a**,**9b** as mixtures of two diastereomers (3 : 2), their total yield being about 75–80%.

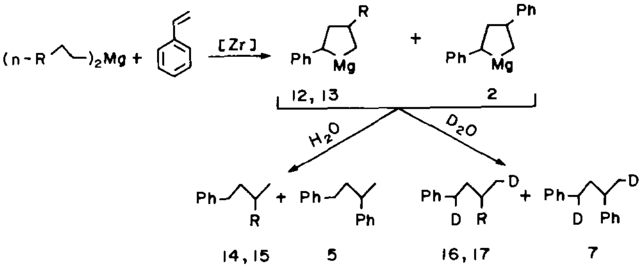
Treatment of **1** and **2** with Me_2SiCl_2 leads to *cis*- and *trans*-1,1,3-trimethyl-5-phenylsilacyclopentanes

(10a,10b) and trans-1,1-dimethyl-2,4-diphenylsilacyclopentane **(11)**:



A total yield of **10a**, **10b** and **11** in the experiments described consists of no less than 75% (**10a,10b**: **11**, 25 : 75).

We studied the following reactions of styrene with $(n\text{-}C_4H_9)_2Mg$ and $(n\text{-}C_6H_{13})_2Mg$ in the presence of Cp_2ZrCl_2 to elucidate any other possible ways for the involvement of OMCs in the cyclometallation under the optimal conditions found earlier (20–25 °C; 7 h: ether : THF, 1 : 1):

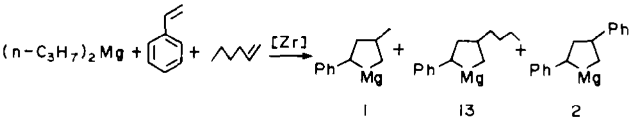


R = C_2H_5 (12, 14, 16); R = C_4H_9 (13, 15, 17)

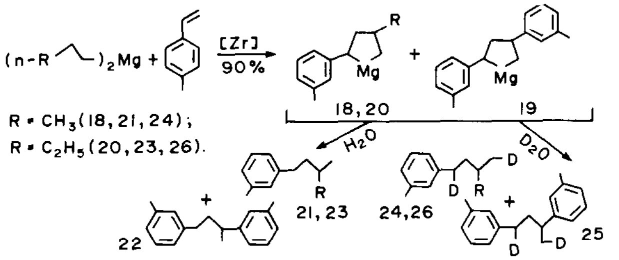
It was ascertained that the cyclometallation followed the pattern common for all the OMCs, used and, irrespective of the ratio of starting reagents, α,β′-disubstituted MCPs **12**, **13** and **2** were found in all experiments. The hydrolysis of the MCPs led to hydrocarbons **14**, **15** and **5** respectively. Following deuterolysis of **12**, **13** and **2**, there arose deuterated hydrocarbons **16**, **7** and **17**, **7**. The position of deuterium atoms in the latters confirmed a formation of five-membered cyclic OMCs. Similarly to the reaction with $(n\text{-}C_3H_7)_2Mg$, the product yield depends on the ratio of the starting reagents. One may establish strict control over the composition of the resultant MCPs by varying the styrene:OMC ratio. The activity of all the dialkyl magnesium derivatives studied in our experimental work was almost the same.

To prepare mixed alkyl- substituted and aryl-substituted MCPs, we studied the simultaneous cyclometallation of styren and hexene-1 (1:1). It should be noted that we did not find any alkenyl organomagnesium compounds during the reaction. These compounds are usually formed in reactions of aliphatic α-olefins with *n*-alkyl magnesium derivatives, which will be discussed later on in this work.

Thus styrene and hexane-1 react with an equimolar amount of $(n\text{-}C_3H_7)_2Mg$, giving rise to 2-phenyl-4-butylmagnesiumcyclopentane **(13)** in addition to **1** and **2** in the ratios 35:30:35 respectively and with about 85% total yield:



To obtain the effects of the nature and disposition of the alkyl substituents in the starting reagents on the reaction direction and selectivity, we conducted reactions of *ortho*-, *meta*-and *para*-methylstyrenes and *para*-tert-butylstyrene with $(n\text{-}C_3H_7)_2Mg$ and $(n\text{-}C_4H_9)_2Mg$. The *Ortho*- or *para*-positioned CH_3 group in styrene blocks the cyclometallation, while the *meta*-positioned methyl group does not interfere in the course of the reaction:

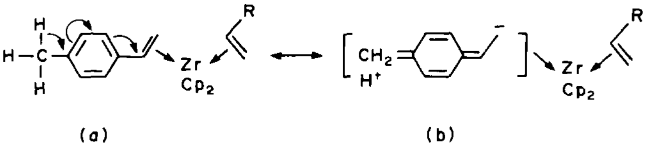


R = CH_3 (18, 21, 24);
R = C_2H_5 (20, 23, 26).

The structures of **18–20** were confirmed by the fact that their hydrolysis resulted in hydrocarbons **21–23**, and also by the 1,4-positioned deuterium atoms in **24–26**.

The reason that the methyl-substituted styrenes behave as in the catalytic cyclometallation is most probably due to the additional contribution of electrons, made in the presence of a polarizing agent because the methyl substituents are *ortho* and *para* positioned in the aromatic nuclei. This agent is zirconocene "Cp_2Zr" formed during the reaction [10]. The polarization effect of zirconocene for *para*-methylstyrene may be demonstrated by Scheme 1.

It is clear Scheme 1 that the resonance structure in Scheme 1(b) seems to make the major contribution to the complexation, leading to a stable system, and thus preventing cyclometallation. Following this version, one may assume that the tert-butyl group *para* positioned

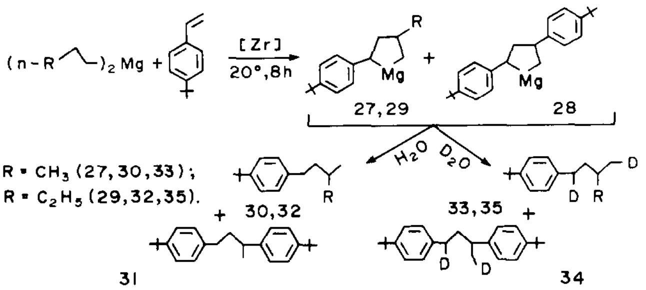


(a) (b)

Scheme 1.

in a styrene molecule would surpress the effect of superconjugation. Indeed, the catalytic cyclometallation of *para*-tert-butylstyrene with *n*-alkyl magnesium derivatives results in related substituted MCPs **27–29** with 75–85% yields.

The MCPs **27–29** are easily transformed into the hydrocarbons **30–35** in reactions with H_2O and D_2O:



The **27**:**28** and **29**:**28** ratios were as 70:30 and 40:60 respectively.

To expand the range of application of the catalytic cyclometallation, and to determine any possible ways for the involvement of cyclic olefins in the reaction, we studied reactions of norbornenes (NBs) with *n*-alkyl magnesium derivatives.

The research was done with bicyclo[2.2.1] heptene (**36**), spiro {bicyclo[2.2.1] hept-2-en-7,1-cyclopropane} (**37**) and endo-tricyclo[5.2.1.0^{2,6}]-3,8-decadiene (**38**) as the olefins, and with $(n\text{-}C_3H_7)_2Mg$ and $(n\text{-}C_4H_9)_2Mg$ as the OMCs. Note that, in the presence of Cp_2ZrCl_2 the reactions of Et_2Mg with the NBs follow the pattern of carbomagnesiation [17], whereas the cyclometallation may be observed starting from $(n\text{-}C_3H_7)_2Mg$.

The optimal conditions for the cyclometallation of the stated norbornenes, similarly to the reactions of styrenes, are as follows: 25°C for 7–8 h; a mixture of solvents Et_2O and THF (1 : 1); catalyst concentration, 2–3 wt.% as calculated for the olefin taken.

The OMCs **39–41** are formed with about 80% total yield in the reaction of **36** with an equimolar amount of R_2Mg (R≡n-C_3H_7 or n-C_4H_9) in the presence of Cp_2ZrCl_2 under the stated conditions. During the reaction, liberation of propane or butane occurs and this depends on the starting OMC. The gaseous product contains up to 5–6% of propylene or butene-1 respectively.

Hydrolysis or deuterolysis of the reaction mixture resulting from the interaction of $(n\text{-}C_3H_7)_2Mg$ and an NB led to *exo*-2-(1^1-methyl)ethylbicyclo[2.2.1]heptane (**42**) and *exo*, *exo*-2,2^1-bis-bicyclo[2.2.1]heptyl (**43**) or in partially deuterated *exo*-2-(1^1-deuteromethyl)ethyl-3-deuterobicyclo[2.2.1]heptane (**44**) and *exo*, *exo*-2,2^1-bis-3-deuterobicyclo[2.2.1]heptyl (**45**). The products were isolated by distillation in vacuum and identified by the use of spectral methods.

In the reactions with $(n\text{-}C_4H_9)_2Mg$, **43** and *exo*-2-(1^1-methyl)propylbicyclo[2.2.1] heptane (**46**) or **45** and *exo*-2-(1^1-deuteromethyl)propyl-3-deuterobicyclo[2.2.1] heptane (**47**) respectively, were obtained:

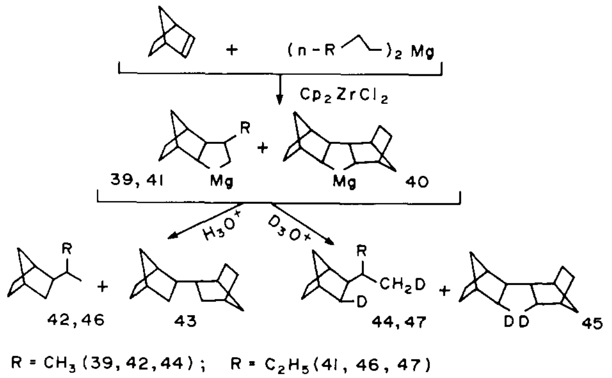
Table 2
The effect of the ratio of starting reagents on the yield of products and composition during cyclometallation of norbornenes with $(n\text{-}C_3H_7)_2Mg$ [a]

NB:$(n\text{-}C_3H_7)_2Mg$	Yield of **39**+**40** (%)	Product ratio (%)	
		39	**40**
2:1	58	29	71
1:1	81	80	20
1:2	86	95	5
1:3	98	99	1
1:1 [b]	95	11	89
1:1 [c]	40	26	74

[a] Cp_2ZrCl_2:$(n\text{-}C_3H_7)_2Mg$ = 2.5:100; ether-THF (1:1) as a solvent; 20°C; 8 h; $(n\text{-}C_3H_7)_2Mg$ concentration, 0.6 mmol ml^{-1}. The yields of **39** and **40** were found by the products of reaction mixture hydrolysis, as calculated for the starting NB. The reaction features for $(n\text{-}C_4H_9)_2Mg$ were the same as for $(n\text{-}C_3H_7)_2Mg$.

[b] 40°C; 4 h.

[c] Et_2O; 20°C; 8 h.



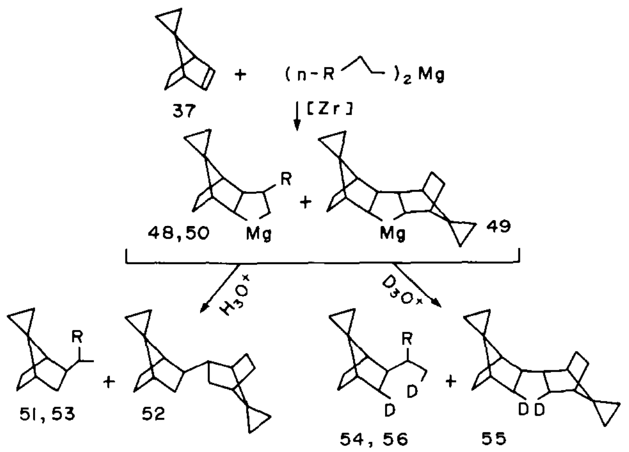
As for the cyclometallation of styrenes [16], a proper choice of the reaction conditions is of great importance for that the cyclometallation of NBs could work selectively enough and high yields could be obtained (Table 2). Note that a higher amount of the starting OMC promotes an increased selectivity for **39**, reaching 99%. The reaction temperature contributes much to the yield and composition of the products. The content of **40** is increased up to 89% at a higher reaction temperature (up to 40°C).

According to the spectral assignments obtained for **42–47**, it was concluded that NB reacts with R_2Mg in the presence of Cp_2ZrCl_2 via *exo*-cyclometallation. This results in three- and five-membered metallocycles, where the MCP fragment is *exo* oriented.

To estimate the effect of the olefin's structure upon the cyclometallation direction and stereochemistry, we conducted the reactions of **37** and **38** with R_2Mg(R≡n-C_3M_7 or n-C_4H_9) in the presence of 3 wt.% Cp_2ZrCl_2 under the conditions stated above. Thus the reaction of **37** afforded the MCPs **48**, **49** and **50**, **49** with about

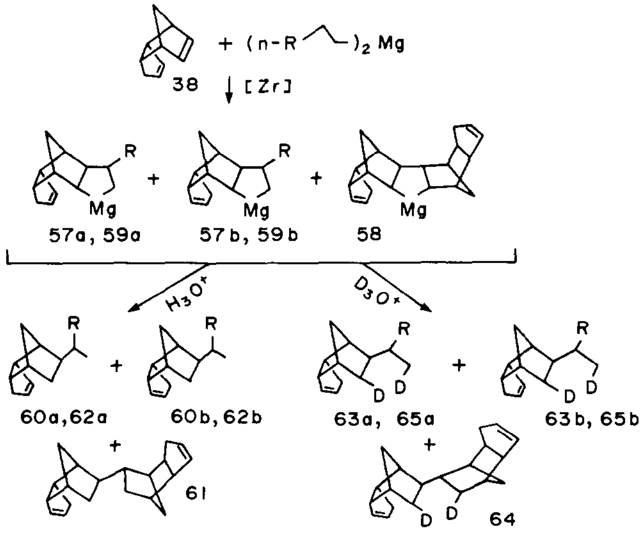
80% total yield. The reaction proceeded similarly to that of **36**.

Hydrolysis and deuterolysis of the obtained metallocycles led directly to *exo*-substituted norbornanes **51**, **55** and **56** respectively:



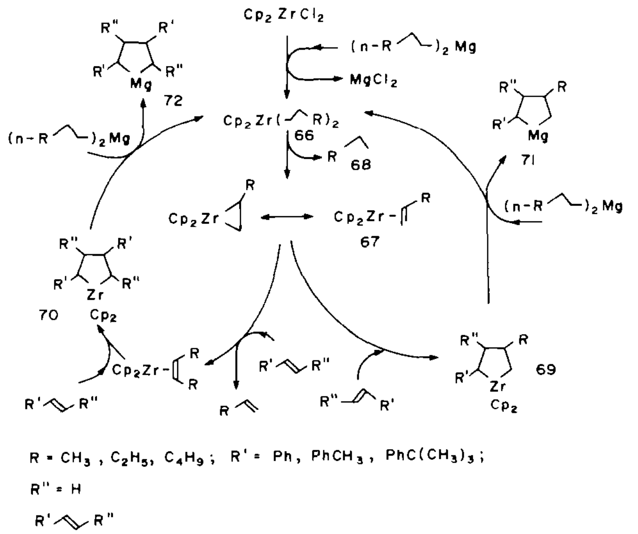
R = CH_3(48,51,54); R = C_2H_5(50,53,56)

Similar results were obtained for the cyclometallation of *endo*-dicyclopentadiene (**38**) under otherwise equal conditions. The reaction afforded a mixture of five-membered regioisomeric MCPs **57a**, **57b**, **59a** and **59b**, consisting of one molecule of the *endo*-dicyclopentadiene, a magnesium atom and an alkyl radical and an MCP **58** formed from two molecules of **38** and a magnesium atom. After hydrolysis and deuterolysis of the resultant OMC mixture, hydrocarbons **60–65** were isolated and given spectral assignments in terms of their structures and ratios:



R = CH_3(57a, 57b, 60a, 60b, 63a, 63b)
R = C_2H_5(59a, 59b, 62a, 62b, 65a, 65b)

The **60a**:**60b**, **62a**:**62b**, **63a**:**63b** and **65a**:**65b** regioisomer ratios were all 3:2.



R = CH_3, C_2H_5, C_4H_9; R' = Ph, $PhCH_3$, $PhC(CH_3)_3$;
R'' = H
R'⌃R''

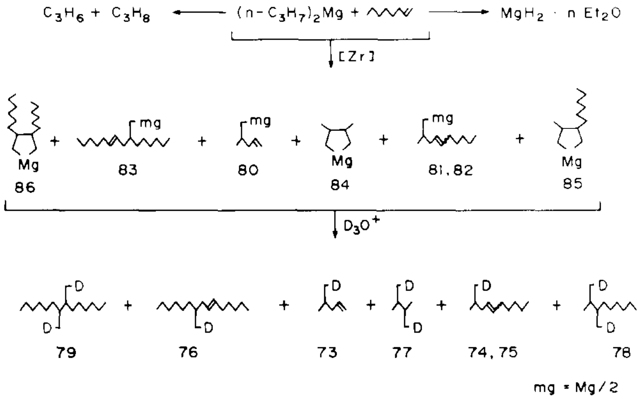
Scheme 2.

Accounting for the reported results on the cycloalumination of olefins with R_3Al, catalyzed by zirconium complexes [9,18,19], the available data on the mechanism of decomposition of dialkyl zirconium derivatives and the synthesis of zirconocene–alkene complexes [20,21], and also our own experimental results, we suggest Scheme 2 for a sequence of the elementary steps in the cyclometallation of olefins with *n*-R_2Mg in the presence of Cp_2ZrCl_2. From scheme 2, it follows that a dialkylzirconium complex **66** is formed first. Then, **66** is decomposed to give a zirconocene–alkene complex **67** and an alkane **68**; the latter corresponds to the alkyl radical in the starting OMC. After this, ZCPs **69** and **70** arise and then are remetallated with OMC to result finally in **71** and **72** respectively, and in regeneration of **66**.

Therefore, the catalytic cyclomagnesiation of the olefins under the consideration holds to the common pattern and results in substituted MCPs.

As opposed to the unambiguously proceding reactions of styrenes and NBs with n-R_2Mg, assisted by Cp_2ZrCl_2, the reactions of α-olefins with n-alkyl magnesium derivatives (*n*-R_2Mg; R≡C_3H_7, C_4H_9 etc.) afford primarily acyclic alkenylmagnesium compounds (AMCs).

Thus the reaction of an equimolar amount of (*n*-$C_3H_7)_2Mg$ with 1-octene in the presence of 5 wt.% Cp_2ZrCl_2 (20°C; 20 h; Et_2O) leads to liberation of a mixture of propane and propylene (3:2). Among the products of the reaction mixture deuterolysis, there were found monodeuterated alkenes **73–76** and vicinal dimethyldideuteroalkanes **77–79**, which indicated that AMCs **80–83** and 3,4-disubstituted MCPs **84–86** were formed during the reaction (Scheme 3). It is interesting that the resultant OMC contain fewer hydrogen atoms than the starting OMC and olefin do. The "superfluous" hydrogen atoms are accepted by the excessive



Scheme 3.

molecules of $(n\text{-}C_3H_7)_2Mg$, that undergo reductive elimination by their Mg–C bonds. Indeed, in the course of the reaction propane is liberated and precipitation occurs, the content of which corresponds to the brutto-formula MgH_2–$n$$Et_2O$ (n varies from 0.5 to 1.5). Also hydrogen is liberated also during hydrolysis or deuterolysis of the reaction mixture, which provides evidence for the presence of soluble hydrides as HMgR. The reaction of 1-octene with $n\text{-}C_3H_7MgBr$ requires a much longer time for completion (40–45 h). The reaction products are the same as for the case with $(n\text{-}C_3H_7)_2Mg$, except for the insoluble precipitate. It is most likely that, instead of MgH_2, there appears HMgBr which is very soluble in the solvent. At higher reaction temperatures (up to 80°C), the reaction rate increases, which affords a product **83** (Table 3). The same effect may be attained with an excessive amount of the starting olefin. Our attempts to gain selectivity for the rest of the reaction products failed. The optimal OMC:olefin ratio that would allow one to reach the maximum conversion of the starting olefin was a 1.5:1.

The product yields and ratios for the reaction of $(n\text{-}C_3H_7)_2Mg$ with 1-octene, catalyzed by Cp_2ZrCl_2, are given in Table 4.

Proceeding from $(n\text{-}C_3H_7)_2Mg$ and $n\text{-}C_3H_7MgBr$ to the next members of the OMC homologous series, $(n\text{-}C_4H_9)_2Mg$ and $(n\text{-}C_6H_{16})_2Mg$, all the features of the reaction considered in this work remain unchanged. The higher OMC formed may be subdivided into three groups with respect to a hydrocarbon radical structure (Scheme 4).

Table 3
Product yields and ratios in the reaction of $(n\text{-}C_3H_7)_2Mg$ with 1-octene [a], with respect to the reaction temperature

Temperature (°C)	Conversion of 1-octene (%)	Product ratio (%)				
		74	**75**	**76**	**78**	**79**
25	5	0.5	–	4.0	–	0.5
35	11	2.0	1.0	6.0	1.0	1.0
50	23	–	–	22.0	–	1.0
60	–	–	–	–	–	–
80	60	–	–	58.0	–	2.0

[a] The products were obtained after deuterolysis of the reaction mixture, and identified by GLC. Reaction conditions; $(n\text{-}C_3H_7)_2Mg$:1-octene: [Zr], 150:100:2, ether; 1 h; $C_{OMC} = 1.7$ mmol ml^{-1}.

Table 4
Product yields and ratios for the reaction of $n\text{-}(C_3H_7)_2Mg$ with 1-octene [a]

Compound	1-octene	**74**	**75**	**76**	**78**	**79**
Yield(%)	2	25	5	56	10	2

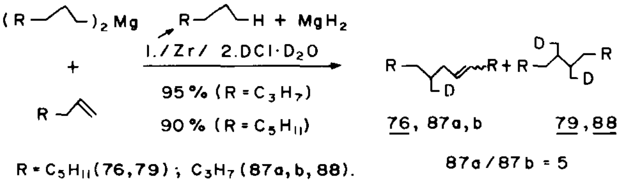
[a] OMC: 1-octene: [Zr], 150:100:5; ether; 20°C;20 h; $C_{OMC} = 1.0$ mmol ml^{-1}, as found by the results of gas-liquid chromatography (GLC) of the products of deuterolysis of the reaction mixture.

Group A includes OMCs having their hydrocarbon radicals formed from two molecules of the starting olefin; the content of these OMCs is the highest in the product mixture.

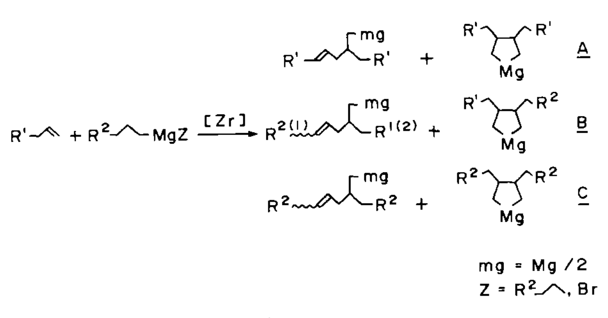
Group B includes OMCs having their hydrocarbon radicals built up from one molecule of the starting olefin and one molecule of the starting OMC;

Group C includes OMCs with their hydrocarbon radicals built up from two hydrocarbon remainders of the starting OMC. The content of these OMCs is the lowest in the product mixture.

If the numbers of carbon atoms are the same in the hydrocarbon radical of the starting OMCs and in the starting α-olefin as in $(n\text{-}C_6H_{13})_2Mg$ and 1-hexene or in $(n\text{-}C_8H_{17})_2Mg$ and 1-octene, deuterolysis of the reaction mixture affords exclusively deuteroalkenes **76**, **87** and dimethyldeuteroalkanes **79**, **88**:



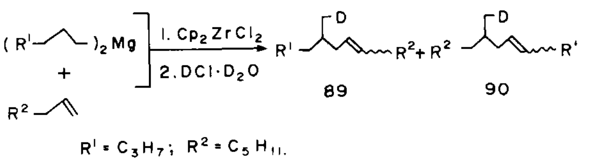
We found that different α-olefins and n-alkyl magnesium derivatives showed similar activities in the reaction. As an example, during the reaction of an equimolar mixture of 1-hexene and 1-octene with $(n\text{-}C_3H_7)_2Mg$ for 5 hours, the olefins were converted by 16% and 18% respectively. The reaction of 1-octene



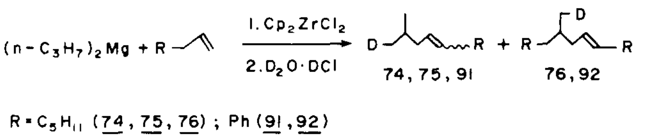
Scheme 4.

with $(n\text{-}C_6H_{13})_2Mg$ and $(n\text{-}C_9H_{19})_2Mg$ led to 21% and 23% conversion respectively of the olefin.

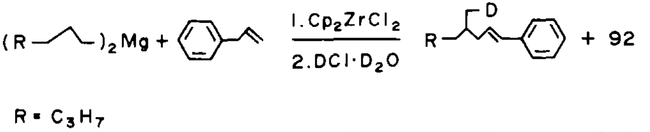
The structures of the resultant AMC from the group B depend sometimes on the nature of the starting reagents. Thus $(n\text{-}C_6H_{13})_2Mg$ reacts with 1-octene (or $(n\text{-}C_8H_{17})_2Mg$ reacts with 1-hexene) to yield a mixture of isomeric products **89** and **90** having their double bonds of different positions and configurations:



On the contrary, the reaction of $(n\text{-}C_3H_7)_2Mg$ with 1-octene or allylbenzene affords AMCs having one double bond only in the fragment of their hydrocarbon radical which corresponds to that in the starting olefin:



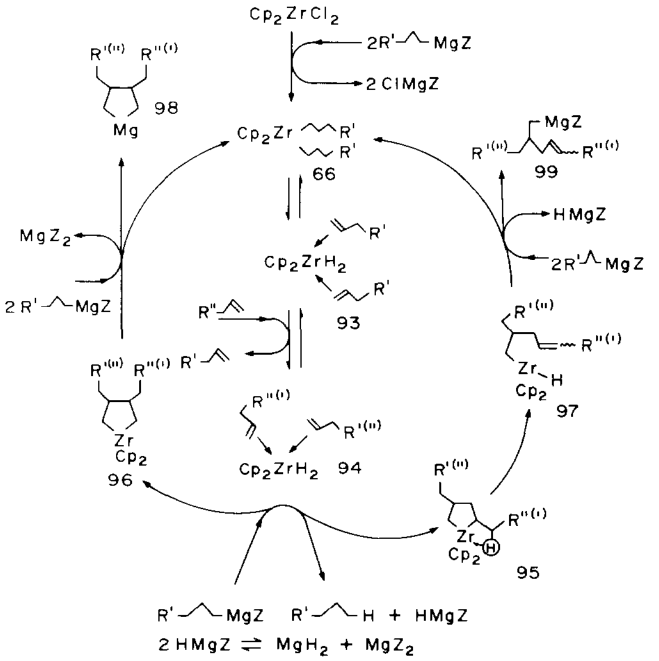
A similar effect may be observed in the reaction of $(n\text{-}C_6H_{13})_2Mg$ with allylbenzene:



It is important that the double bonds are strictly fixed between c(4) and c(5) atoms, counting from the magnesium atom, in the hydrocarbon radicals of all the resultant AMCs.

As may be concluded from the above results, we revealed a new catalytic reaction of n-alkyl magnesium derivatives with α-olefins, leading to AMCs.

Judging from the structures and compositions of the resultant reaction products, one may assume that the reaction would occur even through intermediate ZCP complexes. Scheme 5 may be considered reasonable for the reaction giving AMCs. Cp_2ZrCl_2 reacts with the starting OMC to give the dialkyl zirconium complex **66**. The latter complex eliminates reversibly 2 mol of the alkene, thus transforming into hydride complexes **93** and **94**, each containing two molecules of the coordinated olefin (eliminated or starting olefin molecules). Owing to an essential predominance of the starting olefin over the eliminated define, **94**, which contains two coordinated molecules of the starting olefin, would prevail in the product mixture.

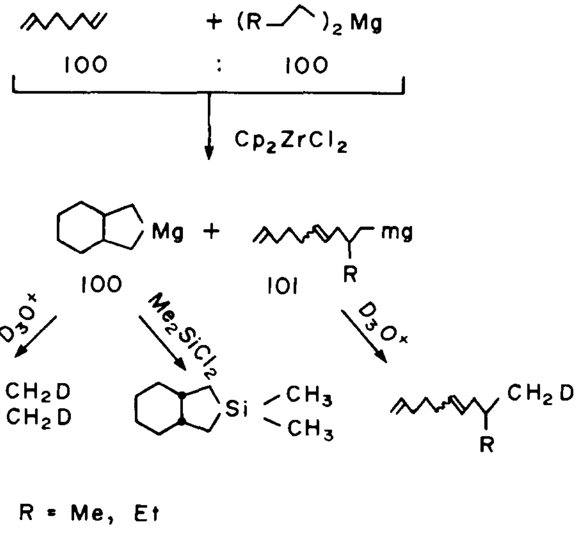


Scheme 5.

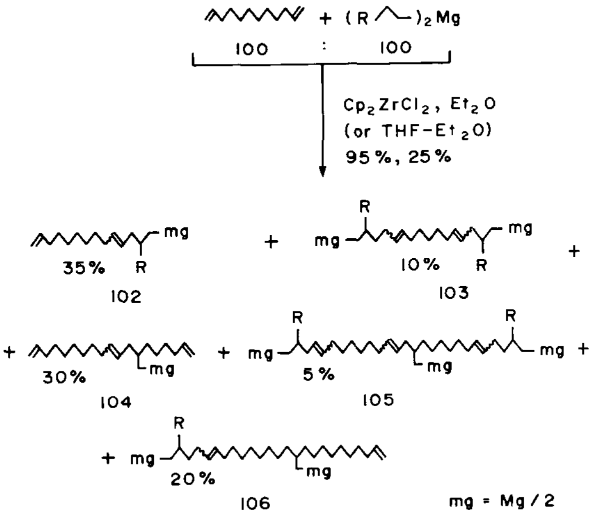
The complex **94** reacts with an excess of the starting OMC, acting as an acceptor of hydrogen, and is transformed into α-, β- and β,β'-disubstituted ZCPs **95** and **96**, the amount of the latter being much less than that of the former probably owing to some steric factors. The β,β'-disubstituted ZCPs are known to be rather unstable [22]; hence we can assume that **95** becomes isomerized rapidly into a more stable alkenyl hydride **97**; the hydrogen atoms are β eliminated exclusively from the acyclic CH_2 group. The hydride β elimination in β,β'-disubstituted metal cycles is somewhat hindered [22]; so **96** is stable under our experimental conditions. Finally, remetallation of **96** and **97** yields related OMOs **98** and **99** respectively.

In our subsequent experiments, we tried to conduct the cyclomagnesiation of α, ω-dienes. As a result, the reactions of n-alkyl magnesium derivatives with α, ω-dienes afforded both MCPs and acyclic AMCs under our experimental conditions.

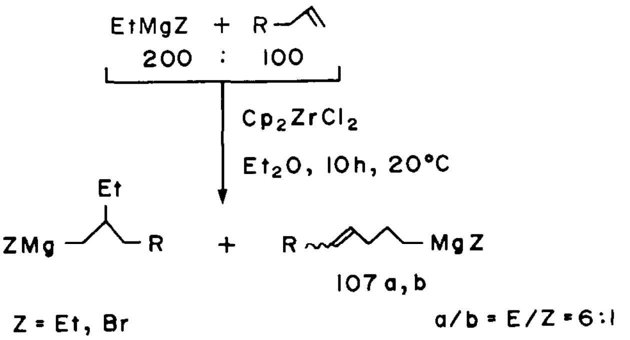
As an example, 1,7-octadiene reacts with $(n\text{-}C_3H_7)_2Mg$ or $(n\text{-}C_4H_9)_2Mg$ (3 wt.% Cp_2ZrCl_2; THF–Et_2O; 20°C; 7 h) to give a mixture of OMCs **100** and **101** (6 : 1) with about 90% total yield:



This reaction conducted without THF yields exclusively **100**. At the same time a mixture of AMCs **102–106** results from the reaction of an α, ω-diene having a longer hydrocarbon chain:



Recently, we managed to carry out some reactions of α-olefins with Et_2Mg and EtMgBr, leading preferentially to an AMC **107**. The reaction is successful only if it is conducted in a solution of Et_2O with an Mg:olefin starting reagent ratio of 2:1:

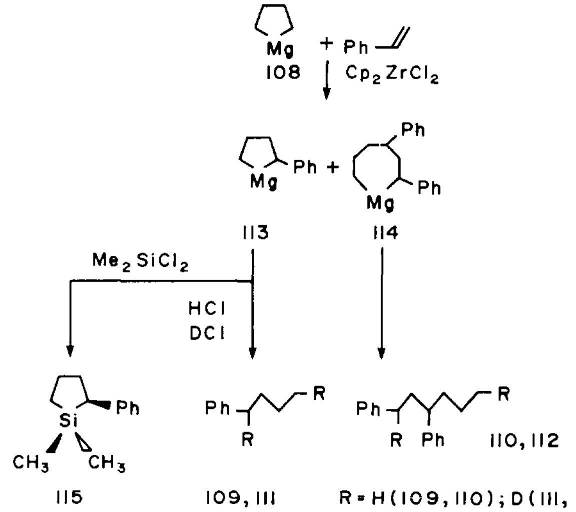


All the facts stated for the reactions of α-olefins with *n*-alkyl magnesium derivatives, assisted by Cp_2ZrCl_2, provide substantial evidence in favour of a common pattern of the reactions that are promising for the synthesis of higher alkenyl magnesium compounds and olefins of various structures.

To develop a new synthetic procedure for MCPs, to gain experimental evidence to the formation of ZCPs via an intramolecular cyclometallation of olefins with R_2Mg, and to find possible ZCP remetallation with OMCs, we studied reactions of unsubstituted MCPs with styrene in THF, catalyzed by Cp_2ZrCl_2.

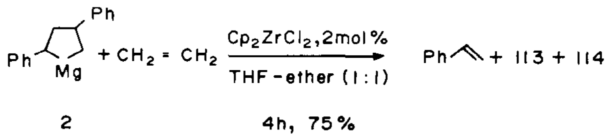
The reaction of styrene with **108** in a 1:1 ratio, catalyzed by 2 wt% Cp_2ZrCl_2, in a THF solution at 25°C for 1.5 h affords a mixture of organometallic compounds with about 75% total yield as calculated for the starting styrene, and ethylene with about 95% yield as calculated for **108**. Upon decomposition of the reaction products, assisted by HCl or DCl, butylbenzene (**109**) (about 95%) and 1,3-diphenylhexane (**110**) (about 5%), or 1,4-dideutero-1-phenylbutane (**111**) (about 95%) and 1,6-dideutero-1,3-diphenylhexane (**112**) (about 5%) respectively, are formed.

The structures of the hydrocarbons **109–112** indicate that the reaction products represent the OMCs in which the magnesium atom is bound up simultaneously to C′ and C(4) or C′ and C(6) carbon atoms of the hydrocarbon chain. In other words, 2-phenylmagnesiumcyclopentane (**113**) and a small amount of 2,4-diphenylmagnesiumcycloheptane (**114**) may be found in the reaction mixture during the cyclometallation and remetallation:



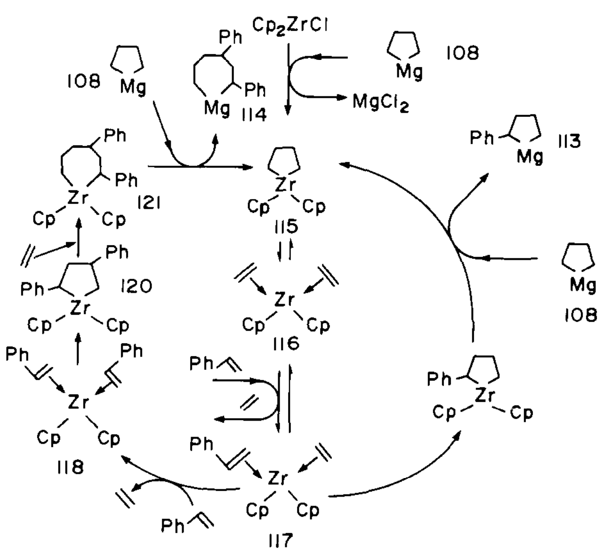
To furnish some more reliable proof for the structure of **113**, it was treated with Me_2SiCl_2, which afforded 1,2-dimethyl-2-phenylsilacyclopentane (**115**) with a 80% yield. The resultant magnesiacycloalkane **113** was built up of an ethylene molecule and a styrene molecule, while **114** was built up of two styrene molecules and an ethylene molecule.

To carry out an alternative synthesis of **113** and **114**, we conducted the reaction of 2,4-diphenylmagnesiumcyclopentane (**2**) which was prepared in situ via the cyclometallation of styrene with $(n\text{-}C_3H_7)_2Mg$, with ethylene. The reaction yielded 75% of styrene and a mixture of **113** and **114** in the ratios 65:13:22 respectively:



This serves a good confirmation for our assumption that the zirconacycloalkanes work as the key intermediates during the formation of magnesia-cycloalkanes.

Proceeding from the results of our experiments, we constructed Scheme 6 for the transformations of ethy-



Scheme 6.

lene, styrene, **108** and **2**, catalyzed by Cp_2ZrCl_2. In the first step, the remetallation of **108** with Cp_2ZrCl_2 gives 1,4-tetramethylene-bis(cyclopentadienyl)zirconium (**115**) which breaks and transforms into a bis-ethylene complex **116** under the reaction conditions [20]. Because of an excessive amount of styrene in the reaction mixture, ethylene is pushed out from the coordination sphere of **116**, which leads to the π-complexes **117** and **118**. Further intramolecular cyclometallation in **117** and **118** results in the ZCPs **119** and **120** respectively. Following the introduction of an ethylene molecule by the Zr–C bond, **120** is transformed into 2,4-diphenyl-1,6-hexamethylene-bis(cyclopentadienyl)zirconium (**121**). The interaction of **119** and **121** with **108** leads to the related magnesiacycloalkanes **113** and **114**, and also to regeneration of the starting active intermediate **115**.

Therefore our research in the field of transformations of OMCs with linear and cyclic olefins, catalyzed by the complex Cp_2ZrCl_2, led to a series of new reactions such as (i) cyclomagnesiation of olefins, (ii) oxidative coupling of α-olefins with the starting OMC, resulting in AMCs, in which the double bond is shifted for one carbon atom, and (iii) transformation of an MCP into a different cyclic OMC.

All these reactions have good potentials for organic and organometallic synthesis as well as for metal complex catalysis.

3. Experimental part

All the experiments were conducted in an atmosphere of dry argon. Solutions of dialkyl magnesium derivatives were prepared as reported elsewhere [23]. Starting styrenes were obtained according to the known procedures [24]. Compounds **10a**, **10b**, **11** and **115** were synthesized as reported by Xiong and Ricke [25]. The hydrocarbons were at least 99% pure. Compound **108** was synthesized according to the method of Holtkamp et al. [26]. The solvents were dried according to the standard procedures. The Grignard reagents were prepared as usual.

IR spectra were obtained on a UR-20 spectrometer (using thin layers). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 instrument (tetramethylsilane was used as an internal standard, and $CDCl_3$ as solvent). Mass spectra were obtained in a Finnigan-420 Chromatomass spectrometer. GLC analyses were done, following the required treatment of the reaction mixtures, on a Chrom-5 instrument having a flame-ionizing detector, 5% SE-30 and 30% PEG-6000 as fixed phases on N-AW-DMCS-Chromatone 3.7 m and 2.4 m columns at operating temperatures of 50–300°C and 50–170°C respectively. To analyze silicon-containing products, a catarometer was used with methyltrifluor–propylsiloxane rubber as a fixed phase on an Inertone-super 2.4 m columns, at 50–300°C. Gaseous hydrocarbons were analyzed on a Chrom-4 instrument, with columns of 6 m length and 3 mm diameter, with hexadecane on silica gel as a fixed phase, at 25°C. A column filled with activated coal and a detecting catarometer were used to analyze H_2. The products **10a** and **10b** were separated by column chromatography.

3.1. General procedure for the cyclometallation of styrenes and norbornenes with n-alkyl magnesium derivatives

A glass reaction vessel fixed on a magnetic stirrer was filled with a solution of OMC (20 mmol) in ether ($C_{OMC} = 1.4$ mmol ml^{-1}), styrene or NB (20 mmol), Cp_2ZrCl_2(0.116 g, 0.4 mmol) and THF (14 ml). The mixture was stirred at 25°C for 7–8 h, cooled to 0°C, hydrolyzed with 5% HCl in H_2O or DCl in D_2O, extracted with an ether and dried with $MgSO_4$. After evaporation of the solvent, the mixture was analyzed by GLC. Individual products were isolated by vacuum rectification. The gaseous portion of the reaction mixture was analyzed by GLC. The reaction mixture was oxidized with oxygen as reported elsewhere [27].

3.2. General procedure for reactions of organomagnesium compounds with α-olefins

Cp_2ZrCl_2(0.2 mmol) and α-olefin (20 mmol) were added in turn to an ester solution of n-R_2Mg (30 mmol) or n-RMgBr (60 mmol). The mixture was stirred at about 20°C until precipitation took place; then the precipitate was separated, washed with dry ester (3 × 50 ml), dried and subjected to elemental analysis. The liquid portion of the reaction mixture was cooled to

0°C and hydrolyzed with DCl in D_2O; then the organic layer was separated, dried with $MgSO_4$ and analyzed by GLC. Individual compounds were isolated by preparative chromatography and vacuum rectification.

3.3. Reaction of the magnesiacyclopentane **108** with styrene

A 100 ml glass vessel fixed on a magnetic stirrer was filled with a solution of **108** (30 mmol) in THF (0.52 mmol ml^{-1}), styrene (3.12 g, 30 mmol) and Cp_2ZrCl_2 (0.175 g, 0.6 mmol). The mixture was stirred at 20–25°C for 1.5 h, cooled to 0°C and hydrolyzed with HCl in H_2O or DCl in D_2O. The reaction products were isolated as described above.

The reaction of **2** with ethylene was carried out in a steel autoclave ($V = 100$ cm^3) at 25°C (12.5 and 25 atm), with a **2** : ethylene ratios of 1 : 1 and 1 : 2.

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