New effective reagent [Cp₂ZrH₂ · ClAlEt₂]₂ for alkene hydrometallation

Lyudmila V. Parfenova *, Rushana F. Vil'danova, Svetlana V. Pechatkina,
Leonard M. Khalilov, Usein M. Dzhemilev

Institute of Petrochemistry and Catalysis, Russian Academy of Sciences, 450075 Ufa, Prospect Oktyabrya 141, Russian Federation

Abstract

New bimetallic complex [Cp₂ZrH₂ · ClAlEt₂]₂ (**1**) was synthesized, and its reactivity in hydrometallation reaction with the following alkenes was studied: hept-1-ene, okt-1-ene, α-methylstyrene, (1S)-β-pinene, (+)-camphene. Complex **1** shows the highest reactivity among the other known Al,Zr-bimetallic complexes: [Cp₂ZrH₂ · ClAlBu$_2^i$]₂ (**2**), [Cp₂ZrH₂ · AlEt₃]₂ (**3**), [Cp₂ZrH₂ · AlBu$_3^i$]₂ (**4**) and [Cp₂ZrH₂ · HAlBu$_2^i$] (**5**) as well as organoaluminium compounds (OAC): ^{i}Bu₂AlH, ^{i}Bu₃Al and ^{i}Bu₂AlCl in presence of Zr catalysts. Chlorine containing complexes **1** and **2** appear to be more effective in alkene hydrometallation, and relative hydrometallation rates are (1S)-β-pinene ⩽ (+)-camphene < α-methylstyrene < oct-1-ene < hept-1-ene. Hydrometallation of (1S)-β-pinene and its subsequent oxidation with I₂ run with high diastereoselectivity and yield *trans*-myrtanol. However, the diastereoselectivity of (+)-camphene hydrometallation is less than that for (1S)-β-pinene, and the reaction gives predominately *endo*-camphanol.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Hydrometallation; Al,Zr-complexes; Organoaluminium compounds; Organozirconium compounds; *trans*-Myrtanol; *endo*-Camphanol

1. Introduction

More than 30 years passed since the moment when the first zirconium hydrides: Cp₂ZrHCl and Cp₂ZrH₂ were synthesized by Wailes et al. [1]. The hydrozirconation reagent Cp₂ZrHCl, or Schwartz reagent, has been widely used in laboratory practice. Under the mild conditions the reagent hydrometallates alkenes of different structure to obtain functional derivatives. According to Schwartz [2], the relative rates of the alkenes hydrozirconation are α-alkene > *cis*-alkene > *trans*-alkene > exocyclic alkene > cyclic alkene > trisubstituted alkene. The last three alkenes react with Cp₂ZrHCl at temperature higher than 40 °C. Among the bicyclic hydrocarbons with various double bond screening degrees the hydrozirconation rates are: norbonene > sabinene > camphene > β-pinene [3]; moreover,

Cp₂ZrHCl generally attaches to the less hindered side of the alkene.

Unlike Schwartz reagent, Cp₂ZrH₂ did not become useful in synthesis because of instability of dialkyl zirconocenes which are formed during the reactions with alkenes. The dialkyl zirconocenes are disposed to the disproportionation to give zirconocene "Cp₂Zr" and a mixture of alkane and alkene in mole ratio 1:1 [4a]. Furthermore, the reaction of Cp₂ZrH₂ with acetylenes provides zirconocyclopentadienes [4b].

Along with the mentioned above zirconium hydrides, the isobutylalanes (HAlBu$_2^i$, ClAlBu$_2^i$, AlBu$_3^i$) are widely used for the alkene reduction in the presence of Zr catalysts.

We recently established the formation of hydride Al,Zr-complexes during mechanism studies for the alkenes hydroalumination by HAlBu$_2^i$, ClAlBu$_2^i$ and AlBu$_3^i$ in the presence of Cp₂ZrCl₂ catalyst [5]. As a result, new complex [Cp₂ZrH₂ · ClAlBu$_2^i$]₂ (**2**) was found and shown to be a key intermediate of the reaction (Scheme 1).

* Corresponding author. Tel.: +7 3472 313527; fax: +7 3472 312750.
  E-mail addresses: luda_parfenova@yahoo.com, ink@anrb.ru (L.V. Parfenova).
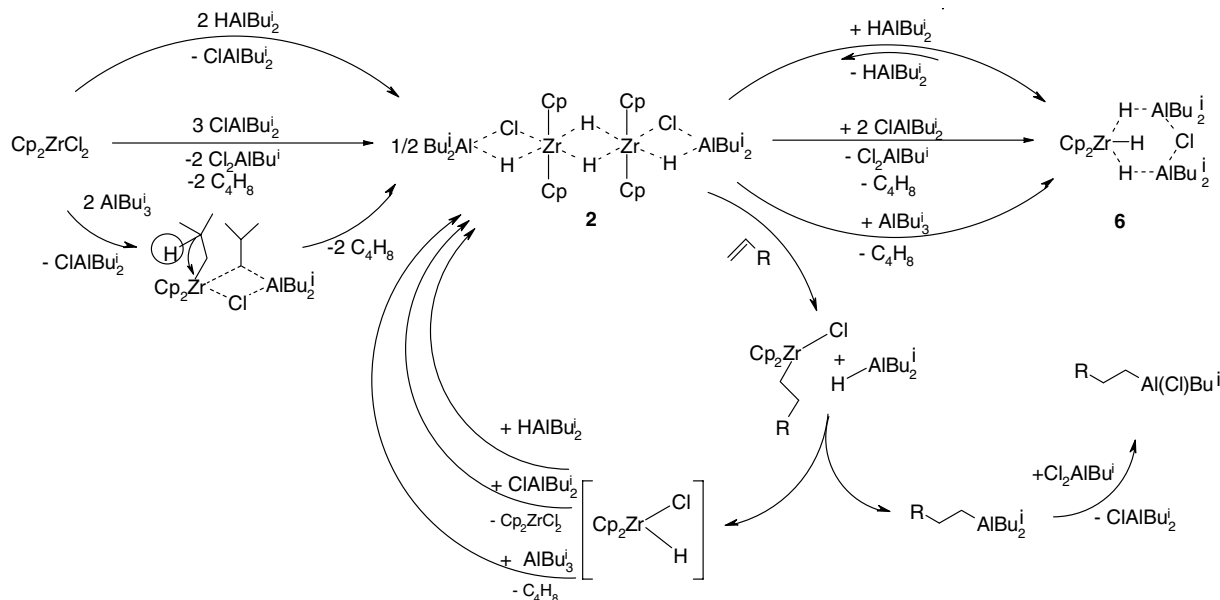
Scheme 1.

The structure of complex **2** was established by the means of both NMR spectroscopy and encounter synthesis from $[Cp_2ZrH_2]_2$ and $ClAlBu_2^i$. Moreover, the dimeric structure of the complex was confirmed by cryoscopy. Further, complex **2** can transform into trihydride complex $Cp_2ZrH_2 \cdot ClAlBu_2^i \cdot HAlBu_2^i$ (**6**), which does not react with alkenes. However, complex **6** reduces carbonyl compounds [6] and acetylenes [7]. Moreover, complex **2** coordinates the alkene to form alkyl complex $Cp_2ZrCl(CH_2CH_2R)$ and $HAlBu_2^i$, which further rapidly transmetallates zirconocene alkylchloride and gives both diisobutylalkylaluminium and Cp_2ZrHCl. Independently from the nature of initial OAC, Cp_2ZrHCl immediately transforms into complex **2**, thus closing the hydrometallation catalytic cycle.

Furthermore, during the study of the hydroalumination mechanism we synthesized bimetallic hydride complexes **3** [8], **4** [5], **5** [9] by the encounter synthesis as represented on Scheme 2. It was shown that all these complexes react with alkenes and form alkylalanes [5].

In this paper we present novel complex $[Cp_2ZrH_2 \cdot ClAlEt_2]_2$ (**1**), which is related to complex **2**. The aims of the work are the following: study of alkene hydroalumination with

new bimetallic complex **1** and complexes **2**–**5**; comparison of their reactivity; analysis of stereoselectivity of both (1S)-β-pinene and (+)-camphene hydrometallation by complex **1**.

2. Results and discussion

2.1. Synthesis and structure of $[Cp_2ZrH_2 \cdot ClAlEt_2]_2$ (1)

Complex **1** was synthesized by treating the $[Cp_2ZrH_2]_2$ with 2 equiv. of $ClAlEt_2$ in C_6H_6 at room temperature analogous to that of complex **2** [5].
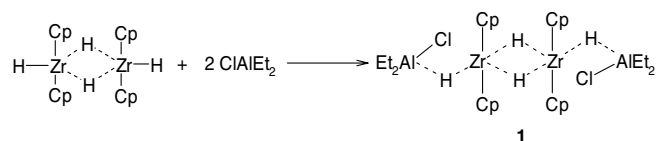
NMR ^{1}H spectrum of complex **1** is very similar to that reported for complex **2** [5]. Complex **1** exhibits widened triplet signal of the bridge Zr–H–Zr hydrogen at −2.68 ppm with $^2J = 4.2$ Hz. The signal of the bridge Zr–H–Al hydrogen is located at −0.91 ppm. It is wider than that in Zr–H–Zr fragment, and it is not splitted into the multiplet. On the other hand, both complexes **3** and **4** (type $[Cp_2ZrH_2 \cdot AlR'_3]_2$) exhibit two sharp triplets for the both bridge hydrogens [5]. Broadening of the signals of hydride atoms in complexes **1** and **2** can be explained both by the increase in the rate of intramolecular exchange between bridge and terminal hydrides and by the shift of the equilibrium from the dimeric to monomeric form of the complexes. The temperature behavior of the both dynamic processes is similar to that in $[Cp_2ZrH_2]_2$ [10]. The study of the molecular weight of complex **1** by cryoscopy in ben-
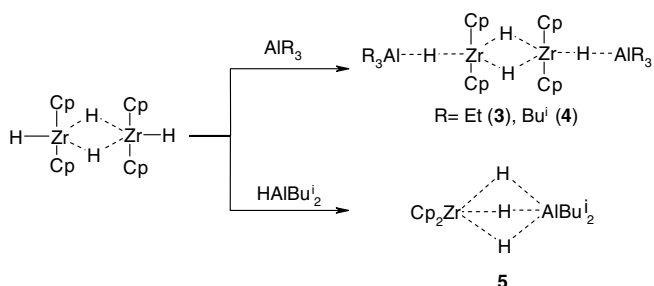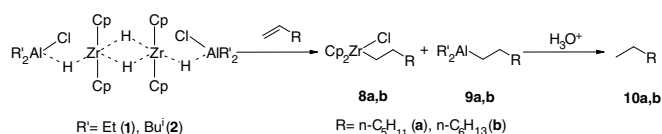

Scheme 2.

zene confirmed the dimeric structure of this compound. The experimental value of the molecular weight was 640 g mol^{-1}, while the theoretical weight is equal to 688 g mol^{-1}.

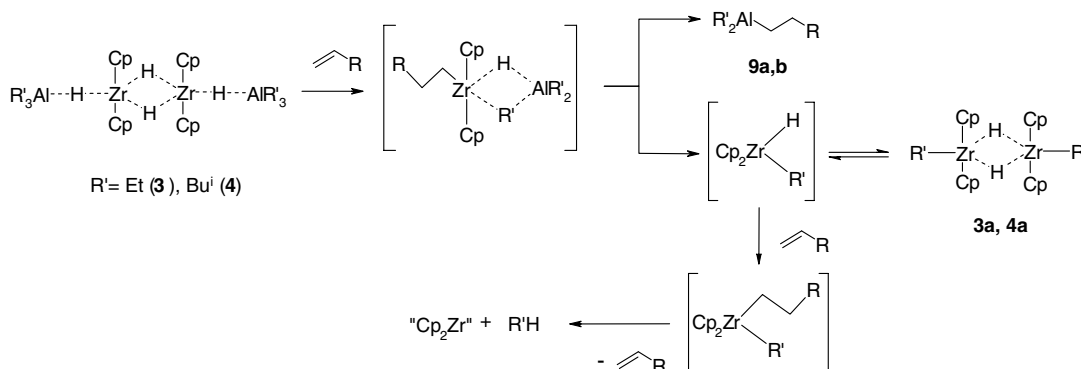## 2.2. Reactivity of complexes 1–5 in reactions with α-alkenes

Complexes **1–5** were evaluated in the reactions with α-alkenes (hept-1-ene (**7a**), oct-1-ene (**7b**)) in C$_6$H$_6$ at room temperature and different mole ratios of complex to alkene: 1:2 and 1:4. The NMR observation of the reactions shows that the hydrometallation products: zirconocene alkylchlorides **8a,b** and alkylalanes **9a,b** are formed in mole ratio 1:1. The NMR spectra of **8a,b** and **9a,b** correlate with the data presented in Ref. [5].

R'= Et (**1**), Bu^i(**2**)   R= n-C$_5$H$_{11}$ (**a**), n-C$_6$H$_{13}$(**b**)

However, the hydrometallation of alkenes with complexes **3** and **4** proceeds more complex than that with complexes **1** and **2** (Scheme 3). For example, at the mole ratio 1:2 we observed formation of alkylalanes **9a,b** and alkylhydride complexes **3a** and **4a**, which are similar to the complexes described in the Schwartz work [11].

The increase of the alkene concentration to the mole ratio of 1:4 leads to the broadening of the Cp-rings signals in the NMR spectra. Analysis of the gaseous products which appear in this reaction shows that for complex **3** the isolation of ethane and for complex **4** the formation of isobutane is observed. Probably, the presence of an additional quantity of alkene accelerates the well-known process of zirconocene alkylhydrides (**3a** and **4a**) decomposition into both "Cp$_2$Zr" and alkanes R'H [11]. The interaction of complex **5** with alkenes is similar to that for complexes **3** and **4**.

Comparison of complexes **1–5** reactivity was carried out in the reaction with alkene **7a** at the mole ratio 1:2 (Fig. 1). It was
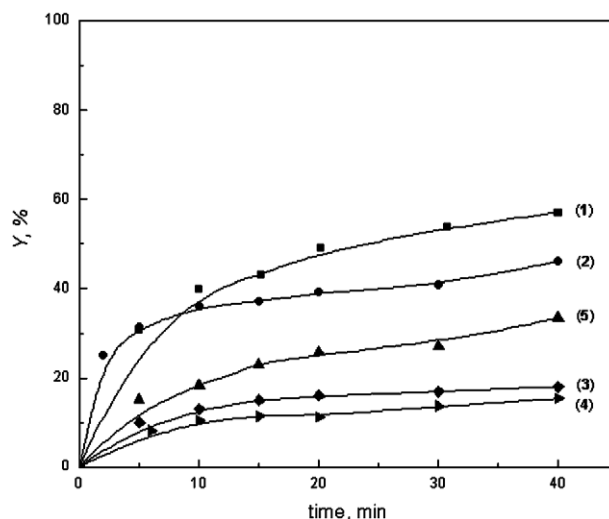
Fig. 1. The yield of heptane (**10a**) in hydrometallation of **7a** with complexes **1–5** at mole ratio of complex to alkene 1:2, vs. time (20 °C, C$_6$H$_6$).

According to Fig. 1 the reactivity of Al,Zr-hydride complexes **1–5** rises in the series **4** ⩽ **3** < **5** < **2** < **1**. Therefore, complexes **1** and **2** are the most active among the bimetallic Al,Zr-hydride complexes studied by us. Probably, compared to trialkylalanes AlR'$_3$, the chlorine containing OACs ClAlR'$_2$ increase the rate of the intramolecular exchange between bridge and terminal hydrides in dimer [Cp$_2$ZrH$_2$]$_2$ and, consequently, shift the equilibrium between the dimeric and monomeric forms. This "shaking" of dimer [Cp$_2$ZrH$_2$]$_2$ under the action of ClAlR'$_2$ eases the process of alkene introduction into Zr–H bond.

Moreover, the reactivity of complexes **1** and **2** is higher than that of Schwartz reagent. For example, the yield of **10a** in the reaction of **7a** with Cp$_2$ZrHCl for 6 h in C$_6$H$_6$ at 20 °C was 70%, whereas for complexes **1** and **2** the corresponding alkane yield of 87% was achieved after only 1 h. We link the reason of this higher reactivity with the both high solubility of the studied complexes in hydrocarbon solvents and additional activation of [Cp$_2$ZrH$_2$]$_2$ due to the complex formation in reaction with ClAlR'$_2$.

Further, the influence of complex **1** to alkene **7a,b** mole ratio on the yields of alkanes **10a,b** was studied. It was

R'= Et (**3**), Bu^i (**4**)

Scheme 3.

shown that the yield of **10a,b** during the first 20 min of the reaction at the mole ratio of 1:2 is two times higher than that at the mole ratio of 1:4. After that, the dependence of the alkane yield vs. the reaction time for both ratios becomes equal. Therefore, it could be concluded that all four hydride atoms in complex **1** participate in the hydrometallation process.

2.3. Reactivity of alkenes in the reactions with complexes 1 and 2

Further we studied the interactions of complexes **1** and **2** in C_6H_6 at room temperature with the following alkenes: α-methylstyrene (**7c**), (+)-camphene (**7d**), (1S)-β-pinene (**7e**). It was shown that complexes **1** and **2** react with **7c–e** similarly to that with α- alkenes **7a,b**; as a result of the reaction, zirconocene alkylchlorides **8c–e** and alkylalanes **9c–e** are formed in mole ratio 1:1 (Scheme 4).

Hydrolysis of the hydrometallation products gives alkanes **10c–e**, whose yields vs. both the initial reagents ratio and the reaction time are presented in Table 1. Under the optimal conditions at the mole ratio of 1:2 the maximal yield of the products **10a,b** is close to 87% after 1 h of the reaction, whereas the isopropylbenzene (**10c**), camphane (**10d**) and pinane (**10e**) yields of 86%, 78% and 84% were observed after 1.5, 2.0 and 2.5 h, correspondingly. It is interesting that catalytic hydroalumination of β-pinene by $HAlBu_2^i$ in the presence of $ZrCl_4$ [12] at

60 °C for 12 h after hydrolysis gave pinane at the yield of 69%.

As follows from Table 1, the studied alkenes reactivity in hydrometallation by complexes **1** and **2** is (1S)-β-pinene ≤ (+)-camphene < α-methylstyrene < oct-1-ene < hept-1-ene.

2.4. Stereoselectivity of Bicyclic Olefin Hydrometallation by Complex 1

In order to study the stereoselectivity of complex **1** reaction with both (+)-camphene and (1S)-β-pinene we obtained alcohols **11d** and **11e** by oxidation with dried oxygen and consequent hydrolysis of the hydrometallation products **8d,e** and **9d,e**. In these reactions the yield of alcohols was fairly low; for example, the formation of *trans*- and *cis*-mirtanols (**11e**) proceeds with the yield of about 57%. Further, the yield of the alcohols was increased after carrying out the additional transmetallation stage of **8d,e** by $ClAlR'_2$ as shown in Scheme 4 without isolation of the organozirconium compound from the mixture. During this reaction we observed formation of Cp_2ZrCl_2 and OACs **9d** or **9e**. The oxidation of **9d** or **9e** and the subsequent hydrolysis provided compounds **11e** and **11d** at the yields of 82% and 71% accordingly.

The correlation between the obtained alcohol stereoisomers was established by both the technique of optical rotation angle $[\alpha]_D$ measurement and the means of ^1H and ^{13}C
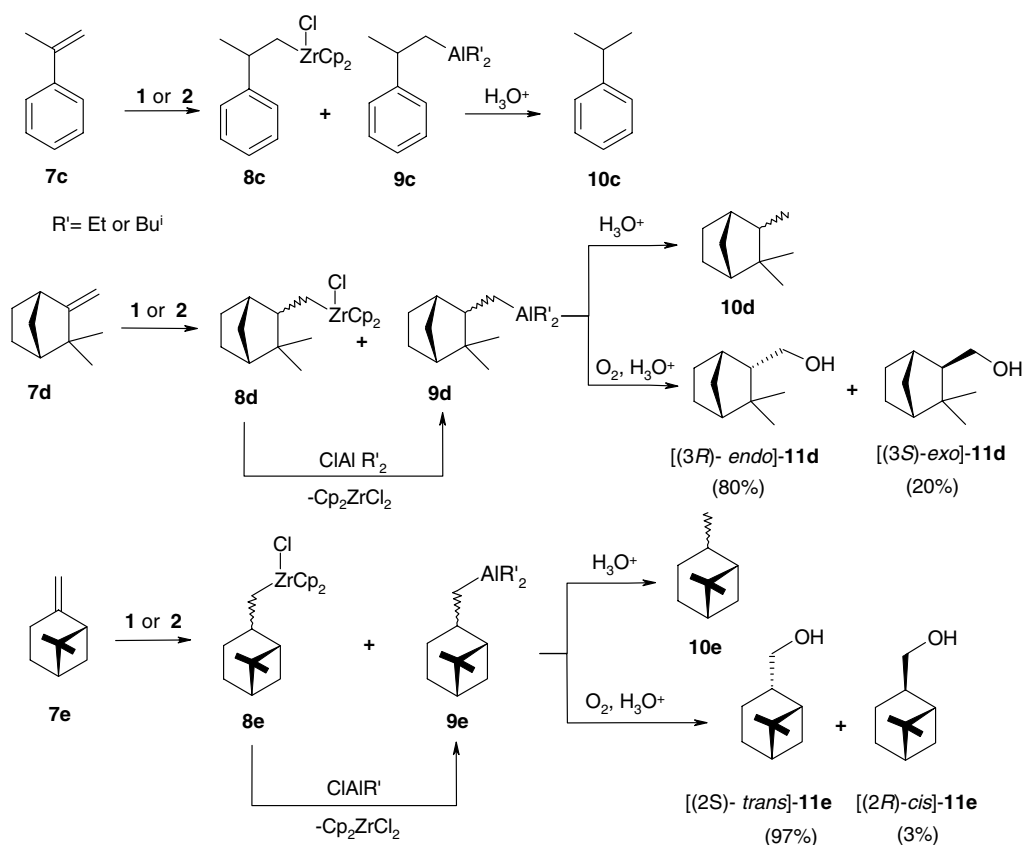
Scheme 4.

Table 1
Yield of hydrometallation products vs. complex nature, reagents concentration and reaction time (C_6H_6, 20 °C)

Complex	Alkene	Mole ratio	Time (h)	Hydrolysis products	Yield (%)
1	Hept-1-ene (**7a**)	1:2	0.25	Heptane (**10a**)	79
			1		87
	Oct-1-ene (**7b**)	1:2	0.25	Octane (**10b**)	76
			1		82
		1:4	0.25		31
			3		80
	α-Methylstyrene (**7c**)	1:2	0.25	Isopropylbenzene (**10c**)	64
			1.5		86
	(+)-Camphene (**7d**)	1:2	2	Camphane (**10d**)	78
		1:4	2		71
	(1S)-β-pinene (**7e**)	1:2	0.25	Pinane (**10e**)	34
			2.5		83
2	**7a**	1:2	0.25	**10a**	78
			1		83
	7b	1:2	0.25	**10b**	74
			1		80
	7c	1:2	0.25	**10c**	61
			1.5		84
	7e	1:2	2	**10e**	81
3	**7a**	1:2	1	**10a**	19
4	**7a**	1:2	1	**10a**	17
5	**7a**	1:2	1	**10a**	43

NMR spectroscopy [13,14]. It was found that the hydrometallation of (1S)-β-pinene by complex **1** runs with high diastereoselectivity and mainly provides *trans*-isomer **11e** (*trans/cis* ratio 97:3). However, the diastereoselectivity of (+)-camphene hydrometallation is less than that of (1S)-β-pinene, and the reaction and subsequent oxidation with I_2 give *endo*-camphanol (*endo/exo* ratio: 80:20).

By the beginning of our studies the literature data contained contradictory information concerning the stereoselectivity of the bicyclic alkenes reducing. However, an opinion that the attachment of small molecules (BH_3, $HAlBu_2^i$) to bicyclic alkenes proceeds at the least sterically hindered side of the double bond was common for literature sources. For example, in Ref. [15] devoted to oxidative camphene hydroboration with BH_3 a mixture of diastereomers with predomination of *endo*-camphanol (*endo/exo* ratio 80:20) was obtained. The same reaction with β-pinene produces *cis*-mirtanol at high yield [16].

The camphene hydrozirconation by Schwartz reagent at 80 °C and further oxidation of the reaction products also provides *endo*-camphanol (*endo/exo* ratio 97:3) [3]. The β-pinene hydrozirconation provides the excess of *cis*-isomer (*trans/cis* ratio 13:87). The *endo*-isomers formation the authors explained by the isomerization of zirconium σ-complex with the *exo*-configuration of substitutes which was initially formed in the steric control conditions. Furthermore, boron-[15a,16] and organoaluminium [13] *exo*-isomers were shown to be able to transform into more thermodynamically stable *endo*-isomers after heating. It is interesting that

H_2PtCl_6 catalyzed hydrosilylation of β-pinene using $HSiMeCl_2$ or $HSiMe_2Cl$ gives *trans*-isomers [17], whereas no diastereoselectivity was observed in the reaction with camphene [14a].

In our case the high diastereoselectivity of the bicyclic alkenes reaction with complex **1** under the mild conditions is probably caused by the structure of the complex, and, therefore, the bicyclic alkene hydrometallation proceeds at the most hindered *exo*-side with formation of thermodynamically stable *endo*-isomers.

3. Conclusion

Finally, a new bimetallic complex $[Cp_2ZrH_2 \cdot ClAlEt_2]_2$ (**1**) was synthesized, and its reactivity in the reaction of alkenes hydrometallation was studied. Results of the alkenes hydrometallation by hydride Al,Zr-complexes **1–5** show that chlorine containing complexes **1** and **2** are the most active among the complexes studied by us. In these reactions α-alkenes exhibit the highest reactivity. The 1,1′-substituted alkenes (e.g. α-methyl styrene) are less active. The bicyclic alkenes (e.g. camphene and β-pinene) due to electronic and steric factors show the lowest activity in the series of the alkenes examined. Because of the complexes **1** and **2** structure, the hydrometallation of (1S)-β-pinene and (+)-camphene runs with high diastereoselectivity and provides *trans*- and *endo*-alcohols, correspondingly. The new reagent **1** opens the way to the synthesis of not only diastereomerically pure bicyclic alcohols, but also optically active OACs, for example, **9d,e**, which are promising for the purposes of organic and organometallic synthesis.

4. Experimental

4.1. General

All operations were carried out under argon using Schlenk techniques. Solvents were dried by refluxing over either $LiAlH_4$ or *i*-Bu_2AlH and freshly distilled prior to use. (+)-Camphene (**7d**) (Aldrich; 80%) was purchased and used after double recrystallization. (1S)-(−)-β-Pinene (Aldrich 99+%) was used without purification. Commercially available 91.8% $AlEt_3$, 90% $ClAlEt_2$, 95% $ClAlBu_2^i$, 91% $AlBu_3^i$ and 74% $HAlBu_2^i$ were involved into the reactions. Cp_2ZrCl_2 was prepared from $ZrCl_4$(Aldrich, 99.5 %) according to the procedure in Ref. [18]. The Cp_2ZrH_2 and complexes **2–5** were prepared as described previously in Ref. [5]. The NMR spectra ^1H and ^{13}C were recorded at 25 °C on spectrometers JEOL FX-90Q (90 MHz ^1H, 22.5 MHz ^{13}C) and BRUKER AM-300 (300 MHz ^1H, 75 MHz ^{13}C). d_6-Benzene and *d*-chloroform were used as internal standard. Optical rotation angles $[\alpha]_D$ were determined on spectropolarimeter Perkin–Elmer-341. The hydrolysis products of reaction mixture were analyzed on chromatograph "Chrom-5" (flame-ionizing detector, column 2 m × 3 mm 15% "Peg-6000" or 5% "SE-30" on Chromaton N-AW, 50–190 °C). Mass spectra were obtained

on a Finnigan 4021 GLC-mass spectrometer. The yields of the both alkanes and alcohols were calculated with respect to the initial alkene amount.

4.2. Synthesis of [Cp₂ZrH₂ · ClAlEt₂]₂ (1)

A flask equipped with a magnetic stirrer and filled with argon was loaded with Cp_2ZrH_2 (0.6 mmol, 134 mg) and benzene (1.5 ml). $ClAlEt_2$ (0.6 mmol, 0.11 ml) was added dropwise until the precipitate was dissolved. Finally the formation of complex **1** was observed.

^1H NMR (C_6D_6) δ 5.78 (20H, Cp); −0.91 (s, 2H, ZrHAl); −2.68 (br.t, 2H, ZrHZr, $^2J_{HH} = 4.2$ Hz); 1,46 (t, 12H, CH_3, $J = 8.3$ Hz); 0.43 (q, 8H, CH_2, $J = 8.3$ Hz). ^{13}C NMR (C_6D_6) δ 106.35 (Cp), 1.15 (t, C_1), 9.83 (q, C_2). Molecular weight (cryoscopy in benzene): found 640 g mol^{-1}; calc. 688 g mol^{-1}.

4.3. Alkenes 7a–e hydrometallation with complexes 1–5

A flask equipped with a magnetic stirrer and filled with argon was loaded with Cp_2ZrH_2 (0.6 mmol, 134 mg) and benzene (0.5 ml). The OACs (0.6 mmol) were added dropwise until the precipitate was completely dissolved. Formation of complexes **1–5** were obtained. Then, either 0.6 or 1.2 mmol of alkenes **7a–e** were added to reaction mixture. The mixture was stirred for 2 h and the formation of mixture of **8a–e** and **9a–e** at mole ratio 1:1 was observed. For the kinetic study, the samples (0.2 ml) were syringed into tubes filled with argon, and the samples were decomposed with 10% HCl at 0 °C. The decomposition products were extracted with benzene; further, the organic layer was dried over Na_2SO_4 and analyzed by GLC. The products yields are presented in Table 1.

4.4. Oxidation of 9d,e with O₂

An excess of $ClAlEt_2$ or $ClAlBu_2^i$ (0.6 mmol) was added under vigorous stirring to either **8d,e** or **9d,e** mixture, which was prepared as described in Section 4.3. The mixture was stirred for 1 h at r.t. The solution of **9d,e** was blown by dry O_2 and decomposed by 10% HCl at 0 °C. The products were extracted by benzene (3 × 5 ml); the combined organic extracts were dried over Na_2SO_4 and the solvents removed in vacuum. The products were recrystallized from $CHCl_3$. The yield of [(3R)-endo]- and [(3S)-exo]-1R,4S-2,2-dimethylbicyclo[2.2.1]heptan-3-yl-methanol (**11d**) was 71% (endo/exo ratio 80:20). The yield of [(2S)-trans]- and [(2R)-cis]-1S,5S-6,6-dimethylbicyclo[3.1.1]heptan-2-yl-methanol (**11e**) was 82% (trans/cis ratio 97:3). ^1H and ^{13}C NMR spectra were identical to those of authentic sample [14a,14b,14c].

References

[1] (a) B. Kautzner, P.C. Wailes, H. Weigold, J. Chem. Soc., Chem. Commun. D19 (1969) 1105;
(b) P.C. Wailes, H. Weigold, J. Organomet. Chem. 24 (1970) 405.
[2] (a) D.W. Hart, J. Schwartz, J. Am. Chem. Soc. 96 (1974) 8115;
(b) J. Schwartz, J.A. Labinger, Angew. Chem. Int. Ed. Engl. 15 (1976) 333.
[3] M.S. Miftakhov, N.N. Sidorov, G.A. Tolstikov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 28 (1979).
[4] (a) P.C. Wailes, H. Welgold, A.P. Bell, J. Organomet. Chem. 43 (1972) 32;
(b) P.C. Wailes, H. Welgold, A.P. Bell, J. Organomet. Chem. 27 (1971) 373.
[5] L.V. Parfenova, S.V. Pechatkina, L.M. Khalilov, U.M. Dzhemilev, Russ. Chem. Bull. 54 (2005) 316.
[6] L.I. Shoer, J. Schwartz, J. Am. Chem. Soc. 99 (1977) 5831.
[7] B.D. Carr, J. Schwartz, J. Am. Chem. Soc. 101 (1979) 3521.
[8] P.C. Wailes, H. Weigold, A.P. Bell, J. Organomet. Chem. 43 (1972) 29.
[9] L.I. Shoer, K.I. Gell, J. Schwartz, J. Organomet. Chem. 136 (1977) 19.
[10] P.G. Bickley, N. Hao, P. Bougeard, B.G. Sayrr, R. Burns, M. Burns, M.J. McGlinchey, J. Organomet. Chem. 246 (1983) 257.
[11] (a) K.I. Gell, J. Schwartz, J. Am. Chem. Soc. 100 (1978) 3246;
(b) K.I. Gell, B. Posin, J. Schwartz, G.M. Williams, J. Am. Chem. Soc. 104 (1982) 1846.
[12] G.A. Tolstikov, U.M. Dzhemilev, O.S. Vostrikova, A.G. Tolstikov, Izv. AN SSSR. Ser. Khim. (1982) 669.
[13] trans-Myrtanol: H. Benn, J. Brandt, G. Wilke, Liebigs Ann. Chem. (1974) 189.
[14] (a) Camphanol: J. Beckmann, D. Dakternieks, A. Duthie, S.L. Floate, R.C. Foitzik, C.H. Schiesser, J. Organomet. Chem. 689 (2004) 909;
(b) myrtanol: M. Miyazawa, Y. Suzuki, H. Kameoka, Phytochemistry 45 (1997) 935;
(c) myrtanol: K.-Y. Kim, S.-G. Lee, Magn. Reson. Chem. 35 (1997) 451.
[15] (a) R. Dulou, J. Chretien-Bessiere, Bull. Soc. Chim. France (1959) 1362;
(b) J. Lhomme, G. Ourisson, Tetrahedron 24 (1968) 3201.
[16] (a) J.C. Braun, G.S. Fisher, Tetrahedron Lett. 21 (1960) 9;
(b) G. Zweifel, H.C. Brown, J. Am. Chem. Soc. 86 (1964) 393.
[17] D. Wang, T.H. Chan, Tetrahedron Lett. 24 (1983) 1573.
[18] R.Kh. Freidlina, E.M. Brainina, A.N. Nesmeyanov, Dokl. Acad. Nauk SSSR 138 (1969) 1369.