Journal of Organometallic Chemistry, 473 (1994) 117–128

Highly regioselective reaction of zirconocene-alkene complexes with aldehydes or ketones

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(Received December 1, 1993; in revised form March 23, 1994)

Abstract

Reactions of zirconocene-alkene complexes $Cp_2Zr(CH_2{=}CHR)(PR'_3)$ (R = H, Me, Et, SiR''_3 or Ar) with aldehydes or ketones were investigated. Zirconocene-ethylene, -propylene or 1-butene complexes reacted with aldehydes or ketones at terminal carbons of alkenes to give the corresponding alcohols after hydrolysis with a high regioselectivity. A similar type of reaction product was also obtained by a reaction of zirconacyclopentanes with aldehydes. This reaction proceeded via β–β' carbon–carbon bond cleavage of zirconacyclopentanes. A reaction of zirconocene-vinylsilane complexes with ketones afforded 3-trimethylsilyl-1-oxa-2-zirconacyclopentanes with an excellent regioselectivity. Carbon–carbon bond formation occurred exclusively at the terminal carbon of vinylsilanes. Their corresponding γ-silylalcohols were obtained after hydrolysis. The products showed that vinylsilanes reacted with carbonyl compounds at the β-carbon to silyl group. It is in sharp contrast to the conventional reactions of vinylsilanes of which the α-carbon normally attacked electrophiles. The reactions of styrene and its derivatives with pentan-3-one on zirconium gave a mixture of two regioisomers. Substituents of alkenes tend to be in α-position to Zr in 1-oxa-2-zirconacyclopentanes. This orientation showed a different aspect of the formation of 1-oxa-2-zirconacyclopentanes from the alkene-alkene coupling reaction on zirconium. The regioselectivity of the reaction with carbonyl compounds decreased in this order; R = alkyl > silyl > aryl.

Key words: Zirconium; Silicon; Metallocenes; Carbon–carbon bond formation; Aldehyde; Ketone

1. Introduction

Recently a variety of valuable reactions involving organozirconium complexes have been reported [1]. Zirconocene-alkene complexes have been also attractive compounds since the first example, zirconocene-stilbene complex, was prepared and characterized [2,3]. Zirconocene-alkene complexes can be prepared by (i) addition of alkenes to Cp_2ZrBu_2 (Negishi reagent) [2,4], (ii) addition of alkenes to $Cp_2Zr(PMe_3)_2$ [5], (iii) a β-hydrogen abstraction and an elimination of alkanes from zirconocenedialkyls [3,6], (iv) a reaction of Cp_2ZrMe_2 with alkylmagnesium halides [7], (v) replacement of alkenes in zirconocene-alkene complexes $Cp_2Zr(alkene)(PR_3)$ [6b,8]. (vi) β–β' carbon–carbon bond cleavage of a zirconacyclopentane compound [9], or (vii) a reaction of zirconocenealkylalkoxides with alkylmagnesium halides [10].

Recently we reported a highly regioselective carbon–carbon bond formation reaction of zirconocene-alkene complexes **1** with alkenes giving zirconacyclopentanes **2** or **3** [11]. In these reaction products alkyl groups R and R' were in β-position of zirconacyclopentanes **2** with a > 98% regioselectivity, whereas an aryl group R' was in α-position with a > 98% regioselectivity as shown in Scheme 1.

In the course of further investigations of reactions of these zirconocene-alkene complexes, we found a

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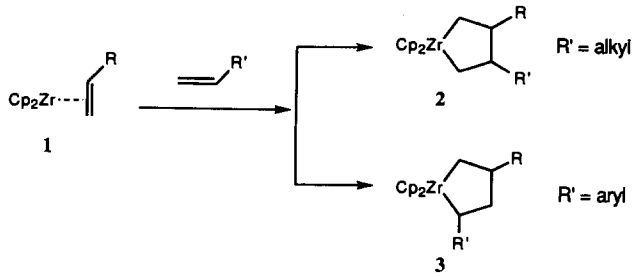


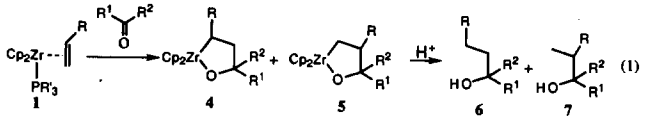
Scheme 1.

regioselective carbon-carbon bond formation reaction of **1** with aldehydes or ketones [12]. Herein we would like to describe the details of the reaction of zirconocene-alkene complexes with aldehydes or ketones with good to excellent selectivities and a reaction of a zirconacyclopentane with aldehydes which gave the same product.

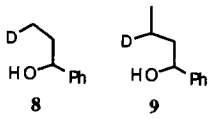
2. Results and discussion

2.1. Reaction of $Cp_2Zr(CH_2{=}CHR)(PMePh_2)$ (R = H, Me, Et) with aldehydes or ketones

It was known that the reaction of zirconocene-stilbene complex [4] or -cyclobutene complexes [13] with acetone gave alcohols after hydrolysis. However, regioselectivities for the reaction of unsymmetrical alkenes have not been reported. As shown in eqn (1) two regioisomers **6** and **7** are possible for unsymmetrical alkenes. Interestingly as shown in Table 1, zirconocene-propene or 1-butene complexes reacted with various aldehydes or ketones to give exclusively **6** after hydrolysis [14].



A reaction of a titanocene-ethylene complex with aldehydes has been reported [15]. The products, 1-oxa-2-titanacyclopentanes, were fully characterized by X-ray analysis recently [16]. The structure of zirconium analog, 1-oxa-2-zirconacyclopentane, has been also determined by X-ray analysis [17]. The reaction mechanism of the reaction of zirconocene-alkene complexes with aldehydes or ketones presumably involves the formation of 1-oxa-2-zirconacyclopentanes **4**. Indeed, deuterolysis of the reaction mixture gave **8** (R = H, R' = Ph) and **9** (R = CH_3, R' = Ph) with 85% and 94% D incorporation, respectively.

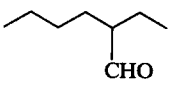
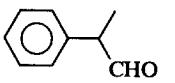
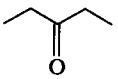
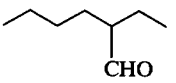
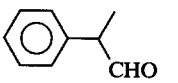
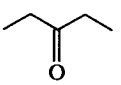
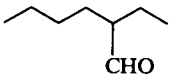
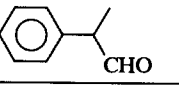


However, unfortunately, monitoring the reaction of **1a** (R = H) with benzaldehyde or 2-phenylpropanal in THF at room temperature by NMR spectroscopy did not show a clean formation of one species such as 1-oxa-2-zirconacyclopentanes. Interestingly, the orientation of alkenes observed here was opposite to that for the reaction of **1** with alkenes. Scheme 2 summarizes the difference in regioselectivities between the reactions of zirconium-alkene complexes with alkenes and with aldehydes or ketones.

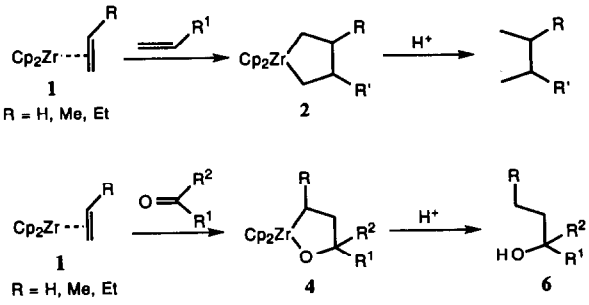
2.2. Reactions of zirconacyclopentanes with aldehydes

It was found that the treatment or zirconacyclopentanes with an aldehyde gave a coupling product of

TABLE 1. Reactions of $Cp_2Zr(CH_2 = CHR)(PMePh_2)$ with aldehydes or ketones (R = H, Ch_3, CH_2CH_3)

R	Aldehydes or Ketones	Time/ h	Yield/ % [a]	Regioselectivity % [b]	
				6	7
H	n-C_7H_{15}CHO	2	97	–	–
H		2	97	–	–
H		1	90	–	–
H	PhCHO	2	95	–	–
H		1	78	–	–
CH_3	n-C_7H_{15}CHO	2	71	> 99	< 1
CH_3		2	46	> 99	< 1
CH_3		3	48	> 99	< 1
CH_3	PhCHO	2	67	> 99	< 1
CH_3		1	40	> 99	< 1
C_2H_5	n-C_7H_{15}CHO	2	29	> 99	< 1
C_2H_5		2	64	> 99	< 1
C_2H_5		3	35	> 99	< 1

[a,b] Determined by GC and NMR spectroscopy.



Scheme 2.

ethyolene with the aldehyde (eqn. (2)) [12]. Zirconacyclopentane **2a** [18], prepared from Cp_2ZrEt_2 and 1-octene, reacted with 2-phenylpropanal to give 2-phenylpentan-3-ol in 73% yield after hydrolysis. This reaction can be explained by the β,β'-carbon–carbon bond activation [19], followed by the formation of 1-oxa-2-zirconacyclopentanes as shown in eqn. (2). The reaction was highly "pair"-selective. Coupling product of 1-octene and 2-phenylpropanal, 4-methyl-2-phenyldecan-3-ol, was not detected. Zirconacyclopentane **2b**, which was prepared from Cp_2ZrCl_2 and $BrMg(CH_2)_4MgBr$, also showed a similar reactivity in the presence of 2-phenylpropanal to afford the same product in 53% yield.

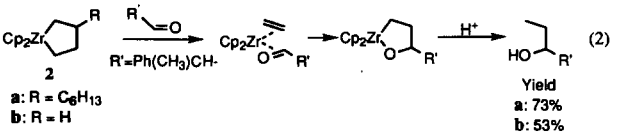
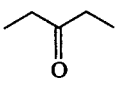
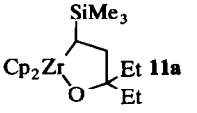
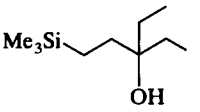
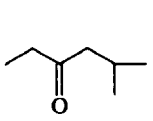
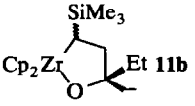
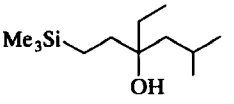
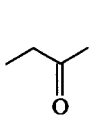
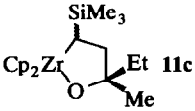
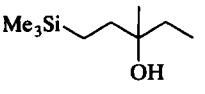
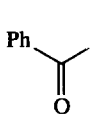
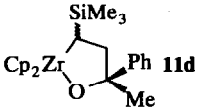
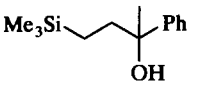
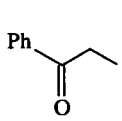
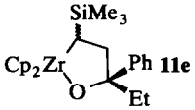
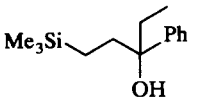
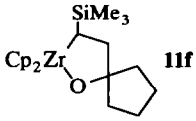
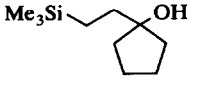
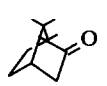
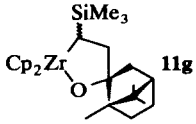
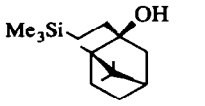


TABLE 2. Formation of 2-di(η^5-cyclpentadienyl)-3-trialkylsilyl-1-oxa-2-zirconacyclopentanes **11** and γ-silylalcohols **12**

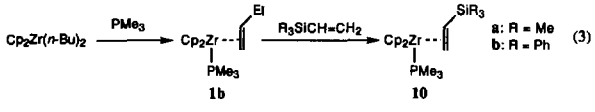
Ketones	1-oxa-2-zircona-cyclopentanes **11**	Yield of **11** [a]/%	γ-silylalchols **12**	Yield of **12** [b]/%	Regioselectivity/%
	 **11a**	88		75	> 98
	 **11b**	71		60	> 95
	 **11c**	77		69	> 95
	 **11d**	87		72	> 97
	 **11e**	83		68	> 98
	 **11f**	85		75	> 97
	 **11g**	90		75	> 98 [c]

[a] By ^1H NMR. [b] Isolated yield. [c] d.e. > 99%.

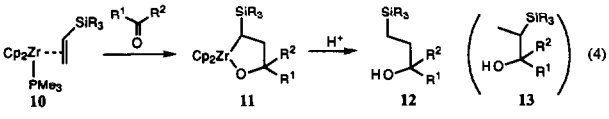
We recently reported the similar reactions of zirconacyclopentenes via β–β' carbon–carbon bond activation with unsaturated compounds such as aldehydes, ketones, nitriles, alkynes and homoallylic halides [20,21].

2.3. *Reaction of $Cp_2Zr(CH_2{=}CHSiR_3)(PMe_3)$ with aldehydes or ketones*

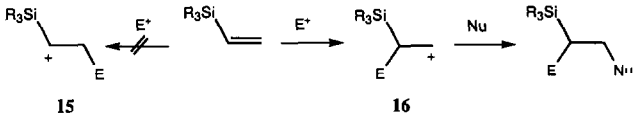
In order to investigate the effect of silyl group, we prepared zirconocene-vinylsilane complexes [22]. Zirconocene-vinylsilane complexes ($Cp_2Zr(CH_2{=}CH\text{-}SiR_3)(PMe_3)$) **10** were cleanly formed (R = Me, 93% yield; R = Ph, 94% yield) by treatment of Cp_2ZrBu_2 (Negishi reagent) with vinylsilanes in the presence of trimethylphosphine (eqn. (3)). Vinylsilanes displaced cleanly 1-butene in Cp_2Zr(1-butene)(PMe_3) **1b** which was formed from Cp_2ZrBu_2 in the presence of PMe_3 [6b]. The NMR spectrum of **10a** indicated that there were two isomers in a ratio of 85:15. The ^1H NMR spectrum of the major isomer showed two singlets at 5.14 and 5.22 ppm, two peaks (ddd) coupled with ^{31}P nucleus at 0.00 and 0.54 ppm, and one doublet of doublet at 0.08 ppm assignable to Cp protons, two terminal protons and an α-proton of vinylsilane, respectively.



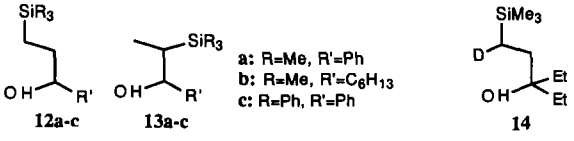
As shown in Table 2, reactions of **10a** with ketones provided 1-oxa-2-zirconacyclopentanes **11** in good yields in contrast to the reaction of **1**. In the case of the reaction with unsymmetrical ketones, a 1:1–2:1 mixture of diastereomers was obtained. In this reaction trimethylphosphine did not inhibit the reactions with ketones, although only weak donating ligands such as diphenylmethylphosphine could be used for the reaction of zirconocene-ethylene, propene or butene complexes. The products **11** were formed in a highly regioselective manner (> 95%), with the silyl group in α-position of 1-oxa-2-zirconacyclopentane. This regioselectivity is similar to the case of the reaction of $Cp_2Zr(CH_2{=}CHR)(PMePh_2)$ (R = H, Me, Et) with aldehydes described above.



Trialkylsilyl groups were known to have a tendency to come to α-position of zirconacyclopentenes [23]. Formation of **11** with vinylsilane indicated the same orientation (eqn. (4)).



Scheme 3.



Hydrolysis of **11** gave the corresponding alcohols, providing a method to prepare γ-silylalcohols as shown in Table 2. Deuterolysis of **11** afforded **14** with > 95% deuterium incorporation. As a general rule, electrophiles (E^+) attack the silicon-bearing carbon atom (α-carbon) of vinylsilanes, due to the β-silicon effect which stabilizes a structure **16** over **15** (Scheme 3) [24]. When a vinylsilane was treated with organometallic reagents such as EtLi followed by a treatment with aldehydes, a carbon-carbon bond formation occurred at the α-carbon of vinylsilanes to give β-silylalcohols [25]. In our reaction with ketones, the carbon-carbon bond was formed at the β-carbon of vinylsilanes to afford γ-silylalcohols.

A reaction of **10a** (R = Me) with benzaldehyde and heptaldehyde, however, gave a mixture of two regioisomers of alcohols **12a–c** and **13a–c** with rather lower regioselectivities, 64% and 55%, respectively. Less bulky carbonyl compounds such as aldehydes were able to attack the vinylsilane on zirconium from trialkylsilyl side (side B) which is more hindered. Vinyltriphenylsilane complex **10b** (R = Ph) with a more bulky substituent, indeed, suppressed an aldehyde attack from the silicon side. γ-Silylalcohol **12c**, which was a resultant of an attack from side A, was predominantly obtained (> 94% regioselectivity) by the reaction of **10b** with benzaldehyde. It is of great interest in comparison with the result of the reactions of zirconocene-propylene or -butene complex with aldehydes which attacked from side A only. It is presumably due to polarized character of vinylsilane described above (Scheme 3). Anionic character of α-carbon stabilized by silyl group might facilitate a nucleophilic attack to carbonyl carbon.

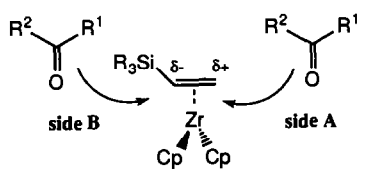
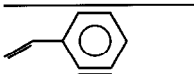
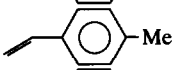
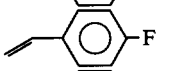
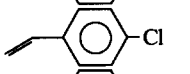
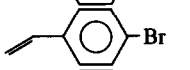
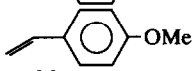
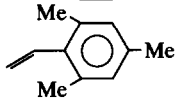


TABLE 3. Coupling reactions of zirconocene-styrene complexes with pentan-3-one

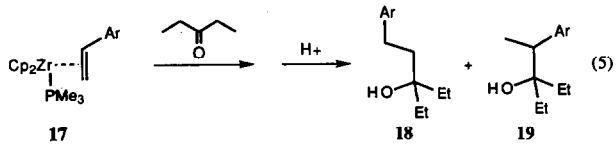
Styrene derivatives	Yield [a] %	Regioselectivity 18:19
	84	63:37
	79	67:33
	83	69:31
	63	65:35
	63	68:32
	84	71:29
	62	> 99:1

[a] Combined yield of **18** and **19**; determined by GC.

To our interest, even triphenylsilyl moiety came to α-position to zirconium in 1-oxa-2-zirconacyclopentane **11** in spite of its bulkiness. A steric repulsion between an electrophile and a trialkylsilyl group on zirconocene-vinylsilane complexes seems to mainly govern the regioselectivity in the formation of **11**.

2.4. Reaction of $Cp_2Zr(CH_2{=}CHAr)(PMe_3)$ with pentan-3-one; regioselectivity in the formation of 1-oxa-2-zirconacyclopentanes

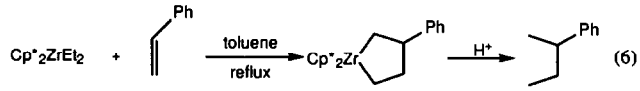
Zirconocene-styrene complex **17** was prepared by a reaction of zirconocene-butene complex with styrene as previously reported [3,6b,26]. This method could be applied for *p*-substituted styrene derivatives.



17 18 19

The complex **17** smoothly reacted with pentan-3-one to give the corresponding alcohols **18** and **19** after hydrolysis as a mixture of regioisomers. The results of the reactions of zirconocene-styrene complexes or its derivatives are summarized in Table 3. In contrast to the results on alkene complexes or vinylsilane complexes, relatively low regioselectivities were observed. Two factors can be taken into considerations for the regioselectivity during the formation of 1-oxa-2-zirconacyclopentanes. One is an electronic factor and the other is a steric factor. Despite a wide range of electronic character of substituents, the reactions of these *p*-substituted styrene complexes showed similar regioselectivities in the formation of corresponding alcohols. On the other hand, 2,4,6-trimethylstyrene, gave 1-(2,4,6-trimethylphenyl)-3-ethylpentan-3-ol as a single product after hydrolysis. Bulky substituents remarkably improved its regioselectivity.

As to the formation of 1-oxa-2-zirconacyclopentanes, two kinds of steric repulsion can be considered. One is a repulsion between Cp ring and a substituent on alkenes, and the other is between an electrophile and a substituent of alkenes. The former might affect the stability of resultant zirconacycles. Indeed, we observed the former steric effect in the formation of a zirconacyclopentane [12]. With pentamethylcyclopentadiene (Cp*), sterically more hindered cyclopentadienyl ligands, a reaction of $Cp^*_2ZrEt_2$ with styrene led to the formation of 1-methylpropylbenzene after hydrolysis with > 99% regioselectivity (eqn. (6), yield 38%) while Cp_2ZrEt_2 gave exclusively butylbenzene. This is due to a steric repulsion between Cp* rings and a phenyl group.



The formation of 1-oxa-2-zirconacyclopentanes presented here, however, revealed the latter steric effect. The result on the reaction of 2,4,6-trimethylstyrene obviously indicated that the steric factor between an aldehydes and an aryl group mainly controlled the regioselectivities in the formation of 1-oxa-2-zirconacyclopentanes. The electrophile attacked from the less hindered side of alkenes on zirconium to form new C–C bond as a result. It can also account for the regioselectivity in the reactions of zirconocene-propene or 1-butene complexes. Therefore the steric repulsion between a substituent and an electrophile seems to overcome that between Cp ligands and a substituent of alkenes. This aspect of the regioselectivity in the reaction of zirconocene-alkene complexes with carbonyl compounds is different from that in an alkene–alkene coupling reaction.

The regioselectivities in the reaction of zirconocene-alkene complexes with electrophiles were summa-

TABLE 4. Comparison of regioselectivities in the reaction of zirconocene-alkene complexes with electrophiles

	R in $Cp_2Zr(CH_2{=}CHR)(PR'_3)$		
	alkyl	silyl	aryl
ketones	> 99%	> 95–99%	63–99%
aldehydes	> 99%	55–94%	[a]

[a] low yield.

rized in Table 4. Relatively higher regioselectivity in the case of propylene or 1-butene complex compared with the case of vinylsilane or styrene complexes cannot be explained by only the steric effect. Although all factors which control the regiochemistry were not clearly elucidated yet, the nucleophilicity of α-carbon of vinylsilanes or styrene might affect the factors.

3. Conclusion

Zirconocene-alkene complexes $Cp_2Zr(CH_2{=}CHR)(PR'_3)$ reacted with aldehydes or ketones to form new carbon-carbon bonds at carbonyl carbons. Substituents on alkenes had a tendency to come to α-position in the formation of zirconacycles. The regioselectivity decreased in the order of R = alkyl > silyl > aryl as shown in Table 4. This showed a different aspect of regioselectivity from that of an alkene-alkene coupling reaction on zirconium. A steric repulsion between a substituent of alkenes and an electrophile has a stronger effect than that between Cp ligands and a substituent of alkenes.

4. Experimental details

All reactions involving organozirconium compounds were carried out under nitrogen. Tetrahydrofuran was dried over sodium. Zirconocene dichloride and propylmagnesium chloride were purchased from Aldrich Chemical Company, Inc. Ethylmagnesium bromide (THF solution) and butyllithium (hexane solution) were purchased from Kanto Chemicals Co. Ltd. ^{1}H (270 MHz) and ^{13}C (67.5 MHz) NMR spectra were recorded on JEOL EX270 NMR spectrometer. Deuterium incorporation was determined by ^{13}C NMR spectra (gated decoupling pulse technique without NOE).

4.1. Reaction of $Cp_2Zr(CH_2{=}CHR)(PMePh_2)$ (R = H, Me, Et) with aldehydes or ketones

4.1.1. Representative procedure; decan-3-ol

Diethylzirconocene was prepared in situ by adding ethylmagnesium bromide in THF (1.0 M, 2.0 mmol) to a solution of zirconocene dichloride (292 mg, 1.0 mmol) in THF (5 mL) at −78°C. The mixture was stirred for 1 h at the same temperature. After addition of diphenylmethylphosphine (200 mg, 1.0 mmol), the mixture was warmed up to room temperature and stirred for 1 h. To this reaction mixture containing the zirconocene-ethylene complex **1a** thus prepared in high yield was added octyl aldehyde (128 mg, 1.0 mmol). After the mixture was stirred for additional 2 h, the yellow solution was quenched with 3 N HCl and extracted with ether. Usual work-up followed by bulb-to-bulb distillation gave decan-3-ol (97% yield). Yields were determined by GC. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.88 (t, J = 7 Hz, 3H), 0.94 (t, J = 8 Hz, 3H), 1.29–1.53 (m, 14H), 3.52 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 9.88, 14.09, 22.68, 25.70, 29.32, 29.71, 30.18, 31.87, 37.01, 73.38.

4.1.2. 4-Ethyloctan-3-ol

Reaction was carried out in a similar manner to the representative procedure using 2-ethylhexanal (128 mg, 1.0 mmol). Title compound was obtained in 97% yield as a 1/1 mixture of diastereomeric isomers. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.90 (t, J = 7 Hz, 3H), 0.94–0.98 (m, 6H), 1.28–1.51 (m, 11H), 3.52 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 10.65, 10.65, 11.83, 11.90, 14.08, 14.08, 21.61, 22.85, 23.16, 23.20, 26.90, 26.95, 28.35, 29.40, 29.72, 29.94, 44.81, 44.85, 75.04, 75.12.

4.1.3. 2-Phenylpentan-3-ol

Title compound was obtained in 90% yield as a 2.7/1 mixture of diastereomeric isomers. For major product, (*R,R*)/(*S,S*)-2-phenylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.9 (t, 3H, J = 7.4 Hz), 1.29 (d, 3H, J = 6.9 Hz), 1.3–1.5 (m, 2H), 2.7 (dq, 1H, J = 6.9Hz), 3.4–3.6 (m, 1H), 7.1–7.4 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ: 10.39, 15.81, 27.57, 45.41, 77.68, 126.29, 127.80, 128.39, 144.83. For minor product, (*R,S*)/(*S,R*)-2-phenylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.97 (t, J = 7.4 Hz, 3H), 1.25 (t, J = 6.9 Hz, 3H), 1.3–1.5 (m, 2H), 2.6–2.8 (m, 1H), 3.4–3.6 (m, 1H), 7.1 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 10.50, 17.90, 27.17, 45.61, 77.32, 126.56, 128.23, 128.44, 143.63.

4.1.4. 1-Phenylpropan-1-ol

Reaction was carried out in a similar manner to the representative procedure using benzaldehyde (106 mg, 1.0 mmol). Title compound was obtained in 90% yield. Quenching the reaction mixture with D_2SO_4 (98% in D_2O) gave 3-deutero-1-phenylpronan-1-ol with 85% D incorporation. Title compound, ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.84 (t, J = 7.6 Hz, 3H), 1.6–1.8 (m, 2H), 4.7 (t, J = 6.6 Hz, 1H), 7.20–7.32 (m, 5H). ^{13}C NMR: δ 10.12, 31.78, 75.83, 126.02, 127.32, 128.28, 144.62. 3-deutero-1-phenylpronan-1-ol, ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.86–0.94 (m, 2H), 1.6–1.8 (m, 2H), 4.59 (t, J = 7 Hz, 1H), 7.20–7.32 (m, 5H). ^{13}C NMR: δ 9.87 (t, $^1J_{C-D}$ = 19.6 Hz), 31.81, 76.03, 125.98, 127.49, 128.41, 144.62.

4.1.5. 3-Ethylpentan-3-ol

Zirconocene-ethylene complex, $Cp_2Zr(CH_2{=}CH_2)(PPh_2Me)$ **1a**, was prepared in the same way as described above. To the solution of **1a** was added pentan-3-one (86 mg, 1.0 mmol) dropwise via syringe throughout 50 min. After the mixture was stirred for additional

10 min, the yellow solution was quenched with 3 N HCl and extracted with ether. Usual work-up followed by bulb-to-bulb distillation gave title compound (78% yield). Yields were determined by GC. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.86 (t, $J = 7.6$ Hz, 9H), 1.46 (q, $J = 7.6$ Hz, 6H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.73, 30.51, 74.73.

4.1.6. Undecan-4-ol

Reaction was carried out in a similar manner to the representative procedure using propylmagnesium chloride (2.0 M diethyl ether solution, 2.0 mmol) instead of ethylmagnesium bromide, and octyl aldehyde (128 mg, 1.0 mmol). Title compound was obtained in Yield 71%. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.88 (t, $J = 7$ Hz, 3H), 0.93 (t, $J = 7$ Hz, 3H), 1.29–1.47 (m, 16H), 3.60 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.06, 14.10, 18.85, 22.67, 25.68, 29.32, 29.71, 31.86, 37.58, 39.74, 71.76.

4.1.7. 5-Ethylnonan-4-ol

Title compound was obtained in 46% yield as a 1/1 mixture of diastereomeric isomers. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.86–0.90 (m, 6H), 0.93 (t, $J = 7$ Hz, 3H), 1.28–1.43 (m, 13H), 3.62 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.09, 14.14, 18.86, 22.69, 25.70, 29.33, 29.72, 31.88, 37.59, 39.75, 71.78.

4.1.8. 2-Phenylhexan-3-ol

Reaction was carried out in a similar manner to the representative procedure using propylmagnesium chloride and DL-2-phenylpropionaldehyde (134 mg, 1.0 mmol). Title compound was obtained in 48% yield as a mixture of diastereomeric isomers. For major product, (*R,R*)/(*S,S*)-2-phenylhexan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.86 (t, $J = 6.6$ Hz, 3H), 1.2–1.5 (m, 4H), 1.28 (d, $J = 7$ Hz, 3H), 2.65 (dq, $J = 7$, 7 Hz, 1H), 3.6–3.7 (m, 1H), 7.1–7.4 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.03, 15.62, 19.23, 36.89, 45.72, 75.92, 126.31, 127.82, 128.41, 144.78. For minor product, (*R,S*)/(*S,R*)-2-phenylhexan-3-ol. ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.41, 17.89, 18.96, 36.64, 46.09, 75.80, 126.58, 128.23, 128.46, 143.59.

4.1.9. 1-Phenylbutan-1-ol

Title compound was obtained in a similar manner to the representative procedure using propylmagnesium chloride and benzaldehyde (106 mg, 1.0 mmol) in 67% yield. Quenching the reaction mixture with D_2SO_4 (98% in D_2O) gave 3-deutero-1-phenylbutan-1-ol with 94% D incorporation. Title compound, ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.92 (t, $J = 7$ Hz, 3H), 1.28–1.34 (m, 1H), 1.38–1.45 (m, 1H), 1.62–1.71 (m, 1H), 1.73–1.83 (m, 1H), 4.65 (t, $J = 7$ Hz, 1H), 7.25–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.96, 19.03, 41.27, 74.43, 125.92, 127.47, 128.42, 144.98. 3-Deutero-1-phenylbutan-1-ol, ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.85, 18.65 (t, $^1J_{C-D} = 19$ Hz), 41.10, 74.34, 125.91, 127.42, 128.37, 144.94.

4.1.10. 3-Ethylhexan-3-ol

Zirconocene-propylene complex, $Cp_2Zr(CH_2{=}CH{-}CH_3)(PPh_2Me)$, was prepared in the same way as described above. To a solution of the propylene complex was added pentan-3-one (86 mg, 1.0 mmol) dropwise via syringe throughout 50 min. After the mixture was stirred for additional 10 min, the yellow solution was quenched with 3 N HCl and extracted with ether. Usual work-up followed by bulb-to-bulb distillation gave title compound (40% yield). Yields were determined by GC. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.82 (t, $J = 7.4$ Hz, 6H), 0.89 (t, $J = 7$ Hz, 3H), 1.42 (q, $J = 7.4$ Hz, 4H), 1.2–1.4 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.70, 14.70, 16.61, 30.98, 40.61, 74.59.

4.1.11. Dodecan-5-ol

Reaction was carried out in a similar manner to the representative procedure using butyllithium (1.6 M hexane solution, 2.0 mol) instead of ethylmagnesium bromide, and octyl aldehyde (128 mg, 1.0 mmol). Title compound was obtained in 29% yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.88 (t, $J = 6.9$ Hz, 3H), 0.91 (t, $J = 6.9$ Hz, 3H), 1.2–1.6 (m, 18H), 3.6–3.8 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.12, 14.12, 22.74, 22.84, 25.75, 27.92, 29.40, 29.77, 31.93, 37.25, 37.55, 72.09.

4.1.12. 6-Ethyldecan-5-ol

Title compound was obtained in 64% yield as a *ca.* 1/1 mixture of diastereomeric isomers. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.89–0.93 (m, 9H), 1.18–1.43 (m, 15H), 3.61 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 11.92, 11.99, 14.11, 14.11, 21.70, 21.70, 22.85, 22.85, 23.19, 23.19, 28.42, 28.42, 28.61, 28.61, 29.41, 29.41, 29.82, 29.97, 33.82, 33.82, 45.27, 45.27, 73.51, 73.59.

4.1.13. 2-Phenylheptan-3-ol

Reaction was carried out in a similar manner to the representative procedure using butyllithium and DL-2-phenylpropionaldehyde (134 mg, 1.0 mmol). Title compound was obtained in 35% yield as a mixture of diastereomeric isomers. For major product, (*R, R*)/(*S, S*)-2-phenylheptan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.86 (t, $J = 7$ Hz, 3H), 1.2–1.5 (m, 6H), 1.29 (d, $J = 6.9$ Hz, 3H), 2.7–2.8 (m, 1H); 3.5–3.7 (m, 1H). 7.1–7.4 (m, 5H). ^{13}C NMR: δ: 14.05, 15.49, 22.66, 28.25, 34.41, 45.62, 76.15, 126.29, 127.80, 128.39, 144.78. For minor product, (*R, S*)/(*S, R*)-2-phenylheptan-3-ol. ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.05, 17.93, 22.79, 27.92, 34.16, 46.04, 76.03, 126.17, 128.21, 128.46, 143.57.

4.2. Reactions of zirconacyclopentanes with aldehydes

4.2.1. A reaction of 1,1-(η^5-cyclopentadienyl)-3-hexylzirconacyclopentane (2a)

1,1-(η^5-Cyclopentadienyl)-3-hexylzirconacyclopentane **2a** was prepared in situ from Cp_2ZrCl_2, EtMgBr and 1-octene by reported method [18]. To a solution of **2a** in THF was added DL-2-phenypropionaldehyde (134 mg, 1.0 mmol) at room temperature. After stirring for 1 h, the reaction mixture was quenched with dil. HCl. Usual work-up gave 2-phenylpentan-3-ol as a 2:1 mixture of diastereoisomers (yield 73% by GC).

4.2.2. A reaction of 1,1-(η^5-cyclopentadienyl)zirconacyclopentane (2b)

To a solution of Cp_2ZrCl_2 (292 mg, 1.0 mmol) in THF (5 mL) was added $BrMg(CH_2)_4MgBr$ (1.0 mmol) at −78°C. After stirring for 1 h, DL-2-phenylpropionaldehyde (134 mg, 1.0 mmol) was added to the reaction mixture at −10°C. The reaction mixture was warmed up to room temperature and was stirred for 1 h. Quenching with dil. HCl and usual work-up gave 2-phenylpentan-3-ol as a mixture of diastereoisomers (yield 53% by GC).

4.3. Preparation of zirconocene-vinylsilane complexes

4.3.1. Representative procedure; $Cp_2Zr(CH_2{=}CHSiMe_3)(PMe_3)$ (10a)

To a solution of Cp_2ZrCl_2 (292 mg, 1 mmol) in THF (5 mL) was added butyllithium (1.6 M hexane solution, 2 mmol) at −78°C. After stirring for 1 h at same temperature, trimethylphosphine (1.0 M THF solution, 1.3 M) and vinyltrimethylsilane (110 mg, 1.1 mmol) was added and the mixture was allowed to be warmed up to room temperature. The reaction mixture was stirred for 1 h. Observation by ^{1}H NMR showed formation of title compound (93% yield by ^{1}H NMR) as a 85:15 mixture of isomers. Major isomer, ^{1}H NMR (C_6D_6/THF, Me_4Si): δ −0.82 (dd, J = 13.3, 14.2 Hz, 1H), 0.00 (ddd, $^3J_{P-H}$ = 5.4 Hz, $^2J_{H-H}$ = 5.4, $^3J_{H-H}$ = 14.2 Hz, 1H), 0.17 (s, 9H), 0.54 (ddd, $^3J_{P-H}$ = 10.5 Hz, $^2J_{H-H}$ = 5.6 Hz, $^3J_{H-H}$ = 13.3, 1H), 1.15 (d, $^2J_{P-H}$ = 5.6 Hz, 6H), 5.14 (d, $^3J_{P-H}$ = 1.7 Hz, 5H), 5.22 (d, $^3J_{P-H}$ = 1.7 Hz, 5H). ^{13}C NMR (C_6D_6/THF, Me_4Si): δ 2.08, 17.12, 17.39, 21.20, 99.33, 100.95. Minor isomer, ^{1}H NMR (C_6D_6/THF, Me_4Si): δ 0.10 (s, 9H, $Si(CH_3)_3$), 1.23 (d, $^3J_{P-H}$ = 5.6 Hz, 9H, $P(CH_3)_3$), 5.14 (d, $^3J_{P-H}$ = 1.7 Hz, 5H, Cp), 5.22 (d, $^3J_{P-H}$ = 2.0 Hz, 5H, Cp). ^{13}C NMR (C_6D_6/THF, Me_4Si): δ 3.38 ($Si(CH_3)_3$), 18.1 ($P(CH_3)_3$), 100.47 (Cp), 102.08 (Cp).

4.3.2. $Cp_2Zr(CH_2{=}CHSiPh_3)(PMe_3)$ (10b)

Reaction was carried out similarly to the preparation of $Cp_2Zr(CH_2{=}CH(SiMe_3)(PMe_3)$ using vinyltriphenylsilane (315 mg 1.1 mmol). The reaction mixture was stirred for 12 h. ^{1}H NMR spectrum showed formation of title compound (94% yield by ^{1}H NMR) as a single isomer. ^{1}H NMR (C_6D_6, Me_4Si): δ 0.08 (dd, J = 13.5, 13.5 Hz, 1H), 0.45 (ddd, $^2J_{H-H}$ = 6 Hz, $^3J_{H-H}$ = 13.5 Hz, J_{P-H} = 6 Hz, 1H), 0.71 (d, $^2J_{P-H}$ = 5.9 Hz, 9H), 0.87 (ddd, $^2J_{H-H}$ = 6.1 Hz, $^3J_{H-H}$ = 13.5 Hz, J_{P-H} = 9.4 Hz, 1H), 4.88 (d, J_{P-H} = 2.0 Hz, 5H), 5.13 (d, J_{P-H} = 1.7 Hz, 5H), 7.16–7.34 (m, 9H), 8.10–8.14 (m, 6H). ^{13}C NMR (C_6D_6, Me_4Si): δ 8.39 (J_{C-P} = 2.5 Hz), 16.68 (J_{C-P} = 18.3 Hz), 22.17 (J_{C-P} = 14.7 Hz), 99.98, 101.38, 127.65, 128.23, 136.91, 141.24.

4.4. Reaction of $Cp_2Zr(CH_2{=}CHSiR_3)(PMe_3)$ (R = Me, Ph) with ketones

4.4.1. Formation of 2,2-bis(η^5-cyclopentadienyl)-5,5-diethyl-3-trimethylsilyl-1-oxa-2-zirconacyclopentane (11a)

To a solution of Cp_2ZrCl_2 (0.292 g, 1 mmol) in THF (5 mL) was added dropwise hexane solution of butyllithium (1.68 M, 2.0 mmol) at −78°C. After stirring for 1 h at −78°C, trimethylvinylsilane (110 mg, 1.1 mmol) and trimethylphosphine (1.0 M in THF, 1.3 mmol) were added and the reaction mixture was warmed to room temperature and stirred for an additional hour. Zirconocene-vinylsilane complex was formed quantitatively in this stage. To the reaction mixture was added pentan-3-one (86 mg, 1.0 mmol) and it was stirred for 1 h. ^{1}H NMR observation showed the formation of title compound in 88% yield (by ^{1}H NMR). After removal of volatile, residue was dissolved in benzene and followed by filtration. Filtrate was dried up and oily solid was obtained. Products were characterized by ^{1}H and ^{13}C NMR. ^{1}H NMR (C_6D_6, Me_4Si): δ 0.10 (s, 9H), 0.17 (t, J = 7.6 Hz, 3H), 0.81 (t, J = 7.6 Hz, 3H), 1.3–1.5 (m, 1H), 1.43 (q, J = 7.6 Hz, 2H), 1.6–1.7 (m, 1H), 2.40 (dd, ^2J = 15 Hz, ^3J = 3.3 Hz, 1H), 2.45 (dd, J = 3.3, 15 Hz, 1H), 2.85 (dd, ^2J = 15 Hz, ^3J = 15, Hz, 1H), 5.92 (s, 5H), 6.02 (s, 5H). ^{13}C NMR: δ 1.13, 8.13, 9.16, 28.39, 32.40, 45.12, 52.61, 88.39, 111.43, 112.49.

4.4.2. 2,2-Bis(η^5-cyclopentadienyl)-5-ethyl-5-(2-methylpropyl)-3-trimethylsilyl-1-oxa-2-zirconacyclopentane (11b)

Reaction was carried out in a similar manner to the representative procedure using 5-methylhexan-3-one (114 mg, 1.0 mmol). Title compound was obtained in 71% yield with > 95% regioselectivity as a 1:1 mixture of diastereomeric isomers. For *trans*-isomer, ^{1}H NMR (C_6D_6, Me_4Si): δ 0.10 (s, 9H); 0.82 (t, J = 7.6 Hz, 3H), 0.95 (d, J = 6.5 Hz, 3H), 1.06 (d, J = 6.5 Hz, 3H), 1.3–1.4 (m, 1H), 1.5–1.7 (m, 3H), 2.35–2.55 (m, 2H), 2.75–2.95 (m, 1H), 5.90 (s, 5H), 6.01 (s, 5H). ^{13}C NMR

(C_6D_6, Me_4Si): δ: 1.35, 9.79, 24.68, 24.76, 24.79, 34.93, 44.75, 46.36, 54.99, 89.33, 111.49, 112.62. For *cis*-isomer, ^1H NMR (C_6D_6, Me_4Si): δ 0.10 (s, 9H); 0.80 (t, $J = 7.6$ Hz, 3H), 0.97 (d, $J = 6.5$ Hz, 3H), 0.98 (d, $J = 6.5$ Hz, 3H), 1.2–1.4 (m, 2H); 1.5–1.7 (m, 2H), 2.35–2.55 (m, 2H), 2.75–2.95 (m, 2H), 5.97 (s, 5H), 6.04 (s, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 1.30, 9.42, 24.79, 25.47, 25.52, 29.15, 45.82, 48.72, 55.85, 89.55, 111.49, 112.62.

4.4.3. 2,2-Bis(η⁵-cyclopentadienyl)-5-ethyl-5-methyl-3-trimethylsilyl-1-oxa-2-zirconacyclopentane (11c)

Title compound was obtained in 77% yield with > 95% regioselectivity as a 1:1 mixture of diastereomeric isomers. For *trans*-isomer, ^1H NMR (C_6D_6, Me_4Si): δ 0.10 (s, 9H), 0.87 (t, $J = 7.4$ Hz, 3H), 1.15 (s, 3H), 1.2–1.4 (m, 1H), 1.7–1.9 (m, 1H), 2.2–2.5 (m, 1H), 2.5–2.6 (m, 1H), 2.9 (dd, $^2J = 13.5$ Hz, $^3J = 13.5$ Hz, 1H), 5.91 (s, 5H), 6.02 (s, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 1.19, 8.90, 26.99, 32.67, 46.09, 54.86, 85.87, 111.39, 112.51. For *cis*-isomer, ^1H NMR (C_6D_6, Me_4Si): δ 0.10 (s, 9H), 0.87 (t, $J = 7.4$ Hz, 3H), 1.07 (s, 3H), 1.4–1.5 (m, 1H), 1.7–1.8 (m, 1H), 2.2–2.5 (m, 1H), 2.4–2.5 (m, 1H), 2.90 (dd, $^2J = 13.5$ Hz, $^3J = 13.5$ Hz, 1H), 5.93 (s, 5H), 6.01 (s, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 1.19, 9.29, 24.83, 37.09, 45.64, 54.80, 86.32, 111.46, 112.61.

4.4.4. 2,2-Bis(η⁵-cyclopentadienyl)-5-methyl-5-phenyl-3-trimethylsilyl-1-oxa-2-zirconacyclopentane (11d)

Title compound was obtained in 87% yield with > 97% regioselectivity as a 1.3:1 (*trans*:*cis*) mixture of diastereomeric isomers. For *trans*-isomer, ^1H NMR (C_6D_6, Me_4Si): δ 0.06 (s, 9H), 1.34 (s, 3H); 2.21 (dd, $^3J = 3$, 9 Hz, 1H), 3.1–3.3 (m, 2H), 5.80 (s, 5H), 6.07 (s, 5H), 7.1–7.4 (m, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 1.04, 34.09, 48.70, 54.12, 87.80, 111.53, 112.55, 125.75, 128.04, 128.47, 150.01. For *cis*-isomer, ^1H NMR (C_6D_6, Me_4Si): δ 0.09 (s, 9H), 1.46 (s, 3H), 2.71 (dd, $^3J = 3$ Hz, $^3J = 9$ Hz, 1H), 2.86 (dd, $^3J = 3$ Hz, $^3J = 9$ Hz, 1H), 3.1–3.3 (m, 1H), 5.95 (s, 5H), 6.02 (s, 5H), 7.1–7.4 (m, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 1.24, 30.17, 46.95, 56.13, 86.23, 111.62, 112.77, 124.16, 128.42, 152.82. one carbon overlapped with a solvent signal.

4.4.5. 2,2-Bis(η⁵-cyclopentadienyl)-5-ethyl-5-phenyl-3-trimethylsilyl-1-oxa-2-zirconacyclopentane (11e)

Title compound was obtained in 83% yield with > 98% regioselectivity as a 1:1 mixture of diastereomeric isomers. For *trans*-isomer, ^1H NMR (C_6D_6, Me_4Si): δ 0.02 (s, 9H), 0.61 (t, $^3J = 7.5$ Hz, 3H), 1.5–1.7 (m, 2H), 2.15 (dd, $^3J = 4.3$ Hz, $^3J = 12.2$ Hz, 1H), 3.0–3.2 (m, 2H), 5.79 (s, 5H), 6.06 (s, 5H), 7.1–7.4 (m, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 1.00, 9.15, 39.00, 48.00, 52.72, 90.74, 111.50, 112.49,126.59, 127.8, 128.41, 147.62. For *cis*-isomer, ^1H NMR (C_6D_6, Me_4Si): δ 0.02 (s, 9H), 0.62 (t, $^3J = 7.3$ Hz, 3H), 1.3–1.4 (m, 1H), 2.1–2.3 (m, 1H), 2.65 (dd, $^3J = 3.4$ Hz, $^3J = 13.6$ Hz, 1H), 2.8 (dd, $^2J = 13.6$ Hz, $^3J = 3.4$ Hz, 1H), 3.0–3.2 (m, 1H), 5.94 (s, 5H), 5.98 (s, 5H), 7.1–7.4 (m, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 1.20, 8.07, 34.02, 46.76, 56.15, 88.73, 111.53, 112.61, 124.90, 127.64, 128.41, 150.31.

4.4.6. 2,2-Bis(η⁵-cyclopentadienyl)-5-cyclopentyl-3-trimethylsilyl-1-oxa-2-zirconacyclopentane (11f)

Title compound was obtained in 85% yield with > 97% regioselectivity. ^1H NMR (C_6D_6, Me_4Si): δ 0.10 (s, 9H); 1.4–1.8 (m, 8H), 2.46 (dd, $^3J = 3.3$ Hz, $^3J = 13.8$ Hz, 1H); 2.6 (dd, $^3J = 3.3$ Hz, $^2J = 13.5$ Hz, 1H), 3.15 (dd, $^2J = 13.5$ Hz, $^3J = 14$ Hz, 1H), 5.92 (s, 5H), 6.00 (s, 5H). ^{13}C NMR: δ 1.28, 24.21, 24.54, 39.84, 40.85, 48.49, 53.99, 95.92, 111.68, 112.57.

4.4.7. Preparation of 11g

Reaction was carried out in a similar manner to the representative procedure using camphor (152 mg, 1.0 mmol). Title compound was obtained in 90% yield with > 98% regioselectivity and as a 2:1 mixture of diastereomeric isomers. For major isomer, ^1H NMR (C_6D_6, Me_4Si): δ 0.08 (s, 9H), 0.82 (s, 3H), 0.94 (s, 3H), 0.97 (s, 3H); 0.8–0.9 (m, 1H), 1.3–1.4 (m, 2H), 1.5–1.7 (m, 1H), 1.6–1.7 (m, 2H), 2.1–2.2 (m, 1H), 2.25 (dd, $^2J = 13$ Hz, $^3J = 3$ Hz, 1H), 2.45 (dd, $^3J = 3$ Hz, $^3J = 13$ Hz, 1H), 3.15 (dd, $^2J = 13$ Hz, $^3J = 13$ Hz, 1H), 5.91 (s, 5H), 6.01 (s, 5H). ^{13}C NMR (C_6D_6, Me_4Si): δ 1.21, 11.92, 20.83, 21.84, 27.41, 30.43, 45.76, 45.76, 46.86, 49.42, 53.26, 54.34, 97.17, 111.67, 112.42. For minor isomer, ^1H NMR (C_6D_6, Me_4Si): δ 5.95 (s, 5H, Cp), 5.99 (s, 5H, Cp). ^{13}C NMR (C_6D_6, Me_4Si): δ 1.55, 14.33, 21.67, 22.20, 27.89, 31.04, 45.86, 50.14, 50.23, 51.72, 53.41, 54.11, 95.72, 110.86, 112.19.

4.5. Synthesis of γ-silylalcohols via Zr-promoted coupling reaction of trimethylvinylsilane with ketones

4.5.1. Representative procedure; 3-ethyl-1-trimethylsilylpentan-3-ol

To a solution of Cp_2ZrCl_2 (292 mg, 1 mmol) in THF (5 mL) was added dropwise hexane solution of butyllithium (1.68 M, 2 mmol) at −78°C. After stirring for 1 h at −78°C, trimethylvinylsilane (110 mg, 1.1 mmol) and trimethylphosphine (1.0 M in THF, 1.3 mmol) were added and the reaction mixture was warmed to room temperature and stirred for an additional hour, at which time pentan-3-one (86 mg, 1.0 mmol) was added. After 1 h, the reaction mixture was quenched with 3 N HCl, extracted with Et_2O, washed with $NaHCO_3$, brine and dried over $MgSO_4$. Filtration fol-

lowed by concentration provided 141 mg (75% isolated yield) of the title compound with > 99% regioisomeric purity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ −0.03 (s, 9H), 0.35–0.45 (m, 2H), 0.82 (t, J = 7.6 Hz, 6H), 1.2 (bs, 1H), 1.3–1.4 (m, 2H), 1.47 (q, J = 7.6 Hz, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ −1.91, 7.67, 9.54, 30.37, 31.79, 75.04.

4.5.2. 3,5-Dimethyl-1-trimethylsilylhexan-3-ol

Title compound was prepared similarly from 4-methyl-2-pentanone (100 mg, 1.0 mmol) in 60% isolated yield and with a > 95% regioisomeric purity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ −0.03 (s, 9H), 0.4–0.45 (m, 2H), 0.93 (d, J = 7.6 Hz, 3H), 0.95 (d, J = 7.6 Hz, 3H), 1.13 (s, 3H), 1.2 (bs, 1H), 1.34 (d, J = 5.9 Hz, 2H), 1.35–1.45 (m, 2H), 1.65–1.68 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ −1.90, 10.13, 24.11, 24.71, 24.89, 26.65, 36.72, 49.58, 73.82.

4.5.3. 3-Phenyl-1-trimethylsilylpentan-3-ol

Reaction was carried out in a similar manner to the representative procedure using propiophenone (134 mg, 1 mmol). Title compound was obtained in 68% isolated yield and with a > 98% regioisomeric purity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ −0.04 (s, 9H), 0.20 (ddd, J = 15.0, 15.0, 4.9 Hz, 1H), 0.45 (ddd, J = 15.0, 15.0, 4.9 Hz, 1H), 0.76 (t, J = 7.2 Hz, 3H), 1.65–1.8 (m, 4H), 2.0 (bs, 1H), 7.2–7.55 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ −1.95, 7.83, 9.36, 34.84, 36.30, 77.70, 125.48, 126.09, 127.85, 145.85.

4.5.4. 2-Phenyl-4-trimethylsilylbutan-2-ol [27]

Title compound was prepared similarly from acetophenone (120 mg, 1 mmol) in 72% isolated yield and with a > 97% regioisomeric purity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ −0.04 (s, 9H), 0.2–0.5 (m, 2H), 1.53 (s, 3H), 1.65–1.9 (m, 2H), 2.05 (bs, 1H), 7.15–7.55 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ −1.93, 10.02, 29.54, 38.06, 75.27, 124.88, 126.36, 128.03, 147.81.

4.5.5. 3-Methyl-1-trimethylsilylpentan-3-ol

Title compound was obtained in 68% isolated yield and with a > 98% regioisomeric purity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ −0.04 (s, 9H), 0.4–0.45 (m, 2H), 0.84 (t, J = 7.2 Hz, 3H), 1.08 (s, 3H), 1.3–1.4 (m, 2H), 1.35 (bs, 1H), 1.48 (q, J = 7.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ −1.95, 8.28, 9.93, 25.78, 33.29, 35.04, 73.29.

4.5.6. 1-(2-Trimethylsilylethyl)cyclopentanol

Title compound was obtained in 75% isolated yield and with a > 97% regioisomeric purity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ −0.04 (s, 9H), 0.45–0.55 (m, 2H), 1.4 (bs, 1H), 1.45–1.6 (m, 8H), 1.75–1.8 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ −1.92, 10.76, 24.01, 35.25, 39.13, 83.23.

4.5.7. 1-(2-Trimethylsylilethyl)borneol

Title compound was obtained similarly from D-camphor (152 mg, 1.0 mmol) in 75% isolated yield and with a > 98% isomeric purity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ −0.03 (s, 9H), 0.35–0.65 (m, 2H), 0.82 (s, 3H), 0.83 (s, 3H), 0.85–1.0 (m, 2H), 1.08 (s, 3H), 1.2–1.5 (m, 5H), 1.6–1.7 (m, 2H), 1.87 (dt, (J = 13.2, 3.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ −1.86, 10.10, 10.84, 20.92, 21.53, 27.08, 30.28, 33.10, 44.96, 45.69, 49.65, 52.09, 81.13.

4.6. Reaction of $Cp_2Zr(CH_2{=}CHAr)(PMe_3)$ with diethylketone

4.6.1. Representative procedure; 1-phenyl-3-ethylpentan-3-ol / 2-phenyl-3-ethylpentan-3-ol

To a solution of Cp_2ZrCl_2 (292 mg, 1.0 mmol) in THF (5 mL) was added dropwise hexane solution of butyllithium (1.68 M, 2 mmol) at −78°C. After stirring for 1 h at −78°C styrene (114 mg, 1.1 mmol) and trimethylphosphine (1.0 M in THF, 1.2 mmol) were added and the reaction mixture was warmed to room temperature and stirred for an additional hour, at which time pentan-3-one (86 mg, 1.0 mmol) was added. After 3 h, the reaction mixture was quenched with 3N HCl, extracted with Et_2O, washed with $NaHCO_3$, brine and dried over $MgSO_4$. Evaporation followed by purification with column chromatography provided the title compounds (84% combined yield). Ratio of two regioisomers was 1-phenyl-3-ethylpentan-3-ol/2-phenyl-3-ethylpentan-3-ol = 63/37. Yields were determined by gas chromatography. Major product, 1-phenyl-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.90 (t, J = 7 Hz, 6H), 1.54 (q, J = 7 Hz, 4H), 1.63 (s, 1H, OH), 1.69–1.75 (AA'BB', 2H), 2.59–2.65 (AA'BB', 2H), 7.14–7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.77, 29.85, 30.87, 40.33, 74.52, 125.64, 128.25, 128.34, 142.71. Minor product, 2-phenyl-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.87 (t, J = 7 Hz, 6H), 1.15–1.45 (m, 2H) 1.28 (d, J = 7 Hz, 3H), 1.56 (q, J = 7 Hz, 2H), 2.85 (q, J = 7 Hz, 1H), 7.17–7.31 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.69, 8.01, 15.29, 27.31, 29.09, 45.46, 75.92, 126.31, 128.05, 129.20, 143.74.

4.6.2. 1-(4-Methylphenyl)-3-ethylpentan-3-ol / 2-(4-methylphenyl)-3-ethylpentan-3-ol

Title compounds were prepared similarly from 4-methylstyrene (118 mg, 1.0 mmol) in 79% combined yield. Ratio of two regioisomers was 67/33. Major product, 1-(4-methylphenyl)-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.87 (t, J = 8 Hz, 6H), 1.49

(q, $J = 8$ Hz, 4H), 1.64–1.70 (AA'BB', 2H), 2.28 (s, 3H), 2.52–2.59 (AA'BB', 2H), 7.05 (s, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.85, 20.95, 29.49, 30.93, 40.57, 74.48, 128.21, 129.09, 135.00, 139.75. Minor product, 2-(4-methylphenyl)-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.82 (t, $J = 7$ Hz, 3H), 0.86 (t, $J = 8$ Hz, 3H), 1.17 (s, 1H, OH), 1.15–1.44 (m, 2H) 1.26 (d, $J = 7$ Hz, 3H), 1.55 (q, $J = 7$ Hz, 2H), 2.31 (s, 3H), 2.82 (q, $J = 7$ Hz, 1H), 7.07–7.17 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.59, 7.89, 15.22, 20.86, 27.14, 28.97, 44.91, 75.74, 128.66, 128.95, 135.65, 140.47.

4.6.3. 1-(4-Fluorophenyl)-3-ethylpentan-3-ol / 2-(4-fluorophenyl)-3-ethylpentan-3-ol

Title compounds were obtained in 83% combined yield. Ratio of two regioisomers was 69/31. Major product, 1-(4-fluorophenyl)-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.89 (t, $J = 7$ Hz, 6H), 1.52 (q, $J = 7$Hz, 4H), 1.65–1.71 (AA'BB', 2H), 1.79 (s, 1H, OH), 2.56–2.62 (AA'BB', 2H), 6.89–6.97 (m, 2H), 7.09–7.16 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.66, 28.93, 30.73, 40.34, 74.36, 114.91 (d, $|^2J_{C-F}| = 21$ Hz), 129.45 (d, $|^3J_{C-F}| = 7$ Hz), 138.27 (d, $|^4J_{C-F}| = 4$ Hz), 161.02 (d, $|^1J_{C-F}| = 243$ Hz). Minor product, 2-(4-fluorophenyl)-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.82 (t, $J = 7$ Hz, 3H), 0.87 (t, $J = 7$ Hz, 3H), 1.02–1.50 (m, 2H), 1.26 (d, $J = 7$ Hz, 3H), 1.56 (q, $J = 7$ Hz, 2H), 2.84 (q, $J = 7$ Hz, 1H), 6.92–7.01 (m, 2H), 7.18–7.26 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.66, 8.01, 15.54, 27.49, 29.06, 44.76, 75.92, 114.71 (d, $|^2J_{C-F}| = 21$ Hz), 130.49 (d, $|^3J_{C-F}| = 7$ Hz), 139.50 (d, $|^4J_{C-F}| = 4$ Hz), 161.54 (d, $|^1J_{C-F}| = 244$ Hz).

4.6.4. 1-(4-Chlorophenyl)-3-ethylpentan-3-ol / 2-(4-chlorophenyl)-3-ethylpentan-3-ol

Title compounds were obtained in 63% combined yield. Ratio of two regioisomers was 65/35. Major product, 1-(4-chlorophenyl)-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.88 (t, $J = 7$ Hz, 6H), 1.51 (q, $J = 7$ Hz, 4H), 1.63–1.70 (AA'BB', 2H), 2.55–2.61 (AA'BB', 2H), 7.10 (d, 8 Hz, 2H), 7.10 (d, 8 Hz, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.84, 29.25, 30.89, 40.25, 74.46, 128.43, 129.65, 131.34, 141.26. Minor product, 2-(4-chlorophenyl)-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.81 (t, $J = 8$ Hz, 3H), 0.87 (t, $J = 8$ Hz, 3H), 1.07 (s, 1H, OH), 1.13–1.40 (m, 2H) 1.25 (d, $J = 7$ Hz, 3H), 1.56 (q, $J = 7$ Hz, 2H), 2.82 (q, $J = 7$ Hz, 1H), 7.18–7.26 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.64, 8.00, 15.36, 27.48, 29.06, 44.91, 75.88, 128.07, 130.49, 131.98, 142.35.

4.6.5. 1-(4-Bromophenyl)-3-ethylpentan-3-ol / 2-(4-bromophenyl)-3-ethylpentan-3-ol

Title compounds were obtained in 63% combined yield. Ratio of two regioisomers was 68/32. Major product, 1-(4-bromophenyl)-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.88 (t, $J = 8$ Hz, 6H), 1.51 (q, $J = 8$ Hz, 4H), 1.64–1.70 (AA'BB', 2H), 2.54–2.60 (AA'BB', 2H), 7.03–7.08 (m, 2H), 7.10 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.84, 29.29, 30.87, 40.20, 74.46, 119.33, 130.06, 131.37, 141.74. Minor product, 2-(4-bromophenyl)-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.81 (t, $J = 8$ Hz, 3H), 0.86 (t, $J = 8$ Hz, 3H), 1.11 (s, 1H, OH), 1.01–1.46 (m, 2H) 1.25 (d, $J = 7$ Hz, 3H), 1.56 (q, $J = 7$ Hz, 2H), 2.80 (q, $J = 7$ Hz, 1H), 7.13–7.17 (m, 2H), 7.38–7.42 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.66, 8.00, 15.33, 27.49, 29.06, 44.98, 75.83, 120.09, 130.91, 131.00, 142.91.

4.6.6. 1-(4-Methoxyphenyl)-3-ethylpentan-3-ol / 2-(4-methoxyphenyl)-3-ethylpentan-3-ol

Title compounds were obtained similarly from 4-vinylanisole (134 mg, 1.0 mmol) in 84% combined yield. Ratio of two regioisomers was 71/29. Major product, 1-(4-methoxyphenyl)-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.88 (t, $J = 8$ Hz, 6H), 1.50 (q, $J = 8$ Hz, 4H), 1.64–1.70 (AA'BB', 2H), 2.52–2.58 (AA'BB', 2H), 3.73 (s, 3H), 6.77–6.83 (m, 2H), 7.06–7.11 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.60, 28.72, 30.64, 40.34, 54.90, 74.22, 113.57, 128.91, 134.61, 157.39. Minor product, 2-(4-methoxyphenyl)-3-ethylpentan-3-ol. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.82 (t, $J = 7$ Hz, 3H), 0.86 (t, $J = 8$ Hz, 3H), 1.15–1.46 (m, 2H), 1.25 (d, $J = 7$ Hz, 3H), 1.55 (q, $J = 7$ Hz, 2H), 2.81 (q, $J = 7$ Hz, 1H), 3.76 (s, 3H), 6.80–6.85 (m, 2H), 7.14–7.19 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.69, 8.01, 15.45, 27.30, 29.00, 44.56, 55.13, 75.92, 113.42, 130.03, 135.67, 158.09.

4.6.7. 1-(2,4,6-Trimethylphenyl)-3-ethylpentan-3-ol

Title compound was prepared similarly from 2,4,6-trimethylstyrene (146 mg, 1.0 mmol) in 62% yield with a $> 99\%$ regioisomeric purity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.90 (t, $J = 7$ Hz, 6H), 1.35 (s, 1H, OH), 1.48–1.58 (m, 6H), 2.22 (s, 3H), 2.28 (s, 6H), 2.56–2.63 (AA'BB', 2H), 6.81 (s, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 7.91, 19.64, 20.77, 23.16, 30.71, 37.63, 74.59, 128.95, 134.84, 135.63, 136.12.

4.7. Formation of zirconacyclopentane with $Cp^*_2ZrEt_2$ and styrene

Ethylmagnesium bromide (2 mmol) was added to the suspension of $Cp^*_2ZrCl_2$ (433 mg, 1.0 mmol) in toluene (5 mL) at -78°C and the mixture was stirred for 1 h at room temperature. After adding styrene, the reaction mixture was stirred and warmed up to reflux temperature. To the mixture 3 N HCl was added to quench the reaction and usual work-up gave 2-phenylbutane as a single product (yield 38% by GC).

Acknowledgments

The authors thank the Japanese Ministry of Education, Science and Culture and the Kawakami Memorial Foundation for support of this study. We also thank Prof. Ei-ichi Negishi for his useful information.

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