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Novel Type of Carbozirconation Reaction of Alkynes[1]

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Abstract: Novel type of carbozirconation reaction of alkynes is reported. Treatment of zirconocene-alkyne complexes, zirconacyclopentenes, or zirconacyclopentadienes with allylic compounds gave allylzirconation products of alkynes. Carbozirconation of alkynes with zirconacyclopentenes or zirconacyclopentadienes involved β,β'-C-C bond cleavage reaction of zirconacycles. Reactions of zirconacyclopentenes with homoallyl bromides afforded allylcyclopropane derivatives as carbozirconation products.

1. INTRODUCTION

Carbometalation of unsaturated hydrocarbons is an attractive reaction from the viewpoint of synthetic application of organometallic chemistry.[2] Although allylmetalation of alkynes is a valuable reaction among them, only allylmetals containing Li, Mg, B, Zn or Al have been used.[2,3] In addition, the allylmetalation with such allylmetals always involves a problem of regioselectivity. The formation of a new C-C bond can take place at the α- or γ-carbon of an allylic moiety. This regioselectivity depends on its mechanism, and the reactions often give a mixture of two isomers.

On the other hand, zirconium mediated or catalyzed organic reactions have been extensively explored for the last two decades.[4] Particularly, the reductive coupling of alkynes with other unsaturated compounds on zirconocene species has been intensively investigated.[5,6] We have reported previously the zirconium mediated functionalization of unactivated alkynes via the formation of zirconacyclopentenes.[6] This reaction could afford alcohols, ketones or halides as organic products involving the formation of new C-C bonds. In concern with the allylmetalation, zirconium mediated allylzincation of alkynes[7] or zirconium catalyzed allylalumination[8] has been reported by Negishi. However, allylzirconocene compounds, which are easily prepared by the reaction of Cp_2ZrCl_2 with allyl Grignard[9] or by the oxidative addition of allylic ethers to a 'zirconocene equivalent'[10,11,12] (Cp_2ZrBu_2: Negishi reagent), are inert for the allylzirconation of alkynes.

Recently we found that the zirconium-ethylene complex **1**[13] reacted with an allylic ether to afford the allylzirconation product of ethylene.[14] Furthermore, this reaction could be catalytic as an allylation reaction in the presence of EtMgBr.[14,15] The reaction proceeded via a five membered zirconacyclopentane intermediate **2**, and elimination of the β-alkoxy group from **2** was the key step (eq 1).

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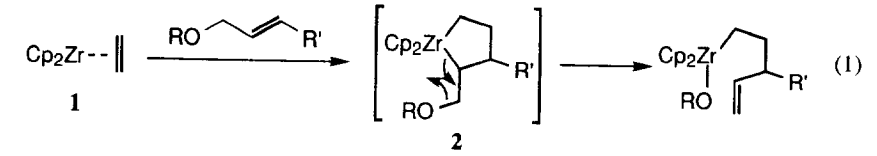
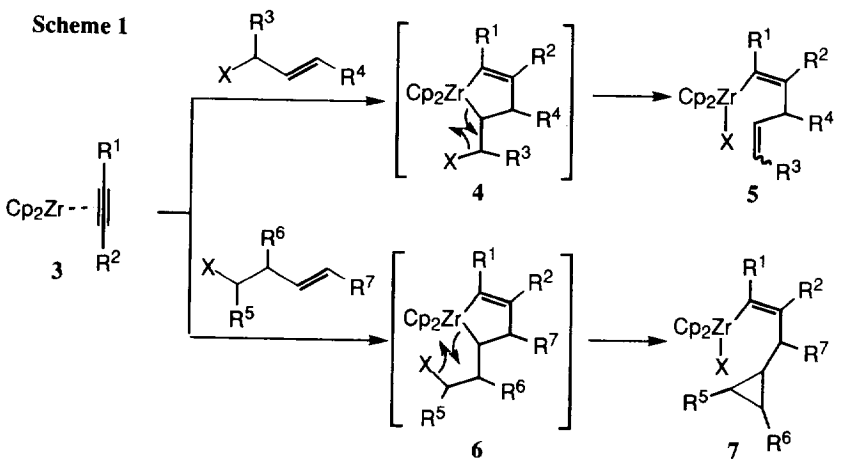
This information led us to the idea that a similar reaction may also proceed with a combination of usual alkynes and the zirconocene such as **3**. Coupling of alkynes on zirconium with allylic compounds would give zirconacyclopentenes **4** that have a substituent at the α-carbon of the zirconacycles with a leaving group at the β-position. β-Elimination of the leaving group from **4** resulted in the allylated product **5** (Scheme 1). Furthermore, we have investigated the possibility of γ-elimination from zirconacyclopentenes **6** which would give **7** involving the formation of a cyclopropane ring.



(1)

Scheme 1



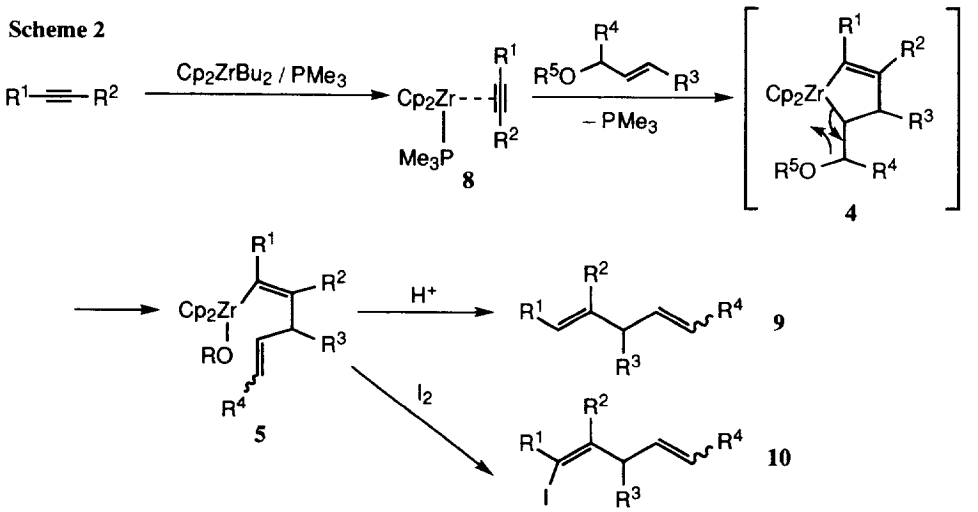
In this paper we describe full details of this novel type of carbozirconation of alkynes which involves elimination reactions from α-substituents of zirconacyclopentene derivatives.

2. RESULTS AND DISCUSSION

2.1. Allylation of alkynes via zirconocene-alkyne complexes (Method A); Mechanistic consideration

To achieve the allylzirconation reaction of alkynes, the first step should be the coupling of alkynes with allylic ethers on zirconium to form **4**. One accessible way to **4** is the reaction of zirconocene-alkyne complex **8** with an allylic compound. Preparation and reactions of zirconocene-alkyne complexes have already been investigated by several groups.[16] Zirconocene-alkyne complexes have been prepared by the following two methods: (i) adding alkynes and stabilizing reagents such as phosphines[16a,c,f] and DMAP[16g] to Cp_2ZrBu_2 (Negishi reagent); (ii) hydrozirconation of alkynes to produce $Cp_2Zr(CR{=}CHR')Cl$, followed by methylation with MeLi and β-hydrogen abstraction from the alkenyl ligand.[16b,d,e] The former method (i) is more convenient for our purpose. For terminal alkynes, however, method (i) did not give **8** in good yields, therefore the latter method (ii) was useful for terminal alkynes.[17]

Scheme 2

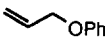
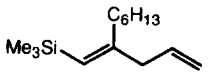
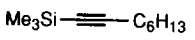
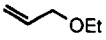
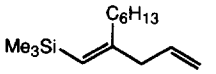
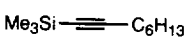
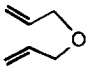
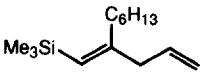
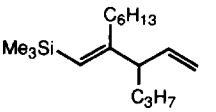
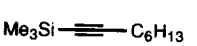
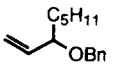
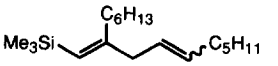
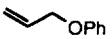
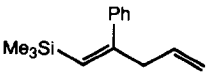
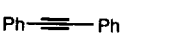
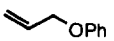
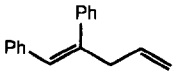
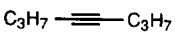
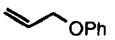
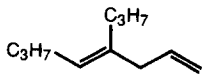
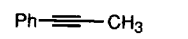
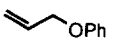
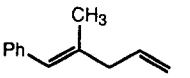
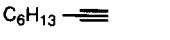
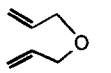
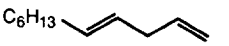


Results are shown in Table 1. Alkynes on zirconium reacted with allylic ethers to afford allylated products **9** in good to excellent yields after hydrolysis. Treatment of the reaction mixture with iodine afforded the corresponding alkenyl iodides **10**, showing that the products were alkenylzirconium species. Various allylic ethers can be used for the reaction. Substituted allylic ethers, *trans*-2-hexenyl phenyl ether and 3-benzyloxy-1-octene, also gave allylated products. It is noteworthy that the C-C bond formation occurred exclusively at the γ-position of allylic ethers. Reactions of 1-(trimethylsilyl)alkynes gave the allylated products **9** and **10** with high regioselectivity. Since a trimethylsilyl group stabilizes α-carbanions, α-silyl-alkenylzirconium compounds such as **5** (R^1 = Me_3Si) were favored as products as usually observed.[16e] This caused the high regioselectivity. The same type of regioselectivity or orientation was also observed in the case of silyl substituted alkynes for other allylmetalation reactions such as allylzincation.[7] 1-Phenylpropyne and 1-octyne, however, gave mixtures of regioisomers. Addition of Zr and an allyl group to an alkyne was perfectly *syn* in all cases as usually observed.

A plausible mechanism for this allylzirconation of alkynes involves the zirconacyclopentene intermediate **4**. Though the formation of allylzirconocene species in the reaction of Cp_2ZrBu_2 with allylic ethers has been proposed,[18] direct addition of the allylzirconocene to alkynes did not take place under the present conditions. Two isomers, **4a** and **4b**, can be considered as possibilities in the coupling of alkynes with allylic ethers. Even though **4b** might be formed,[19] transformation of **4b** via β-β' C-C bond cleavage in the zirconacyclopentene[20] would afford **4a** under some conditions as observed for allylation of alkenes.[14] Finally, the complex **4a**, in which the -CH(R)OR group occupies the α-position of the zirconacyclopentene, allows β-elimination of an -OR group to give the allylzirconation product **5**. This irreversible β-alkoxy elimination step from **4a** to **5** is totally responsible for inducing the reaction. This mechanism can account for high regioselectivity in C-C bond formation at the γ-position of allylic ethers.

Hydrolysis products of the zirconacyclopentene intermediate **4b** were not observed by gas chromatography in a reasonable amount probably due to the short lifetime of **4b**. The complex **5a** (R^1= Me_3Si, R^2= Ph, R^3= H, R^4= H, R^5= Ph) was formed quantitatively and characterized by NMR spectroscopy.

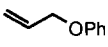
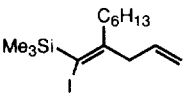
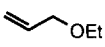
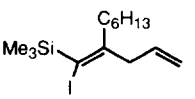
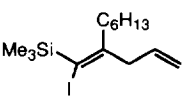
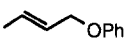
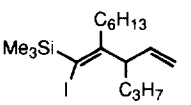
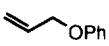
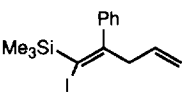
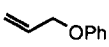
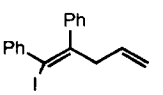
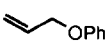
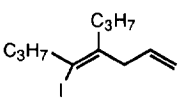
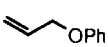
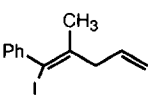
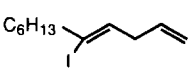
Table 1. Allylzirconation Reactions of Alkynes by the Reactions of Zirconocene Alkyne Complexes with Allylic Ethers; *Formation of Hydrolysis Products*[a]

Run	Alkyne	Allylic ether	Temp /°C	Time /h	Hydrolysis product **9**	Yield /%	Isomeric purity/%
1			35	3		81	97
2			35	6		80	95
3			35	3		94	>99
4			50	48		72	>99
5			35	24		80	b
6			35	3		97	98
7			35	24		97	>99
8			35	1		67	>99
9			35	24		76	62
10[c]			35	24		73	d

a) Yields were determined by GC. Unless otherwise mentioned, the alkyne complex was prepared by the method (i) with PMe_3. b) cis:trans = 58:42. c) Zirconocene(1-octyne)(PMe_3) was prepared by method (ii).[16d] d) 2-hexyl-1,4-pentadiene:(E)-1,4-undecadiene = 78:22.

Table 1 (continued).

Allylzirconation Reactions of Alkynes by the Reactions of Zirconocene-alkyne Complexes with Allylic Ethers; *Formation of Alkenyl Iodides*[a]

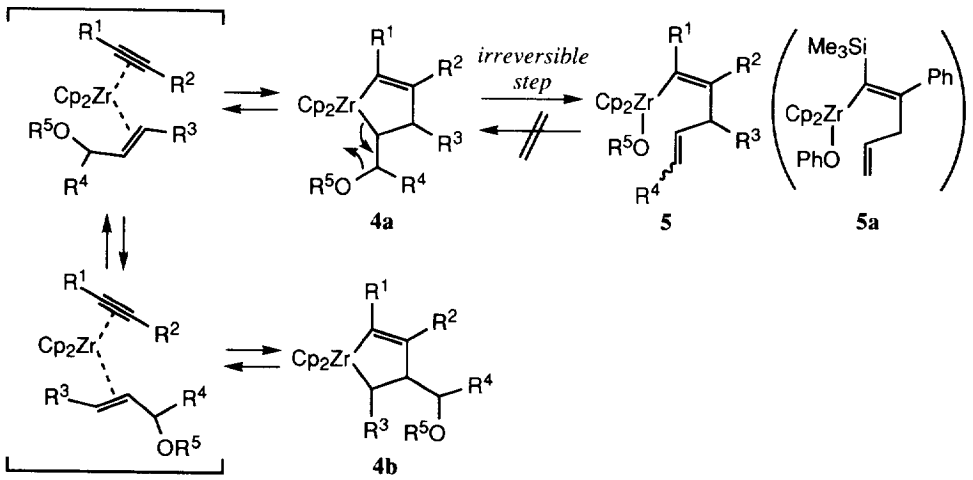
Run	Alkyne	Allylic ether	Temp /℃	Time /h	Iodinolysis product **10**	Yield /%	Isomeric purity/%
1	$Me_3Si-\equiv-C_6H_{13}$		35	3		84	99
2	$Me_3Si-\equiv-C_6H_{13}$		35	6		72	96
3	$Me_3Si-\equiv-C_6H_{13}$		35	3		88	>99
4	$Me_3Si-\equiv-C_6H_{13}$	C_3H_7 	50	48		75	>99
5	$Me_3Si-\equiv-Ph$		35	3		94	98
6	$Ph-\equiv-Ph$		35	24		87	>99
7	$C_3H_7-\equiv-C_3H_7$		35	1		71	>99
8	$Ph-\equiv-CH_3$		35	24		76	60
9[b]	$C_6H_{13}-\equiv$		35	24		56	c

a) Yields were determined by GC. Unless otherwise mentioned, the alkyne complex was prepared by the method (i) with PMe_3. b) Zirconocene(1-octyne)(PMe_3) was prepared by method (ii)[16d].

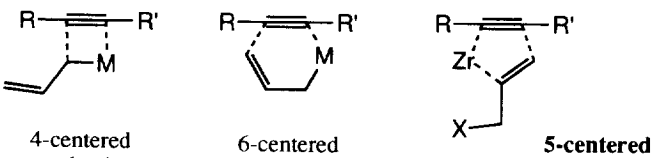
c) 1-iodo-2-hexyl-1,4-pentadiene:(Z)-5-iodo-1,4-undecadiene = 81:19.

The ^{1}H NMR spectrum of **5a** showed a singlet peak at 6.03 ppm which was assigned to Cp and the ^{13}C NMR signals were consistent with the structure.

Scheme 3



Mechanistic studies of conventional allylmetalations using allylmetals suggested that four-centered and six-centered transition state were plausible.[2] The formation of a mixture of regioisomers is due to these two mechanisms. The mechanism of the present reaction that we are describing here involves the five-membered zirconacyclopentenes for allylzirconation of alkynes and is quite different from those of conventional allylmetalation.[21] This five-centered mechanism is responsible for the high regioselectivity of this allylzirconation reactions.

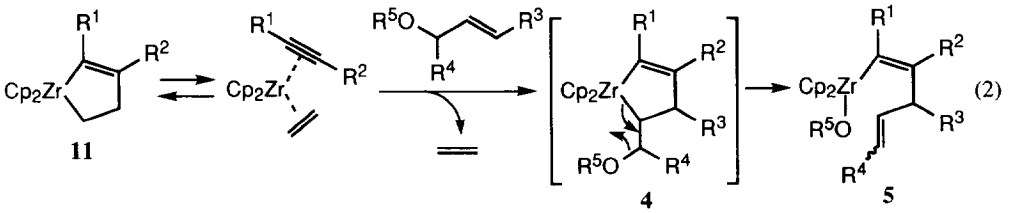


2.2. Allylation of alkynes via zirconacyclopentenes (Method B)

The method for the allylzirconation via the zirconocene-alkyne complex **8** (method A) gave satisfactory results especially for 1-(trimethylsilyl)alkynes or 1-phenylalkynes. This method, however, gave the allylzirconation products in relatively low yields for alkyl substituted alkynes such as 4-octyne. Thus we derived another method using zirconacyclopentene complexes (Method B).

We recently reported a convenient preparative method for zirconacyclopentene **11** and its reactivity.[6] **11** was prepared quantitatively from Cp_2ZrEt_2 and corresponding alkynes. When **11** was treated with unsaturated compounds such as aldehydes, ketones and alkynes, it showed similar behavior to the zirconocene-alkyne complexes. Cleavage of the β-β' C-C bond in the zirconacycle occurred and the ethylene part was replaced by another unsaturated compound to give a new metalacyclic species. It has been reported

that zirconocene-alkyne complex **8** also reacted with aldehydes, ketones and other alkynes to give a new zirconacycle. This reactivity of **11** can be interpreted as it behaving as a "zirconocene-alkyne complex equivalent". Therefore zirconacyclopentene **11** could be used for preparation of **4** using allylic compounds (eq 2).[1c]



11 showed similar reactivity to **8** and treatment of **11** with allylic ethers gave allylated products as expected. The results are shown in Table 2. The reaction using 4-octyne was remarkably improved. The allylation of alkyl substituted alkynes could be improved by this method. Although 1-trimethylsilyl-1-alkynes gave a rather lower yield in contrast to method A, their products also showed high regioselectivity. Deuterolysis of the reaction mixture of run 1 gave the deuterated compound 4-deutero-3-propyl-1,4-octadiene with 94% D incorporation, showing that the alkenylzirconium species **5** was the product of this reaction. Thus, these two methods A and B can complement each other.

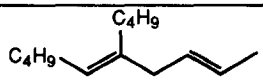
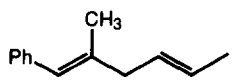
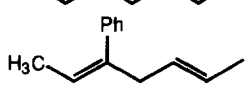
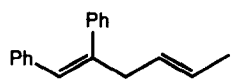
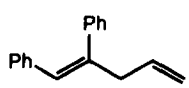
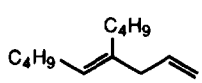
Table 2. Allylzirconation Reactions of Alkynes via Zirconacyclopentenes[a]

Run	Alkyne	Allylic ether	Temp /°C	Time /h	Hydrolysis Product **9**	Yield /%	Isomeric purity/%
1	C_3H_7—≡—C_3H_7	OPh	50	3	C_3H_7, C_3H_7	91	-
2	C_3H_7—≡—C_3H_7	O	35	1	C_3H_7, C_3H_7	99	-
3	C_4H_9—≡—C_4H_9	$OSiMe_3$	50	1	C_4H_9, C_4H_9	97	-
4	C_3H_7—≡—C_3H_7	C_5H_{11}, OBn	50	24	C_3H_7, C_3H_7, C_5H_{11}	60	cis/tr = 66:34
5	Ph—≡—Ph	OPh	r.t.	3	Ph, Ph	89	>99
6	Ph—≡—CH_3	O	35	3	CH_3, Ph	91[b]	regiosel. = 65%
7	Me_3Si—≡—C_6H_{13}	OPh	35	24	C_6H_{13}, Me_3Si	68	96
8	Me_3Si—≡—Ph	OPh	35	3	Ph, Me_3Si	56	98

a) Yields were determined by GC. b) Combined yield of regioisomers

In order to investigate the scope of the reaction, we tried some other allylic compounds. Generally, halogens are good leaving groups and allyl halides are the most typical allylic compounds in this kind of reaction.[22] However, they were not suitable for the method A since they interact with trialkylphosphines first. The zirconacyclopentene technique (Method B), on the other hand, does not require phosphine ligands. Hence this method has an advantage in allowing allylic halides to participate in the reaction. Results of the allylation with allylic halides are shown in Table 3. Allylation products, in fact, were obtained when the zirconacyclopentenes were treated with allylic chlorides. Interestingly, the products obtained from the reactions of 3-chloro-1-butene were selectively *trans*-isomers. It is in sharp contrast with the case of allylic ethers, in which 34:66 to 42:58 mixtures of *trans* and *cis* isomers were obtained. The allylation occurred only at the γ-position of the allylic moiety. Other substituted allylic chlorides such as crotyl chloride and metallyl chloride did not give positive results. Allyl bromide has not given satisfactory results so far. Only a small amount (<10% yield) of the allylation products were obtained and the starting alkyne was liberated in the reaction mixture, in the case of allyl bromide with 5-decyne.

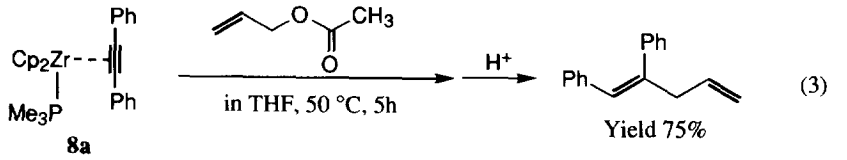
Table 3. Allylzirconation of Alkynes using Allylic Chlorides via Zirconacyclopentenes[a]

Run	Alkyne	Allylic chloride	Temp /°C	Time /h	Product **9**	Yield /%	Stereosel. /%
1	$C_4H_9-\equiv-C_4H_9$		50	3		53	91
2	$Ph-\equiv-CH_3$		50	6		46	91
						32	97
3	$Ph-\equiv-Ph$		50	1		79	>99
4	$Me_3Si-\equiv-C_4H_9$				N.R.	-	-
5	$Ph-\equiv-Ph$		r.t.	1		95	-
6	$C_4H_9-\equiv-C_4H_9$		r.t.	1		69	-

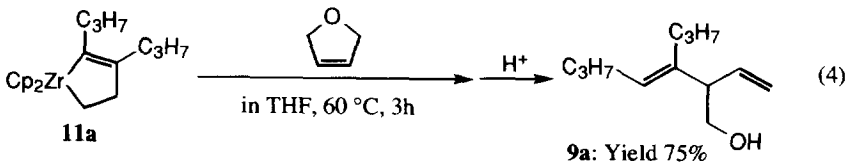
a) Yields were determined by GC.

Allyl esters could also be used for the reaction. Treatment of Cp_2Zr(1,2-diphenylacetylene)(PMe_3) **8a** with allyl acetate (method A) gave (*Z*)-1,2-diphenyl-1,4-pentadiene in 75% yield (eq 3). Cyclic allylic ethers such as 2,5-dihydrofuran also afforded the desired product **9a** in the reaction with zirconacyclopentene **11a** ($R^1=R^2=C_3H_7$) (method B, eq 4). Buchwald and co-worker have reported a reaction of a zirconocene-

cyclooctyne complex, which was prepared from cyclooctenyllithium, with 2,5-dihydrofuran, although there was no report for other alkynes.[23]



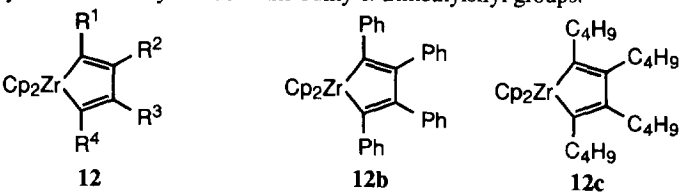
(3)

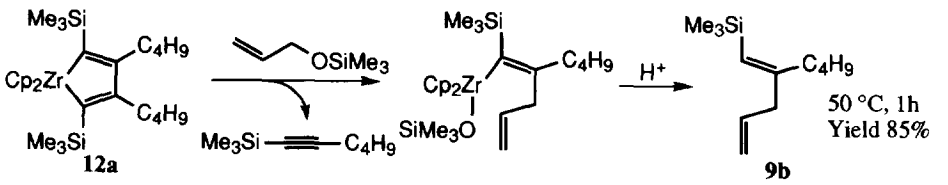


(4)

2.3 Allylation of alkynes via zirconacyclopentadienes

Zirconacyclopentanes[24] and zirconacyclopent-2-enes[21] showed β-β' C-C bond cleavage in their reactions. In the reactions of zirconacyclopentadiene **12**, however, this type of C-C bond activation has been rarely observed.[5e,17] During the course of our investigation, we found that zirconacyclopentadiene **12a** (R^1=R^4=Me_3Si, R^2=R^3=C_4H_9) reacted with allyl trimethylsilyl ether to result in the allylation of the alkyne (eq 5). The product (*E*)-2-*n*-butyl-1-(trimethylsilyl)-1,4-pentadiene **9b** was obtained in 85% yield after hydrolysis. This reaction should involve cleavage of the β-β' C-C bond in **12**. This reaction, however, did not occur in other zirconacyclopentadienes such as **12b** and **12c**. This uncommon reactivity of **12a** might be because of instability of the metalacycle due to the bulky α-trimethylsilyl groups.





(5)

2.4. Allylation of alkynes with acetals; formation of vinyl ethers

Introduction of a functional group to the allylation products is also attractive. Although several examples of allylmetalation are known so far, it is relatively difficult to use the functionalized allylmetals. In order to explore this subject in our allylation reactions, we investigated the reaction with α,β-unsaturated acetals. α,β-Unsaturated acetals, which contain an allyl ether moiety, were expected to afford a functionalized allylic moiety in the products **14** (Scheme 4). Both methods A and B could be used for the reactions and the results are described in Table 4.

Acrolein diethyl acetal was used for the reactions. After hydrolysis of the reaction mixture, vinyl ethers **15** were obtained as the products. Treatment of the products with acid can convert them into aldehydes. The C-C bond formation proceeded exclusively at the terminal carbon of

Scheme 4

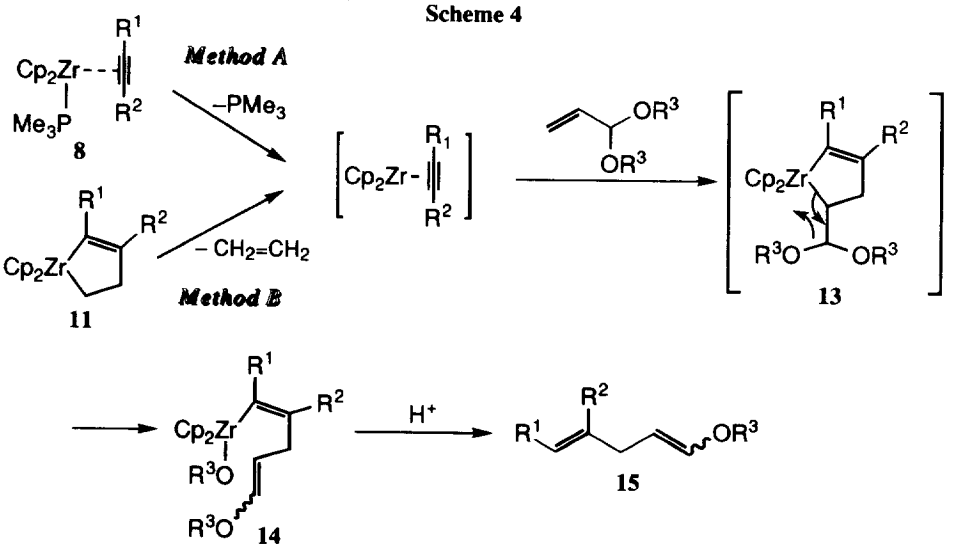
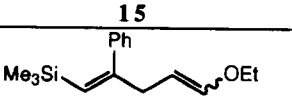
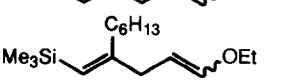
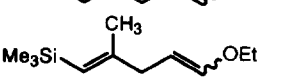
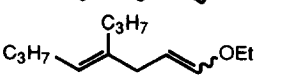
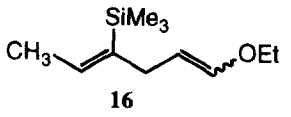


Table 4. Reactions of Alkynes with Acetals Mediated by Zirconium; *Formation of Vinyl Ethers*[a]

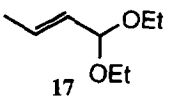
Alkyne	Method[b]	Temp /°C	Time /h	Hydrolysis product **15**	Yield /%	Regiosel. for alkyne/%	cis:trans for vinyl ether
$Me_3Si-\equiv-Ph$	A	35	1		71	>98	53:47
$Me_3Si-\equiv-C_6H_{13}$	A	35	1		75	>98	48:52
$Me_3Si-\equiv-CH_3$	A	35	1		81[c]	89	41:59
$C_3H_7-\equiv-C_3H_7$	B	r.t.	48		61	-	49:51

a) Yields were determined by GC.
b) Method A: via zirconocene-alkyne complexes, Method B: via zirconacyclopentenes.
c) Combined yield of regioisomers

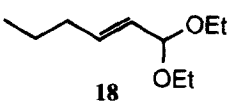
acrolein diethyl acetal in a same way as described above. For 1-trimethylsilyl-2-phenylacetylene and 1-trimethylsilyl-1-octyne, regioselectivity was very high (>98%). In the case of 1-trimethylsilyl-1-propyne, ca. 10% of the regioisomer **16** was observed. The *cis:trans* ratio for the vinyl ether moiety was approximately 1:1. β-Substituted acetals such as **17** and **18** did not give the desired products even at 60 °C.



16



17



18

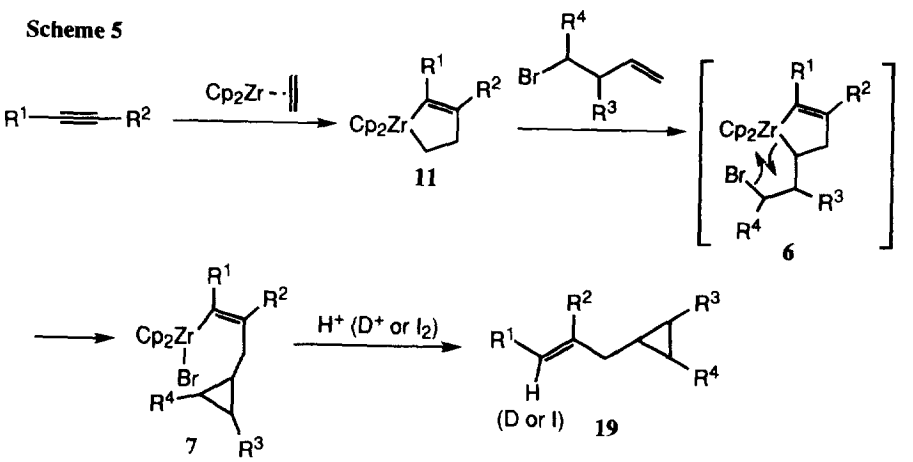
2.5. Carbometalation of alkyne using homoallylic compounds; formation of allylcyclopropanes

As described above, β-elimination from the α-stem of the zirconacycle was the key step of the allylzirconation of alkynes. This information prompted us to pursue the possibility of γ-elimination from the zirconacyclopentenes. Thus we investigated reactions of alkynes with homoallylic compounds. Homoallylic ethers, however, were not reactive towards the zirconocene-alkyne complexes or zirconacyclopentenes. No γ-elimination products were observed.

Finally we found that treatment of the zirconacyclopentenes with homoallylic bromides gave cyclopropane products **19** after hydrolysis in good yields (Scheme 5). Results of the reactions are shown in Table 5. Internal alkynes, such as 4-octyne, 3-hexyne, and diphenylacetylene. afforded the corresponding allylcyclopropane derivatives in good yields with high isomeric purity (Run, 1,7,9). Deuterolysis and iodinolysis products revealed the formation of **7** in the reaction mixtures (Run 2, 8, 10). The stereochemistry of the alkenyl moieties was very selective (highly selective *syn* addition) as observed for the allylation reactions of alkynes described above. 1-(Trimethylsilyl)alkynes did not give positive results (Run 13, 14). Similar low reactivity of 1-(trimethylsilyl)alkynes was observed in the allylation reactions via zirconacyclopentenes (method B).

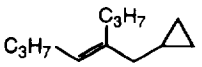
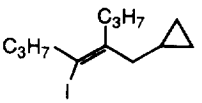
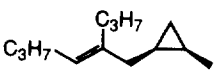
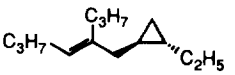
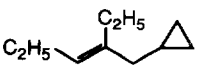
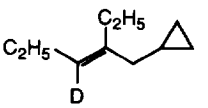
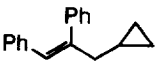
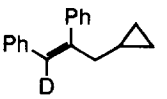
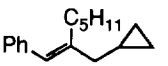
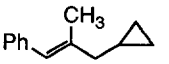
Substituted homoallylic bromides were investigated. When a methyl group was at the δ-position in the homoallylic moiety, only an alkyne dimer was obtained in ca. 40 % yield based on zirconium. No desired product was detected (Run 3). An α-substituted homoallylic bromide produced predominantly the *cis*-isomer for the disubstituted cyclopropane moiety (R^1=R^2=C_3H_7, R^3=H, R^4=Me) (Run 5), whereas an β-substituted one gave the *trans*-isomer as a main product (R^1=R^2=C_3H_7, R^3=Et, R^4=H) (Run 6). The stereochemistry of disubstituted cyclopropane derivatives was determined by a known method.[25]

Scheme 5



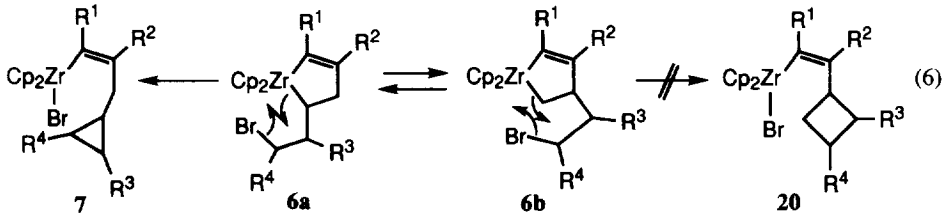
11 6 7 19

Table 5. Reactions of Alkynes with Homoallylic Bromides; *Formation of Cyclopropanes*

Run	Alkyne	Homoallylic halide	Temp /°C	Time /h		Main product **19**	Yield[a] /%	Isomeric purity/%
1	$C_3H_7-\equiv-C_3H_7$	Br	r.t.	24	H^+		68	>99
2	$C_3H_7-\equiv-C_3H_7$	Br	r.t.	24	I_2		50	>99
3	$C_3H_7-\equiv-C_3H_7$	Br	65	24	H^+	b	0	-
4	$C_3H_7-\equiv-C_3H_7$	OPh	50	12	H^+	N.R.[c]	0	-
5	$C_3H_7-\equiv-C_3H_7$	Br	50	24	H^+		64	74[d,e]
6	$C_3H_7-\equiv-C_3H_7$	Br, Et	40	24	H^+		59	74[d,f]
7	$C_2H_5-\equiv-C_2H_5$	Br	r.t.	24	H^+		70	>98
8	$C_2H_5-\equiv-C_2H_5$	Br	r.t.	24	D^+		70	(95)[g]
9	Ph-≡-Ph	Br	r.t.	12	H^+		80	>98
10	Ph-≡-Ph	Br	r.t.	24	D^+		71	(94)[g]
11	Ph-≡-C_5H_{11}	Br	40	24	H^+		68	>98
12	Ph-≡-Me	Br	r.t.	24	H^+		85	85[h]
13	$Me_3Si-\equiv-SiMe_3$	Br	50	24	H^+	N.R.[c]	0	-
14	$Me_3Si-\equiv-Me$	Br	40	12	H^+	b	0	-
15[i]	$C_6H_{13}-\equiv$	Br	r.t.	12	H^+		59	77[j]

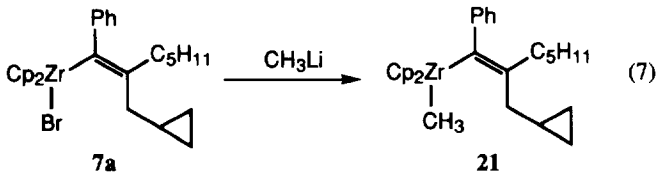
a) Yields were determined by GC. Combined yields of isomers. b) Alkyne dimer was formed. c) No desired products. d) A mixture of stereoisomers of cyclopropane moiety. e) Cis:trans = 74:26. f) Cis:trans = 26:74. g) Deuterium incorporation. h) Two regioisomers for Me and Ph groups of phenylpropyne were obtained in a ratio of 85:15. i) This reaction was carried out using zirconocene-alkyne complex without PMe_3 prepared by method (ii).[16d] j) Two regioisomers for C_6H_{13} group of 1-octyne were obtained in a ratio of 77:23.

A plausible mechanism for these reactions is as follows. The intermediates **11** reacted with double bond of homoallylic bromides to afford α-substituted zirconacyclopentene compounds **6**. Sequential γ-bromine abstraction by the zirconium metal and attack by the alkyl carbon attached to zirconium produced **7**. Hydrolysis (deuterolysis or iodinolysis) gave the corresponding compounds **19**. Other possible orientations of the double bond in the homoallylic bromides in the reaction with **11** gives β-substituted **6b**. If similar δ-bromine abstraction occurs, cyclobutane derivatives **20** should be formed (eq 6). However, the cyclobutane compounds were not detected. Even though **6b** was formed in the reaction, it would be converted into **6a** by isomerization.[26] Recently Whitby et al. showed that the reaction of the zirconocene η^2-imine complex with homoallyl bromide produced cyclopropane compounds.[27] They also suggested that its intermediate was a zirconacycle with the bromoethyl substituent in the α-position.



(6)

The zirconium containing intermediate species **7a** was investigated by NMR study. The NMR spectra indicated that the complex **7a** was formed in 72% yield. However, the spectra were not clear enough. Therefore the complex **7a** was converted into the methylated compound **21** in 93% yield using MeLi (eq 7). The ^{1}H- and ^{13}C-NMR spectra of **21** clearly showed all the protons and carbons which were consistent with the structure.



(7)

3. CONCLUSION

In conclusion, our current work represents novel carbozirconation reactions of alkynes. These reactions are summarized by the following points. (i) Zirconocene-alkyne complexes reacted with allylic compounds to afford the allylzirconation products. (ii) Zirconacyclopentenes, which are prepared from alkynes and Cp_2ZrEt_2, also gave the allylzirconation products when treated with allylic compounds. (iii) Zirconacyclopentadiene with α-trimethylsilyl groups also showed similar reactivity toward allylic ethers. The allylation proceed via β-β' C-C bond cleavage in the reactions of the zirconacyclopentenes and the zirconacyclopentadienes. (iv) The allylation reaction proceeds via a five-membered ring intermediate and subsequent β-elimination. High γ-selectivity of the C-C bond formation in the allylation is explained by this mechanism. This mechanism is uncommon compared with conventional allylmetalation mechanisms. (v) An α,β-unsaturated acetal was used for the allylation reactions to give vinyl ether derivatives as the products. (vi) The reactions of homoallyl bromides with the zirconacyclopentenes afforded allylcyclopropane derivatives as the carbozirconation products. Further investigation of this region is now in progress.

EXPERIMENTAL

General

All reactions involving organozirconium compounds were carried out under a nitrogen atmosphere. Teterahydrofuran was dried over sodium/benzophenone and then distilled. Zirconocene dichloride was purchased from Aldrich Chemical Company, Inc. Ethylmagnesium bromide (THF solution) and butyllithium (hexane solution) were purchased from Kanto Chemicals Co. Ltd. Other organic chemicals were purchased from Tokyo Chemical Industry Co., Ltd. or Wako Pure Chemical Ind., Ltd. Some alkynes were prepared by known methods. ^{1}H (270 MHz) and ^{13}C (67.5 MHz) NMR spectra were recorded on a JEOL EX270 NMR spectrometer, infrared spectra on a Shimadzu FTIR-4200, GC-MS on a Shimadzu GCMS-QP1000EX and high resolution mass spectroscopy on a Shimadzu-Kratos CONCEPT IS. Deuterium incorporation was determined by ^{13}C NMR spectra (gated decoupling pulse technique without NOE).

Allylation of alkynes via zirconocene-alkyne complexes (method A)

Representative Procedure; (Z)-2-phenyl-1-trimethylsilyl-1,4-pentadiene. Typical procedure for the allylation of alkynes via the zirconocene-alkyne complex is as follows. To Cp_2ZrBu_2 prepared from Cp_2ZrCl_2(365 mg, 1.25 mmol) and 2 equiv of *n*-BuLi (1.6 M hexane solution, 2.5 mmol) in 5 mL of THF was added 1.5 mmol of PMe_3 (1.25 mL of 1.0M solution in THF) at -78°C. The mixture was warmed up to room temperature and stirred for 1 h. To this mixture was added 1-phenyl-2-(trimethylsilyl)acetylene (174 mg, 1.0 mmol) at room temperature. Zirconocene alkyne complex **8** was cleanly formed after 1h. After addition of allyl phenyl ether (268 mg, 2.0 mmol), the mixture was stirred for 3h at 35 °C. The reaction mixture was quenched with 3.0 N HCl, extracted with Et_2O, washed with saturated aqueous $NaHCO_3$ and brine and then dried over $MgSO_4$. Purification by flash column chromatography (hexane) gave the title compound (97% yield based on alkyne with 98% regioselectivity). The yield was determined by GC. The product was characterized by ^{1}H and ^{13}C NMR and high resolution mass spectroscopy. ^{1}H NMR ($CDCl_3$, Me_4Si): δ -0.19 (s, 9H), 3.34 (dq, *J* = 7, 1 Hz, 2H), 4.99-5.06 (m, 2H), 5.59 (t, *J* = 1 Hz, 1H), 5.75-5.91 (m, 1H), 7.13-7.17 (m, 2H), 7.24-7.32 (m, 3H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 0.66, 47.36, 117.08, 127.61, 128.38, 128.58, 136.54, 144.66, 158.05. High resolution mass spectroscopy, calcd for $C_{14}H_{20}Si$: 216.1334, found: 216.1326.

(E)-2-n-Hexyl-1-trimethylsilyl-1,4-pentadiene. The title compound was prepared in a similar manner to that described above, using 1-(trimethylsilyl)-1-octyne (0.182 g, 1.0 mmol) instead of 1-phenyl-2-(trimethylsilyl)-acetylene. Yield 81% (by GC) with 97% regioselectivity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.09 (s, 9H), 0.89 (t, *J* = 7 Hz, 3H), 1.29-1.40 (m, 8H), 2.08-2.14 (dd, *J* = 7, 8 Hz, 2H), 2.80-2.83 (dd, *J* = 7, 1 Hz, 2H), 4.99-5.05 (m, 2H), 5.20 (dd, *J* = 1, 1 Hz, 1H), 5.73-5.88 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 0.38, 14.07, 22.62, 29.02, 29.60, 31.81, 36.24, 43.45, 115.95, 124.24, 136.89, 158.00. High resolution mass spectroscopy, calcd for $C_{14}H_{28}Si$: 224.1960, found: 224.1951.

(1E)-2-n-Hexyl-1-(trimethylsilyl)-1,4-decadiene. The title compound was obtained as a mixture of two isomers, (1*E*,4*Z*)/(1*E*,4*E*)=58/42. 80% combined yield (by GC). ^{1}H NMR ($CDCl_3$, Me_4Si): δ -0.08 (s, *E-isomer*), 0.00 (s, Z), 0.78-0.83 (m, CH_3 x 4), 1.16-1.35 (m), 1.90-2.05 (m), 2.66 (d, *J* = 5 Hz, 2H, *E-isomer*), 2.72 (d, *J* = 6.9 Hz, *Z-isomer*), 5.10-5.12 (m), 5.23-5.44 (m). ^{13}C NMR ($CDCl_3$, Me_4Si): δ (1*E*,4*Z*-isomer) 0.41, 14.09, 14.09, 22.62, 22.66, 27.19, 29.06, 29.24, 29.38, 31.59, 31.86, 36.41, 36.80, 123.45, 127.40, 131.35, 158.58; (1*E*,4*E*-isomer) 0.41, 14.09, 14.09, 22.57, 22.66, 29.24, 29.67, 29.67, 31.39, 31.86, 32.56, 36.19, 42.39, 123.59, 128.08, 132.40, 159.08. High resolution mass spectroscopy; calcd for $C_{19}H_{38}Si$: 294.2743, found: 294.2753.

(Z)-1,2-Diphenyl-1,4-pentadiene. Yield 97% with >99% stereoselectivity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 3.22 (dd, J = 7, 1 Hz, 2H), 5.04-5.14 (m, 2H), 5.81-5.96 (m, 1H), 6.45 (s, 1H), 6.91-7.54 (m, 10H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 45.35, 117.30, 126.91, 127.61, 127.70, 128.49, 129.12, 129.23, 129.69, 136.52, 137.98, 141.84, 141.88.

(E)-4-Allyl-4-octene. 67% yield by method A (by GC). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.887 (t, 3H, J = 7 Hz), 0.894 (t, 3H, J = 7 Hz), 1.37 (tq, 2H, J = 7, 7 Hz), 1.40 (tq, 2H, J = 7, 7 Hz), 1.99 (dt, 2H, J = 7, 7 Hz), 2.00 (t, 2H, J = 7 Hz), 2.74-2.69 (m, 2H), 4.99 (ddt, 1H, $|^2J|$ = 2 Hz, ^3J = 10 Hz, $|^4J|$ = 1.2 Hz), 5.02 (ddt, 1H, $|^2J|$ = 2 Hz, ^3J = 17 Hz, $|^4J|$ = 1.5 Hz), 5.16 (t, 1H, J = 7 Hz), 5.78 (ddt, 1H, J = 10, 17, 7 Hz). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.93, 14.14, 21.47, 23.23, 29.99, 32.22, 41.60, 115.36, 126.25, 137.63, 137.68. MS (EI) *m/e* 152 (M^+). High resolution mass spectroscopy; calcd for $C_{11}H_{20}$: 152.1565, found: 152.1565.

(E)-1-Phenyl-2-methyl-1,4-pentadiene/(Z)-4-phenyl-1,4-hexadiene. Obtained as a 62/38 mixture of two regioisomers, in 67% combined yield (by GC). *1-Phenyl-2-methyl-1,4-pentadiene.* ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.85 (d, J = 1 Hz, 3H), 2.90 (d, J = 7 Hz, 2H), 5.06-5.15 (m, 2H), 5.72-5.96 (m, 1H), 6.30 (s, 1H), 7.15-7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 17.83, 44.96, 116.33, 125.96, 126.43, 128.01, 128.80, 136.40, 137.27, 139.73. *2-phenyl-1-methyl-1,4-pentadiene.* ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.58-1.61 (dq, J = 7, 1 Hz, 3H), 3.06-3.09 (dq, J = 7, 1 Hz, 2H), 4.95-5.04 (m, 2H), 5.56 (dt, J = 7 Hz, 1H), 5.72-5.96 (m, 1H), 7.15-7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.75, 43.34, 115.78, 122.23, 125.73, 127.98, 128.50, 136.66, 138.42, 140.09. High resolution mass spectroscopy; calcd for $C_{12}H_{14}$: 158.1096, found: 158.1098.

(E)-1,4-Undecadiene/2-n-hexyl-1,4-pentadiene. Obtained as a 78/22 mixture of two regioisomers, in 73% combined yield (by GC). *(E)-1,4-Undecadiene.* ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.88 (t, J = 6.6 Hz, 3H, 11), 1.20-1.45 (m, 8H), 1.99 (dt, J = 6.6, 6.6 Hz, 2H, 6), 2.73 (dd, J = 6, 6 Hz, 2H, 3), 4.94-5.08 (m, 2H, 1), 5.34-5.51 (m, 2H, 2,4), 5.74-5.90 (m, 1H, 5). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.11, 22.66, 28.88, 29.49, 31.77, 32.61, 36.78, 114.70, 127.49, 131.86, 137.54. *2-n-Hexyl-1,4-pentadiene.* ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.11, 22.66, 27.62, 29.07, 31.77, 36.01, 40.79, 109.70, 115.92, 136.62, 148.52. High resolution mass spectroscopy; calcd for $C_{11}H_{20}$: 152.1565, found: 152.1565.

Allylation of alkynes via zirconocene-alkyne complexes (method A); iodination products.

Representative procedure; (E)-1-iodo-2-phenyl-1-(trimethylsilyl)-1,4-pentadiene. The allylzirconation reaction was carried out by the same method as detailed above. Typical procedure for iodinolysis of the allylzirconation products is as follows. To the reaction mixture was added slightly excess of iodine in THF solution at 0 °C. After stirring at room temperature overnight, the reaction mixture was quenched with 3.0 N HCl and the usual workup gave the title compound (97% yield based on alkyne with 98% regioselectivity). Yield was determined by GC. ^{1}H NMR ($CDCl_3$, Me_4Si): δ -0.12 (s, 9H), 3.46-3.49 (dd, J = 7, 1 Hz, 2H), 5.01-5.08 (m, 2H), 5.64-5.79 (m, 1H), 7.03-7.10 (m, 2H), 7.24-7.31 (m, 3H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 0.85, 52.28, 112.52, 117.03, 127.94, 128.41, 132.79, 141.88, 157.34. High resolution mass spectroscopy, calcd for $C_{14}H_{19}ISi$: 342.0301, found: 342.0302.

(E)-2-n-Hexyl-1-iodo-1-(trimethylsilyl)-1,4-pentadiene. 72-88% yield (by GC) with 96-99% isomerical purities. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.29 (s, 9H), 0.89 (t, J = 7 Hz, 3H), 1.18-1.43 (m, 8H), 2.25-2.28 (dd, J = 6, 3 Hz, 2H), 3.18-3.22 (ddd, J =7, 2, 1 Hz, 2H), 5.06-5.16 (m, 2H), 5.71-5.86 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 2.10, 14.05, 22.59, 29.31, 29.40, 31.66, 35.54, 49.02, 108.98, 116.33, 134.19, 157.18. High resolution mass spectroscopy, calcd for $C_{14}H_{27}ISi$: 350.0927, found: 350.0934.

(Z)-2-n-Hexyl-1-iodo-3-n-propyl-1-(trimethylsilyl)-1,4-pentadiene. 75% yield (by GC) with >99% isomerical purity. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.30 (s, 9H), 0.86-0.95 (m, 6H), 1.16-1.43 (m, 12H), 2.29

(t, J = 7.2 Hz, 2H), 3.80 (m, 1H), 4.76-5.15 (m, 2H), 5.70-5.83 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 2.13, 14.09, 14.27, 20.18, 22.59, 29.30, 29.44, 31.80, 33.64, 35.51, 58.85, 107.90, 115.29, 137.88, 156.27. High resolution mass spectroscopy; calcd for $C_{17}H_{33}ISi$: 392.1398, found: 392.1386.

(E)-1,2-Diphenyl-1-iodo-1,4-pentadiene. 87% yield by GC. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 3.58 (d, J = 6.6 Hz, 2H), 5.07-5.22 (m, 2H), 5.75-5.90 (m, 1H), 6.95-7.11 (m, 10H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 49.27, 101.27, 116.78, 126.66, 127.58, 127.74, 128.30, 128.98, 129.81, 131.57, 133.44, 139.76, 146.11. High resolution mass spectroscopy; calcd for $C_{17}H_{15}I$: 346.0220, found: 346.0234.

(Z)-5-Iodo-4-n-propyl-1,4-octadiene. 71% yield by the method A (by GC). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.87-0.94 (m, 6H), 1.35-1.48 (m, 2H), 1.49-1.63 (m, 2H), 2.15 (t, J = 7.9 Hz, 2H), 2.51 (t, J = 7.4 Hz, 2H), 3.02 (d, J = 6.6 Hz, 2H), 5.03-5.13 (m, 2H), 5.67-5.82 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 12.94, 14.02, 21.83, 23.09, 33.67, 43.04, 46.99, 106.38, 113.90, 134.73, 141.67. High resolution mass spectroscopy; calcd for $C_{11}H_{19}I$: 278.0533, found: 278.0540.

(Z)-1-Iodo-2-methyl-1-phenyl-1,4-pentadiene/(E)-5-iodo-4-phenyl-1,4-hexadiene. Obtained as a 60:40 mixture of two isomers. 76% combined yield (by GC). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.69 (s), 2.39 (s), 3.18 (d, J=5.9 Hz), 3.33 (dt, J=6.6, 1.5 Hz), 4.98-5.24 (m, 2H), 5.63-5.90 (m, 1H), 7.07-7.33 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 19.08, 31.82, 48.45, 49.04, 95.87, 99.24, 116.44, 116.53, 126.97, 127.37, 128.08, 128.19, 128.19, 128.77, 133.62, 133.92, 139.53, 140.84, 143.61, 144.62. High resolution mass spectroscopy; calcd for $C_{12}H_{13}I$: 284.0062, found: 284.0051.

(Z)-5-Iodo-1,4-undecadiene/2-n-hexyl-1-iodo-1,4-pentadiene. Obtained as a 81/19 mixture of two regioisomers, in 73% combined yield (by GC). *(Z)-5-Iodo-1,4-undecadiene.* ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.89 (t, J = 6.6 Hz, 3H), 1.25-1.35 (m, 6H), 1.52 (tt, J = 7.1 Hz, 2H), 1.99 (dt, J = 6.6, 6.6 Hz, 2H), 2.48 (td, ^3J = 7.3 Hz, ^4J = 0.8 Hz, 2H), 2.88 (dd, J = 6.4, 6.4 Hz, 2H), 5.00-5.13 (m, 2H), 5.51 (tt, ^3J = 6.9 Hz, ^4J = 1.2 Hz, 1H), 5.65-5.87 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.07, 22.59, 27.87, 29.33, 31.57, 40.70, 45.21, 111.18, 115.52, 131.73, 134.86. *2-n-Hexyl-5-iodo-1,4-pentadiene.* ^{1}H NMR ($CDCl_3$, Me_4Si): δ 2.18 (td, ^3J = 7.5 Hz, ^4J = 1 Hz, 2H), 2.97 (ddd, ^3J = 6.6, ^4J = 1.5, 1.5 Hz, 2H), 5.94 (t, ^4J = 1.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.07, 22.59, 27.62, 28.82, 31.57, 37.20, 41.81, 75.43, 116.57, 133.91, 149.52. High resolution mass spectroscopy; calcd for $C_{11}H_{19}I$: 278.0532, found: 278.0529.

Reaction of Cp_2Zr(1-phenyl-2-(trimethylsilyl)acetylene)(PMe_3) with ally phenyl ether; preparation of **5a**.
To a solution of Cp_2ZrCl_2 (1.461 g, 5.0 mmol) in THF (20 mL) was added dropwise *n*-BuLi (1.6 M in *n*-hexane, 6.25 mL, 10.0 mmol) at -78 °C and stirred for 1h. After addition of trimethylphosphine (1.0 M in THF, 5.5 mmol) at -78 °C, the reaction mixture was gradually warmed up to room temperature and stirred for 1h, and then 1-phenyl-2-(trimethylsilyl)acetylene (0.872 g, 5.0 mmol) was added. After stirring for 3h at room temperature, allyl phenyl ether (0.670 mg, 5.0 mmol) was added and the mixture was stirred at 35 °C overnight. The solvent was then removed *in vacuo* and the residue was washed with hexane and extracted with C_6D_6. ^{1}H- and ^{13}C NMR observation indicated the quantitative formation of **5a**. ^{1}H NMR (Me_4Si, C_6D_6): δ 0.02 (s, 9H), 2.76 (ddd, J=6.3, 1.6, 1.3 Hz, 2H), 4.87-4.96 (m, 2H), 5.69-5.84 (m, 1H), 6.03 (s, 10H), 6.59-6.64 (m, 2H), 6.85-6.91 (m, 1H), 7.04-7.26 (m, 7H). ^{13}C NMR (Me_4Si, C_6D_6): δ 3.94, 50.89, 112.00, 115.94, 118.47, 119.87, 126.25, 127.89, 129.00, 129.72, 136.96, 148.70, 158.29, 164.78, 185.21.

Allylation of alkynes via zirconacyclopentenes (method B)
Representative procedure; (E)-4-allyl-4-octene. Typical procedure for the allylation reactions of alkynes via zirconacyclopentenes is as follows. To a solution of Cp_2ZrCl_2 (365 mg, 1.25 mmol) in THF (5 mL) was

added ethylmagnesium bromide (0.93 M THF solution; 2.5 mmol) at -78 °C and was stirred for 1 h. After 4-octyne (110 mg, 1.0 mmol) was added, the reaction mixture was allowed to warm up to 0 °C. Zirconacyclopentene **11a** (R^1=R^2=C_3H_7) was yielded in ca. 90% based on 4-octyne after 3h. Allyl phenyl ether (168 mg, 1.25 mmol) was then added and the mixture was stirred for 3 h at 50 °C. After quenching with 3N HCl, the usual workup gave the title compound in 91% yield. Yields were determined by GC. The product was characterized by ^{1}H and ^{13}C NMR, GC-MS and high resolution mass spectroscopy, and compared with an authentic sample prepared by a known method.

(E)-5-Allyl-5-decene. The title compound was prepared in a similar manner to the case of (*E*)-4-allyl-4-octene using 5-decyne and allyl trimethylsilyl ether, instead of 4-octyne and allyl phenyl ether. Yield 97% (by GC). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.85-0.95 (m, 6H), 1.2-1.4 (m, 8H), 1.9-2.1 (m, 4H), 2.71 (dd, ^3J = 6.9 Hz, ^4J = 1 Hz, 2H), 4.95-5.10 (m, 2H), 5.14 (t, *J* = 7.3 Hz, 1H), 5.76 (ddt, *J* = 17, 10.2, 6.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.08, 14.08, 22.50, 22.84, 27.58, 29.87, 30.62, 32.34, 41.62, 115.36, 126.18, 137.63, 137.73.

5-Propyl-4,7-tridecadiene; (4E,7E)/(4E,7Z) = 34:66 mixture. The reaction was carried out in a similar manner to that described above, using 3-benzyloxyoct-1-ene instead of allyl phenyl ether. Yield 60% (GC). ^{1}H NMR ($CDCl_3$, Me_4Si, as a mixture of (4*E*,7*E*)/(4*E*,7*Z*)): δ 0.86-0.94 (m), 1.22-1.44 (m), 1.93-2.07 (m), 2.64 (d, 2H, *J* = 5.0 Hz, *E-isomer*), 2.71(d, 2H, *J* = 6.6 Hz, *Z-isomer*), 5.10-5.20 (m), 5.29-5.50(m). ^{13}C NMR ($CDCl_3$, Me_4Si, as a mixture of (4*E*,7*E*)/(4*E*,7*Z*)): δ 13.91, 14.11, 14.18, 21.44, 21.55, 22.57, 22.61, 23.22, 27.12, 29.27 29.42, 29.92, 31.41, 31.59, 32.17, 32.40, 32.52, 34.72, 40.36, 125.39, 125.55, 128.03, 128.68, 130.85, 131.75, 138.22, 138.56. High resolution mass spectroscopy; calcd for $C_{16}H_{30}$: 222.2348, found: 222.2353.

Allylation reactions of alkynes with allylic chlorides

Representative procedure; (2E,5E)-5-n-butyl-2,5-decadiene. To a solution of Cp_2ZrCl_2 (365 mg, 1.25 mmol) in THF (5 mL) was added ethylmagnesium bromide (0.9 M THF solution, 2.5 mmol) at -78 °C. After stirring for 1h at the same temperature, 5-decyne (138 mg, 1.0 mmol) was added and the reaction mixture was allowed to warm up to room temperature. The mixture was stirred for 1h, and then was added 3-chloro-1-butene (135 mg, 1.5 mmol) and stirred for an additional hour at 50 °C. The reaction mixture was quenched with 3N HCl, washed with $NaHCO_3$ and dried over $MgSO_4$. Filtration followed by concentration and bulb-to-bulb distillation gave the title compound (yield 48% by GC) accompanied by 5% of a stereoisomer. Ratio of stereoisomers 2*E*/2*Z* was 91:9. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.89 (t, *J* = 6.9 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H), 1.2-1.4 (m, 8H), 1.65-1.70 (m, 3H), 1.95-2.05 (m, 4H), 2.60-2.65 (m, 2H), 5.11 (t, *J* = 7.3 Hz, 1H), 5.35-5.45 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.05, 14.05, 17.92, 22.48, 22.82, 27.55, 29.79, 30.58, 32.36, 40.34, 125.51, 125.86, 129.91, 138.56. IR (cm^{-1}): 2959(s), 2928(s), 2874(s), 2861(s), 1458(m), 1379(m), 968(s). High resolution mass spectroscopy; calcd for $C_{14}H_{26}$: 194.2035, found: 194.2042.

(1E,4E)-2-Methyl-1-phenyl-1,4-hexadiene/(2Z,5E)-3-phenyl-2,5-heptadiene. The reaction was carried out in a similar manner to that described above using 1-phenyl-1-propyne (116 mg, 1.0 mmol) instead of 5-decyne. Usual workup gave a mixture of isomers in 78% combined yield by GC. *(1E,4E)-2-Methyl-1-phenyl-1,4-hexadiene.* ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.70 (d, *J* = 4.3 Hz, 3H), 1.83 (d, *J* = 1 Hz, 3H), 2.82 (d, *J* = 4.3 Hz, 2H), 5.45-5.60 (m, 2H), 6.27 (s, 1H), 7.1-7.3 (m, 5H). 13C : 1.57 (d, *J* =7.3 Hz, 3H), 1.60-1.65 (m, 3H), 2.95-3.05 (m, 2H), 5.45-5.60 (m, 3H), 7.1-7.3 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 17.86, 17.95, 43.59, 125.21, 125.60, 126.92, 127.96, 128.82, 128.88, 138.22, 138.62. *(2Z,5E)-3-phenyl-2,5-heptadiene.* ^{13}C NMR ($CDCl_3$, Me_4Si): δ 14.72, 17.90, 42.08, 121.36, 126.34, 126.34, 127.65, 128.88, 129.04, 140.63, 141.27. High resolution mass spectroscopy calcd for $C_{13}H_{16}$ 172.1252, found: 172.1246.

(1Z,4E)-1,2-Diphenyl-1,4-hexadiene. The title compound was obtained in 79% yield by GC. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 1.65-1.70 (m, 3H), 3.14 (d, *J* = 1.3 Hz, 2H), 5.45-5.55 (m, 2H), 6.41 (s, 1H), 6.9-7.3 (m, 10H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 17.95, 43.49, 126.14, 126.56, 126.84, 127.26, 127.80, 128.25,

128.41, 128.55, 129.02, 137.48, 141.56, 142.12. IR (cm^{-1}): 3023(m), 2966(m), 2932(m), 1599(m), 1493(m), 968(m), 756(m), 696(s). High resolution mass spectroscopy; calcd for $C_{18}H_{18}$: 234.1409, found: 234.1409.

Reaction of Cp_2Zr(1,2-diphenylacetylene)(PMe_3) with allyl acetate, (Z)-1,2-diphenyl-1,4-pentadiene. Cp_2Zr(1,2-diphenylacetylene)(PMe_3) was prepared in the same way as described above from Cp_2ZrCl_2/2eq *n*-BuLi (Negishi reagent), 1,2-diphenylacetylene and trimethylphosphine. To a solution of this complex (1.25 mmol) in THF (5 mL) was added allyl acetate (150 mg, 1.5 mmol) and the mixture was stirred for 5h at 50 °C. Hydrolysis and the usual workup gave the title compound in 75% yield (by GC).

*Reaction of **11a** with 2,5-dihydrofuran, (E)-2-Vinyl-3-propylhept-3-en-1-ol (**9a**).* Zirconacyclopentene **11a** was prepared in a similar manner to that described above. 2,5-Dihydrofuran (70 mg, 1.0 mmol) was added to a THF solution of **11a** (1.0 mmol) and the mixture was warmed up to 60 °C. After stirring for 3h, hydrolysis with 3N HCl and the usual workup gave the **9a** in 75% yield (by GC). ^1H NMR ($CDCl_3$, Me_4Si): δ 0.90 (t, J = 7.3 Hz, 6H), 1.30-1.46 (m, 4H), 1.48-1.60 (m, 1H), 1.95-2.07 (m, 4H), 2.80-2.90 (m, 1H), 3.49-3.70 (m, 2H), 5.08-5.15 (m, 2H), 5.22 (t, J = 7.3 Hz, 1H), 5.66-5.81 (m, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.87, 14.29, 22.23, 23.11, 29.90, 32.40, 53.01, 63.95, 116.31, 127.40, 138.25, 138.70. High resolution mass spectroscopy; calcd for $C_{12}H_{22}O$: 182.1671, found: 182.1671.

*Allylation of 1-(trimethylsilyl)-1-hexyne via zirconacyclopentadiene **12a***

To a solution of Cp_2ZrCl_2 (292 mg, 1.0 mmol) in THF was added *n*-butyllithium (1.6 M hexane solution, 2.0 mmol) at -78 °C and the mixture was stirred for 1 h at the same temperature. After adding 1-(trimethylsilyl)-1-hexyne (309 mg, 2.0 mmol), the reaction mixture was warmed up to room temperature and stirred for 1h. Zirconacyclopentadiene **12a** was formed quantitatively at this stage. Allyl trimethylsilyl ether (260 mg, 2.0 mmol) was then added to the solution of **12a** and the mixture was stirred for 1h at 50 °C. Quenching the reaction mixture with 3N HCl and the usual workup gave (*E*)-4-*n*-butyl-1-(trimethylsilyl)-1,4-pentadiene **9b**. 85% yield (by GC).

Reactions of zirconocene-alkyne complexes with acetals: formation of vinyl ethers

Representative procedure; 4-n-hexyl-5-trimethylsilyl-1,4-pentadienyl ethyl ether (52:48 mixture of (1E,4E)/(1Z,4E)). To a solution of Cp_2ZrCl_2 (1.0 mmol, 292 mg) in THF (5 mL) was added *n*-butyllithium (1.6M hexane solution, 2.0 mmol) at -78 °C and stirred for 1h. After adding trimethylphosphine (1.0M in THF, 1.1 mmol) the reaction mixture was warmed up to room temperature and was stirred for 1h. Addition of 1-(trimethylsilyl)-1-octyne (1.0 mmol, 182 mg) gave zirconocene(1-(trimethylsilyl)-1-octyne)(PMe_3) complex in 90-95% yield after 2h. To this reaction mixture, acrolein diethyl acetal (2.0 mmol, 260 mg) was added and the mixture was stirred at 35 °C for 1h. After hydrolysis and the usual workup, the title compound was obtained in 75% yield with >98% of regioselectivity for Me_3Si and C_6H_{13} groups. ^1H NMR ($CDCl_3$, Me_4Si, as a (1*E*,4*E*)/(1*Z*,4*E*) mixture 52:48): δ 0.09 (s), 0.85-0.91 (m), 1.21-1.30 (m), 2.08-2.14 (m), 2.66 (d, 2H, J = 7.6 Hz, 1*E-isomer*), 2.86 (d, 2H, J = 7.3 Hz, 1*Z-isomer*), 3.70-3.83 (m), 4.37 (q, 1H, J = 6.3 Hz, 1*Z-isomer*), 4.75 (dt, 1H, J = 12.5, 6 Hz, 1*E-isomer*), 5.22 (s), 5.99-6.02 (m, 1H, 1*Z-isomer*), 6.21 (d, 1H, J = 12.5 Hz, 1*E-isomer*). ^{13}C NMR ($CDCl_3$, Me_4Si, as a (1*E*,4*E*)/(1*Z*,4*E*) mixture 52:48): δ 0.41, 14.09, 14.81, 15.29, 22.64, 29.06, 29.11, 29.63, 31.84, 33.53, 36.06, 36.33, 37.18, 64.67, 67.51, 102.03, 104.80, 122.59, 123.14, 145.26, 147.10, 159.17, 159.46. High resolution mass spectroscopy; calcd for $C_{16}H_{32}OSi$: 268.2222, found: 268.2232.

4-phenyl-5-trimethylsilyl-1,4-pentadienyl ethyl ether (47:53 mixture of (1E,4E)/(1Z,4E)). Yield 71% (by GC). ^1H NMR ($CDCl_3$, Me_4Si): δ –0.01-0.01 (m), 1.37 (t, J = 7 Hz, 3H), 1.44 (t, J =7 Hz, 3H), 3.14-3.18 (m, 2H, 1*E-isomer*), 3.36-3.41 (m, 2H, 1*Z-isomer*), 3.86-3.95 (m), 4.56-4.64 (m, 1H, 1*Z-isomer*), 4.92-5.04 (m, 1H, 1*E-isomer*), 5.78-5.81 (m), 6.15-6.20 (m, 1H, 1*Z-isomer*), 6.38 (d, J = 13 Hz, 1H, 1*E-*

isomer), 7.3-7.7 (m). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 0.09, 0.13, 14.77, 15.26, 36.66, 40.50, 64.73, 67.53, 101.13, 103.83, 126.31, 126.74, 126.81, 126.88, 127.60, 127.74, 127.96, 128.01, 128.19, 131.97, 145.53, 147.53, 158.24, 158.96. High resolution mass spectroscopy; calcd for $C_{16}H_{24}OSi$: 260.1596, found 260.1586.

4-Methyl-5-trimethylsilyl-1,4-pentadienyl ethyl ether (59:41 mixture of (1E,4E)/(1Z,4E)). 72% combined yield. Regioselectivity for Me_3Si and CH_3 groups was 89%. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.09 (s), 1.20-1.30 (m), 1.76 (s, 1H, *E-isomer*), 1.78 (s, 1H, *Z-isomer*), 2.64 (d, 2H, J = 7.6 Hz, *E-isomer*), 2.84 (d, 2H, J = 7.3 Hz, *Z-isomer*), 3.69-3.82(m), 4.35-4.41 (m, 1H, *Z-isomer*), 4.77 (dt, 1H, J = 12.5, 7.6 Hz, *E-isomer*), 5.24 (s), 6.02 (d, 1H, J = 6.3 Hz, *Z-isomer*), 6.22 (d, 1H, J = 12.5 Hz). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 0.09, 14.79, 15.29, 21.47, 21.67, 36.77, 40.63, 64.65, 67.55, 101.78, 104.40, 122.37, 123.02, 145.41, 147.20, 154.36, 154.70. High resolution mass spectroscopy; calcd for $C_{11}H_{22}OSi$: 198.1440, found: 198.1435.

Reactions of zirconacyclopentenes with acetals

Formation of 4-propyl-1,4-octadienyl ethyl ether (51:49 mixture of (1E,4E)/(1Z,4E)). Zirconacyclopentane **11a** (R^1=R^2=C_3H_7) was prepared in a similar manner to that shown above. To this **11a** in THF was added acrolein diethyl acetal and the mixture was stirred for 48h at room temperature. Hydrolysis of the reaction mixture and the usual workup gave the title compound in 61% yield (by GC). ^1H NMR ($CDCl_3$, Me_4Si): δ 0.85-0.92 (m), 1.20-1.54 (m), 1.93-2.02 (m), 2.57 (d, 2H, J = 7.3 Hz, 1*E-isomer*), 2.74-2.78 (m, 2H, *Z-isomer*), 3.66-3.81 (m), 4.30-4.39 (m, 1H, 1*Z-isomer*), 4.72 (dt, 1H, J = 12.5 Hz, J = 5.5 Hz, 1*E-isomer*), 5.13-5.20 (m), 5.97 (dt, 1H, J = 6.3 Hz, J = 1.3 Hz, 1*Z-isomer*), 6.20 (d, 1H, J = 12.5 Hz, 1*E-isomer*). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 13.96, 14.20, 14.84, 15.35, 21.56, 23.31, 23.34, 30.03, 31.54, 32.13, 32.34, 35.38, 64.55, 67.51, 102.59, 105.57, 124.85, 125.35, 138.70, 139.00, 145.08, 146.77.

Reactions of zirconacyclopentenes with homoallylic bromides

Representative procedure; 2-(cyclopropylmethyl)-1-phenyl-1-heptene. Typical procedure for the reactions of zirconacyclopentenes **11** with 4-bromo-1-butene is as follows. To a solution of zirconocene dichloride (365 mg; 1.25 mmol) in THF (3 mL) was added THF solution of ethylmagnesium bromide (1.04 M, 2.5 mmol) at -78 °C and the mixture was stirred for 1 h. After 1-phenyl-1-heptyne (173 mg, 1.0 mmol) was added the reaction mixture was allowed to warm up to 0 °C and stirred for 2 h. And then 4-bromo-1-butene (204 mg, 1.5 mmol) was added and the reaction mixture was stirred at 40 °C for 12 h. Quenching of the sample with 3N HCl and the usual workup gave the title compound in 68% yield by GC. The product was characterized by ^1H and ^{13}C NMR, GC-MS and high resolution mass spectroscopy. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.08-0.16 (m, 2H), 0.48-0.56 (m, 2H), 0.80-0.95 (m, 1H), 0.87 (t, J = 6.9 Hz, 3H), 1.20-1.36 (m, 4H), 1.42-1.54 (m, 2H), 2.06 (dd, J = 6.8, 1.1 Hz, 2H), 2.26 (dd, J = 9.6, 7.0 Hz, 2H), 6.39 (s, 1H), 7.14-7.33 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 5.53, 10.45, 14.84, 23.28, 28.89, 31.89, 32.80, 42.81, 125.34, 126.55, 128.78, 129.42, 139.52, 144.52. High resolution mass spectroscopy; calcd for $C_{17}H_{24}$: 228.1881, found: 228.1878.

(E)-4-(Cyclopropylmethyl)-4-octene. Yield 68% by GC. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.01-0.08 (m, 2H), 0.40-0.48 (m, 2H), 0.68-0.83 (m, 1H), 0.84-0.96 (m, 6H), 1.25-1.54 (m, 4H), 1.87 (d, J = 6.9 Hz, 2H), 1.97-2.10 (m, 4H), 5.23 (t, 1H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 4.64, 9.90, 13.91, 14.21, 21.65, 23.32, 29.83, 32.56, 41.83, 124.81, 139.37. High resolution mass spectroscopy; calcd for $C_{12}H_{22}$: 166.1720, found: 166.1722.

(Z)-4-(Cyclopropylmethyl)-5-iodo-4-octene. Yield 50% by GC. ^1H NMR ($CDCl_3$, Me_4Si): δ 0.16-0.23 (m, 2H), 0.41-0.48 (m, 2H), 0.76-0.95 (m, 7H), 1.32-1.50 (m, 2H), 1.52-1.64 (m, 2H), 2.21 (d, J = 6.6

Hz, 2H), 2.24-2.30 (m, 2H), 2.51 (t, J = 7.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 4.28, 9.81, 12.92, 14.12, 22.03, 23.07, 33.84, 43.04, 46.54, 105.16, 144.18. High resolution mass spectroscopy; calcd for $C_{12}H_{21}I$: 292.0690, found: 292.0688.

(E)-4-(2-methylcyclopropyl)methyl-4-octene. The title compound was obtained as a 74:26 mixture of cis:trans isomers of the cyclopropane ring. Yield 64% by GC. ^{1}H NMR ($CDCl_3$, Me_4Si): δ -0.28 (q, J = 4.3 Hz, 1H, *cis*), 0.14-0.22 (m, 2H, *trans*), 0.37-0.48 (m, 2H, *trans*), 0.59-0.69 (m, 1H, *cis*), 0.70-0.83 (m, 2H, *cis*), 0.85-0.93 (m, 6H, *both isomers*), 1.01 (d, J = 5.7 Hz, 3H, *cis*), 1.02 (d, J = 8.9 Hz, 3H, *trans*), 1.29-1.55 (m, 4H, *both isomers*), 1.83-2.10 (m, 6H, *both isomers*), 5.20 (t, J = 6.9 Hz, 1H, *trans*), 5.27 (t, J = 6.9 Hz, 1H, *cis*). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 9.56, 12.09, 12.94, 13.01, 13.26, 13.91, 14.21, 14.36, 18.74, 18.96, 21.62, 21.71, 23.32, 29.79, 29.85, 32.54, 32.72, 35.35, 41.40, 124.42, 124.54, 139.42, 139.57. High resolution mass spectroscopy; calcd for $C_{13}H_{24}$: 180.1876, found: 180.1878.

(E)-4-(2-ethylcyclopropyl)methyl-4-octene. The title compound was obtained as a 26:74 mixture of cis:trans isomers of the cyclopropane ring. Yield 59% by GC. ^{1}H NMR ($CDCl_3$, Me_4Si): δ -0.26 (q, J = 4.0 Hz, 1H, *cis*), 0.15-0.22 (m, 2H, *trans*), 0.34-0.52 (m, 2H, *trans*), 0.61-0.81 (m, 3H, *cis*), 0.85-1.03 (m, 9H, *both isomers*), 1.12-1.45 (m, 6H, *both isomers*), 1.77-2.09 (m, 6H, *both isomers*), 5.21 (t, J = 6.9 Hz, 1H, *trans*), 5.23 (t, J = 7.6 Hz, 1H, *cis*). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 10.89, 11.64, 13.71, 13.91, 14.21, 14.47, 14.61, 17.54, 17.83, 20.77, 21.60, 21.67, 21.94, 23.32, 27.28, 29.81, 29.87, 32.47, 32.67, 35.54, 41.44, 124.47, 124.63, 139.48, 139.58. High resolution mass spectroscopy; calcd for $C_{14}H_{26}$: 194.2035, found: 194.2043.

(E)-3-(Cyclopropylmethyl)-3-hexene. Yield 70% by GC. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.01-0.07 (m, 2H), 0.41-0.46 (m, 2H), 0.68-0.85 (m, 1H), 0.956 (t, J = 7.6 Hz, 3H), 0.964 (t, J = 7.6 Hz, 3H), 1.88 (d, J = 6.6 Hz, 2H), 1.95-2.12 (m, 4H), 5.19 (t, J = 7.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 4.64, 9.85, 13.35, 14.81, 20.81, 23.41, 41.46, 125.82, 140.55.

(E)-3-(Cyclopropylmethyl)-4-deutero-3-hexene. Yield 70% by GC with 95% D incorporation. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.01-0.07 (m, 2H), 0.41-0.48 (m, 2H), 0.70-0.90 (m, 1H), 0.956 (t, J = 7.6 Hz, 3H), 0.962 (t, J = 7.6 Hz, 3H), 1.88 (d, J = 7.0 Hz, 2H), 1.98-2.12 (m, 4H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 4.62, 9.81, 13.33, 14.79, 20.68, 23.38, 41.37, 125.44 (t, $|^1J_{CD}|$ = 23 Hz), 140.45.

(Z)-3-Cyclopropyl-1,2-diphenyl-1-propene. Yield by 80% by GC (78% isol.). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.07-0.13 (m, 2H), 0.40-0.50 (m, 2H), 0.76-0.93 (m, 1H), 2.35 (dd, J = 7.0, 1.3 Hz, 2H), 6.52 (s, 1H), 6.89-7.31 (m, 10H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 4.71, 9.70, 45.43, 125.84, 126.04, 126.74, 127.78, 128.43, 128.48, 129.02, 137.54, 141.90, 143.27. High resolution mass spectroscopy; calcd for $C_{18}H_{18}$: 234.1409, found: 234.1415.

(Z)-3-Cyclopropyl-1-deutero-1,2-diphenyl-1-propene. Yield 71% by GC with 94% D incorporation. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.07-0.12 (m, 2H), 0.42-0.49 (m, 2H), 0.76-0.90 (m, 1H), 2.35 (d, J = 6.9 Hz, 2H), 6.90-7.31 (m, 10H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 4.71, 9.67, 45.36, 125.47 (t, $|^1J_{CD}|$ = 23 Hz), 126.04, 126.73, 127.77, 128.42, 128.45, 128.97, 137.43, 141.88, 143.16. High resolution mass spectroscopy; calcd for $C_{18}H_{17}D$: 235.1471, found: 235.1481.

(E)-3-Cyclopropyl-2-methyl-1-phenyl-propene. The title compound was obtained in 72% yield by GC with 13% yield of regioisomer. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.11-0.17 (m, 2H), 0.48-0.55 (m, 2H), 0.80-0.92 (m, 1H), 1.91 (d, J = 1.3 Hz, 3H), 2.06 (dd, J = 6.9, 0.6 Hz, 2H), 6.36 (s, 1H), 7.14-7.35 (m, 5H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 4.65, 9.70, 18.20, 45.34, 124.47, 125.77, 128.00, 128.89, 138.70, 139.30. High resolution mass spectroscopy; calcd for $C_{13}H_{16}$: 172.1252, found: 172.1259.

1-Cyclopropyl-2-nonene/1-cyclopropyl-2-methylene-octane, (77:23 mixture). Combined yield 59% (by GC). ^{1}H NMR ($CDCl_3$, Me_4Si): δ 0.01-0.11 (m), 0.37-0.51 (m, 2H), 0.64-0.82 (m), 0.88 (t, J = 6.3 Hz), 1.27-

1.55 (m), 1.90 (d, J = 6.6 Hz), 1.97-2.08 (m), 4.71 (d, J = 1 Hz), 4.84 (s), 5.38-5.50 (m). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 4.04, 4.64, 9.52, 10.66, 14.11, 22.66, 27.82, 28.88, 29.15, 29.60, 31.77, 32.65, 36.42, 37.27, 41.02, 108.48, 129.07, 130.74, 150.28. High resolution mass spectroscopy; calcd for $C_{12}H_{22}$: 166.1722, found: 166.1717.

Reaction of a zirconacyclopentene with 4-bromo-1-butene, formation of the intermediate ***21***.
To a solution of zirconocene dichloride (365 mg; 1.25 mmol) in THF (3 mL) was added THF solution of ethylmagnesium bromide (1.04 M, 2.5 mmol) at -78 °C and the mixture was stirred for 1h. After 1-phenyl-1-heptyne (173 mg, 1.0 mmol) was added the reaction mixture was allowed to warm up to 0 °C and stirred for 2 h. Then 4-bromo-1-butene (204 mg, 1.5 mmol) was added and the reaction mixture was stirred at 40 °C for 12 hours. Addition of 15 mL of hexane to the reaction mixture lead to the precipitation of Mg salts. The clear solution was transferred to another Schlenk tube and pumped off. The remaining oil was dissolved in benzene and treated with MeLi (1.05 M in ether, 0.4 mmol) at 0 °C. The reaction mixture was allowed to warm up to the room temperature and NMR analysis showed the formation of $Cp_2Zr(Me)$(2-(cyclopropylmethyl)-1-phenyl-1-heptenyl) **21** in 93% yield by ^1H NMR. ^1H NMR (THF-d_8, Me_4Si): δ -1.19 (s, 3H), 0.17-0.20 (m, 2H), 0.50-0.55 (m, 2H), 0.78 (t, J = 7 Hz, 3H), 0.7-0.9 (m, 1H), 1.0-1.5 (m, 6H), 1.6-2.0 (m, 4H), 5.99 (s, 10H), 7.0-7.2 (m, 5H). ^{13}C NMR (THF-d_8, Me_4Si) δ 5.34, 10.53, 14.12, 22.96, 25.97, 29.22, 32.69, 34.03, 43.02, 109.27, 125.41, 128.39, 130.62, 143.47, 143.70.

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