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A Cp_2TiCl_2-Me_3Al (1 : 4) Reagent System: An Efficient Reagent for Generation of Allylic Titanocene Derivatives from Vinyl Halides, Vinyl Ethers and Carboxylic Esters

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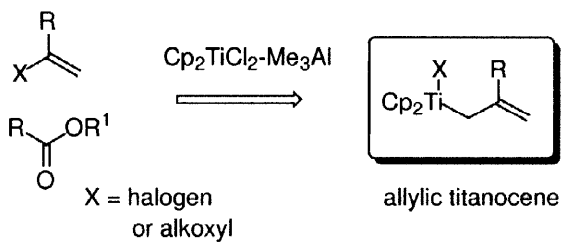
Abstract: The reagent prepared in advance by stirring a mixture of a Cp_2TiCl_2–Me_3Al (a 1 : 4 ratio) reagent system in toluene for 3 days is found to be effective in generating allylic titanocene on treatment with vinyl halides, vinyl ethers and carboxylic esters in THF. The process for the generation of an allylic titanocene species from these starting materials was suggested to proceed through a formation of titanacyclobutane and the subsequent elimination of the halogen or alkoxyl group. The generated allylic titanocene intermediate was proved to be an allylic Ti(IV) species and showed the typical reactivity to carbonyl compounds.

Introduction

Allylic metal reagent is one of the important reagents in diastereo- and/or enantioselective syntheses of organic molecules and has been widely applied to the syntheses of natural products.[1] Hence, the search for a new procedure for the generation of allylic organometals is a significant project. Recent development for the generation[2] of allyllic titanium (Ti) and/or zirconium (Zr) from allylic ethers through the oxidative addition of low-valent dialkoxytitanium–olefin[2d] and/or zirconocene–1-butene[2e,3] complexes opened the new synthetic possibility.[2d,e,f] However, it is still required that the new preparative method of the allylic titanium and/or zirconium species from *non-allylic starting materials* since a new procedure to prepare an allylic metal species from *non-allylic starting material* leads to a new possibility in the organic synthesis. In a literal sense, the hydrozirconation[4] reaction of allene derivatives is a notable example for the preparation of an allylic zirconocene species from the non-allylic starting material.[5] In our preliminary communication, we reported the formation of allylic titanocene complex from vinyl halides by treating with a pregenerated Cp_2TiCl_2–Me_3Al (1 : 4) reagent in the presence of a Lewis base at 70 ℃.[6] Herein we describe the full acount for the generation of an allylic titanocene complex from non-allylic starting materials; vinyl halides, vinyl ethers and carboxylic ester derivatives.



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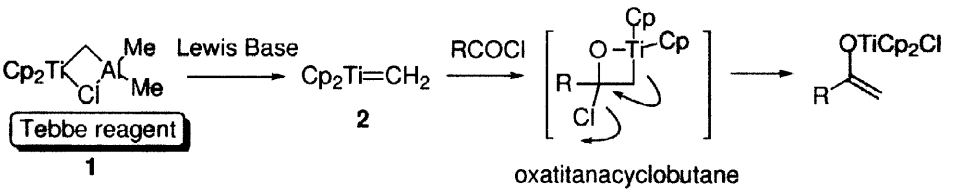
Tebbe reagent **1** which can be generated from Cp_2TiCl_2–Me_3Al (1 : 2) is a efficient reagent for a mild methylenation of carbonyls[7] and for an olefin metathesis.[8] The Tebbe reagent **1** is known to yield *in situ* titanocene methylene complex **2** in the presense of Lewis base.[7b] It has been reported that the titanocene methylene complex **2** reacts with acid chloride to give a titanocene enolate through a β-elimination reaction in an oxatitanacyclobutane intermediate.[9]



As a working hypothesis, the treatment of Tebbe reagent **1** with vinyl derivatives **3** (X = halogen or alkoxyl) in the presence of Lewis base would be expected to give a transient titanacyclobutane **4** which is an intermediate for the olefin metathesis reaction.[8] When the β-elimination process of the leaving group in titanacyclobutane **4** occurs irreversively in competition with the reversible olefin metathesis process, allylic titanocene species **5** would be formed (Figure 1). It has also been reported the unique reactions of **2** toward the alkyl and/or allylic halide to give a methylene homologated compounds through a radical ion mechanism.[10] Thus, it is very interesting to test about the reactivity of vinyl halide derivatives with the Tebbe reagent **1**.

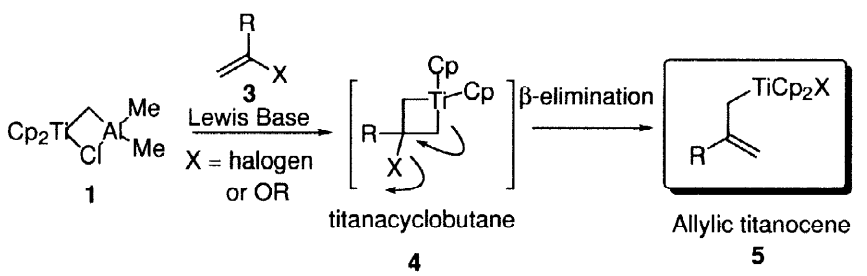
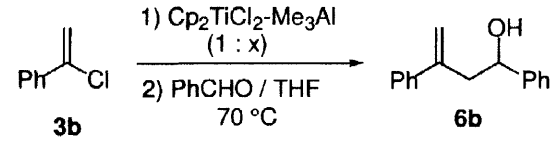


Figure 1. A Hypothetical pathway for the formation of allylic titanocene 5 from vinyl compounds.

Result and Discussion

The reaction of α-chlorostyrene **3b** in the presence of THF as a Lewis base with the Tebbe reagent **1** (1 eqiv – 3 equiv), which is prepared in toluene according to the reported procedure,[7a] and the subsequent addition of benzaldehyde to the reaction mixture did not yield a detectable amount of the allylation product (Scheme 1). To our delight, the addition of an excess amount of Me_3Al to a 1 : 1 mixture of **3b** in THF and Tebbe reagent **1** in toluene followed by heating to 70 ℃ and the subsequent addition of benzaldehyde in THF gave an allylation product **6b**. The yield of **6b** was increased up to 50 % by adding two more equiv of Me_3Al to Tebbe reagent **1**, a totally 1 : 4 molar ratio of Cp_2TiCl_2 and Me_3Al with respect to **3b** (Scheme 1). Further addition of Me_3Al did not improve the yield of the product; and besides the addition of BF_3•OEt_2 instead of Me_3Al to the Tebbe reagent **1** failed to yield **6b**. The use of THF as a Lewis basic co-solvent and the heating of the reaction mixture to 70 ℃ are requisite to bring about the present reaction in reasonable yields. It is also required to stir a 1 : 4 mixture of Cp_2TiCl_2–Me_3Al in toluene for 3 days at ambient temperature prior to the addition of a solution of **3b** in THF.

Scheme 1



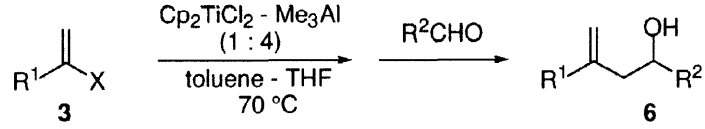
3b **6b**

Cp_2TiCl_2-Me_3Al (1 : x)	yield (%)
1 : 2[a]	-
1 : 3	25
1 : 4	50

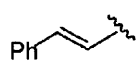
[a] Tebbe reagent

The generality of the present procedure was confirmed by treating α-halovinyl or α-alkoxyvinyl derivatives **3** (X = halogen or alkoxyl) with aldehydes (Table 1). Cyclohexanone also yielded allylation product **7** in good yield under the same reaction conditions (Scheme 2). Although the yields of **6** from vinyl ether derivatives (**3h**, **3i**) were lower compared to vinyl halides, it is obvious that the vinyl ether derivatives can be used as a precursor for the present reaction (entries 13 and 14, Table 1). One drawback to the present procedure is its inapplicability to the β-halovinyl or β-alkoxyvinyl derivatives, regioisomer of **3**, probably due to the regiochemical problem in the formation of the supposed intermediate **4** and/or the competitive olefin metathesis reaction.[11]

Table 1. Generation of Allyltitanocene Derivatives and Its Reactions with Aldehydes.

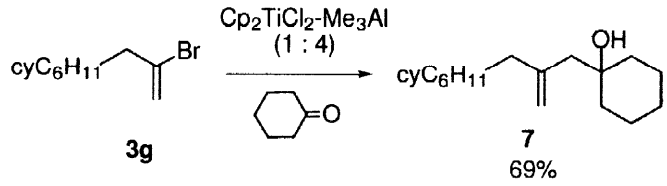


3 **6**

entry	R^1	X	3	R^2	6	yield (%)[a]
1	H	Br	**3a**	Ph	**6a**	47
2	Ph	Cl	**3b**	Ph	**6b**	50
3				$PhCH_2CH_2$	**6c**	74
4	p-MeOPhCH_2	Cl	**3c**	$PhCH_2CH_2$	**6d**	93
5	CH_3	Cl	**3d**	Ph	**6e**	58
6				$PhCH_2CH_2$	**6f**	58
7		Br	**3e**	Ph	**6e**	60
8				$PhCH_2CH_2$	**6f**	80
9	$cyC_6H_{11}CH_2$	Cl	**3f**	Ph	**6g**	60
10		Br	**3g**	$PhCH_2CH_2$	**6h**	87
11				cyC_6H_{11}	**6i**	60
12					**6j**	66
13	Ph	OCH_3	**3h**	$PhCH_2CH_2$	**6c**	41
14		OBn	**3i**		**6c**	39

[a] Isolated yield.

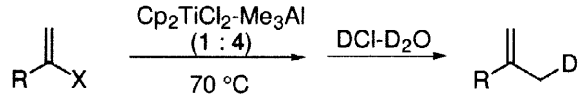
Scheme 2



3g 7 69%

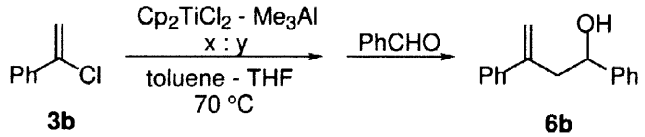
The results described in Table 1 suggest the presence of allylic titanocene species **5** (X = halogen or alkoxyl) as a reactive intermediate in the reaction medium. The presence of **5** was supported by the fact that the 20 % DCl/D_2O–treatment of the reaction mixture of **3c** and the Cp_2TiCl_2–Me_3Al (1 : 4) reagent gave a monodeutrated compound **8** at more than 95 % deuterium content (89 % chemical yield) (Scheme 3).[12] Furthermore, a stoichiometric requirement of Cp_2TiCl_2 with respect to **3** suggests the presence of **5** (Scheme 4). Thus, the treatment of **3b** with a reagent, which is generated from 0.5 equiv of Cp_2TiCl_2 and 2 equiv of Me_3Al, and the subsequent reaction with benzaldehyde gave **6b** in 20 % yield. Semi-catalytic use (0.1 equiv) of Cp_2TiCl_2 under the presence of 4 equiv of Me_3Al otherwise identical to the aforementioned conditions yielded less than 5 % of **6b**. The kinetic study for the reaction of Cp_2TiCl_2 with greater than 2 equiv of Me_3Al suggested the presence of a highly reactive complex which is derived from the Tebbe reagent and excess Me_3Al in a prolonged reaction.[13] Although the structure of the active complex is unclear, the same complex might be involved in the present allylic titanocene formation.

Scheme 3



3c R=4-MeOPhCH$_2$, X=Cl **8** 89 % yield >95 % D

Scheme 4



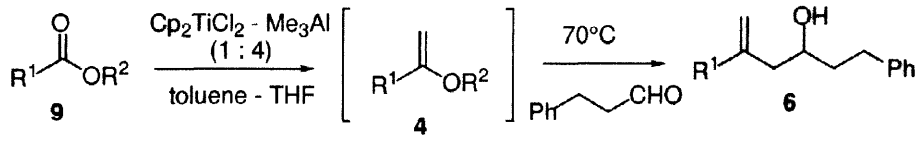
3b **6b**

Cp_2TiCl_2 - Me_3Al x : y	yield %)
1.5 : 6	50
0.5 : 2	20
0.1 : 2	< 5

The reactions of vinyl ether derivatives (**3h** and **3i**) described in Table 1 (entries 12, 13) suggest to us the possibility of the direct conversion of carboxylic ester derivatives to **5** (X = alkoxyl) since the similarity of the Cp_2TiCl_2–Me_3Al (1 : 4) reagent in the present reaction to the Tebbe reagent **1** which efficiently converts carboxylic esters to vinyl ethers.[14] In other words, the reactions of carboxylic ester derivatives **9** with two-fold excess at least or more of the preformed Cp_2TiCl_2–Me_3Al (1 : 4) reagent would directly generate **5** (X = alkoxyl) via vinyl ethers **3** (X = alkoxyl) as a primary intermediate and **4** (X = alkoxyl) as a secondary intermediate. Thus, the treatment of 1 equiv of **9** in the presence of THF with the preformed 3 equiv solution of Cp_2TiCl_2–Me_3Al (1 : 4) in toluene as described and the subsequent reactions with aldehydes gave **6** in fair yields (Table 2). It should be mentioned that the addition of the excess aldehyde (2 equiv with respect to Cp_2TiCl_2) increased the yield of **6**, significantly (entries 6, 7 and 10, Table 2). The allylic titanocene species **5** (X = alkoxyl) from carboxylic ester **9d** also gave an allylically monodeuterated compound **10** in high yield (83 % chemical yield and >95 %D content) (Scheme 5).

These observations indicate that the formation of **5** (X = alkoxyl) from esters **9** is quite high but the reaction with aldehyde is hampered by the presence of excess reagent.

Table 2. Generation of Allylic Titanocene Derivatives from Carboxylic Esters

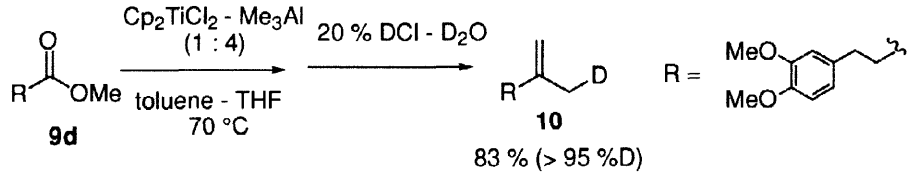


9 **4** **6**

entry	R^1	R^2	**9**	yield of **6** (%)[a]	
1	Ph	Ph		15	**6c**
2		CH_2CF_3		34	**6c**
3		Me		41	**6c**
4	Me	Bn		36	**6f**
5		Et		48	**6f**
6		6-heptenyl	**9a**	49 (70)	**6f**
7	$CH_3(CH_2)_{14}$	Me	**9b**	47 (78)	**6k**
8	$CH_3(CH_2)_3$			42	**6l**
9	$MeO(CH_2)_2$			36	**6m**
10	2-MeOPh$(CH_2)_2$		**9c**	40 (55)	**6n**

a) Isolated yield. Yields in parenthesis are the results by the use of 2 equivalents of aldehyde with respect to Cp_2TiCl_2.

Scheme 5

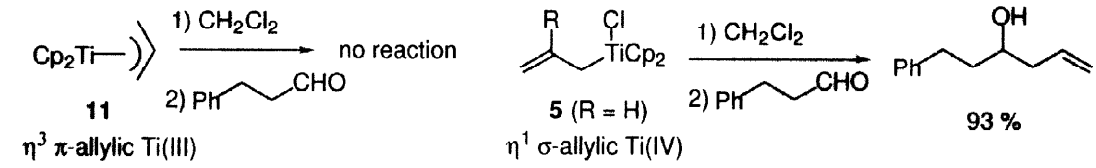


9d **10**

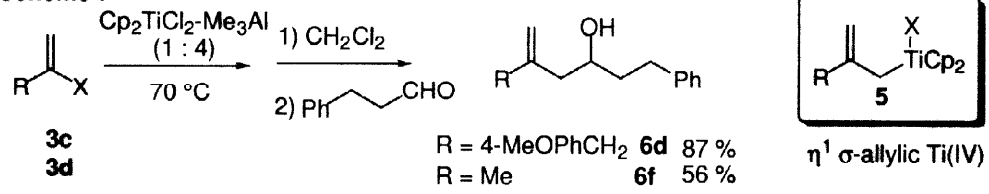
83 % (> 95 %D)

As an intrinsic character of titanium metal, two stable valence states of allylic titanocene derivatives [π-allylic Ti(III) complex **11** and σ-allylic Ti(IV) complex **5**] have been known.[15] Both of the allylic species react with carbonyls and/or D_2O to give homoallylic alcohol and/or an allylically monodeutrated compound, respectively. It has also been known that π-allylic Ti(III) complex **11** does not survive under the treatment of CH_2Cl_2, while the η^1 σ-allylic Ti(IV) complex **5** (R = H) with CH_2Cl_2 remained unchanged (Scheme 6).[15,16] The reaction of the allylic titanocene intermediate generated through our present procedure showed the unchanged reactivity to the aldehyde after the treatment of CH_2Cl_2 (Scheme 7). Thus, we conclude that the valence state of the titanium metal in the present allylic titanocene species **5** is not η^3 π-allylic Ti(III) **11** but the η^1 σ-allylic Ti(IV) **5**.

Scheme 6



Scheme 7



By taking into consideration the observed results and the similarity of the reactivity of the present reagent system to the Tebbe reagent **1**, the formation of allylic titanocene derivatives **5** in the present study from non-allylic starting materials, vinyl halides, vinyl ethers and simple carboxylic ester derivatives, can be explained by the formation of titanacyclobutane **4** (X = halogen or alkoxyl) as an intermediate and the subsequent β-elimination of the halogen or alkoxyl group as we have postulated in Figure 1. Although the exact role of the excess Me_3Al requisite for the present reaction is unclear yet, it might contribute to the elimination of the halogen or alkoxyl function of **4**, or to the enhancement of the reactivity of Tebbe reagent **1**.[13] It is also worth mentioning that the complex and multi-mechanistic nature of the Cp_2TiCl_2–Me_3Al reagent system in carbometalation of an acetylenic compound has been reported by Negishi et al.[17]

Conclusion

We developed a new and efficient procedure to generate an allylic titanocene species from non-allylic starting materials – vinyl halides, vinyl ethers and/or carboxylic esters – through a reaction of the preformed Cp_2TiCl_2 – Me_3Al (1 : 4) reagent using a toluene-THF solvent system. It was confirmed that a stoichiometric amount of Cp_2TiCl_2 with respect to the starting material was required and the valence state of the generated allylic titanocene species was a Ti(IV) species. The present procedure has opened up new possibility for the generation of Ti(IV) allylic derivatives. Especially, the direct conversion of carboxylic ester compounds to allylic titanocene derivatives would add a new and/or alternative strategy in organic synthesis.

Experimental

All nonaqueous reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Dichloromethane (CH_2Cl_2) and toluene were distilled from calcium hydride. NMR spectra were measured at 300 or 400 MHz for ^1H and 75.5 or 100.6 MHz for ^{13}C. Materials were obtained from commercial suppliers and used without further purification unless otherwise noted. Fuji silysia silica gel BW-80S was used for column chromatography and pre-packed column CPS-223L-1 (Kusano Kagaku Kikai Works Co., Japan) were used for medium pressure liquid chromatography (MPLC). Compounds **3a**, **3f** were prepared by the reported procedure.[18]

2-Chloro-3-cyclohexylprop-1-ene (3f)

To a 1M solution of $cyC_6H_{11}ZnI$[18] in THF (40mL, 40 mmol) was added CuCN (3.63g, 40.0 mmol) and LiCl (3.4g, 80.0 mmol) at -40 ℃. After the mixture was cooled at -78 ℃, 2,3-dichloro-1-propene (4.7 mL, 5.64 g, 50.0 mmol) was added dropwise and the mixture was stirred at ambient temperature for 1 h. Under ice-cooling sat. aq. NH_4Cl was added and the mixture was extracted with ether. The combined

organic layer was washed with brine, dried over $MgSO_4$ and filtered. The filtrate was concentrated *in vacuo* to give a crude product which was distilled under vacuum to give pure **3f** (5.4 g, 84 %) as an oily material. **3f**: Bp. 76.0 - 77.0 °C / 15mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 - 0.96 (m, 2 H), 1.07 – 1.35 (m, 3 H), 1.57 - 1.79 (m, 6 H), 2.19 (dd, *J* = 1.0, 6.9 Hz, 2 H), 5.07 (dd, *J* = 1.0, 1.9 Hz, 1 H), 5.15 (d, *J* = 1.9 Hz, 1 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.1, 26.4, 32.6, 35.0, 47.0, 112.9, 141.6; EIMS *m/z* 160.1 ($C_9H_{15}{}^{37}Cl$, M^+), 158.1 ($C_9H_{15}{}^{35}Cl$, M^+), 123.2 ($C_9H_{15}{}^+$); HRMS. Calcd for $C_9H_{15}Cl$: 158.086228. Found: 158.085205.

1-(2-chloroprop-2-enyl)-4-methoxybenzene (3c)

To a solution of 4-methoxyphenyl magnesium bromide generated from 4-bromoanisole (2.85 g, 15.0 mmol) and Mg (383.0 mg, 15.8 mmol) in THF (5 mL) was added $CuMe_2{\bullet}SMe_2$ (617 mg, 3.0 mmol) at 0 °C and the mixture was stirred at the same temperature for 1 h. After addition of 2,3-dichloro-1-propene (1.7 mL, 2.04 g, 18.0 mmol) to the mixture at 0 °C and the stirring for 1 h at the same temperature, the reaction was quenched by adding sat. aq. NH_4Cl and extracted with ether. The combined organic layer was washed with brine, dried over $MgSO_4$ and filtered. The filtrate was concentrated to dryness to give a crude oil which was purified by silica gel column chromatography (hexane – ethyl acetate = 10 : 1) to give **3b** (760 mg, 30 %) as a colorless oil. **3c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.57 (brs, 2 H), 3.80 (s, 3 H), 5.12 (dd, *J* = 1.2, 2.4 Hz, 1 H), 5.23 (s, 1 H), 6.87 (d, *J* = 8.7 Hz, 2 H), 7.16 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 44.5, 55.0, 113.1, 113.8, 128.8, 129.9, 142.0, 158.5; EIMS *m/z* 184.1 ($C_{10}H_{11}O^{37}Cl$, M^+), 182.1 ($C_{10}H_{11}O^{35}Cl$, M^+), 147.1 ($C_{10}H_{11}O^+$), 121.1 ($C_8H_9O^+$); Anal. Calcd for $C_{10}H_{11}OCl$: C, 65.76; H, 6.07. Found: C, 65.53; H, 6.25.

1-Phenylbut-3-en-1-ol (6a)

To a solution of Cp_2TiCl_2 (374 mg, 1.5.0 mmol) in toluene (3 mL) was added Me_3Al (15 % in toluene, 2.9 mL, 6.0 mmol) at ambient temperature and the solution was stirred for 3 days at the same temperature. A 1 M solution of 1-bromoethene **3a** in THF (1 mL, 1.0 mmol) in THF was added to the reagent mixture at 0 °C and the resulting mixture was stirred for 0.5 h at ambient temperature and for 10 h at 70 °C. After the reaction mixture was cooled to 0 °C, a solution of benzaldehyde (160 mg, 1.5 mmol) in THF (5 mL) was added and the mixture was stirred at ambient temperature for 3 h. After an addition of 1M solution of NaOH under ice-cooling, the mixture was filtered through a Celite pad, and the filtrate was extracted with ether. The combined organic layer was washed with brine and dried over $MgSO_4$. The filtered ether solution was concentrated to dryness *in vacuo* to give a crude oil. Purification by column chromatography (silica gel, hexane – ethyl acetate = 5 : 1 – 3 : 1) gave 1-phenylbut-3-en-1-ol **6a** (70.0 mg, 0.47 mmol, 50 %) as a colorless oil which was identical to the authentic sample.

1,3-Diphenylbut-3-en-1-ol (6b)

To a solution of Cp_2TiCl_2 (374 mg, 1.5.0 mmol) in toluene (3 mL) was added Me_3Al (15 % in toluene, 2.9 mL, 6.0 mmol) at ambient temperature and the solution was stirred for 3 days at the same temperature. A solution of 1-chloro-1-phenylethene **3b** (139 mg, 1.0 mmol) in THF was added to the reagent mixture at 0 °C and the resulting mixture was stirred for 0.5 h at ambient temperature and for 10 h at 70 °C. After the reaction mixture was cooled to 0 °C, a solution of benzaldehyde (160 mg, 1.5 mmol) in THF (5 mL) was added and the mixture was stirred at ambient temperature for 3 h. After an addition of 1M solution of NaOH under ice-cooling, the mixture was filtered through a Celite pad, and the filtrate was extracted with ether. The combined organic layer was washed with brine and dried over $MgSO_4$. The filtered ether solution was concentrated to dryness *in vacuo* to give a crude oil. Purification by column chromatography (silica gel, hexane – ethyl acetate = 5 : 1 – 3 : 1) gave 1,3-diphenyl-3-buten-1-ol **6b** (112.1 mg, 0.5 mmol, 50 %) as a colorless oil. The structure of **6a** was confirmed by comparison with the authentic sample.[18]

1,5-Diphenylhex-5-en-3-ol (6c).

According to the procedure described for **6b**, 1-chloro-1-phenylethene **3b** (139 mg, 1.0 mmol) and 3-phenylpropanal (200 mg, 1.5 mmol) gave **6c** (187 mg, 0.74 mmol, 74 %). **6c**: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67 (d, J = 3.2 Hz, 1 H), 1.78 – 1.87 (m, 2 H), 2.53 - 2.72 (m, 2 H), 2.75 - 2.88 (m, 2 H), 3.66 – 3.76 (brm, 1 H), 5.17 (d, J = 1.1 Hz, 1 H), 5.42 (d, J = 1.5 Hz, 1 H), 7.15 – 7.41 (m, 10 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 31.9, 38.5, 43.7, 68.9, 115.2, 125.7, 126.1, 127.6, 128.2, 128.3, 140.4, 142.0, 145.2; IR (neat) ν 3422 (br) cm^{-1}; EIMS *m/z* 252.1 (M^+), 91.1 ($C_7H_7^+$); HRMS. Calcd for $C_{18}H_{20}O$: 252.151415. Found: 252.153149.

1-Phenyl-5-(4-methoxybenzyl)hex-5-en-3-ol (6d).

According to the procedure described for **6b**, 1-(2-chloroprop-2-enyl)-4-methoxybenzene **3c** (182 mg, 1.0 mmol) and 3-phenylpropanal (200 mg, 1.5 mmol) gave **6d** (200 mg, 93 %). **6d**: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67 (d, J = 3.0 Hz, 1 H), 1.71 - 1.80 (m, 2 H), 2.08 (dd, J = 9.3, 14.0 Hz 1 H), 2.21 (dd, J = 3.9, 14.0 Hz, 1 H), 2.66 (dt, J = 8.2, 14.0 Hz, 1 H), 2.81 (dt, J = 6.6, 14.0 Hz, 1 H), 3.28 (d, J = 4.4 Hz, 2 H), 3.68 -3.78 (brm, 1 H), 3.80 (s, 3 H), 4.90 (d, J = 1.5 Hz, 1 H), 4.92 (brs, 1 H), 6.83 (d, J = 8.7 Hz, 2 H), 7.06 (d, J = 8.7 Hz, 2 H), 7.18 - 7.22(m, 3 H), 7.25 - 7.32 (m, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 31.9, 38.6, 41.9, 43.7, 55.1, 68.1, 113.7, 114.3, 125.7, 128.27, 128.34, 129.8, 131.0, 142.0, 146.1, 158.0; IR (neat) ν 3419 (br) cm^{-1}; EIMS *m/z* 296.1 (M^+), 121.0 ($C_8H_9O^+$), 71.1 ($C_6H_5^+$); Anal. Calcd for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16. Found: C, 80.92; H, 8.18.

3-Methyl-1-phenylbut-3-en-1-ol (6e)[19]

According to the procedure described for **6b**, 2-chloro-1-propene **3d** (1.0 M THF solution, 1.0 mL, 1.0 mmol) and benzaldehyde (160 mg, 1.5 mmol) gave **6e** (93.8 mg, 58 %). **6e**: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.81 (t, J = 1.4 Hz, 3 H), 2.11 (d, J = 2.4 Hz, 1 H), 2.43 (dd, J = 1.0, 6.9 Hz 2 H), 4.82 (dt, J = 2.4, 6.9 Hz, 1 H), 4.85 - 4.88 (dm, J = 1.4 Hz, 1 H), 4.92 - 4.95 (dm, J = 1.4 Hz, 1 H), 7.25 – 7.41 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.3, 48.2, 71.4, 113.9, 125.7, 127.3, 128.3, 142.3, 144.0; IR (neat) ν 3395 (br) cm^{-1}; EIMS *m/z* 162.1 (M^+), 107.1 ($C_7H_7O^+$), 91.1 ($C_7H_7^+$), 77.1 ($C_6H_5^+$); Anal. Calcd for $C_{11}H_{14}O$: C, 81.44; H, 8.70. Found: C, 81.19; H, 8.38.

5-Methyl-1-phenylhex-5-en-3-ol (6f)[20]

According to the procedure described for **6b**, 2-chloro-1-propene **3d** (1.0 M THF solution, 1.0 mL, 1.0 mmol) and 3-phenylpropanal (200 mg, 1.5 mmol) gave **6f** (110 mg, 0.58 mmol, 58 %). **6f**: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 -1.84 (m, 6 H), 2.14 (ddd, J =0.8, 9.1, 13.7 Hz, 1 H), 2.24 (ddd, J =0.8, 3.8, 13.7 Hz, 1 H), 2.71 (dt, J = 8.2, 13.5 Hz, 1 H), 2.84 (dt, J =7.7, 13.5 Hz, 1 H), 3.71 - 3.81 (brm, 1 H), 4.81 (d, J = 0.8 Hz, 5 H), 4.89 (t, J =1.7 Hz, 1 H), 7.15-7.32 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 22.4, 32.0, 38.7, 46.2, 68.0, 113.5, 125.7, 128.24, 128.33, 142.1, 142.5; IR (neat) ν 3390 (br) cm^{-1}; EIMS *m/z* 190.2 (M^+), 105.1 ($C_8H_9^+$), 91.1 ($C_7H_7^+$); Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 81.99; H, 9.59.

2-Cyclohexyl-1-phenylprop-2-en-1-ol (6g)[18]

According to the procedure described for **6b**, 1-chloro-1-cyclohexylethene **3f** (159 mg, 1.0 mmol) and benzaldehyde (160 mg, 1.5 mmol) gave **6g** (147 mg, 60 %). The structure of **6g** was confirmed by comparison with the authentic sample.[18]

2-Cyclohexyl-5-phenylpent-1-en-3-ol (6h)

According to the procedure described for **6b**, 1-bromo-1-cyclohexylethene **3g** (204 mg, 1.0 mmol) and 3-phenylpropanal (200 mg, 1.5 mmol) gave **6h** (236 mg, 87 %). **6h**: Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77 -0.98 (m, 2 H), 1.10 - 1.47 (m, 4 H), 1.60 - 1.74 (m, 5 H), 1.75 -1.98 (m, 5 H), 2.07 (dd, J = 9.3, 14.0 Hz, 1 H), 2.24 (dd, J = 3.6, 14.0 Hz, 1 H), 2.70 (dt, J =8.0, 14.0 Hz, 1 H), 2.84 (dt, J =7.8, 14.0 Hz, 1 H), 3.67 - 3.77 (brm, 1 H), 4.86 (s, 2 H), 7.16-7.32 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.2, 26.3, 26.5, 32.1, 32.9, 33.5, 35.5, 38.7, 44.0, 44.2, 68.0, 113.7, 125.7, 128.3, 128.4,

142.1, 144.9; IR (neat) ν 3393 (br) cm^{-1}; EIMS *m/z* 272.1 (M^+), 91.1 ($C_7H_7^+$); CIMS *m/z* 273.2 (M^++1); Anal. Calcd for $C_{19}H_{28}O$: C, 83.77; H 10.36. Found: C, 83.39; H, 10.35.

1,3-DiCyclohexylbut-3-en-1-ol (6i)

According to the procedure described for **6b**, 1-bromo-1-cyclohexylethene **3g** (204 mg, 1.0 mmol) and cyclohexanecarbaldehyde (170 mg, 1.5 mmol) gave **6i** (151 mg, 60 %). **6i**: Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 0.74 - 1.45 (m, 12 H), 1.60 - 1.92 (m, 12 H), 1.93 - 2.04 (m, 2 H), 2.26 (dd, *J* = 2.7, 14.0 Hz, 1 H), 3.40 - 3.47 (brm, 1 H), 4.86 (s, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.2, 26.3, 26.6, 28.1, 29.1, 32.8, 33.7, 35.6, 41.0, 43.4, 43.8, 72.5, 113.5, 145.5; IR (neat) ν 3454 (br) cm^{-1}; EIMS *m/z* 250.2 (M^+); CIMS *m/z* 251.2 (M^++1); HRMS. Calcd for $C_{17}H_{30}O$: 250.229666 Found: 250.229015.

(*E*)-5-(Cyclohexylmethyl)-1-phenylhexa-1,5-dien-3-ol (6j)

According to the procedure described for **6b**, 1-bromo-1-cyclohexylethene **3g** (204 mg, 1.0 mmol) and (*E*)-cinnamualdehyde (200 mg, 1.5 mmol) gave **6j** (179 mg, 66 %). **6j**: Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 0.77 - 0.98 (m, 2 H), 1.10 - 1.35 (m, 3 H), 1.37 - 1.51 (m, 1 H), 1.60 - 1.77 (m, 5 H), 1.90 -2.06 (m, 3 H), 2.27 (dd, *J* = 8.8, 14.0 Hz, 1 H), 2.37 (dd, *J* = 4.5, 14.0 Hz, 1 H), 4.37 - 4.46 (brm, 1 H), 4.90 (brs, 1 H), 4.92 (brs, 1 H), 6.24 (dd, *J* = 6.2, 15.9 Hz, 1 H), 6.64 (d, *J* = 15.9 Hz, 1 H), 7.20 -7.41 (m, 5 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 26.2, 26.3, 26.5, 33.0, 33.5, 35.5, 44.1, 44.2, 69.9, 114.1, 126.4, 127.5, 128.5, 130.0, 131.7, 136.7, 144.2; IR (neat) ν 3433 (br) cm^{-1}; EIMS *m/z* 270.2 (M^+), 91.1 ($C_7H_7^+$); Anal. Calcd for $C_{19}H_{26}O$: C, 84.39; H 9.69, Found: C, 84.12; H 9.71.

1-[2-(Cyclohexylmethyl)prop-2-enyl]cyclohexan-1-ol (7)

According to the procedure described for **6b**, 1-bromo-1-cyclohexylethene **3g** (204 mg, 1.0 mmol) and cyclohexanone (147 mg, 1.5 mmol) gave **7** (163 mg, 69 %). The structure of 7 was confirmed by comparison with the authentic sample.[18]

4-[(2-Deuteromethyl)prop-2-enyl]-1-methoxybenzene (8)

According to the procedure described for **6b**, **3c** (182 mg, 1.0 mmol) was treated with Cp_2TiCl_2-Me_3Al (1 : 4) reagent followed by the addition of 20 % DCl-D_2O. The mixture was extracted with ether, and the combined organic layer was washed with sat. aq. $NaHCO_3$ and brine successively. After the ether solution was dried over $MgSO_4$ and filtrated, the filtrate was concentrated to dryness to give a crude oil. The crude product was purified by silica gel column chromatography (hexane – ethyl acetate = 40 : 1 – 20 : 1) to give **8** (146 mg, 89 %) as a colorless oil. **8**: ^1H NMR (300 MHz, $CDCl_3$) δ 1.65(brs, 2 H), 3.26 (brs, 2 H), 3.79 (s, 3 H), 4.71 (brs, 1 H), 4.78 (brs, 1 H), 6.83 (d, *J* = 8.7 Hz, 2 H), 7.10 (d, *J* = 8.7 Hz, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 21.7 (dd, *J* = 19.3 Hz), 43.7, 55.2, 111.5, 113.6, 129.8, 131.8, 145.5, 157.9; EIMS *m/z* 163.1 (M^+), 121.1 ($C_8H_9O^+$); HRMS. Calcd for $C_{11}H_{13}DO$: 163.110742. Found: 163.110978.

Reactions of carboxylic ester compounds with Cp_2TiCl_2-Me_3Al (1 : 4)

1) Reaction of hept-6-enyl acetate (9a)

To a solution of Cp_2TiCl_2 (374 mg, 1.5 mmol) in toluene (3 mL) was added Me_3Al (15 % in toluene, 2.9 mL, 6.0 mmol) at ambient temperature and the solution was stirred for 3 days at the same temperature. A solution of the hept-6-enyl acetate **9a** (78 mg, 0.5 mmol) in THF (1 mL) was added to the above reagent mixture at 0 ℃ and the resulting mixture was stirred for 0.5 h at ambient temperature and for 10 h at 70 ℃. After the reaction mixture was cooled to 0 ℃, a solution of 3-phenylpropanal (400 mg, 3.0 mmol) in THF (5 mL) was added and the mixture was stirred at ambient temperature for 3 h. After an addition of 1M solution of NaOH under ice-cooling, the mixture was filtered through a Celite pad, and the filtrate was extracted with ether. The combined organic layer was washed with brine and dried over $MgSO_4$. The filtered ether solution was concentrated to dryness in vacuo to give a crude oil. Purification by column chromatography (silica gel, hexane – ethyl acetate = 5 : 1 – 3 : 1) gave **6f** (67 mg, 70 %) which was

identical to the authentic sample.[20]

2) Reaction of methyl palmitate (9b).

5-Pentadecyl-1-phenylhex-5-en-3-ol (6k).

According to the procedure described for the reaction of hept-6-enyl acetate (**9a**), methyl palmitate **9b** (135 mg, 0.5 mmol) and 3-phenylpropanal (400 mg, 3.0 mmol) were reacted to give **6k** (151 mg, 78 %) as a colorless oil. **6k**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.85 - 0.91 (m, 3 H), 1.26 (brs, 24 H), 1.35 - 1.50 (m, 2 H), 1.75 - 1.84 (m, 3 H), 2.00 (t, J = 7.5 Hz, 2 H), 2.10 (dd, J = 9.6, 13.7 Hz, 1 H), 2.27 (dd, J = 3.6, 13.7 Hz, 1 H), 2.70 (dt, J = 8.2, 14.0 Hz, 1 H), 2.84 (dt, J = 7.9, 14.0 Hz, 1 H), 3.68 - 3.78 (brm, 1 H), 4.83 (brs, 1 H), 4.89 (d, J = 1.7 Hz, 1 H), 7.15 -7.32 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 27.8, 29.4, 29.5, 29.7, 31.9, 32.2, 35.9, 38.8, 44.6, 68.1, 112.3, 125.8, 128.37, 128.43, 142.2, 146.8; IR (neat) ν 3435 (br) cm^{-1}; CIMS *m/z* 387.2 (M^++1); Anal. Calcd for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C, 83.59; H, 12.26.

3) Reaction of methyl valerate.

2-Butyl-6-phenyl-1-hexen-4-ol (6l).

According to the procedure described for the reaction of **9a**, methyl valerate (76 mg, 0.5 mmol) and 3-phenylpropanal (200 mg, 1,5 mmol) were reacted to give **6l** (46 mg, 42 %) as a colorless oil. **6l**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 3 H), 1.24 - 1.47 (m, 4 H), 1.74 - 1.84 (m, 3 H), 2.00 (t, J = 7.6 Hz 2 H), 2.11 (dd, J = 9.4, 13.8 Hz, 1 H), 2.27 (dd, J = 3.4, 13.8 Hz, 1 H), 2.70 (dt, J = 8.0, 14.0 Hz, 1 H), 2.84 (dt, J = 7.9, 14.0 Hz, 1 H), 3.70 - 3.76 (brm, 1 H), 4.83 (brs, 1 H), 4.89 (d, J = 1.7 Hz, 1 H), 7.15 -7.30 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ14.0, 22.4, 29.9, 32.2, 35.6, 38.8, 44.6, 68.1, 112.3, 125.8, 128.38, 128.44, 142.2, 146.8; IR (neat) ν 3397 (br) cm^{-1}; CIMS *m/z* 233.3 (M^++1); Anal, Calcd for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.38; H, 10.55.

4) Reaction of methyl 3-methoxypropanoate.

5-(2-Methoxyethyl)-1-phenylhex-5-en-3-ol (6m).

According to the procedure described for the reaction of **9a**, methyl 3-methoxypropanoate (60 mg, 0.5 mmol) and 3-phenylpropanal (200 mg, 1,5 mmol) were reacted to give **6m** (42 mg, 36 %) as a colorless oil. **6m**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.70 -1.86 (m, 2 H), 2.08 -2.37 (m, 5 H), 2.70 (dt, J = 8.5, 13.7 Hz, 1 H), 2.83 (ddd, J = 6.3, 9.1, 13.7 Hz, 1 H), 3.34 (s, 3 H), 3.47 - 3.54 (m, 2 H), 3.75 (brm, 1 H), 4.94 (s, 1 H), 4.96 (s, 1 H), 7.15 - 7.31 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 32.2, 35.8, 38.8, 44.9, 58.6, 68.5, 71.4, 114.3, 125.8, 128.37, 128.45, 142.2, 143.8; IR (neat) n 3424 (br) cm^{-1}; EIMS *m/z* 234.1 (M^+), 91.1 ($C_7H_7^+$); CIMS *m/z* 235.2 (M^++1); Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.72; H, 9.40.

5) Reaction of methyl 3-(2-methoxyphenyl)propanoate (9c).

5-[2-(2-Methoxyphenyl)ethyl]-1-phenylhex-5-en-3-ol (6n).

According to the procedure described for the reaction of **9a**, methyl 3-(2-methoxyphenyl)propanoate (97 mg, 0.5 mmol) and 3-phenylpropanal (400 mg, 3.0 mmol) were reacted to give **6n** (85 mg, 55 %) as a colorless oil. **6n**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.75 -1.84 (m, 3 H), 2.15 (dd, J = 9.3, 14.0 Hz, 1 H), 2.26 - 2.38 (m, 1 H), 2.64 - 2.89 (m, 4 H), 3.72 - 3.80 (m, 4 H),4.87 (brs, 1 H), 4.93 (d, J = 1.4 Hz, 1 H), 6.82 - 6.91 (m, 2 H), 7.09 -7.32 (m, 7 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9, 32.1, 35.9, 38.8, 44.9, 55.2, 68.2, 110.2, 112.7, 120.4, 125.8, 127.2, 128.37, 128.43, 129.7, 130.2, 142.2, 146.5, 157.4; IR (neat) ν 3433 (br) cm^{-1}; EIMS *m/z* 310.2 (M^+), 121.1 ($C_8H_9O^+$), 91.1 ($C_7H_7^+$); Anal. Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.24; H, 8.50.

6) Reaction of methyl benzoate

According to the procedure described for the reaction of **9a**, methyl benzoate (68 mg, 0.5 mmol) and 3-phenylpropanal (200 mg, 1.5 mmol) were reacted to give **6n** (52 mg, 41 %) as a colorless oil.

4-(3-Deuteromethylbut-3-enyl)-1,2-dimethoxybenzene (10)

According to the procedure described for the reaction of hept-6-enyl acetate (**9a**), methyl 3-(3,4-dimethoxyphenyl)propanoate (**9d**) (104 mg, 0.5 mmol) was reacted with 20 % DCl-D_2O. Purification by silica gel column chromatography (hexane – ethyl acetate = 1 : 20 – 1 : 10) gave **10** (86 mg, 83 %). **10:** Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76 (brs, 2 H), 2.27 – 2.35 (m, 2 H), 2.67 - 274 (m, 2 H), 3.86 (s, 3 H), 3.88 (s, 3 H), 4.72 (brs, 1 H), 4.74 (brs, 1 H), 6.71 - 6.76 (m, 2 H), 6.78 - 6.82 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3 (dd, J = 1.4 Hz), 33.8, 39.7, 55.8, 55.9, 110.2, 111.2, 111.7, 120.0, 134.9, 145.4, 147.1, 148.7; EIMS *m/z* 207.1 (M^+), 151.1 ($C_9H_{11}O_2^+$); HRMS. Calcd for $C_{13}H_{17}DO_2$:207.136957. Found: 207.136974.

Reactions of allylic titanocene derivatives with aldehydes in the presence of CH_2Cl_2

1) Reaction of 3c

According to the procedure described for **6d**, 1-(2-chloroprop-2-enyl)-4-methoxybenzene **3c** (182 mg, 1.0 mmol) was treated with Cp_2TiCl_2-Me_3Al (1 : 4). After the mixture was treated with CH_2Cl_2 (5 mL) under ice-cooling, 3-phenylpropanal (200 mg, 1.5 mmol) was added and the workup of the reaction mixture gave **6d** (258 mg, 87 %).

2) Reaction of 3d.

As described for **3c**, 2-bromopropene (0.088 mL, 120 mg, 1 mmol) was treated with Cp_2TiCl_2-Me_3Al (1 : 4). After the mixture was treated with CH_2Cl_2 (5 mL) under ice-cooling, 3-phenylpropanal (200 mg, 1.5 mmol) was added and the workup of the reaction mixture gave **6f** (107 mg, 56 %).

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