Titanocene-Catalyzed Carbosilylation of Alkenes and Dienes Using Alkyl Halides and Chlorosilanes

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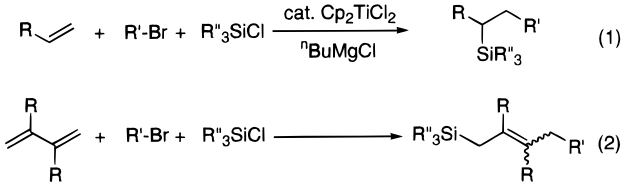
A new method for regioselective carbosilylation of alkenes and dienes has been developed by the use of a titanocene catalyst. This reaction proceeds efficiently at 0 °C in THF in the presence of Grignard reagents by the combined use of alkyl halides (R′−X, X = Br or Cl) and chlorotrialkylsilanes ($R_3''Si-Cl$) as the alkylating and silylating reagents, respectively. Terminal alkenes having aryl or silyl substituents ($YRC{=}CH_2$, Y = Ar or Me_3Si, R = H or Me) afford addition products $YRC(SiR''_3)-CH_2R'$ in good yields, whereas 1-octene and internal alkenes were sluggish. When 2,3-disubstituted 1,3-butadienes were used instead of alkenes, alkyl and silyl units are introduced at the 1- and 4-positions giving rise to allylsilanes in high yields under similar conditions. The present reaction involves (i) addition of alkyl radicals toward alkenes or dienes, and (ii) electrophilic trapping of benzyl- or allylmagnesium halides with chlorosilanes. The titanocene catalyst plays important roles in generation of these active species, i.e., alkyl radicals and benzyl- or allylmagnesium halides.

Introduction

Carbosilylation of carbon−carbon unsaturated bonds is a synthetically very useful reaction for introduction of silicon functionalities into organic molecules with concomitant construction of carbon skeletons via carbon−carbon bond formation. There have already been developed several methods for the carbosilylation of alkynes. The simple examples are Lewis acid-catalyzed addition of allylsilanes[1] and palladium−catalyzed addition of Me_3SiCN[2a] or strained silacyclic compounds such as silacyclopropene,[2b] -propane,[2c] and -butanes.[2d] Vinylsilanes were also obtained from terminal alkynes by the combined use of Me_3SiI and organotin[2e] or -zinc[2f] compounds in the presence of Pd(0). As for the reactions involving carbon−carbon double bonds, it is known that 1,3-dienes[3] and allenes[4] are carbosilylated to give allylsilanes, in which π-allyl palladium species play an important role as a key intermediate. However, carbosilylation of alkenes has not been attained so far. Recently we have established new methodologies to introduce alkyl or silyl groups into alkenes and dienes using early transition metal catalysts such as titanocene[5] and zirconocene.[6] During the course of our study, we wish to report herein the titanocene-catalyzed regioselective carbosilylation of alkenes and dienes by the combined use of alkyl halides and chlorotrialkylsilanes in the presence of Grignard reagents (eqs 1 and 2).



Results and Discussion

For example, to a THF solution of styrene, chlorotriethylsilane (1.1 equiv), a catalytic amount of titanocene dichloride (0.05 equiv), and ^{n}BuMgCl (2.2 equiv) was added *tert*-butyl bromide (1.1 equiv) at 0 °C for 10 min under nitrogen, and the solution was stirred for 1 h. The NMR analysis of the crude mixture indicated the formation of the addition product (**1**) in 96%. This reaction is highly regioselective to yield a single regioisomer possessing *tert*-butyl group at the terminal carbon and triethylsilyl group at the benzylic carbon (Table 1, run 1). It is known that double alkylation[5a] and double silylation[5b] can take place under similar conditions; however, any byproducts arising from such reactions were not formed. The use of EtMgCl instead of ^{n}BuMgCl afforded **1** in 50% yield, but **1** was not obtained when ^{i}PrMgBr or PhMgCl was employed. As shown in runs 2, 5, and 6, this reaction proceeds efficiently when secondary bromides were used. Primary alkyl bromides can also be employed as the alkylating reagents, but the reaction is somewhat less efficient, affording moderate yields of products (runs 3, 4). When chloro-substituted substrates were used, the reaction took place site selectively at the bromo functional group leaving the chloro substituents

(1) Asao, N.; Yoshikawa, E.; Yamamoto, Y. *J. Org. Chem.* **1996**, *61*, 4874−4875.

(2) Pd-catalyzed carbosilylation: (a) Chatani, N.; Hanafusa, T. *J. Chem. Soc., Chem. Commun.* **1985**, 838−839. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879−3880. (c) Saso, H.; Ando, W. *Chem. Lett.* **1988**, 1567−1570. (d) Sakurai, H.; Imai, T. *Chem. Lett.* **1975**, 891−894. (e) Chatani, N.; Amishiro, N.; Murai, S. *J. Am. Chem. Soc.* **1991**, *113*, 7778−7780. (f) Chatani, N.; Amishiro, N.; Morii, T.; Yamashita, T.; Murai, S. *J. Org. Chem.* **1995**, *60*, 1834−1840.

(3) Obora, Y.; Tsuji, Y.; Kawamura, T. *J. Am. Chem. Soc.* **1995**, *117*, 9814−9821.

(4) Wu, M.; Yang, F.; Cheng, C. *J. Org. Chem.* **1999**, *64*, 2471−2474.

(5) (a) Terao, J.; Saito, K.; Nii, S.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1998**, *120*, 11822−11823. (b) Terao, J.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1998**, *39*, 9697−9698.

(6) (a) Terao, J.; Torii, K.; Saito, K.; Kambe, N.; Baba, A.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2653−2656. (b) Terao, J.; Watanabe, T.; Saito, K.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1998**, *39*, 9201−9204.

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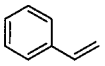
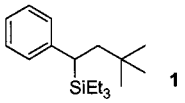
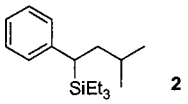
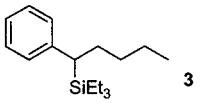
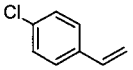
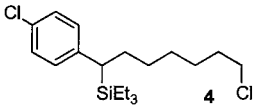
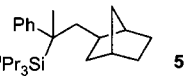
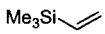
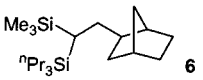
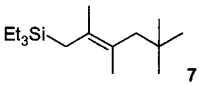
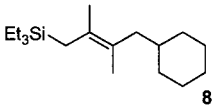
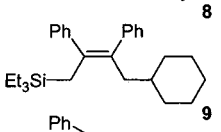
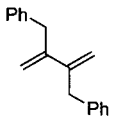
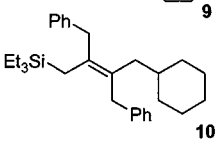
Table 1. Titanocene-Catalyzed Carbosilylation Using Alkyl Halides and Chlorosilanes[a]

run	alkene or diene	R-X	R'_3Si-Cl	time (h)	product	yield (%)[b]
1		^{t}Bu-Br	Et_3Si-Cl	1	 **1**	96(95)
2		^{i}Pr-Br	Et_3Si-Cl	1	 **2**	85(84)
3		^{n}Pr-Br	Et_3Si-Cl	1	 **3**	51(41)
4		ClC_5H_{10}-Br	Et_3Si-Cl	4	 **4**	48(40)
5		2-Norbornyl-Br	$^n Pr_3Si$-Cl	6	 **5**	85(74)
6		2-Norbornyl-Br	$^n Pr_3Si$-Cl	6	 **6**	66(35)
7		^{t}Bu-Br	Et_3Si-Cl	2	 **7**	83(78) *E*/*Z* = 96/4
8		^{t}Bu-Cl	Et_3Si-Cl	6	**7**	76(64) *E*/*Z* = 98/2
9		*cyclo*-Hex-Cl	Et_3Si-Cl	6	 **8**	66(53) *E*/*Z* = 97/3
10		*cyclo*-Hex-Br	Et_3Si-Cl	2	 **9**	82(80) *E*/*Z* = 10/90
11		*cyclo*-Hex-Br	Et_3Si-Cl	4	 **10**	95(92) *E*/*Z* = 80/20

[a] For details of reaction conditions and product characterization, see Experimental Section. [b] NMR yield. Isolated yield is in parentheses.

intact, giving rise to **4** in 48% yield (run 4). α-Methylstyrene efficiently underwent carbosilylation (run 5), but styrenes having a substituent (Me or Ph) at the β-position did not afford the desired products. In addition to aryl-substituted alkenes, a vinylsilane underwent carbosilylation to give the corresponding *gem*-disilyl product (**6**) in a good yield (run 6). Under similar conditions, 1-octene and 1-phenyl-1-propyne did not give the desired products.

When 2,3-dimethyl-1,3-butadiene was treated with *tert*-butyl bromide and Et_3SiCl under identical conditions, alkyl and silyl units are introduced at the 1- and 4-positions forming **7** in high yield with an *E*/*Z* ratio of 96/4 (run 7). It should be noted that secondary and tertiary alkyl chlorides can be employed as suitable alkylating reagents in this reaction, giving **7** and **8** in good yields although longer reaction time was required (runs 8, 9). Phenyl- and benzyl-substituted 1,3-butadienes also gave the corresponding products in 82% and 95% yields, respectively (runs 10, 11), whereas desired products were not obtained from isoprene and 1,3-butadiene.

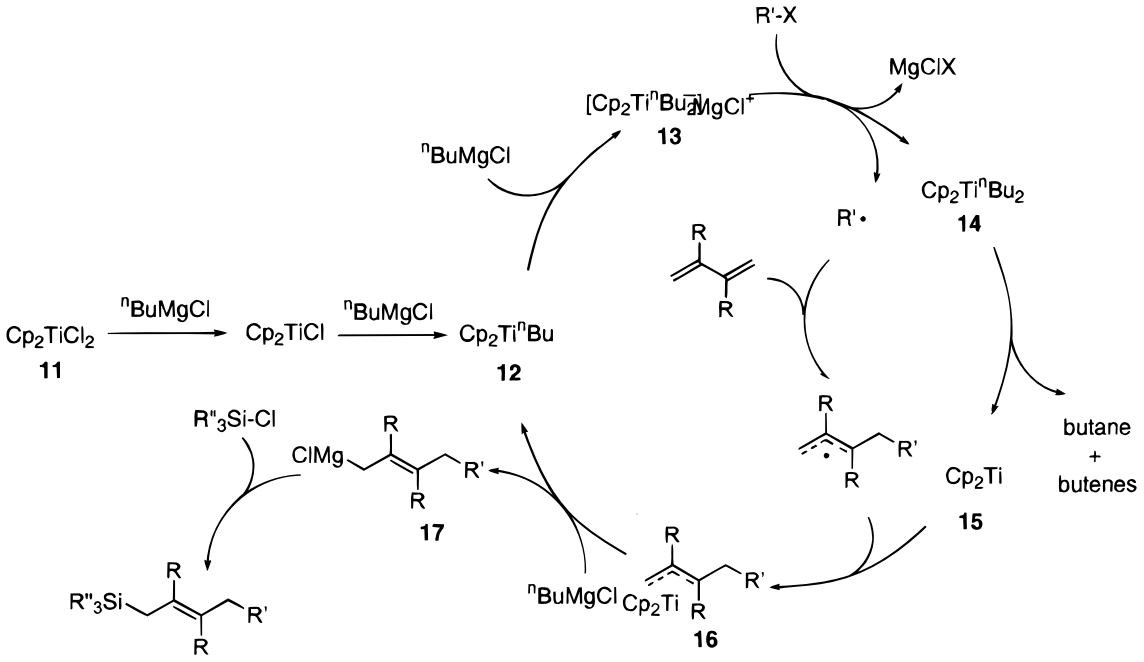
A plausible pathway of this reaction is outlined in Scheme 1 for the case of dienes. Titanocene dichloride (**11**) reacts with ^{n}BuMgCl to generate dibutyltitanate(III) complex (**13**) via Cp_2TiCl[7] and butyltitanocene (**12**).[8] One electron transfer from **13** to alkyl halides leads to the cleavage of the C−X bond to give the corresponding alkyl radical[9] along with dibutyltitanocene (**14**), which

(7) For the formation of Cp_2TiCl from Cp_2TiCl_2 and alkyl Grignard reagents, see: Martin, H. A.; Jellinek, F. *J. Organomet. Chem.* **1968**, *12*, 149−161.

(8) Reaction of Cp_2TiCl with ^{n}BuLi affords the thermally instable **12**, see: (a) Klei, E.; Telgen, J. H.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *209*, 297−307. (η^5-$C_5Me_5)_2Ti^nPr$ was formed by the reaction of (η^5-$C_5Me_5)_2TiCl$ with ^{n}PrMgBr, see: (b) Luinstra, G. A.; ten Cate, L. C.; Heeres, H. J.; Pattiasina, J. W.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3227−3237.

(9) It is known that alkyl radicals are generated in the titanocene-catalyzed reduction of alkyl bromides with ^{i}PrMgBr. Rilatt, J. A.; Kitching, W. *Organometallics* **1982**, *1*, 1089−1093.

Scheme 1. A Plausible Pathway of Titanocene-Catalyzed Carbosilylation of Dienes



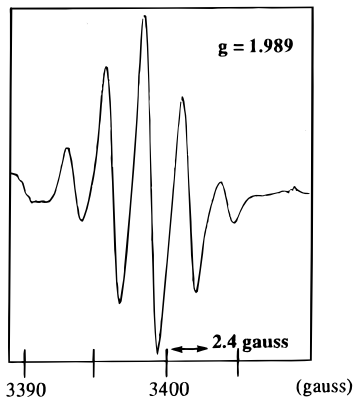


Figure 1. ESR spectrum of $[Cp_2Ti^nBu_2]^-MgCl^+$.

readily forms Cp_2Ti (**15**) via β-hydrogen elimination.[10] Addition of thus-formed alkyl radical to a diene at the terminal carbon affords allyl radical species, which recombines with **15** to give the corresponding allyl titanium complex (**16**). Subsequent transmetalation[11] of **16** with ^{n}BuMgCl gives the corresponding allyl Grignard reagent (**17**) along with regeneration of **12**. Then **17** reacts with a chlorosilane to give carbosilylation product. Arylalkenes may react similarly via benzylic, instead of allylic, intermediates. The evidence shown below supports this reaction pathway.

First, we tested the intermediacy of a Ti(III) ate complex as follows. Cp_2TiCl_2 (0.025 M) was treated with a large excess of ^{n}BuMgCl (1 M) at 0 °C in THF. The ESR spectrum of the resulting dark brown solution (Figure 1) showed a quintet hyperfine splitting at g = 1.989 with a coupling constant of 2.4 G which might be ascribable to the coupling with the four equivalent α-hydrogens of the two butyl groups of **13**. This is quite similar to the ESR spectrum of $[Cp_2TiEt_2]^-$ Li^+ (g = 1.991, 2.3 G) generated by the reaction of Cp_2TiCl_2 with EtLi.[12] Addition of cyclohexyl bromide into the THF solution of **13** quickly changed the color to green, and the ESR signal disappeared. This result is in accord with the SET process in Scheme 1 (**13** to **14**).

To confirm the radical mechanism for the carbon−carbon bond forming step, we carried out the reaction of styrene using (bromomethyl)cyclopropane as the alkylating reagent. This reaction afforded the sole carbosilylation product (**18**) having 3-butenyl units at the terminal carbon in 49% yield, and the corresponding product containing cyclopropylmethyl group was not detected in the resulting mixture (eq 3). This result can be explained by the evidence that the rate constant of the ring opening of cyclopropylmethyl radical, $k = 1.3 \times 10^8$ s^{-1} at 25 °C,[13] is much faster than the addition of primary radicals to styrene, $k = 5.4 \times 10^4$ M^{-1} s^{-1} at 25 °C.[14] Since the rearrangement of cyclopropylmethylmagnesium bromide to $CH_2{=}CHCH_2CH_2MgBr$ is a slow process with $t_{1/2}$ = 30 h in THF at 27 °C,[15] it is unlikely that alkylation at the terminal carbon is an

(10) It is reported that **14** decomposes rapidly at −50 °C forming **15** along with a 1:1 mixture of *n*-butane and butenes. McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6529−6536.

(11) Transmetalation of vinyltitanocene complexes with ^{i}PrMgBr is known. Gao, Y.; Sato, F. *J. Chem. Soc., Chem. Commun.* **1995**, 659−660.

(12) Brintzinger, H. H. *J. Am. Chem. Soc.* **1967**, *89*, 6871−6877.

(13) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024−7026.

(14) Citterio, A.; Arnoldi, A.; Minisci, F. *J. Org. Chem.* **1979**, *44*, 2674−2682.

(15) Silver, M. S.; Shafer, P. R.; Nordlander, J. E.; Ruchardt, C.; Roberts, J. D. *J. Am. Chem. Soc.* **1960**, *82*, 2646−2647.

(16) $(C_5Me_5)_2Ti(CH_2{=}CH_2)$ complex has been isolated and well catalyzed. The crystal structure of this complex is more similar to a (titanacyclopropane) δ-coordination rather than a π-coordination structure, see: Cohen, S. A.; Auburn, P. R.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 1136−1143.

(17) Martin, H. A.; Jellinek, F. *Angew. Chem.* **1964**, *76*, 274. Chen, J.; Kai, Y.; Kasai, N.; Yasuda, H.; Yamamoto, H.; Nakamura, A. *J. Organomet. Chem.* **1991**, *407*, 191−205.

(18) Allyl Grignard reagents react with chlorosilanes much faster than alkyl Grignard reagents. For example, a reaction of $CH_2{=}CHCH_2$-MgCl with ^{n}Pr$_3$SiCl was complete within 1 min at 0 °C in THF to give the corresponding allylsilane, whereas only a trace amount (<1%) of butyltripropylsilane was formed under identical conditions when ^{n}BuMgCl was used.

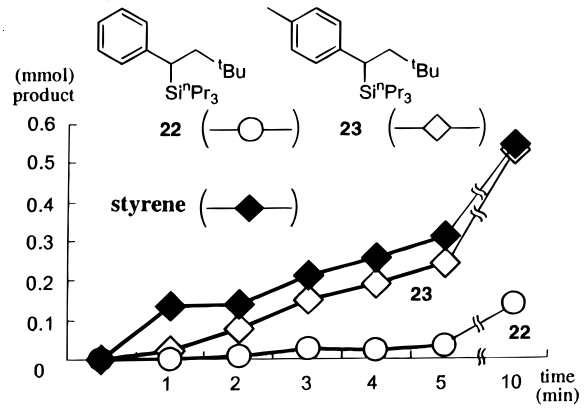
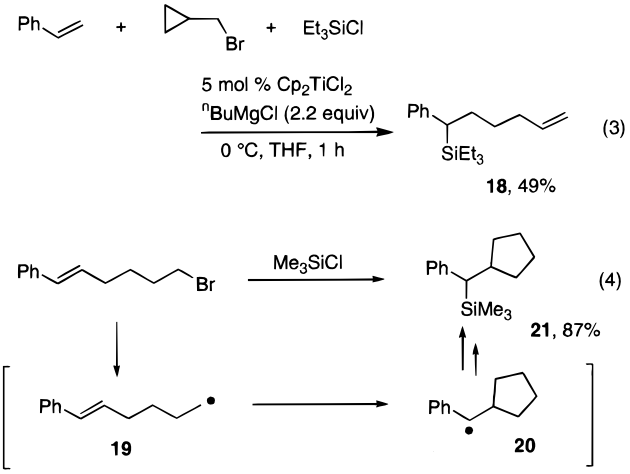
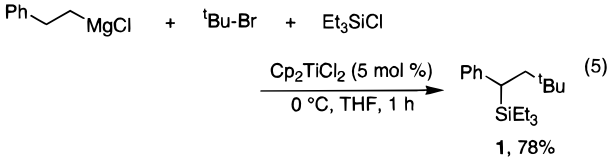


Figure 2. Reaction of *p*-methylstyrene (2 mmol) with ^{t}BuBr (2 mmol) and $^{n}Pr_3SiCl$ (2 mmol) using $PhCH_2CH_2MgCl$ (2 mmol) in the presence of Cp_2TiCl_2 (0.1 mmol) at 0 °C in THF.

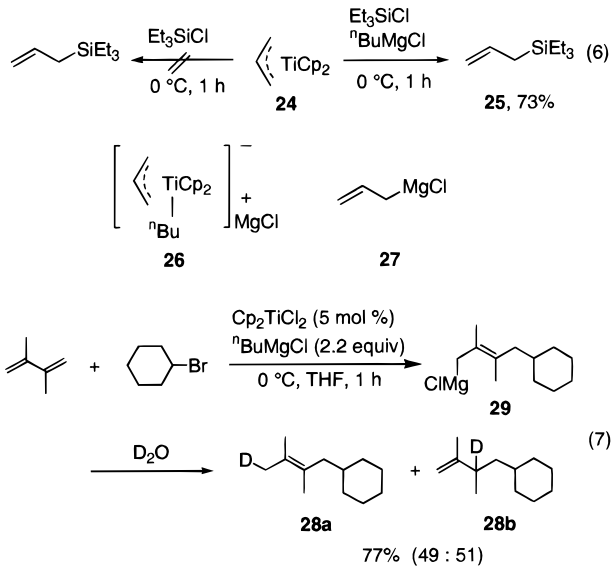
anionic process. Furthermore, when the reaction of 6-bromo-1-phenyl-1-hexene with Me_3SiCl was performed under the identical conditions, only the cyclized product (**21**) was obtained probably via 5-exo cyclization from **19** to **20** (eq 4).



An alternative route leading to **16** is the addition of alkyl radicals toward alkenes or dienes moiety coordinated to titanocene rather than toward free molecules. Such a possibility was examined in the case of styrene. According to Scheme 1, when $PhCH_2CH_2MgCl$ is used instead of ^{n}BuMgCl, styrene should be formed. So, we carried out the reaction of *tert*-butyl bromide and Et_3SiCl (1 equiv) with $PhCH_2CH_2MgCl$ (2.2 equiv) using 5 mol % of Cp_2TiCl_2 in the absence of alkenes. Under similar conditions, **1** was obtained in 78% yield as a single product, indicating that styrene generated in situ was incorporated in this catalytic cycle (eq 5). We then conducted a similar reaction using $^{n}Pr_3SiCl$ (1 equiv) as the silylating reagent in the presence of *p*-methylstyrene (1 equiv), and the yields of the products at different reaction time were plotted in Figure 2. A carbosilylated product (**23**) from *p*-methylstyrene was formed predominantly at any stage of the reaction over **22**, which is derived from in situ generated styrene. It should also be noted that only a trace amount of **22** was formed at the early stage of the reaction (reaction time <1 min) whereas the yield of **23** increased continually from the beginning of the reaction. Taking into account these results and a hypothesis that β-elimination of $Cp_2Ti(CH_2CH_2Ph)_2$ yields $Cp_2Ti(CH_2{=}CHPh)$ which then can undergo ligand exchange with *p*-methylstyrene, it is likely that alkyl radicals attack free alkenes rather than titianocene−alkene complexes.[16]



To shed light on the active species of the subsequent silylation step, allyltitanocene complex (**24**) was prepared by the reported procedure[17] and examined its reactivity toward chlorosilanes. When a THF solution of **24** and Et_3SiCl (1 equiv) was stirred at 0 °C for 1 h, no reaction took place. On the other hand, **25** was formed in 73% yield when a similar reaction was performed in the presence of a stoichiometric amount of ^{n}BuMgCl (eq 6). These results suggest that chlorosilane reacted with an ate complex (**26**) or with allylmagnesium chloride (**27**)[18] which was formed by transmetalation from **24** via **26**. Although a possibility that titanocene ate complexes such as **26** react directly with chlorosilanes cannot be ruled out, the following evidence supports that the transmetalation does proceed under the conditions employed. A reaction of 2,3-dimethyl-1,3-butadiene with cyclohexyl bromide (1.1 equiv) was conducted at 0 °C for 1 h in the absence of chlorosilane. Subsequent addition of D_2O afforded monoalkylated compound (**28**) containing a deuterium at the allylic positions in 77% yield as a mixture of regioisomers (eq 7). This result indicates that the titanocene complex catalyzes the carbon−carbon bond formation even in the absence of chlorotrialkylsilanes giving rise to **29**.



Conclusions

A new method for carbosilylation of alkenes and dienes has been developed by the aid of a titanocene catalyst. This reaction proceeds efficiently under mild conditions using alkyl halides and chlorotrialkylsilanes, which can rarely been employed in catalytic reactions promoted by late transition metals. The present reaction involves (i) addition of alkyl radicals toward alkenes or dienes in the

carbon−carbon bond forming step and (ii) electrophilic trapping of benzyl- or allylmagnesium halides with chlorosilanes in the carbon−silicon bond forming step. The titanocene catalyst plays important roles for generating active key species to promote these crucial steps, i.e., (iii) alkyl radicals are formed by electron transfer from titanocene ate complexes to alkyl halides and (iv) benzyl- or allylmagnesium halides are formed by transmetalation of Ti(III) complexes with Grignard reagents.

Experimental Section

General Methods. THF was distilled just before use from benzophenone ketyl. 6-Bromo-1-phenyl-1-hexene was prepared by the reaction of 6-chrolo-1-phenyl-1-hexene[19] with LiBr following a literature.[20] Other alkenes, dienes, and Grignard reagents were used as purchased without further purification. Analytical and purification procedures for NMR, IR, MS, GC-MS, elemental analysis, and HPLC were the same as mentioned before.[5a]

3,3-Dimethyl-1-phenyl-1-(triethylsilyl)butane (1). Into a 10 mL glass vessel containing styrene (114 mg, 1.10 mmol), Et_3SiCl (181 mg, 1.20 mmol), and a catalytic amount of Cp_2TiCl_2 (13 mg, 0.05 mmol) was added a THF solution of ^{n}BuMgCl (0.90 M in THF, 2.70 mL, 2.43 mmol). *tert*-Butyl bromide (169 mg, 1.23 mmol) was added by a syringe to the solution kept at 0 °C over the period of 10 min under nitrogen. After stirring for 40 min, ca. 2 mL of 1 N HCl aq was added to the solution at 0 °C, and the mixture was warmed to 20 °C. A saturated aqueous NH_4Cl solution (50 mL) was added, and the product was extracted with ether (50 mL), dried over $MgSO_4$, and evaporated to give an orange crude product (96% NMR yield). Purification by HPLC with $CHCl_3$ as an eluent afforded 286 mg (95%) of **1** in pure form. IR (neat) 2953, 2909, 2876, 1466, 1006, 789, 750, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18−7.02 (m, 5H), 2.28 (d, J = 11.2 Hz, 1H), 1.89 (dd, J = 10.4, 11.2 Hz, 1H), 1.57 (d, J = 10.4 Hz, 1H), 0.87 (t, J = 7.6 Hz, 9H), 0.74 (s, 9H), 0.48 (q, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 127.8, 127.7, 123.6, 43.6, 33.1, 30.6, 30.1, 7.7, 2.4; MS (EI) *m*/*z* (relative intensity, %) 276 (M^+, 12), 248 (21), 247 (100), 115 (31); HRMS calcd for $C_{18}H_{32}Si$: 276.2273, found 276.2281. Anal. Calcd for $C_{18}H_{32}Si$: C, 78.18; H, 11.66. Found: C, 78.20; H, 11.58.

3-Methyl-1-phenyl-1-(triethylsilyl)butane (2). A mixture of styrene (93 mg, 0.89 mmol), isopropyl bromide (123 mg, 1.00 mmol), Et_3SiCl (148 mg, 0.98 mmol), and ^{n}BuMgCl (0.90 M in THF, 2.20 mL, 2.00 mmol) was cooled to 0 °C, and Cp_2TiCl_2 (11 mg, 0.04 mmol) was added. After stirring for 1 h, similar workup as mentioned above afforded an orange crude product (85% NMR yield). Purification by HPLC gave 195 mg (84%) of **2**. IR (neat) 2953, 2911, 2875, 766, 727, 713, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26−7.03 (m, 5H), 2.28 (dd, J = 2.8, 12.8 Hz, 1H), 1.90 (ddd, J = 2.8, 12.8, 13.2 Hz, 1H), 1.48−1.34 (m, 1H), 1.36−1.30 (m, 1H), 0.87 (t, J = 7.6 Hz, 9H), 0.82 (d, J = 6.2 Hz, 3H), 0.78 (d, J = 6.2 Hz, 3H), 0.49 (q, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 127.82, 127.80, 123.9, 38.9, 31.6, 26.2, 24.2, 20.8, 7.7, 2.5; MS (EI) *m*/*z* (relative intensity, %) 262 (M^+, 12), 234 (18), 233 (100), 232 (10), 115 (8); HRMS calcd for $C_{17}H_{30}Si$: 262.2117, found 262.2108. Anal. Calcd for $C_{17}H_{30}Si$: C, 77.78; H, 11.52. Found: C, 77.64; H, 11.56.

1-Phenyl-1-(triethylsilyl)pentane (3). A mixture of styrene (90 mg, 0.86 mmol), propyl bromide (119 mg, 0.98 mmol), Et_3SiCl (143 mg, 0.95 mmol), and ^{n}BuMgCl (0.90 M in THF, 2.11 mL, 1.90 mmol) was cooled to 0 °C, and then Cp_2TiCl_2 (11 mg, 0.04 mmol) was added. After stirring for 1 h, similar workup as mentioned above afforded an orange crude product (51% NMR yield). Purification by HPLC gave 92 mg (41%) of **3**. IR (neat) 2955, 2875, 1458, 1016, 782, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23−7.03 (m, 5H), 2.13 (dd, J = 3.2, 12.4 Hz, 1H), 1.83−1.77 (m, 1H), 1.72−1.68 (m, 1H), 1.40−1.02 (m, 4H), 0.87 (t, J = 8.0 Hz, 9H), 0.82 (t, J = 6.8 Hz, 3H), 0.49 (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 127.8, 127.8, 124.0, 34.2, 31.7, 29.6, 22.6, 14.1, 7.7, 2.6; MS (EI) *m*/*z* (relative intensity, %) 262 (M^+, 17), 235 (6), 234 (20), 233 (100), 117 (6), 115 (24); HRMS calcd for $C_{17}H_{30}Si$: 262.2117, found 262.2137. Anal. Calcd for $C_{17}H_{30}Si$: C, 77.78; H, 11.52. Found: C, 77.65; H, 11.49.

7-Chloro-1-(4-chrolophenyl)-1-(triethylsilyl)heptane (4). To a THF solution (10 mL) of *p*-chlorostyrene (405 mg, 2.92 mmol), 1-bromo-5-chloropentane (1110 mg, 5.99 mmol), Et_3SiCl (910 mg, 6.03 mmol), and ^{n}BuMgCl (0.90 M in THF, 9.00 mmol) was added Cp_2TiCl_2 (79.5 mg, 0.32 mmol) at 0 °C. After stirring for 4 h, similar workup gave an orange crude product (48% NMR yield). Purification by HPLC afforded 419 mg (40%) of **4**. IR (neat) 2933, 2875, 2857, 1489, 1012, 837, 718 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 3.41 (t, J = 6.7 Hz, 2H), 2.04 (d, J = 12.2 Hz, 1H), 1.74−1.59 (m, 4H), 1.30−1.11 (m, 5H), 1.03−1.00 (m, 1H), 0.81 (t, J = 8.0 Hz, 9H), 0.42 (q, J = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 129.6, 128.9, 128.0, 45.1, 33.8, 32.7, 29.7, 29.2, 28.7, 26.8, 7.7, 2.5; MS (EI) *m*/*z* (relative intensity, %) 358 (M^+, 2), 208 (26), 151 (18), 140 (17), 138 (49), 131 (15), 115 (100), 87 (85), 59 (26); HRMS calcd for $C_{19}H_{32}SiCl_2(^{35}Cl)$: 358.1650, found 358.1648. Anal. Calcd for $C_{19}H_{32}SiCl_2$: C, 63.49; H, 8.97. Found: C, 63.73; H, 9.08.

2-[2-Phenyl-2-(tripropylsilyl)propyl]norbornane(5). To a mixture of α-methylstyrene (119 mg, 1.01 mmol), 2-norbornyl bromide (427 mg, 2.44 mmol), and ^{n}Pr$_3$SiCl (494 mg, 2.56 mmol) was added ^{n}BuMgCl (0.90 M in THF, 4.40 mL, 4.00 mmol). A catalytic of amount of Cp_2TiCl_2 (24.5 mg, 0.10 mmol) was added to the solution at 0 °C and stirred for 6 h. The similar workup gave an orange crude product (85% GC yield). Purification by HPLC afforded 276 mg (74%) of **5** as a mixture of isomers with ca. 1:1 ratio indicated by ^{1}H and ^{13}C NMR. The ^{1}H NMR showed two singlet peaks of methyl protons at 1.36 and 1.31 ppm, which are more reasonably assigned to those of a diastereomer pair having different configurations at the benzylic carbons rather than to those of a mixture of *exo*, *endo* isomers with the same stereochemistry at the benzylic carbons. A 1:1 mixture of diastereomers: IR (neat) 2951, 2867, 1495, 1454, 1064, 804, 787, 745, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.01 (m, 5H), 2.26−1.39 (m, 4H), 1.37−0.85 (m, 18H), 0.83 (t, J = 7.2 Hz, 9H), 0.38 (t, J = 9.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (147.4, 147.3), (127.5, 127.4), (126.8, 126.6), 123.6 (1 C), (45.1, 44.6), (44.1, 43.6), 42.1 (1 C), (38.2, 38.1), (37.1, 36.2), (36.1, 35.8), (33.5, 33.1), (29.9, 29.6), (28.8, 28.5), (21.4, 21.0), (19.09, 19.05), 18.0 (1 C), (13.93, 13.89); MS (EI) *m*/*z* (relative intensity, %) 370 (M^+, 17), 287 (2), 245 (3), 212 (37), 187 (6), 157 (100), 115 (51), 73 (15), 59 (6), 45 (6); HRMS (EI) calcd for $C_{25}H_{42}Si$: 370.3056, found 370.3048. Anal. Calcd for $C_{25}H_{42}Si$: C, 81.00; H, 11.42. Found: C, 80.80; H, 11.37.

2-[2-Trimethylsilyl-2-tripropylsilyl)ethyl]norbornane (6). To a mixture of trimethylvinylsilane (113 mg, 1.13 mmol), 2-norbolnyl bromide (354 mg, 2.02 mmol), and ^{n}Pr$_3$SiCl (388 mg, 2.01 mmol) was added ^{n}BuMgCl (0.90 M in THF, 3.30 mL, 3.00 mmol). A catalytic of amount of Cp_2TiCl_2 (24.5 mg, 0.06 mmol) was added to the solution at 0 °C and stirred for 6 h. Similar workup gave an orange crude product (66% GC yield). Purification by HPLC afforded 140 mg (35%) of **6** as a mixture of diastereomers with ca. 1:1 ratio as in the case of **5**. ^{13}C NMR showed two singlet peaks assinable to methyl carbons of trimethylsilyl group at 1.00 and 0.86 ppm with similar intensities. A 1:1 mixture of diastereomers: IR (neat) 2951, 2926, 2868, 1455, 1247, 1065, 1015, 894, 853, 832, 758, 683 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.15 (s, 1H), 1.95−1.90 (m, 1H), 1.52−0.87 (m, 17H), 0.94 (t, J = 7.20 Hz, 9H), 0.59−0.47 (m, 6H), 0.04- -0.12 (m, 1H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (44.4, 44.1), (40.7, 39.7), (38.5, 38.1), (36.6, 36.5), (35.3, 35.1), (33.0, 32.9), (30.3, 30.2), (29.1, 29.0), 19.0 (3 C), 18.0 (3 C), 16.7 (3 C), (8.57, 8.21), (1.00, 0.86); MS (EI)

(19) 6-Chloro-1-phenyl1-1-hexene was prepared by the reaction of styrene with 1-bromo-4-chlorobutane in the presence of ^{n}BuMgCl (2 M in Et_2O) using Cp_2TiCl_2 as the catalyst (unpublished result). The details will be published in due course.

(20) Li, X.; Singh, S. M.; Labrie, F. *Synth. Commun.* **1994**, *24*, 733−743.

m/*z* (relative intensity, %) 310 (26), 309 (90), 268 (15), 267 (57), 208 (20), 207 (100), 180 (16), 179 (63), 165 (62), 157 (32), 152 (10), 129 (25), 115 (36), 101 (23), 87 (19), 73 (42), 59 (32), 42 (13); HRMS calcd for $C_{20}H_{41}Si_2(M\text{-}CH_3)^+$: 337.2747, found 337.2721. Anal.Calcd for $C_{21}H_{44}Si_2$: C, 71.50; H, 12.57. Found: C, 71.28; H, 12.69.

(*E*)-2,3,5,5-Tetramethyl-1-triethylsilyl-2-hexene (7). To a mixture of 2,3-dimethyl-1,3-butadiene (160 mg, 1.94 mmol), Et_3SiCl (598 mg, 3.98 mmol), ^{n}BuMgCl (0.90 M in THF, 6.7 mL, 6.0 mmol), and Cp_2TiCl_2 (25 mg, 0.10 mmol) was added slowly a THF solution of *tert*-butyl bromide (0.47 M, 5.00 mL, 2.35 mmol) using a dropping funnel over a period of 1 h at 0 °C. After stirring for 2 h, similar workup gave an orange crude product (83% NMR yield). Purification by HPLC afforded 387 mg (78%) of **7**. ^{1}H NMR shows a mixture of stereoisomers with an *E*/*Z* ratio of 96/4: IR (neat) 2954, 2911, 2876, 1466, 1016, 774, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (*E* isomer) δ 2.00 (s, 2H), 1.65 (s, 3H), 1.63 (s, 3H), 1.54 (s, 2H), 0.95 (t, J = 7.9 Hz, 9H), 0.90 (s, 9H), 0.55 (q, J = 7.9 Hz, 6H); NOE difference measurement: irradiation of methylene protons at δ 2.00 (-CH_2-^{t}Bu) caused enhancement of the methyl protons at δ 1.65 (6.7%) and 1.63 (2.1%), while no enhancement was observed for methylene protons at δ 1.54 (-CH_2-SiEt$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) (*E* isomer) δ 128.8, 123.6, 48.3, 33.8, 30.7, 22.5, 22.2, 21.0, 7.7, 4.4; MS (EI) *m*/*z* (relative intensity, %) 254 (M^+, 30), 225 (67), 197 (27), 115 (100), 87 (21), 59 (16); HRMS calcd for $C_{16}H_{34}Si$: 254.2430, found 254.2434. Anal. Calcd for $C_{16}H_{34}Si$: C, 75.50; H, 13.46. Found: C, 75.47; H 13.50.

Preparation of 7 Using *tert*-Butyl Chloride. To a mixture of 2,3-dimethyl-1,3-butadiene (168 mg, 2.04 mmol), *tert*-butyl chloride (268 mg, 2.89 mmol), Et_3SiCl (460 mg, 3.05 mmol), and ^{n}BuMgCl (0.90 M in THF, 6.7 mL, 6.0 mmol) was added Cp_2TiCl_2 (25.3 mg, 0.10 mmol) at 0 °C under nitrogen. After stirring for 6 h, similar workup gave an orange crude product (76% NMR yield). Purification by silica gel column chromatography with hexane as an eluent afforded 323 mg (64%) of **7** as a mixture of stereoisomers (*E*/*Z* = 98/2).

(*E*)-1-Cyclohexyl-2,3-dimethyl-4-triethylsilyl-2-butene (8). To a mixture of 2,3-dimethyl-1,3-butadiene (162 mg, 1.97 mmol), cyclohexyl chloride (591 mg, 4.98 mmol), Et_3SiCl (466 mg, 3.09 mmol), and ^{n}BuMgCl (0.90 M in THF, 6.66 mL, 6.00 mmol) was added Cp_2TiCl_2 (26 mg, 0.11 mmol) at 0 °C under nitrogen. After stirring for 6 h, similar workup gave an orange crude product (66% NMR yield). Purification by HPLC with $CHCl_3$ as an eluent afforded 290 mg (53%) of **8**. ^{1}H NMR as a mixture of stereoisomers (*E*/*Z* = 97/3): IR (neat) 2921, 2875, 2852, 774, 752, 737 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (*E* isomer) δ 1.90 (d, J = 7.8 Hz, 2H), 1.72−1.62 (m, 3H), 1.62 (s, 3H), 1.58 (s, 3H), 1.53 (s, 2H), 1.45−1.30 (m, 1H), 1.27−1.05 (m, 4H), 0.94 (t, J = 8.0 Hz, 9H), 0.93−0.81 (m, 3H), 0.53 (q, J = 8.0 Hz, 6H); NOE difference measurement: irradiation of methylene protons at δ 1.90 (-CH_2-cyclohexyl) caused enhancement of methyl protons at δ 1.62 (3.6%) and 1.58 (2.2%), while no enhancement was observed for methylene protons at δ 1.53 (-CH_2-SiEt$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) (*E* isomer) δ 126.4, 123.8, 42.5, 37.4, 33.7, 26.9, 26.7, 21.3, 20.8, 19.8, 7.6, 4.4; MS (EI) *m*/*z* (relative intensity, %) 280 (M^+, 94), 251 (100), 115 (43); HRMS calcd for $C_{18}H_{36}Si$: 280.2586, found 280.2567. Anal. Calcd for $C_{18}H_{36}Si$: C, 77.06; H, 12.93. Found: C, 76.78; H, 12.74.

(*Z*)-1-Cyclohexyl-2,3-diphenyl-4-triethylsilyl-2-butene (9). To a mixture of 2,3-diphenyl-1,3-butadiene (209 mg, 1.01 mmol), cyclohexyl bromide (248 mg, 1.52 mmol), Et_3SiCl (247 mg, 1.65 mmol), and ^{n}BuMgCl (0.90 M in THF, 2.78 mL, 2.50 mmol) was added Cp_2TiCl_2 (13 mg, 0.05 mmol) at 0 °C. After stirring for 2 h, similar workup gave an orange crude product (82% NMR yield). Purification by HPLC with $CHCl_3$ as an eluent afforded 325 mg (80%) of **9** as a mixture of stereoisomers (*E*/*Z* = 10/90); IR (neat) 2950, 2922, 2874, 2851, 772, 755, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (*Z* isomer) δ 7.03−6.87 (m, 10H), 2.43 (d, J = 6.84 Hz, 2H), 2.11 (s, 2H), 1.73−1.56 (m, 5H), 1.48−0.94 (m, 6H), 0.81 (t, J = 8.0 Hz, 9H), 0.37 (q, J = 8.0 Hz, 6H); NOE difference measurement: irradiation of methylene protons at δ 2.11 (−CH_2-cyclohexyl) caused 4.7% enhancement of methylene protons at δ 2.43 (-CH_2-SiEt$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) (*Z* isomer) δ 144.4, 143.5, 136.1, 133.2, 129.7, 126.9, 126.8, 125.0, 124.7, 42.3, 36.3, 33.2, 26.6, 26.3, 21.2, 7.2, 3.6; MS (EI) *m*/*z* (relative intensity, %) 404 (M^+, 100), 375 (16), 116 (10), 115 (75), 87 (33), 59 (10); HRMS calcd for $C_{28}H_{40}Si$: 404.2899, found 404.2904. Anal. Calcd for $C_{14}H_{40}Si$: C, 83.10; H, 9.96. Found: C, 82.72; H, 9.81.

(*E*)-1-Cyclohexyl-2,3-di(phenylmethyl)-4-triethylsilyl-2-butene (10). To a mixture of 2,3-dibenzyl-1,3-butadiene (230 mg, 0.98 mmol), cyclohexyl bromide (326 mg, 2.00 mmol), Et_3SiCl (323 mg, 2.14 mmol), and ^{n}BuMgCl (0.90 M in THF, 3.33 mL, 3.00 mmol) was added Cp_2TiCl_2 (14 mg, 0.06 mmol) at 0 °C. After stirring for 4 h, similar workup gave an orange crude product (95% NMR yield). Purification by silica gel column chromatography with hexane as an eluent afforded 391 mg (92%) of **10** as a mixture of stereoisomers (*E*/*Z* = 80/20): IR (neat) 2921, 2874, 2851, 734, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) (*E* isomer) δ 7.30−7.17 (m, 10H), 3.42 (s, 4H), 1.95 (d, J = 7.1 Hz, 2H), 1.72−1.63 (m, 6H), 1.58 (s, 2 H), 1.49−1.46 (m, 1H), 1.26−1.10 (m, 4H), 0.95 (t, J = 7.9 Hz, 9H), 0.60 (q, J = 7.9 Hz, 6H); NOE difference measurement: irradiation of methylene protons at δ 1.95 (-CH_2-cyclohexyl) caused 3.8% enhancement of the benzyl protons at δ 3.42, while no enhancement was observed for methylene protons at δ 1.58 (-CH_2−SiEt$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) (*E* isomer) δ 140.9, 140.7, 131.9, 129.5, 128.3, 128.2, 127.9, 127.8, 125.5, 125.4, 39.4, 39.0, 38.1, 37.9, 33.7, 26.6, 26.5, 17.9, 7.5, 4.3; MS (EI) *m*/*z* (relative intensity, %) 432 (M^+, 82), 403 (13), 349 (5), 225 (10), 163 (6), 143 (5), 129 (4), 116 (13), 115 (100), 91 (11), 87 (41), 59 (13); HRMS calcd for $C_{30}H_{44}Si$: 432.3212, found 432.3216. Anal. Calcd for $C_{30}H_{44}Si$: C, 83.26; H, 10.25. Found: C, 83.39; H, 10.32.

6-Phenyl-6-triethylsilyl-1-hexene (18). To a mixture of styrene (96 mg, 0.92 mmol), (bromomethyl)cyclopropane (137 mg, 1.02 mmol), Et_3SiCl (155 mg, 1.03 mmol), and ^{n}BuMgCl (0.90 M in THF, 2.3 mL, 2.07 mmol) was added Cp_2TiCl_2 (11 mg, 0.04 mmol) at 0 °C under nitrogen. After stirring for 1 h, similar workup gave an orange crude product (49% NMR yield). Purification by HPLC with $CHCl_3$ as an eluent afforded 81 mg (32%) of **18**. IR (neat) 3023, 2952, 2934, 2875, 1450, 769, 714, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.03 (m, 5H), 5.73 (tdd, J = 6.6, 10.3, 18.5 Hz, 1H), 4.94 (d, J = 18.5 Hz, 1H), 4.89 (d, J = 10.3 Hz, 1H), 2.14 (dd, J = 3.2, 12.4 Hz, 1H), 2.08−1.91 (m, 2H), 1.89−1.79 (m, 1H), 1.77−1.66 (m, 1H), 1.45−1.34 (m, 1H), 1.29−1.14 (m, 1H), 0.87 (t, J = 7.8 Hz, 9H), 0.49 (q, J = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 138.7, 127.9, 127.8, 124.1, 114.1, 34.0 33.7, 29.3, 28.7, 7.7, 2.5; MS (EI) *m*/*z* (relative intensity, %) 274 (M^+, 0.5), 246 (21), 245 (100), 217 (6), 115 (15); HRMS calcd for $C_{18}H_{30}Si$: 274.2117, found 274.2110. Anal. Calcd for $C_{18}H_{30}Si$: C, 78.75; H, 11.02. Found: C, 78.45; H, 11.03.

[Phenyl(trimethylsilyl)methyl]cyclopentane (21). To a mixture of 6-bromo-1- phenyl-1-hexene (189 mg, 0.79 mmol), Me_3SiCl (250 mg, 2.31 mmol), and Cp_2TiCl_2 (12 mg, 0.05 mmol) was added THF solution of ^{n}BuMgCl (0.90 M, 2.44 mL, 2.20 mmol). After stirring for 1 h, similar workup gave an orange crude product (87% NMR yield). Purification by HPLC with $CHCl_3$ as an eluent afforded 156 mg (85%) of **21**. IR (neat) 3021, 2952, 2869, 1248, 859, 835, 743, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.17 (m, 2H), 7.07−6.99 (m, 3H), 2.36−2.25 (m, 1H), 1.94−1.92 (m, 1H), 1.83 (d, J = 11.2 Hz, 1H), 1.71−1.32 (m, 5H), 1.25−1.13 (m, 1H), 0.99−0.89 (m, 1H), −0.066 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 127.9, 127.7, 124.0, 43.9, 42.7, 34.4, 33.4, 25.7, 24.2, −1.13; MS (EI) *m*/*z* (relative intensity, %) 232 (M^+, 16), 158 (53), 135 (12), 91 (8), 74 (11), 73 (100); HRMS calcd for $C_{15}H_{24}Si$: 232.1647, found 232.1649. Anal. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41. Found: C, 77.68; H, 10.61.

1-Cyclohexyl-2,3-dimethyl-4-deuterio-2-butene (28a) and 4-Cyclohexyl-2,3-dimethyl-3-deuterio-1-butene (28b). To a mixture of 2,3-dimethyl-1,3-butadiene (158 mg, 1.93 mmol), cyclohexyl bromide (367 mg, 2.26 mmol), and ^{n}BuMgCl (0.90 M in THF, 4.90 mL, 4.40 mmol) was added Cp_2TiCl_2 (26 mg, 0.11 mmol) at 0 °C under nitrogen. After stirring for 1 h, ca. 2 mL of D_2O was added to the solution at 0 °C. Similar workup gave an orange crude product (77% NMR yield).

Purification by HPLC with $CHCl_3$ as an eluent afforded 205.2 mg (64%) of product as a mixture of **28a** and **28b**. IR (neat) 2921, 2851, 1642, 1448, 1373, 1151, 887 cm^{-1}; MS (EI) *m*/*z* (relative intensity, %) 167 (M^+, 62), 123 (25), 85 (100), 71 (54), 70 (42), 56 (35), 55 (78), 42 (12), 41 (31); HRMS calcd for $C_{12}H_{21}D$: 167.1783, found 167.1781. Anal. Calcd for $C_{12}H_{21}D$: C, 86.14; H and D, 13.86 Found: C, 85.88; H and D, 13.52. An aliquot of the mixture was subjected to HPLC again using $CHCl_3$ as an eluent in order to separate these isomers. **28a**: ^1H NMR (400 MHz, $CDCl_3$) δ 1.91 (d, J = 7.32 Hz, 2H), 1.66−1.61 (m, 13H), 1.40−1.37 (m, 1H), 1.24−1.11 (m, 3H), 0.96−0.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.4, 124.5, 42.3, 37.1, 33.6, 26.9, 26.7, 20.7, 20.5 (t, J = 19.4 Hz), 19.1. **28b**: ^1H NMR (400 MHz, $CDCl_3$) δ 4.66 (s, 2H), 1.74−1.64 (m, 8H), 1.29−1.04 (m, 6H), 0.96 (s, 3H), 0.90−0.77 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 109.0, 43.0, 37.6 (t, J = 19.7 Hz), 35.2, 33.9, 33.5, 26.9, 26.6, 20.2, 18.8.

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