Selected Paper

Titanocene-Catalyzed Alkylation of Aryl-Substituted Alkenes with Alkyl Halides

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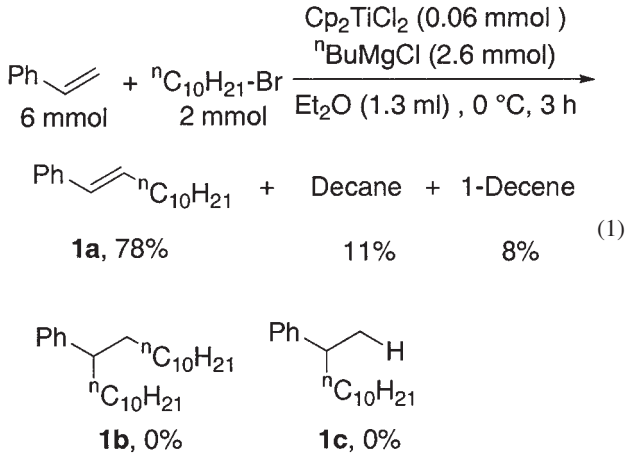
Aryl-substituted alkenes (ArHC=CH_2) react with alkyl halides (R–X, X = Br or Cl) in the presence of a catalytic amount of [Cp_2TiCl_2] and ^{n}BuMgCl in Et_2O to give alkylated alkenes (ArHC=CHR). This reaction proceeds regio- and stereoselectively under mild conditions to afford *E*-olefins. Primary and secondary alkyl bromides and secondary alkyl chlorides can be used as suitable alkylating reagents. The reactions of aliphatic alkenes, such as 1-octene and internal alkenes, were sluggish. When *t*-alkyl halides are employed, alkylative dimerization of alkenes proceeds exclusively to give symmetrical *vic*-diarylalkanes. These reactions involve addition of alkyl radicals to arylalkenes to form benzyl radicals as a carbon–carbon bond-forming step. Dimerization of thus formed benzyl radicals affords symmetrical alkanes and β-hydrogen elimination from benzyltitanocene intermediates gives alkylated alkenes. A possibility that titanocene activates alkenes as radical accepters was also proposed.

The Mizoroki–Heck reaction provides a useful method for preparation of substituted alkenes[1] by way of introducing aryl, alkenyl, benzyl, allyl, and alkynyl groups at the vinylic carbons. However, this reaction, in general, cannot be applied for introduction of alkyl groups having one or more β-hydrogen(s) due to the facile β-hydrogen elimination from the σ-alkylpalladium intermediate.[2] In terms of this type of transformation that uses alkyl halides, regardless of the mechanisms, a few catalytic systems have been developed by the aid of late transition metals such as nickel[3] and cobalt.[4] During the course of our study on early transition metal-catalyzed alkylation of alkenes,[5] we found that titanocene catalyzes a Mizoroki–Heck type transformation of arylalkenes with alkyl halides in the presence of ^{n}BuMgCl and some representative results were reported.[6] Herein, we wish to reveal experimental details as well as the scope and limitations of this reaction and to discuss its reaction pathway. Alkylative dimerization of styrenes is also described.

Results

Into a mixture of 1-bromodecane (2 mmol), styrene (3.0 equiv), and a catalytic amount of [Cp_2TiCl_2] (0.03 equiv) was added an ether solution of ^{n}BuMgCl (2 M, 1.3 mL, 1.3 equiv); this solution was stirred for 3 h at 0 °C under nitrogen. The NMR analysis of the crude mixture indicated the formation of (*E*)-1-phenyl-1-dodecene (**1a**) in 78% yield based on alkyl bromide with >98% regio- and stereoselectivity. The product was obtained in pure form in 63% yield along with decane and 1-decene in 11% and 8% yields, respectively (Eq. 1).[7] When only one equivalent of styrene was used, the yield of **1a** decreased to 52% and those of decane and 1-decene increased to 25% and 18% yields, respectively. We have already reported that double alkylation[5a] of arylalkenes took place in THF under similar conditions; however, such an addition product (**1b**) was not formed in ether. Under the same conditions, 1-chlorodecane and 1-iododecane were ineffective. Since it is also known that [Cp_2ZrCl_2] catalyzes hydroalkylation[5b,8] of arylalkenes using alkyl bromides and Grignard reagents in THF at 50 °C, we checked the resulting mixture carefully but no evidence for the presence of hydroalkylation product (**1c**) was detected.



(1)

The use of other primary bromides afforded the corresponding products (**2**–**5**, Chart 1) with perfect regio- and stereoselec-

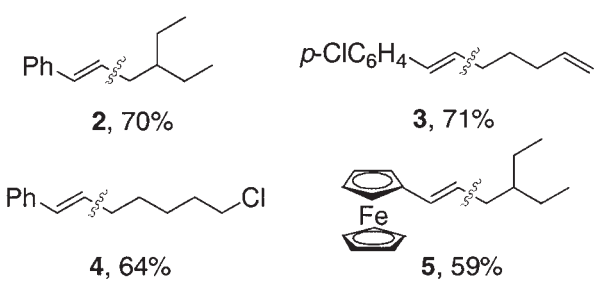


Chart 1.

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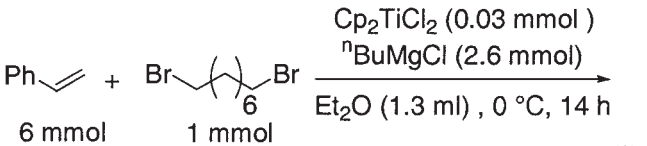
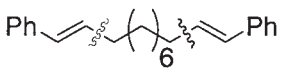
tivities under similar conditions to those for Eq. 1. The reactions of internal alkenes and 1-alkenes bearing no aryl group are sluggish. This feature enabled successful introduction of carbon chains having a carbon–carbon double bond to give rise to **3** in 71% yield. The results that **3** and **4** were obtained in good yields show that chloro substituents on sp^2- and primary sp^3-carbons were not affected in this reaction system. Vinylferrocene also underwent alkylation to give **5** in 59% yield. When 1,8-dibromooctane was employed, two styryl groups could be introduced, one at each of the terminal carbons, affording **6** in 40% isolated yield after HPLC purification (Eq. 2).

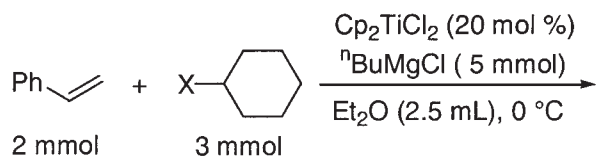


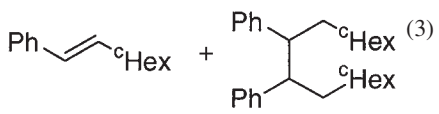
(2)



6, 40%

When secondary alkyl bromides were employed, a similar reaction proceeded, but it competed with a different reaction. For example, cyclohexyl bromide gave the corresponding product **7** in 46% yield along with 28% of **8** as a 1:1 mixture of diastereomers under the same conditions as those for Eq. 1. However, the use of a large amount of the titanocene catalyst (20 mol%) and 1.5 equivalents of bromide increased the yield of **7** to 84% (based on styrene) and suppressed the formation of **8** (8%). This reaction also proceeded with cyclohexyl chloride to give **7** in 65% yield, although longer reaction time (72 h) was required (Eq. 3).





(3)

X	**7**	**8**
Br	84%	8%
Cl	65%	5%

The product ratio of **7** over **8** was plotted against the amounts of the titanocene catalyst in Fig. 1. Increasing the titanocene catalyst leads to the preferred formation of **7** and the ratio obeys first-order kinetics on the concentration of the catalyst. This result affords important information about the reaction mechanisms (vide infra).

It is also noteworthy that an alkylative dimerization product **9** was obtained in 53% yield (based on styrene) as the sole product when *t*-butyl bromide was employed (Eq. 4).

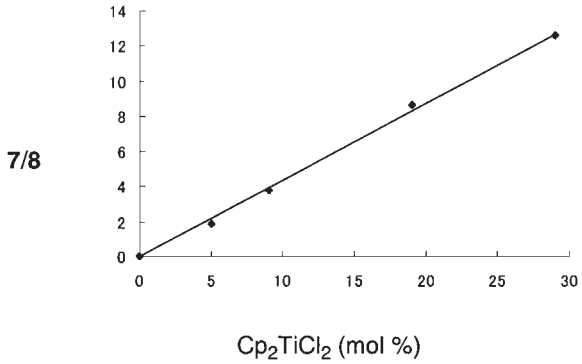
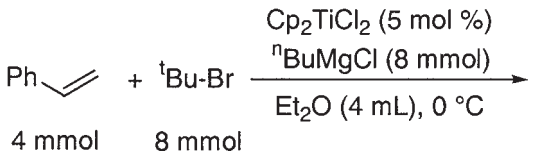
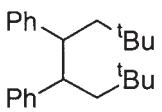


Fig. 1. A plot of **7**/**8** for the amount of titanocene catalyst. The reactions were run in the presence of 5, 9, 19, and 30 mol% of [Cp_2TiCl_2], 2 mmol of styrene, 1.5 equiv of cyclohexyl bromide, 2.5 equiv of ^{n}BuMgCl in 5 mL of Et_2O at 0 °C.

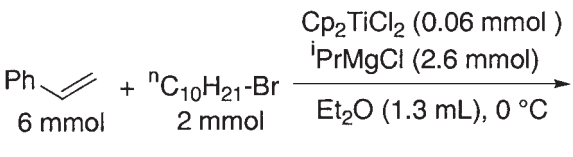


(4)

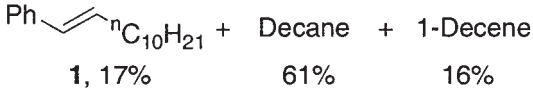


9, 53% (a 1:1 mixture of diastereomers)

This result is in accordance with the known evidence that [Cp_2TiH], which can be generated from [Cp_2TiCl_2] and isopropyl Grignard reagent under similar conditions, catalyzes hydromagnesiation[9] of alkynes, dienes, and alkenes or reduction[7] of alkyl halides. When a reaction of styrene with decyl bromide was performed by using ^{i}PrMgCl instead of ^{n}BuMgCl, the desired product **1a** was obtained in only 17% yield and the reduction of 1-bromodecane proceeded predominantly to give decane and 1-decene in 61% and 16% yields, respectively (Eq. 5).

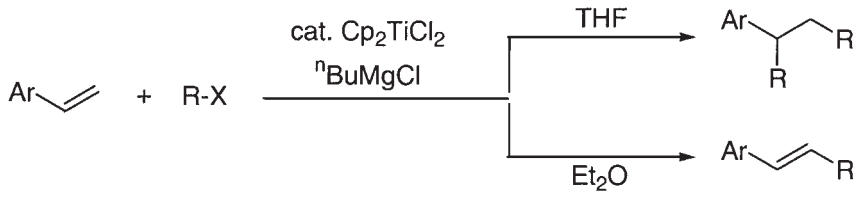


(5)



Discussion

We have revealed that arylalkenes react with alkyl halides in the presence of [Cp_2TiCl_2] and ^{n}BuMgCl to give dialkylated products when the reaction was performed in THF and that this reaction involves addition of alkyl radicals to arylalkenes. Change of the solvent from THF to ether drastically changed the reaction course as shown in this report (Scheme 1). The formation of **9** (Eq. 4) can reasonably be explained by the coupling of a benzyl radical formed by the addition of a *t*-butyl radical to



Scheme 1.

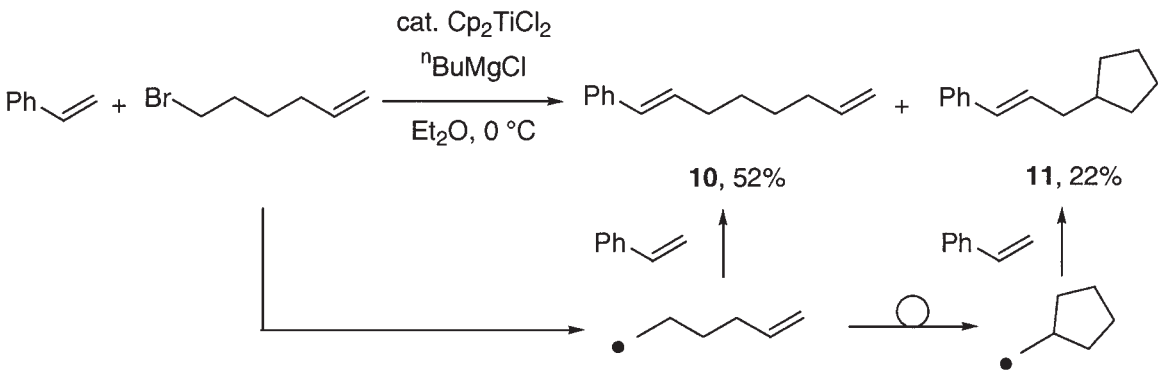


Chart 2.

styrene. Similar Mizoroki–Heck type transformations using Co[4] were explained by radical mechanisms. Taking into account these examples, we would like to propose that the present reaction also likely involves radical intermediates.

In order to examine the possibility of this radical mechanism, a reaction of styrene with 6-bromo-1-hexene was carried out. This reaction afforded cyclopentylmethyl substituted styrene **11** in 22% yield along with direct alkylation product **10** in 52% yield (Chart 2). The formation of **11** strongly support a radical mechanism, i.e., 5-exo cyclization of the 5-hexenyl radical to cyclopentylmethyl radical which then adds to styrene to form a carbon–carbon bond.[10]

To examine the role of titanocene complex in this process, we then carried out the reaction of styrene with 6-bromo-1-hexene in the presence of different amounts of the titanocene catalyst and the ratio of **10** over **11** was plotted against the amount of [Cp_2TiCl_2] used in Fig. 2. It should be noted that the formation of **10** was favored under higher concentration of the titanocene catalyst and a simple linear correlation was obtained. If

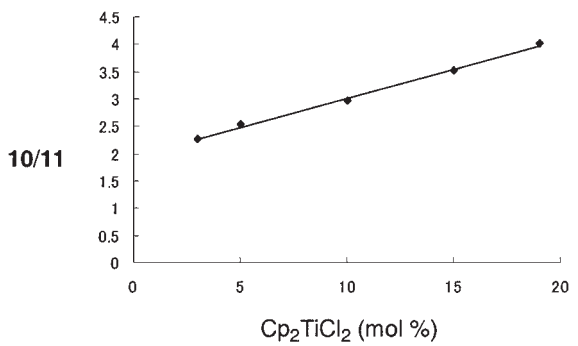
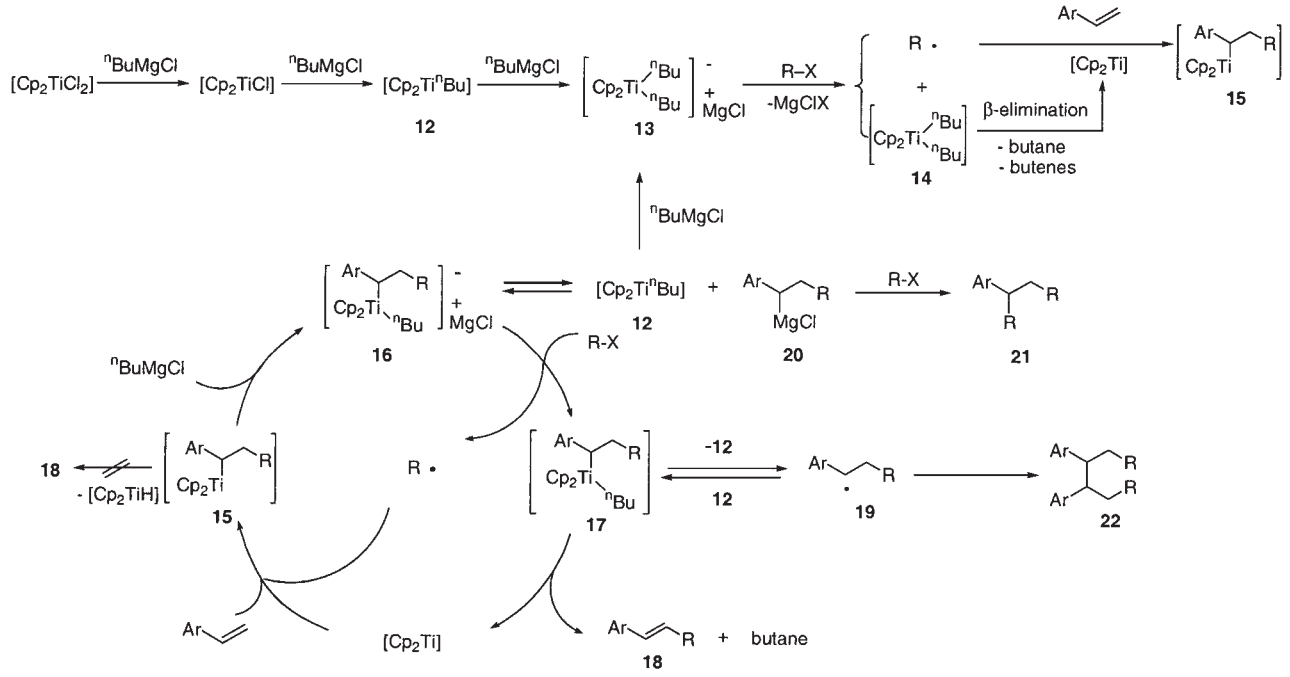


Fig. 2. A plot of **10**/**11** for the amount of titanocene catalyst. The reactions were run in the presence of 3, 5, 10, 15, and 19 mol% of [Cp_2TiCl_2], 1 equiv of 5-hexenyl bromide, 3 equiv of styrene, 1.3 equiv of ^{n}BuMgCl in 1.3 mL of Et_2O at 0 °C for 30 min.

intermolecular cyclization of 5-hexenyl radical competes with its addition to styrene, this interesting phenomenon suggests that titanocene accelerates the addition of 5-hexenyl radical toward styrene, implying the possibility that a titanocene complex activates the double bond toward radical addition to alkenes via complexation.

Reaction Pathways. Taking into account the above results as well as the evidence shown below, we propose a possible reaction pathway in Scheme 2, where the dialkyltitanate(Ⅲ) species[11] serves as the key intermediate. Titanocene dichloride reacts with ^{n}BuMgCl to afford dibutyltitanate(Ⅲ) complex (**13**) via [Cp_2TiCl][12] and butyltitanocene (**12**).[13] One electron transfer from **13** to alkyl halide gives an alkyl radical along with dibutyltitanocene (**14**), which readily forms [Cp_2Ti(Ⅱ)] via β-hydrogen elimination.[14] The successive addition of the thus formed alkyl radical to a [Cp_2Ti(Ⅱ)]–alkene complex or to free alkene, followed by the reaction with [Cp_2Ti], affords the benzyltitanium complex (**15**). This process constitutes the initiation step, and **15** promotes the catalytic cycle of the present alkylation in a similar way via benzylbutyltitanate(Ⅲ) complex (**16**) and benzylbutyltitanocene (**17**). Product (**18**) is formed by the siteselective β-hydrogen elimination from **17**. Although it is also possible that **15** undergoes β-hydrogen elimination leading to **18**, this pathway seems unlikely because this process forms the [Cp_2TiH], which should give reduction products of alkyl halides (vide supra).

The fact that the use of ^{t}BuBr exclusively afforded a coupling product **22** (R = ^{t}Bu) instead of the corresponding substitution product **18** can reasonably be understood by assuming the equilibrium between **17** and **19** + **12**. The steric bulkiness of R would shift this equilibrium toward **19** and also retard the β-elimination leading to **18**. As the result, dimerization of **19** to **22** predominates. This hypothesis also explains the result shown in Fig. 1, i.e., higher concentration of the Ti catalyst shifts this equilibrium toward **17**, resulting in the suppression of the formation of **22**.



Scheme 2.

Finally, we should refer to the unique effect of solvents in this $[Cp_2TiCl_2]/^n$BuMgCl catalytic system, i.e., ether affords substitution products **18**, whereas *vic*-dialkylated products **21** are obtained in THF.[5a] We think that in either solvent, **16** is formed as a common intermediate which then undergoes electron transfer in ether or transmetallation in THF. This different behavior of **16** might be explained by assuming a equilibrium between **16** and **12** + **20**. Benzylmagnesium chloride (**20**) reacts with alkyl halides to give **21** only in a strongly coordinating solvent such as THF. In ether, **20** does not react with alkyl halides and recombines with $[Cp_2Ti^nBu]$, to regenerate **16**, which transfers an electron to alkyl halides to give **17**. This is in accordance with the fact that double alkylation in THF is complete within an hour, but the present substitution reaction is relatively slower and requires a few hours or longer reaction time.

Conclusions

A new method for substitution of a vinylic hydrogen with an alkyl group (a Mizoroki–Heck type transformation) was developed by a titanocene catalyst in the presence of ^{n}BuMgCl. This reaction can proceed regio- and stereoselectively under mild conditions to afford *E*-olefins using primary and secondary alkyl halides. The Ti catalyst would play an important role in generation of alkyl radicals from alkyl halides via electron transfer from Ti(Ⅲ) ate complexes and in reconstruction of carbon–carbon double bonds by β-hydrogen elimination from Ti(Ⅳ) intermediates. A possibility that titanocene activates carbon–carbon double bonds toward alkyl radical attack is proposed. It was also revealed that use of tertiary alkyl halides affords alkylative homocoupling of styrenes to form symmetrical *vic*-diarylalkanes.

Experimental

General Methods. THF was distilled just before use from sodium diphenylketyl. Grignard reagents, titanocene dichloride, arylalkenes, and alkyl halides are 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]

(*E*)-1-Phenyl-1-dodecene (1a). Into a 10-mL glass vessel containing styrene (631 mg, 6.06 mmol), 1-bromodecane (452 mg, 2.04 mmol), and ^{n}BuMgCl (2.0 M in ether, 1.3 mL, 2.60 mmol) cooled at 0 °C was added $[Cp_2TiCl_2]$ (18 mg, 0.07 mmol) under nitrogen. After stirring for 3 h, ca. 2 mL of 3 M HClaq (5 mL) was added to the solution at 0 °C; the mixture was warmed to room temperature and a saturated aqueous NH_4Cl solution (50 mL) was added. The product was extracted with ether (50 mL), dried over $MgSO_4$, and evaporated to give an orange crude product (78% NMR yield based on 1-bromodecane). Purification by HPLC with $CHCl_3$ as the eluent afforded 314 mg (63%) of **1a**. IR (neat) 3025, 2955, 2924, 2853, 1466, 962, 742, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.16 (m, 5H), 6.37 (d, J = 15.9 Hz, 1H), 6.22 (dt, J = 15.9, 6.6 Hz, 1H), 2.20 (dt, J = 6.9, 6.6 Hz, 2H), 1.48–1.42 (m, 2H), 1.30–1.27 (m, 14H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 131.1, 129.5, 128.3, 126.6, 125.7, 33.2, 32.1, 29.8, 29.7, 29.56, 29.49, 29.39, 29.35, 22.9, 14.3; MS (EI) m/z (relative intensity, %) 244 (M^+, 100), 243 (30), 242 (27), 241 (11), 117 (28); HRMS calcd for $C_{18}H_{28}$ 244.2191, found 224.2192; Anal. Calcd for $C_{18}H_{28}$: C, 88.45; H, 11.55%. Found: C, 88.28; H, 11.72%.

(*E*)-4-Ethyl-1-phenyl-1-hexene (2). A mixture of styrene (647 mg, 6.21 mmol), 1-bromo-2-ethylbutane (327 mg, 1.98 mmol), and ^{n}BuMgCl (2 M in ether, 1.3 mL, 2.60 mmol) was cooled to 0 °C, and $[Cp_2TiCl_2]$ (16 mg, 0.06 mmol) was added. After stirring for 3.5 h, ca. 2 mL of 3 M HClaq was added to the solution at 0 °C. Similar workup to that mentioned above afforded an orange crude product (70% NMR yield). Purification by HPLC gave 203 mg (54%) of **2**. IR (neat) 3025, 2961, 2929, 2873, 1459, 965, 734, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.08 (m, 5H), 6.29 (d, J = 15.9 Hz, 1H), 6.12 (dt, J = 15.9, 7.3 Hz, 1H), 2.10 (t, J = 7.3 Hz, 2H), 1.29–1.24 (m, 5H), 0.81 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 130.6, 129.6, 128.3,

126.6, 125.7, 41.2, 36.6, 25.6, 11.2; MS (EI) m/z (relative intensity, %) 188 (M^+, 100), 187 (19), 117 (57), 115 (13); HRMS calcd for $C_{14}H_{20}$ 188.1565, found 188.1571; Anal. Calcd for $C_{14}H_{20}$: C, 89.30; H, 10.71%. Found: C, 88.88; H, 10.35%.

(*E*)-1-Chloro-4-(1,6-heptadienyl)benzene (3). To a mixture of *p*-chlorostyrene (872 mg, 2.87 mmol), 1-bromo-4-pentene (327 mg, 2.19 mmol), and ^{n}BuMgCl (2 M in ether, 1.3 mL, 2.60 mmol) was added [Cp_2TiCl_2] (15 mg, 0.06 mmol) at 0 °C under nitrogen. After stirring for 6.5 h, ca. 2 mL of 3 M HClaq was added to the solution at 0 °C. Similar workup to that mentioned above afforded an orange crude product (71% NMR yield). Purification by HPLC gave 289 mg (64%) of **3**. IR (neat) 2928, 1490, 1092, 965, 912 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (br s, 4H), 6.31 (d, $J = 15.9$ Hz, 1H), 6.17 (dt, $J = 15.9$, 6.8 Hz, 1H), 5.82 (ddt, $J = 17.8$, 10.3, 6.8 Hz, 1H), 5.02 (dd, $J = 17.8$, 1.5 Hz, 1H), 4.97 (dd, $J = 10.3$, 1.5 Hz, 1H), 2.20 (dt, $J = 6.8$, 7.8 Hz, 2H), 2.10 (dt, $J = 6.8$, 7.1 Hz, 2H), 1.55 (quintet, $J = 7.1$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 136.1, 132.1, 131.2, 128.7, 128.4, 127.1, 114.6, 33.3, 32.5, 28.6; MS (EI) m/z (relative intensity, %, ^{35}Cl) 206 (M^+, 35), 171 (100), 138 (63), 129 (69), 115 (76), 91 (40); HRMS calcd for $C_{13}H_{15}Cl$ (^{35}Cl) 206.0862, found 206.0863; Anal. Calcd for $C_{13}H_{15}Cl$: C, 75.54; H, 7.31%. Found: C, 75.35; H, 7.51%.

(*E*)-7-Chloro-1-phenyl-1-heptene (4). To a mixture of styrene (650 mg, 6.24 mmol), 1-bromo-5-chloropentene (392 mg, 2.11 mmol), and ^{n}BuMgCl (2 M in ether, 1.3 mL, 2.60 mmol) was added [Cp_2TiCl_2] (15 mg, 0.06 mmol) at 0 °C under nitrogen. After stirring for 6 h, ca. 2 mL of 3 M HClaq was added to the solution at 0 °C. Similar workup to that mentioned above afforded an orange crude product (64% NMR yield). Purification by HPLC gave 211 mg (48%) of **4**. IR (neat) 3025, 2976, 2928, 2856, 1640, 1490, 1092, 1012, 992, 965, 912, 839, 821, 797 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.17 (m, 5H), 6.38 (d, $J = 15.9$ Hz, 1H), 6.21 (dt, $J = 15.9$, 6.8 Hz, 1H), 3.54 (t, $J = 6.8$ Hz, 2H), 2.24–2.22 (m, 2H), 1.81 (t, $J = 6.8$ Hz, 2H), 1.54–1.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 130.4, 129.9, 128.3, 126.7, 125.8, 45.1, 32.9, 32.6, 28.7, 26.6; MS (EI) m/z (relative intensity, %, ^{35}Cl) 208 (M^+, 78), 117 (100), 115 (56), 104 (62), 91 (37); HRMS calcd for $C_{13}H_{17}Cl$ (^{35}Cl) 208.1019, found 208.1017; Anal. Calcd for $C_{13}H_{17}Cl$: C, 74.81; H, 8.21%. Found: C, 74.77; H, 8.29%.

(*E*)-(4-Ethyl-1-hexenyl)ferrocene (5). To a mixture of vinylferrocene (639 mg, 3.01 mmol), 1-bromo-2-ethylbutane (170 mg, 1.03 mmol), and ^{n}BuMgCl (2 M in ether, 0.65 mL, 1.30 mmol) was added [Cp_2TiCl_2] (10 mg, 0.04 mmol) at 0 °C under nitrogen. After stirring for 5 h, ca. 2 mL of 3 M HClaq was added to the solution at 0 °C. Similar workup to that mentioned above afforded an orange crude product (59% NMR yield). Purification by HPLC gave 140 mg (46%) of **5**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.07 (d, $J = 15.6$ Hz, 1H), 5.76 (dt, $J = 15.6$, 7.3 Hz, 1H), 4.29 (s, 2H), 4.15 (s, 2H), 4.09 (s, 5H), 2.04 (dd, $J = 7.3$, 6.1 Hz, 2H), 1.37–1.23 (m, 5H), 0.89 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.4, 126.7, 84.3, 69.0, 68.1, 66.3, 41.1, 36.5, 25.6, 11.3; MS (EI) m/z (relative intensity, %) 296 (M^+, 100), 225 (12), 224 (16), 223 (14); HRMS calcd for $C_{18}H_{24}Fe$ 296.1227, found 296.1228; Anal. Calcd for $C_{18}H_{24}Fe$: C, 72.98; H, 8.16%. Found: C, 72.88; H, 8.25%.

(*E*)-1,12-Diphenyl-1,11-dodecadiene (6). To a mixture of styrene (615 mg, 5.91 mmol), 1,8-dibromooctane (266 mg, 0.98 mmol), and ^{n}BuMgCl (2 M in ether, 1.3 mL, 2.60 mmol) was added [Cp_2TiCl_2] (5 mg, 0.02 mmol) at 0 °C under nitrogen. After stirring for 14 h, ca. 2 mL of 3 M HClaq was added to the solution at 0 °C. Similar workup to that mentioned above and purification by HPLC gave 125 mg (40%) of **6**. IR (KBr) 2918, 2844, 1463, 1448, 964, 746, 732, 687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.15 (m, 10H), 6.37 (d, $J = 15.9$ Hz, 2H), 6.21 (dt, $J = 15.9$, 6.8 Hz, 2H), 2.19 (dt, $J = 6.8$, 6.9 Hz, 4H), 1.50–1.44 (m, 4H), 1.33–1.31 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 131.0, 129.6, 128.3, 126.6, 125.7, 33.2, 29.6, 29.5, 29.3; MS (EI) m/z (relative intensity, %) 318 (M^+, 100), 129 (40), 117 (71), 115 (69), 104 (33), 91 (46); HRMS calcd for $C_{24}H_{30}$ 318.2348, found 318.2353; Anal. Calcd for $C_{24}H_{30}$: C, 90.51; H, 9.49%. Found; C, 90.30; H, 9.49%.

(*E*)-(2-Cyclohexylethenyl)benzene (7). In a manner similar to that described for preparation of **1** using styrene (209 mg, 2.01 mmol), cyclohexyl bromide (484 mg, 2.97 mmol), and ^{n}BuMgCl (2.0 M in ether, 2.5 mL, 5.0 mmol) and [Cp_2TiCl_2] (103 mg, 0.41 mmol), an orange crude product (84% NMR yield based on styrene) was obtained. Purification by HPLC with $CHCl_3$ as the eluent afforded **7** as colorless liquid (264 mg, 71% yield). IR (neat) 3025, 2924, 2851, 1448, 964, 745, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.15 (m, 5H), 6.34 (d, $J = 15.9$ Hz, 1H), 6.17 (dd, $J = 15.9$, 6.9 Hz, 1H), 2.16–2.08 (m, 1H), 1.82–1.74 (m, 4H), 1.69–1.66 (m, 1 H), 1.38–1.12 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 136.6, 128.3, 127.1, 126.6, 125.8, 41.2, 33.1, 26.3, 26.2; MS (EI) m/z (relative intensity, %) 186 (M^+, 66), 129 (21), 128 (19), 115 (22), 104 (100), 91 (16); HRMS calcd for $C_{14}H_{18}$ 186.1409, found 186.1421; Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%. Found: C, 90.12; H, 9.71%.

Preparation of 7 Using Cyclohexyl Chloride. To a mixture of styrene (221 mg, 2.12 mmol), cyclohexyl chloride (353 mg, 2.98 mmol), and ^{n}BuMgCl (2 M in ether, 2.5 mL, 5 mmol) was added [Cp_2TiCl_2] (74 mg, 0.33 mmol) at 0 °C under nitrogen. After stirring for 72 h, ca. 2 mL of 3 M HClaq was added to the solution at 0 °C. Similar workup to that mentioned above afforded an orange crude product (65% NMR yield).

1,4-Dicyclohexyl-2,3-diphenylbutane (8). To a mixture of styrene (927 mg, 8.90 mmol), cyclohexyl bromide (480 mg, 2.94 mmol), and ^{n}BuMgCl (2 M in ether, 1.95 mL, 3.90 mmol) was added [Cp_2TiCl_2] (23 mg, 0.09 mmol) at 0 °C under nitrogen. After stirring for 24 h, a 1:1 mixture of diastereomers **8** (28% GC yield based on styrene) was obtained along with **7** (46% NMR yield based on styrene). One of diastereomers was isolated in 7% yield (38 mg) by recrystallization as white crystal. IR (KBr) 2919, 2853, 1444, 758, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.13 (m, 10H), 2.77–2.74 (m, 2H), 1.71–1.68 (m, 2H), 1.55–0.50 (m, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 128.2, 127.9, 125.7, 49.5, 42.4, 34.7, 34.6, 31.8, 26.7, 26.3, 26.1; MS (EI) m/z (relative intensity, %) 188 (47), 187 (100), 106 (65), 92 (29); HRMS calcd for $C_{28}H_{38}$ 374.2974, found 374.2968; Anal. Calcd for $C_{28}H_{38}$: C, 89.78; H, 10.22%. Found: C, 89.56; H, 10.14%.

2,2,7,7-Tetramethyl-4,5-diphenyloctane (9). To a mixture of styrene (417 mg, 4.00 mmol), *t*-butyl bromide (821 mg, 5.99 mmol), and ^{n}BuMgCl (2 M in ether, 4 mL, 8 mmol) was added [Cp_2TiCl_2] (50.4 mg, 0.20 mmol) at 0 °C under nitrogen. After stirring for 10 h, ca. 2 mL of 3 M HClaq was added to the solution at 0 °C. Similar workup to that mentioned above afforded an orange crude product (53% NMR yield based on styrene). Purification by HPLC gave 238 mg (37%) of **9**. IR (KBr) 3026, 2954, 2864, 1495, 1474, 1452, 1364, 761, 701, 592 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.05 (m, 10H), 2.74–2.70 (m, 2H), 1.59–1.52 (m, 2H), 1.45–1.37 (m, 2H), 0.56 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 129.2, 127.6, 125.6, 50.3, 46.9, 31.1, 30.28, 30.25, 30.22; MS (EI) m/z (relative intensity, %)

161 (31), 160 (100), 145 (17), 105 (86), 57 (71); HRMS calcd for $C_{24}H_{34}$ 322.2661, found 322.2632; Anal. Calcd for $C_{24}H_{34}$: C, 89.37; H, 10.63%. Found: C, 89.32; H, 10.63%.

(*E*)-(3-Cyclopentyl-1-propenyl)benzene (11). To a mixture of styrene (613 mg, 2.87 mmol), 6-bromo-1-hexene (334 mg, 2.05 mmol), and ^{n}BuMgCl (2 M in ether, 1.3 mL, 2.6 mmol) was added [Cp_2TiCl_2] (17 mg, 0.07 mmol) at 0 °C under nitrogen. After stirring for 3 h, ca. 2 mL of 3 M HClaq was added to the solution at 0 °C. Similar workup to that mentioned above afforded 22% NMR yield of **11** along with 52% NMR yield of **10**. Purification by HPLC gave 65 mg (17%) of **11**. IR (neat) 3025, 2949, 2866, 963, 741, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.16 (m, 5H), 6.37 (d, $J = 15.9$ Hz, 1H), 6.23 (dt, $J = 15.9$, 7.1 Hz, 1H), 2.21 (dd, $J = 7.1$, 7.5 Hz, 2H), 1.98–1.88 (quintet, $J = 7.5$ Hz, 1H), 1.78–1.76 (m, 2H), 1.62–1.52 (m, 4H), 1.23–1.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 130.4, 130.0, 128.3, 126.6, 125.8, 40.1, 39.5, 32.5, 25.3; MS (EI) m/z (relative intensity, %) 186 (M^+, 100), 118 (22), 117 (92), 115 (46), 104 (80), 91 (25); HRMS calcd for $C_{14}H_{18}$ 186.1409, found 186.1410; Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74%. Found: C, 89.96; H, 9.51%.

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