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Tetrahedron
Tetrahedron 63 (2007) 6635–6641

Nickel-catalyzed dimerization coupling reactions of vinyl Grignard reagents with 3, 4-membered cyclic ethers and chlorosilanes

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Received 15 February 2007; revised 29 March 2007; accepted 9 April 2007
Available online 13 April 2007

Dedicated to the late Emeritus Professor Yoshihiko Ito of Kyoto University

Abstract—Vinyl Grignard reagents reacted with cyclic ethers in the presence of a nickel catalyst giving rise to 2:1 coupling products **1** regioselectively. When chlorosilanes were used instead of cyclic ethers, 2:2 component coupling products **6** were obtained. A plausible reaction pathway via 1,3-butadiene–nickel complex and (2-butene-1,4-diyl)magnesium was proposed.

1. Introduction

Since the discovery of the formation of Grignard reagents by the reaction of organic halides with magnesium metal in 1901,[1a] numerous efforts have been devoted to developing their synthetic applications especially to carbon–carbon bond forming reactions.[1] Epoch-making in this field was the introduction of transition metal catalysts in Grignard chemistry that provided novel synthetic methodologies by cross-coupling reactions.[1e–h] We have been working on C–C and C–Si bond forming reactions using Grignard reagents catalyzed by Zr, Ti, Ni, or Pd involving ate-complex intermediates.[2] During the course of these studies, we have recently found that Ni catalyzes the alkylative dimerization of vinyl Grignard reagents with alkyl fluorides giving rise to 2-alkyl-3-butenyl Grignard reagents.[3] As an extension of this work, we report herein Ni-catalyzed regioselective coupling of vinyl Grignard reagents with cyclic ethers and chlorosilanes to give 2:1 or 2:2 coupling products, respectively.

2. Results and discussion

2.1. Nickel-catalyzed 2:1 coupling reaction of vinyl Grignard reagents with cyclic ethers

A typical example is as follows. To a mixture of cyclopentene oxide (1.0 mmol) and $NiCl_2(PPh_3)_2$ (0.03 mmol) was added vinyl magnesium chloride (2.2 mmol) in THF (1.7 mL) at 25 °C under nitrogen, and the resulting mixture was stirred for 3 h at the same temperature. The NMR analysis of the crude mixture indicated the formation of *trans*-2-(1-methyl-2-propenyl)cyclopentanol **1a** in 79% yield. The product was obtained as 1:1.3 mixture of diastereomers in 66% yield by column chromatography with pentane/ether=6:4 as the eluent (Table 1, entry 1). Entry 2 shows a successful example of large scale preparation (50 mmol of cyclopentene oxide) under the identical conditions, where 5.07 g (72%) of **1a** was obtained in pure form by distillation. When $NiCl_2$ was used instead of $NiCl_2(PPh_3)_2$, **1a** was formed in 62% NMR yield (entry 3). Under the same conditions, $PdCl_2(PPh_3)_2$ and Cp_2TiCl_2 were ineffective (entries 4 and 5). When cyclododecene oxide (trans/cis=33:67) was used, only *cis*-cyclododecene oxide reacted with vinyl Grignard reagent to afford coupling product **1b** as 1:1 mixture of diastereomers (entry 6).[4] Isobutylene oxide gave coupling product **1c** in poor yield (20%) (entry 7). The use of oxetanes also afforded the corresponding 2:1 coupling products **1d** and **1e** in 62% and 50% yields, respectively (entries 8 and 9). However, no reaction took place with substituted vinyl Grignard reagents such as MeCH=CHMgBr, CH_2=CMeMgBr and PhCH=CHMgBr.

When a reaction of cyclopentene oxide with vinyl Grignard reagent was quenched with D_2O, 79% yield of monodeuterated compound **3** (*d*-content 94%) as 1:1.3 mixture of diastereomers was formed. This result implies that the butenyl Grignard reagent **2** is formed in the present reaction. As a synthetic application of thus-formed **2**, we attempted to synthesize bicyclic ester **5** via intramolecular esterification of **4** formed by the reaction of **2** with CO_2. Into a solution of **2** prepared in situ under similar conditions of entry 1 in Table 1, dry ice was added at

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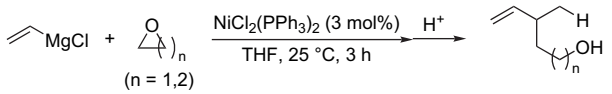
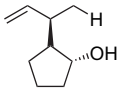
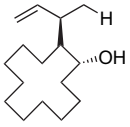
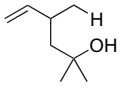
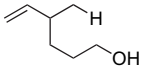
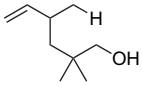
0040–4020/$ - see front matter © 2007 Published by Elsevier Ltd.
doi:10.1016/j.tet.2007.04.013

Table 1. Ni-catalyzed 2:1 coupling reaction of vinyl Grignard reagent with cyclic ethers[a]



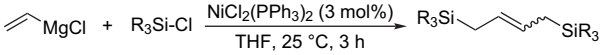
Entry	Epoxide (oxetane)	Product		Yield[b] (%)
1			**1a**	79 (66)
2				(72)[c]
3				62[d]
4				0[e]
5				0[f]
6	 (*trans/cis* = 33/67)		**1b**	66 (61)
7			**1c**	25 (20)[g]
8			**1d**	73 (62)
9			**1e**	64 (50)

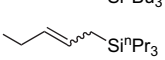
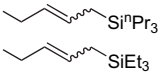
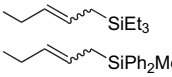
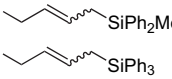
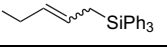
[a] The reaction was carried out in THF at 25 °C for 3 h using epoxide/oxetane (1.0 mmol), vinyl Grignard reagent (2.2 mmol) and $NiCl_2(PPh_3)_2$ (0.03 mmol).
[b] NMR yield. Isolated yield is in parentheses.
[c] Reaction was carried out on a 50 mmol scale.
[d] $NiCl_2$ was used.
[e] Cp_2TiCl_2 was used.
[f] $PdCl_2(PPh_3)_2$ was used.
[g] Reaction was carried out on a 3.0 mmol scale.

25 °C. After treating with 3 N HCl and stirring at 40 °C for 2 h, the desired bicyclic ester **5** was obtained in 37% yield (Eq. 1).

of 77:23. No evidence for the formation of regioisomers of **6a** was detected. The product was obtained in pure form in 66% yield by a recycling preparative HPLC using $CHCl_3$ as an eluent (Table 2, entry 1). In this reaction, tributylvinylsilane was formed in 3% yield as a byproduct probably via the direct reaction of vinyl magnesium chloride with $^nBu_3SiCl$. Other trialkyl and phenyl substituted chlorosilanes afforded the corresponding 2:2 coupling products in good yield (entries 3–6). When Cp_2TiCl_2 was used instead of $NiCl_2(PPh_3)_2$, **6a** was obtained in 37% NMR yield (entry 2),[5] whereas no reaction took place with $PdCl_2(PPh_3)_2$.

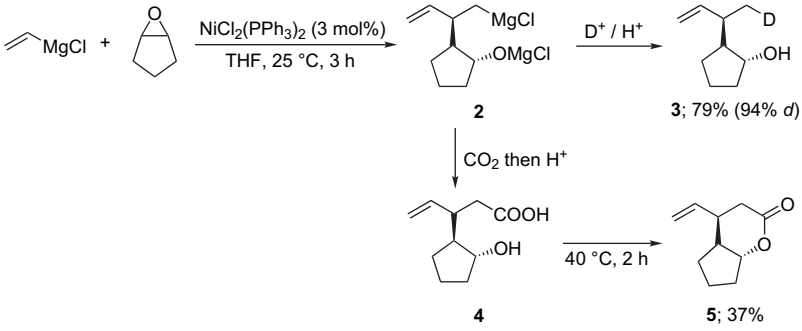
Table 2. Ni-catalyzed 2:2 coupling reaction of vinyl Grignard reagent with chlorosilanes[a]



Entry	Chlorosilane	Product		Yield[b] (%)	*E*/*Z*[c]
1	$^nBu_3Si$–Cl		**6a**	86 (66)	77/23
2[d]				37	79/21
3	$^nPr_3Si$–Cl		**6b**	84 (69)	79/21
4	Et_3Si–Cl		**6c**	79 (58)	77/23
5	Ph_2MeSi–Cl		**6d**	(48)	60/40
6[e]	Ph_3Si–Cl		**6e**	82 (79)	71/29

[a] The reaction was carried out in THF at 25 °C for 3 h using chlorosilane (1.0 mmol), vinyl Grignard reagent (1.5 mmol) and $NiCl_2(PPh_3)_2$ (0.03 mmol).
[b] NMR yield. Isolated yield is in parentheses.
[c] Determined by GC or NMR.
[d] Cp_2TiCl_2 was used as a catalyst.
[e] At 0 °C, 5 h.

No reaction took place when MeCH=CHMgBr and CH_2=CMeMgBr were used, although coupling product **7** was obtained in 71% yield from PhCH=CHMgBr (Eq. 2). We have already reported that Cp_2TiCl_2 catalyzes similar dimerization silylation of vinyl Grignard reagent with chlorosilanes.[5] However, in this Ti-catalyzed reaction system,

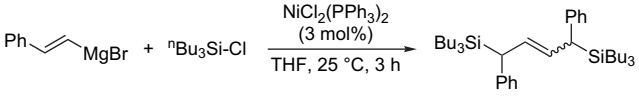


(1)

substituted Grignard reagents including PhCH=CHMgBr did not afford the corresponding products **7** at all.

2.2. Nickel-catalyzed 2:2 coupling reaction of vinyl Grignard reagents with chlorosilanes

When chlorosilanes were employed instead of cyclic ethers, dimerization disilylation proceeded regioselectively under identical conditions to afford 1,4-disilyl-2-butenes (**6**). For example, $^nBu_3SiCl$ (1.0 mmol) reacted with vinyl magnesium chloride (1.5 mmol) in THF (1.2 mL) in the presence of $NiCl_2(PPh_3)_2$ (0.03 mmol) at 25 °C for 3 h to give 1,4-bis(tributylsilyl)-2-butene **6a** in 86% yield with an *E*/*Z* ratio

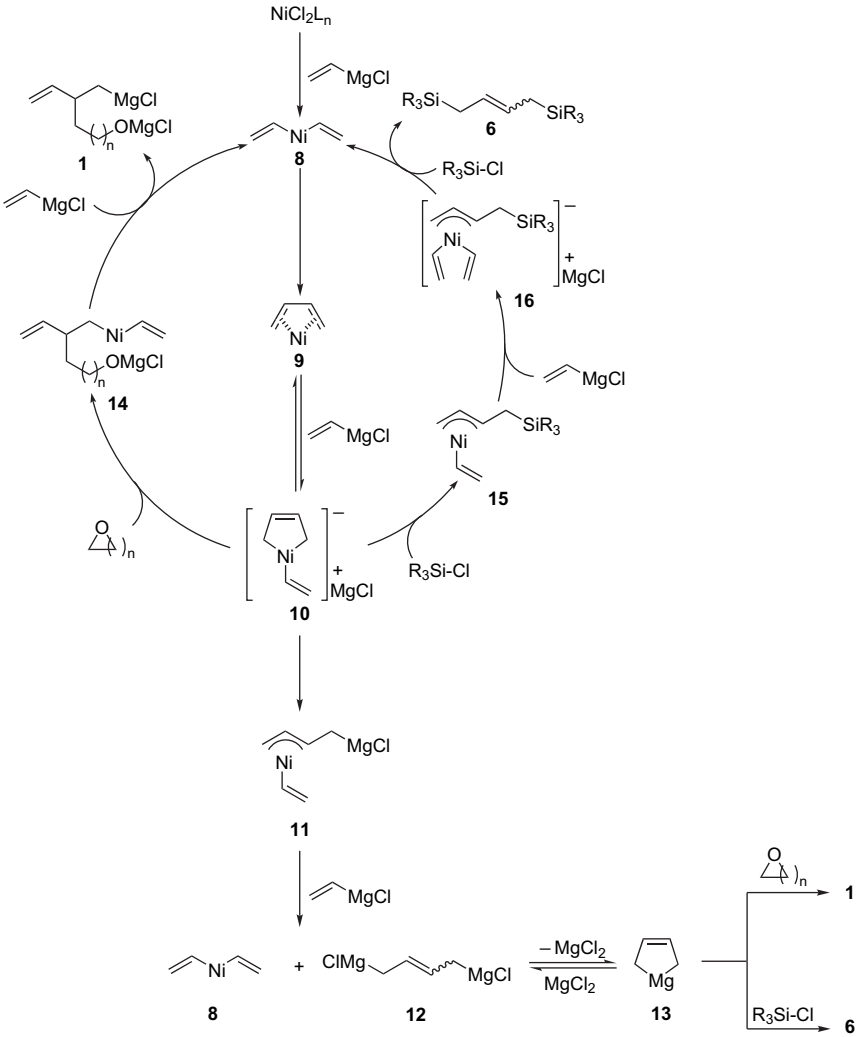


(2)

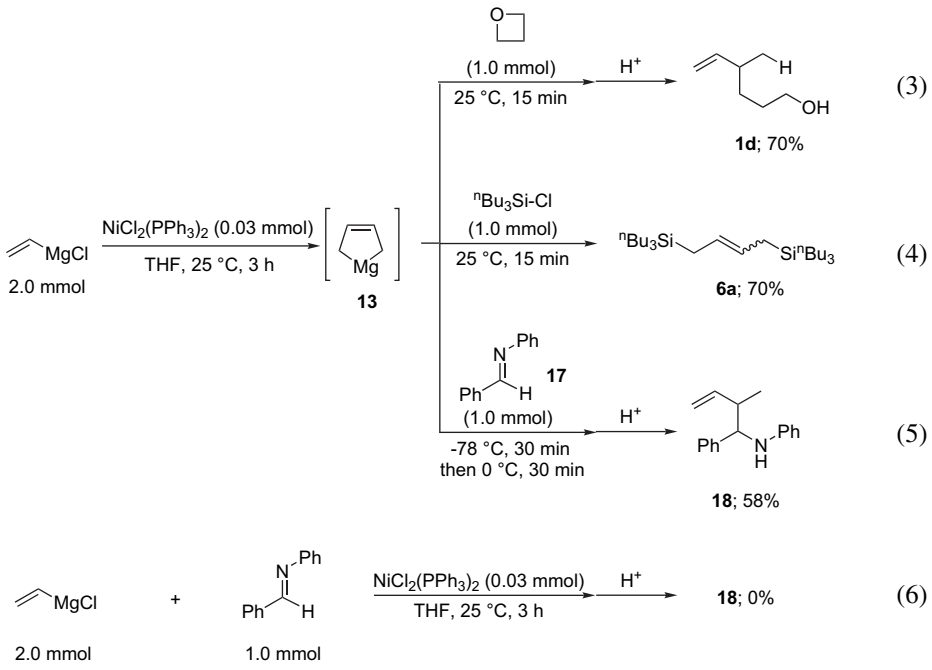
2.3. Reaction mechanisms

Plausible reaction pathways for the present reaction are outlined in Scheme 1. Nickel(II) is reduced by vinyl Grignard reagent to afford Ni(0) via the divinylnickel complex **8**.[6] Thus-formed butadiene–nickel complex **9** reacts with another vinyl Grignard reagent to afford the π-allylnickel complex **11** via nickelate complex **10**.[7] Transmetallation of **11** with vinyl Grignard reagent affords **8** and (2-butene-1,4-diyl)magnesium **13** via diallyl Grignard reagent **12**. Compound **13** (and/or **12**) reacts with cyclic ethers at an internal carbon to give **1** and with chlorosilanes at a terminal carbon to give **6**. Alternatively, direct reaction of **10** with cyclic ethers and chlorosilanes may form the corresponding coupling products **1** or **6** along with regeneration of **8** via vinyl nickel intermediates **14** or **16**, respectively. Although a possibility of these alternative pathways cannot be ruled out, the following evidence supports the formation of **13** in this reaction system.

It is known that (2-butene-1,4-diyl)magnesiums react with epoxides at the β-carbon to give the corresponding 2-alkyl-3-butenyl Grignard reagents[8] and react with chlorosilanes at α-carbon giving rise to 1,4-disilyl-2-butenes.[9] In order to confirm the intermediary of **13** in the present reaction system, we conducted the reaction of $NiCl_2(PPh_3)_2$ (0.03 mmol) with vinyl magnesium chloride (1.5 mmol) at 25 °C in the absence of cyclic ethers and chlorosilanes. After stirring for 3 h, the reaction mixture was treated at 25 °C for 15 min with cyclopentene oxide and tributylchlorosilane separately. GC analysis of the resulting reaction mixture showed the formation of **1d** and **6a** in 70% yield (Eqs. 3 and 4). The elongation of reaction time to 3 h did not improve the products' yields at all. These results suggest that **13** is formed from vinyl Grignard reagents in the presence of Ni. When the reaction was conducted using Cp_2TiCl_2 instead of $NiCl_2(PPh_3)_2$ under the identical conditions and by the same procedure as Eq. 3, **1d** was not formed. Although these yields were slightly lower than the results of one pot reaction system as shown in entry 1 of Tables 1 and 2, this method can be applied to more reactive electrophiles that are not tolerant to vinyl Grignard reagent. For example, homoallylic amine **18** was obtained as a mixture of diastereomers (*erythro*/*threo*=94:6) by the reaction of thus-formed **13** with imine **17**,[10] which cannot be used in one pot reaction system since the direct reaction of vinyl Grignard reagent with imine predominates (Eqs. 5 and 6).



Scheme 1. A plausible reaction pathway.



3. Conclusion

In conclusion, we have developed Ni-catalyzed regioselective coupling of vinyl Grignard reagents with cyclic ethers or chlorosilanes to give 2:1 and 2:2 coupling products, respectively. The present reaction may involve the formation of (2-butene-1,4-diyl)magnesium (**13**) from vinyl Grignard reagents by the aid of Ni catalysts and its electrophilic trapping with cyclic ethers or chlorosilanes. This reaction would provide a new method for generation of (2-butene-1,4-diyl)-magnesium species (**13**) from vinyl Grignard reagents by Ni catalyst as an addition to known methods using 1,3-butadiene and activated Mg. Mechanistic details are currently under investigation.

4. Experimental

4.1. General experimental method

^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL JNM-Alice 400 (400 MHz and 100 MHz, respectively) spectrometer. Chemical shifts are reported in parts per million (δ) downfield from internal tetramethylsilane. Infrared spectra were recorded with a Perkin–Elmer FT-IR (Model 1600). Both conventional and high resolution mass spectra were recorded with a JEOL JMS-DX303HF spectrometer. GC mass spectra (EI) were obtained using a JMS-mate operating in the electron impact mode (70 eV) equipped with an RTX-5 30MX.25MMX.25U column. HPLC separations were performed on a recycling preparative HPLC (Japan Analytical Industry Co. Ltd., Model LC-908) equipped with JAIGEL-1H and -2H columns (GPC) using $CHCl_3$ as an eluent. Column chromatography was conducted using Kanto Chemical Co., Inc. silica gel 60 (63–210 μm). Elemental analyses were performed on a Perkin Elmer 240C apparatus. GC yields were determined using octane as an internal standard. Vinyl Grignard reagent (Kanto Chemical Company), chlorotriethylsilane (Shin-Etsu Chemical Company), chlorotriphenylsilane, chlorotributylsilane, chlorotripropylsilane (Aldrich Chemical Company), cyclopentene oxide, isobutylene oxide, oxetane, 3,3-dimethyl oxetane, diphenylmethylchlorosilane, benzylideneaniline, $NiCl_2(PPh_3)_2$ (Tokyo Chemical Industry Company) were purchased and used as received.

4.2. General procedure for nickel-catalyzed 2:1 coupling reaction of vinyl Grignard reagents with cyclic ethers (Table 1)

To a mixture of cyclic ethers (1.0 mmol) and $NiCl_2(PPh_3)_2$ (19.6 mg, 0.03 mmol) was added vinyl magnesium chloride (1.30 M in THF, 1.7 mL, 2.2 mmol) at 25 °C. After stirring for 3 h, aqueous 1 N HCl was added and the products were extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated to give crude products. Purification by column chromatography on silica gel gave the corresponding products (**1a**–**1e**).

4.2.1. *trans*-2-(1-Methyl-2-propenyl)cyclopentanol (1a). Purification by column chromatography on silica gel (pentane/ether=6:4) gave 90 mg (66%) of **1a** (96% purity determined by GC). The following spectral and analytical data were obtained from 1:1.3 mixture of diastereomers. IR (NaCl): 3344, 2957, 2876, 1639, 1452, 1343, 1027, 996, 911 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87–5.69 (m, 1H), 5.10–4.95 (m, 2H), 3.99–3.90 (m, 1H), 2.25–2.16 (m, 0.6H), 2.08–1.99 (m, 0.4H), 1.93–1.53 (m, 6H), 1.31–1.20 (m, 2H), 1.08 (d, J=6.8 Hz, 1.7H), 1.01 (d, J=6.6 Hz, 1.3H); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor): δ (142.2, 144.2), (113.64, 113.62), (76.5, 77.3), (53.5, 53.4), (40.1, 42.8), (35.4, 34.4), (27.6, 28.9), (22.4, 21.7), (18.6, 18.9); MS (CI) *m/z* (relative intensity, %): 141 (M+1, 14), 124 (9), 123 (100), 84 (3), 81 (9), 67 (3); HRMS (CI) calcd for $C_9H_{17}O$ (M+1): 141.1201, found: 141.1264.

4.2.2. *trans*-2-(1-Methyl-2-propenyl)cyclododecanol (1b). Purification by column chromatography on silica gel (hexane/ether=9:1) gave 145 mg (61%) of **1b** (97% purity determined by GC) as a mixture of diastereomers derived from *cis*-1,2-epoxycyclododecane with ca. 1:1 ratio indicated by ^{1}H and ^{13}C NMR. A 1:1 mixture of diastereomers. IR (NaCl): 3382, 2932, 2863, 1636, 1469, 1445, 1001, 907 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.05–5.92 (m, 1H), 5.10–4.98 (m, 2H), 3.79–3.72 (m, 1H), 2.68–2.58 (m, 0.5H), 2.58–2.50 (m, 0.5H), 1.74–1.25 (m, 22H), 1.08 (d, J=7.1 Hz, 1.5H), 1.05 (d, J=7.1 Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 143.9, 113.8, 112.6, 72.0, 71.7, 43.6, 43.5, 37.6, 37.0, 32.9, 32.6, 25.2, 24.8, 24.6, 24.53, 24.50, 24.33, 24.27, 24.13, 24.11, 24.06, 23.99 (2C), 23.92, 23.7, 23.6, 23.4, 21.2, 21.1, 18.0, 16.5; MS (EI) *m/z* (relative intensity, %): 238 (M^+, 12), 123 (10), 121 (12), 111 (16), 110 (10), 109 (33), 108 (10), 107 (13), 98 (15), 97 (25), 96 (24), 95 (55), 94 (18), 93 (17), 84 (27), 83 (54), 82 (25), 81 (53), 80 (11), 79 (16), 71 (19), 70 (76), 69 (60), 68 (25), 67 (45), 57 (23), 56 (40), 55 (100), 53 (11), 43 (17), 41 (40); HRMS calcd for $C_{16}H_{30}O$: 238.2297, found: 238.2294. Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.50; H, 12.85.

4.2.3. 2,4-Dimethyl-5-pentene-2-ol (1c). This reaction was carried out on a 3.0 mmol scale. Purification by column chromatography on silica gel (pentane/ether=6:4) gave 78 mg (20%) of **1c** (97% purity determined by GC). IR (NaCl): 3404, 2970, 2926, 1640, 1456, 1378, 1159, 908 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.81 (ddd, J=8.8 Hz, 10.0 Hz, 17.2 Hz, 1H), 5.09–4.94 (m, 2H), 2.50–2.39 (m, 1H), 1.74 (s, 1H), 1.60 (dd, J=9.6 Hz, 14.2 Hz, 1H), 1.49 (dd, J=4.0 Hz, 14.2 Hz 1H), 1.24 (s, 3H), 1.20 (s, 3H), 1.03 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 113.2, 71.5, 50.1, 35.2, 30.4, 29.4, 22.7; MS (CI) *m/z* (relative intensity, %): 129 (M+1, 0.8), 112 (9), 111 (100), 95 (1), 69 (4); HRMS (CI) calcd for $C_8H_{17}O$ (M+1): 129.1201, found: 129.1277.

4.2.4. 4-Methyl-5-hexen-1-ol (1d). Purification by column chromatography on silica gel (pentane/ether=6:4) gave 70 mg (62%) of **1d** (96% purity determined by GC). IR (NaCl): 3324, 3077, 2936, 1640, 1420, 1374, 1058, 910, 682 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.69 (ddd, J=7.2 Hz, 10.1 Hz, 17.2 Hz, 1H), 4.99–4.92 (m, 2H), 3.64 (t, J=7.2 Hz, 2H), 2.14 (qtd, J=7.2 Hz, 7.2 Hz, 7.2 Hz, 1H), 1.62–1.51 (m, 2H), 1.40–1.31 (m, 3H), 1.00 (d, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 112.7, 63.1, 37.7, 32.7, 30.6, 20.4; MS (EI) *m/z* (relative intensity, %): 114 (M^+, 0.1), 113 (0.1), 96 (9), 95 (6), 83 (12), 82 (8), 81 (100), 71 (27), 70 (86), 69 (15), 68 (77), 67 (30), 58 (11), 57 (27), 56 (22), 55 (95), 54 (17), 53 (19), 42 (14), 41 (37), 39 (20); HRMS calcd for $C_7H_{14}O$: 114.1045, found: 114.1042. Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.35; H, 12.08.

4.2.5. 2,2,4-Trimethyl-5-hexen-1-ol (1e). Purification by column chromatography on silica gel (pentane/ether=7:3) gave 70 mg (50%) of **1e** (98% purity determined by GC). IR (NaCl): 3334, 2955, 2244, 1643, 1456, 1365, 1040, 908 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.69 (ddd, J=8.6 Hz, 10.3 Hz, 17.2 Hz, 1H), 5.02–4.87 (m, 2H), 3.36 (d, J=11.0 Hz, 1H), 3.28 (d, J=11.0 Hz, 1H), 2.35–2.25 (m, 1H), 1.42–1.36 (m, 2H), 1.22 (dd, J=14.0 Hz, 3.6 Hz, 1H), 1.01 (d, J=6.8 Hz, 3H), 0.90 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 112.0, 71.7, 45.4, 35.9, 34.6, 25.2, 24.4, 23.9; MS (CI) *m/z* (relative intensity, %): 143 (M+1, 100), 126 (3), 125 (32), 83 (7), 69 (19); HRMS (CI) calcd for $C_9H_{19}O$ (M+1): 143.1358, found: 143.1437.

4.3. *trans*-2-(1-Deuteriomethyl-2-propenyl)cyclopentanol (3)

To a mixture of cyclopentene oxide (84.0 mg, 1.00 mmol) and $NiCl_2(PPh_3)_2$ (19.6 mg, 0.03 mmol) was added vinyl magnesium chloride (1.35 M in THF, 1.6 mL, 2.2 mmol) at 25 °C. After stirring for 3 h, D_2O was added and the products were extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated to give yellow crude products (79% NMR yield). Purification by column chromatography on silica gel (pentane/ether=6:4) gave 90 mg (64%) of **3** (96% purity determined by GC). The following spectral and analytical data were obtained from 1:1.3 mixture of diastereomers. IR (NaCl): 3354, 2956, 2873, 1639, 1450, 1435, 1419, 1344, 1301, 1027, 996, 910 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87–5.69 (m, 1H), 5.09–4.95 (m, 2H), 4.00–3.91 (m, 1H), 2.32–2.16 (m, 0.6H), 2.07–1.99 (m, 0.4H), 1.93–1.50 (m, 6H), 1.31–1.20 (m, 2H), 1.08–1.04 (m, 1.2H), 1.02–0.98 (m, 0.8H); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor): δ (142.4, 144.4), (113.76, 113.75), (76.7, 77.5), (53.6, 53.5), (40.1, 42.7), (35.5, 34.5), (27.7, 28.9), (22.4, 21.8), (18.3, 18.6) (t, J=19.3 Hz); MS (CI) *m/z* (relative intensity, %): 142 (M+1, 16), 125 (10), 124 (100), 123 (4), 82 (5), 67 (2); HRMS (CI) calcd for $C_9H_{16}DO$ (M+1): 142.1263, found: 142.1337.

4.4. *trans*-4-Vinyl-hexahydro-cyclopenta[*b*]pyran-2-one (5)

To a mixture of cyclopentene oxide (85.1 mg, 1.01 mmol) and $NiCl_2(PPh_3)_2$ (19.6 mg, 0.03 mmol) was added vinyl magnesium chloride (1.30 M in THF, 1.7 mL, 2.2 mmol) at 25 °C. After stirring for 3 h, CO_2 was added to the solution. After stirring for 30 min, aqueous 3 N HCl (2 mL) was added to the solution and the mixture was stirred for 2 h at 40 °C. The product was extracted with ether, dried over Na_2SO_4 and evaporated to give an orange crude product. The NMR and GC analyses of the crude mixture indicated the formation of **5** (95% purity determined by GC) as 1:1.3 mixture of diastereomers. Purification by HPLC afforded 62 mg (37%) of **5** as a mixture of diastereomers with ca. 1:5 ratio due to the loss of the minor isomer. Major diastereomers. IR (NaCl): 3436, 2957, 2874, 1732, 1640, 1438, 1418, 1256, 1187, 918 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67 (ddd, J=7.2 Hz, 10.0 Hz, 17.2 Hz, 1H), 5.10–5.03 (m, 2H), 4.10 (td, J=10.2 Hz, 7.6 Hz, 1H), 2.89–2.81 (m, 1H), 2.44–2.35 (m, 2H), 2.18–2.10 (m, 1H), 1.96–1.60 (m, 4H), 1.29–1.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 139.1, 115.2, 84.0, 46.1, 41.5, 35.3, 29.2, 25.0, 19.3; MS (EI) *m/z* (relative intensity, %): 166 (M^+, 5), 138 (10), 124 (28), 95 (26), 82 (16), 81 (18), 80 (100), 79 (31), 68 (10), 67 (21), 54 (11), 53 (10), 41 (10); HRMS (EI) calcd for $C_{10}H_{14}O_2$: 166.0994, found: 166.0995. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.35; H, 8.65.

4.5. General procedure for nickel-catalyzed 2:2 coupling reaction of vinyl Grignard reagents with chlorosilanes (Table 2)

To a mixture of chlorosilanes (1.0 mmol) and $NiCl_2(PPh_3)_2$ (19.6 mg, 0.03 mmol) was added vinyl magnesium chloride (1.30 M in THF, 1.2 mL, 1.5 mmol) at 25 °C. After stirring for 3 h, aqueous 1 N HCl was added and the products were extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated to give crude products. Purification by HPLC or recrystallization afforded the corresponding products (**6a**–**6e**).

4.5.1. 1,4-Bis(tributylsilyl)-2-butene (6a). Purification by HPLC with $CHCl_3$ as eluent afforded 150.2 mg (66%) of **6a** (98% purity determined by GC). IR (NaCl): 2957, 2921, 2872, 2857, 1464, 1376, 1194, 1082, 886, 789, 762, 728 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.29–5.18 (m, 2H), 1.43–1.39 (m, 4H), 1.36–1.22 (m, 24H), 0.88 (t, J=6.8 Hz, 18H), 0.54–0.47 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): (trans isomer) δ 124.5, 26.8, 26.1, 18.4, 13.8, 11.9; (cis isomer) δ 123.2, 26.8, 26.2, 13.8, 13.6, 12.2; MS (EI) *m/z* (relative intensity, %) 452 (M^+, 11), 199 (94), 143 (100), 101 (12), 87 (13), 59 (14); HRMS calcd for $C_{28}H_{60}Si_2$: 452.4233, found: 452.4224. Anal. Calcd for $C_{28}H_{60}Si_2$: C, 74.25; H, 13.35. Found: C, 74.26; H, 13.07.

4.5.2. 1,4-Bis(tripropylsilyl)-2-butene (6b) [CAS Registry Number 349152-14-3]. Purification by HPLC with $CHCl_3$ as eluent afforded 126.3 mg (69%) of **6b** (99% purity determined by GC). Spectroscopic data were in agreement with those of previously published material.[5] ^1H NMR (400 MHz, $CDCl_3$): (trans isomer) δ 5.21–5.18 (m, 2H), 1.41–1.40 (m, 4H), 1.38–1.28 (m, 12H), 0.97–0.91 (t, J=7.2 Hz, 18H), 0.54–0.49 (m, 12H); (cis isomer) δ 5.28–5.15 (m, 2H), 1.45–1.40 (m, 4H), 1.38–1.28 (m, 12H), 0.97–0.91 (t, J=7.2 Hz, 18H), 0.54–0.49 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): (trans isomer) δ 124.1, 18.5, 18.4, 17.3, 15.0; (cis isomer) δ 122.8, 18.6, 18.5, 17.4, 15.1.

4.5.3. 1,4-Bis(triethylsilyl)-2-butene (6c). Purification by HPLC with $CHCl_3$ as eluent afforded 83 mg (58%) of **6c** (99% purity determined by GC). IR (NaCl): 2952, 2874, 1464, 1417, 1238, 1154, 1016, 812, 751, 722 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.29–5.21 (m, 2H), 1.45–1.42 (m, 4H), 0.96–0.91 (m, 18H), 0.56–0.48 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): (trans isomer) δ 124.4, 17.3, 7.4, 3.2; (cis isomer) δ 123.1, 12.6, 7.4, 3.3; MS (EI) *m/z* (relative intensity, %): 284 (M^+, 15), 140 (11), 117 (4), 116 (12), 115 (100), 111 (9), 88 (6), 87 (69), 83 (4), 59 (19), 58 (3); HRMS (EI) calcd for $C_{16}H_{36}Si_2$: 284.2356, found: 284.2355.

4.5.4. 1,4-Bis(methyldiphenylsilyl)-2-butene (6d). Purification by HPLC with $CHCl_3$ as eluent afforded 108 mg (48%) of **6d** (99% purity determined by GC). IR (NaCl): 3068, 3010, 2956, 1588, 1487, 1427, 1250, 1155, 1113, 834, 804, 788, 731, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): (trans isomer) δ 7.50–7.24 (m, 20H), 5.32–5.30 (m, 2H), 1.96–1.94 (m, 4H), 0.40 (s, 6H); (cis isomer) δ 7.50–7.24 (m, 20H), 5.38–5.35 (m, 2H), 1.89 (d, J=6.3 Hz, 4H), 0.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): (trans isomer) δ 136.9, 134.5, 129.1, 127.7, 124.8, 20.3, −4.9; (cis isomer) δ 136.9, 134.5, 129.2, 127.8, 123.5, 15.4, −4.6; MS (EI) *m/z* (relative intensity, %) 448 (M^+, 4), 259 (3), 236 (5), 199 (5), 198 (20), 197 (100), 181 (3), 174 (10), 165 (2), 158 (2), 119 (2), 105 (5); HRMS calcd for $C_{30}H_{32}Si_2$: 448.2043, found: 448.2047. Anal. Calcd for $C_{30}H_{32}Si_2$: C, 80.30; H, 7.19. Found: C, 80.14; H, 7.21.

4.5.5. 1,4-Bis(triphenylsilyl)-2-butene (6e). Purification by recrystallization with chloroform/hexane afforded 211 mg (79%) of **6e**. IR (KBr): 3065, 3009, 2486, 1427, 1397, 1172, 1112, 1063, 998, 966, 766, 732, 700, 517, 478 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52–7.25 (m, 30H), 5.49–5.41 (m, 2H), 2.28–2.06 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): (trans isomer) δ 135.5, 134.7, 129.2, 127.6, 125.1, 19.6; (cis isomer) δ 135.5, 134.7, 129.3, 127.6, 123.8, 14.6; MS (EI) *m/z* (relative intensity, %) 572 (M^+, 3), 261 (6), 260 (24), 259 (100), 236 (2), 181 (6), 180 (2), 105 (2); HRMS calcd for $C_{40}H_{36}Si_2$: 572.2356, found: 572.2352. Anal. Calcd for $C_{40}H_{36}Si_2$: C, 83.86; H, 6.33. Found: C, 83.59; H, 6.13.

4.6. 1,4-Bis(tributylsilyl)-1,4-diphenyl-2-butene (7)

To a mixture of chlorotributylsilane (235 mg, 1.00 mmol) and $NiCl_2(PPh_3)_2$ (19 mg, 0.03 mmol) was added a THF solution of β-phenyl vinyl magnesium bromide (0.52 M in THF, 2.9 mL, 1.5 mmol) at 25 °C under nitrogen. After stirring for 3 h, similar workup as mentioned above afforded yellow crude products (88% NMR yield). Purification by HPLC with $CHCl_3$ as an eluent afforded 215 mg (71%) of **7**. IR (NaCl): 2956, 2922, 2871, 2857, 1464, 1081, 886, 764, 744, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.23–7.02 (m, 10H), 5.88–5.74 (m, 2H), 3.38–3.01 (m, 2H), 1.30–1.01 (m, 24H), 0.88–0.68 (m, 18H), 0.55–0.33 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): (trans isomer) δ 143.2, 128.4, 127.9, 127.2, 124.1, 40.6, 27.0, 26.1, 13.9, 11.3; (cis isomer) δ 143.1, 128.0, 127.0, 126.6, 124.0, 35.5, 26.9, 26.1, 13.8, 11.1; MS (EI) *m/z* (relative intensity, %) 604 (M^+, 3), 348 (5), 291 (2), 199 (100), 143 (92), 87 (22), 59 (29); HRMS calcd for $C_{40}H_{68}Si_2$: 604.4859, found: 604.4868. Anal. Calcd for $C_{40}H_{68}Si_2$: C, 79.39; H, 11.33. Found: C, 79.21; H, 11.13.

4.7. *N*-(2-Methyl-1-phenyl-3-butenyl)phenylamine (18) [CAS Registry Number 80188-13-2]

Vinyl magnesium chloride (1.30 M in THF, 1.5 mL, 2.0 mmol) was added to $NiCl_2(PPh_3)_2$ (19.6 mg, 0.03 mmol) at 25 °C. After stirring for 3 h, benzylideneaniline (181.2 mg, 1.00 mmol) was added to the solution at −78 °C. After stirring for 30 min, the solution was warmed to 0 °C and stirred at 0 °C for an additional 30 min. The product was extracted with ether, dried over $MgSO_4$ and evaporated to give an orange crude product. Purification by column chromatography on silica gel (hexane/ether=8:2) gave 137 mg (58%) of **18** as a mixture of diastereomers (*erythro*/*threo*=94:6). The stereochemistries were determined by comparison of their NMR data with the reported ones;[11] *erythro*-isomer: ^1H NMR (400 MHz, $CDCl_3$): δ 7.36–7.20 (m, 5H), 7.06–7.02 (m, 2H), 6.62–6.58 (m, 1H), 6.46 (d, J=7.8 Hz, 2H), 5.75 (ddd, J=7.6 Hz, 10.1 Hz, 17.5 Hz, 1H), 5.20–5.15 (m, 2H), 4.22 (br, 1H), 4.07 (d, J=7.1 Hz, 1H), 2.56–2.47 (m, 1H), 1.01 (d, J=6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 142.6, 140.5, 129.0, 128.3, 127.2, 127.0, 117.1, 116.2, 113.3, 62.3, 45.2, 17.3.

References and notes

1. (a) Grignard, V. *Ann. Chim.* **1901**, *24*, 433; (b) *Organomagnesium Methods in Organic Synthesis*; Wakefield, B. J., Ed.; Academic: London, 1995; (c) *Grignard Reagents New Developments*; Richey, H. G., Jr., Ed.; Wiley: Chichester, UK, 2000; (d) Shinokubo, H.; Oshima, K. *Eur. J. Org. Chem.* **2004**, 2081; (e) Tamura, M.; Kochi, J. *J. Am. Chem. Soc.* **1971**, *93*, 1487; (f) Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 4374; (g) Corriu, R. J. P.; Masse, J. P. *J. Chem. Soc., Chem. Commun.* **1972**, 144; (h) Fouquet, G.; Schlosser, M. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 82.
2. (a) Terao, J.; Kambe, N. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 663; (b) Terao, J.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1998**, *39*, 9697; (c) Terao, J.; Torii, K.; Saito, K.; Kambe, N.; Baba, A.; Sonoda, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 2653; (d) Terao, J.; Oda, A.; Ikumi, A.; Nakamura, A.; Kuniyasu, H.; Kambe, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 3412; (e) Terao, J.; Oda, A.; Kambe, N. *Org. Lett.* **2004**, *6*, 3341; (f) Fujii, Y.; Terao, J.; Kuniyasu, H.; Kambe, N. *J. Organomet. Chem.* **2007**, *692*, 375; (g) Terao, J.; Kambe, N. *Chem. Rec.* **2007**, *7*, 57.
3. Terao, J.; Watabe, H.; Kambe, N. *J. Am. Chem. Soc.* **2005**, *127*, 3656.
4. The reaction of *trans*-cyclododecene oxide with Grignard reagent is very slow: Michel, D.; Schlosser, M. *Tetrahedron* **2000**, *56*, 4253.
5. Watabe, H.; Terao, J.; Kambe, N. *Org. Lett.* **2001**, *3*, 1733.
6. (a) Whitesides, G. M.; Casey, C. P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379; (b) Semmelhack, M. F.; Helquist, P.; Jones, L. D.; Keller, L.; Mendelson, L.; Ryono, L. S.; Smith, J. G.; Stauffer, R. D. *J. Am. Chem. Soc.* **1981**, *103*, 6460.
7. For magnesium nickelate complexes, see: Kaschube, W.; Pörschke, K. R.; Angermund, K.; Krüger, C.; Wilke, G. *Chem. Ber.* **1988**, *121*, 1921.
8. Sell, M. S.; Xiong, H.; Rieke, R. D. *Tetrahedron Lett.* **1993**, *34*, 6007.
9. (a) Richter, W. J. *Synthesis* **1982**, 1102; (b) Richer, W. J. *J. Organomet. Chem.* **1985**, *289*, 45; (c) Rieke, R. D.; Xiong, H. *J. Org. Chem.* **1991**, *56*, 3109.
10. Sell, M. S.; Klein, W. R.; Rieke, R. D. *J. Org. Chem.* **1995**, *60*, 1077.
11. Andrade, C. K. Z.; Azevedo, N. R.; Oliveira, G. R. *Synthesis* **2002**, 928.