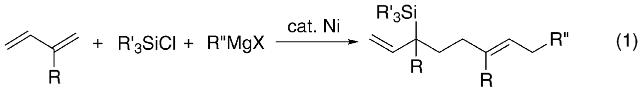
Carbosilylation-Dimerization

Nickel-Catalyzed Dimerization and Carbosilylation of 1,3-Butadienes with Chlorosilanes and Grignard Reagents**

Jun Terao, Akihiro Oda, Aki Ikumi,
Akifumi Nakamura, Hitoshi Kuniyasu, and
*Nobuaki Kambe**

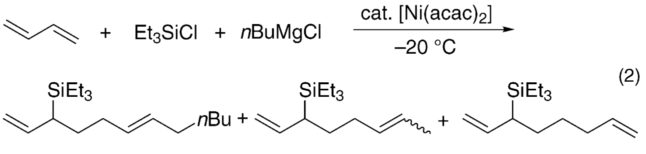
Ni^0 reacts with 1,3-butadienes to form octadienediyl–nickel complexes, which play an important role as key intermediates in the oligomerization of butadienes.[1,2] This reaction demonstrates extreme synthetic utility as a straightforward method for the formation of C_8 building blocks in organic synthesis. The cycloaddition of butadienes is one of the most successful transformations of this type.[1d,3] However, many attempts toward the synthesis of functionalized oligomers (i.e. telomerization) by using Ni catalysts resulted in the formation of mixtures of products.[1b,4] We have recently developed new methods for the regioselective addition of silicon and/or carbon functionalities to alkenes or dienes in the presence of early-transition-metal catalysts, such as zirconium complexes[5] and titanium complexes.[6] During the course of these studies, we found that Ni catalyzes the dimerization and carbosilylation of butadienes in the presence of chlorosilanes and Grignard reagents to give rise to 1,6-dienes with high regio- and stereoselectivity [Eq. (1)].



(1)

When a catalytic amount of $[Ni(acac)_2]$ (0.05 mmol; acac = acetylacetone) was added to a solution of isoprene (2 mmol), chlorotriethylsilane (1 mmol), and *n*BuMgCl (1.2 mmol) in THF (1.3 mL) at −20 °C, and the resulting mixture was stirred for a further 18 hours at the same temperature, compound **1**, with Et_3Si and *n*Bu groups at positions 3 and 8 of its dimerized isoprene skeleton, was isolated in 87 % yield ($E/Z = 76:24$) from the crude mixture by HPLC, with $CHCl_3$ as the eluent (Table 1, entry 1). No regioisomers of **1** were formed in the reaction. When $NiCl_2$ and $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) were used as catalysts, **1** was obtained in yields of 78 and 80 %, respectively, but no reaction took place in the presence of nickel catalysts with phosphane ligands, such as $[(PPh_3)_2NiCl_2]$, $[(dppe)NiCl_2]$ (dppe = ethane-1,2-diylbis(diphenylphosphane), or $[(dppp)NiCl_2]$ (dppp = propane-1,3-diylbis(diphenylphosphane), under identical conditions. This reaction also proceeded efficiently when a phenyl-substituted chlorosilane (Table 1, entries 2, 6, and 7) and/or a secondary alkyl Grignard reagent (Table 1, entries 2, 3, and 5) were used. The use of a cyclohexyl Grignard reagent with isoprene led to the formation of only the *E* isomer of the product (Table 1, entry 3). The reaction of 2-nonyl-1,3-butadiene with Et_3SiCl and *i*BuMgCl gave a mixture of stereoisomers **8** in a 40:60 ratio and 42 % yield (Table 1, entry 8).

When unsubstituted 1,3-butadiene was used, the coupling products were obtained not only regioselectively but also stereoselectively in all cases examined (Table 1, entries 4–7). A phenyl and a vinyl Grignard reagent could also be used to prepare the allyl arene **6** and the triene **7**, respectively, in good yields (Table 1, entries 6 and 7). However, the reaction of a primary alkyl Grignard reagent gave the desired product **9** in only moderate yield (32 %), along with the hydrosilylated products **10a** and **10b** in 27 and 29 % yields, respectively [Eq. (2)]. The desired product was not obtained when



(2)

9, 32% **10a**, 27% **10b**, 29%

---

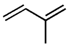
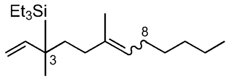
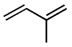
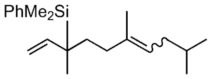
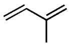
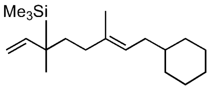
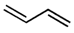
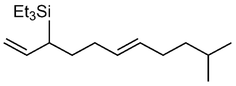
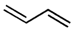
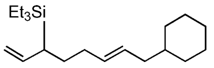
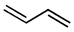
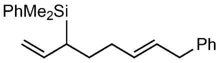
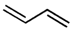
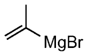
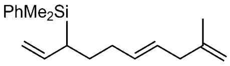
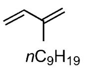
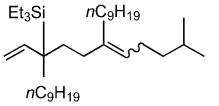
[*] Prof. Dr. N. Kambe, Dr. J. Terao, A. Oda, A. Ikumi, A. Nakamura, Dr. H. Kuniyasu
Department of Molecular Chemistry and Frontier Research Center
Graduate School of Engineering, Osaka University
Suita, Osaka 565-0871 (Japan)
Fax: (+81) 6-6879-7390
E-mail: kambe@chem.eng.osaka-u.ac.jp

[**] This research was supported financially through a grant from the Ministry of Education, Culture, Sports, Science, and Technology of Japan and by the JSPS COE program. We thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University for MS and HRMS measurements as well as elemental analyses.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

DOI: 10.1002/ange.200351579

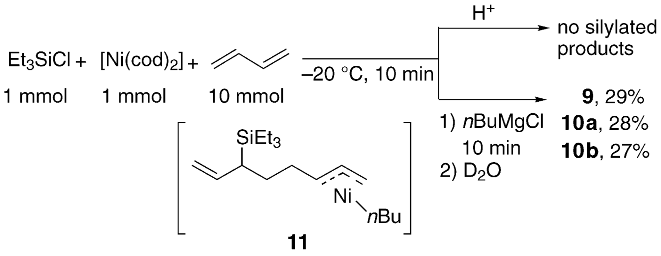
Table 1: Ni-catalyzed regioselective coupling of 1,3-dienes with Grignard reagents and chlorosilanes.[a]

Entry	Diene	R'_3SiCl	R″MgX	Product		Yield [%][b]	*E*/*Z*[c]
1		Et_3SiCl	*n*BuMgCl		**1**	87	76:24
2		$PhMe_2SiCl$	*i*PrMgCl		**2**	86	92:8
3		Me_3SiCl	*c*-$C_6H_{11}MgCl$		**3**	84	100:0
4		Et_3SiCl	*i*BuMgCl		**4**	78	100:0
5		Et_3SiCl	*c*-$C_6H_{11}MgCl$		**5**	93	100:0
6		$PhMe_2SiCl$	PhMgBr		**6**	78	100:0
7		$PhMe_2SiCl$			**7**	76	100:0
8		Et_3SiCl	*i*BuMgCl		**8**	42	40:60[d]

[a] For experimental details, see Supporting Information. [b] Yields of isolated products. [c] Determined by GC. [d] Ratio of the stereoisomers: their stereochemistry was not assigned.

MeMgCl[7] or *t*BuMgCl was used. Under identical conditions, 2,3-dimethyl-1,3-butadiene and 1,4-diphenyl-1,3-butadiene did not react.

We carried out several control experiments to prove the reaction pathway and product selectivity. For example, Et_3SiCl, a stoichiometric amount of $[Ni(cod)_2]$, and excess 1,3-butadiene (10 equiv) were stirred as a solution in THF for 10 min at −20 °C. The reaction was quenched with HCl (1 N, 1.5 mL), and analysis of the mixture by NMR spectroscopy and GC–MS showed no evidence for the formation of silylated products. However, when 1 equivalent of *n*BuMgCl was added to the reaction mixture prior to quenching with D_2O, a mixture of the monosilylated compounds **9**, **10a**, and **10b** (Scheme 1) was obtained in a similar total yield and ratio to those shown in Equation 2.

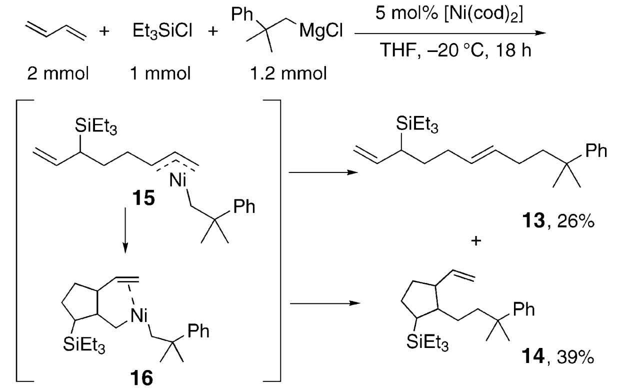


Scheme 1. Significance of the Grignard reagent: Treatment of 1,3-butadiene with Et_3SiCl and [Ni(cod)] in the presence and in the absence of *n*BuMgCl.

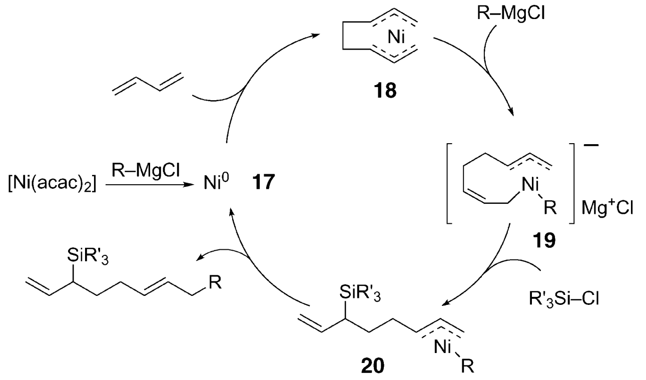
These results suggest that Grignard reagents do, in fact, promote the C–Si bond-forming step. The fact that the hydrosilylated products **10a** and **10b** did not contain deuterium may suggest that a hydrogen atom of the butyl group of the Grignard reagent was transferred to **10a** and **10b**. The formation of the coupling product **9** and hydrosilylated products **10a** and **10b** can be rationalized by assuming a common intermediate **11**, the reaction of which leads to **9** through reductive elimination of the allyl and *n*Bu groups or to **10a** and **10b** through β-hydrogen elimination. This β-hydrogen-elimination process may be disfavored when isoprene (Table 1, entry 1) or *i*BuMgCl (Table 1, entry 4) is used, because of steric reasons, thus resulting in the selective formation of coupling products **1** and **4**, respectively.

We then tested the reaction in the presence of a primary alkyl Grignard reagent with no β-hydrogen atom. The reaction of 1,3-butadiene with Et_3SiCl and $PhMe_2CCH_2MgCl$ afforded the expected coupling product **13** in 26 % yield along with cyclized compound **14** (39 %; Scheme 2). The latter compound might be formed via **16**, generated by insertion of the terminal carbon–carbon double bond into the allyl–nickel bond of **15**, as reductive elimination from **15** to give **13** is probably retarded because of steric reasons.

A plausible reaction pathway, which takes into account the above evidence, is shown in Scheme 3. The reaction of $[Ni(acac)_2]$ with a Grignard reagent affords Ni^0 (**17**), which reacts with butadiene and a Grignard reagent to give η^1,η^3-octadienediyl–nickelate complex **19**[8] via η^3,η^3-octadienediyl–



Scheme 2. Reaction of a primary alkyl Grignard reagent that bears no β-hydrogen atom.



Scheme 3. A plausible reaction pathway.

nickel complex **18** or its η^1,η^3 isomer.[9a] Complex **19** then reacts with a chlorosilane at the γ allylic carbon atom to form an allyl complex **20**.[9] The subsequent reductive elimination of **20** affords the coupling product and regenerates **17** to complete the catalytic cycle.

In conclusion, a new method for the highly regioselective nickel-catalyzed four-component coupling[10] of two diene molecules, a chlorosilane, and a Grignard reagent has been developed. This reaction affords 1,6-dienes with an allyl silane unit[11] under mild conditions and, when unsubstituted 1,3-butadiene is used, proceeds stereoselectively to produce only *trans* olefins. This study provides the first example of a C–Si bond-forming reaction that involves chlorosilanes and is catalyzed by a late transition metal.[12]

Experimental Section

5: A solution of Et_3SiCl (152 mg, 1.0 mmol) and a catalytic amount of [Ni(acac)$_2$] (12 mg, 0.05 mmol) in THF (1.2 mL) was cooled to −78 °C, and 1,3-butadiene (45 mL at 20 °C under 1 atm, 2.0 mmol) was added through a syringe. c-$C_6H_{11}MgCl$ (2 M in Et_2O, 0.6 mL, 1.2 mmol) was then added at the same temperature and the mixture was warmed to −20 °C and stirred for a further 18 h. The reaction was quenched with HCl (1 N), and the mixture was extracted with diethyl ether to afford the yellow crude product, which was purified by HPLC to give **5** (292 mg, 93 %). IR (neat): $\tilde{\nu} = 2920, 2875, 2851, 1625, 968, 894, 730, 696\ \text{cm}^{-1}$; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): $\delta = 5.62$ (dt, $J = 17.1, 10.0$ Hz, 1H), 5.41–5.26 (m, 2H), 4.86 (dd, $J = 10.0, 1.7$ Hz, 1H), 4.82 (d, $J = 17.1$ Hz, 1H), 2.17–2.08 (m, 1H), 1.92–1.82 (m, 3H), 1.75–1.62 (m, 6H), 1.47 (dt, $J = 6.1, 7.8$ Hz, 2H), 1.26–1.07 (m, 4H), 0.94 (t, $J = 8.4$ Hz, 9H), 0.92–0.82 (m, 2H), 0.54 ppm (q, $J = 8.4$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): $\delta = 140.2$, 130.9, 129.1, 111.8, 40.8, 38.3, 33.3, 33.2, 32.2, 31.4, 28.8, 26.8, 26.5, 7.8, 2.4 ppm; MS (EI): m/z (%): 306 (0.1), 277 (7), 169 (18), 115 (100), 87 (58), 59 (47); HRMS (m/z): calcd for $C_{20}H_{38}Si$ (M^+): 306.2743, found 306.2745; elemental analysis: calcd for $C_{20}H_{38}Si$: C 78.35, H 12.49; found: C 78.19, H 12.57.

Received: April 4, 2003 [Z51579]

Keywords: dienes · Grignard reagents · multicomponent reactions · nickel · silanes

---

[1] a) P. W. Jolly, G. Wilke, *The Organic Chemistry of Nickel*, Academic Press, New York, **1975**; b) W. Keim, A. Behr, M. Röper in *Comprehensive Organometallic Chemistry, Vol. 8* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1982**, pp. 371–462; c) W. Keim, *Angew. Chem.* **1990**, *102*, 251–260; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 235–244; d) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49–92.

[2] We recently reported that octadienediyl–nickel complexes show unique catalytic activity in C(sp^3)–C(sp^3) coupling reactions of alkyl halides with RMgX: J. Terao, H. Watanabe, A. Ikumi, H. Kuniyasu, N. Kambe, *J. Am. Chem. Soc.* **2002**, *124*, 4222–4223; J. Terao, A. Ikumi, H. Kumiyasu, N. Kambe, *J. Am. Chem. Soc.* **2003**, *125*, 5646–5647.

[3] S. McN. Sieburth, N. T. Cunard, *Tetrahedron* **1996**, *52*, 6251–6282.

[4] For a Ni-catalyzed reaction of 1,3-butadiene with Me_2Zn and a ketone, see: a) M. Kimura, S. Matsuo, K. Shibata, Y. Tamaru, *Angew. Chem.* **1999**, *111*, 3586–3589; *Angew. Chem. Int. Ed.* **1999**, *38*, 3386–3388; for reviews of Pd-catalyzed reactions, see: b) J. Tsuji, *Palladium Reagents and Catalysts*, Wiley, Chichester, **1995**, pp. 422–449; c) F. Bouachir, P. Grenouillet, D. Neibecker, J. Poirier, I. Tkatchenko, *J. Organomet. Chem.* **1998**, *569*, 203–215.

[5] a) J. Terao, K. Torii, K. Saito, N. Kambe, A. Baba, N. Sonoda, *Angew. Chem.* **1998**, *110*, 2798–2801; *Angew. Chem. Int. Ed.* **1998**, *37*, 2653–2656; b) J. Terao, T. Watanabe, K. Saito, N. Kambe, N. Sonoda, *Tetrahedron Lett.* **1998**, *39*, 9201–9204.

[6] a) J. Terao, K. Saito, S. Nii, N. Kambe, N. Sonoda, *J. Am. Chem. Soc.* **1998**, *120*, 11 822–11 823; b) S. Nii, J. Terao, N. Kambe, *J. Org. Chem.* **2000**, *65*, 5291–5297.

[7] Direct reaction with the chlorosilane predominated.

[8] For a similar η^1,η^3-octadienediyl–nickelate complex reported for Li, see: S. Hole, P. W. Jolly, R. Mynott, R. Salz, *Z. Naturforsch. B* **1982**, *37*, 675–676.

[9] a) An η^1,η^3-octadienediyl–nickel complex reacts with H^+ at the γ allylic carbon: R. Benn, B. Büssemeier, S. Holle, P. W. Jolly, R. Mynott, I. Tkatchenko, G. Wilke, *J. Organomet. Chem.* **1985**, *279*, 63–86; b) an η^1,η^3-octadienediyl–palladium complex also reacts with Me_2HSiCl at the γ position: P. W. Jolly, R. Mynott, B. Raspel, K.-P. Schick, *Organometallics* **1986**, *5*, 473–481; c) an η^1-allyl–palladium complex reacts with electrophiles at the γ position: H. Kurosawa, A. Urabe, K. Miki, N. Kasai, *Organometallics* **1986**, *5*, 2002–2008.

[10] For recent reviews of Ni-catalyzed multicomponent coupling reactions, see: a) J. Montgomery, *Acc. Chem. Res.* **2000**, *33*, 467–473; b) S. Ikeda, *Acc. Chem. Res.* **2000**, *33*, 511–519.

[11] Allyl silanes play an important role in organic synthesis as useful intermediates in a number of synthetic transformations; see: T.-Y. Luh, S.-T. Liu in *The Chemistry of Organic Silicon Compounds, Vol. 2* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1998**, pp. 1793–1868.

[12] The oxidative addition of chlorosilanes to late transition metals tends to be sluggish as a result of the strong Si–Cl bond energy; see: H. Yamashita, M. Tanaka, M. Goto, *Organometallics* **1997**, *16*, 4696–4704, and references therein; for the Zr-catalyzed silylation of olefins with chlorosilanes, see reference [5a].