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Formation of 1,4-Disilyl-2-butenes from Vinyl Grignard Reagent and Chlorosilanes Catalyzed by a Titanocene Complex

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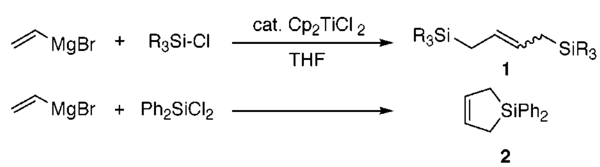
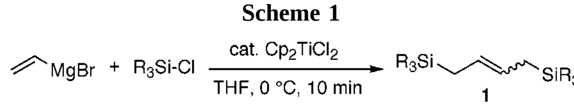
ABSTRACT



Symmetrical 1,4-disilyl-2-butenes 1 have been prepared by the reaction of vinyl Grignard reagent with chlorosilanes. This reaction proceeds efficiently in the presence of a catalytic amount of titanocene dichloride at 0 °C in THF. When dichlorodiphenylsilane was used, 1,1-diphenyl-1-silacyclo-3-pentene 2 was obtained in a good yield.

Titanocene dichloride catalyzes the reduction of alkyl, aryl, and vinyl bromides;[1a,b] aryl chlorides;[1c] alkoxy- and halo-silanes;[1d] ketones;[1e] esters,[1f] and carboxylic acid[1g] by the aid of alkyl Grignard reagents. This Cp_2TiCl_2/RMgX system can also be applied to the hydromagnesation of alkynes, dienes, and alkenes.[1a,2] We have recently developed regioselective introduction of alkyl and/or silyl functionalities to alkenes and dienes by the use of Cp_2TiCl_2 as a catalyst in the presence of ^{n}BuMgCl.[3] In these reactions, however, Grignard reagents have been used as the reducing reagent of titanocene complexes or as the hydrogen source and their carbon moieties have never been incorporated in the products. Herein, we wish to disclose a new type of titanocene-catalyzed transformation using vinyl Grignard reagents and chlorosilanes giving rise to 1,4-disilyl-2-butenes as shown in Scheme 1.

Scheme 1



For example, into a mixture of chlorodimethylphenylsilane (2.85 mmol) and a catalytic amount of titanocene dichloride (0.05 equiv) was added a THF solution of vinyl Grignard reagent (0.95 M in THF, 3 mL, 1.0 equiv) at 0 °C, and the solution was stirred for 10 min. The NMR analysis of the crude mixture indicated the formation of 1,4-bis(dimethyl-phenylsilyl)-2-butene[4] (**1a**; $R_3Si = PhMe_2Si$) in 94% yield with an *E*/*Z* ratio of 74/26 (Table 1, run 1). The product

(1) (a) Colomer, E.; Corriu, R. *J. Organomet. Chem*. **1974**, *82*, 367−373. (b) Rilatt, J. A.; Kitching, W. *Organometallics* **1982**, *1*, 1089−1093. (c) Hara, R.; Sato, K.; Sun, W. H.; Takahashi, T. *J. Chem. Soc., Chem. Commun.* **1999**, 845−846. (d) Corriu, R. J. P.; Meunier, B. *J. Organomet. Chem*. **1974**, *65*, 187−194. (e) Sato, F.; Jinbo, T.; Sato, M. *Tetrahedron Lett.* **1980**, *21*, 2171−2174. (f) Sato, F.; Jinbo, T.; Sato, M. *Tetrahedron Lett.* **1980**, *21*, 2175−2178. (g) Sato, F.; Jinbo, T.; Sato, M. *Synthesis* **1981**, 871.

(2) Sato, F. *J. Organomet. Chem*. **1985**, *285*, 53−64. Gao, Y.; Sato, F. *J. Chem. Soc. Chem. Commun.* **1995**, 659−660 and references therein.

(3) (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. (c) Nii, S.; Terao, J.; Kambe, N. *J. Org. Chem.* **2000**, *65*, 5291−5297.

(4) The products **1a**−**c** and **2** are known compounds, and their yields and *E*/*Z* ratios were determined by NMR. Registry nos.: **1a**, 60404-57-1; **1b**, 3528-12-9; **1c**, 58458-84-7, 84812-44-2; **2**, 34106-93-9.

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Table 1. Silylative Homocoupling of Vinylmagnesium Bromide

run	catalyst	clorosilane	product	yield (%)[a]	E/Z
1	Cp_2TiCl_2	$PhMe_2Si$-Cl	**1a**	94 (86)	74/26
2		Me_3Si-Cl	**1b**	83	72/28
3		Et_3Si-Cl	**1c**	68 (61)	76/24
4		Pr_3Si-Cl	**1d**	64	82/18
5		Me_3SiMe_2Si-Cl	**1e**	72, 86[b]	64/36
6	Cp_2ZrCl_2	$PhMe_2Si$-Cl	**1a**	<1	
7	$TiCl_4$		**1a**	8	
8	$Ti(O^iPr)_4$		**1a**	6	
9	Cp_2HfCl_2		**1a**	0	

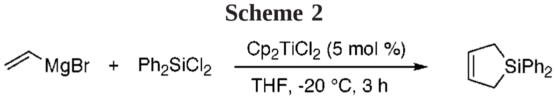
[a] NMR yield. Isolated yield is in parentheses. [b] At −20 °C, 10 min.

was obtained in pure form in 86% yield by a recycling preparative HPLC using $CHCl_3$ as an eluent. In this reaction, only a trace amount of $CH_2{=}CHSiMe_2Ph$ (<1%) was formed as a byproduct, probably via direct reaction of $CH_2{=}CHMgBr$ with $PhMe_2SiCl$. The elongation of the reaction time did not lead to the change of *E/Z* ratio.

Table 1 summarizes the results of this silylative coupling of vinyl Grignard reagent. Chlorotrialkylsilanes can also be employed as the silylation reagents to give the desired products[4,5] (**1b**, R = Me; **1c**, R = Et; **1d**, R = ^{n}Pr) in good yields (runs 2−4). Under similar conditions, chloropentamethyldisilane also gave the corresponding product[6] (**1e**, $R_3Si = Me_3SiMe_2Si$) in 72% yield (run 5). The yield increased to 86% when the reaction was conducted at −20 °C for 10 min. Substituted vinyl Grignard reagents, such as α-methyl or β-methyl vinylmagnesium bromides, were sluggish under the same conditions. When Cp_2ZrCl_2 was used as a catalyst, only a trace amount of **1a** was obtained under the identical conditions (run 6). The use of $TiCl_4$ and $Ti(O^iPr)_4$ in place of Cp_2TiCl_2 afforded 8% and 6% yields of **1a**, respectively (runs 7 and 8), but no reaction took place with Cp_2HfCl_2 (run 9).

When dichlorodiphenylsilane (0.5 equiv) was treated with vinyl Grignard reagent at −20 °C for 3 h, cyclization predominated to afford 1,1-diphenyl-1-silacyclo-3-pentene[4] (**2**) in 73% yield (Scheme 2).

Scheme 2



2, 73%

A plausible reaction pathway is shown in Scheme 3. Titanocene dichloride reacts with 2 equiv of $CH_2{=}CHMgBr$ to generate divinyltitanocene complex **3**, which readily forms titanocene−butadiene complex **4** or its *s*-trans isomer via reductive coupling.[7,8] Then, **4** would isomerize to titanacyclopentene **5**.[9] The successive transmetalation of **5** with vinyl Grignard reagent affords allylmagnesium species **6**, which reacts with chlorosilane to give allylsilane **7** carrying a titanocene group on the other allylic position. Subsequent transmetalation of **7** with $CH_2{=}CHMgBr$ followed by trapping with a chlorosilane gives the corresponding product along with regeneration of **3**.

We carried out the following control experiments to examine the validity of this reaction pathway. Since a small amount of the vinylsilane was formed as a byproduct (<5%) in the present silylation reaction, we first examined whether the double silylated product is formed via vinylsilanes as an intermediate.[10] When a reaction of chlorotripropylsilane (1.0 equiv) with vinyl Grignard reagent under identical conditions as run 4 in Table 1 was carried out at 0 °C for 10 min in the presence of $CH_2{=}CHSiEt_3$ (1.0 equiv), **1d** was obtained as the sole product in 49% yield and 92% of unreacted $CH_2{=}CHSiEt_3$ was recovered. When the reaction was conducted for 2 h, the yield of **1d** was improved to 62%. This result rules out the intermediacy of vinylsilanes.

It is known that Cp_2TiCl_2 reacts with $CH_2{=}CHLi$ at low temperature in the presence of tetramethylethylenediamine (TMEDA) to give butadiene and $Cp_2Ti(TMEDA)$.[7a] On the other hand, it was also reported that titanocene alkenylidene complexes were prepared from titanocene dichloride with 2 equiv of vinyl Grignard reagents.[11] So, we tested whether the reductive coupling of divinyltitanocene **3** giving rise to 1,3-butadiene does take place under the conditions employed. Titanocene dichloride was treated with 2 equiv of vinylmagnesium bromide in THF at −78 °C. After stirring for 1 h, the solution was warmed to 0 °C over 5 min and stirred for another 5 min at the same temperature. NMR analysis

(5) **Data for 1d:** IR (neat) 2954, 2925, 2868, 1459, 1409, 1332, 1202, 1067, 1004, 815, 738 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (trans isomer) δ 5.21−5.18 (m, 2 H), 1.41−1.40 (m, 4 H), 1.38−1.28 (m, 12 H), 0.97−0.91 (t, J = 7.2 Hz, 18 H), 0.54−0.49 (m, 12 H); (cis isomer) δ 5.28−5.15 (m, 2 H), 1.45−1.40 (m, 4 H), 1.38−1.28 (m, 12 H), 0.97−0.91 (t, J = 7.2 Hz, 18 H), 0.54−0.49 (m, 12 H); ^{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; MS (EI) *m/z* (relative intensity, %) 368 (M^+, 10), 158 (15), 157 (100), 116 (12), 115 (90), 87 (17), 73 (27), 59 (9), 45 (10); HRMS calcd for $C_{22}H_{48}Si_2$ 368.3295, found 368.3292. Anal. Calcd for $C_{22}H_{48}Si_2$: C, 71.65; H, 13.12. Found: C, 71.84; H, 13.32.

(6) **Data for 1e:** IR (neat) 2950, 2893, 1244, 833, 809, 723, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) (trans isomer) δ 5.23-5.19 (m, 2 H), 1.49−1.47 (m, 4 H), 0.05 (s, 18 H), 0.02 (s, 12 H); (cis isomer) 5.31−5.28 (m, 2 H), 1.49−1.47 (m, 4 H), 0.06 (s, 18 H), 0.04 (s, 12 H); ^{13}C NMR (100 MHz, $CDCl_3$) (trans isomer) δ 124.2, 20.6, −2.0, −4.5. (cis isomer) δ 122.9, 15.8, −2.0, −4.5; MS (EI) *m/z* (relative intensity, %) 316 (M^+, 10), 243 (14), 169 (8), 155 (40), 132 (21), 131 (100), 116(15), 73(50); HRMS calcd for $C_{14}H_{36}Si_4$ 316.1894, found 316.1902. Anal. Calcd for $C_{14}H_{36}Si_4$: C, 53.08; H, 11.45. Found: C, 53.07; H, 11.02

(7) (a) Beckhaus, R.; Thiele, K.-H. *J. Organomet. Chem.* **1986**, *317*, 23−31. (b) Beckhaus, R.; Flatau, S.; Trojanov, S.; Hofmann, P. *Chem. Ber*. **1992**, *125*, 291−299. (c) Beckhaus, R. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 686−713.

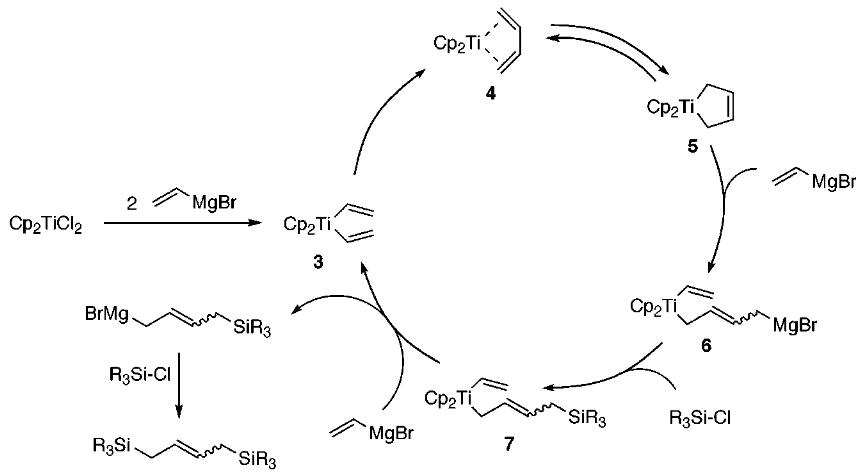
(8) Similar reaction has also been reported for zirconocene, i.e., Cp_2ZrCl_2 reacts with $CH_2{=}CHLi$ to form $Cp_2Zr(CH{=}CH_2)_2$, which undergoes reductive coupling to afford butadiene. Beckhaus, R.; Thiele, K.-H. *J. Organomet. Chem*. **1984**, *268*, C7−C8.

(9) It is known that isomerization of zircocene−butadiene complex to zirconacyclopentene was suggested, see: (a) Erker, G.; Wicher, J.; Engel, K.; Rosenfeldt, F.; Dietrich, W.; Krüger, C. *J. Am. Chem. Soc.* **1980**, *102*, 6344−6346. (b) Yasuda, H.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 723−742.

(10) It is also reported that homodimerization of vinyl silane catalyzed by transition metal gives 1,4-disilyl-butenes: (a) Yur'ev, V. P.; Gailyunas, G. A.; Yusupova, F. G.; Nurtdinova, G. V.; Monakhova, E. S.; Tolstikov, G. A. *J. Organomet. Chem*. **1979**, 169, 19−24. (b) Kretschmer, W. P.; Troyanov, S. I.; Meetsma, A.; Hessen, B.; Teuben. J. H. *Organometallics* **1998**, *17*, 284−286.

(11) Petasis, N. A.; Hu, Y.-H. *J. Org. Chem.* **1997**, *62*, 782−783.

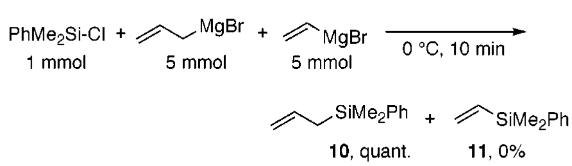
Scheme 3. A Plausible Pathway of Ti-Catalyzed Double Silylative Vinyl Coupling



of this solution, after addition of THF-d_8, indicated the formation of 1, 3-butadiene in 64% yield. We have already reported that 1,4-disilyl-2-butenes were formed by the reaction of 1,3-butadiene with 2 equiv of chlorosilane and ^{n}BuMgCl in the presence of a catalytic amount of Cp_2TiCl_2.[3b] This result also supports the intermediary of butadiene.

To support the intermediary of allyl Grignard reagents, we examined their reactivities toward chlorosilanes. To a mixture of $CH_2{=}CHCH_2MgBr$ (5 mmol) and $CH_2{=}CHMgBr$ (5 mmol) in THF (10 mL) was added $PhMe_2SiCl$ (1 mmol) at 0 °C, and the mixture was stirred for 10 min. The NMR analysis of the crude mixture indicated the formation of allylsilane (**10**) quantitatively, but vinylsilane (**11**) was not detected at all (Scheme 4). This result suggests

Scheme 4



that allyl Grignard reagents react with chlorosilanes much faster than $CH_2{=}CHMgBr$.

An alternative pathway from **5** to **7** was proposed by a referee, i.e., reaction of **5** with R_3SiCl to give $Cp_2TiClCH_2$-$CH{=}CHCH_2SiR_3$ followed by the transmetalation with $CH_2{=}CHMgBr$ leading to **7**. However, this might be ruled out by the evidence that a reaction of Cp_2TiCl_2 with 2 equiv of $CH_2{=}CHMgBr$ in the presence of Me_3SiCl followed by protonolysis did not afford any silylated products.

In conclusion, a novel silylative coupling of vinylmagnesium bromides with chlorosilanes has been developed by the aid of a titanocene catalyst. Many reactions catalyzed by titanocene complexes using Grignard reagents have been reported, in which Grignard reagents have been employed as reducing reagents of titanocene complexes or as hydrogen sources. This reaction is unique because organic moieties of Grignard reagents are incorporated in the products, which has never been achieved by the use of Cp_2TiCl_2 as a catalyst before this. The present reaction would involve reductive coupling of divinyltitanocene complex in the carbon−carbon bond forming step and electrophilic trapping of allylmagnesium intermediates with chlorosilanes.

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