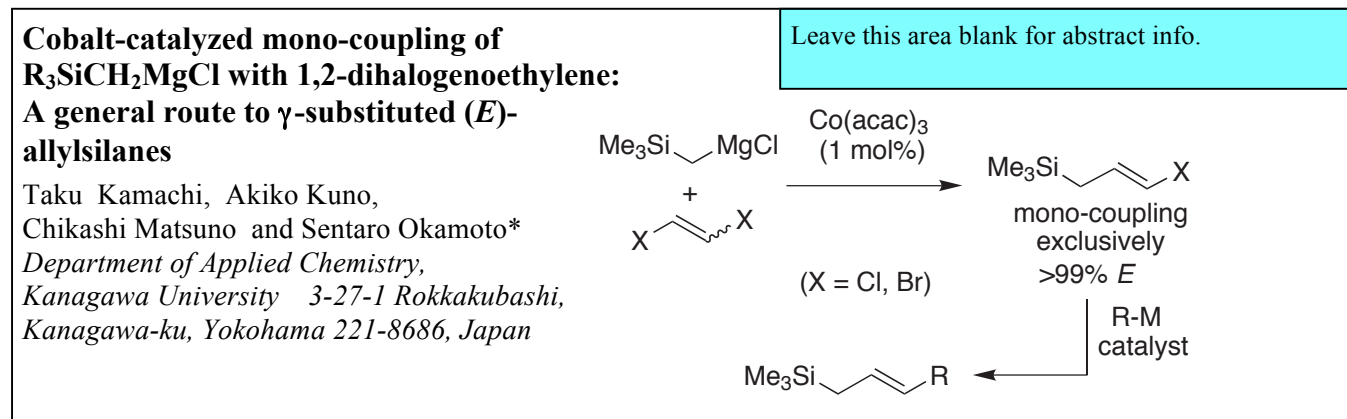


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Cobalt-catalyzed mono-coupling of R_3SiCH_2MgCl with 1,2-dihalogenoethylene: A general route to γ -substituted (*E*)-allylsilanes

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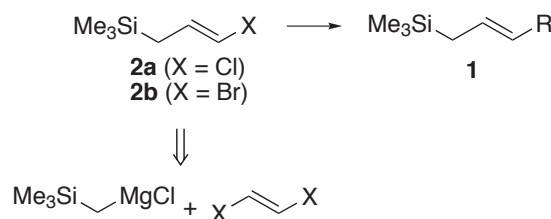
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Abstract—The reaction of trimethylsilylmethylmagnesium chloride ($TMSCH_2MgCl$) with 1,2-dihalogenoethylene in the presence of 1 mol% of Co(II) or Co(III) acetylacetonate in THF or THF-NMP proceeded exclusively in a mono-coupling pathway to provide 3-trimethylsilyl-1-halogeno-1-propene with >99% of *E* geometry in high yield, which was converted to a variety of γ -substituted allylsilanes by Ni- or Pd-catalyzed coupling with organometallic compounds. © 2011 Elsevier Science. All rights reserved

Allylsilanes are versatile compounds in organic synthesis useful as an allylating reagent or a starting material.¹ Therefore, numerous methods have been developed for their preparation, and several substituted allylsilanes as well as simple unsubstituted ones have become obtainable from commercial sources. γ -Substituted allylsilane **1** is an important member in the chemistry field that has been widely used in inter- and intramolecular reactions in the presence of a Lewis acid or F^- with a variety of electrophiles such as carbonyl, imino and iminium compounds and α,β -unsaturated carbonyl compounds, where high regio- and/or stereoselectivity has often been attained. Therefore, development of a general method for their preparation is desired.² Herein we describe an efficient preparation of (*E*)-3-silyl-1-halogeno-1-propene (**2**)³ by a selective Co-catalyzed mono-coupling of 1,2-dihalogenoethylene with $TMSCH_2MgCl$ (TMS = trimethylsilyl), which allows a general access to (*E*)- γ -substituted allylsilanes **1** by the metal-catalyzed cross-coupling with a variety of organometallic reagents (Scheme 1).

First, we investigated a transition metal-catalyzed coupling reaction of (*E*)-1,2-dichloroethylene (>99% *E*), which is commercially available at low price, with $TMSCH_2MgCl$ to find conditions for selective production

Scheme 1

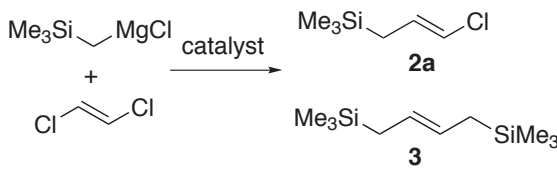


of mono-coupling product **2a**. Thus, (*E*)-1,2-dichloroethylene (4.0 mmol) was treated with $TMSCH_2MgCl$ ⁴ (2.0 mmol) in the presence of 1 mol% of Ni, Pd, Co or Fe catalyst precursor. As can be seen from Table 1 summarizing the results, nickel-catalyzed reactions⁵ afforded a mixture of (*E*)-3-trimethylsilyl-1-chloro-1-propene (**2a**) and 1,4-bis(trimethylsilyl)-2-butene (**3**) (entries 1-4).⁶ It was noteworthy that the reaction with Ni- PPh_3 complexes gave **2a** predominantly (entries 1 and 2) but Ni-complexes with a bidentate phosphine ligand such as $Cl_2Ni(dppp)$ and $Cl_2Ni(dppb)$ catalyzed production of **3** mainly (entries 3 and 4). As shown in entries 6-8, to our delight, the reaction catalyzed by $Co(acac)_2$ or $Co(acac)_3$ proceeded smoothly with nearly complete selectivity of mono-coupling to provide **2a** in excellent yield, the isomeric purity of which was found to be >99% *E* by GC and 500 MHz ¹H NMR analyses.⁷ In these reactions, use of NMP (*N*-methylpyrrolidin-2-one) as an additive affected the reaction rate but not the yield and selectivity

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(entries 6 and 7). Cahiez originally reported the reaction of 1,2-dichloroethylene with alkyl-Grignard reagents providing mono-coupling products exclusively where addition of NMP as a co-solvent was suggested for attaining good yield.⁸ The yield of the reaction carried out here was somewhat better than those of the reaction with the usual alkyl-Grignard reagents reported by Cahiez. It can be assumed that the absence of β -hydride in TMSCH₂MgCl might avoid other reaction(s) than the desired coupling. With these results, we carried out 20 mmol scale synthesis and **2a** could be isolated in pure form by distillation in 90% yield. Pd- and Fe-compounds did not catalyze this reaction (entries 5 and 9).

Table 1^a

entry	catalyst (1 mol%)	conditions	yield, % ^b	
			2a	3
				
1 ^c	Br ₂ Ni(PPh ₃) ₂ + 2PPh ₃	0 °C, 30 min benzene-ether	78	15
2	Cl ₂ Ni(PPh ₃) ₂ + 2PPh ₃	0 °C to r.t., 2.5 h ether	33	20
3	Cl ₂ Ni(dppp) ₂	0 °C to r.t., 2.5 h ether	10	87
4	Cl ₂ Ni(dppb) ₂	0 °C to r.t., 2.5 h ether	5	32
5	Cl ₂ Pd(PPh ₃) ₂	0 °C to r.t., 12 h THF-ether	trace	trace
6	Co(acac) ₃	0 °C, 5 h THF	86	0
7	Co(acac) ₃	0 °C, 15 min THF-NMP (4:1)	88	0
8	Co(acac) ₂ ^d	0 °C, 15 min THF-NMP (4:1)	81	0
9	Fe(acac) ₂	0 °C to r.t., 1.5 h THF-NMP (4:1)	trace	trace

^aReactions were performed using 2.0 mmol of Grignard reagent, 4.0 mmol of 1,2-dichloroethylene and 1 mol% of catalyst. ^bGC yield. ^cSee ref. 1. 5 equiv of 1,2-dichloroethylene was used.

^dTetrahydrate was used.

dppp: 1,3-bis(diphenylphosphino)propane

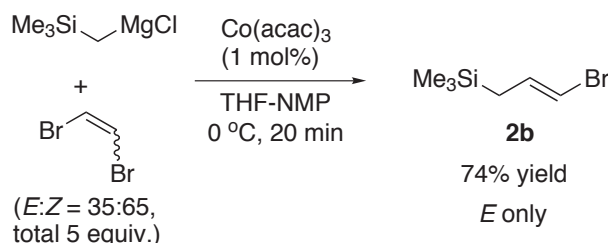
dppb: 1,4-bis(diphenylphosphino)butane

acac: acetylacetonato

Next we tried a Co-catalyzed coupling of TMSCH₂MgCl with (*Z*)-1,2-dichloroethylene and, unfortunately, found that the reaction did not proceed at all. However, the results prompted us to carry out the reaction with a mixture of (*E*)- and (*Z*)-1,2-dibromoethylene which is commercially available at low price. Thus, a mixture of *E*- and *Z*-isomers

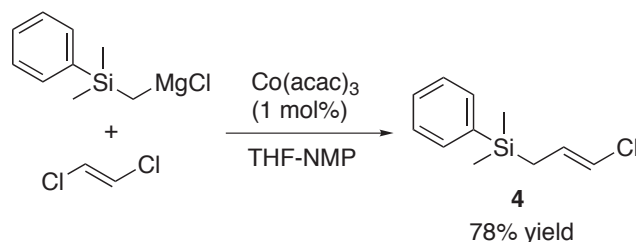
of 1,2-dibromoethylene (*E:Z* = 35:65, total 5 equiv.) was treated with TMSCH₂MgCl in the presence of 1 mol% of Co(acac)₃ in THF-NMP (Scheme 2). As expected, only (*E*)-3-trimethylsilyl-1-bromopropene (**2b**) was produced in good yield of 74%.

Scheme 2



Similarly, γ -halogenoallylsilanes having a silyl moiety other than trimethylsilyl could be prepared without loss of yield and selectivity (Scheme 3).⁷

Scheme 3



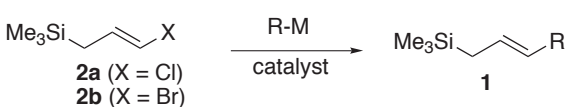
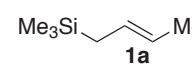
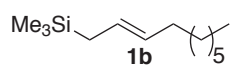
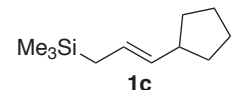
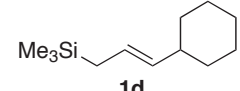
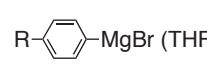
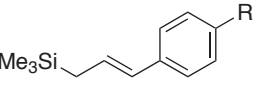
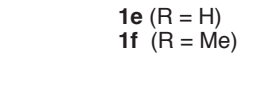
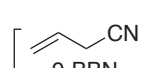
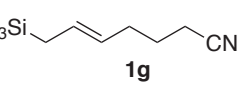
With γ -halo-(*E*)-allylsilanes **2a** and **2b** in hand, we carried out their conversion to **1** by transition metal-catalyzed coupling reactions. As can be seen from Table 2 summarizing the several representative results, **1** with methyl as well as normal and secondary alkyl and aryl groups could be readily prepared by the Ni-catalyzed coupling with the corresponding Grignard reagent (Kumada-Tamao reaction).⁵ It is noteworthy that the Suzuki-Miyaura coupling⁹ of bromide **2b** with boranes was effective for synthesis of **1** having a functional group as shown in entry 5.

In addition to use of **2** as a substrate for metal-catalyzed coupling reactions, as illustrated in Scheme 4, **2a** and **2b** are useful as an equivalent of 3-silyl-1-propynyl and 3-silyl-1-propenyl anions. Thus, treatment of **2a** with LDA (2 equiv.) and the following addition of aldehyde afforded the corresponding adduct, whereas (*E*)-allylic alcohol was obtained by treatment of **2b** with *t*-BuLi and then aldehyde.¹⁰

In conclusion, we have developed a selective mono-coupling reaction of R₃SiCH₂MgCl with 1,2-dihaloethylene which opens up a general method for preparation of γ -substituted (*E*)-allylic silanes. Further

study for the preparation and synthetic utilization of functionalized allylsilanes is underway in our laboratories.

Table 2

			
entry	2	R-M (solvent) catalyst (mol%)	product yield, % ^a
1	2a	MeMgI (ether) Cl ₂ Ni(dppp) (2)	 1a 95 ^b
2	2a	<i>n</i> -C ₆ H ₁₃ MgBr (THF) Cl ₂ Ni(dppp) (2)	 1b 83
3	2a	<i>c</i> -C ₅ H ₉ MgCl (ether) Cl ₂ Ni(dppp) (2)	 1c 59
4	2a	<i>c</i> -C ₆ H ₁₁ MgCl (ether) Cl ₂ Ni(dppp) (2)	 1d 93
5	2a	R-  -MgBr (THF) Cl ₂ Ni(dppp) (2)	 1e (R = H) 91
6			 1f (R = Me) 95
7	2b	 Cl ₂ Pd(dppf) (4) K ₃ PO ₄	 1g 58

^aIsolated yield unless otherwise indicated. Reaction was not optimized. ^bGC yield.

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- An *E*- and *Z*-mixture of **2a** or **2b** has been prepared from the corresponding 1,3-dihalopropene by the reaction with Cl₃SiH and the following methylation with MeMgBr. For preparation and synthetic utilization of **2**, see: for **2a**, (a) Ochiai, M.; Fujita, E. *J. Chem. Soc., Chem. Commun.*, **1980**, 1118. (b) Ochiai, M.; Fujita, E. *Tetrahedron Lett.*, **1980**, *21*, 4369. For **2b**, (c) Nishiyama, H.; Narimatsu, S.; Itoh, K. *Tetrahedron Lett.*, **1981**, *22*, 5289. (d) Angell, R.; Parsons, P. J.; Naylor, A.; Tyrrell, E. *Synlett*, **1992**, 599. (e) Parsons, P. J.; Angell, R.; Naylor, A.; Tyrrell, E. *J. Chem. Soc., Chem. Commun.*, **1993**, 366.
- Prepared from TMSCH₂Cl and magnesium turnings in ether or THF and titrated by using acid and base. Yields shown in Table 1 and Scheme 2 were based on the amount of the Grignard reagent used.
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- One of the authors (SO) reported the preparation of **2a** by the reaction shown in entry 1 on Table 1, in which **2a** was obtained by distillation as a benzene solution: Okamoto, S.; Tani, K.; Sato, F.; Sharpless, K. B.; Zargarian, D. *Tetrahedron Lett.*, **1993**, *34*, 2509.
- ¹H NMR (CDCl₃, 500 MHz): **2a**; δ 5.87 (dt, *J* = 13, 8.5 Hz, 1H), 5.51 (d, *J* = 13 Hz, 1H), 1.48 (d, *J* = 8.5 Hz, 2H), 0.03 (s, 9H). **2b**; δ 6.16 (dt, *J* = 13, 8.5 Hz, 1H), 5.82 (dt, *J* = 13, 1.0 Hz, 1H), 1.52 (dd, *J* = 1.0, 8.5 Hz, 2H), 0.06 (s, 9H). **4**; δ 7.39-7.57 (m, 5H), 5.90 (ddt, *J* = 1.0, 13, 8.5 Hz, 1H), 5.77 (dd, *J* = 1.0, 13 Hz, 1H), 1.75 (d, *J* = 8.5 Hz, 2H), 0.35 (s, 6H).
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- Miyaura, N.; Suzuki, A. *Chem. Rev.*, **1995**, *95*, 2457.
- CrCl₂-Mediated reaction of **2b** with aldehydes providing δ -trimethylsilyl allylic alcohols has been reported: see references 3d and 3e.

Scheme 4

