Note

Direct construction of silicon–silicon bond by using the low-valent titanium reagent

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Abstract

The reductive dimerization or polymerization of organochlorosilanes has been achieved by using the low-valent titanium reducing agent other than the alkali metals that are invariable used in the Wurtz-type coupling reaction. Applying this method, the corresponding disilanes or poly(methylvinylsilane) was obtained in good yields. The poly(methylvinylsilane) synthesized by this method is highly pure with a high molecular weight and a narrow molecular weight distribution ($M_w/M_n = 1.6$, $M_n = 16,860$).
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1. Introduction

The silicon-containing polymers have been widely investigated in recent decades because of their potential applications in the fields of advanced materials [1]. Much attention is, therefore, being focused on the development of synthetic routs [2–6]. However, the most commonly used approach for the construction of the silicon–silicon bond is the Wurtz-type reaction of halosilanes with an alkali metal (the Kipping method) [7]. Nevertheless, this method suffers from drastic reaction conditions, thus few functional groups, unless well protected, can withstand such conditions so substitutents are generally limited to alkyl, aryl, silyl groups, etc. [2d]. Alternative reducing agents were widely investigated by Jones for the reductive polymerization of dichloromethylphenylsilane, and demonstrated that the Wurtz synthesis of poly(methylphenylsilane) can be carried out with yttrium and pyrophoric lead metals although the reaction is slow (7–30 days) [8]. Recently, Ogawa groups reported the Sm/SmI$_2$ mixed system induced reductive coupling of organochlorosilanes, which gave the dislanes and poly(methylphenylsilane) in good yields [9]. In our studies for the construction of Group 14 element linkages, we found that the low-valent titanium is a versatile reagent for the synthesis of polysilanes. Herein we describe the results of reductive dimerization or polymerization of organochlorosilanes with the low-valent titanium as the alternative reducing agent.

Low-valent titanium has been extensively investigated as a versatile reagent in organic synthesis, especially with its exceptional ability to promote reductive coupling of many functional groups [10]. Thus, the low-valent titanium was considered promising as a mild reducing agent for dimerization or polymerization of chlorosilanes. Herein we described the direct construction of the silicon–silicon bond using the low-valent titanium reagent.
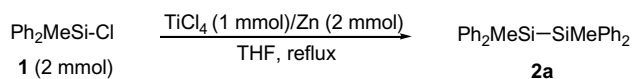
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2. Results and discussion

As a starting point for the synthesis of disilanes, initially, we chose to study the conversion of chlorodiphenylmethylsilane to the disilane mediated by the Zn/TiCl$_4$ reagent (Scheme 1). When chlorodiphenylmethylsilanes (1) was treated with the low-valent titanium (TiCl$_4$/Zn) at reflux in dry THF for 20 h to give dimethyltetraphenyldisilane (2a) in 88% isolated yield. When the reaction was carried out in other solvents other than THF, such as dry DME, toluene or CH$_3$CN, the reaction failed (entries 1–3).

On the basis of the result obtained with the chlorodiphenylmethylsilane, we investigate the possibility of extending this methodology to other trisubstituted chlorosilanes (R$_3$SiCl). As shown in Table 2, substituted aromatic chlorosilanes could take place smoothly reductive dimerization under the optimized reaction conditions (Table 1, entry 5) to give the corresponding disilanes in good yields, in which the vinyl group was not affected (entry 6). It should be noted that reduced by the low-valent titanium reagent, aliphatic chlorosilane, such as t-butyldimethylchlorosilane also can be undergone the reductive dimerization giving di-t-butyltetramethyldisilane in 81% isolated yield (entry 7).

With the success for the synthesis of disilanes, the reductive polymerization of dichloromethylvinylsilane was also investigated under the above-mentioned reaction conditions, since the known methods for the polysilane synthesis are not very satisfactory [2d]. When dichloromethylvinylsilane (2 mmol) was treated with TiCl$_4$ (2 mmol)/Zn (4 mmol) in refluxing THF (50 mL) for 24 h, poly(methylvinylsilane) was isolated although the yield is low (Table 3, entry). Interestingly, when samarium was used as the co-reductant, the poly(methylvinylsilane) was obtained in moderate yield (entry 2) [11]. An increase of yield could be achieved by prolonging the reaction time (entry 3), and the molecular weight distribution of the poly(methylvi-

Ph$_2$MeSi-Cl $\xrightarrow[\text{THF, reflux}]{\text{TiCl}_4 \text{ (1 mmol)/Zn (2 mmol)}}$ Ph$_2$MeSi—SiMePh$_2$

1 (2 mmol)   **2a**

Scheme 1.

Table 1
The reductive dimerization of chlorodiphenylmethylsilane promoted by the low-valent titanium reagent[a]

Entry	Solvent	Time (h)	Yields[b] (%)
1	DME	10	NR
2	Toluene	10	NR
3	CH$_3$CN	10	NR
4	THF	12	50
5	THF	20	88
6[c]	THF	24	NR

[a] Unless otherwise noted, chlorodiphenylmethylsilane (2 mmol) were allowed to react with Zn powder (2 mmol) and TiCl$_4$ (1 mmol) in THF 65 °C, toluene 110 °C, DME 84 °C, CH$_3$CN 82 °C for 10–24 h.
[b] Isolated yields based on (1) used.
[c] At room temperature.

Table 2
The reductive dimerization of trisubstituted chlorosilanes (R$_3$SiCl) promoted by the TiCl$_4$/Zn system[a]

R$_1$R$_2$R$_3$Si-Cl $\xrightarrow[\text{THF(40 mL), reflux}]{\text{TiCl}_4\text{(1 mmol)/Zn (2 mmol)}}$ R$_1$R$_2$R$_3$Si-SiR$_1$R$_2$R$_3$

1 (2 mmol)   **2**

Entry	Chlorosilanes	Products		Yields[b] (%)
1	MePh$_2$SiCl	MePh$_2$SiSiPh$_2$Me	2a	90
2	Me$_2$PhSiCl	Me$_2$PhSiSiPhMe$_2$	2b	91
3	Ph$_3$SiCl	Ph$_3$SiSiPh$_3$	2c	80
4	MePhHSiCl	MePhHSiSiHPhMe	2d	64
5	Ph$_2$HSiCl	Ph$_2$HSiSiHPh$_2$	2e	70
6	VinylPh$_2$SiCl	VinylPh$_2$SiSiPh$_2$Vinyl	2f	85
7	^{t}BuMe$_2$SiCl	^{t}BuMe$_2$SiSiMe$_2$Bu^t	2g	81

[a] Unless otherwise noted, organochlorosilanes (2 mmol) were allowed to react with Zn (2 mmol) and TiCl$_4$ (1 mmol) in THF at 56 °C for 24 h.
[b] Isolated yield based on chlorosilane (1) used.

Table 3
The reductive polymerization of dichloromethylvinylsilane promoted by the low-valent titanium agent

Entry	Reducing agent	Time (h)	Yield[a,b] (%)	M_w	M_n	M_w/M_n
1	TiCl$_4$/Zn	24	11	12,870	9426	1.3
2	TiCl$_4$/Zn/Sm	12	56	17,870	8122	2.2
3	TiCl$_4$/Zn/Sm	24	84	26,976	16,860	1.6
4[c]	TiCl$_4$/Zn/Sm	24	0			

[a] Isolated yields based on 3 used.
[b] Purified by precipitation from THF–EtOH.
[c] At room temperature.

nylsilane) obtained by this method is much narrow ($M_w/M_n = 1.6$, $M_n = 16,860$).

The polymer was purified by precipitation from its THF solution with EtOH, followed by freeze-drying. The product was identified as a polysilane polymer based on the analysis of ^{1}H NMR, IR, and UV spectra. The molecular weight distribution of this polymer was determined by gel permeation chromatography (GPC) calibrated by polystyrene standards with chloroform as the eluent.

In conclusion, the efficient reductive dimerization or polymerization of chlorosilanes has been achieved by using the low-valent titanium reagent. Applying this method, the corresponding disilanes and poly(methylvinylsilane) were obtained in good yields. Further studies on the synthesis of functional polysilanes with this reducing agent are now underway.

3. Experimental

^{1}H and ^{13}C NMR spectra were recorded on a BRUKER AV-400 MHz instrument as CDCl$_3$ solution using TMS as an internal standard. Chemical shifts (δ) are reported in

ppm and coupling constants J are given in Hz. GC–MS were measured with TRANCE 2000 DSQ mass spectrometer. The UV and UV–Vis spectra were recorded with a Shimadzu UV 2200 spectrometer. IR spectra were taken as thin films with a NICOLET 5700 infrared spectrometer. GPC was performed with Water 1525. Elemental analysis was performed on a VARIO EL-III instrument. Melting points are uncorrected. Column chromatography was performed with silica gel (Wako Pure Chemical Industries, Ltd., Wakogel C-300). Thin-layer chromatography was performed on 0.25 mm E. Merck silica gel plates (GF-254).

3.1. Materials

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. Sodium metal, magnesium, zinc, samarium metal and titanium chloride were commercially available products. Ethanol and toluene were purified by distillation prior to use. The starting material chlorosilanes and all solvents of column chromatography were used without further purification. All reactions were conducted under a nitrogen atmosphere.

3.2. General procedure for the synthesis of disilanes (2a–2g)

As a representative example, the preparation of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane(MePh$_2$SiSiPh$_2$Me) is described. A dry 100 mL flask was charged with Zn powder (2 mmol), TiCl$_4$ (0.11 mL, 1 mmol) and THF (50 mL). The mixture was refluxed for 2 h under nitrogen. When black slurry was formed, a solution of chlorodiphenylmethylsilane (2 mmol) in THF (5 mL) was added to the reaction mixture immediately. The black reaction mixture was stirred for another 20 h in refluxing THF. After cooled to room temperature, the mixture was quenched with dilute ice-cold hydrochloric acid (1 mol/L, 30 mL), and extracted with ether (3 × 40 mL). The combined organic layer was washed with saturated NaHCO$_3$ solution and brine, dried over anhydrous MgSO$_4$, and filtered off. The solvent was concentrated under reduced pressure. The residue recrystallized from ethanol to give the product MePh$_2$SiSiPh$_2$Me (2a). This disilane was identified by comparison with an authentic compound (IR, GC–MS and NMR), which was described in the literature [12].

3.3. General procedure for the synthesis of poly(methylvinylsilane)

In a 100 mL three-necked flask equipped with a reflux condenser and a dropping funnel was placed samarium powder (4 mmol), zinc powder (20 mmol), TiCl$_4$ (1.1 mL, 10 mmol), and freshly distilled (sodium/benzophenone ketyl) THF (60 mL) under nitrogen atmosphere. The mixture was refluxed for 2 h under nitrogen. When black slurry was formed, dichloromethylvinylsilane (10 mmol) was dropped to the reaction mixture. Then the flask was set in an oil bath maintained at 70 °C. The reaction mixture

was refluxed for 24 h, and then cooled to the room temperature. The reaction mixture was quenched with EtOH (5 mL), poured into the ice-cold hydrochloric acid (1 mol/L, 30 mL), and then extracted with ether (3 × 50 mL). The combined organic layer was washed with saturated NaHCO$_3$ solution and brine, dried over anhydrous MgSO$_4$, and filtered off. The solvent was removed under reduced pressure, providing a white crude product. The residual crude polymer was dissolved in THF (6 mL), and precipitated by the addition of ethanol (100 mL) to the solution. The molecular weight of the polymer was determined by gel permeation chromatography (GPC) calibrated by polystyrene standards with chloroform as the eluent. Poly(methylvinylsilane) (4a): 588 mg (84%); ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.06 (s, 3H), 5.35–5.40 (m, 3 H); IR (KBr), 2956, 1261, 1105, 1066, 983, 886, 815 cm^{-1}; UV: $\lambda_{max} = 346$ nm; $M_w/M_n = 1.6$, $M_n = 16,860$; Anal. Calc. for C$_3$H$_6$Si: C, 51.42; H, 8.57. Found: C, 51.20; H, 8.79%.

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