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Practical method for the synthesis of polysilanes using Mg and Lewis acid system

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Dedicated to the memory of Professor Yoshihiro Matsumura

Abstract

Reduction of dichlorosilanes with Mg metal in the presence of Lewis acid and LiCl was found to be the highly practical method for the synthesis of polysilanes.

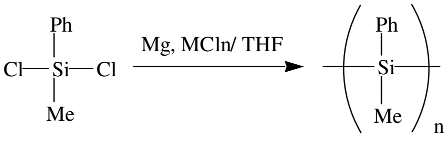
Polysilanes (PS) attracted much attention in recent years because their interesting electronic and photochemical properties stem from σ-conjugation of Si–Si bond.[1] Although some synthetic methods of PS such as the Wurtz coupling reaction,[2] dehydrogenative coupling of primary silanes,[3] the anionic polymerization of masked disilenes,[4] and the ring opening polymerization of strained cyclosilanes[5] have been reported so far, these methods are not practical. On the basis of our continuing studies on the electroreductive synthesis of PS using Mg electrodes,[6–10] we have examined the exploitation of new practical method for the synthesis of PS.

In this Letter we wish to report that the reduction of dichlorosilane (**1**) with Mg metal in the presence of Lewis acid (MCl_n) (Scheme 1) is a highly useful method for the synthesis of PS (**2**) under extremely mild reaction conditions.

As shown in Table 1, the reduction of **1** in the presence of LiCl or $FeCl_2$ did not give **2**, however, that of **1** with LiCl and $FeCl_2$ gave **2** in reasonable yield. Thus the reduction of **1** in the presence of LiCl and some Lewis acids was examined (Table 2).

The results summarized in Table 2 show that the effect of Lewis acid is dramatic and the use of $AlCl_3$ (run 1), $SnCl_2$ (run 5), and $MgCl_2$ (run 6) did not give **2**. The use of other Lewis acids gave **2** and that of $ZnCl_2$ gave the best result (run 7).[11]

The reaction was carried out as follows: Into a 30 mL round-bottomed flask were added dichlorosilane (30 mmol), THF (30 ml, dried over Na), Mg powder (30 mmol), LiCl (20 mmol), and Lewis acid (4 mmol) and the mixture was stirred for 2 h at room temperature. The reaction mixture was poured into an ice cold solution of HCl (1 M/dm^3, 100 mL) and the aqueous solution was extracted with ether (50 mL × 3). The combined organic layers were washed twice with 50 mL of brine, dried over



1 **2**

Scheme 1. Reduction of dichlorosilane.

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Table 1
Effect of metal chloride catalysts in the preparation of polysilane

Run	MCl_n	M_n[a]	M_w/M_n	Yield[b] (%)
1	LiCl	—	—	0
2	$FeCl_2$	—	—	0
3	LiCl + $FeCl_2$	6600	3.1	50

[a] Determined by GPC based on polystyrene standard.
[b] Isolated yield based on **1**.

Table 2
Effect of lewis acid catalysts in preparation of polysilane **2**

Run	MCl_n	M_n[a]	M_w/M_n	Yield of **2**[b] (%)
1	$AlCl_3$	2500	2.02	Trace
2	$CuCl_2$	6150	2.56	44
3	$FeCl_2$	6600	2.79	50
4	$FeCl_3$	4280	2.40	46
5	$SnCl_2$	—	—	0
6	$MgCl_2$	—	—	0
7	$ZnCl_2$	8970	2.18	64

[a] Determined by GPC based on polystyrene standard.
[b] Isolated yield based on **1**.

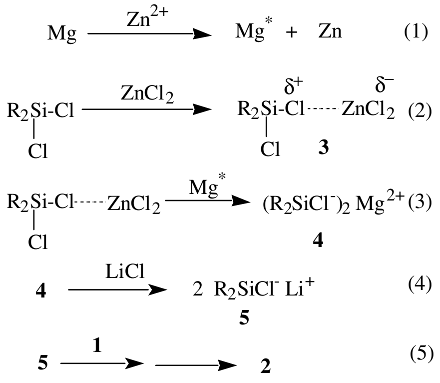
Table 3
Reduction of chlorosilanes

Run	Chlorosilane	Yield of PS (**6**–**8**)[a] (%)	M_n[b]	M_w/M_n
1	Ph_2SiCl_2	100 (**6**)	1000	1.10
2	$PhSiCl_3$	75.8 (**7**)	1380	1.41
3	$HexMeSiCl_2$ $PhMeSiCl_2$[c]	35.8 (**8**)	6200	1.48

[a] Isolated yield based on chlorosilanes.
[b] Determined by GPC based on polystyrene standard.
[c] 1:1 Mixture of $HexMeSiCl_2$ and $PhMeSiCl_2$ was reacted under conditions same as that of **1**. ^1H NMR of **8** indicated that the ratio of PhMeSi and HexMeSi units in **8** was 4:1.

$MgSO_4$, and concentrated. The products were purified by reprecipitation from hexane. The reactions shown in Tables 1–3 were carried out under similar conditions as described above. Scale-up of the reaction was also attained. For example the reduction of **1** (1 kg, 5.24 mol) under similar reaction conditions gave **2** in 70% yield. The synthesis of other PS shown in Table 3 was carried out under similar reaction conditions shown above. The molecular weight of polysilane was determined by GPC based on polystyrene standard,. The product showed reasonable NMR and IR spectra for the assigned structures.[12]

In addition, the effect of Lewis acid was also observed in the structures of PS. For example, ^1H NMR of PS **2a** prepared by using $ZnCl_2$ and **2b** prepared by using $FeCl_2$ showed similar signals at δ −1.00 to −0.70 (m, SiMe), and 6.30–7.70 (m, ring protons), however, exact proportion between methyl protons and ring proton of **2a** was 3.10:5.00 and that of **2b** was 3.30:5.00. This means that **2b** has some blanched structure of Si chain compared with **2a**. This is also supported by ^{29}Si NMR of **2** because the spectra of **2a** showed signal at δ −43 to −38 (m) and that of **2b** showed two kinds of signals at δ −43 to −38 (m) and −33 (m). The latter signal of **2b** indicates the existence of blanched Si chain. Thus the use of stronger Lewis acid resulted in the partial cleavage of bond between Si and aromatic ring and the formation of blanched PS.[13]



Scheme 2. Reaction mechanism.

Although the mechanism of the formation of **2**, especially, the role of LiCl, is not always clear, one of the plausible mechanisms is as follows: The reduction of $ZnCl_2$ with Mg [(1) in Scheme 2] forms the activated Mg (Mg^*), namely, the surface of Mg metal is activated by this reaction, and dichlorosilane is also activated by $ZnCl_2$ [(2) in Scheme 2]. The reduction of activated dichlorosilane (**3**) with Mg^* affords the corresponding silyl anion having Mg counter ion (**4**) [(3) in Scheme 2]. The nucleophilicity of **4** is not enough to react with **1**, however, the cation exchange reaction of **4** to **5** may take place in the presence of LiCl [(4) in Scheme 2]. The nucleophilicity of **5** is enough to react with **1** and form **2** [(5) in Scheme 2].[14]

The reaction is also applicable to the synthesis of other PS. As shown in Table 3, the reduction of $PhMeSiCl_2$ (run 1) and $PhSiCl_3$ (run 2) gave the corresponding PS (**6** and **7**, respectively) in reasonable yields. Although the reduction of $HexMeSiCl_2$ under same reduction conditions did not give PS, the reduction of a mixture of $HexMeSiCl_2$ and $PhMeSiCl_2$ (1:1) (run 3) gave the corresponding copolymer (**8**).[15]

In conclusion the synthesis of PS using Mg–Lewis acid system is highly useful for the practical method since the reaction can be carried out under mild reaction conditions, and the scale-up (kg scale) of the reaction is also easily attained.

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11. The use of the strong Lewis acid such as $AlCl_3$ resulted in the cleavage of the Si–Si bonds of formed PS and resulted in the decrease of the yields.
12. IR (KBr) 3050, 2960, 1430, 1250, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -1.00 to -0.70 (m, 3H, SiMe), 6.30–7.70 (m, 5H, ring protons).
13. The structure of **2** prepared by the electroreduction of **1** was determined to be similar to **2a**. This was confirmed by ^{29}Si NMR.[9]
14. We had previously reported that the electrontransfer reduction of dichlorosilanes formed anionic intermediate.[9]
15. (**6**) IR (KBr) 3068, 2956, 1428 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.10–7.80 (m, 10H, ring protons). (**7**) IR (KBr) 3050, 2960, 1430 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.30–7.70 (m, 15H, ring protons). (**8**) IR (KBr) 3060, 2960, 1430 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ -1.00 to -0.70 (m, 6H, SiMe), 0.10–1.10 (m, 2.6H), 6.30–7.70 (m, 4H, ring protons).