

Synthesis of 1,2-Bis(trimethylsilyl)benzene Derivatives from 1,2-Dichlorobenzenes Using a Hybrid Metal Mg/CuCl in the Presence of LiCl in 1,3-Dimethyl-2-imidazolidinone

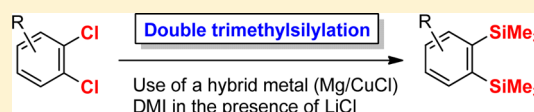
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S Supporting Information

ABSTRACT: A practical and safe synthesis of 1,2-bis(trimethylsilyl)-benzene from 1,2-dichlorobenzene and Me₃SiCl was achieved by use of a hybrid metal of Mg and CuCl in the presence of LiCl in 1,3-dimethyl-2-imidazolidinone (DMI). This method does not require a toxic HMPA, provides a high yield of the product under mild conditions, and is also applied to synthesis of substituted 1,2-bis(trimethylsilyl)benzenes and poly(trimethylsilyl)benzenes.

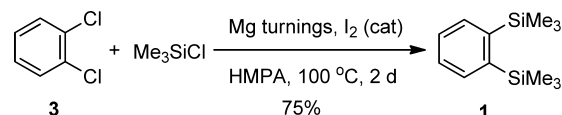


Arylsilanes are useful intermediates in organic synthesis and utilized for several functional group transformations,¹ and palladium-catalyzed Hiyama coupling reactions.² Recently, much attention has been paid to organosilicone compounds as functional materials applicable for optoelectronic devices due to the presence of $\sigma^*-\pi^*$ conjugation.³ In addition, it has been suggested that bifunctional disilylbenzene derivatives are valuable compounds for key materials as a building block for functional materials.⁴

1,2-Bis(trimethylsilyl)benzene (**1**) is a useful starting material for preparing an efficient hypervalent iodine-benzyne precursor, (phenyl)[2-(trimethylsilyl)phenyl]iodonium triflate (**2**).⁵ The 1,2-bis(trimethylsilyl)benzenes are also used for synthesis of 9,10-dihydro-9,10-diboraanthracene as the building block of luminescent boron-containing polymers⁶ and functional materials⁷ and 9,10-dimethyl-9,10-diboraanthracene, which is a powerful Lewis acid catalyst.⁸ Furthermore, synthesis of functionalized 1,2-bis(trimethylsilyl)benzenes has been furnished by C–H activation and functionalization of the parent 1,2-bis(trimethylsilyl)benzene.⁹ Although there are interesting applications, the chemistry of 1,2-disilylbenzene derivatives has not been greatly studied. This is because 1,2-bis(trimethylsilyl)benzene has some serious problems in the synthesis. Therefore, development of synthetic methods of silylbenzenes is a challenging research subject which will be indispensable to development of promising organosilicon chemistry, organic synthesis, and functional materials.

Previously, we reported the most reliable and convenient method for synthesis of 1,2-bis(trimethylsilyl)benzene, which is furnished by the reaction of 1,2-dichlorobenzene with chlorotrimethylsilane in the presence of Mg and a catalytic amount of iodine in HMPA (Scheme 1).^{5,10} However, this method suffers the use of toxic, carcinogenic HMPA¹¹ as solvent and the severe conditions of high temperature and long reaction time.

Scheme 1. Representative Procedure for Synthesis of **1**



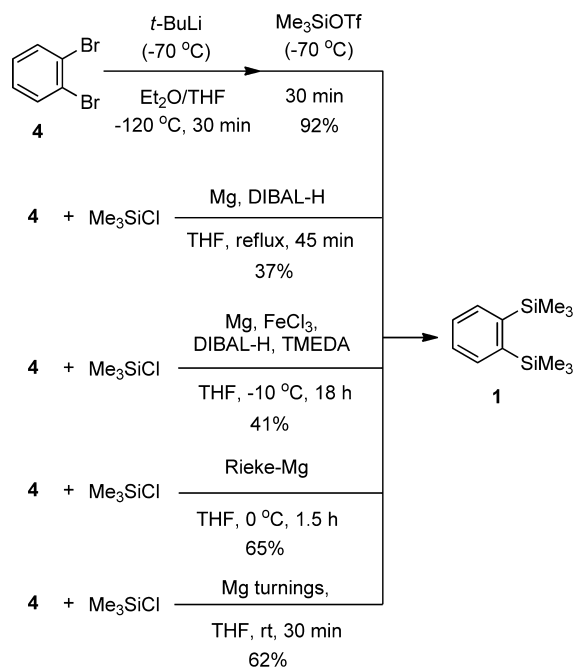
For these reasons, some alternative methods using 1,2-dibromobenzene, instead of 1,2-dichlorobenzene, have been recently reported for synthesis of 1,2-bis(trimethylsilyl)benzene, as outlined in Scheme 2. Bettinger and Filthaus reported synthesis of 1,2-bis(trimethylsilyl)benzene using a specific and controlled procedure: lithiation of 1,2-dibromobenzene with *t*-BuLi cooled at -70 °C in THF/Et₂O at -120 °C followed by silylation with Me₃SiOTf cooled at -70 °C.¹² This procedure needs very low temperature conditions, expensive chemicals, and inconvenient operation.

Wegner et al. reported more convenient methods for synthesis of 1,2-bis(trimethylsilyl)benzene.¹³ One method uses Mg activated with DIBAL-H. Another one includes Mg activated with FeCl₃ and DIBAL-H in the presence of TMEDA. However, the yields of bis(trimethylsilyl)benzene are 37 and 41%, respectively. Wagner et al. reported improved methods using Rieke Mg and Mg activated by 1,2-dibromoethane,¹⁴ giving 1,2-bis(trimethylsilyl)benzene in 65 and 62% yields, respectively.

Although the synthesis of 1,2-bis(trimethylsilyl)benzene has been performed by several methods shown in Scheme 2, most methods do not give the product in a high yield, and an expensive 1,2-dibromobenzene is essential as starting material in any case. The method using lithiation with *t*-BuLi needs special and inconvenient operation. Therefore, the desirable

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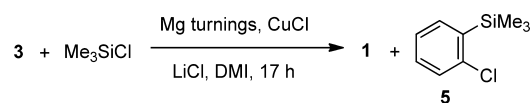
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Scheme 2. Recently Reported Methods for Synthesis of **1**

synthetic method should involve a convenient procedure, a high yield of the product, and a cheap 1,2-dichlorobenzene as a starting material without toxic HMPA. However, to the best of our knowledge, there are no reports on such a safe and cheap method of preparing 1,2-bis(trimethylsilyl)benzenes starting from 1,2-dichlorobenzenes. Recently, Katagiri et al. reported that a reagent composed of Mg and CuCl caused reductive silylation of trifluoroacetates in 1,3-dimethyl-2-imidazolizone (DMI).¹⁵ Inspired by this result, we envisaged a hybrid Grignard reagent prepared from Mg and CuCl for synthesis of 1,2-bis(trimethylsilyl)benzene from 1,2-dichlorobenzene. Here, we report for the first time an efficient synthesis of 1,2-bis(trimethylsilyl)benzene from 1,2-dichlorobenzene without HMPA as a solvent.

First, we examined the reaction temperature roughly under the conditions of Mg turnings and CuCl in DMI (Table 1, entries 1–3). The reaction of 1,2-dichlorobenzene with chlorotrimethylsilane at room temperature for 17 h gave 1,2-bis(trimethylsilyl)benzene (**1**) and 1-chloro-2-trimethylsilylbenzene (**5**) in 7 and 60% yields, respectively. The reaction at 90 °C for 17 h afforded the product **1** in 50% yield, but further increasing the temperature to 120 °C resulted in a slight decrease in the yield of **1** (44%).

Since Krasovskiy and Knochel clarified that addition of LiCl to *i*-PrMgCl or *s*-BuMgCl promotes selective halogen–metal exchange,¹⁶ we expected that the addition of LiCl would assist the silylation reaction more effectively. Under the above conditions at 90 °C, the addition of LiCl was examined (Table 1, entries 4–7). Surprisingly, we observed that 1,2-bis(trimethylsilyl)benzene was only formed in 52% yield when an equimolar amount of LiCl was added. Since the formation of 1-chloro-2-(trimethylsilyl)benzene was controlled completely, the addition effect of LiCl is critical. When the quantity of LiCl was increased to 4 or 8 mmol, the yield of the product also increased, but further increments of LiCl decreased the yield. The best result was obtained when LiCl of 8 mmol was used. Next, we examined three kinds of magnesium available commercially, i.e., Mg turnings, Mg powder (99.0%), and Mg

Table 1. Optimization of the Reaction Conditions^a

entry	LiCl (mmol)	temp (°C)	yield ^b (%)	
			1	5
1	0	rt	7	60
2	0	90	50	11
3	0	120	44	3
4	1	90	52	0
5	4	90	60	0
6	8	90	72	0
7	12	90	53	0
8 ^c	8	90	84	0
9 ^d	8	90	89	0
10 ^{d,e}	8	90	45	12
11 ^{d,f}	8	90	2	67
12 ^g		100	0	0

^aConditions: Mg turnings (8 mmol), CuCl (1 mmol), LiCl, **3** (1 mmol), Me₃SiCl (16 mmol), and DMI (10 mL) for 17 h at 90 °C.

^bYields were determined by ¹H NMR. ^cMg powder (99.0%) (8 mmol) was used instead of Mg turnings. ^dMg powder (99.9%) (8 mmol) was used instead of Mg turnings. ^eDMI (2 mL) was used. ^fDMI (5 mL) and THF (5 mL) were used. ^gConditions: **3** (1 mmol), Me₃SiCl (4 mmol), Mg (4 mmol), a catalytic amount of I₂, and DMI (10 mL) at 100 °C for 48 h.

powder (99.9%) (Table 1, entries 8 and 9). Although a good yield of the product was obtained even by using Mg turnings, use of Mg powder gave the better result. When Mg powder with high purity was used, the product was formed in 89% yield.

When the amount of DMI was decreased to 2 mL, the yield of the product was decreased to 47% and the monosilylated product was also formed (entry 10). Use of a 1:1 mixture of DMI and THF drastically decreased the product and afforded the monosilylated product in 67% yield (entry 11), suggesting that addition of THF was not desirable as solvent. Furthermore, we examined the reaction under the original conditions⁵ using DMI instead of HMPA (entry 12). However, none of the product was formed, and 1,2-dichlorobenzene was recovered. Therefore, the addition of CuCl and LiCl is essential to promote the bis-silylation.

Since the optimum temperature in the presence of LiCl was not examined in detail, the temperature effect was examined again. The results are given in Table 2. In order to compare with the conditions at 90 °C (entry 4), the reaction in a temperature lower than 90 °C was considered. The reaction at 0 °C afforded **1** and **5** in 12 and 67% yields, respectively (entry 1). At 25 °C, **1** and **5** were formed in 43 and 56% yields, respectively (entry 2). When the reaction was conducted at still higher 55 °C, **1** was only formed in 93% yield (entry 3). These results indicate that the bis-silylation reaction takes place stepwise through the monosilylated product. To recognize the utility of this method, the reaction was applied a 50 mmol scale (entry 4). This result shows that this reaction can be scaled up easily.

With the optimized conditions for the disilylation reaction in hand, we explored the scope of this reaction, as shown in Table 3. As a substrate of the bis-silylation reaction, we chose dichlorotoluenes (**6a** and **6b**), dichloroanisoles (**6c** and **6d**), 1,2-dichloro-4-fluorodichlorobenzene (**6e**), 1,2,4-trichloroben-

Table 2. Effect of Temperature in the Presence of LiCl^a

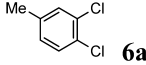
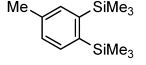
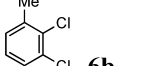
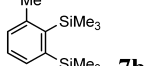
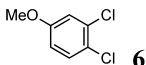
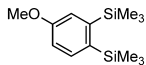
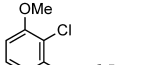
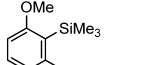
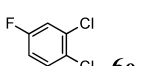
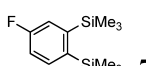
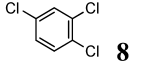
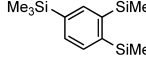
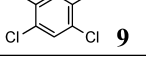
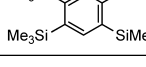
$$3 + \text{Me}_3\text{SiCl} \xrightarrow[\text{LiCl, DMI, 17 h}]{\text{Mg, CuCl}} 1 + 5$$

entry	temp (°C)	yield of 1 ^b (%)	yield of 5 ^b (%)
1	0	12	67
2	25	43	56
3	55	93	0
4 ^c	55	87	0
5 ^d	90	89	0

^aConditions: Mg powder (8 mmol), CuCl (1 mmol), LiCl (8 mmol), 3 (1 mmol), Me₃SiCl (16 mmol), and DMI (10 mL) for 17 h. ^bYields were determined by ¹H NMR. ^cMg powder (400 mmol), CuCl (50 mmol), LiCl (400 mmol), 3 (50 mmol), Me₃SiCl (800 mmol), and DMI (300 mL) were used. ^dSame as Table 1, entry 9.

Table 3. Silylation of 1,1-Dichlorobenzene Derivatives^a

$$\text{R-C}_6\text{H}_3\text{Cl}_2 + \text{Me}_3\text{SiCl} \xrightarrow[\text{LiCl, DMI, 55 }^\circ\text{C, 17 h}]{\text{Mg, CuCl}} \text{R-C}_6\text{H}_3\text{SiMe}_3_2$$

Entry	Substrate	Product	Yield (%) ^b
1	 6a	 7a	92
2 ^[c]	 6b	 7b	56
3	 6c	 7c	87
4	 6d	 7d	50
5	 6e	 7e	88
6	 8	 10	88
7	 9	 11	78

^aConditions: Mg powder (8 mmol), CuCl (1 mmol), LiCl (8 mmol), substrate (1 mmol), Me₃SiCl (16 mmol), and DMI (10 mL) for 17 h. ^bIsolated yields by column chromatography. ^cReaction time, 36 h.

zene (8), and 1,2,4,5-tetrachlorobenzene (9). When the reaction of 6a was conducted under the optimized conditions, 3,4-bis(trimethylsilyl)toluene (7a) was obtained in 92% yield. However, a similar reaction of 6b decreased the yield (50%) of the corresponding bis-silylated toluene 7b presumably due to the steric hindrance. Similar results were obtained in the case of dichloroanisoles, which gave the corresponding bis-silylated anisoles (7c and 7d) in 87 and 56% yields, respectively. The reaction of a fluorinated dichlorobenzene, 1,2-dichloro-4-fluorobenzene (6e), also proceeded efficiently to afford 1-fluoro-3,4-bis(trimethylsilyl)benzene (7e) in 88% yield. Even in the case of 1,2,4-trichlorobenzene (8) and 1,2,4,5-tetrachlorobenzene (9), use of the same conditions as above gave 1,2,4-tris(trimethylsilyl)benzene (10) and 1,2,4,5-tetrakis(trimethylsilyl)benzene (11) in 88 and 78% yields, respectively. This result suggests that the present silylation reaction is also

applicable for polysilylation. Although these reactions are preliminary experiments, these results suggest that the present procedure is useful for the silylation reaction of various dichlorobenzene derivatives.

The bis-silylation reaction is explained as follows. A hybrid metal prepared from Mg powder and CuCl showed a drastic behavior in the bis-silylation reaction of 1,2-dichlorobenzene derivatives using DMI solvent in the presence of LiCl. The role of CuCl is considered to enhance the reduction ability by depositing Cu(0) on the magnesium surface.¹⁵ Addition of LiCl in DMI increases the polarity of the solvent system to promote electron transfer. In addition, as suggested by Krasovskiy and Knochel,¹⁶ the addition of LiCl may break the polymeric aggregate of Grignard reagents generated in situ to increase the reactivity. As a result, electron transfer efficiently takes place to produce 2-chlorophenylmagnesium chloride, which reacts with chlorotrimethylsilane to give 1-chloro-2-(trimethylsilyl)benzene (5). The similar reaction of 5 successively occurs to form 1,2-bis(trimethylsilyl)benzene (1). The successive process is supported by the selective formation of monosilylated product 5 in the reaction at low temperature. In addition, we examined the reaction of 1,2-dibromobenzene under the present conditions to compare the reactivity. 1,2-Dibromobenzene showed a high reactivity and reacted even at 0 °C with a good yield.

In summary, we have demonstrated that a hybrid Grignard reagent composed Mg and Cu is highly effective for bis-silylation of 1,2-dichlorobenzene with chlorotrimethylsilane in DMI. This approach provides an effective synthesis of 1,2-bis(trimethylsilyl)benzene with a high yield. A number of previously inaccessible but potentially useful substituted 1,2-disilylbenzenes can now be synthesized in a straightforward synthesis. Therefore, it is the most outstanding method in the synthesis of 1,2-bis(trimethylsilyl)benzene reported to date. This method is also applicable for synthesis of substituted 1,2-bis(trimethylsilyl)benzene derivatives and poly(trimethylsilyl)benzenes.

EXPERIMENTAL SECTION

Reaction of 1,2-Dichlorobenzene (3) with Chlorotrimethylsilane in the Presence of Mg, CuCl, and LiCl in DMI. To a mixture of Mg turnings (8 mmol), CuCl (1 mmol), LiCl (the amount given in Table 1), and chlorotrimethylsilane (16 mmol) in DMI (10 mL) was added 3 (1 mmol). The mixture was gradually heated to the temperature described in Table 1 and stirred for 17 h. After being cooled to room temperature, the reaction mixture was poured into a mixture of saturated NaHCO₃, hexane, and ice. The resulting precipitates were filtered off, and the filtrate was extracted with hexane. The combined organic extract was washed with brine, dried over anhydrous Na₂SO₄, and concentrated by a rotary evaporator. The yield of the products was determined by ¹H NMR. The products were separated by column chromatography on silica gel with hexane as eluent.

1,2-Bis(trimethylsilyl)benzene (1).^{5b} The product was obtained in 93% yield (Table 2, entry 3) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 0.37 (s, 18H), 7.31–7.34 (m, 2H), 7.65–7.68 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 2.5, 128.2, 135.6, 146.1.

1-Chloro-2-(trimethylsilyl)benzene (5).¹⁷ The product was obtained in 60% yield (Table 1, entry 1) as colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 0.38 (s, 9H), 7.20–7.35 (m, 3H), 7.43–7.46 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 0.8, 125.9, 129.2, 130.5, 135.6, 138.7, 141.0.

General Procedure for Preparation of 1,2-Bis(trimethylsilyl)arenes. To a mixture of Mg powder (8 mmol), CuCl (1 mmol), LiCl (8 mmol), DMI (10 mL), and chlorotrimethylsilane (16 mmol) was added 1,2-dichloroarene (1 mmol). The mixture was gradually heated

to 55 °C and stirred at that temperature for 17 h. After being cooled to room temperature, the reaction mixture was poured into a mixture of saturated NaHCO₃, hexane, and ice. The resulting precipitates were filtered off, and the filtrate was extracted with hexane. The combined organic extract was washed with brine, dried over anhydrous Na₂SO₄, and concentrated by a rotary evaporator. The crude product was purified by column chromatography on silica gel with hexane or hexane/CH₂Cl₂ as eluent or distilled under reduced pressure.

1-Methyl-3,4-bis(trimethylsilyl)benzene (7a).^{5b} The product was obtained as a colorless oil: yield 0.218 g (92%); ¹H NMR (300 MHz, CDCl₃) δ 0.35 (s, 9H), 0.36 (s, 9H), 2.34 (s, 3H), 7.16 (d, J = 7.5 Hz), 7.49 (s, 1H), 7.58 (d, J = 7.5 Hz); ¹³C NMR (75 MHz, CDCl₃) δ 1.96, 2.02, 21.4, 128.6, 135.4, 136.2, 137.1, 142.2, 145.9.

1-Methyl-2,3-bis(trimethylsilyl)benzene (7b).^{5b} The product was obtained as a colorless oil: yield 0.132 g (56%); ¹H NMR (300 MHz, CDCl₃) δ 0.38 (s, 9H), 0.45 (s, 9H), 2.51 (s, 3H), 7.12–7.24 (m, 2H), 7.51–7.54 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 5.2, 5.8, 27.0, 129.1, 132.5, 135.0, 145.7, 146.6, 148.6.

1-Methoxy-3,4-bis(trimethylsilyl)benzene (7c). The product was obtained as a colorless oil: yield 0.220 g (87%); ¹H NMR (300 MHz, CDCl₃) δ 0.34 (s, 9H), 0.38 (s, 9H), 3.80 (s, 3H), 6.84 (dd, J = 2.7, 8.4 Hz, 1H), 7.24 (d, J = 2.8 Hz, 1H), 7.61 (d, J = 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 2.7, 2.9, 54.9, 110.7, 128.2, 129.1, 134.4, 148.1, 164.9; HRMS (EI) calcd for C₁₃H₂₄O₂Si₂ 252.1366, found 252.1363.

1-Methoxy-2,3-bis(trimethylsilyl)benzene (7d). The product was obtained as a colorless oil: yield 0.136 g (50%); ¹H NMR (300 MHz, CDCl₃) δ 0.345 (s, 9H), 0.352 (s, 9H), 3.78 (s, 3H), 6.84–6.87 (m, 1H), 7.24–7.32 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 2.7, 3.0, 54.9, 110.8, 128.2, 129.2, 134.4, 148.0, 164.9; HRMS (EI) calcd for C₁₃H₂₄O₂Si₂ 252.1366, found 252.1365.

1-Fluoro-3,4-bis(trimethylsilyl)benzene (7e).¹⁴ The product was obtained as colorless oil: yield 0.212 g (88%); ¹H NMR (300 MHz, CDCl₃) δ 0.35 (s, 9H), 3.36 (s, 9H), 6.98 (dt, J = 3.0, 8.4 Hz, 1H), 7.35 (dd, J = 3.0, 10.8 Hz, 1H), 7.63 (dd, J = 6.6, 8.4 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 1.7, 2.0, 114.3 (d, J = 18.6 Hz), 122.0 (d, J = 17.3 Hz), 137.3 (d, J = 6.2 Hz), 141.3, 149.7, 164.3.

1,2,4-Tris(trimethylsilyl)benzene (10).¹⁸ The product was obtained as colorless crystals: mp 41–42 °C; yield 0.259 g (88%); ¹H NMR (300 MHz, CDCl₃) δ 0.27 (s, 9H), 0.36 (s, 9H), 0.38 (s, 9H), 7.49 (d, J = 7.5 Hz, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.83 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ –1.0, 2.1, 2.2, 132.9, 134.5, 139.3, 140.0, 144.7, 146.5.

1,2,4,5-Tetrakis(trimethylsilyl)benzene (11).¹⁹ The product was obtained as colorless crystals: mp 169–170 °C; yield 0.286 g (78%); ¹H NMR (300 MHz, CDCl₃) δ 0.37 (s, 36H), 7.96 (s, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 1.8, 141.5, 144.8.

■ ASSOCIATED CONTENT

Supporting Information

¹H and ¹³C NMR spectra of new products 7c and 7d. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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