Boron–Metal Exchange Reaction of Silylboranes with Organometallic Reagents: A New Route to Arylsilyl Anions

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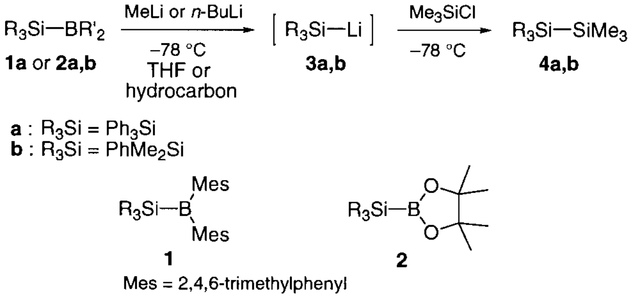
The boron–metal exchange reaction of (arylsilyl)boranes with alkyllithiums, potassium *tert*-butoxide, and methylmagnesium bromide affords the corresponding silyllithium, silylpotassium, and silylmagnesium compounds, respectively. Especially, the boron–lithium exchange reaction occurs even in hydrocarbon solvents such as toluene and hexane as well as in THF.

Silyl anions[1] are versatile reagents for silicon–carbon and silicon–silicon bond formation reactions in organic synthesis. Silyl anions are conventionally obtained by reactions of chlorosilanes with alkali metal, reaction of hydrosilanes with alkali metal hydride, and cleavage of the silicon–silicon bond in disilanes by organometallic nucleophiles, most of which are carried out in polar aprotic solvents such as Et_2O, THF, DME, and HMPA,[1] but not in hydrocarbon solvents.[2]

The tin–lithium exchange reaction of silylstannanes with alkyllithiums has been established by our group and other groups as a new route to silyllithiums under mild conditions.[3] This method, however, often causes a problem of a competitive silicon–lithium exchange reaction arising from nucleophilic attack on the silicon atom, producing a stannyllithium, due to the slight difference in the electronegativity[4] between tin (1.96) and silicon (1.90). Upon searching for suitable substrates to solve this problem, we focused on the silylboranes.[5] Since the boron atom is receptive toward nucleophiles due to its vacant 2p orbital, the reaction of a silylborane[6] with an alkyllithium is expected to cause a boron–lithium exchange reaction to produce a silyllithium.

(Triphenylsilyl)boranes having aryl (**1**)[5c] and alkoxy (**2**) substituents on the boron were exposed to alkyllithiums (RLi), as shown in Scheme 1 and Table 1. When the silylborane **1a** in THF was treated with MeLi (1.1 mol dm^{-3} in Et_2O, 2 mol amt.) at −78 °C for 0.5 h, triphenylsilyllithium (**3a**) was formed in 71% yield (run 1).[7] The yield of **3a** was estimated after conversion to the disilane **4a** by trapping with Me_3SiCl. Under similar reaction conditions, **2a** afforded **3a**, which was also trapped as **4a** in 87% yield (run 2). In contrast, a silyldiaminoborane, $Ph_3SiB(N\textit{i}\text{-}Pr_2)_2$, was thoroughly unreactive towards MeLi. The formation of the silyllithium **3a** was also confirmed by the NMR analysis. The ^{29}Si NMR spectra of **3a** prepared from the reaction of **2a** with MeLi displayed a signal at δ −9.1 in THF, which was identical with the reported value.[8] The reaction of the (phenyldimethylsilyl)borane[5d,e,g] **2b** with MeLi also gave the corresponding silyllithium **3b**, being trapped as **4b** in 62% yield (run 3).

The boron–lithium exchange reaction was examined also in hydrocarbon solvents,[2] which are usually much less effective for formation of silyl anions (Scheme 1 and Table 1). A hexane solution of *n*-BuLi was used instead of a diethyl ether solution of MeLi. Although excess *n*-BuLi (1.6 mol dm^{-3} in hexane, 4 mol amt.) was required to consume **1a** (run 4) and **2a** (run 5) in toluene and **2b** (run 6) in hexane at −78 °C,[9] the silyllithiums **3a** and **3b** were formed in moderate to high yields. In contrast, a tin–lithium exchange reaction of the silylstannane **5** did not occur in the hydrocarbon solvents under similar reaction conditions, indicative of the efficiency of the boron–lithium exchange reaction.



Scheme 1.

Table 1. Preparation of Silyllithiums **3** from silylboranes **1** and **2**

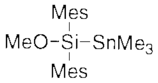
Run	Silylborane	RLi[a,b]	Solvent	Silyllithium	Yield of **4**/%
1	**1a**	MeLi (2)	THF	**3a**	71
2	**2a**	MeLi (2)	THF	**3a**	87
3	**2b**	MeLi (2)	THF	**3b**	62
4	**1a**	*n*-BuLi (4)	toluene	**3a**	90
5	**2a**	*n*-BuLi (4)	toluene	**3a**	57
6	**2b**	*n*-BuLi (4)	hexane	**3b**	61

[a] A diethyl ether solution of MeLi (1.1 mol dm^{-3}) or a hexane solution of *n*-BuLi (1.6 mol dm^{-3}). [b] Mol amount in parentheses.

A functionalized silyllithium[3a–c] can be obtained in a hydrocarbon solvent by this methodology. Treatment of the [(methoxy)dimesitylsilyl]borane **6** with *n*-BuLi in toluene at −78 °C produced the [(methoxy)silyl]lithium **7**, being trapped as **8** in 88% yield, as shown in Scheme 2. The ^{29}Si NMR resonance of **7** in toluene appeared at δ 40.6, being downfield-shifted from that in THF at δ 31.6 (Δδ = +9.0).[10] In contrast, **7** was obtained in a very low yield (8% yield of **8**) by the reaction of the tin counterpart **9** with *n*-BuLi under similar reaction conditions.[11]

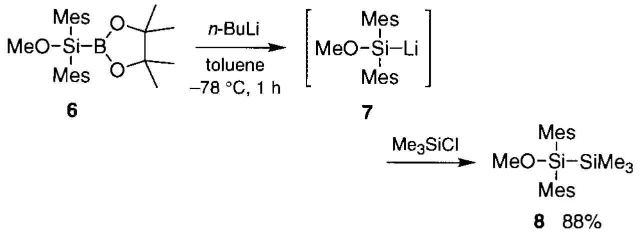
$PhMe_2Si{-}SnMe_3$

5



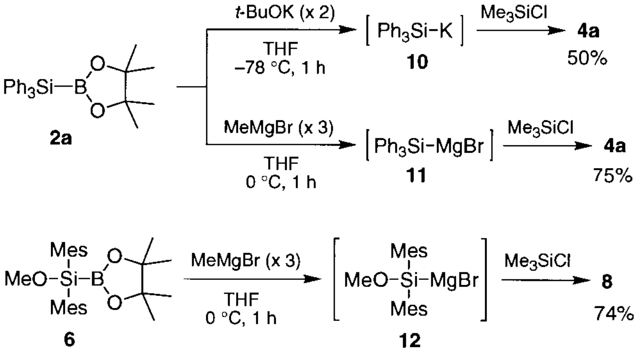
$$MeO{-}\overset{\displaystyle Mes}{\underset{\displaystyle Mes}{Si}}{-}SnMe_3$$

9



Scheme 2.

This boron–metal exchange methodology could be extended to prepare other silyl–metal compounds, as shown in Scheme 3. The reaction of **2a** with *t*-BuOK (1.0 mol dm^{-3} in THF, 2 mol amt.) in THF at –78 °C afforded the silylpotassium compound **10**, being trapped as **4a** in 50% yield.[8a] The reaction of **2a** with MeMgBr (0.9 mol dm^{-3} in THF, 3 mol amt.) in THF at 0 °C afforded the silylmagnesium compound **11**, being trapped as **4a** in 75% yield. The [(alkoxy)silyl]magnesium compound **12** was obtained from **6** in a similar manner (74% yield of **8**). It is noted that only a few methods have been reported for preparation of silylmagnesium compounds.[12]



Scheme 3.

In summary, we have found that the boron–metal exchange reactions of the (arylsilyl)boranes with MeLi, *n*-BuLi, *t*-BuOK, and MeMgBr are useful for the preparation of arylsilyl anions. Especially, the boron–lithium exchange reaction occurs even in the hydrocarbon solvents. This may be useful for elucidation of structures of silyllithiums in hydrocarbon solvents, study of solvent effect on the reaction of silyllithiums, and tuning of the reactivity of silyllithiums for selective organic synthesis. Variation of the substituents on the silicon atom in this methodology and application to organic synthesis are now under investigation.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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7 Typical procedure: To a solution of **2a** (173 mg, 0.45 mmol) in THF (3 mL) was added methyllithium in Et$_2$O (1.14 mol dm^{-3}, 0.78 mL, 0.9 mmol) at –78 °C. The reaction mixture was stirred at the same temperature for 30 min to give **3a**. To the solution of **3a** was added trimethylchlorosilane (0.14 mL, 1.1 mmol) at –78 °C, and the reaction mixture was warmed to the ambient temperature. After usual workup, **4a** was obtained in 87% yield after column chromatography on silica gel.

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9 The choice of the solvent depends on the solubility of the silylboranes.

10 A similar downfield shift was reported in the ^{29}Si resonance of **2a** in THF-d_8 (δ –9.0) and that in toluene-d_8 (δ 9.28) ($\Delta\delta$ 18.28), see ref 8.

11 The starting material **9** was recovered in 55% yield and the side product, (MeO)Mes$_2$Si-SnMe$_2$*n*-Bu, was obtained in 34% yield.

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