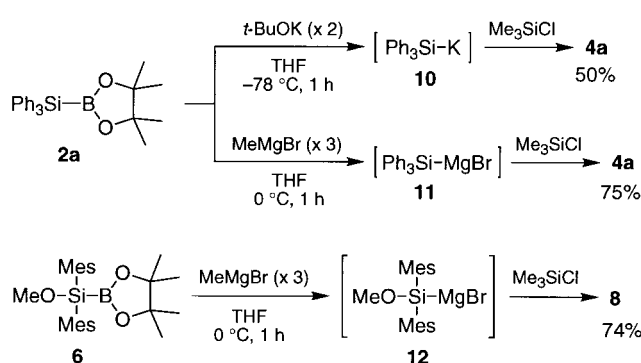


Scheme 2.

This boron–metal exchange methodology could be extended to prepare other silyl–metal compounds, as shown in Scheme 3. The reaction of **2a** with  $t\text{-BuOK}$  (1.0 mol  $\text{dm}^{-3}$  in THF, 2 mol amt.) in THF at  $-78\text{ }^\circ\text{C}$  afforded the silylpotassium compound **10**, being trapped as **4a** in 50% yield.<sup>8a</sup> The reaction of **2a** with  $\text{MeMgBr}$  (0.9 mol  $\text{dm}^{-3}$  in THF, 3 mol amt.) in THF at  $0\text{ }^\circ\text{C}$  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.<sup>12</sup>



Scheme 3.

In summary, we have found that the boron–metal exchange reactions of the (arylsilyl)boranes with  $\text{MeLi}$ ,  $n\text{-BuLi}$ ,  $t\text{-BuOK}$ , and  $\text{MeMgBr}$  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.

We thank the Ministry of Education, Culture, Sports, Science and Technology, Japan, for the Grant-in-Aids for COE Research on Elements Science, No. 12CE2005 and for Scientific Research Nos. 12042241 and 12750763.

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

#### References and Notes

- Reviews: a) K. Tamao and A. Kawachi, *Adv. Organomet. Chem.*, **38**, 1 (1995). b) P. D. Lickiss and C. M. Smith, *Coord. Chem.*

- Rev.*, **145**, 75 (1995). c) J. Belzner and U. Dehnert, "The Chemistry of Organic Silicon Compounds," ed. by Z. Rappoport and Y. Apeloig, John-Wiley & Sons, Chichester (1998), Vol. 2, pp 779–826.
- The reaction of bis(silyl)zinc, -cadmium, and -mercury with lithium is almost the sole method using hydrocarbon solvents: a) K. W. Klinkhammer, *Chem. Eur. J.*, **3**, 1418 (1997). b) M. Nanjo, A. Sekiguchi, and H. Sakurai, *Bull. Chem. Soc. Jpn.*, **71**, 741 (1998), and references cited therein.
- a) A. Kawachi and K. Tamao, *Bull. Chem. Soc. Jpn.*, **70**, 945 (1997). b) A. Kawachi and K. Tamao, *J. Am. Chem. Soc.*, **122**, 1919 (2000). c) A. Kawachi, H. Maeda, H. Nakamura, N. Doi, and K. Tamao, *J. Am. Chem. Soc.*, **123**, 3143 (2001). d) M. Omote, T. Tokita, Y. Shimizu, I. Imae, E. Shirakawa, and Y. Kawakami, *J. Organomet. Chem.*, **611**, 20 (2001).
- Pauling's electronegativity: J. Emsley, "The Elements," 2nd ed., Clarendon Press, Oxford (1992).
- Examples of preparations and reactions of silylboranes; a) W. Biffar and H. Nöth, *Angew. Chem., Int. Ed. Engl.*, **19**, 58 (1980). b) J. D. Buynak and B. Geng, *Organometallics*, **14**, 3112 (1995). c) E. Bonnefon, M. Birot, J. Dunogues, J.-P. Pillot, C. Courseille, and F. Taulle, *Main Group Metal Chem.*, **19**, 761 (1996). d) M. Sugimoto, H. Nakamura, T. Matsuda, and Y. Ito, *J. Am. Chem. Soc.*, **120**, 4248 (1998). e) M. Sugimoto, T. Matsuda, and Y. Ito, *Organometallics*, **19**, 4647 (2000). f) S. Onozawa, Y. Hatanaka, and M. Tanaka, *Chem. Commun.*, **1997**, 1229. g) T. Hata, H. Kitagawa, H. Masai, T. Kurahashi, M. Shimizu, and T. Hiyama, *Angew. Chem. Int. Ed.*, **40**, 790 (2001).
- Studies on nucleophilic substitution at boron atoms: a) A. Cowley and J. L. Mills, *J. Am. Chem. Soc.*, **91**, 2911 (1969). b) B. Glavinovski and S. K. Brownstein, *Can. J. Chem.*, **59**, 3012 (1980). c) E. Müller and H.-B. Bürgi, *Helv. Chim. Acta*, **70**, 511 (1987). d) S. Toyota, T. Futawaka, M. Asakura, H. Ikeda, and M. Oki, *Organometallics*, **17**, 4155 (1998). e) M. Yamashita, Y. Yamamoto, K.-y. Akiba, and S. Nagase, *Angew. Chem. Int. Ed.*, **39**, 4055 (2000), and references cited therein.
- Typical procedure: To a solution of **2a** (173 mg, 0.45 mmol) in THF (3 mL) was added methyllithium in  $\text{Et}_2\text{O}$  (1.14 mol  $\text{dm}^{-3}$ , 0.78 mL, 0.9 mmol) at  $-78\text{ }^\circ\text{C}$ . 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  $-78\text{ }^\circ\text{C}$ , 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.
- a) E. Bunzel, T. K. Venkatchalam, B. Eliasson, and U. Edlund, *J. Am. Chem. Soc.*, **107**, 303 (1985). b) U. Edlund, T. Lejon, T. K. Venkatchalam, and E. Bunzel, *J. Am. Chem. Soc.*, **107**, 6408 (1985). c) H. V. R. Dias, M. M. Olmstead, K. Ruhlandt-Senge, and P. P. Power, *J. Organomet. Chem.*, **462**, 1 (1993).
- The choice of the solvent depends on the solubility of the silylboranes.
- A similar downfield shift was reported in the  $^{29}\text{Si}$  resonance of **2a** in THF- $d_8$  ( $\delta$   $-9.0$ ) and that in toluene- $d_8$  ( $\delta$   $9.28$ ) ( $\Delta\delta$   $18.28$ ), see ref 8.
- The starting material **9** was recovered in 55% yield and the side product,  $(\text{MeO})\text{Me}_2\text{Si-SnMe}_2n\text{-Bu}$ , was obtained in 34% yield.
- Reaction of chlorosilanes with magnesium: a) R. Goddard, C. Krüger, N. A. Ramadan, and A. Ritter, *Angew. Chem., Int. Ed. Engl.*, **34**, 1030 (1995). b) K. Tamao, M. Asahara, T. Saeki, and A. Toshimitsu, *Angew. Chem. Int. Ed.*, **38**, 3316 (1999). Lithium–magnesium exchange reaction between silyllithiums and Grignard reagents: c) H. Hayami, M. Sato, S. Kanemoto, Y. Morizawa, K. Oshima, and H. Nozaki, *J. Am. Chem. Soc.*, **105**, 4491 (1983). d) D. L. Comins and M. O. Killpack, *J. Am. Chem. Soc.*, **114**, 10972 (1992). e) A. Kawachi and K. Tamao, *J. Organomet. Chem.*, **601**, 259 (2000). Cobalt–magnesium exchange reaction of silylcobalt compounds and Grignard reagents: f) E. Colomer and R. J. P. Corriu, *J. Organomet. Chem.*, **133**, 159 (1977).