ORGANOMETALLICS

Volume 26, Number 19, September 10, 2007

Communications

o-(Fluorodimethylsilyl)phenyllithium as a Versatile Reagent for Preparation of Unsymmetrical, Silicon-Functionalized *o*-Disilylbenzenes

Atsushi Kawachi,* Atsushi Tani, Koji Machida, and Yohsuke Yamamoto

Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526, Japan

Received February 21, 2007

*Summary: o-(Fluorodimethylsilyl)phenyllithium (**1**) was prepared by bromine−lithium exchange between o-$C_6H_4(SiMe_2F)$-Br (**2**) and t-BuLi in Et_2O at −78 °C. The electrophilic Si−F functionality in **1** is not attacked by the nucleophilic aryllithium moiety at that temperature. ^7Li, ^{19}F, and ^{29}Si NMR analyses supported by DFT calculations suggested that the structure of **1** involves an intramolecular coordination of the fluorine substituent to the lithium atom. Reactions of **1** with halosilanes produced unsymmetrical, silicon-halogenated o-disilylbenzenes **4**.*

(Fluorosilyl)benzenes have received much attention in organic synthesis as well as in material science because (i) their reactions with nucleophiles allow facile functional group transformations on the silicon;[1] (ii) the fluorosilyl group can be converted into a hydroxyl group through Tamao−Fleming oxidation;[2] (iii) (fluorosilyl)benzenes serve as aromatic components in silicon-based cross-coupling reactions;[3] and (iv) they are also potential building blocks in silicon-containing π-conjugated polymers represented by disilanylene−phenylene polymers.[4]

o-(Fluorosilyl)phenyl alkali metal species could be good precursors for a variety of (fluorosilyl)benzenes required in the above-mentioned applications. However, such species have received little attention, perhaps because it was believed that they are so unstable that they readily lose LiF and dimerize to give 9,10-dihydro-9,10-disilaanthracenes. We report the preparation and reactions of *o*-(fluorodimethylsilyl)phenyllithium (**1**), in which the electrophilic Si−F functionality is compatible with the nucleophilic phenyllithium moiety at low temperatures. This reagent allows us to obtain unsymmetrical, silicon-halogenated *o*-disilylbenzenes.[5]

o-Bromo(fluorodimethylsilyl)benzene (**2**) selectively underwent bromine−lithium exchange[6] with 1 molar equiv of *t*-BuLi in Et_2O at −78 °C, leaving the Si−F functionality intact to afford aryllithium **1**, as shown in Scheme 1.[7] Whereas **1** easily dimerized to form 9,10-dihydro-9,10-disilaanthracene[8] **3** in 97% yield during warming up to 0 °C,[9] **1** reacted with HMe_2SiCl (1.1 molar equiv) at −78 °C to give 1,2-disilylbenzene **4a** in

---

* Corresponding author. E-mail: kawachi@sci.hiroshima-u.ac.jp.

(1) Herzog, U. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; John-Wiley & Sons: Chichester, 2001; Vol. 3, pp 469−490.

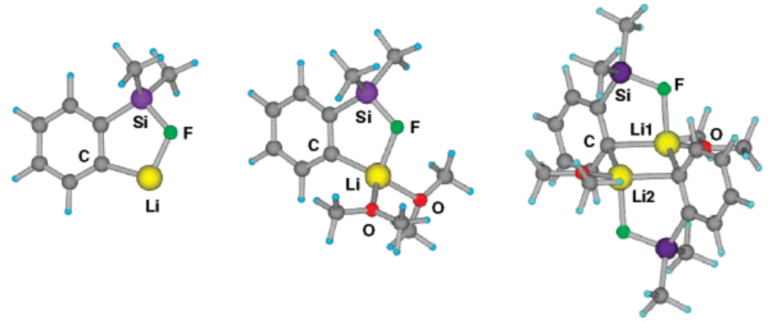
(2) Recent reviews: (a) Tamao, K. *Adv. Silicon Chem.* **1996**, *3*, 1. (b) Fleming, I. *Chemtracts-Org. Chem.* **1996**, *9*, 1.

(3) Recent reviews: (a) Hiyama, T. In *Metal-Catalyzed Cross-Coupling Reactions*; Diederich, F., Stang, P. J., Eds.; Wiley-VCH: Weinheim, Germany, 1998; pp 421−453. (b) Hiyama, T.; Shirakawa, E. *Top. Curr. Chem.* **2002**, *219*, 61.

(4) Recent examples of disilanylene−phenylene polymers: (a) Kashimura, S.; Ishifune, M.; Yamashita, N.; Bu, H.-B.; Takebayashi, M.; Kitajima, S.; Yoshiwara, D.; Kataoka, Y.; Nishida, R.; Kawasaki, S.-i.; Murase, H.; Shono, T. *J. Org. Chem.* **1999**, *64*, 6615. (b) Kira, M.; Tokura, S. *Organometallics* **1997**, *16*, 1100. (c) Ohshita, J.; Watanabe, T.; Kanaya, D.; Ohsaki, H.; Ishikawa, M.; Ago, H.; Tanaka, K.; Yamabe, T. *Organometallics* **1994**, *13*, 5002. (d) Ishikawa, M.; Sakamoto, H.; Ohshita, J. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 3281.

(5) Examples of preparations of unsymmetrical, silicon-functionalized *o*-disilylbenzenes: (a) Tamao, K.; Yao, H.; Tsutsumi, Y.; Abe, H.; Hayashi, T.; Ito, A. *Tetrahedron Lett.* **1990**, *31*, 2925. (b) Tamao, K.; Hayashi, T.; Ito, Y. *Organometallics* **1992**, *11*, 2099. (c) Ishikawa, M.; Sakamoto, H.; Tabuchi, T. *Organometallics* **1991**, *10*, 3173. (d) Ohshita, J.; Niwa, H.; Ishikawa, M. *Organometallics* **1996**, *15*, 4632. (e) Chen, W.; Shimada, S.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **2001**, *30*, 1096. (f) Kira, M.; Tokura, S. *Chem. Lett.* **1994**, *23*, 1459.

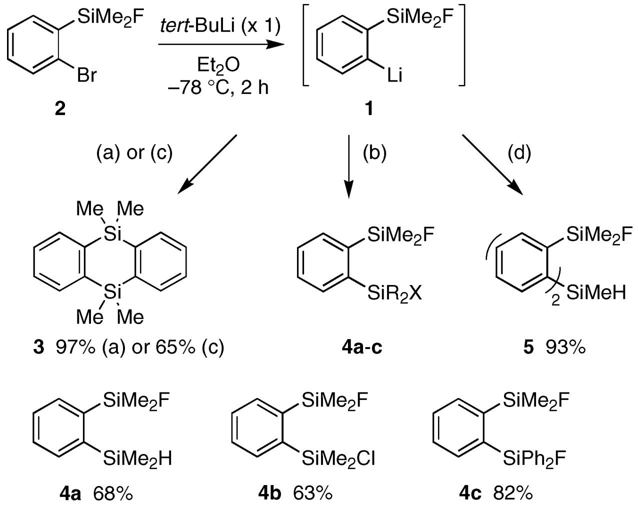
10.1021/om070161c CCC: $37.00 © 2007 American Chemical Society
Publication on Web 08/11/2007



	I	II	III	*observed*
Si–F (Å)	1.717	1.691	1.683	
Li–F (Å)	1.831	1.988	2.002	
C–Li (Å)	1.996	2.077	2.248 (Li1) 2.196 (Li2)	
$\delta(^7Li)$	4.2	2.6	3.2	2.3
$\delta(^{19}F)$	−163.0	−162.9	−157.8	−162.4
$\delta(^{29}Si)$	40.5	29.6	27.8	24.0

Figure 1. Calculated structures and GIAO NMR shifts δ (ppm) of **I**, **II**, and **III**.

Scheme 1. Preparation and Reactions of 1



(a) –78 °C, 1 h; 0 °C, 2.5 h.
(b) X-SiR$_2$Y = Cl-SiMe$_2$H (x 1.1), Cl-SiMe$_2$Cl (x 1.1), or F-SiPh$_2$F (x 1.1) / –78 °C, 1 h; 0 °C, 2.5 h.
(c) ClSiMe$_3$ (x 1.1) / –78 °C, 1 h; 0 °C, 2.5 h.
(d) Cl$_2$SiMeH (x 1.1) / –78 °C, 1 h; 0 °C, 2.5 h.

68% yield. Aryllithium **1** also reacted with dihalosilanes such as Me$_2$SiCl$_2$ (1.1 molar equiv)[10] and Ph$_2$SiF$_2$ (1.1 molar equiv), giving **4b** and **4c** in 63% and 82% yields, respectively. Such unsymmetrical, silicon-halogenated *o*-disilylbenzenes are difficultly accessible by conventional methods,[5] and **4a**−**c** were synthesized for the first time by the present method.[7] These silicon-halogenated disilylbenzenes could serve not only as the precursors of disilanylene−phenylene polymers[4] but also as bidentate Lewis acids.[5b] Unexpectedly, **1** did not react with Me$_3$SiCl, which is more sterically demanding than the halosilanes employed above. Instead, LiF elimination occurred and the dimerized product **3** was formed in 68% yield. In contrast, the reaction of **1** with a less sterically demanding dihalosilane, HMeSiCl$_2$, produced bis[*o*-(fluorosilyl)phenyl]silane **5** in 93% yield (based on **2**).[7]

The multinuclear NMR spectra of **1** were observed at −80 °C. The $^7Li\{^1H\}$ NMR spectra of **1** exhibited a singlet at δ = 2.3,[11,12] which lies in the range of the reported ^7Li shifts of aryllithiums in ethereal solvents.[13] The ^{19}F resonance was found at δ = −162.4 as a singlet.[12] The $^{29}Si\{^1H\}$ NMR spectrum showed a doublet at δ = 24.0, and the Si−F coupling constant ($^1J_{Si-F}$ = 259 Hz) was reduced relative to that of **2** ($^1J_{Si-F}$ = 278 Hz).

In order to obtain further insights into the structure of **1**, we performed DFT calculations and NMR shift prediction with the GIAO method.[14,15] DFT calculations displayed the five-membered-ring fluorine-chelated structure[16] **I** (Li···F distance is 1.831 Å) as an energy minimum, as shown in Figure 1. The computed

---

(6) Kawachi, A.; Zaima, M.; Tani, A.; Yamamoto, Y. *Chem. Lett.* **2007**, *36*, 362.

(7) Characterizations of new substances, **1**, **2**, **4**, and **5** are shown in the Supporting Information.

(8) (a) Janzen, E. G.; Pickett, J. B. *J. Am. Chem. Soc.* **1967**, *89*, 3649. (b) McCarthy, W. Z.; Corey, J. Y.; Corey, E. R. *Organometallics* **1984**, *3*, 255.

(9) ^{29}Si NMR measurements of **1** in Et$_2$O at variable temperatures indicated that the dimerization of **1** started to occur between −40 and −50 °C.

(10) The yield of **4b** was improved to 90% using 2.2 molar equiv of Me$_2$SiCl$_2$. In contrast, reaction of **1** with 0.5 molar equiv of Me$_2$SiCl$_2$ afforded a mixture of **4b**, bis[*o*-(fluorodimethylsilyl)phenyl]dimethylsilane, and **3** in the molar ratio of 46:23:31 (^1H NMR analysis).

(11) ^7Li chemical shifts were referenced to external LiCl in MeOH (0.3 M) (δ = 0 ppm).

(12) The anticipated $^7Li-^{19}F$ scalar coupling was not observed perhaps because the temperature was not low enough to slow Li−Li exchange. As an example of the observation of $^7Li-^{19}F$ coupling, see: (a) Stalke, D.; Klingebiel, U.; Sheldrick, G. M. *J. Organomet. Chem.* **1988**, *344*, 37. See also: (b) Stalke, D.; Whitmire, K. H. *J. Chem. Soc., Chem. Commun.* **1990**, 833.

(13) Elschenbroich, Ch.; Salzer, A. *Organometallics*, 2nd, revised ed.; VCH: Weinheim, Germany, 1992; Chapter 5, pp 19−37.

(14) All calculations were performed with the Gaussian 98 program package on the HIT HPC-PA264U-6CPU model: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Oritz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, M. W.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) The structures were optimized by using DFT calculations at the B3LYP/6-31+G(d) level. The GIAO (gauge-independent atomic orbital) nuclear magnetic shielding tensors were calculated at the RHF/6-311+G-(2d,p) level using optimized structures at the B3LYP/6-31+G(d) level. The obtained tensors were converted into the corresponding chemical shifts referenced to the tensors of Li$^+$(MeOH)$_4$ ($\delta(^7Li)$ = 0), CFCl$_3$ ($\delta(^{19}F)$ = 0), and SiMe$_4$ ($\delta(^{29}Si)$ = 0) calculated at the same level.

NMR shifts of **I** ($\delta(^{7}\text{Li})_{\text{calcd}} = 4.2$; $\delta(^{19}\text{F})_{\text{calcd}} = -162.9$; $\delta(^{29}\text{Si})_{\text{calcd}} = 40.5$) are in agreement with the experimental ^{19}F NMR value, but not with the ^{7}Li NMR or ^{29}Si NMR value. Thus, coordinating solvents were included in the optimization. Solvation of **I** with two dimethyl ether molecules produced **II**, which is stabilized by 26 kcal/mol relative to **I** and retains the Li···F interaction (Li···F distance is 1.988 Å) (Figure 1). The calculated NMR shifts ($\delta(^{7}\text{Li})_{\text{calcd}} = 2.6$; $\delta(^{19}\text{F})_{\text{calcd}} = -162.9$; $\delta(^{29}\text{Si})_{\text{calcd}} = 29.6$) are in good agreement with the experimental values. The aggregation of **I** should also be considered. Plausible dimer structure **III**,[1717,18] having a pseudoinversion center in the C_2Li_2 core, was also calculated, as was the NMR shift (Figure 1). The formation of **III** with the release of two molecules of Me_2O is energetically preferable by 5 kcal/mol compared to the two molecules of monomer **II**. The computed NMR shifts ($\delta(^{7}\text{Li})_{\text{calcd}} = 3.2$; $\delta(^{19}\text{F})_{\text{calcd}} = -157.8$; $\delta(^{29}\text{Si})_{\text{calcd}} = 27.8$) were in moderate agreement with the experimental values. Thus, chelated, monosolvated dimer **III** as well as chelated, bis-solvated monomer **II** could be the plausible structure of **1** in Et_2O. We also mention that elongation of the Si−F bond in **II** and **III** (1.691 Å in **II**; 1.683 Å in **III**) compared to that in the calculated structure of **2** (1.630 Å)[16] is consistent with the reduction of $^{1}J_{\text{Si-F}}$ in **1** mentioned above.

In conclusion, we have shown that *o*-(fluorosilyl)phenyllithium **1** is prepared by the bromine−lithium exchange reaction of aryl bromide **2** in high yield at low temperature and that **1** reacts with chlorosilanes to give unsymmetrical, silicon-halogenated *o*-disilylbenzenes. NMR and computational studies suggest that **1** adopts the five-membered-ring fluorine-chelated structure. Further study on the structure and reactivity of **1** is in progress at our laboratory.

Acknowledgment. This work was supported by Grants-in-Aid for Scientific Research, Nos. 17550038 and 18037052, the latter of which corresponds to Priority Area “Advanced Molecular Transformations of Carbon Resources” from the Ministry of Education, Culture, Sports, Science and Technology, Japan. We wish to express our profound gratitude to Professor Atsutaka Kunai and Professor Joji Ohshita at Hiroshima University for allowing us to use preparative GC and GC-mass instruments in their laboratories for the analysis of **2** and **4a**−**c**. We also thank Mr. Daisuke Kajiya, the Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University, for measurement of high-resolution mass spectra. This paper is dedicated to the memory of the late Professor Emeritus Yoshihiko Ito.

Supporting Information Available: Experimental details and physical data of compounds **1**−**5** and computational details of **I**, **II**, and **III**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070161C

---

(16) Five-membered-ring amine-chelated aryllithiums have been well-characterized: (a) Jastrzebski, Johann, T. B. H.; van Koten, G.; Konijn, M.; Stam, C. H. *J. Am. Chem. Soc.* **1982**, *104*, 5490. (b) Belzner, J.; Schär, D.; Dehnert, U.; Noltemeyer, M. *Organometallics* **1997**, *16*, 285. (c) Reich, H. J.; Gudmundsson, B. Ö. *J. Am. Chem. Soc.* **1996**, *118*, 6074. (d) Reich, H. J.; Goldenberg, W. S.; Gudmundsson, B. Ö.; Sanders, A. W.; Kulicke, K. J.; Simon, K.; Guzei, I. A. *J. Am. Chem. Soc.* **2001**, *123*, 8067.

(17) Reich et al.[16c,d] demonstrated that *o*-(dimethylaminomethyl)phenyllithium, which is structurally analogous to **1**, forms three isomeric chelated dimers in ethereal solvents: one with both nitrogens coordinated to one lithium of the dimer and two in which each lithium bears one chelating group. We performed preliminary calculations for the three corresponding plausible isomers and found that **III** is the most stable isomer among them: see Supporting Information.

(18) The structure of **2** was optimized by using DFT calculations at the B3LYP/6-311+G(2d,p) level.