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Preparation and oxidative coupling of bis[*o*-(hydrosilyl)phenyl]cuprates and bis[*o*-(fluorosilyl)phenyl]cuprates

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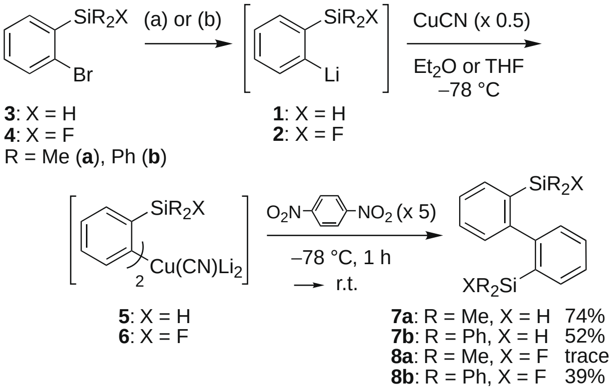
ABSTRACT

Bis[*o*-(hydrosilyl)phenyl]cuprates and bis[*o*-(fluorosilyl)phenyl]cuprates were prepared by reacting [*o*-(hydrosilyl)phenyl]lithiums and [*o*-(fluorosilyl)phenyl]lithiums, respectively, with copper salts, such as CuCN and $Cu(OPiv)_2$. The phenylcuprates underwent oxidative coupling to afford 2,2′-bis(hydrosilyl)biphenyls and 2,2′-bis(fluorosilyl)biphenyls.

1. Introduction

Recently, we reported the preparation of [*o*-(hydrosilyl)phenyl]-lithiums **1** (R = Me (**a**), Ph (**b**)) and [*o*-(fluorosilyl)phenyl]lithiums **2** (R = Me (**a**), Ph (**b**)) by Br–Li exchange of corresponding aryl bromides **3** and **4**, respectively, with *tert*-butyllithium (Scheme 1).[1] Phenyllithiums **1** and **2** reacted with halosilanes and haloboranes to form silicon-functionalized *o*-disilylbenzenes[1b] and *o*-(boryl)silylbenzenes.[1c] Then, we turned our attention to exchange of the counter cation (Li^+) in **1** and **2** with other metals in order to explore the synthetic utility of the *o*-silylphenyl anions. Here, we report the conversion of **1** and **2** into bis(*o*-silylphenyl)cuprates **5** and **6** and the oxidative coupling of **5** and **6**, forming silicon-functionalized 2,2′-disilylbiphenyls **7** and **8**.[2] The aim of this work is to confirm whether the hydrosilyl and fluorosilyl groups are compatible with intramolecular phenylcuprates and survive oxidative coupling at the *ortho* position.

First, we investigated the preparation of bis(*o*-silylphenyl)cuprates **5** and **6** and the oxidative coupling of them according to Lipshutz's procedure (Table 1 and Scheme 1).[3] [*o*-(Dimethylsilyl)phenyl]lithium (**1a**) was prepared from phenyl bromide **3a** with *tert*-BuLi in Et_2O at −78 °C (Scheme 1).[1] Treatment of **1a** with copper cyanide (0.5 equiv) at the same temperature afforded bis[*o*-(dimethylsilyl)phenyl](cyano)cuprate **5a**.[4] Introduction of gaseous oxygen into the solution of **5a** at −78 °C or −110 °C yielded 2,2′-bis(dimethylsilyl)biphenyl (**7a**) in moderate yields (Table 1, entries 1 and 2). Whereas treatment of **5a** with 3 equiv of *p*-dinitrobenzene[5] as an oxidant at −78 °C afforded the comparable yield of **7a** (Table 1, entry 3), the yield of **7a** was increased (74% yield) when 5 equiv of *p*-dinitrobenzene was used (Table 1, entry 4). The same treatment performed at −110 °C, however, resulted in a lower yield (43% yield) (Table 1, entry 5). In contrast, bis[*o*-(fluorodimethylsilyl)phenyl]cuprate **6a** afforded only a trace amount of **8a**, and dimerized product **9a** was obtained as a major product (**8a**/**9a** = 6/94 in ^1H NMR spectra) under the same reaction conditions (Scheme 1). The highly electrophilic fluorodimethylsilyl group in **6a** was easily attacked by the highly nucleophilic phenyl-



(a) for **3a** and **4a**: *tert*-BuLi (x 1)/ Et_2O/–78 °C, 2 h
(b) for **3b** and **4b**: *tert*-BuLi (x 2)/ THF/ −78 °C, 1 h

Scheme 1. Preparation and reaction of **5** and **6**.

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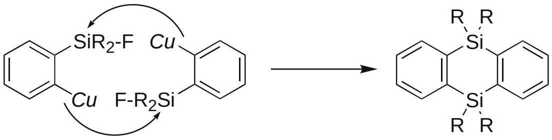
Table 1
Oxidative coupling of bis[*o*-(dimethylsilyl)phenyl](cyano)cuprate **5a**

Entry	Oxidant	Temp (°C)	Time (h)	Yield of **7a** (%)
1	O_2	78	0.5	48
2	O_2	−110	0.5	54
3	*p*-Dinitrobenzene (×3)	−78	1	45
4	*p*-Dinitrobenzene (×5)	−78	1	74
5	*p*-Dinitrobenzene (×5)	−110	1	43

cuprate moiety in another molecule of **6a** even at the low temperature (Scheme 2).

Lipshutz's procedure was also applicable to phenyl derivatives **1b** and **2b**. The reaction of phenyl bromides **3b** and **4b** with *tert*-butyllithium (2 equiv) in THF at −78 °C provided phenyllithiums **1b** and **2b**,[6] which were treated with copper cyanide (0.5 equiv) to give phenylcuprates **5b** and **6b**, respectively (Scheme 1). Subsequent oxidation with *p*-dinitrobenzene (5 equiv) at −78 °C for 1 h produced 2,2′-bis(diphenylsilyl)biphenyls **7b** in 52% yield and **8b** in 39% yield. Corresponding dimerized product **9b** was not obtained perhaps because sterically demanding phenyl groups on the silicon retarded the nucleophilic substitution reaction in **6b** (Scheme 2).

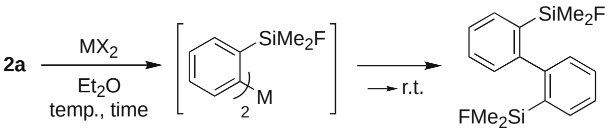
In order to achieve oxidative coupling of the *o*-(fluorodimethylsilyl)phenyl anion, we examined several combinations of **2a** with copper(II) salts (MX_2),[7,8] in which bis[*o*-(fluorosilyl)phenyl]cuprate **10a**–**M** (**M** = Cu) was postulated as an intermediate, as shown in Scheme 3. It was expected that organocuprate **10a**–**M** (**M** = Cu) had lower reactivity toward the fluorosilyl group than cyanocuprate **6a**, retarding the formation of **9a**. In each reaction, phenyllithium **2a** was treated with MX_2 in Et_2O at −78 °C for 1 h,[8] and then the reaction mixture was allowed to warm to ambient temperature. The product ratio was determined by ^1H NMR spectroscopy, and the results are summarized in Table 2. Copper(II) dichloride[8a] exclusively provided **9a** (**8a**/**9a** = 5/95) (Table 2, entry 1), and copper(II) bis(triflate) ($Cu(OTf)_2$)[8b] also preferred the formation of **9a** to that of **8a** (ca. 10% yield) (**8a**/**9a** = 22/78) (Table 2, entry 2). In contrast, copper(II) bis(pivalate) ($Cu(OPiv)_2$)[8c,9] afforded **8a** (ca. 40% yield) in higher yield than **9a** (**8a**/**9a** = 92/8) (Table 2, entry 3). The other metal(II) salt, cobalt(II) dichloride,[8d] facilitated the dimerization rather than the formation of **8a** via **10a**–**M** (**M** = Co), giving **9a** (**8a**/**9a** = 3/97) (Table 2, entry 4). We also treated **2a** with tris(acetylacetonate)iron(III) ($Fe(acac)_3$)[8e,10] (1.1 equiv) in Et_2O at −78 °C for 1 h, which preferred **8a** (ca. 30% yield) to **9a** (**8a**/**9a** = 90/10), but a small amount of disiloxane **11** was formed together. The reason for the successful result in the case of Cu $(OPiv)_2$ remains unclear, but it may be partly due to the high solubility of copper(II) pivalate in Et_2O, which leads to the complete conversion of **2a** into **10a**–**M** (**M** = Cu) at the low temperature. Finally, as the optimized conditions, we demonstrated that treatment of **2a** with $Cu(OPiv)_2$ (3 equiv) in Et_2O at −60 °C for 24 h provided biphenyl **8a** in 66% yield together with a small amount of **9a** (**8a**/**9a** = 93/7) (Scheme 4).



6a R = Me
6b R = Ph

9a R = Me
9b R = Ph

Scheme 2. Dimerization of **6**.



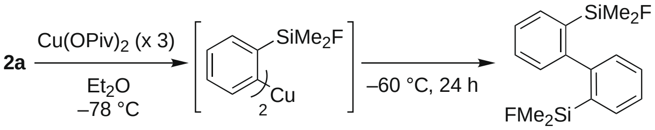
10a-M

8a

Scheme 3. Preparation and reaction of **10a**.

Table 2
Oxidative coupling of bis[*o*-(fluorodimethylsilyl)phenyl]metals **10a**–**M** (**M** = Cu, Co)

Entry	MX_2	Temp (°C)	Time (h)	**8a**:**9a**
1	$CuCl_2$ (×2)	−78	1	5:95
2	$Cu(OTf)_2$ (×1)	−78	1	22:78
3	$Cu(OPiv)_2$ (×3)	−78	1	92:8
4	$CoCl_2$ (×0.5)	−78	1	3:97



10a-Cu

8a 66%
(**8a**/**9a** = 93/7)

Scheme 4. Oxidative coupling of **2a** using $Cu(OPiv)_2$.

In summary, we prepared bis[*o*-(hydrosilyl)phenyl]cuprates **5** and bis[*o*-(fluorosilyl)phenyl]cuprates **6**, which lead to corresponding silicon-functionalized 2,2′-disilylbiphenyls **7** and **8** by oxidative coupling. The present reactions demonstrate for the first time that the hydrosilyl and fluorosilyl functionalities are compatible with organocuprates at low temperatures and survive oxidative coupling at the *ortho* position.

2. Experimental

Preparation of **5a** *and its oxidative coupling:* A solution of *tert*-BuLi in pentane (1.53 mol/L, 14.0 mL, 21.4 mmol) was added to a solution of **3a** (4.70 g, 21.8 mmol) in Et_2O (40 mL) at −78 °C over 8 min. The reaction mixture was stirred at that temperature for 2 h. The resulting solution of **1a** was transferred via a Teflon tube to a suspension of CuCN (902 mg, 10.1 mmol) in Et_2O (20 mL) at −78 °C over 7 min. The reaction mixture was allowed to warm to ambient temperature with vigorous stirring until the solution became homogeneous (for ca. 16 min). Then the resulting solution of **5a** was cooled again to −78 °C. A suspension of *p*-dinitrobenzene (17.0 g, 101 mmol) in Et_2O (100 mL) was added to the solution of **5a** at −78 °C over 15 min. The reaction mixture was stirred at the same temperature for 1 h, and was then allowed to warm to room temperature. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The resulting residue was diluted with hexane (100 mL) and filtered. The filtrate was concentrated in vacuo to give a brown oil (2.57 g). The oil was subjected to column chromatography on silica gel (100 mL) using hexane as eluent ($R_f = 0.6$) to give **7a** (2.19 g, 74% yield) as a colorless oil. Compound **7a**: ^1H NMR ($CDCl_3$, δ): 0.01 (d, $J = 4$ Hz, 6H), 0.03 (d, $J = 4$ Hz, 6H), 4.09 (sept, $J = 4$ Hz, 2H), 7.21–7.23 (m, 2H), 7.33-7.40 (m, 4H), 7.58–7.60 (m, 2H). ^{13}C NMR ($CDCl_3$, δ): −3.05, −3.02, 126.66, 128.45, 129.64, 134.65, 136.47, 149.64. $^{29}Si\{^1H\}$ NMR ($CDCl_3$, δ): −18.7 (d of sept, $^1J_{Si-H} = 191$ Hz, $^2J_{Si-H} = 6$ Hz). Anal. Calcd for $C_{16}H_{22}Si_2$: C, 71.04; H, 8.20. Found: C, 70.79; H, 8.24.

Preparation of **5b** *and its oxidative coupling:* A solution of *tert*-BuLi in pentane (1.58 mol/L, 1.3 mL, 2.0 mmol) was added to a solution of **3b** (339 mg, 1.0 mmol) in THF (2.0 mL) at −78 °C over 2 min. The reaction mixture was stirred at that temperature for

1 h to give a solution of **1b**. A suspension of CuCN (45 mg, 0.50 mmol) in THF (1.0 mL) was transferred via a Teflon tube to the solution of **1b** at −78 °C over 3 min. The reaction mixture was allowed to warm to ambient temperature with vigorous stirring until the solution became homogeneous (for ca. 3 min). The resulting solution of **5b** was cooled again to −78 °C. A suspension of *p*-dinitrobenzene (840 mg, 5.0 mmol) in THF (3.0 mL) was added to the solution of **5b** at −78 °C over 2 min. The reaction mixture was stirred at the same temperature for 1 h, and was then allowed to warm to room temperature. The volume of the reaction mixture was reduced to ca. 3 mL by evaporation. The concentrated reaction mixture was diluted with hexane (10 mL) and filtered. The filtrate was concentrated in vacuo to give a brown solid (353 mg). The solid was subjected to column chromatography on silica gel (15 mL) using hexane/AcOEt (20:1) as eluent (R_f = 0.23) to give a white solid (247 mg), which was recrystallized from CH_2Cl_2/hexane to afford **7b** (134 mg, 52% yield) as colorless crystals. Compound **7b**: mp: 138–139 °C. ^{1}H NMR ($CDCl_3$, δ): 4.94 (s, 2H), 6.94 (d, J = 7 Hz, 2H), 7.16 (t, J = 7 Hz, 4H), 7.23–7.46 (m, 22H). ^{13}C NMR ($CDCl_3$, δ): 126.51, 127.77, 127.80, 128.83, 129.38, 129.40, 130.21, 132.66, 133.84, 134.26, 135.67, 135.85, 136.24, 149.87. ^{29}Si{^{1}H} NMR ($CDCl_3$, δ): −22.9 (d, $^1J_{Si-H}$ = 206 Hz, $^4J_{Si-H}$ = 5 Hz). Anal. Calcd for $C_{36}H_{30}Si_2$: C, 83.34; H, 5.83. Found: C, 83.21; H, 5.75.

Preparation of **6b** *and its oxidative coupling:* A solution of *tert*-BuLi in pentane (1.58 mol/L, 1.3 mL, 2.0 mmol) was added to a solution of **4b** (360 mg, 1.0 mmol) in THF (2.0 mL) at −78 °C over 3 min. The reaction mixture was stirred at that temperature for 1 h to give a solution of **2b**. A suspension of CuCN (45 mg, 0.50 mmol) in THF (1.0 mL) was transferred via a Teflon tube to the solution of **2b** at −78 °C over 3 min. The reaction mixture was stirred at −78 °C for 12 min to give a homogeneous solution of **6b**. A suspension of *p*-dinitrobenzene (850 mg, 5.0 mmol) in THF (3.0 mL) was added to the solution of **6b** at −78 °C over 2 min. The reaction mixture was stirred at the same temperature for 1 h, and was then allowed to warm to room temperature. The volume of the reaction mixture was reduced to ca. 3 mL by evaporation. The concentrated reaction mixture was diluted with hexane (10 mL) and filtered. The filtrate was concentrated in vacuo to give a brown solid (365 mg). This solid was washed with hexane to yield pure **8b** (108 mg, 39% yield) as colorless crystals. Compound **8b**: **m**p: 139–140 °C. ^{1}H NMR ($CDCl_3$, δ): 6.91 (d, J = 8 Hz, 2H), 7.14 (ddd, J = 8 Hz, 8 Hz, and 1 Hz, 2H), 7.23–7.34 (m, 18H), 7.38–7.43 (m, 4H), 7.48 (dd, J = 8 Hz and 1 Hz, 2H). ^{13}C NMR ($CDCl_3$, δ): 126.40, 127.71, 129.69, 130.08, 130.36 (d, $^3J_{C-F}$ = 14 Hz), 132.15 (d, $^2J_{C-F}$ = 16 Hz), 133.33 (d, $^2J_{C-F}$ = 17 Hz), 133.71 (d, $^2J_{C-F}$ = 17 Hz), 134.46, 134.48, 135.10, 135.97, 136.00, 149.30. ^{19}F NMR ($CDCl_3$, δ): −165.67 (s). ^{29}Si{^{1}H} NMR ($CDCl_3$, δ): −4.7 (d, $^1J_{Si-F}$ = 283 Hz). Anal. Calcd for $C_{36}H_{28}F_2Si_2$: C, 77.94; H, 5.09. Found: C, 77.54; H, 5.30.

Preparation of **10a** *and its oxidative coupling:* A solution of *tert*-BuLi in pentane (1.53 mol/L, 0.35 mL, 0.54 mmol) was added to a solution of **4a** (124 mg, 0.53 mmol) in Et_2O (10 mL) at −78 °C over 3 min. The reaction mixture was stirred at that temperature for 2 h. A suspension of $Cu(OPiv)_2$ (421 mg, 1.58 mmol) in Et_2O (1.0 mL) was added to the resulting solution of **1a** at −78 °C over 5 min. The reaction mixture was stirred at −60 °C for 24 h, and was then allowed to warm to room temperature. The reaction mixture was diluted with hexane (10 mL) and filtered. The filtrate was concentrated in vacuo. The resulting residue was diluted with hexane (10 mL) and filtered. The filtrate was concentrated in vacuo to give a greenish oil (71 mg). The oil was subjected to bulb-to-bulb distillation (115–125 °C (bath temperature)/0.1 mmHg) to yield **8a** with small amount of **9a** (total 58 mg, **8a**:**9a** = 93:7, 66% yield of **8a**) as a colorless oil. Compound **8a**: ^{1}H NMR ($CDCl_3$, δ): 0.00 (d, $^3J_{F-H}$ = 8 Hz, 6H), 0.15 (d, $^3J_{F-H}$ = 8 Hz, 6H), 7.28–7.31 (m, 2H), 7.45–7.48 (m, 4H), 7.75–7.78 (m, 2H). ^{13}C NMR ($CDCl_3$, δ): −0.73 (d, $^2J_{C-F}$ = 16 Hz), 0.90 (d, $^2J_{C-F}$ = 16 Hz), 127.05, 129.44, 129.82, 134.11 (d, $^3J_{C-F}$ = 3 Hz), 135.67 (d, $^2J_{C-F}$ = 15 Hz), 148.54 (d, $^3J_{C-F}$ = 3 Hz). ^{19}F NMR ($CDCl_3$, δ): −158.19 (sept, $^3J_{F-H}$ = 8 Hz). ^{29}Si{^{1}H} NMR ($CDCl_3$, δ): 20.5 (d, $^1J_{Si-F}$ = 280 Hz). Anal. Calcd for $C_{16}H_{20}F_2Si_2$: C, 62.70; H, 6.58. Found: C, 62.41; H, 6.85.

Acknowledgments

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