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Polyarylene Synthesis by Cross-Coupling with HOMSi Reagents

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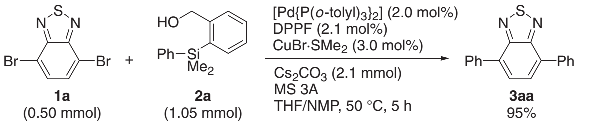
Cross-coupling reaction of dibromoarenes with HOMSi reagents (organo[2-(hydroxymethyl)phenyl]dimethylsilanes), or alternatively bromoarenes with arylene-bisHOMSi reagents, proceeded smoothly in the presence of a Pd catalyst and a weak base, and ter- or quaterarenes are produced in excellent yields. The present reaction was successfully applied to polyarylene synthesis using 4,7-dibromobenzothiadiazole or a 2,7-dibromofluorene derivative along with a 2,7-fluorenylene-bisHOMSi reagent.

Polymers containing conjugated π-electron systems play key roles in many electronic organic materials such as sensors, semiconductors, photovoltaic cells (PVC), field-effect transistors (FET), and optical devices (e.g., organic light-emitting diodes).[1] Thus invention of efficient synthetic methods for π-conjugated polymers has grown to be an important issue in synthetic organic chemistry. Metal-catalyzed cross-coupling reaction of dihaloarenes with organobimetallic reagents is a powerful tool to synthesize polyarylenes straightforwardly.[2,3] To obtain high-molecular-weight polymers, use of highly reactive cross-coupling reaction is essential. So far, the Suzuki–Miyaura coupling has been employed to this end. However, the polymer synthesis is often accompanied by nontrivial contaminant formation attributed mainly to the boron reagents.[4,5] In this sense, organosilicon-based cross-coupling is considered to be advantageous. In particular, recently invented aryl[2-(hydroxymethyl)-phenyl]dimethylsilanes, simply called HOMSi reagents, smoothly cross-couple with a range of haloarenes to give the corresponding biaryls in the presence of a Pd catalyst and weak base in preference to the coupling active groups like boryl and stannyl groups.[6,7] Thus, it is reasonable to apply the HOMSi-based cross-coupling to simultaneous multiple bond forming reactions and polymer synthesis. Herein we report that the Pd-catalyzed cross-coupling reaction of dihaloarenes with HOMSi reagents, or haloarenes with arylene-bisHOMSi reagents, works well to give ter- to quinquaryl derivatives. The cross-coupling reaction is finally shown to be applicable to polyarylene synthesis.

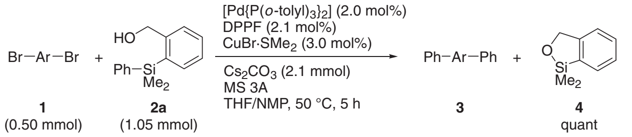


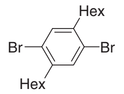
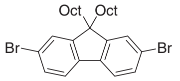
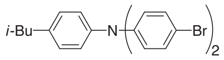
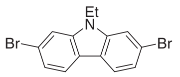
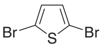
(1)

It is well recognized that the polymer synthesis by the cross-coupling reaction requires careful control of the catalyst system including ligand and base in addition to stoichiometic ratio of dihaloarenes and organobimetallic reagents for the preparation of high-molecular-weight polymers. In this regard, HOMSi reagents have advantages of easy handing and purification as well as cyclic silyl ether formation. On the other hand, for a single carbon–carbon bond formation, HOMSi reagents are generally used slightly in excess.[6] Thus, we started our research by scrutinizing the cross-coupling conditions for the stoichiometric coupling of 4,7-dibromobenzothiadiazole (**1a**) with phenyl-HOMSi reagent **2a**.

After screening various parameters of reaction conditions, we found that the reaction of **1a** and **2a** in a molar ratio of 1.0:2.1 proceeded smoothly in the presence of $[\mathrm{Pd}\{\mathrm{P}(o\text{-tolyl})_3\}_2]$ (2.0 mol %), DPPF (= 1,1′-bis(diphenylphosphino)ferrocene) (2.1 mol %), $\mathrm{CuBr{\cdot}SMe_2}$ (3.0 mol %), $\mathrm{Cs_2CO_3}$ (4.2 equiv), MS 3A (200 mg mmol^{-1}) in THF/NMP at 50 °C for 3 h to give 4,7-diphenylbenzothiadiazole (**3aa**) in 95% yield (eq 1). The scope of dibromoarenes **1** was proven to be broad as demonstrated in Table 1. Substituted aryl electrophiles such as 1,4-dibromo-2,5-dihexylbenzene (**1b**) and 2,7-dibromo-9,9-dioctylfluorene (**1c**) gave the corresponding terphenyl and quaterphenyl derivatives **3ba** and **3ca** in 94% and 92% yields respectively (Entries 1 and

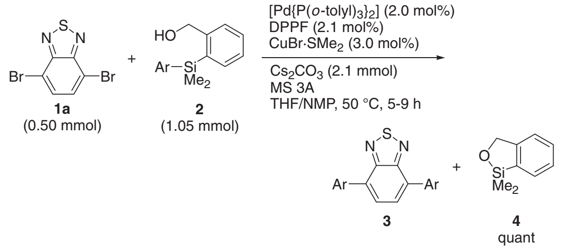
Table 1. Cross-coupling reaction of dihaloarenes **1** with **2a**[a]

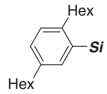
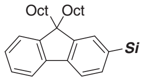
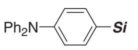
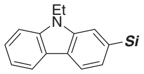
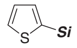


Entry	1		Product	Yield/%[b]
1		**1b**	**3ba**	94
2		**1c**	**3ca**	92
3		**1d**	**3da**	98
4		**1e**	**3ea**	90
5		**1f**	**3fa**	90

[a]Unless otherwise noted, a mixture of **1** (0.50 mmol), **2a** (1.05 mmol), $[\mathrm{Pd}\{\mathrm{P}(o\text{-tolyl})_3\}_2]$ (0.010 mmol), DPPF (0.011 mmol), $\mathrm{CuBr{\cdot}SMe_2}$ (0.015 mmol), $\mathrm{Cs_2CO_3}$ (2.10 mmol), MS 3A (100 mg), THF (0.75 mL), and NMP (0.25 mL) was heated at 50 °C for 5 h.[11] NMP: *N*-methylpyrrolidone. [b]Isolated yield.

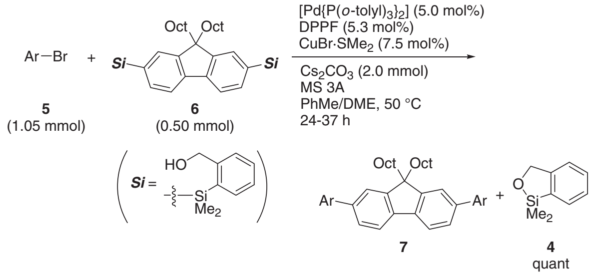
Table 2. Cross-coupling reaction of **1a** with **2**[a]

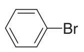
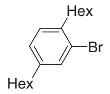
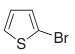
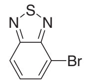


Entry	**2**		Product	Yield/%^{b}
1		**2b**	**3ab**	99
2		**2c**	**3ac**	87
3		**2d**	**3ad**	76
4		**2e**	**3ae**	91
5		**2f**	**3af**	99

[a]Unless otherwise noted, a mixture of **1a** (0.50 mmol), **2** (1.05 mmol), [Pd{P(*o*-tolyl)$_3$}$_2$] (0.010 mmol), DPPF (0.011 mmol), CuBr•SMe$_2$ (0.015 mmol), Cs$_2$CO$_3$ (2.1 mmol), MS 3A (100 mg), THF (0.75 mL), and NMP (0.25 mL) was heated at 50 °C for 5–9 h.[11] [b]Isolated yield.

Table 3. Cross-coupling reaction of bromoarenes **5** with **6**[a]



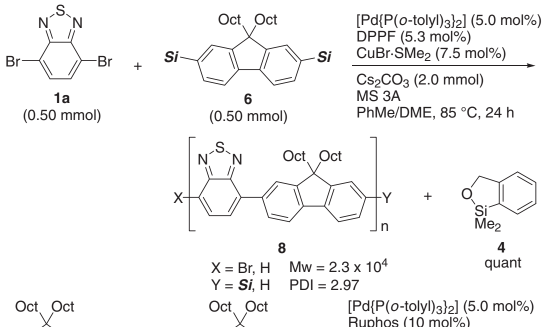
Entry	**5**		Product	Yield/%^{b}
1		**5a**	**7a** (= **3ca**)	91
2		**5b**	**7b**	72
3		**5c**	**7c**	80
4[c]		**5d**	**7d**	94

[a]Unless otherwise noted, a mixture of **5** (1.05 mmol), **6** (0.50 mmol), [Pd{P(*o*-tolyl)$_3$}$_2$] (0.025 mmol), DPPF (0.026 mmol), CuBr•SMe$_2$ (0.038 mmol), Cs$_2$CO$_3$ (2.0 mmol), MS 3A (100 mg), PhMe (0.75 mL), and DME (0.25 mL) was heated at 50 °C.[11] DME: 1,2-dimethoxyethane. [b]Isolated yield. [c]Reaction run on a 0.20 mmol scale.

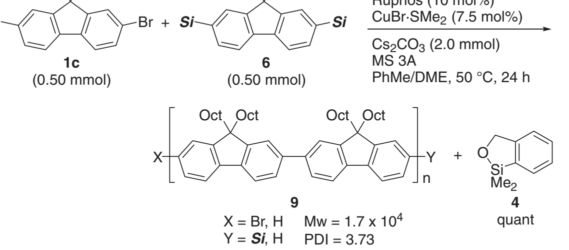
2). Dibromo derivative of triarylamine **1d** reacted with **2a** to afford **3da** in a quantitative yield (Entry 3). Dibromoheteroarenes **1e** and **1f** also underwent the phenyl coupling in excellent yields (Entries 4 and 5).

Having succeeded in the cross-coupling of dibromoarenes with phenyl-HOMSi reagent **2a**, we turned our attention to the reaction of other aryl- and heteroaryl-HOMSi reagents **2b**–**2f** with 4,7-dibromobenzothiadiazole (**1a**) as a coupling partner.[8] As summarized in Table 2, the teraryl and quateraryl synthesis proceeded without any problems. Perturbation by an ortho substituent is minimum (Entry 1). When fluorenyl-HOMSi reagent **2c** was used, the corresponding quinquaryl derivative **3ac** was obtained in 87% yield (Entry 2). Diphenylamino group did not hamper the reaction, but the isolated yield of **3ad** was slightly lower (Entry 3). Heteroaryl groups such as 2-carbazoyl and 2-thienyl groups tolerated the coupling reaction conditions to give **3ae** and **3af** in 91% and 99% yields, respectively (Entries 4 and 5). To the best of our knowledge, the cross-coupling reaction of 4,7-dibromobenzothiadiazole with a 2-thienylsilane reagent has never been performed before.

The scope of the reaction of bromoarenes with a fluorenylene-bisHOMSi reagent **6**, as an organobimetallic coupling partner is summarized in Table 3. The reaction of **6** (0.50 mmol) with bromobenzene (**5a**) (1.05 mmol) proceeded smoothly in the presence of [Pd{P(*o*-tolyl)$_3$}$_2$] (5 mol %), DPPF (5.3 mol %), CuBr•SMe$_2$ (7.5 mol %), Cs$_2$CO$_3$ (4.0 equiv) and MS 3A (200 mg mmol^{-1}) in toluene/DME at 50 °C for 24 h to give **7a** (identical to **3ca**) in 91% yield (Entry 1). Dihexyl substituents in bromobenzene **5b** did not seriously hamper the reaction to give the corresponding bisarylated fluorene **7b** in 72% yield (Entry 2). Heteroaryl electrophiles also reacted with **6** to give the corresponding quateraryls **7c** and **7d** in good and excellent yields (Entries 3 and 4).



(2)



(3)

Finally, the cross-coupling reaction was applied to dibromoarenes **1** and fluorenylene-bisHOMSi reagent **6** to give the corresponding conjugated polyarylenes (eqs 2 and 3). Copolymerization of **1a** and **6** in strictly equimolar amounts under the optimized conditions proceeded smoothly to give poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) with M_w of 2.3×10^4 (PDI 2.97) (eq 2).[9] F8BT is attracting specific interest as a photovoltaic and light-emitting material.[10] 4,7-Dibromo-9,9-dioctylfluorene (**1c**) also reacted with **6** to give a polyfluorene with M_w of 1.7×10^4 (PDI 3.73) in almost quantitative yield (eq 3).

In summary, we have demonstrated that HOMSi-based cross-coupling is an efficient and straightforward strategy for simultaneous multiple cross-coupling and polymer synthesis. Further application to construction of polyarylene frameworks is in progress in our laboratories.

References and Notes

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5 Polymer synthesis by the Suzuki–Miyaura cross-coupling reaction is accompanied by formation of boronic acids, which tend to precipitate in organic phase and hamper the formation of high-molecular-weight polymers. Thus polymer synthesis by this cross-coupling reaction is carried out often in an organic–aqueous biphase system to let boronic acid residue move to aqueous phase. However, the presence of water often is apt to trigger protodeborylation. In sharp contrast, HOMSi-based cross-coupling reaction coproduces cyclic silyl ether **4** which acts like an organic solvent, and water cosolvent is not necessary. Therefore, HOMSi-based cross-coupling reaction is free of salt precipitation and protodesilylation.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.