

# Regioselective Synthesis of Multisubstituted Benzenes by Palladium-Catalyzed Intermolecular Reaction of $\beta$ -Iodo- $\beta$ -silylstyrenes with Alkynes

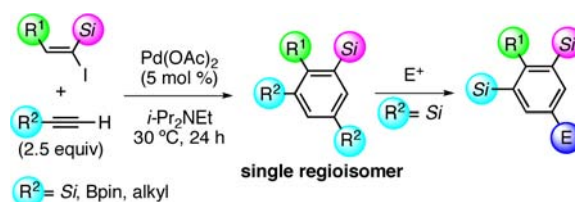
Hidenori Kinoshita, Hirotohi Takahashi, and Katsukiyo Miura\*

Department of Applied Chemistry, Graduate School of Science and Engineering,  
Saitama University, 255 Shimo-ohkubo, Sakura-ku, Saitama 338-8570, Japan

kmiura@apc.saitama-u.ac.jp

Received April 19, 2013

## ABSTRACT



The Pd-catalyzed reaction between  $\beta$ -iodo- $\beta$ -silylstyrenes and terminal alkynes in  $i$ -Pr<sub>2</sub>NEt gave 1,2,3,5-tetrasubstituted benzenes with complete regioselection. The use of certain silylacetylenes as alkynes enabled efficient synthesis of 1,3,5-trissilyl-2-arylbenzenes, which could be transformed into other multisubstituted benzenes by displacement of the silyl groups.

Multisubstituted benzenes are quite ubiquitous building blocks of various compounds ranging from biologically active natural products to functional materials. Therefore, a number of methods for constructing multisubstituted benzenes have so far been developed.<sup>1,2</sup> In particular, transition-metal-catalyzed reactions among three two-carbon units provide easy access to the structural motifs. Cyclotrimerization of alkynes is a well-known example

of these reactions.<sup>3,4</sup> As another intriguing example, the Pd-catalyzed cascade reaction of 2-bromoalkenediynes is useful for the synthesis of tricyclic compounds containing a benzene ring (Scheme 1).<sup>5</sup> In contrast to the successful intramolecular process, to the best of our knowledge, its intermolecular version using independent haloalkenes and alkynes has not been applied to the efficient synthesis of

(1) For selective examples using transition metal catalysis, see: (a) Rubina, M.; Conley, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2006**, *128*, 5818. (b) Hara, H.; Hirano, M.; Tanaka, K. *Org. Lett.* **2008**, *10*, 2537. (c) Tsuji, H.; Yamagata, K.; Fujimoto, T.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 7792. (d) Kuninobu, Y.; Nishi, M.; Yasuda, S.; Takai, K. *Org. Lett.* **2008**, *10*, 3009. (e) Izawa, Y.; Pun, D.; Stahl, S. S. *Science* **2011**, *333*, 209.

(2) For selective examples of nontransition-metal-mediated reactions, see: (a) Crone, B.; Krisch, S. F.; Umland, K.-D. *Angew. Chem., Int. Ed.* **2010**, *49*, 4661. (b) Yang, F.; Qiu, Y.-F.; Ji, K.-G.; Niu, Y.-N.; Ali, S.; Liang, Y.-M. *J. Org. Chem.* **2012**, *77*, 9029. (c) Diallo, A.; Zhao, Y.-L.; Wang, H.; Li, S.-S.; Ren, C.-Q.; Liu, Q. *Org. Lett.* **2012**, *14*, 5776.

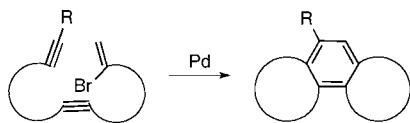
(3) (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (b) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: New York, 1991; Vol. 5, p 1129. (c) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49. (d) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901. (e) Kotha, S.; Brahmachary, E.; Lahiri, K. *Eur. J. Org. Chem.* **2005**, 4741. (f) Yamamoto, Y. *Curr. Org. Chem.* **2005**, *9*, 503. (g) Gandon, V.; Aubert, C.; Malacria, M. *Chem. Commun.* **2006**, 2209.

(4) For selective examples of intermolecular [2 + 2 + 2] cyclotrimerization, see: (a) Ozerov, O. V.; Ladipo, F. T.; Patrick, B. O. *J. Am. Chem. Soc.* **1999**, *121*, 7941. (b) Li, J.; Jiang, H.; Chen, M. *J. Org. Chem.* **2001**, *66*, 3627. (c) Tanaka, K.; Shirasaka, K. *Org. Lett.* **2003**, *5*, 4697. (d) Takeuchi, R.; Nakaya, Y. *Org. Lett.* **2003**, *5*, 3659. (e) Yamamoto, Y.; Ishii, J.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2004**, *126*, 3712. (f) Yamamoto, Y.; Ishii, J.; Nishiyama, H.; Itoh, K. *J. Am. Chem. Soc.* **2005**, *127*, 9625. (g) Tanaka, K.; Nishida, G.; Ogino, M.; Noguchi, K. *Org. Lett.* **2005**, *7*, 3119. (h) Tanaka, K.; Toyoda, K.; Wada, A.; Shirasaka, K.; Hirano, M. *Chem.—Eur. J.* **2005**, *11*, 1145. (i) Hilt, G.; Volger, T.; Hess, W.; Galbiati, F. *Chem. Commun.* **2005**, 1474. (j) Hilt, G.; Hess, W.; Volger, T.; Hengst, C. *J. Organomet. Chem.* **2005**, *690*, 5170. (k) Saino, N.; Amemiya, F.; Tanabe, E.; Kase, K.; Okamoto, S. *Org. Lett.* **2006**, *8*, 1439. (l) Goswami, A.; Ito, T.; Okamoto, S. *Adv. Synth. Catal.* **2007**, *349*, 2368. (m) Hilt, G.; Hengst, C.; Hess, W. *Eur. J. Org. Chem.* **2008**, 2293. (n) Xu, Y.-L.; Pan, Y.-M.; Wu, Q.; Wang, H.-S.; Liu, P.-Z. *J. Org. Chem.* **2011**, *76*, 8472.

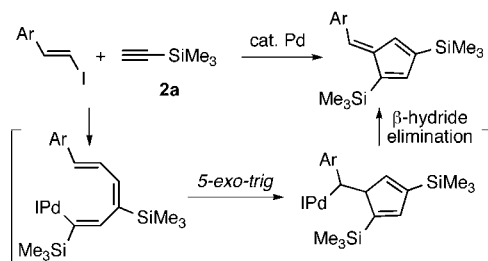
(5) (a) Meyer, F. E.; de Meijere, A. *Synlett* **1991**, 777. (b) Negishi, E.; Harring, L. S.; Owczarczyk, Z.; Mohamud, M. M.; Ay, M. *Tetrahedron Lett.* **1992**, *33*, 3253. (c) Negishi, E.; Ay, M.; Sugihara, T. *Tetrahedron* **1993**, *49*, 5471. (d) Tokan, W. M.; Meyer, F. E.; Schweizer, S.; Parsons, P. J.; de Meijere, A. *Eur. J. Org. Chem.* **2008**, 6152.

multisubstituted benzenes.<sup>6,7</sup> In this context, Lee et al. have reported that the Pd-catalyzed intermolecular reaction of (*E*)- $\beta$ -iodostyrenes with 2 equiv of trimethylsilylacetylene (**2a**) provides substituted fulvenes (Scheme 2).<sup>6</sup> The fulvene formation can be explained by a cascade mechanism involving intermolecular double carbopalladation of alkenylpalladiums and 5-exo-trig cyclization (intramolecular carbopalladation) of the resultant trienylpalladiums. We therefore expected that introduction of a bulky group at the position  $\alpha$  to iodine would prevent the 5-exo-trig cyclization to achieve an intermolecular benzene-forming reaction. Herein we report that the Pd-catalyzed reaction of  $\beta$ -iodo- $\beta$ -silylstyrenes **1** with terminal alkynes **2** is valuable for regioselective synthesis of multisubstituted benzenes.

**Scheme 1.** Pd-Catalyzed Cascade Reaction of 2-Bromoalkenediynes



**Scheme 2.** Pd-Catalyzed Intermolecular Reaction of  $\beta$ -Iodostyrenes with **2a**



The reaction of  $\beta$ -iodo- $\beta$ -silylstyrene **1a** with **2a** was chosen to determine the viability of benzene construction from haloalkenes and alkynes (Table 1). Initially, in the presence of a catalytic amount of Pd(OAc)<sub>2</sub> (5 mol %) and Et<sub>3</sub>N (1.2 equiv), the reaction was conducted in THF at room temperature for 24 h. To our delight, the desired tetrasubstituted benzene **3a** was obtained as a single regioisomer even in low yield (entry 1). When Et<sub>3</sub>N was used as both base and solvent, the yield of **3a** was largely improved (entry 2). Use of a reduced amount of Pd(OAc)<sub>2</sub> decreased the yield (entry 3). Other Pd(II) salts also catalyzed the benzene construction to afford **3a** in moderate

yields (entries 4–6), while the reactions catalyzed by Pd(PPh<sub>3</sub>)<sub>4</sub> and Pd/C resulted in recovery of **1a** (entries 7 and 8). Screening of amines revealed that *i*-Pr<sub>2</sub>NEt was the most effective among the amines examined (entries 2 and 9–12). A slightly elevated temperature retarded the formation of **3a** (entry 13). The (*Z*)-isomer of **1a** was also subjected to the Pd-catalyzed reaction. However, **3a** was not obtained at all with recovery of (*Z*)-**1a** (entry 14).

**Table 1.** Reaction of Iodoalkene **1a** with **2a**<sup>a</sup>

entry	Pd cat.	base and solvent	yield (%) <sup>b</sup>
1 <sup>c</sup>	Pd(OAc) <sub>2</sub>	Et <sub>3</sub> N + THF	31
2	Pd(OAc) <sub>2</sub>	Et <sub>3</sub> N	83 (70)
3 <sup>d</sup>	Pd(OAc) <sub>2</sub>	Et <sub>3</sub> N	64
4	PdCl <sub>2</sub>	Et <sub>3</sub> N	65
5	PdBr <sub>2</sub>	Et <sub>3</sub> N	58
6	Na <sub>2</sub> PdCl <sub>4</sub>	Et <sub>3</sub> N	66
7	Pd(PPh <sub>3</sub> ) <sub>4</sub>	Et <sub>3</sub> N	0 <sup>e</sup>
8	Pd/C	Et <sub>3</sub> N	0 <sup>e,f</sup>
9	Pd(OAc) <sub>2</sub>	Et <sub>2</sub> NH	0 <sup>f</sup>
10	Pd(OAc) <sub>2</sub>	pyridine	0 <sup>e</sup>
11	Pd(OAc) <sub>2</sub>	Bu <sub>3</sub> N	78
12	Pd(OAc) <sub>2</sub>	<i>i</i> -Pr <sub>2</sub> NEt	84 (90)
13 <sup>g</sup>	Pd(OAc) <sub>2</sub>	<i>i</i> -Pr <sub>2</sub> NEt	69
14 <sup>h</sup>	Pd(OAc) <sub>2</sub>	<i>i</i> -Pr <sub>2</sub> NEt	0 <sup>i</sup>

<sup>a</sup> Unless otherwise noted, all reactions were carried out with **1a** (0.50 mmol), **2a** (1.25 mmol), a catalyst (0.025 mmol), and an amine (0.5 mL) at 30 °C for 24 h. <sup>b</sup> The yield was determined by <sup>1</sup>H NMR analysis using dibenzyl ether as an internal standard. The isolated yield is shown in parentheses. <sup>c</sup> THF (1.0 mL) and Et<sub>3</sub>N (0.084 mL) were used. <sup>d</sup> With Pd(OAc)<sub>2</sub> (0.013 mmol). <sup>e</sup> Recovery of **1a**: 53% (entry 7), 30% (entry 8), 79% (entry 10). <sup>f</sup> A complex mixture of unidentified products was obtained mainly. <sup>g</sup> The reaction was conducted at 40 °C. <sup>h</sup> (*Z*)-Isomer of **1a** was used. <sup>i</sup> (*Z*)-**1a** was recovered quantitatively.

With the optimal reaction conditions in hand (Table 1, entry 12), various iodoalkenes **1** were subjected to the reaction with **2a** (Table 2). The reaction of iodoalkene **1b**, bearing a TMS group as R<sup>2</sup>, resulted in a low yield of the desired product **3b** (entry 1). Introduction of a TBS group, that is, a bulky and relatively electron-donating group as R<sup>2</sup>, diminished the reactivity further (entry 2). Iodoalkenes **1d** and **1e** showed moderate reactivity toward the Pd-catalyzed annulation (entries 3 and 4). When the phenyl group on silicon in **1e** was modified by a CF<sub>3</sub> group, the benzene construction proceeded more efficiently (entry 5). In the case where R<sup>2</sup> is a triphenylsilyl group, the corresponding tetrasubstituted benzene **3g** was obtained in high yield although the reaction required a prolonged time to completion (entry 6). The structure of **3g** was clearly

(6) Lee, G. C. M.; Tobias, B.; Holmes, J. M.; Harcourt, D. A.; Garst, M. E. *J. Am. Chem. Soc.* **1990**, *112*, 9330. In this report, they mentioned that the Pd-catalyzed reaction of  $\alpha$ -bromostyrene with **2a** gave 1-phenyl-3,5-bis(trimethylsilyl)benzene in only 2% yield.

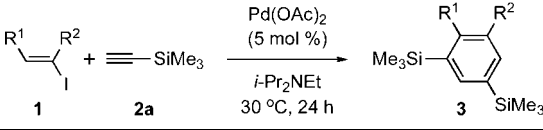
(7) For the Pd-catalyzed reaction of iodoarenes with alkynes leading to naphthalenes, see: Kawasaki, S.; Satoh, T.; Miura, M.; Nomura, M. *J. Org. Chem.* **2003**, *68*, 6836. The present Pd-catalyzed reaction of iodobenzene with **2a** in *i*-Pr<sub>2</sub>NEt did not give any benzannulation product.

(8) For electronic effects of silyl groups, see: (a) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds Part 2*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: Chichester, 1989; Chapter 14, p 893. (b) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed.* **1994**, *33*, 938.

confirmed by X-ray structure analysis (CCDC 914507). These results with the variation of the silyl group ( $R^2$ ) in **1** indicate that the reaction efficiency becomes higher as the electron-withdrawing ability of the substituents on silicon increases.<sup>8</sup> Thus the electronic effect rather than the steric effect is more important to the benzene formation. From this information, it is expected that substrate **1** bearing an electron-withdrawing group such as a carbonyl group as  $R^2$  can show high reactivity. The reaction of iodoalkene **1h** bearing an ethoxycarbonyl group, however, gave a complex mixture of unidentified products with a trace amount of **3h** (entry 7). Similarly nonsilylated  $\beta$ -iodostyrenes **1i** ( $R^2 = \text{Me}$ ) and **1j** ( $R^2 = \text{Ph}$ ) were not suitable for the benzene construction (entries 8 and 9). These results clearly indicate that the directing effects of silyl groups effectively promote the reaction leading to **3**.

The scope of **1** was investigated also by varying the substituent  $R^1$ . The electronic bias by  $p$ -CF<sub>3</sub> and  $p$ -OEt groups on the benzene ring did not affect the reaction efficiency (entries 10 and 11). The *ortho*-substitution in the substrate **1m** allowed an efficient benzene ring formation to **3m** (entry 12). When  $R^1$  was a methyl group, only a trace amount of the desired product was obtained and most of iodoalkene **1n** remained intact (entry 13).

**Table 2.** Scope and Limitations of  $\beta$ -Iodo- $\beta$ -silylstyrenes<sup>a</sup>

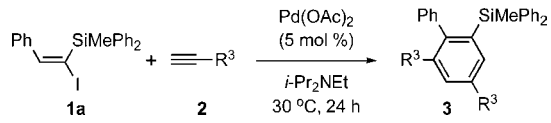
				
entry	<b>1</b>		<b>3</b>	yield (%) <sup>b</sup>
	$R^1$	$R^2$		
1	<b>1b</b>	Ph	<b>3b</b>	27 <sup>c</sup>
2	<b>1c</b>	Ph	<b>3c</b>	trace <sup>c</sup>
3	<b>1d</b>	Ph	<b>3d</b>	52
4	<b>1e</b>	Ph	<b>3e</b>	60
5	<b>1f</b>	Ph	<b>3f</b>	76
6	<b>1g</b>	Ph	<b>3g</b>	84 <sup>d</sup>
7	<b>1h</b>	Ph	<b>3h</b>	trace <sup>c</sup>
8	<b>1i</b>	Ph	<b>3i</b>	trace <sup>c,e</sup>
9	<b>1j</b>	Ph	<b>3j</b>	7 <sup>f</sup>
10	<b>1k</b>	$p$ -CF <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	<b>3k</b>	93
11	<b>1l</b>	$p$ -EtO-C <sub>6</sub> H <sub>4</sub>	<b>3l</b>	86
12	<b>1m</b>	$o$ -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub>	<b>3m</b>	92
13	<b>1n</b>	Me	<b>3n</b>	trace <sup>c</sup>

<sup>a</sup> The reaction was carried out with **1** (0.5 mmol), **2** (1.25 mmol), and Pd(OAc)<sub>2</sub> (0.025 mmol) in *i*-Pr<sub>2</sub>NEt (0.5 mL) at 30 °C for 24 h. <sup>b</sup> Isolated yield. <sup>c</sup> A complex mixture of unidentified products was obtained mainly. <sup>d</sup> The reaction was carried out for 48 h. The reaction for 24 h provided **3g** in 67% yield. <sup>e</sup> With 22% recovery of **1i**. <sup>f</sup> With 65% recovery of **1j**.

We next turned our attention to the scope of alkynes **2** (Table 3). Silylacetylenes **2o**, **2p**, and **2q** underwent the reaction of **1a** to give the corresponding tetrasubstituted benzenes in good yields (entries 1–3). In contrast, the reaction with triethylsilylacetylene (**2r**) resulted in a low

yield of **3r** (entry 4). Intriguingly, the use of 2-ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2s**)<sup>9</sup> as the alkyne afforded diborylbenzene **3s** in 46% isolated yield (entry 5). Hex-1-yne (**2t**), a simple alkyne, is also usable for the present aromatic ring formation. The reaction with a large excess of **2t** and higher loading of Pd(OAc)<sub>2</sub> for an elongated time gave **3t** in 67% yield (entry 6). With phenylacetylene (**2u**), no desired product was obtained (entry 7). In this case, the Sonogashira coupling occurred in preference to the benzene construction. Internal alkynes such as 1-(trimethylsilyl)-prop-1-yne and 1-phenylprop-1-yne were not reactive to **1a** under the Pd-catalyzed conditions. It is probably due to the steric hindrance around the triple bond, which inhibits intermolecular interaction between intermediary alkenyl-palladiums and internal alkynes (*vide infra*).

**Table 3.** Scope and Limitations of Alkynes<sup>a</sup>

				
entry	<b>2</b>		<b>3</b>	yield (%) <sup>b</sup>
	$R^3$			
1	<b>2o</b>	SiMe <sub>2</sub> Ph	<b>3o</b>	93
2	<b>2p</b>	SiMePh <sub>2</sub>	<b>3p</b>	89
3	<b>2q</b>	SiMe <sub>2</sub> ( <i>Oi</i> -Pr)	<b>3q</b>	80
4	<b>2r</b>	SiEt <sub>3</sub>	<b>3r</b>	34 <sup>c,d</sup>
5	<b>2s</b>	BPin	<b>3s</b>	46 <sup>d</sup>
6	<b>2t</b>	$n$ -C <sub>4</sub> H <sub>9</sub>	<b>3t</b>	67 <sup>e</sup>
7	<b>2u</b>	Ph	<b>3u</b>	0 <sup>f</sup>

<sup>a</sup> See footnote a in Table 2. <sup>b</sup> See footnote b in Table 2. <sup>c</sup> With 12% recovery of **1a**. <sup>d</sup> Other products could not be identified. <sup>e</sup> With hex-1-yne (2.5 mmol) and Pd(OAc)<sub>2</sub> (0.1 mmol) for 48 h. <sup>f</sup> The Sonogashira coupling product was formed with many unidentified products.

We further attempted the regioselective synthesis of a pentasubstituted benzene using diyne **2v**, bearing terminal and internal triple bonds (Scheme 3).<sup>10</sup> As expected, the desired product **3v** was obtained as a single regioisomer in 53% yield under the modified reaction conditions.

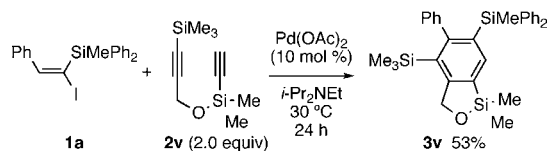
Similar to the proposed mechanism for the Pd-catalyzed cyclization of 2-bromoalkenediynes (Scheme 1), a plausible mechanism for the present benzene-forming reaction involves oxidative addition of iodoalkenes **1** to a Pd(0) species followed by double carbopalladation of alkenyl-palladiums **4** with alkynes **2** (Scheme 4). The resultant

(9) (a) Yamamoto, Y.; Hattori, K.; Ishii, J.; Nishiyama, H. *Tetrahedron* **2006**, *62*, 4294. (b) Geny, A.; Leboeuf, D.; Rouquié, G.; Vollhardt, K. P. C.; Malacria, M.; Gandon, V.; Aubert, C. *Chem.—Eur. J.* **2007**, *13*, 5408. (c) Iannazzo, L.; Vollhardt, K. P. C.; Malacria, M.; Aubert, C.; Gandon, V. *Eur. J. Org. Chem.* **2011**, 3283.

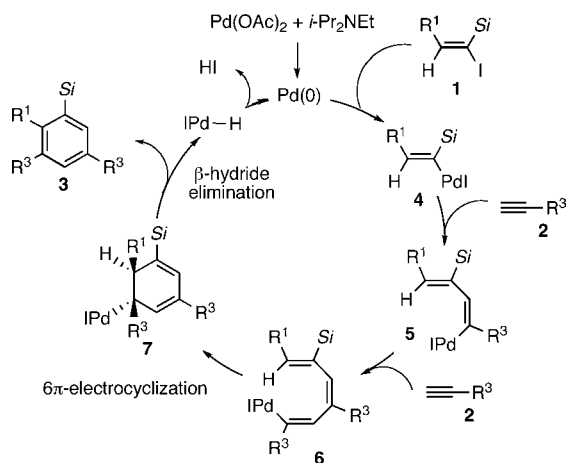
(10) The Pd-catalyzed reaction of  $\beta$ -halostyrenes with 1,6-diynes was reported to yield fulvene derivatives. Silverberg, L. J.; Wu, G.; Rheingold, A. L.; Heck, R. F. *J. Organomet. Chem.* **1991**, *409*, 411.

(11) Judging from the report by Lee and co-workers (Scheme 2 and ref 6), the regioselective double carbopalladation of **4** via **5** is expected to proceed smoothly. We therefore propose the reaction mechanism via **6**. However, an alternative path involving [4 + 2] cycloaddition of **5** to **2** (ref 5d) cannot be ruled out.

**Scheme 3.** Reaction Using Diyne **2v**



**Scheme 4.** A Plausible Mechanism



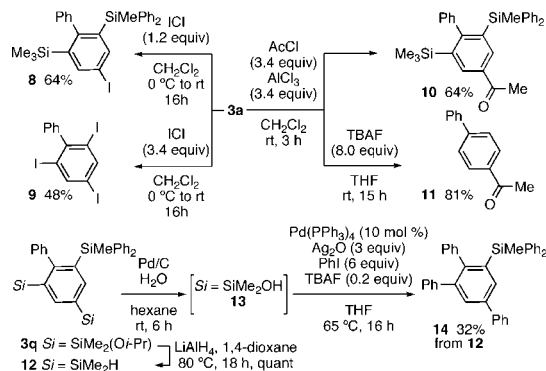
trienylpalladium intermediate **6** undergoes disrotatory  $6\pi$ -electrocyclization to convert to cyclohexadienylpalladium intermediate **7**.<sup>5d,11</sup>  $\beta$ -Hydride elimination of **7** associated with *i*-Pr<sub>2</sub>NEt forms substituted benzenes with regeneration of the Pd(0) species. As described above, the introduction of a Ph<sub>2</sub>MeSi group into **1** is quite effective in promoting the benzene formation. Although the substitution at the position  $\alpha$  to iodine serves to prevent the formation of fulvenes,<sup>12</sup> the silyl group should have other important roles in the reaction course. One of them is presumably to facilitate the initial oxidative addition step by its  $\alpha$ -carbanion stabilizing effect ( $\alpha$ -effect).<sup>9a,13</sup> In addition, the bulky silyl group would fix the conformation of **6** as an *s-cis,cis*-form to assist the  $6\pi$ -electrocyclization. Probably the high reactivity of silylacetylenes also originates from electronic and steric effects of the silyl group. The  $\alpha$ -effect would accelerate the carbopalladation step, and the conformational fixation by the silyl group may facilitate the cyclization step.

(12) Under the present conditions, the reaction of (*E*)- $\beta$ -iodostyrene ( $R^1 = \text{Ph}$ ,  $R^2 = \text{H}$  in **1**) with **2a** in *i*-Pr<sub>2</sub>NEt gave the corresponding fulvene in 12% yield (Scheme 2). No benzene formation was observed.

(13) Igawa, K.; Tomooka, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 232.

(14) Fang, Y.; Xia, W.; He, M.; Liu, B.; Hasebe, K.; Terano, M. *J. Mol. Catal. A: Chem.* **2006**, *247*, 240.

**Scheme 5.** Derivatization of **3a** and **3q**



Finally, we demonstrated the synthetic utility of 2-phenyl-1,3,5-trisilylbenzenes **3a** and **3q** (Scheme 5). Iodode-silylation of **3a** with ICl (1.2 equiv) took place at the least hindered position to give monoiodinated product **8**. With 3.4 equiv of ICl, 2,4,6-triiodobiphenyl (**9**) was obtained in moderate yield. Treatment of **3a** with AcCl–AlCl<sub>3</sub> (3.4 equiv) provided monoacetylated product **10** regioselectively without multiacetylated products. Acetylation of **3a** followed by desilylation with TBAF formed *p*-phenylacetophenone (**11**) in good yield. Silylated benzene **3q** could be converted into triphenylbenzene **14** in 32% yield via the Pd-catalyzed cross-coupling between iodobenzene and silanol **13** under unoptimized conditions.<sup>14,15</sup> The structure of **14** was confirmed by X-ray crystal structure analysis (CCDC 928695).

In conclusion, we have succeeded in the regioselective synthesis of multisubstituted benzenes by the Pd-catalyzed intermolecular reaction of  $\beta$ -iodo- $\beta$ -silylstyrenes with terminal alkynes, especially, silylacetylenes. The silyl groups in these substrates play important roles for efficient benzene construction. The multisilylated benzenes obtained are useful as synthetic intermediates for regiocontrolled synthesis of multifunctionalized benzenes.

**Acknowledgment.** We thank Prof. Dr. Yasushi Nishihara (Okayama Univ.) for his helpful input on the synthesis of ethynylboronates.

**Supporting Information Available.** Experimental procedures, characterization data, and crystallographic data for **3g** and **14** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

(15) Napier, S.; Marcuccio, S. M.; Tye, H.; Whittaker, M. *Tetrahedron Lett.* **2008**, *49*, 3939.

The authors declare no competing financial interest.