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Rhodium-Catalyzed Anti Selective Cross-Addition of Bis(trimethylsilyl)acetylene to Diarylacetylenes via Carbon−Silicon Bond Cleavage

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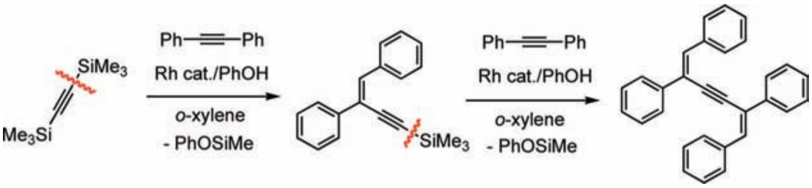
ABSTRACT



The addition of bis(trimethylsilyl)acetylene to diarylacetylenes proceeds efficiently and selectively in a formal anti fashion in the presence of [Rh(OH)(cod)]$_2$/bisphosphine and phenol as catalyst and activator, respectively, accompanied by cleavage of one of the C−Si bonds to produce the corresponding (*Z*)-enynes. The products can further couple with the same or a different diarylacetylene molecule to give rise to (*Z*,*Z*)-1,2,5,6-tetraaryl-1,5-hexadien-3-ynes that show relatively strong solid-state fluorescence.

Alkyne coupling reactions such as the dimerization of terminal alkynes via C(sp)-H bond cleavage are of genuine synthetic utility in preparing π-conjugated enyne compounds.[1] However, the selective cross-dimerization of two different alkynes is, in general, still difficult because the formation of cross- and homocoupled regio- and stereoisomers is possible. Thus, minute control of the reaction is a major challenge. One of the rare, leading examples is the palladium-catalyzed reaction of internal alkynes having an electron-withdrawing group as acetylene acceptors.[2a] Such reactions have been successfully achieved by using other transition metals.[2] Notably, some selective catalytic cross-addition reactions of terminal silylacetylenes as acetylene donors to terminal and internal alkynes have recently been disclosed.[3]

Meanwhile, the selective cross-addition reactions other than those involving C−H bond cleavage are known. Thus, metal or ketone masked terminal alkynes involving stannyl- and boryl-acetylenes and propargyl alcohols have been reported to react via C−M and C−C bond cleavages.[4] We recently reported that in the presence of a rhodium catalyst,

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(2) (a) Pd: Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Ruhter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698. (b) Lucking, U.; Pfaltz, A. *Synlett* **2000**, 1261. (c) Chen, L.; Li, C.-J. *Tetrahedron Lett.* **2004**, *45*, 2771. (d) Ru: Yi, C. S.; Liu, N. *Organometallics* **1998**, *17*, 3158. (e) Rh: Weng, W.; Guo, C.; Çelenligil-Çetin, R.; Foxman, B. M.; Ozerov, O. V. *Chem. Commun.* **2006**, 197. (f) Ito, J.; Kitase, M.; Nishiyama, H. *Organometallics* **2007**, *26*, 6412. (g) Ir: Hirabayashi, T.; Sakaguchi, S.; Ishii, Y. *Adv. Synth. Catal.* **2005**, *347*, 872. (h) Ti Akita, M.; Yasuda, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 480. (i) U: Wang, J.; Kapon, M.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S. *Inorg. Chim. Acta* **2002**, *334*, 183.

(3) (a) Ru: Katayama, H.; Yari, H.; Tanaka, M.; Ozawa, F. *Chem. Commun.* **2005**, 4336. (b) Rh: Katagiri, T.; Tsurugi, H.; Funayama, A.; Satoh, T.; Miura, M. *Chem. Lett.* **2007**, *36*, 830. (c) Nishimura, T.; Guo, X.-X.; Ohnishi, K.; Hayashi, T. *Adv. Synth. Catal.* **2007**, *349*, 2669. (d) Pd: Tsukada, N.; Ninomiya, S.; Aoyama, Y.; Inoue, Y. *Org. Lett.* **2007**, *9*, 2919.

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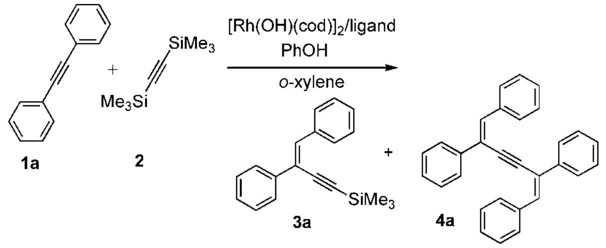
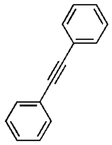
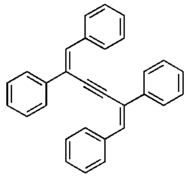
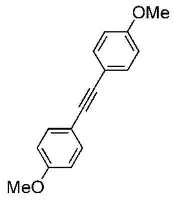
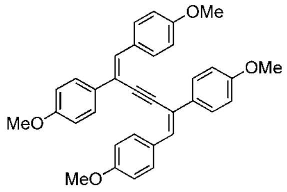
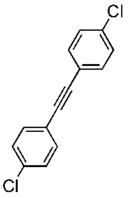
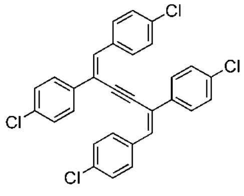
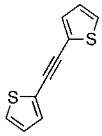
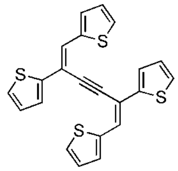
Table 1. Reaction of Diphenylacetylene (**1a**) with Bis(trimethylsilyl)acetylene (**2**) to Produce Enyne **3a** and Dienyne **4**[a]



entry	ligand	time (h)	**3a**, % yield[b] (*E*/*Z*)	**4a**, % yield[c]
1	dppb	2	67 (10:90)	13
2	dCypb	2	76 (64)[d] (4:96)	10
3	dppf	2	77 (8:92)	8
4	dppp	2	56 (54:46)	trace
5[e]	dCypb	2	73 (3:97)	19
6[f]	dCypb	2	23 (22:78)	15
7[g]	dCypb	4	trace	0
8[h]	dCypb	4	0	0
9[i]	dCypb	4	14 (21:79)	0
10[j]	dCypb	4	2	0

[a] Reaction conditions: [**1a**]/[**2**]/[Rh]/[ligand]/[PhOH] = 1:2:0.03:0.03:3 (in mmol), in *o*-xylene (4 mL) at 130 °C under N_2. [b] GC yield based on the amount of **1a** used. [c] GC yield based on the half amount of **1a** used. [d] Isolated yield. [e] [**2**] = 1.2 (mmol). [f] [PhOH] = 1 (mmol). [g] H_2O (3 mmol) in place of PhOH. [h] Without PhOH. [i] $[Rh(Cl)(cod)]_2$ in place of $[Rh(OH)(cod)]_2$. [j] $[Ir(OH)(cod)]_2$ in place of $[Rh(OH)(cod)]_2$.

Table 2. Reaction of Diarylacetylenes (**1**) with Bis(trimethylsilyl)acetylene (**2**) to Produce Dienynes **4**[a]

entry	**1**	time (h)	product, % yield[b]
1[c]	 **1a**	24	 **4a**, 58 (68)
2	**1a**	12	**4a**, 70 (76)
3[d]	**1a**	6	**4a**, 69 (77)
4	 **1b**	8	 **4b**, 81
5[d]	**1b**	2 + 2[e]	**4b**, 82
6[d]	 **1c**	24	 **4c**, 22
7	 **1d**	60	 **4d**, 63
8[d]	**1d**	2 + 2[e]	**4d**, 60

[a] Reaction conditions: [**1**]/[**2**]/[Rh]/[dCypb]/[ArOH] = 1.2:0.5:0.025:0.025:1.5 (in mmol), in refluxing *o*-xylene (4 mL) under N_2. ArOH = 3,4,5-$(MeO)_3C_6H_2OH$. [b] GC yield based on the amount of **2** used. Value in parentheses is GC yield. [c] Reaction with PhOH in place of ArOH. [d] KF (0.1 mmol) was added. [e] KF was added after 2 h and then stirred for 2 h.

the reaction of γ-arylated *tert*-propargyl alcohols with bis(trimethylsilyl)acetylene selectively proceeds via cleavage of the C(sp)−C(sp^3) and C(sp)−Si bonds to afford the corresponding 1-aryl-4-trimethylsilyl-(*E*)-enynes.[5] The reaction is one of the rare examples for alkyne−alkyne coupling leading to enynes through C−Si bond cleavage, while the desilylative coupling with aryl and vinyl halides has been well studied.[6] Thus, the enyne products can be readily converted to π-conjugated fluorescent dihydrofuran derivatives by desilylative Sonogashira coupling and base-promoted cyclization. In the course of our further study of alkyne coupling reactions, we have found that diarylacetylenes also undergo rhodium-catalyzed cross-addition with the bis(silyl)acetylene in a formal anti fashion via cleavage of the C−Si bond by adding phenol as activator. This is in marked contrast to the reaction with terminal silylacetylenes under similar conditions, where syn addition predominates.[3b,c] The present products can further couple with the same or a different diarylacetylene molecule to give rise to (*Z*,*Z*)-1,2,5,6-tetraaryl-1,5-hexadien-3-ynes that show relatively strong solid-state fluorescence.

In an initial attempt, diphenylacetylene (**1a**) (1 mmol) was treated with bis(trimethylsilyl)acetylene (**2**) (2 mmol) in the presence of $[Rh(OH)(cod)]_2$ (0.015 mmol, 3 mol % Rh), dppb (0.03 mmol), and phenol (3 mmol) as catalyst, ligand, and activator, respectively, in *o*-xylene at 130 °C for 2 h. The expected cross-addition product **3a** was formed in 67% yield with an *E*/*Z* ratio of 10:90 together with a small amount of dienyne **4a** (entry 1 in Table 1). The formation of phenoxytrimethylsilane as byproduct was also detected by GC−MS. The yield of **3a** and its *E*/*Z* ratio were improved up to 76% and 4:96 by using dCypb [$Cy_2P(CH_2)_4PCy_2$] as ligand in place of dppb (entry 2). Other bidentate ligands involving dppf and dppp were not superior to dCypb (entries 3 and 4). Reducing the amount of **2a** to 1.2 mmol little affected the reaction (entry 5), while the reaction with a reduced amount of phenol was sluggish (entry 6). It was also confirmed that the reaction did not take place in the absence of phenol or with use of water in place of phenol (entries 7 and 8). Related

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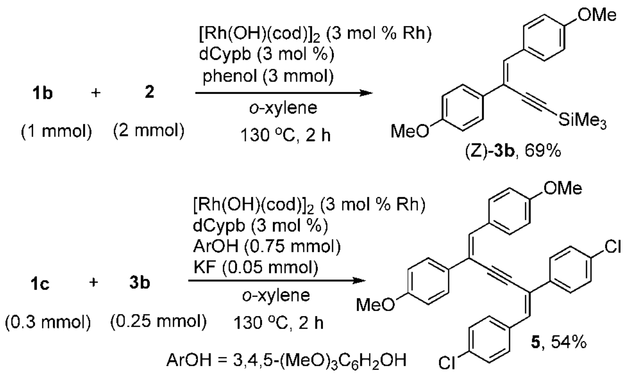
(5) Horita, A.; Tsurugi, H.; Funayama, A.; Satoh, T.; Miura, M. *Org. Lett.* **2007**, *9*, 2231.

(6) (a) Hiyama, T.; Shirakawa, E. *Top. Curr. Chem.* **2002**, *219*, 61. (b) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, U. K., 2004, pp 201–229.

metal complexes, $[Rh(Cl)(cod)]_2$ and $[Ir(OH)(cod)]_2$, as catalysts were not effective for this reaction (entries 9 and 10).

We next examined the selective synthesis of the 2:1-coupled dienyne **4a**. The reaction of **1a** (1.2 mmol) with **2** (0.5 mmol) using $[Rh(OH)(cod)]_2$ and dCypb in refluxing *o*-xylene for 24 h afforded **4a** in 58% isolated yield (entry 1 in Table 2) It is noted that **4a** had exclusively *Z*,*Z*-configuration. The use of an electron-rich phenolic compound, 3,4,5-$(MeO)_3C_6H_2OH$, in place of phenol itself was found to more effectively promote the reaction (entry 2). The use of KF (20 mol %) together with 3,4,5-$(MeO)_3$-C_6H_2OH further accelerated the reaction, and it was completed within 6 h to give **4a** in 69% yield (entry 3). Bis(4-methoxyphenyl)acetylene (**1b**) and bis(2-thienyl)acetylene (**1d**) were also reacted with **2** to give the corresponding dienynes **4b** and **4d** with good yields (entries 4 and 7). Addition of KF, after the first 1:1 coupling was completed by heating for 2 h, was found to effectively promote the second reaction (entries 5 and 8). In contrast, the reaction of bis(4-chlorophenyl)acetylene (**1c**) was sluggish even using KF. As depicted in Scheme 1, however, the sequential reactions of **1b** with **2** and the product (*Z*)-**3b** with **1c** gave crossed-dieneyne **5** with a good yield.

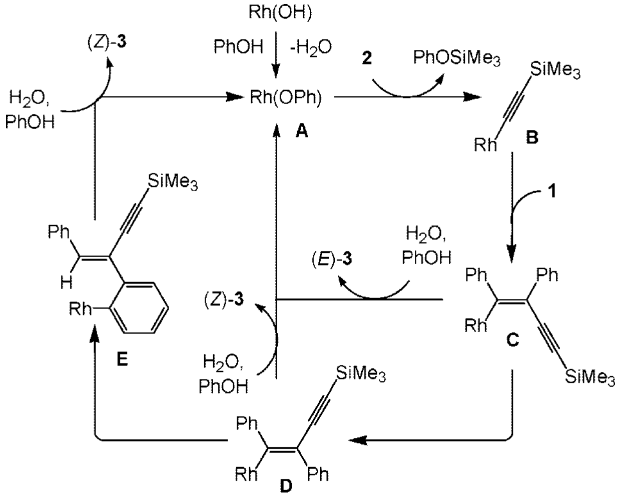
Scheme 1



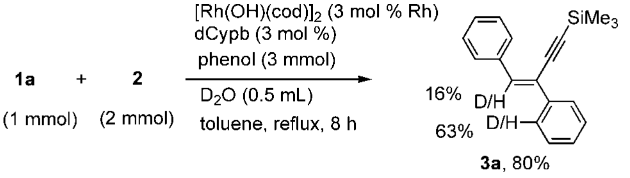
The dienynes **4** and **5** that consist of a π-conjugated six-carbon scaffold may exhibit fluorescent properties.[7] Interestingly, **4a**−**c** and **5** were found to show relatively strong fluorescence in their solid state in a range of 458−506 nm, and are relatively more luminous than or comparable to tris(8-hydroxyquinolino)aluminum (Alq_3), which is a typical green emitter, by a factor range of 3.7−1: **4a** 2.2 (458 nm), **4b** 3.7 (466 nm), **4c** 1.2 (491 nm), **5** 1.0 (506 nm) (see also Figure S1 in the Supporting Information). The fluorescent efficiency of **4b** is especially remarkable. However, they showed only weak fluorescence in solution.

A plausible mechanism for the formation of enyne **3** is illustrated in Scheme 2, in which neutral ligands are omitted. At the initial stage, the reaction of phenol with a hydroxyrhodium(I) species gives phenoxyrhodium **A** and the transmetalation between **A** and **2** with liberation of phenoxytrimethylsilane gives silylalkynylrhodium **B**.[8] The successive insertion of **1** to the rhodium−carbon bond affords vinylrhodium **C**. (*Z*)-Enyne **3** is formed by protonolysis after the geometrical isomerization of **C** to **D**, probably via a zwitterionic form.[9] It should be noted that the reaction of **1a** with **2** in the presence of D_2O was found to give **3a** deuterated at the ortho position of the 2-phenyl group (63%) as well as the expected 1-vinyl position (16%) (Scheme 3).

Scheme 2



Scheme 3



This suggests that arylrhodium **E** that is formed by the 1,4-migration of rhodium from the vinyl position to the ortho position participates in the termination step.[10] The deuterium distribution indicates that the termination takes place mainly in **E** rather than **D**, which may enhance the anti selectivity. It is also worth noting that in our previous work the rhodium-catalyzed reaction of **1a** with *tert*-butyldimethylsilylacetylene was observed to occur selectively in a syn manner, where the termination by protonolysis with acetylenic hydrogen is

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(7) Only an isomer of 1,2,5,6-tetraphenyl-1,5-hexadien-3-yne is known. It seems to be the same with **4a**. Israelshvilli, S.; Edlitz-Pfeffermann, J. *J. Am. Chem. Soc.* **1952**, *74*, 5780.

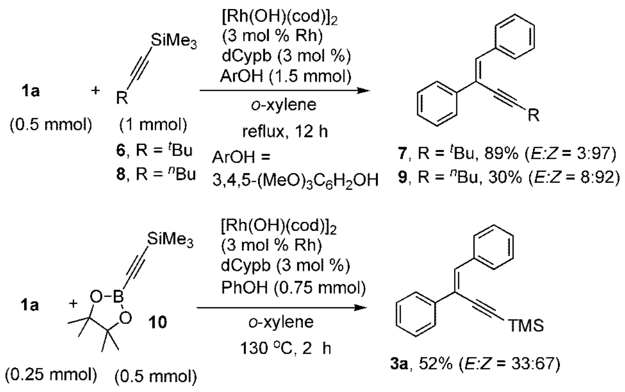
(8) (a) Fangou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169. (b) Müller, J.; Tschampel, M.; Pickardt, J. J. *Organomet. Chem.* **1988**, *355*, 513. (c) Yamane, M.; Uera, K.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 477.

(9) (a) Ojima, I.; Clos, N.; Donovan, R. J.; Ingallina, P. *Organometallics* **1990**, *9*, 3127. (b) Jun, C. H.; Crabtree, R. H. *J. Organomet. Chem.* **1993**, *447*, 177.

(10) (a) Oguma, K.; Miura, M.; Satoh, T.; Nomura, M. *J. Am. Chem. Soc.* **2000**, *122*, 10464. (b) Hayashi, T.; Inoue, K.; Taniguchi, N.; Ogasawara, M. *J. Am. Chem. Soc.* **2001**, *123*, 9918.

relatively fast. Thus, participation of desilylated monosilylacetylene in the present reaction is considered to be, if any, only little. The electron-rich phenol in combination with KF seems to effectively enhance the reaction step of **3** with the corresponding aryloxyrhodium **A** in the second coupling.

Scheme 4



The formation of **4** and **5** indicates that other internal silylacetylenes may react under the present conditions. It was found that 3,3-dimethyl-1-trimethylsilyl-1-butyne (**6**) efficiently couples with **1a** to afford enyne **7** in 89% yield with an *E/Z* ratio of 3:97. The reaction of 1-trimethylsilyl-1-hexyne (**8**) also gave the expected enyne **9**, albeit the yield was low. 1-Phenyl-2-trimethylsilylacetylene was far less reactive and only a small amount of the coupled product (less than 5%) was detected by GC−MS. These results suggest that relatively bulky and electron-rich silylacetylenes are suitable for the present reaction. The reaction of 4-octyne as acetylene acceptor, however, did not take place. We also examined the coupling of boryl(silyl)acetylene **10** with **1a**. In this case, **3a** was obtained as the single major product. This is attributable to higher reactivity of the boryl function.[4b]

In summary, we have developed a rhodium-catalyzed stereoselective cross-addition of bis(trimethylsilyl)acetylene to diarylacetylenes to selectively produce the corresponding (*Z*)-enynes. This represents a rare example of alkyne-alkyne coupling via C(sp)−Si bond cleavage. The absence of terminal acetylene hydrogen is a crucial factor for the high *Z*-selectivity. This reaction also enables us to construct a stereodefined and highly fluorescent π-conjugated dienyne system.

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Supporting Information Available: Standard experimental procedure and characterization data for new compounds. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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