Synthesis of Siloles via Rhodium-Catalyzed Cyclization of Alkynes and Diynes with Hexamethyldisilane

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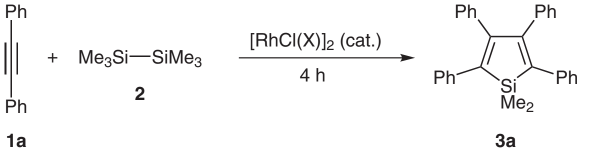
Abstract: A rhodium-catalyzed silylative cyclization of alkynes and 1,6-diynes with hexamethyldisilane is described. These reactions enable the synthesis of densely substituted silole derivatives through the use of a rhodium(I)–norborna-2,5-diene complex as a catalyst.

Key words: alkynes, cyclization, diynes, rhodium, siloles

Heteroles and metalloles belong to a class of compounds that have unique photophysical and electronic properties because of the delocalization of their π-electrons.[1] Among them, siloles have received much attention because of their low-lying LUMO.[2] A series of catalytic reactions that can be used to synthesize silole skeletons have been reported recently.[3–5] Herein, we report a silole-forming reaction catalyzed by a rhodium(I) complex in which alkynes and a disilane are used. 1,6-Diynes can be converted to fused bicyclic siloles through similar reactions.

Bis-silylation reactions of alkynes are generally catalyzed by group 10 metal complexes.[6] Recent reports on the successful use of silylrhodium(I) species in catalytic addition[7] and substitution reactions[8] prompted us to investigate the bis-silylation of alkynes catalyzed by rhodium(I) complexes. In an attempt to carry out the addition of silylrhodium(I) to alkynes, diphenylacetylene (**1a**) and hexamethyldisilane (**2**, 3 equiv to **1a**) were reacted in THF in the presence of 5 mol% of $[RhCl(nbd)]_2$ (10 mol% Rh, nbd = norborna-2,5-diene) at 50 °C. However, instead of the expected bis-silylation product, 1,1-dimethyl-2,3,4,5-tetraphenylsilole (**3a**) was formed in 62% GC yield (Table 1, entry 1). Unlike the corresponding nickel-catalyzed silole-forming reaction, which utilizes *sym*-tetramethyldisilane as the silicon source,[5a] this rhodium-catalyzed 2:1 coupling of **1a** and **2** involves the cleavage of not only the Si–Si bond but also the Si–C bond of **2**. A rhodium(I) complex ligated by cycloocta-1,5-diene (COD) exhibited almost no catalytic activity, indicating that the nature of bidentate diene ligands plays a prominent role in the outcome of the reaction (entry 2). The yield of **3a** improved to 76% when 30 mol% of NBD was added as an additive (entry 3). A slight decrease in yield was observed when the reaction was carried out using one equivalent of **2** (entry 4). Reduction of catalyst loading (4 mol% Rh) resulted in the formation of **3a** in 39% yield (entry 5). The reaction proceeded even at room temperature; however, it had lower efficiency (entry 6). Solvents also play an important role in the formation of siloles. THF was the preferred solvent in this case. The use of other solvents such as 1,1,2-trichloroethane (TCE), toluene, and ethanol provided **3a** in 69%, 48%, and 35% yields, respectively (entries 7–9).

Table 1 Optimization of Reaction Conditions[a]



Entry	Equiv of **2**	Catalyst (X, mol%)	NBD (mol%)	Conditions	Yield[b]
1	3	nbd, 5	–	THF, 50 °C	62%
2	3	cod, 5	–	THF, 50 °C	trace
3	3	nbd, 5	30	THF, 50 °C	76%
4	1	nbd, 5	30	THF, 50 °C	53%
5	3	nbd, 2	10	THF, 50 °C	39%
6	3	nbd, 5	30	THF, r.t.	35%
7	3	nbd, 5	30	TCE, 50 °C	69%
8	3	nbd, 5	30	toluene, 50 °C	48%
9	3	nbd, 5	30	EtOH, 50 °C	35%

[a] All reactions were carried out at a concentration of 0.25 M of **1a** in solvent.
[b] Determined by GC analysis with dodecane as an internal standard.

A possible mechanism for the formation of silole **3a** is shown in Scheme 1. First, a rhodium(I) complex reacts with disilane **2** to generate silylrhodium(I) species **A**. Then, the silylrhodation of alkyne **1a** occurs stereoselectively to generate β-silylalkenylrhodium(I) **B**, which undergoes further addition across **1a** to form δ-silyldienylrhodium(I) **C**. Subsequent intramolecular cyclization accompanying the demethylation of the trimethylsilyl group furnishes silole **3a** and methylrhodium(I) **D**. Finally, silylrhodium(I) **A** is regenerated via a reaction with **2** to complete the catalytic cycle; however, the detailed mechanism of the final step (**D** → **A**) is currently unclear.[9] It is probable that the cleavage process of the sil-

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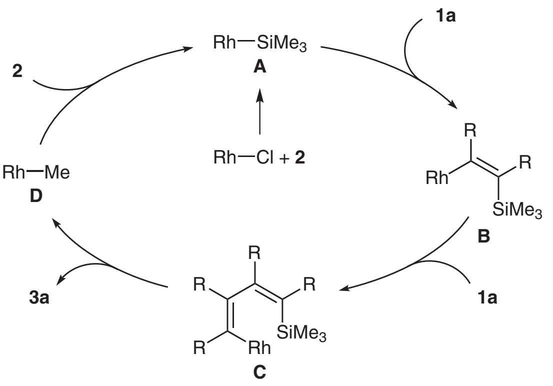
icon–methyl bond (**C** → **D**) is mechanistically related to that observed in the rhodium-catalyzed coupling of 2-silylphenylboronic acids with alkynes.[4c,10] The GC–MS analysis of the reaction mixture revealed the presence of a small quantity of 1,2,3,4-tetraphenylpenta-1,3-diene, which was derived from the successive insertion of **1a** into the Rh–Me bond of **D** and the subsequent protonation of the resulting dienylrhodium(I) with an adventitious proton source.

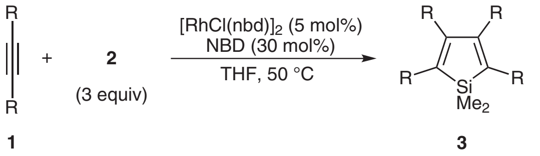


Scheme 1 Proposed mechanism for silole formation

Rate constants for the reaction of alkyne **1a** and disilane **2** were measured by GC using dodecane as an internal standard with the concentration of **2** varying from 0.25 M to 1.50 M. A plot of the initial reaction rate ($\Delta[\mathbf{3a}]/\Delta t$) versus the initial [**2**] was linear ($y = 0.0374x + 0.00858$, $R^2 = 0.9917$), indicating a first-order dependence on the concentration of disilane **2**. This result suggests that the final step (**D** → **A**) may be the turnover-limiting.

With the optimized conditions in hand, the scope of the reaction with various alkynes was investigated. The results obtained when the reaction was carried out using symmetrical internal alkynes **1a**–**e** are summarized in Table 2. Unfortunately, we experienced difficulties while carrying out the chromatographic purification of the products; these difficulties could presumably be ascribed to the byproducts resulting from the oligomerization of alkynes. For the reaction of diphenylacetylene (**1a**), preparative thin-layer chromatography on silica gel was conducted, and this was followed by washing with ethanol to afford analytically pure silole **3a** in 35% isolated yield (entry 1). 4-Tolyl and 3,5-xylyl derivatives (**1b** and **1c**) afforded tetraarylsiloles (**3b** and **3c**) in 38% and 34% yields, respectively (entries 2 and 3). Diphenylacetylenes **1d** and **1e**, which possess electron-donating methoxy and electron-withdrawing trifluoromethyl groups, respectively, also reacted as desired (entries 4 and 5). However, attempts to use aliphatic alkynes such as oct-4-yne and 1,4-bis(benzyloxy)but-2-yne proved to be unsuccessful.

Table 2 Rhodium-Catalyzed Cyclization of Alkynes **1a**–**e** with **2**[a]

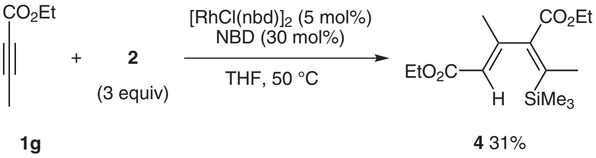


Entry	**1** (R)	Time	**3**	Yield[b]
1	**1a** (Ph)	4 h	**3a**	35%
2	**1b** ($4\text{-MeC}_6\text{H}_4$)	4 h	**3b**	38%
3	**1c** ($3,5\text{-Me}_2\text{C}_6\text{H}_3$)	4 h	**3c**	34%
4	**1d** ($4\text{-MeOC}_6\text{H}_4$)	24 h	**3d**	34%
5	**1e** ($4\text{-F}_3\text{CC}_6\text{H}_4$)	6 h	**3e**	26%

[a] Reaction conditions: alkyne **1**, **2** (3 equiv), $[\text{RhCl(nbd)}]_2$ (5 mol%, 10 mol% Rh), and NBD (30 mol%) were heated in THF (0.25 M) at 50 °C.

[b] Isolated yield after washing with EtOH.

Silole-forming reactions with unsymmetrical alkynes were then examined. The reaction involving 1-phenyl-1-propyne provided an inseparable mixture of products in which three possible isomers were found. When ethyl 2-butynoate (**1f**) was used as the substrate, the corresponding silole was not formed; instead, silyldiene **4** was obtained as the only identifiable product (Scheme 2). The linear diene was produced as a result of the protonation of the δ-silyldienylrhodium(I) intermediate. The reaction involving the use of phenylacetylene failed to give the product.

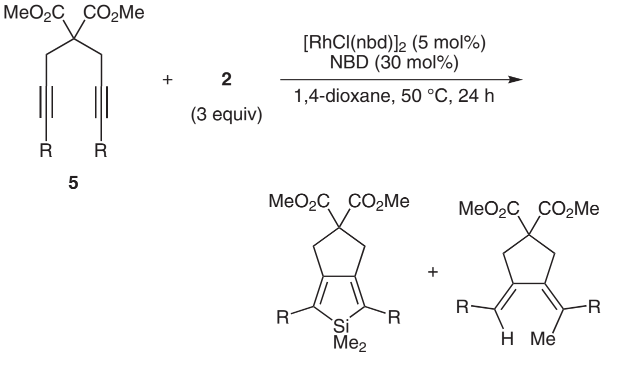


Scheme 2

Next, 1,6-diynes were subjected to the rhodium-catalyzed silole-forming reaction (Table 3). The best results were obtained in 1,4-dioxane, and not in THF, under otherwise identical conditions. Dimethyl 2,2-bis(3-phenylprop-2-ynyl)malonate (**5a**) underwent silole-forming cyclization with disilane **2** to give bicyclic silole derivative **6a** (entry 1).[11] The preparative thin-layer chromatography of the crude reaction mixture afforded **6a** in 65% yield with a small amount (3%) of a by-product. An analysis of the ^{1}H NMR spectra revealed that the by-product was exocyclic diene **7a** that was formed via the cyclization of **5a** with the methylrhodium(I) species instead of silylrhodium(I) (vide supra). After recrystallization from ethanol, analytically pure silole **6a** was isolated in 49% yield (entry 1). The reaction of diyne **5b** (R = $4\text{-MeC}_6\text{H}_4$) with **2** gave silole **6b** and diene **7b** in 66% combined yield (**6b**/**7b** = 82:18) by preparative thin-layer chromatography, and the pure product **6b** was isolated in 48% yield by recrystallization (entry 2). Alkyl-substituted siloles **6c** and **6d** were obtained in poor yields owing to their higher solubility in ethanol (entries 3 and 4). Sterically demanding *o*-tolyl and 1-naphthyl derivatives **5e** and **5f** were good substrates for the reaction, and they furnished the corresponding siloles

6e and **6f** in 52% and 60% isolated yields, respectively, without any noticeable formation of **7** (entries 5 and 6). Although siloles **6g** and **6h**, which have methoxy and bromo groups on the phenyl groups, were obtained in 42% and 46% yields, respectively (entries 7 and 8), the reaction was less efficient when conducted with 4-acetylphenyl derivative **5i**, which gave a mixture of silole **6i** and diene **7i** in favor of **7i** (**6i**/**7i** = 45:55 by ^{1}H NMR; entry 9). No silole formation was observed with 2-pyridyl- and 2-thienyl-substituted diynes.

Table 3 Rhodium-Catalyzed Cyclization of Diynes **5a–i** with **2**[a]



Entry	**5** (R)	Yield[b] (**6** + **7**), ratio[c] (**6**/**7**)	**6** (Yield[d])
1	**5a** (Ph)	65%, 97:3	**6a** (49%)
2	**5b** (4-MeC$_6$H$_4$)	66%, 82:18	**6b** (48%)
3	**5c** (4-*t*-BuC$_6$H$_4$)	55%, 87:13	**6c** (30%)
4	**5d** (3,5-Me$_2$C$_6$H$_3$)	–, –	**6d** (29%)
5	**5e** (2-MeC$_6$H$_4$)	–, >99:<1	**6e** (52%)
6	**5f** (1-naphthyl)	–, –	**6f** (60%)
7	**5g** (4-MeOC$_6$H$_4$)	–, –	**6g** (42%)
8	**5h** (4-BrC$_6$H$_4$)	49%, 94:6	**6h** (46%)
9	**5i** (4-AcC$_6$H$_4$)	33%, 45:55	**6i** (–[e])

[a] Reaction conditions: 1,6-diyne **5**, **2** (3 equiv), $[\mathrm{RhCl(nbd)}]_2$ (5 mol%, 10 mol% Rh), and NBD (30 mol%) were heated in 1,4-dioxane (0.1 M) at 50 °C for 24 h.

[b] Combined yield of **6** and **7** after preparative thin-layer chromatography.

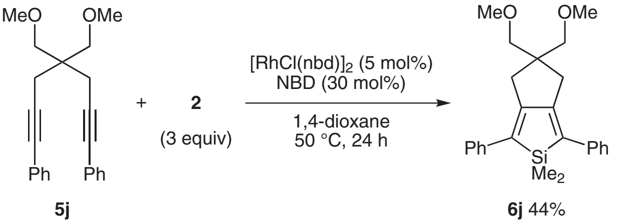
[c] Determined by ^{1}H NMR.

[d] Isolated yield by recrystallization.

[e] Not isolated as a pure compound.

Diyne **5j** tethered by a C(CH$_2$OMe)$_2$ group reacted similarly with **2** to give silole **6j** in 44% isolated yield by recrystallization (66% yield after thin-layer chromatography, **6j**/**7j** = 84:16; Scheme 3). On the other hand, the reaction of 1,6-diynes that were tethered by CH$_2$, O, and NTs groups was sluggish.[12]

In summary, we have developed a silole-forming cyclization reaction of alkynes and 1,6-diynes with hexamethyldisilane catalyzed by $[\mathrm{RhCl(nbd)}]_2$. This cyclization reaction affords various fully substituted siloles from readily available starting materials under mild conditions.



Scheme 3

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

References and Notes

(1) (a) Dubac, J.; Laporterie, A.; Manuel, G. *Chem. Rev.* **1990**, *90*, 215. (b) Hissler, M.; Dyer, P. W.; Réau, R. *Coord. Chem. Rev.* **2003**, *244*, 1. (c) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, *34*, 2.

(2) (a) Yamaguchi, S.; Tamao, K. *J. Chem. Soc., Dalton Trans.* **1998**, 3693. (b) Chen, J.; Cao, Y. *Macromol. Rapid Commun.* **2007**, *28*, 1714. (c) Zhan, X.; Barlow, S.; Marder, S. R. *Chem. Commun.* **2009**, 1948. (d) Liu, J.; Lam, J. W. Y.; Tang, B. Z. *J. Inorg. Organomet. Polym.* **2009**, *19*, 249.

(3) (a) Matsuda, T.; Kadowaki, S.; Goya, T.; Murakami, M. *Org. Lett.* **2007**, *9*, 133. (b) Matsuda, T.; Kadowaki, S.; Murakami, M. *Chem. Commun.* **2007**, 2627. (c) Matsuda, T.; Kadowaki, S.; Yamaguchi, Y.; Murakami, M. *Chem. Commun.* **2008**, 2744. (d) Matsuda, T.; Yamaguchi, Y.; Murakami, M. *Synlett* **2008**, 561. (e) Matsuda, T.; Yamaguchi, Y.; Murakami, M. *Synlett* **2010**, 2743.

(4) (a) Ohmura, T.; Masuda, K.; Suginome, M. *J. Am. Chem. Soc.* **2008**, *130*, 1526. (b) Shimizu, M.; Mochida, K.; Hiyama, T. *Angew. Chem. Int. Ed.* **2008**, *47*, 9760. (c) Tobisu, M.; Onoe, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2009**, *131*, 7506. (d) Ureshino, T.; Yoshida, T.; Kuninobu, Y.; Takai, K. *J. Am. Chem. Soc.* **2010**, *132*, 14324.

(5) For earlier studies on catalytic construction of silole skeletons, see: (a) Okinoshima, H.; Yamamoto, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, *94*, 9263. (b) Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3879. (c) Seyferth, D.; Vick, S. C.; Shannon, M. L.; Lim, T. F. O.; Duncan, D. P. *J. Organomet. Chem.* **1977**, *135*, C37. (d) Schäfer, A.; Weidenbruch, M.; Pohl, S. *J. Organomet. Chem.* **1985**, *282*, 305. (e) Ikenaga, K.; Hiramatsu, K.; Nasaka, N.; Matsumoto, S. *J. Org. Chem.* **1993**, *58*, 5045. (f) Ojima, I.; Fracchiolla, D. A.; Donovan, R. J.; Banerji, P. *J. Org. Chem.* **1994**, *59*, 7594. (g) Palmer, W. S.; Woerpel, K. A. *Organometallics* **1997**, *16*, 1097.

(6) For reviews, see: (a) Han, L.-B.; Tanaka, M. *Chem. Commun.* **1999**, 395. (b) Beletskaya, I.; Moberg, C. *Chem. Rev.* **2006**, *106*, 2320. (c) Suginome, M.; Matsuda, T.; Ohmura, T.; Seki, A.; Murakami, M. In *Comprehensive Organometallic Chemistry III*, Vol. 10; Crabtree, R.; Mingos, M.; Ojima, I., Eds.; Elsevier: Oxford, **2007**, 725.

(7) (a) Walter, C.; Auer, G.; Oestreich, M. *Angew. Chem. Int. Ed.* **2006**, *45*, 5675. (b) Nakao, Y.; Chen, J.; Imanaka, H.; Hiyama, T.; Ichikawa, Y.; Duan, W.-L.; Shintani, R.; Hayashi, T. *J. Am. Chem. Soc.* **2007**, *129*, 9137. (c) Walter, C.; Fröhlich, R.; Oestreich, M. *Tetrahedron* **2009**, *65*, 5513.

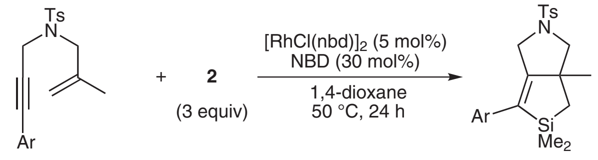
(8) (a) Tobisu, M.; Kita, Y.; Chatani, N. *J. Am. Chem. Soc.* **2006**, *128*, 8152. (b) Tobisu, M.; Ano, Y.; Chatani, N. *Chem. Asian J.* **2008**, *3*, 1585. (c) Tobisu, M.; Kita, Y.; Ano, Y.; Chatani, N. *J. Am. Chem. Soc.* **2008**, *130*, 15982. (d) Kita, Y.; Tobisu, M.; Chatani, N. *Org. Lett.* **2010**, *12*, 1864.

(9) The attempted detection of tetramethylsilane formation was unsuccessful when the reaction was performed in C_6D_6 at 30 °C in a sealed NMR tube.

(10) For Si–Me bond cleavage observed in palladium-catalyzed reactions, see: (a) Rauf, W.; Brown, J. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 4228. (b) Nakao, Y.; Takeda, M.; Matsumoto, T.; Hiyama, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 4447.

(11) The reaction of a diyne with *t*-BuMe$_2$SiH catalyzed by a rhodium(I) complex under an ambient pressure of carbon monoxide reportedly gave a silole via a mechanism involving a Si–Me bond cleavage. See ref. 5f.

(12) When 1,6-enyne **8** was employed as the substrate, analogous silylative cyclization occurred to afford bicyclic dihydrosilole **9** in 44% isolated yield (Scheme 4).



8 (Ar = 4-MeC$_6$H$_4$)

9 44%

Scheme 4