ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2015, **51**, 11378

Received 20th May 2015,
Accepted 4th June 2015

DOI: 10.1039/c5cc04172d

www.rsc.org/chemcomm

Rhodium-catalyzed intramolecular alkynylsilylation of alkynes†

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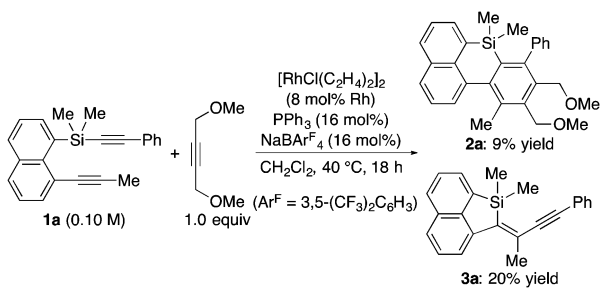
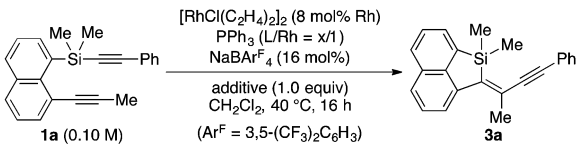
Rhodium-catalyzed intramolecular alkynylsilylation of alkynes is described. The reaction proceeds through *syn*-insertion by a cationic rhodium/triarylphosphine catalyst, representing the first alkynylsilylation of alkynes *via* the cleavage of a C(sp)–Si bond by transition-metal catalysis. A highly enantioselective variant is also described for the creation of a silicon stereogenic center.

Stereoselective insertion of alkynes into carbon–silicon bonds represents a powerful and efficient approach for the synthesis of highly substituted alkenylsilanes. Most of the reported examples employ either strained organosilicon substrates[1] or (Lewis) acid catalysts/additives[2] to promote the reaction to achieve alkyl-,[1a–f] allyl-,[1g–i,2b–e,3] alkenyl-,[1g–j,2f–i,4] aryl-,[1b,k,2h,i] and propargyl/allenylsilylation[2j] of alkynes. More reactive acylsilanes[5] and trimethylsilylcyanide[6] are also known to undergo insertion of alkynes to give 2-acyl- and 2-cyanoalkenylsilanes, respectively. In contrast, virtually no progress has been made for alkyne insertion into alkynylsilanes. In fact, there has been only one report where they described a formal insertion reaction through conjugate addition of 2-silylynamides to acetylenedicarboxylates followed by silyl migration.[7,8] In this communication, we describe the development of rhodium-catalyzed intramolecular alkynylsilylation of alkynes through the cleavage of a C(sp)–Si bond under mild conditions, including a highly enantioselective variant for the construction of a silicon stereogenic center.[9]

During the course of our study directed toward the development of synthetic methods for various silicon-bridged π-conjugated compounds,[10] we attempted to synthesize benzonaphthosiline **2a** from silicon-containing diyne **1a** and 1,4-dimethoxy-2-butyne through a rhodium-catalyzed [2+2+2] cycloaddition reaction.[11] As shown in eqn (1), under the conditions of using a cationic Rh/2PPh$_3$ catalyst generated *in situ*, only 9% yield of the desired product **2a** was obtained and the major product turned out to be an intramolecular alkynylsilylation product **3a** in 20% yield. On the basis of this unexpected result, we decided to focus on the improvement of this alkynylsilylation reaction by rhodium catalysis. To our surprise, however, simple removal of 1,4-dimethoxy-2-butyne from the reaction in eqn (1) did not provide **3a** at all (eqn (2)). We hypothesized that this seemingly inconsistent result might indicate that the coordination of 1,4-dimethoxy-2-butyne to rhodium had a beneficial effect on promoting the alkynylsilylation of **1a**. We then tried to search for an innocent replacement and found that the use of MeCN as an additive gave product **3a** in 51% yield, and a higher yield of 82% was achieved by changing the ratio of Rh/PPh$_3$ from 1/2 to 1/1.[12]



(1)



(2)

x	additive	conv (%)	yield (%)
2	none	52	0
2	MeCN	66	51
1	MeCN	100	82

Under these conditions, several different alkynyl groups on the silicon atom of **1** are tolerated in the present intramolecular alkynylsilylation reaction to give the corresponding **3** in high yields,

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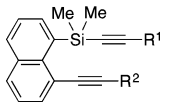
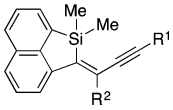
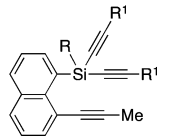
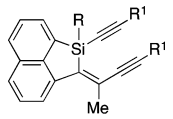
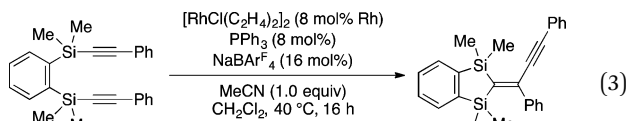
† Electronic supplementary information (ESI) available: Detailed experimental procedures. CCDC 1401151. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc04172d

Table 1 Rhodium-catalyzed alkynylsilylation: scope[a]

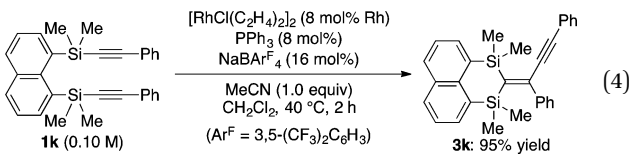
Entry	Substrate	Product	Yield[b] (%)
			
1	**1a** (R^1 = Ph, R^2 = Me)	**3a**	82
2[c]	**1b** (R^1 = 4-MeOC$_6$H$_4$, R^2 = Me)	**3b**	90[d]
3[e]	**1c** (R^1 = 4-ClC$_6$H$_4$, R^2 = Me)	**3c**	93
4[f]	**1d** (R^1 = R^2 = Me)	**3d**	82
5[g]	**1e** (R^1 = Ph, R^2 = *n*-Pr)	**3e**	84
6[c,h]	**1f** (R^1 = R^2 = Ph)	**3f**	82[i]
			
7[g]	**1g** (R = Cy, R^1 = Ph)	**3g**	93
8[c,e]	**1h** (R = Cy, R^1 = Me)	**3h**	82
9[c,h]	**1i** (R = R^1 = Me)	**3i**	73

[a] Conditions: $[RhCl(C_2H_4)_2]_2$ (8 mol% Rh), PPh_3 (8 mol%), $NaBAr_4^F$ (16 mol%), MeCN (1.0 equiv.), CH_2Cl_2 (0.10 M), 40 °C, 16 h. [b] Isolated yield (*Z*-isomer was obtained exclusively unless otherwise noted). [c] The reaction was conducted at 0.05 M substrate concentration. [d] *Z*/*E* = 98/2. [e] The reaction time was 1 h. [f] The reaction was conducted at 80 °C in toluene. [g] The reaction time was 2 h. [h] The reaction was conducted with P(4-MeOC$_6$H$_4$)$_3$ instead of PPh_3. [i] *Z*/*E* = 94/6.

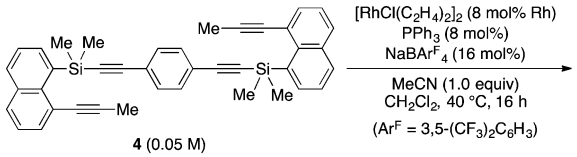
although an elevated temperature is necessary for the reaction of 1-propynyl substituted substrate **1d** (Table 1, entries 1–4). The structure of **3b** was confirmed by X-ray crystallographic analysis, establishing the *syn*-insertion of an alkyne into the alkynylsilane in the present catalysis.[13] With respect to the alkynyl substituent at the 8-position of the naphthalene tether, in addition to alkyl groups such as **1a** and **1e**, aryl groups such as **1f** can also be effectively employed by changing the ligand from PPh_3 to P(4-MeOC$_6$H$_4$)$_3$ (entries 1, 5 and 6). Substrates **1g–1i** having an alkylbis(alkynyl)silyl group at the 1-position are also suitable for the present alkynylsilylation to give **3g–3i** in 73–93% yield (entries 7–9). Furthermore, the reaction is applicable to substrates containing some other tethers as well. As shown in eqn (3) and (4), 1,2-bis(dimethyl(phenylethynyl)silyl)benzene (**1j**) and 1,8-bis(dimethyl(phenylethynyl)silyl)naphthalene (**1k**) similarly undergo intramolecular alkynylsilylation to give products **3j** and **3k** in high yields. The reaction also proceeds smoothly with substrate **4** having two alkynylsilane moieties through the two-fold alkynylsilylation process, giving a highly conjugated product **5** in 78% yield (eqn (5)).[14]

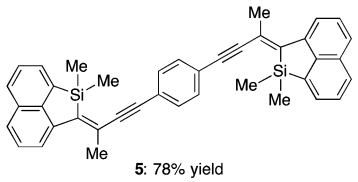


(3)



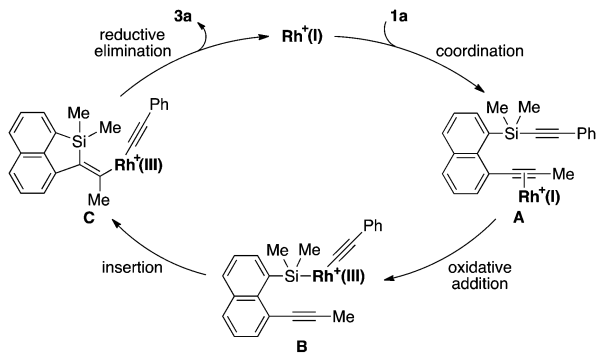
(4)



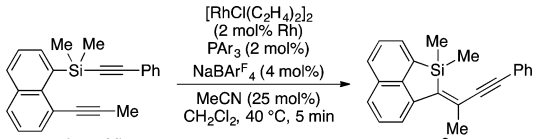


(5)

A proposed catalytic cycle for the reaction of **1a** to **3a** is illustrated in Scheme 1. Coordination of **1a** to cationic rhodium(I) in the form of **A** facilitates the oxidative addition of a C(sp)–Si bond to give intermediate **B**. Successive intramolecular insertion of alkyne into a Si–Rh bond provides alkenyl(alkynyl)rhodium(III) **C**, reductive elimination of which leads to the formation of product **3a** along with regeneration of the cationic rhodium(I) species. Although the role of MeCN is not yet completely understood, it probably stabilizes coordinatively unsaturated rhodium intermediates during the catalytic cycle. To gain some insights into the present catalysis, we conducted the following control experiments as shown in eqn (6) and (7). By changing the electronic properties of the triarylphosphine ligand in the reaction of **1a**, we determined that the reaction proceeds faster by using more electron-rich phosphine ligands (eqn (6)). We also found that electron-deficient alkynylsilanes tend to react faster by changing the *para*-substituent of the arylethynyl group on the silicon of **1** (eqn (7)). Both these results are consistent with the assumption

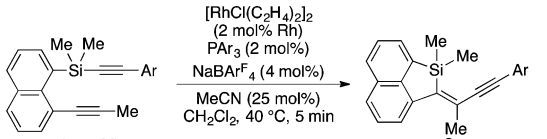


Scheme 1 Proposed catalytic cycle for the rhodium-catalyzed intramolecular alkynylsilylation of **1a**.



(6)

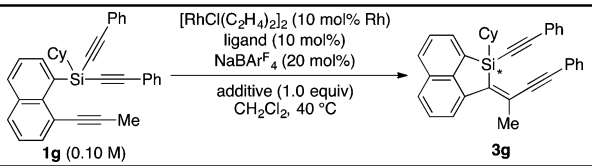
PAr_3	conv. of **1a** (%)	yield of **3a** (%)
P(4-FC$_6$H$_4$)$_3$	23	19
PPh_3	29	29
P(4-MeOC$_6$H$_4$)$_3$	63	61



(7)

Ar	conv. of **1** (%)	yield of **3** (%)
4-MeOC$_6$H$_4$	15	10
Ph	29	29
4-ClC$_6$H$_4$	35	35

Table 2 Rhodium-catalyzed asymmetric alkynylsilylation

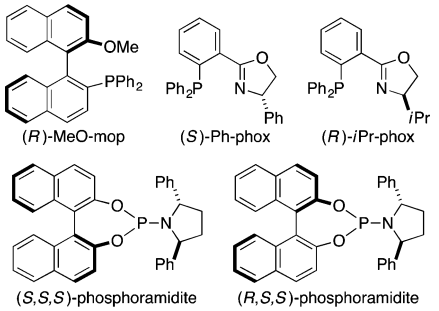


Entry	Ligand	Additive	Yield[a] (%)	ee[b] (%)
1	(*R*)-MeO-mop	MeCN	77	0
2	(*R*)-MeO-mop	None	23	83 (−)
3	(*S*)-Ph-phox	None	74	69 (+)
4	(*R*)-iPr-phox	None	27	42 (−)
5	(*S*,*S*,*S*)-Phosphoramidite	None	60	36 (+)
6	(*R*,*S*,*S*)-Phosphoramidite	None	53	92 (+)
7[c]	(*R*,*S*,*S*)-Phosphoramidite	None	62 (59)[d]	94 (+)

[a] Determined by ^{1}H NMR against an internal standard. [b] Determined by chiral HPLC on a Chiralcel OD-H column with hexane/2-propanol = 98/2. [c] The reaction was conducted at 0.03 M substrate concentration. [d] Isolated yield in parentheses.

that the oxidative addition is the turnover-limiting step in the catalytic cycle, although further evidence is necessary to fully establish the catalytic cycle.

Finally, we have also begun to develop an asymmetric variant of this process.[15] On the basis of the conditions for the nonasymmetric reactions, we conducted a reaction of prochiral **1g** by employing (*R*)-MeO-mop,[16] a chiral monophosphine ligand, in the presence of 1.0 equiv. of MeCN. Under these conditions, 77% yield of **3g** was obtained, but no asymmetric induction was observed at the silicon stereocenter (Table 2, entry 1). In comparison, 83% ee was achieved with the same ligand in the absence of MeCN, but the yield of **3g** became significantly lower (entry 2). To accommodate the nitrogen coordination to the structure of a chiral ligand, we examined (*S*)-Ph-phox,[17] a P,N-bidentate ligand, and found that **3g** was produced in 74% yield in the absence of MeCN with an appreciable ee of 69% (entry 3). Unfortunately, however, further improvement was unsuccessful by using other phosphinooxazoline ligands such as (*R*)-iPr-phox[17] (entry 4). As a different structural motif for the chiral ligand, we also employed phosphoramidite ligands.[18] For example, the use of (*S*,*S*,*S*)-phosphoramidite having a 2,5-diphenylpyrrolidine moiety[19] gave **3g** in 60% yield with 36% ee in the absence of MeCN (entry 5). We subsequently found that significantly higher enantioselectivity (92% ee) could be achieved by changing the ligand to its diastereomer ((*R*,*S*,*S*)-phosphoramidite)[19a,20] with a moderate yield of 53% (entry 6). Both the yield and the ee were slightly improved further by lowering the initial substrate concentration from 0.10 M to 0.03 M to give 62% yield (59% isolated yield) of **3g** with 94% ee (entry 7).



In summary, we have developed rhodium-catalyzed intramolecular alkynylsilylation of alkynes under mild conditions. The reaction proceeds through *syn*-insertion in the presence of a cationic rhodium/triarylphosphine catalyst with MeCN as an additive. Although applicable substrates are currently still limited, this represents the first alkynylsilylation of alkynes *via* the cleavage of a C(sp)–Si bond by transition-metal catalysis. We have also described our preliminary investigation of its asymmetric variant, creating a silicon stereogenic center with high enantioselectivity. Future studies will be directed toward the development of a more general catalyst system to expand the scope of alkynylsilylation of alkynes and related reactions.

Support has been provided in part by Challenging Exploratory Research, the Ministry of Education, Culture, Sports, Science and Technology, Japan. We thank Prof. Takuzo Aida and Dr Yoshimitsu Itoh at The University of Tokyo for the measurement of fluorescence spectra.

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