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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 substrates¹ or (Lewis) acid catalysts/additives² 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 acylsilanes⁵ and trimethylsilylcyanide⁶ 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 silvl 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/2PPh₃ 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 alkynyl-silylation 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/PPh₃ from 1/2 to 1/1.¹²





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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Table 1 Rhodium-catalyzed alkynylsilylation: scope^a



^{*a*} Conditions: [RhCl(C₂H₄)₂]₂ (8 mol% Rh), PPh₃ (8 mol%), NaBAr₄^{*F*} (16 mol%), MeCN (1.0 equiv.), CH₂Cl₂ (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. ^{*c*} 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-MeOC₆H₄)₃ instead of PPh₃. ^{*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, any groups such as 1f can also be effectively employed by changing the ligand from PPh₃ to $P(4-MeOC_6H_4)_3$ (entries 1, 5 and 6). Substrates 1g-1i having an alkylbis(alkynyl)silyl group at the 1-position are also suitable for the present alkynylsilvlation 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



A proposed catalytic cycle for the reaction of 1a to 3a is illustrated in Scheme 1. Coordination of 1a to cationic rhodium(1) 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(1) 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**.





^{*a*} Determined by ¹H 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-phox¹⁷ (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 moiety¹⁹ 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.

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