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Synthesis of 7*H*-Benzo[*e*]naphtho[1,8-*bc*]silines by Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition

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Synthesis of 7*H*-Benzo[*e*]naphtho[1,8-*bc*]silines by Rhodium-Catalyzed [2 + 2 + 2] Cycloaddition

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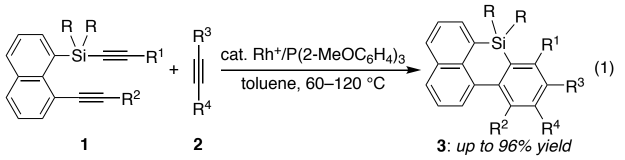
An efficient synthesis of 7*H*-benzo[*e*]naphtho[1,8-*bc*]silines has been developed by a rhodium-catalyzed [2 + 2 + 2] cycloaddition of alkynyl(8-alkynyl-1-naphthyl)silanes with internal alkynes. High chemoselectivity can be realized by employing $P(2\text{-}MeOC_6H_4)_3$ as the ligand for rhodium. Preliminary investigation of its asymmetric variant has also been described to create a silicon stereogenic center with relatively high enantioselectivity.

Keywords: Benzonaphthosilines, Rhodium catalyst, [2 + 2 + 2] Cycloaddition

5*H*-Dibenzo[*b*,*d*]siloles (dibenzosiloles) and related compounds belong to a class of silicon-bridged π-conjugated compounds that can be applied to various optoelectronic materials.[1] In addition to the conventional synthetic process based on the reaction of 2,2'-dimetalated biaryls with dichlorosilanes,[2] dibenzosiloles have been synthesized using a variety of methods including those under transition-metal catalysis.[3] In contrast, structurally related 7*H*-benzo[*e*]naphtho[1,8-*bc*]silines (benzonaphthosilines) possessing a 6-membered silacycle have been significantly less explored to date,[4] which is likely due to the lack of their efficient synthetic methods. In fact, only three isolated approaches were reported to date as far as we are aware: (1) dehydrogenative C–C coupling of methyl(1-naphthyl)(phenyl)silane by pyrolysis,[5] (2) oxidative Si–C coupling of 1-naphthyltriphenylsilane by a radical process,[6] (3) ruthenium-catalyzed cyclization of 5,5-dimethyl-10-(2-propyn-1-ylidene)-5,10-dihydrodibenzo[*b*,*e*]siline,[7] and all of them suffer from either low chemical yields or low chemo-selectivity. To provide a solution to this methodological deficiency, herein we describe the first efficient and selective synthesis of benzonaphthosilines **3** by a rhodium-catalyzed [2 + 2 + 2] cycloaddition of alkynyl(8-alkynyl-1-naphthyl)silanes **1** with internal alkynes **2** (eq 1),[8] including its enantioselective variant for the construction of a silicon stereogenic center.[9,10]



In 2015, we reported that compounds **1** undergo intramolecular alkynylsilylation of alkynes to give compounds **4** with a cationic Rh/PPh_3 catalyst in the presence of MeCN (eq 2), and replacement of MeCN with internal alkynes led to the formation of benzonaphthosilines **3** via [2 + 2 + 2] cycloaddition, albeit with low efficiency.[11] Based on this previous result, we initially examined a reaction of **1a** with diphenylacetylene (**2a**) as a model substrate combination toward the synthesis of benzonaphthosiline **3aa** (Table 1). The use of PPh_3 as the ligand in toluene at 100 °C did provide product **3aa**, but only in 13% yield even after full consumption of substrate **1a** (entry 1). In stark contrast, we subsequently found that 96% yield of **3aa** could be achieved by changing the ligand to $P(2\text{-}MeOC_6H_4)_3$ (entry 2).[12] It is worth mentioning that neither $P(2\text{-}MeC_6H_4)_3$ nor $P(4\text{-}MeOC_6H_4)_3$ could provide **3aa** with that high efficiency (entries 3 and 4). In addition, the use of binap, which is often used as an effective ligand for various rhodium-catalyzed [2 + 2 + 2] cycloaddition reactions,[8] gave no desired compound **3aa** in this case (entry 5).

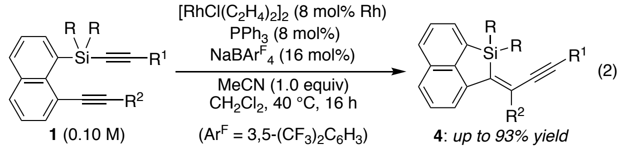
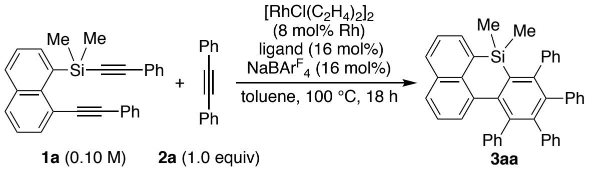


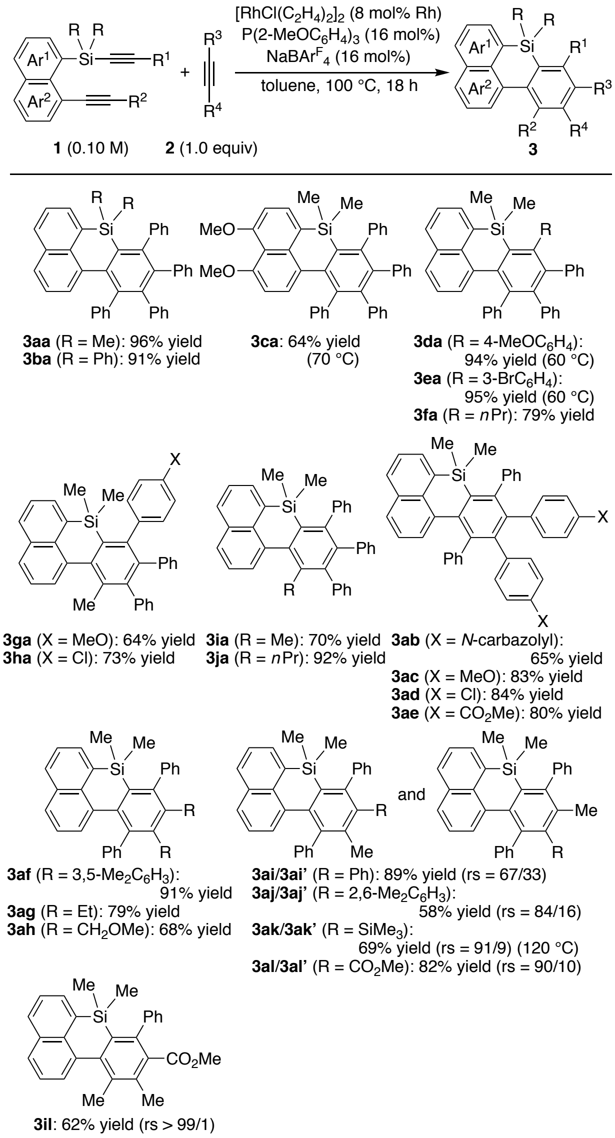
Table 1. Rhodium-catalyzed [2 + 2 + 2] cycloaddition of **1a** with **2a**: Ligand effect.[a]



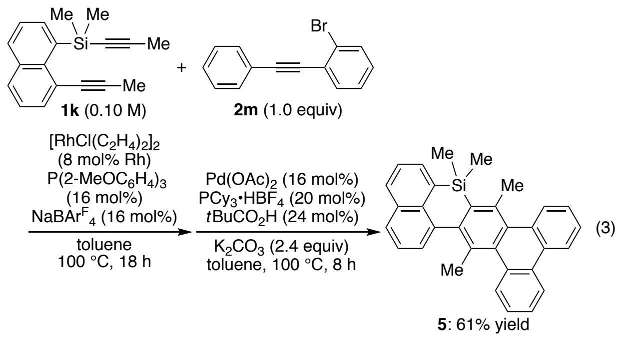
entry	ligand	yield (%)[b]
1	PPh_3	13
2	$P(2\text{-}MeOC_6H_4)_3$	96[c]
3	$P(2\text{-}MeC_6H_4)_3$	17
4	$P(4\text{-}MeOC_6H_4)_3$	30
5	binap[d]	0

[a]Compound **4a** was obtained in 3–11% yield as side product in all entries. [b]Determined by ^1H NMR against internal standard (dimethyl terephthalate). [c]Isolated yield. [d]8 mol% of ligand was used.

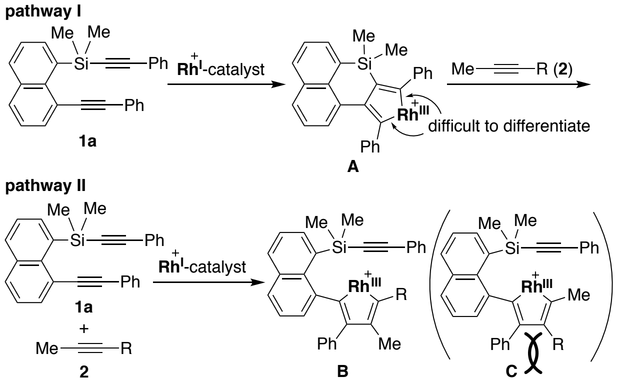
Under the conditions using $P(2\text{-}MeOC_6H_4)_3$ as the ligand, various benzonaphthosilines **3** can be synthesized in reasonably high yields (Scheme 1).[13] For example, in addition to compound **3aa** having a dimethylsilylene bridging unit, diphenylsilylene-bridged benzonaphthosiline **3ba** can be obtained in a similarly high yield (91% yield). Introduction of methoxy groups on naphthalene is also tolerated to give **3ca** (64% yield). With regard to the substituents on the alkynes of **1**, both R^1 and R^2 can be either aryl or alkyl groups as shown in the formation of **3da–3ja** (64–95% yield). The reaction partner **2** can also be changed from diphenylacetylene to various other diarylacetylenes as well as dialkylacetylenes to give corresponding products **3ab–3ah** with similar efficiency (65–91% yield). Unsymmetric alkyne **2i** (R^3 = Ph, R^4 = Me) gave product **3ai** as a regioisomeric mixture in the ratio of 67/33, but relatively high regioselectivity (84/16–91/9) could be achieved by using more biased unsymmetric alkynes such as **2j–2l** to give **3aj–3al**.[14] For the reaction of **1i** with **2l**, product **3il** was obtained in 62% with almost perfect regioselectivity.[14] It is worth noting that the reaction of **1k** with 1-bromo-2-(phenylethynyl)benzene (**2m**) followed by palladium-catalyzed intramolecular C–H arylation[15] leads to naphthotriphenylenosiline **5**, a new silicon-bridged π-conjugated compound, in a facile manner (eq 3).



Scheme 1. Rhodium-catalyzed [2 + 2 + 2] cycloaddition of **1** with **2**: Scope.

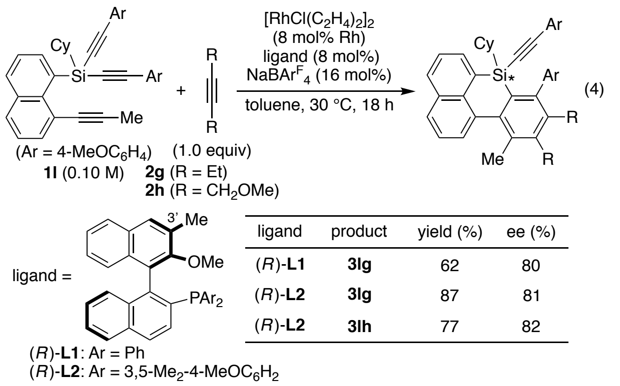


Although the origin of regioselectivity for unsymmetric alkynes is not entirely clear, it could be explained by considering the reaction pathways of the present [2 + 2 + 2] cycloaddition reaction of **1a** with alkyne **2** (Scheme 2). If the reaction proceeds through the formation of rhodacyclopentadiene **A** from **1a** and the rhodium catalyst via pathway I, differentiation of the two carbon–rhodium bonds for the subsequent insertion of alkyne **2** in a position- and regio-selective manner would be highly difficult. In contrast, the selective formation of rhodacyclopentadiene **B** over **C** from **1a**, **2**, and the rhodium catalyst through pathway II could account for the observed regioselectivity, and this selectivity would be reasonable based on the stereo- or electronic bias of the alkyne **2**.



Scheme 2. Possible reaction pathways I and II for the present rhodium-catalyzed [2 + 2 + 2] cycloaddition of **1a** with **2**.

We have also begun to develop an asymmetric variant of this process. On the basis of the ligand effect for the nonasymmetric reactions (Table 1) as well as our previous report on the asymmetric synthesis of related silicon-stereogenic dibenzosiloles,[10d,e] we conducted a reaction of prochiral **1l** with 3-hexyne (**2g**) by employing 3'-methylated (*R*)-MeO-mop ((*R*)-**L1**).[16] As shown in eq 4, the reaction proceeded at 30 °C to give silicon-stereogenic benzonaphthosiline **3lg** in 62% yield with 80% ee, and a slight improvement in the yield and ee was achieved (87% yield, 81% ee) by modification of the aryl groups on the phosphorus atom of the chiral ligand from phenyl to 3,5-dimethyl-4-methoxyphenyl ((*R*)-**L2**). Similarly, the reaction of **1l** with 1,4-dimethoxy-2-butyne (**2h**) under Rh/(*R*)-**L2** catalysis gave **3lh** in 77% yield with 82% ee.



ligand	product	yield (%)	ee (%)
(*R*)-**L1**	**3lg**	62	80
(*R*)-**L2**	**3lg**	87	81
(*R*)-**L2**	**3lh**	77	82

In summary, we have developed an efficient synthesis of benzonaphthosilines by a rhodium-catalyzed [2 + 2 + 2] cycloaddition of alkynyl(8-alkynyl-1-naphthyl)silanes with internal alkynes through the use of P(2-MeOC$_6$H$_4$)$_3$ as ligand for rhodium. We have also described our preliminary investigation of its asymmetric variant, creating a silicon stereogenic center with relatively high enantioselectivity. Future studies will be directed toward the development of functional organic molecules based on the present structural motifs.

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Supporting Information is available on http://dx.doi.org/10.1246/cl.******.

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13 See the Supporting Information for optical properties of selected compounds **3**.

14 CCDC 1976917−1976919 and 1980044 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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