

Rhodium-catalysed intramolecular *trans*-bis-silylation of alkynes to synthesise 3-silyl-1-benzosiloles†

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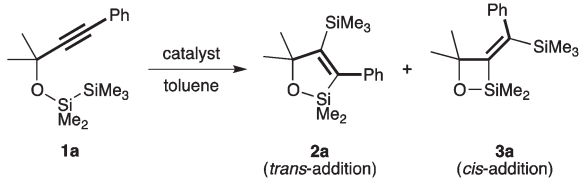
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Intramolecular addition of a Si–Si bond across a C–C triple bond occurs in a *trans* fashion in the presence of rhodium(i) catalysts. The *trans*-bis-silylation reaction of (2-alkynylphenyl)disilanes affords 3-silyl-1-benzosiloles.

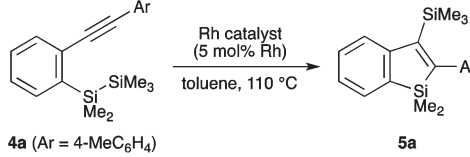
Addition of intermetallic σ -bonds (E–E'; E, E' = Si, B, Sn *etc.*) to alkynes provides a simple and efficient route for the preparation of stereodefined vicinally bismetallated alkenes, which are useful precursors to multisubstituted alkenes.¹ Usually, the 1,2-addition reaction is catalysed by group 10 metal complexes and proceeds *via* a mechanism consisting of oxidative addition, insertion and reductive elimination.^{2,3} As a result, *cis*-adducts form stereoselectively in most cases. A few transition metal catalysed bismetallation reactions afford *trans*-adducts as major products; however, these adducts usually result from *cis*–*trans* isomerisation processes independent of the catalytic addition process.⁴

Extensive studies on the catalytic synthesis of silole (silacyclopentadiene) derivatives have been conducted,⁵ because compounds possessing the silole skeleton exhibit unique properties owing to their low-lying LUMO.⁶ Recently, we reported that the intermolecular reaction of hexamethyldisilane with internal alkynes catalysed by a rhodium(i) complex produces silole derivatives.⁵ⁱ Subsequently, our attention was drawn to the intramolecular variant of this rhodium-catalysed reaction. Herein, we show the first example of a genuine *trans*-selective bis-silylation reaction of alkynes catalysed by rhodium(i) complexes. The reaction enables the synthesis of 3-silyl-1-benzosiloles from (2-alkynylphenyl)disilanes.

When the disilanyl ether of propargylic alcohol **1a** was treated with [RhCl(nbd)]₂ (2.5 mol%, 5 mol% Rh, nbd = norborna-2,5-diene), which is an effective catalyst for the intermolecular reaction of alkynes with disilanes, in toluene at 110 °C for 6 h, 4-silyl-2,5-dihydro-1,2-oxasilole **2a** was produced in 20% yield (Table 1, entry 1). The same reaction performed with RhCl(PPh₃)₃ also resulted in the selective formation of the five-

Table 1 Bis-silylation of disilanyl ether **1a**


Entry	Catalyst (mol%)	Conditions	2a ^a	3a ^a
1	[RhCl(nbd)] ₂ (2.5)	110 °C, 6 h	20%	—
2	RhCl(PPh ₃) ₃ (5)	110 °C, 4 h	20%	—
3	Pd(OAc) ₂ – <i>t</i> -OcNC ^b (2/33)	80 °C, 2.5 h	—	84%

^a Isolated yield. ^b 1,1,3,3-Tetramethylbutyl isocyanide.Table 2 Rhodium-catalysed *trans*-bis-silylation of **4a**


Entry	Catalyst	Time	Isolated yield
1	RhCl(PPh ₃) ₃	20 h	40%
2	[RhCl(nbd)] ₂	16 h	51%
3	[RhCl(CO) ₂] ₂	7 h	66%
4	[RhCl(cod)] ₂	24 h	(Low conv.)

membered ring product **2a** (entry 2). Contrary to the palladium-catalysed bis-silylation of **1** that selectively gave 3-silylmethylene-1,2-oxasilolane **3a** *via* *cis*-addition (entry 3),⁷ the present rhodium-catalysed bis-silylation proceeded exclusively in a *trans* fashion.⁸

As part of our ongoing studies on the synthesis of siloles by *trans*-addition,^{5b,d,k} the *trans*-bis-silylation reaction of (2-alkynylphenyl)disilanes **4** was carried out to synthesise 3-silyl-1-benzosiloles. Reaction conditions were optimised using 2-[2-(*p*-tolylethynyl)phenyl]disilane **4a** as the substrate, and the results are shown in Table 2. The intramolecular *trans*-bis-silylation of

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Table 3 Synthesis of 3-silyl-1-benzosiloles **5** by rhodium-catalysed *trans*-bis-silylation^a

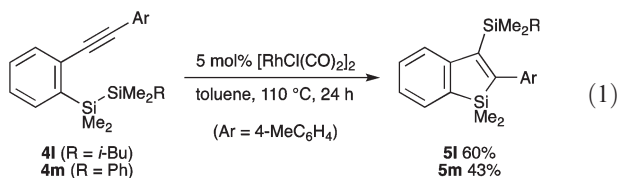
Entry	4 (R)	Isolated yield with	
		[RhCl(CO) ₂] ₂	RhCl(PPh ₃) ₃
1	4b (Ph)	55% ^b	41%
2	4c (3,5-Me ₂ C ₆ H ₃)	64% ^b	36%
3	4d (2-MeC ₆ H ₄)	23% ^{bc}	38%
4	4e (4-MeOC ₆ H ₄)	42%	63% ^d
5	4f (4-O ₂ NC ₆ H ₄)	55% ^b	10% ^b
6	4g (3-AcC ₆ H ₄)	54% ^b	56% ^b
7	4h (5-Me-2-thienyl)	59% ^b	46% ^b
8	4i (Me)	37% ^{cd}	—
9	4j (SiMe ₃)	52% ^{bc}	—
10	4k (H)	16% ^c	—

^a Unless otherwise noted, 2-(alkynylphenyl)disilanes (**4**, 0.20 mmol) were reacted in toluene (1.0 mL) at 110 °C for 3–32 h in the presence of rhodium catalysts (5 mol%). ^b 10 mol% Rh. ^c [RhCl(nbd)]₂ was used instead of [RhCl(CO)₂]₂. ^d Xylene, 130 °C.

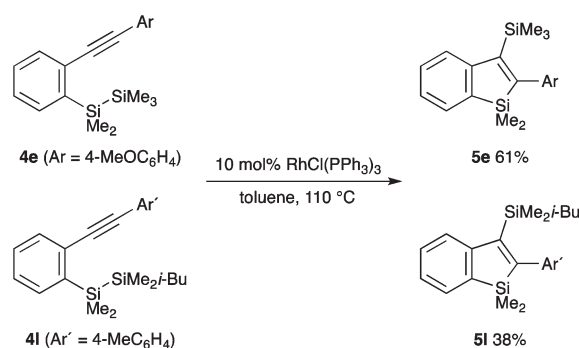
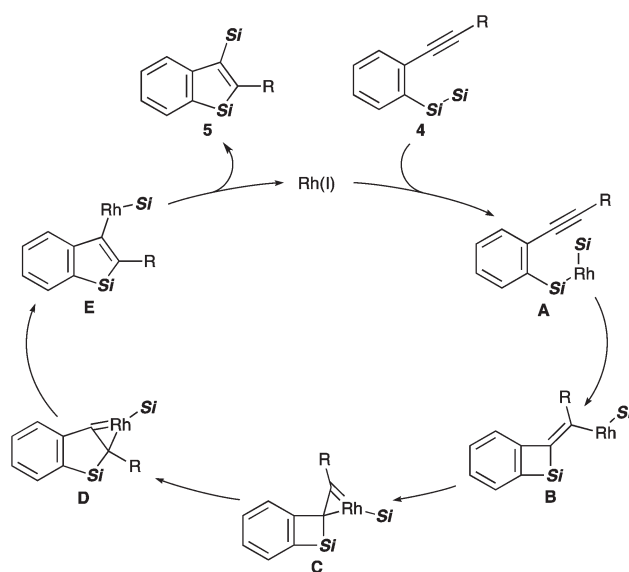
4a proceeded both in the presence of RhCl(PPh₃)₃ and [RhCl(nbd)]₂ to afford 3-silylbenzosilole **5a** in 40% and 51% yields, respectively (entries 1 and 2). The highest yield of **5a** was obtained when [RhCl(CO)₂]₂ was used as the catalyst (entry 3), whereas the reaction was quite sluggish in the presence of [RhCl(cod)]₂ (entry 4).

A variety of (2-alkynylphenyl)disilanes **4** were converted into 3-silyl-1-benzosiloles **5** using rhodium catalysts (Table 3).⁹ The intramolecular *trans*-bis-silylation of phenyl-, 3,5-xylyl- and *o*-tolyl-substituted derivatives **4b–d**, respectively, gave the corresponding benzosiloles **5b–d** in 23–64% yields (entries 1–3). Substrates **4e–g** bearing an electron-donating or electron-withdrawing group on the terminal phenyl substituent were utilised (entries 4–6), and a thienyl substituent was also tolerated (entry 7). Unlike the aryl- and heteroaryl-substituted substrates, alkyl- and silyl-substituted alkynes **4i** and **4j**, respectively, and the substrate bearing a terminal alkyne moiety **4k** failed to yield the desired products in the presence of RhCl(PPh₃)₃; however, they gave the corresponding benzosiloles **5i–k** in 16–52% yields when [RhCl(nbd)]₂ was used as the catalyst (entries 8–10).

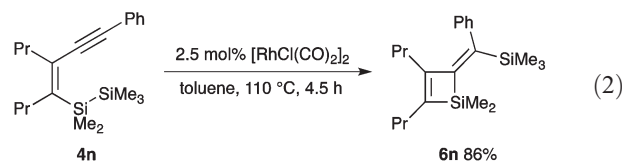
The rhodium-catalysed *trans*-bis-silylation of (2-alkynylphenyl)disilanes tolerated isobutyl (**4l**) and phenyl (**4m**) groups at the terminal silicon atom (eqn (1)).



In contrast to (2-alkynylphenyl)disilanes **4a–l** that gave benzosiloles by *trans*-bis-silylation, ynenyldisilane **4n** exclusively underwent *cis*-bis-silylation in the presence of the rhodium

**Scheme 1** Crossover experiment.**Scheme 2**

catalyst to produce a four-membered silacycle **6n** in 86% yield (eqn (2)).



The reaction mechanism of the present *trans*-bis-silylation is a subject of speculation. In our previous study on the intermolecular reaction of alkynes with hexamethyldisilane,⁵ⁱ a silylrhodium(i) species was expected to be involved in the catalytic cycle. To determine whether the products result from an intermolecular mechanism involving a silylrhodium(i) species, a crossover experiment was conducted. The rhodium(i)-catalysed reaction of a 1 : 1 mixture of **4e** and **4l** afforded **5e** and **5l** without any detectable scrambling (Scheme 1). These results strongly imply that the bis-silylation reaction proceeds *via* an intramolecular process rather than an intermolecular one.

Unlike the bis-silylation of alkynes, hydrosilylation often occurs in a *trans* fashion with various transition metal catalysts.¹⁰ Crabtree claimed that *trans*-hydrosilylation can be

considered by assuming that η^2 -vinyl transition metal (1-metallacyclopentene) intermediates possess electrophilic carbene character and that a 1,2-silyl shift to the electron-deficient centres readily occurs.¹¹ Indeed, the η^2 -vinyl pathway can explain the mechanism of *trans*-bis-silylation, albeit with a lack of experimental evidence for the intermediate species (Scheme 2). Initially, the Si–Si bond of **4** undergoes oxidative addition to a Rh(I) complex to generate bis(silyl)rhodium(III) species **A**,¹² and subsequently, the C–C triple bond inserts intramolecularly into the Rh–Si bond to form (*Z*)- β -silylalkenyl(silyl)rhodium(III) **B** that has a four-membered ring. After isomerisation from **B** to η^2 -vinylrhodium (1-rhodacyclopentene) species **C**, the dimethylsilylene group migrates to the electrophilic carbene carbon to afford intermediate **D**, which then rearranges to another β -silylalkenyl(silyl)rhodium(III) species **E**. Finally, reductive elimination from **E** furnishes 3-silyl-1-benzosilole **5** with the regeneration of the Rh(I) catalyst.

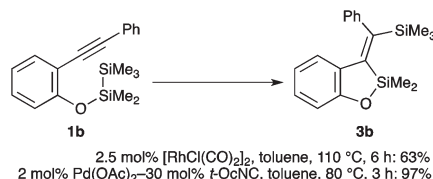
In conclusion, we have developed an intramolecular *trans*-bis-silylation of alkynes catalysed by rhodium(I) complexes, which affords 3-silyl-1-benzosiloles with different functionalities at the 2-position. Although we have suggested a possible mechanism for the *trans*-bis-silylation, further work needs to be directed towards validating the mechanistic hypothesis.

Acknowledgements

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