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Cite this: *Org. Biomol. Chem.*, 2012, **10**, 3175

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

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Received 2nd February 2012, Accepted 1st March 2012
DOI: 10.1039/c2ob25242b

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.

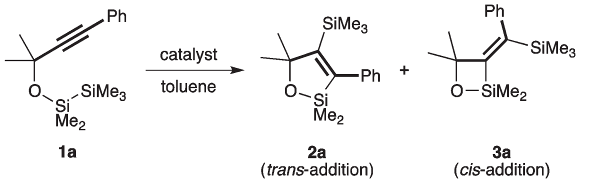
Addition of intermetallic σ-bonds (E–E′; E, E′ = Si, B, Sn *etc.*) to alkynes provides a simple and efficient route for the preparation of stereodefined vicinally bismetallated alkenes, which are useful precursors to multisubstituted alkenes.[1] Usually, the 1,2-addition reaction is catalysed by group 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 $RhCl(PPh_3)_3$ also resulted in the selective formation of the five-membered ring product **2a** (entry 2). Contrary to the palladium-catalysed bis-silylation of **1** that selectively gave 3-silylmethylene-1,2-oxasiletane **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

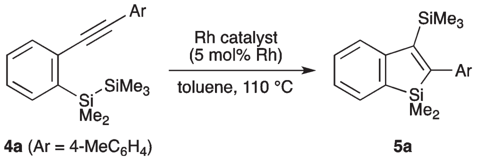
Table 1 Bis-silylation of disilanyl ether **1a**



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	$Pd(OAc)_2$–*t*-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.)

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† Electronic supplementary information (ESI) available: Experimental procedures and characterisation data for new compounds. See DOI: 10.1039/c2ob25242b

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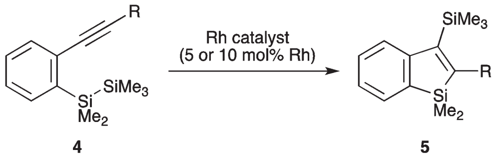
Table 3 Synthesis of 3-silyl-1-benzosiloles **5** by rhodium-catalysed *trans*-bis-silylation[a]



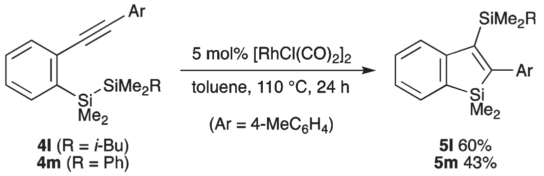
Entry	**4** (R)	Isolated yield with $[RhCl(CO)_2]_2$	Isolated yield with $RhCl(PPh_3)_3$
1	**4b** (Ph)	55%	41%
2	**4c** (3,5-$Me_2C_6H_3$)	64%[b]	36%
3	**4d** (2-MeC_6H_4)	23%[bc]	38%
4	**4e** (4-$MeOC_6H_4$)	42%	63%[d]
5	**4f** (4-$O_2NC_6H_4$)	55%[b]	10%[b]
6	**4g** (3-AcC_6H_4)	54%[b]	56%
7	**4h** (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.

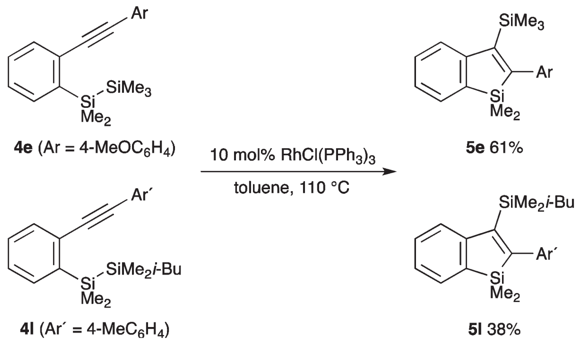
4a proceeded both in the presence of $RhCl(PPh_3)_3$ and $[RhCl(nbd)]_2$ to afford 3-silylbenzosilole **5a** in 40% and 51% yields, respectively (entries 1 and 2). The highest yield of **5a** was obtained when $[RhCl(CO)_2]_2$ was used as the catalyst (entry 3), whereas the reaction was quite sluggish 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 $RhCl(PPh_3)_3$; however, they gave the corresponding benzosiloles **5i–k** in 16–52% yields when $[RhCl(nbd)]_2$ was used as the catalyst (entries 8–10).

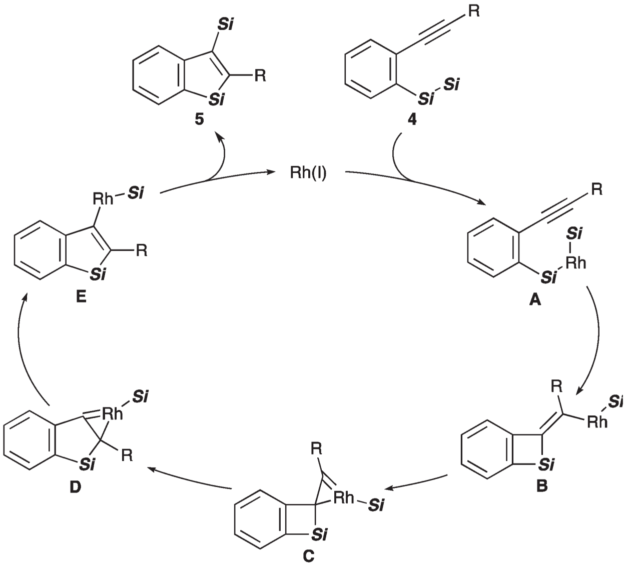
The rhodium-catalysed *trans*-bis-silylation of (2-alkynylphenyl)disilanes tolerated isobutyl (**4l**) and phenyl (**4m**) groups at the terminal silicon atom (eqn (1)).



(1)

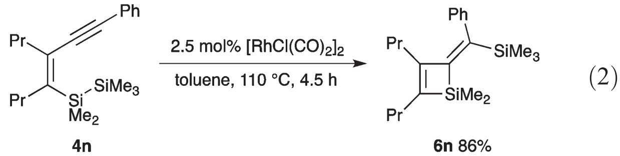


Scheme 1 Crossover experiment.



Scheme 2

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



(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

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considered by assuming that η^2-vinyl transition metal (1-metallacyclopropene) 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-rhodacyclopropene) 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

This work was supported by a Grant-in-Aid for Scientific Research for Young Scientist (B) (No. 23750115) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Notes and references

1 For reviews, see: (*a*) I. Beletskaya and C. Moberg, *Chem. Rev.*, 2006, **106**, 2320; (*b*) M. Suginome, T. Matsuda, T. Ohmura, A. Seki and M. Murakami, in *Comprehensive Organometallic Chemistry III*, ed. R. Crabtree and D. M. P. Mingos, Elsevier, Oxford, 2007, vol. 10, ch. 16, pp. 725–787; (*c*) H. E. Burks and J. P. Morken, *Chem. Commun.*, 2007, 4717; (*d*) C. Pubill-Ulldemolins, A. Bonet, C. Bo, H. Gulyás and E. Fernández, *Org. Biomol. Chem.*, 2010, **8**, 2667.

2 For theoretical studies, see: (*a*) M. Hada, Y. Tanaka, M. Ito, M. Murakami, H. Amii, Y. Ito and H. Nakatsuji, *J. Am. Chem. Soc.*, 1994, **116**, 8754; (*b*) S. Sakaki and T. Kikuno, *Inorg. Chem.*, 1997, **36**, 226; (*c*) Q. Cui, D. G. Musaev and K. Morokuma, *Organometallics*, 1998, **17**, 742.

3 For mechanistic studies, see: (*a*) M. Murakami, T. Yoshida, S. Kawanami and Y. Ito, *J. Am. Chem. Soc.*, 1995, **117**, 6408; (*b*) F. Ozawa, *J. Organomet. Chem.*, 2000, **611**, 332; (*c*) T. Sagawa, K. Ohtsuki, T. Ishiyama and F. Ozawa, *Organometallics*, 2005, **24**, 1670.

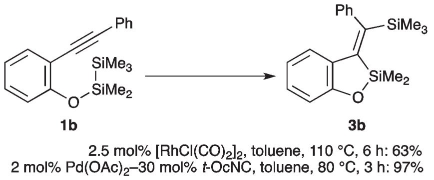
4 (*a*) B. L. Chenard and C. M. Van Zyl, *J. Org. Chem.*, 1986, **51**, 3561; (*b*) T. Hayashi, H. Yamashita, T. Sakakura, Y. Uchimaru and M. Tanaka, *Chem. Lett.*, 1991, **20**, 245; (*c*) T. Ohmura, K. Oshima and M. Suginome, *Chem. Commun.*, 2008, 1416.

5 For recent examples, see: (*a*) T. Matsuda, S. Kadowaki, T. Goya and M. Murakami, *Org. Lett.*, 2007, **9**, 133; (*b*) T. Matsuda, S. Kadowaki and M. Murakami, *Chem. Commun.*, 2007, 2627; (*c*) T. Ohmura, K. Masuda and M. Suginome, *J. Am. Chem. Soc.*, 2008, **130**, 1526; (*d*) T. Matsuda, S. Kadowaki, Y. Yamaguchi and M. Murakami, *Chem. Commun.*, 2008, 5744; (*e*) M. Shimizu, K. Mochida and T. Hiyama, *Angew. Chem., Int. Ed.*, 2008, **47**, 9760; (*f*) M. Tobisu, M. Onoe, Y. Kita and N. Chatani, *J. Am. Chem. Soc.*, 2009, **131**, 7506; (*g*) T. Ureshino, T. Yoshida, Y. Kuninobu and K. Takai, *J. Am. Chem. Soc.*, 2010, **132**, 14324; (*h*) T. Matsuda, Y. Yamaguchi, N. Ishida and M. Murakami, *Synlett*, 2010, 2743; (*i*) T. Matsuda, Y. Suda and Y. Fujisaki, *Synlett*, 2011, 813; (*j*) Y. Liang, S. Zhang and Z. Xi, *J. Am. Chem. Soc.*, 2011, **133**, 9204; (*k*) T. Matsuda, Y. Yamaguchi, M. Shigeno, S. Sato and M. Murakami, *Chem. Commun.*, 2011, **47**, 8697; (*l*) E. Shirakawa, S. Masui, R. Narui, R. Watabe, D. Ikeda and T. Hayashi, *Chem. Commun.*, 2011, **47**, 9714. See also: (*m*) A. S. Dudnik, N. Chernyak, C. Huang and V. Gevorgyan, *Angew. Chem., Int. Ed.*, 2010, **49**, 8729; (*n*) C. Huang, N. Chernyak, A. S. Dudnik and V. Gevorgyan, *Adv. Synth. Catal.*, 2011, **353**, 1285; (*o*) A. Kuznetsov and V. Gevorgyan, *Org. Lett.*, 2012, **14**, 914.

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

7 (*a*) M. Suginome, A. Matsumoto and Y. Ito, *J. Org. Chem.*, 1996, **61**, 4884; (*b*) M. Suginome, A. Takama and Y. Ito, *J. Am. Chem. Soc.*, 1998, **120**, 1930.

8 *trans*-Bis-silylation failed to occur when the tether length was increased by one carbon. For example, 2-[2-(phenylethynyl)phenoxy]disilane (**1b**) led to the formation of the identical five-membered *cis*-bis-silylation product **3b** in both rhodium and palladium catalysts



.

9 Palladium-catalyzed reaction of **4** gave four-membered ring products *via* *cis*-bis-silylation. See ESI.†.

10 (*a*) R. S. Tanke and R. H. Crabtree, *J. Am. Chem. Soc.*, 1990, **112**, 7984; (*b*) I. Ojima, N. Clos, R. J. Donovan and P. Ingallina, *Organometallics*, 1990, **9**, 3127; (*c*) B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.*, 2001, **123**, 12726; (*d*) B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.*, 2003, **125**, 30; (*e*) L. W. Chung, Y.-D. Wu, B. M. Trost and Z. T. Ball, *J. Am. Chem. Soc.*, 2003, **125**, 11578; (*f*) Y. Miyake, E. Isomura and M. Iyoda, *Chem. Lett.*, 2006, **35**, 836; (*g*) V. S. Sridevi, W. Y. Fan and W. K. Leong, *Organometallics*, 2007, **26**, 1157; (*h*) M. V. Jiménez, J. J. Pérez-Torrente, M. I. Bartolomé, V. Gierz, F. J. Lahozand and L. A. Oro, *Organometallics*, 2008, **27**, 224, and references therein.

11 R. H. Crabtree, *New J. Chem.*, 2003, **27**, 771.

12 For bis(silyl)rhodium(III) species, see: (*a*) M. Okazaki, S. Ohshitanai, H. Tobita and H. Ogino, *J. Chem. Soc., Dalton Trans.*, 2002, 2061; (*b*) K. Osakada, K. Hataya, Y. Nakamura, M. Tanaka and T. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 1993, 576; (*c*) M. J. Auburn and S. R. Stobart, *Inorg. Chem.*, 1985, **24**, 318; (*d*) Y. Sunada, Y. Fujimura and H. Nagashima, *Organometallics*, 2008, **27**, 3502.