Gold-catalysed intramolecular *trans*-allylsilylation of alkynes forming 3-allyl-1-silaindenes†

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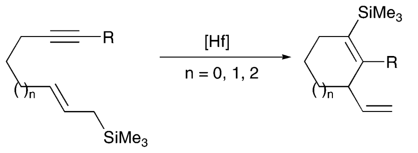
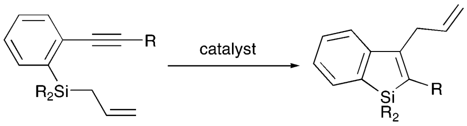
3-Allyl-1-silaindenes are synthesised from alkynes having an allylsilane moiety by a gold-catalysed intramolecular *trans*-allylsilylation reaction.

Enyne cycloisomerisation reactions catalysed by electrophilic transition metal complexes have emerged as a powerful and efficient method for the construction of complex cyclic structures.[1] Yamamoto and his co-workers reported an interesting example using an alkyne tethered to an allylsilane moiety.[2] The intramolecular *trans*-allylsilylation reaction is catalysed by a hafnium complex to afford carbocyclic compounds (eqn (1)). Our interest in the synthesis of silole (silacyclopentadiene) derivatives, which possess unique photophysical and electronic properties,[3] led us to examine the reaction of enynes linked by a slicon-containing tether (eqn (2)). Herein, we report a gold(I)-catalysed intramolecular *trans*-allylsilylation reaction of silicon-tethered enynes furnishing silole cores.[4–6]



(1)



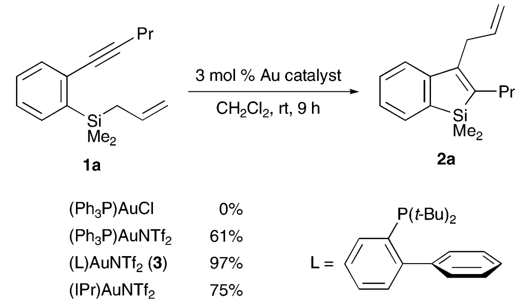
(2)

Gold complexes possess a highly electrophilic character which often works specifically on alkynes.[7] Thus, we examined the use of a gold(I) complex to catalyse a reaction of allyldimethyl[2-(pent-1-ynyl)phenyl]silane (**1a**) (Scheme 1).[8] Whereas a neutral chlorogold(I) complex was ineffective, cationic gold complexes having a bistriflimide counter anion[9] catalysed an intramolecular *trans*-allylsilylation reaction at room temperature to produce 3-allyl-1-silaindene **2a**.[10] The yield of **2a** was significantly affected by the ligand. 2-Di-*tert*-butylphosphinobiphenyl was found to be the ligand of choice, giving **2a** in 97% yield.[11]‡ A gold complex bearing IPr[12] ligand exhibited moderate catalytic activity for the reaction.

The reaction of various sila-enynes **1** having a range of the alkyne substituents (R) was examined using **3** as the catalyst, and the results are listed in Table 1. Methyl, *sec*-alkyl, methoxycarbonyl, alkynyl, and aryl groups were all suitable substituents to give the corresponding 2-substituted 3-allyl-1-silaindenes **1b–j** in moderate to good yield (entries 1–9). Higher catalyst loadings (6–12 mol%) were required to complete the reaction in the case of the cyclopentyl and aryl groups. Notably, a variety of functional groups such as a boryl group and a thienyl group were tolerated in the gold-catalysed reaction. Chloro- and bromoalkyne moieties could be contained in the substituents, producing 2-halo-1-silaindenes **2k** and **2l**, respectively (entries 10 and 11).[13] On the other hand, the substrates possessing a hydrogen (*i.e.*, a terminal alkyne), a bulky *tert*-butyl group, and 2-pyridyl group failed to afford the corresponding 1-silaindenes.

Next, structural variation in the allylsilane moiety was investigated (Table 2). Whereas methylphenylsilylene-bridged sila-enyne **1m** provided 1-silaindene **2m** in good yield (entry 1), diethylsilylene-bridged substrate **2n** was less reactive (entry 2). Methallyl-, crotyl-, and cyclohexenylsilanes **1o–q** also gave the corresponding 1-silaindenes **2o–q** (entries 3–5). The result with **1p** indicated that the allylation took place regioselectively at the γ position. Reaction of allylgermane **1r** occurred in a similar manner to afford 3-allyl-1-germaindene **2r** in 85% yield (entry 6).

The synthesis of 1-silaindene derivatives possessing extended π-conjugation is exemplified in eqn (3) and (4). *m*-Phenylenebis(1-silaindene) **5a** was obtained by two-fold *trans*-allylsilylation of **4a**. An analogous two-fold allylsilylation successfully proceeded with substrate **4b** to afford 1,5-disila-*s*-indacene **5b**.



(Ph$_3$P)AuCl	0%
(Ph$_3$P)AuNTf$_2$	61%
(L)AuNTf$_2$ (**3**)	97%
(IPr)AuNTf$_2$	75%

Scheme 1 Gold-catalysed *trans*-allylsilylation of sila-enyne **1a**.

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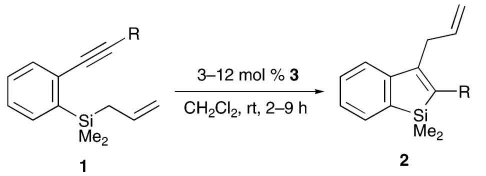
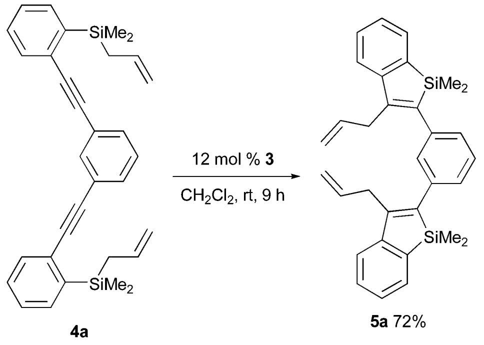
Table 1 Gold-catalysed *trans*-allylsilylation of sila-enynes **1b–l**[a]

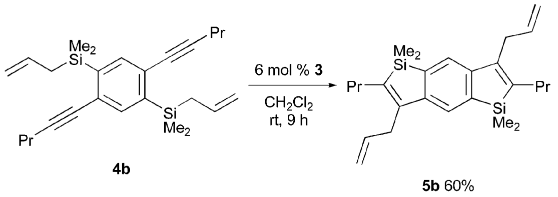


Entry	**1** (R)	mol% Au	**2**	Yield[b]
1	**1b** (Me)	3	**2b**	58%
2	**1c** (cyclopentyl)	6	**2c**	71%[c]
3	**1d** (CO_2Me)	3	**2d**	89%
4	**1e** (C≡CTIPS[d])	3	**2e**	84%
5	**1f** (4-MeC_6H_4)	6	**2f**	75%[e]
6	**1g** (4-(pin)BC_6H_4[f])	6	**2g**	81%
7	**1h** (3-$MeOC_6H_4$)	6	**2h**	71%
8	**1i** (2-FC_6H_4)	12	**2i**	77%
9	**1j** (5-methyl-2-thienyl)	6	**2j**	42%
10[g]	**1k** (Cl)	3	**2k**	79%
11[g]	**1l** (Br)	3	**2l**	77%

[a] Sila-enynes **1b–l** (0.20 mmol) were reacted in the presence of the catalyst **3** (3–12 mol%) in CH_2Cl_2 (2.5 mL) at room temperature for 9 h. [b] Isolated yield by preparative TLC. [c] 33% yield with 3 mol% of **3**. [d] TIPS = triisopropylsilyl. [e] 13% conversion after 1 h. [f] Pin = pinacolato (–$OCMe_2CMe_2O$–). [g] Reaction time: 2 h.



(3)

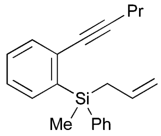
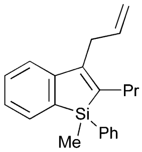
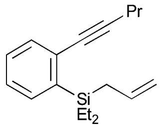
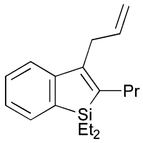
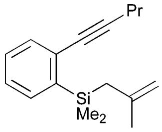
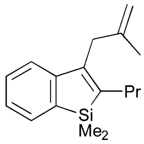
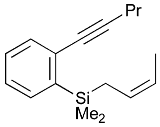
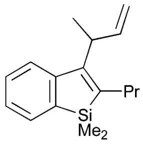
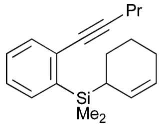
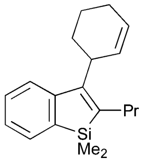
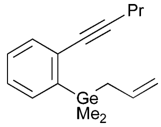
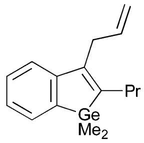


(4)

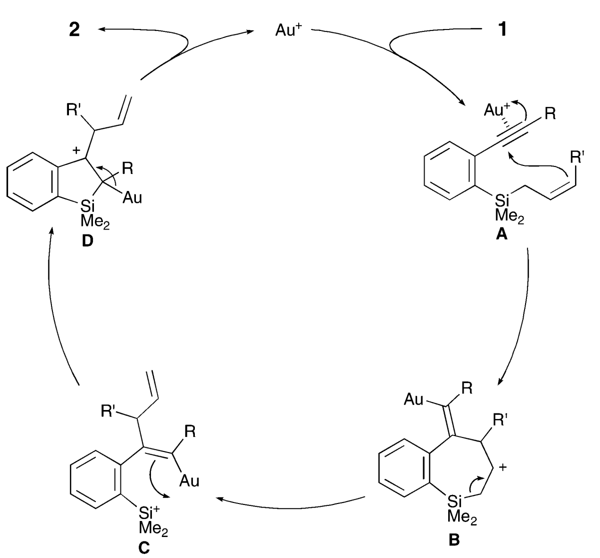
A mechanism conceivable for the production of **2** from **1** is shown in Scheme 2.[14] Initially, the alkyne moiety of **1** activated by electrophilic Au^+ (in **A**) induces intramolecular addition of the pendant allyl group to produce seven-membered ring intermediate **B**. Subsequent ring opening accomplishes allylation to give alkenylgold species **C**, to which the cationic silyl moiety undergoes electrophilic ring closure. Finally, demetalation from alkylgold species **D** furnishes silacycle **2** and regenerates Au^+.[15]

The produced 3-allyl-1-silaindenes **2** exhibited fluorescence upon ultraviolet excitation with 250 nm in hexane solution. Silaindene **2a** emitted fluorescence at 361 nm with quantum efficiency of 0.07, and **5b** at 408 nm with 0.33.

Table 2 Reaction of **1m–r** in the presence of **3**[a]

Entry	**1**	**2**	Yield[b]
1	 **1m**	 **2m**	83%
2[c]	 **1n**	 **2n**	53%
3	 **1o**	 **2o**	83%
4	 **1p**[d]	 **2p**	69%
5	 **1q**	 **2q**	46%
6	 **1r**	 **2r**	85%

[a] Unless otherwise noted, all reactions were carried out in the presence of 3 mol% of **3** in CH_2Cl_2 at room temperature for 9 h. [b] Isolated yield by preparative TLC. [c] 6 mol% of **3** was used. [d] *cis* : *trans* = 93 : 7.



Scheme 2 Mechanism of gold-catalysed intramolecular *trans*-allylsilylation.

In summary, we have developed a new method for the synthesis of 3-allyl-1-silaindenes by a gold-catalysed intramolecular *trans*-allylsilylation reaction of alkynes.

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Notes and references

‡ General procedure: to a Schlenk tube containing [2-PhC_6H_4P-(*t*-$Bu)_2$]$AuNTf_2$ (**3**, 7.0 mg, 9.0 μmol, 3 mol%) under an argon atmosphere was added a solution of allyldimethyl[2-(pent-1-ynyl)-phenyl]silane (**1a**, 72.7 mg, 0.30 mmol) in dichloromethane (0.37 mL). After stirring for 9 h at room temperature, the volatile materials were removed under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane) to give 3-allyl-1,1-dimethyl-2-propyl-1-silaindene (**2a**, 70.2 mg, 97%).

1 Reviews: (*a*) M. Méndez, V. Mamane and A. Fürstner, *Chemtracts*, 2003, **16**, 397; (*b*) A. M. Echavarren and C. Nevado, *Chem. Soc. Rev.*, 2004, **33**, 431; (*c*) C. Bruneau, *Angew. Chem., Int. Ed.*, 2005, **44**, 2328; (*d*) S. Ma, S. Yu and Z. Gu, *Angew. Chem., Int. Ed.*, 2006, **45**, 200; (*e*) C. Nieto-Oberhuber, S. López, E. Jiménez-Núñez and A. M. Echavarren, *Chem.–Eur. J.*, 2006, **12**, 5916; (*f*) L. Zhang, J. Sun and S. A. Kozmin, *Adv. Synth. Catal.*, 2006, **348**, 2271.

2 (*a*) K.-i. Imamura, E. Yoshikawa, V. Gevorgyan and Y. Yamamoto, *J. Am. Chem. Soc.*, 1998, **120**, 5339. For the intermolecular variants, see; (*b*) S. H. Yeon, J. S. Han, E. Hong, Y. Do and I. N. Jung, *J. Organomet. Chem.*, 1995, **499**, 159; (*c*) N. Asao, E. Yoshikawa and Y. Yamamoto, *J. Org. Chem.*, 1996, **61**, 4874; (*d*) E. Yoshikawa, V. Gevorgyan, N. Asao and Y. Yamamoto, *J. Am. Chem. Soc.*, 1997, **119**, 6781; (*e*) N. Asao, H. Tomeba and Y. Yamamoto, *Tetrahedron Lett.*, 2005, **46**, 27.

3 (*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. Matsuda, Y. Yamaguchi and M. Murakami, *Synlett*, 2008, 561.

4 For recent examples of a gold-catalysed intramolecular *cis*-allylsilylation reaction of 4-sila-1,5-enynes, see: (*a*) S. Park and D. Lee, *J. Am. Chem. Soc.*, 2006, **128**, 10664; (*b*) Y. Horino, M. R. Luzung and F. D. Toste, *J. Am. Chem. Soc.*, 2006, **128**, 11364.

5 For related intramolecular allyl migration reactions, see: (*a*) A. Fürstner, F. Stelzer and H. Szillat, *J. Am. Chem. Soc.*, 2001, **123**, 11863; (*b*) A. Fürstner and P. W. Davies, *J. Am. Chem. Soc.*, 2005, **127**, 15024; (*c*) S. Cacchi, *J. Organomet. Chem.*, 1999, **576**, 42.

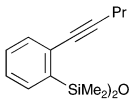
6 For cycloisomerisations of 1,7-enynes, see: (*a*) A. Ochida, H. Ito and M. Sawamura, *J. Am. Chem. Soc.*, 2006, **128**, 16486; (*b*) S. Porcel and A. M. Echavarren, *Angew. Chem., Int. Ed.*, 2007, **46**, 2672; (*c*) N. Cabello, C. Rodríguez and A. M. Echavarren, *Synlett*, 2007, 1753.

7 Reviews: (*a*) A. Hoffmann-Röder and N. Krause, *Org. Biomol. Chem.*, 2005, **3**, 387; (*b*) E. Jiménez-Núñez and A. M. Echavarren, *Chem. Commun.*, 2007, 333; (*c*) D. J. Gorin and F. D. Toste, *Nature*, 2007, **446**, 395; (*d*) A. Fürstner and P. W. Davies, *Angew. Chem., Int. Ed.*, 2007, **46**, 3410; (*e*) Y. Yamamoto, *J. Org. Chem.*, 2007, **72**, 7817; (*f*) A. S. K. Hashmi, *Chem. Rev.*, 2007, **107**, 3180.

8 A reaction in the presence of $HfCl_4$ (CH_2Cl_2, 0 °C) resulted in a complex mixture. No reaction occurred in the presence of $PtCl_2$ (toluene, 80 °C).

9 N. Mézailles, L. Ricard and F. Gagosz, *Org. Lett.*, 2005, **7**, 4133

10 Siloxane **6** was formed in 23% yield in addition to **2a** (61%) in the case of $(Ph_3P)AuNTf_2$



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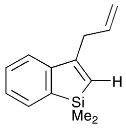
11 Unlike the previous Al- and Hf-catalysed *trans*-allylsilylation reaction of alkynes, the complex **3** failed to promote an intermolecular reaction of allyldimethyl(phenyl)silane with pent-1-ynylbenzene.

12 IPr = Bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

13 Dehalogenated 1-silaindene **7** (*ca.* 14%) was also isolated as the side product. Performing the reaction for a longer period of time than 2 h increased the formation of **7**



7

14 It is premature for us to argue about the mechanism in more detail. A different mechanism can be also assumed to operate depending on the substrates employed.

15 For a related silyldeauration process, see: I. Nakamura, T. Sato, M. Terada and Y. Yamamoto, *Org. Lett.*, 2007, **9**, 4081.