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COMMUNICATION

Gold-catalysed alkenyl- and arylsilylation reactions forming 1-silaindenes†‡

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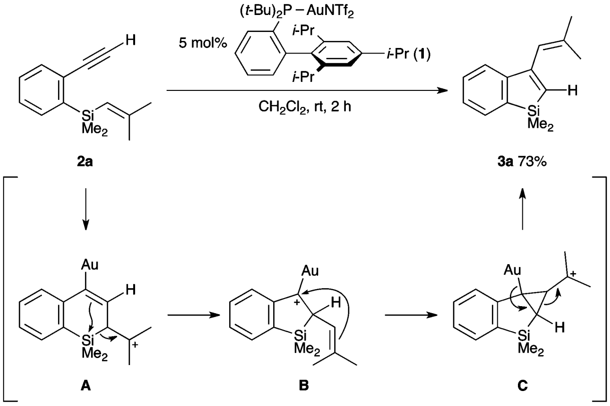
In the presence of gold(I)–phosphine catalysts, alkenyl- and arylsilanes undergo intramolecular cyclisation reactions onto appendant alkyne moieties to afford 1-silaindene derivatives. The reaction pathways vary depending on the substituent on silicon.

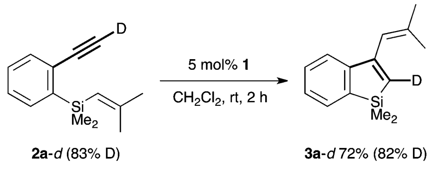
Allylsilanes, alkenylsilanes and arylsilanes undergo carbosilylation across a carbon–carbon triple bond in the presence of various promoters such as Lewis acids and transition metal complexes.[1] We recently reported the gold(I)-catalysed intramolecular *trans*-allylsilylation reaction forming 3-allyl-1-silaindenes.[2] Our continuing interest in the synthesis of silole derivatives[3,4] led us to extend the gold catalysis[5] to alkenylsilylation and arylsilylation reactions. Herein, we report the synthesis of 1-silaindene derivatives[6] by the gold(I)-catalysed intramolecular alkenyl- and arylsilylation reactions.

First, substrates having an ethynyl group were examined. When (2-ethynylphenyl)isobutenyldimethylsilane (**2a**) was treated with a catalytic amount of gold(I) complex **1** bearing a bulky biaryl phosphine ligand (*t*-BuXPhos) at room temperature in dichloromethane for 2 h, intramolecular *trans*-alkenylsilylation occurred across the ethynyl group to afford 3-isobutenyl-1-silaindene **3a** in 73% yield,§ as shown in Scheme 1.[7] We propose a possible mechanistic pathway as depicted therein for the formation of **3a** from **2a**; (i) the cationic gold(I) species of π-acidic character activates the ethynyl group to induce intramolecular nucleophilic attack of the alkene moiety in a 6-*endo* fashion, resulting in the formation of the six-membered ring intermediate **A** having a carbocationic centre β to silicon, (ii) the carbocationic intermediate **A** undergoes skeletal rearrangement to five-membered gold-stabilised carbocation **B**,[8] (iii) the cationic centre in **B** electrophilically attacks the regenerated isobutenyl group to generate tertiary cyclopropylmethyl cation **C** and (iv) the cyclopropyl ring opens with release of the cationic gold(I) species to form 1-silaindene **3a**. Thus, intramolecular *trans*-alkenylsilylation is completed.



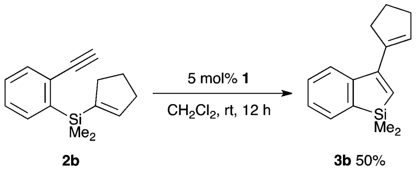
Scheme 1 Gold(I)-catalysed *trans*-alkenylsilylation of **2a**.

A deuterium-labelling experiment was carried out using **2a**-*d* which incorporated a deuterium atom at the terminal position of the ethynyl group (eqn (1)). With the resulting 1-silaindene **3a**-*d*, the deuterium atom was found at the 2-position, staying on the carbon on which it originally resided. This labelling experiment supported that the reaction of **2a** proceeded *via* the *trans*-alkenylsilylation mechanism rather than *via* an enyne metathesis-type mechanism (*vide infra*).



(1)

Cyclopentenylsilane **2b** underwent the *trans*-alkenylsilylation reaction to afford the corresponding silaindene **3b** in 50% yield (eqn (2)).



(2)

The reaction of a substrate having a substituted alkynyl group was also examined (eqn (3)). In the case of alkenylsilane

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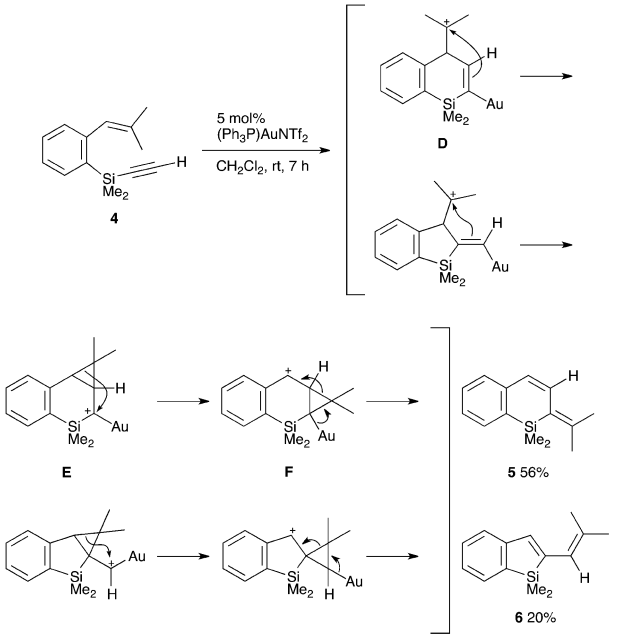
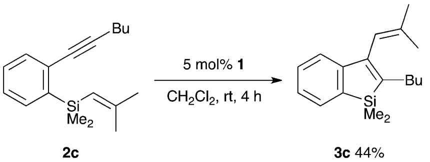
‡ Electronic supplementary information (ESI) available: Experimental procedures and characterisation data for new compounds. See DOI: 10.1039/c1cc12457a



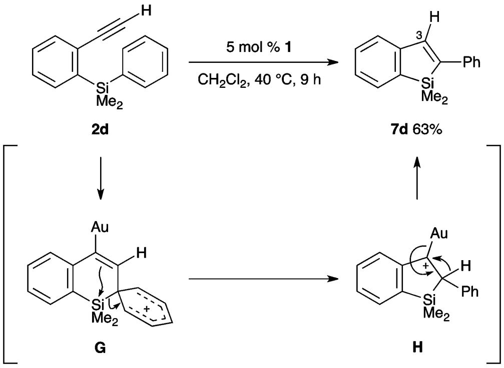
Scheme 2 Gold(I)-catalysed skeletal rearrangement of **4**.

2c possessing a hex-1-ynyl moiety, an analogous alkenylsilylation reaction occurred to produce 1-silaindene **3c** in 44% yield.



(3)

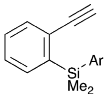
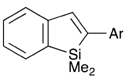
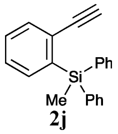
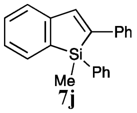
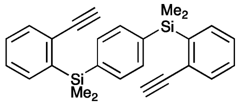
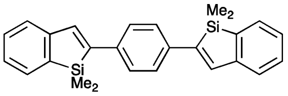
Ethynyl(2-isobutenylphenyl)silane **4** is a constitutional isomer of **2a** in which the ethynyl group and the isobutenyl group were swapped, and its reactivity was examined in comparison with **2a** (Scheme 2). When **4** was subjected to the reaction using $(Ph_3P)AuNTf_2$ as the catalyst, different types of cyclisation reactions took place to give two enyne metathesis-type products **5** and **6** in 76% combined yield. The formation of the two products is attributed to different modes of initial cyclisation. The major product **5** having a 1-silanaphthalene skeleton was formed *via* a skeletal rearrangement initiated with 6-*endo* cyclisation. Alkenylgold intermediate **D** thus formed rearranges to gold-stabilised cyclopropylmethyl cation **E**, which undergoes a further skeletal rearrangement to give cyclopropylgold **F**. Final demetallation furnishes six-membered silacycle **5** having an isopropylidene moiety. On the other hand, the initial cyclisation in a 5-*exo* fashion led to the formation of the minor 1-silaindene product **6** *via* a pathway similar to that mentioned above from **D** to **5**.



Scheme 3 Gold(I)-catalysed 1,1-arylsilylation of **2d**.

We then examined the gold(I)-catalysed reaction of aryl(2-ethynylphenyl)silanes. In marked contrast to the case of alkenylsilanes, phenylsilane **2d** underwent exclusive 1,1-arylsilylation

Table 1 Gold(I)-catalysed 1,1-arylsilylation[a]

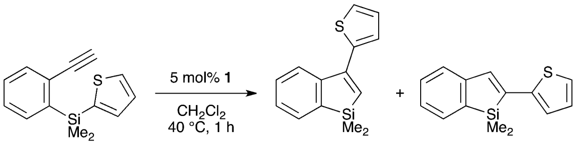
Entry	2	7	Yield[b] (%)
			
1	Ar = 2-MeC_6H_4 (**2e**)	**7e**	52
2	Ar = 3,5-$Me_2C_6H_3$ (**2f**)	**7f**	64
3	Ar = 4-PhC_6H_4 (**2g**)	**7g**	42
4[c]	Ar = 4-$MeOC_6H_4$ (**2h**)	**7h**	24
5	Ar = 4-$CF_3C_6H_4$ (**2i**)	**7i**	Trace
6	 **2j**	 **7j**	60
7[d]	 **2k**	 **7k**	22[e]

[a] Unless otherwise noted, all reactions were carried out in the presence of 5 mol% of **1** in CH_2Cl_2 at 40 °C for 9–18 h. [b] Isolated yield by preparative TLC. [c] Reaction was carried out at rt. [d] 10 mol% of **1** was used. [e] Purified by preparative GPC.

in refluxing dichloromethane in the presence of 5 mol% of **1** to give 2-phenyl-1-silaindene **7d** in 63% yield (Scheme 3).[9] We assume that **7d** was formed by the reaction initiated with 6-*endo* cyclisation, as is the case with **2a–c**. The resulting intermediate **G** undergoes skeletal rearrangement to five-membered gold-stabilised carbocation **H**, which corresponds to **B** in Scheme 1. Finally, the hydride rather than the phenyl group of **H** shifts onto the next carbon[10] with release of the cationic gold(I) species to afford **7d**. Labelled substrate **2d**-*d* having a deuterium atom on the terminal carbon of the ethynyl group was prepared and the gold(I)-catalysed reaction was carried out. A deuterium atom was found at the C(3) position of the product to support the mechanism shown in Scheme 3.

Other results of the intramolecular 1,1-arylsilylation reaction are summarised in Table 1. 2-Tolyl, 3,5-xylyl and 4-biphenyl derivatives (**2e–g**) gave the corresponding 2-aryl-1-silaindenes (**7e–g**) in yields ranging from 42% to 64% (entries 1–3). However, substitution with a methoxy group at the 4-position of the phenyl ring decreased the yield of **7h** to 24% (entry 4), and only a trace amount of the product was obtained with (4-trifluoromethylphenyl)silane **2i** (entry 5). The reaction of triarylsilane **2j** gave the corresponding silaindene **7j** in 60% yield (entry 6). A 2,2′-(1,4-phenylene)bis(1-silaindene) skeleton was constructed by the gold(I)-catalysed reaction of 1,4-phenylenebis[(ethynylphenyl)-silane] **2k** (entry 7). On the other hand, arylsilanes equipped with an internal alkyne moiety failed to undergo arylsilylation even at elevated temperatures.

We carried out the gold(I)-catalysed reaction of 2-thienylsilane **2l**, which exhibited an intermediary reactivity between alkenylsilanes and arylsilanes (eqn (4)). The major product was 3-(2-thienyl)-1-silaindene **3l** (50%), which was formed *via* the *trans*-alkenylsilylation mechanism shown in Scheme 1. 2-(2-Thienyl)-1-silaindene **7l** was also isolated in 17% yield as the minor product, which was formed *via* the 1,1-arylsilylation mechanism shown in Scheme 3.



2l **3l** 50% **7l** 17%

(4)

In conclusion, we have developed the gold(I)-catalysed alkenyl- and arylsilylation reactions to synthesise 1-silaindene derivatives. The substituent on silicon dictates the partitioning between *trans*-1,2-addition and 1,1-addition pathways.

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§ General procedure: to a Schlenk tube containing gold(I) complex **1** (4.8 mg, 5.3 μmol, 5 mol%) was added a solution of (2-ethynylphenyl)dimethyl(2-methylprop-1-enyl)silane (**2a**, 21.6 mg, 0.10 mmol) in dichloromethane (1.0 mL), and the mixture was stirred at rt for 2 h. The reaction mixture was passed through a column of Florisil® (hexane : AcOEt = 10 : 1). After removal of the volatile materials, the residue was subjected to preparative thin-layer chromatography on silica gel (hexane) to afford 1,1-dimethyl-3-(2-methylprop-1-enyl)-1-silaindene (**3a**, 15.8 mg, 73%).

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