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Synthesis of Benzo[*c*]silole derivatives Bearing a Tetrasubstituted Exocyclic C=C Double Bond by Palladium-Catalyzed Domino Reactions.

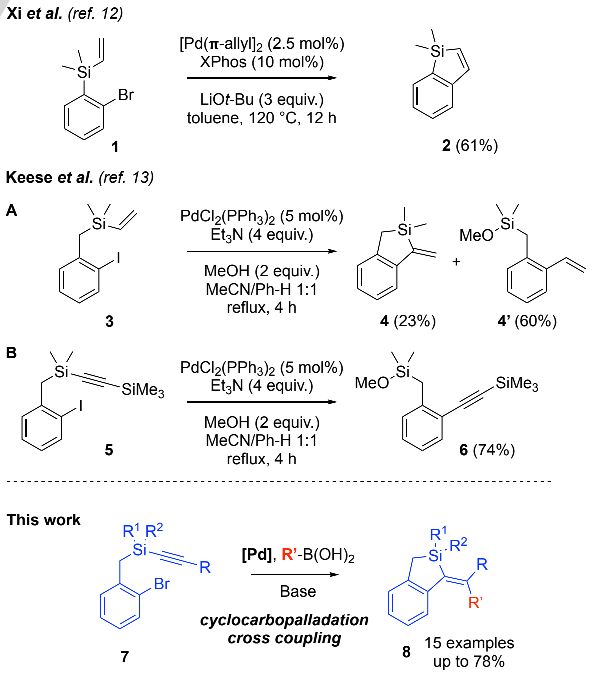
Patrick Wagner,[a] Mihaela Gulea,[a] Jean Suffert,[a] and Morgan Donnard*[a]

In memory of Prof. Robert Corriu who was an inspirational researcher in the field of silicon chemistry.

Abstract: *We are reporting the synthesis of diversely substituted 2,3-dihydro-benzo[c]siloles via an unprecedented palladium catalyzed domino sequence involving a cyclocarbopalladation of an internal silylalkyne. This reaction proceeds with a complete stereoselectivity to lead to a fully substituted exocyclic C=C double bond. Notably the overall domino sequence appears to be crucial to obtain the desired cyclic vinylsilanes.*

Silicon containing heterocycles are highly valuable scaffolds as they have shown specific properties in very different fields such as, non-exhaustively, materials,[1] fragrances[2] and pharmaceuticals.[3,4] Notably, most of the time these specificities are due to the silicon atom itself as it changes dramatically the polarity as well as the conformational characteristics of an organic compound compared to its carbon analog (these effects are encompassed in what is generally called the C/Si switch).[5] Despite an ever-increasing interest in silacyclic compounds, the number of efficient synthetic methodologies to reach these scaffolds remains low in comparison to other heterocycles[6] and it undoubtedly represents the main barrier to the use of such molecules in many fields. For these reasons, we have decided, during the course of our studies to develop original scaffolds,[7] to focus our attention on silacycles. Based on our experience on cascade reactions, we have envisioned that the cyclocarbopalladation of silylalkynes in a domino sequence could represent a straightforward access to this family of compounds with an interesting level of molecular diversification.[8] Interestingly, the resulting vinylsilanes would bear an exocyclic fully substituted carbon-carbon double bond.[9] This singular family of cyclic vinylsilanes are of high interest and represents one of the most challenging sub-classes to synthesize.[10] Many of the methods to access exocyclic vinylsilanes are based on intramolecular modifications of established alkyne hydrosilylation and silylformylation methodologies. In addition, most of the substrates used are silyl ethers when those leading to a cycle incorporating a silicon atom linked to four carbons are more rare.[11] To the best of our knowledge, only two groups have focused their attention on such kind of cyclization on all-carbon quaternary silicon atoms. Notably, none of them have integrated it in a domino sequence. Xi *et al.* reported a 5-*endo*-dig cyclocarbopalladation (Heck-type cyclization) on an acyclic vinylsilane (Scheme 1). This transformation offered the corresponding benzosilole in 61% yield.[12] On their side Keese *et al.*[13] attempted to synthesize benzo[*c*]siloles using 5-*exo* Mizoroki-Heck reactions on vinyl and alkynyl silanes, respectively **3** and **5** (Scheme 1). In the first case (equation A, scheme 1), the reaction led to the targeted compound **4** in a modest 23% yield and notably the major compound **4'** (60% yield) resulted from the migration of the alkene moiety from the silicon atom to the *ortho* position of the aromatic ring. When applied to substrate **5** bearing an alkynylsilane (equation B, Scheme 1), no traces of the silacyclic compound was observed as only the product **6** rising from the migration of the alkyne was obtained in a 74% yield. From these preliminary results, it appeared that the 5-*exo*-dig cyclization would be challenging. We concluded that the product and/or the intermediate in this type of cyclizations was perhaps too sensitive and systematically rearranged to the undesired acyclic silane **6**. Based on this assessment we considered that our approach involving an additional step of cross coupling could overcome this issue by potentially stabilizing the palladium intermediate that would be involved in the Suzuki-Miyaura coupling[14] and also the product of the cyclization by having a more substituted exocyclic C=C double bond. We hoped that all together these stabilizations could be the key to access efficiently the targeted exocyclic vinylsilanes **8**.

Another point that had to be addressed was the usual regioselectivity of carbopalladation reactions on silylalkynes (Figure 1). As reported in the literature the carbo-functionalization classically takes place at the β position of the alkyne installing the palladium on the geminal position of the silicon.[15] Due to the regiospecificity of cyclocarbopalladation reactions when applied to alkynes (*i.e.* syn addition forcing the C=C double bond to be exocyclic), the carbopalladation would have to take place at the α position of the alkynylsilane. For instance Keese neutralized this issue by using a 1,2-disilyl-alkyne (**5**) as substrate (Scheme 1 equation B).



Scheme 1. Cyclocarbopalladation of vinyl and alkynyl silanes.

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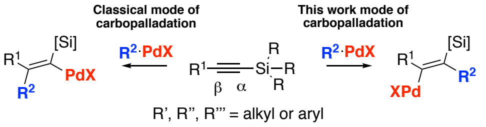


Figure 1. Regioselectivity of the carbopalladation of silylalkynes.

We first prepared, using Keese's synthesis, a range of nine original alkynylsilanes **7a-i** bearing a 2-bromo benzyl group on silicon (Figure 2).[13] Then the reaction conditions were optimized using (2-bromobenzyl)(hept-1-yn-1-yl)dimethylsilane **7a** as substrate and phenyl boronic acid as the coupling partner (Table 1). To start this study we decided to use our classical conditions *i.e.* $Pd(PPh_3)_4$ as catalyst, K_3PO_4 as base in a mixture of 2-MeTHF and H_2O as solvent at 130 °C for 18 h (Table 1, entry 1).[16] To our delight, under these conditions, we succeeded in performing the first cyclocarbopalladation on an alkynylsilane that led to the formation of a silacycle. The domino process was validated as the targeted benzosilole **8a** was obtained in an encouraging 52% yield. Notably, no traces of the direct coupling between the aryl moiety of the starting material and the phenyl boronic acid or of the migration of the alkyne to the *ortho* position of the benzyl silane (compound **8a'**) were detected. A similar result was obtained when the reaction was performed under microwave irradiation at 130 °C during 3 hours. After having confirmed that the presence of water has a beneficial effect on the yield of this domino transformation (Table 1, entry 2), we turned our attention to the influence of the catalytic system. To do so, we have decided to use $Pd(OAc)_2$ as palladium source in addition to diverse phosphines. Monophosphine ligands such as PPh_3 and SPHOS led to similar results to $Pd(PPh_3)_4$ (Table 1, entries 3 & 4). The use of a more hindered ligand like $P(Cy)_3$ resulted in a dramatic decrease of the conversion and the desired product **8a** was obtained in only 12% yield (Table 1, entry 5). The use of a more electron donating phosphine ligand as $P(2\text{-furyl})_3$ led to product **8a** in 34% yield with the rest of the reaction mixture mainly remaining as starting material (Table 1, entry 6). Remarkably, bisphosphine ligands such as BINAP or Xantphos drove the reaction to a complete inversion of selectivity as product **8a'** was exclusively obtained in good yields (Table 1, entries 7 & 8).

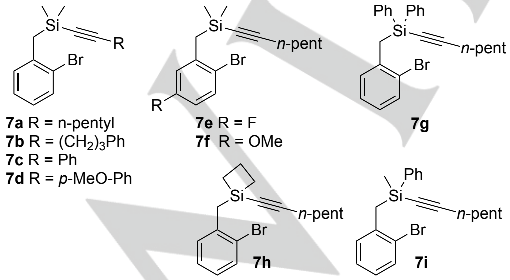
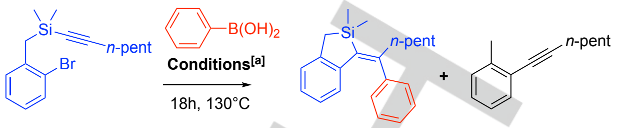


Figure 2. Substrates synthesized to study the domino reaction.

Table 1. Synthesis of benzosiloles starting from silylalkynes and reaction optimisation.

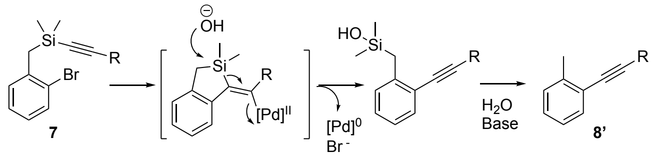


7a **8a** **8a'**

Entry	Catalyst/ligand	Base	Solvent	Yield (ratio **8a/8a'**)
1	$Pd(PPh_3)_4$	K_3PO_4	2-MeTHF/H_2O	52 (1:0)
2	$Pd(PPh_3)_4$	K_3PO_4	2-MeTHF	40 (1:0)
3	$Pd(OAc)_2/PPh_3$	K_3PO_4	2-MeTHF/H_2O	57 (1:0)
4	$Pd(OAc)_2$/SPhos	K_3PO_4	2-MeTHF/H_2O	50 (1:0)
5	$Pd(OAc)_2/P(Cy)_3$	K_3PO_4	2-MeTHF/H_2O	12 (1:0)
6	$Pd(OAc)_2/P(Furyl)_3$	K_3PO_4	2-MeTHF/H_2O	34 (1:0)
7	$Pd(OAc)_2$/Binap	K_3PO_4	2-MeTHF/H_2O	78 (0:1)
8	$Pd(OAc)_2$/Xantphos	K_3PO_4	2-MeTHF/H_2O	80 (0:1)
9	$Pd(OAc)_2/PPh_3$	K_2CO_3	2-MeTHF/H_2O	55 (1:0)
10	$Pd(OAc)_2/PPh_3$	Na_2CO_3	2-MeTHF/H_2O	26 (1:0)
11	$Pd(OAc)_2/PPh_3$	Cs_2CO_3	2-MeTHF/H_2O	45 (1:0)
12	$Pd(OAc)_2/PPh_3$	K_3PO_4	Toluene/H_2O	63 (1:0)
13	$Pd(OAc)_2/PPh_3$	K_3PO_4	MeCN/H_2O	06 (1:0)
14	$Pd(OAc)_2/PPh_3$	K_3PO_4	1,4-dioxane/H_2O	32 (1:0)
15	$Pd(OAc)_2/PPh_3$	Na_2CO_3	1,4-dioxane/H_2O	52 (1:0)
16[b]	$Pd(OAc)_2/PPh_3$	Na_2CO_3	1,4-dioxane/H_2O	68 (1:2)
17[b, c]	$Pd(OAc)_2/PPh_3$	Na_2CO_3	1,4-dioxane/H_2O	73 (2:1)
18[b, d]	$Pd(OAc)_2/PPh_3$	Na_2CO_3	1,4-dioxane/H_2O	78 (1:0)

[a] The reactions were performed under argon using Pd complex (10 mol%), ligand when required (20 mol%), base (3 equiv.), phenyl boronic acid (1.5 equiv.), silane **7a** (1 equiv.) at 0.1 M concentration in the indicated solvent. [b] Addition of TBAI (25 mol%). [c] Reaction performed at 100 °C. [d] Reaction performed at 70 °C.

We can then hypothesize that the use of BINAP or Xantphos decreases dramatically the kinetics of the transmetallation with the coupling partner and so favors the competition with the β-elimination of the palladium species. This hypothesis is supported by the result of a control experiment that consisted of setting up the reaction without any coupling partner. In that case the compound **8a'** was obtained in 76% yield as the sole product. These observations support that the success of this approach lies on the overall domino process (*i.e.* cyclocarbopalladation/Suzuki-Miyaura reaction). According to Keese's experimental observations and ours, the most probable hypothesis for the formation of compound **8a'** is based on the attack of an hydroxide ion on the silicon that results in the opening of the silacycle coming from the carbopalladation step and the β-elimination of the palladium (II) complex (Scheme 2).

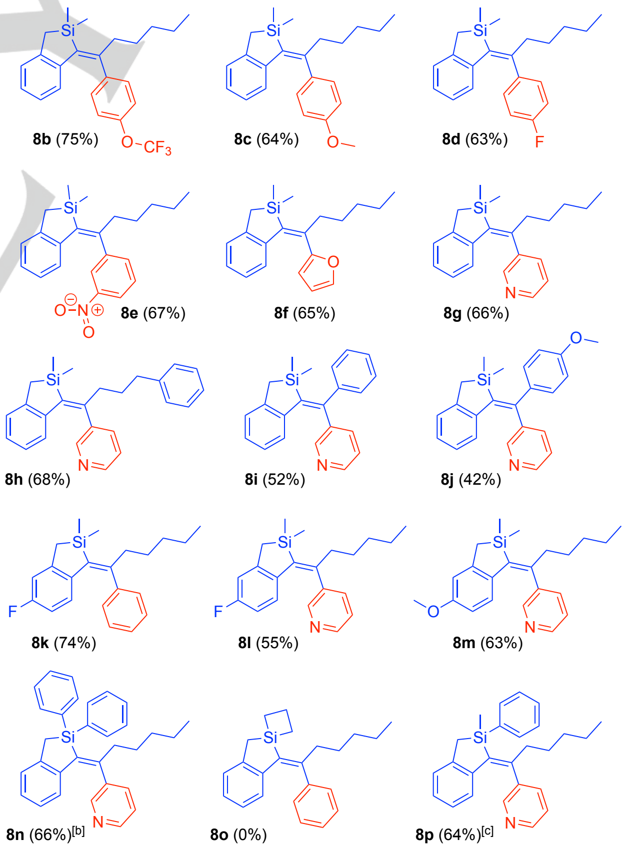


Scheme 2. Potential mechanism for the formation of **8'** from silane **7**.

In followup studies, we decided to turn our attention to the effects of the base under our optimal conditions to date (*i.e.* $Pd(OAc)_2/PPh_3$,130°C, 2-MeTHF/H_2O as solvent). Substituting K_3PO_4 by K_2CO_3 appeared to have no effect on the yield and the selectivity of the reaction (table 1, entry 9), whereas the use of Na_2CO_3 or Cs_2CO_3 gave the desired compound in yields reduced by 30% and 10%, respectively (Table 1, entry 10 & 11). We then focused our attention on the effects of the solvent. When the reaction was performed in toluene, the desired compound was obtain selectively in a respectable 63% yield (Table 1, entry 12). The use of acetonitrile yielded only traces of compound **8a'** and starting material **7a** was mainly degradated (Table 1, entry 13). 1,4-dioxane was then tested and resulted in only a modest 32% yield of **8a** (Table1, entry 14). Remarkably, in this solvent, when the base was shifted from potassium phosphate to sodium carbonate, the yield of **8a** increased by 20% (52%, Table 1, entry 15). The use of an additivie such as TBAI increased the yield by 15% but with a clear erosion of the selectivity in favor of the desilylated product **8a'** (**8a**/**8a'** 1:2) (Table 1, entry 16). Lowering the reaction temperature to 100°C allowed for an equivalent yield but with a complete inversion of selectivity in favor of the desired silacyclic product (**8a**/**8a'** 2:1) (Table 1, entry 17). Finally, our best result was obtained when the reaction was performed with $Pd(OAc)_2/PPh_3$ as catalyst, sodium carbonate as base in a mixture of water in 1,4-dioxane at 70°C. In that case compound **8a** was obtained selectively in a synthetically useful 78% yield after 18 h (table 1, entry 18).

With these optimized conditions in hand we then decided to study the scope and limitations of the reaction (Table 2). For a first time, the influence of the coupling partner was evaluated. Toward this end, we performed the reaction by using the silane **7a** as substrate in presence of various subtituted aryl boronic acids. Pleasingly, substituting the aromatic ring of the boronic acid with an eletron-donating group such as OCF_3 group at the *para* position gave the targeted benzosilole **8b** in a similar 75% yield. Notably, when (4-methoxyphenyl)boronic acid was used as coupling partner, the efficiency of the reaction slightly decreased and the desired product **8c** was obtained in 64% yield. When electron withdrawing groups such as a fluorine or a nitro group were used in position 4 of the arylboronic acid the respective benzosiloles **8d** and **8e** were obtained in comparable yields (63% and 67%). The use of heteroarylboronic acids as coupling partners did not affect the behavior of the domino process. For instance, products **8f** and **8g** bearing a furyl and a pyridyl group respectively were attained in about 65% yield. For a second time we investigated the effects of the substitution on the alkyne moiety. Logically, replacing the heptynyl chain by a 5-phenylpent-1-yn-1-yl chain (substrate **7b**) did not impact the quality of the reaction as the corresponding product **8h** was obtained in a similar 68% yield. However, when the alkyne was substituted with an aryl group the yield decreased significantly. For instance, substrates **7c** and **7d,** bearing a phenyl and a *p*-methoxyphenyl respectively, were submitted to the domino sequence and the corresponding products **8i** and **8j** were reached in 52% and 42% yields, respectively. Next, we focused on the effect of substitution on the benzyl moiety worn by the silicon. Pleasingly, the presence of an electron-withdrawing group such as fluorine at the position 5 of the aromatic ring (substrate **7e**) did not impact the efficiency of the reaction and the targeted vinylsilanes **8k** and **8l** were obtained in comparable yields to those obtained with an unsubstituted benzyl group (respectively 74% and 55%). Interestingly, the electron-rich subtrate **7f**, bearing a methoxy group, led efficiently to the desired vinylsilane **8m** in a slightly lower yield (63%). Finally, the influence of the substituents on the silicon atom has been investigated. When performed on substrate **7g** bearing two phenyl groups, the reaction led only to traces of the corresponding silacycle **8n**. However, this issue was easily overcome by using $Pd(PPh_3)_4$ as catalyst and **8n** was obtained in a good 66% yield. Unfortunately, substrate **7h** bearing a siletane did not convert to the targeted spirocyclic product **8o**. The reaction led only to a degradation of the starting

Table 2. Scope of the domino carbopalladation/Suzuki-Miyaura coupling sequence.[a]



[a] The reactions were performed under argon at 70 °C for 18 h using $Pd(OAc)_2$ (10 mol%), PPh_3 (20 mol%), Na_2CO_3 (3 equiv.), TBAI (0.25 equiv.), boronic acid (1.5 equiv.), silane **7** (1 equiv.) at 0.1 M concentration in the indicated solvent; [b] $Pd(PPh_3)_4$ as catalyst; [c] Reaction performed at 90°C.

material. Presumably, this can be explained by the specific reactivity of strained silacycles when brought into contact with palladium complexes.[17] Finally, when substrate **7i**, bearing a silicon centre linked to four different substitutents, was submitted to our optimal reaction conditions, no traces of the desired product **8p** were detected but increasing the temperature to 90°C allowed us to reach this vinylsilane in a 64% yield.

In conclusion, an unprecedented synthesis of cyclic vinylsilanes bearing an exocyclic fully substituted carbon-carbon double bond has been developed. This approach is based on the first examples of palladium-catalyzed domino reaction involving a cyclocarbopalladation of (*o*-bromobenzyl)alkynylsilanes. This transformation is tolerant to a broad range of substitutions both on the silylalkyne and the aryl coupling partner. The overall domino process appeared to be essential to avoid a competitive migration of the alkynyl moiety. At the present time our group is extending this methodology to the synthesis of other families of silacycles and the results of these investigations will be reported in due course.

Acknowledgements

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Keywords: silacycle • carbopalladation • domino • vinylsilane • palladium

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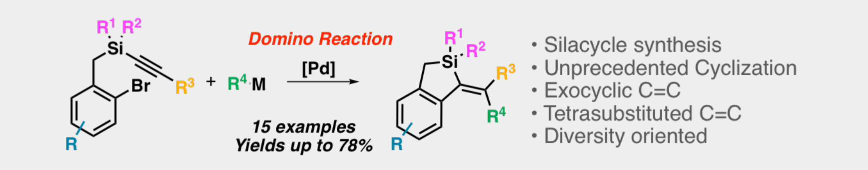

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Synthesis of Benzo[c]silole Derivatives Bearing a Tetrasubstituted Exocyclic C=C Double Bond by Palladium-Catalyzed Domino Reactions.

Silicon prefers to play dominos. The synthesis of diversely substituted benzo[*c*]silole derivatives via an unprecedented domino sequence involving the cyclocarbopalladation of an internal silylalkyne is reported. This reaction proceeds with a complete stereoselectivity to lead to a fully substituted exocyclic C=C double bond. Notably the domino sequence appears to be crucial to the success of this approach.