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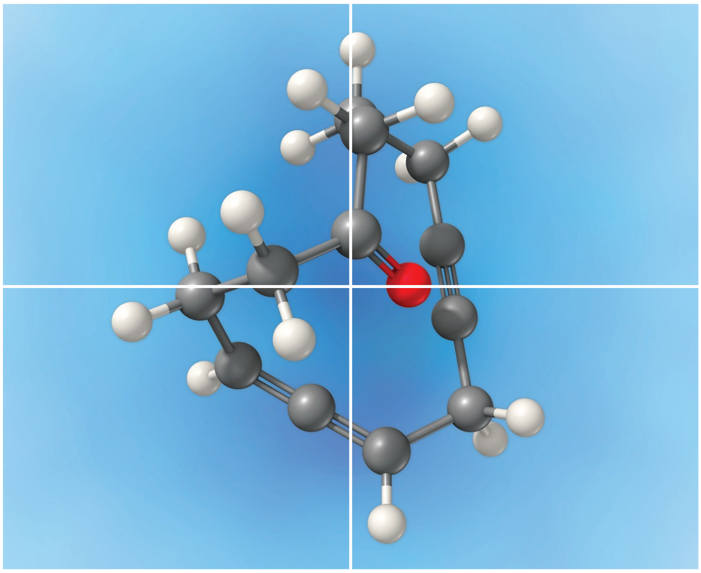

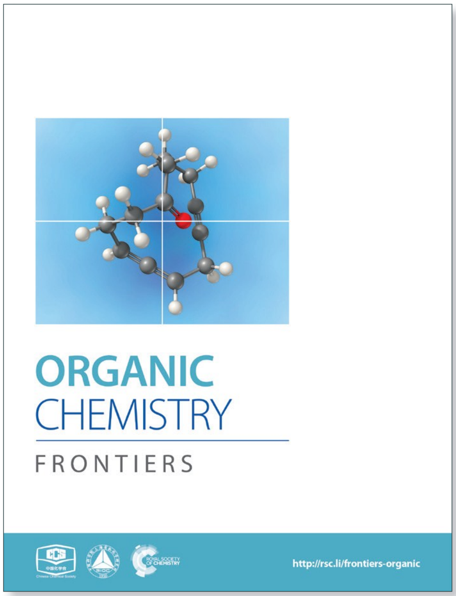

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ARTICLE

Synthesis of silafluorenes and silaindenes via silyl radicals from arylhydrosilanes: intramolecular cyclization and intermolecular annulation with alkynes

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Intramolecular homolytic aromatic silylation of biphenyl-2-hydrosilanes via silyl radicals has been developed for the synthesis of silafluorenes. Moreover, silaindenes are synthesized via a silyl radical cascade process, assembling internal alkynes with readily available arylhydrosilanes by C-H and Si-H cleavage and C-C and C-Si bond formation in one step. These represent a new simple and efficient approach towards the synthesis of benzosilole derivatives.

Siloles (silacyclopentadienes) and their π-extended derivatives, such as silaindenes and silafluorenes, have attracted considerable interests because of their application as building blocks or structural moieties in organic electronics materials.[1,2] Conventional synthetic approaches towards silole derivatives (Scheme 1) employed the reactions of di-chlorosilane with highly reactive organometallic reagents[3] and intramolecular reductive cyclization of alkynyl silanes.[4] Recently, transition metal-catalyzed approaches have also been developed to synthesize diverse siloles,[5] silaindenes[6] and silafluorenes[6b,7] derivatives under mild conditions. While these synthetic methods have greatly improved the accessibility to silaindenes and silafluorenes, most of them start from difunctionalized precursors, such as 2,2'-dihalobiaryls,[3a-e,7e] silicon-bridged diynes,[7a,7g] 2-(arylsilyl)aryl triflate,[7b,c] (2'-bromobiphen-2-yl)silane,[7f] 2-trimethylsilylarylboronic acid[6b,6f] and 2-trimethylsilyl arylbromide.[6e,6h] To the best of our knowledge, no precedent synthetic method toward silaindenes from *ortho*-unsubstituted arylsilanes through direct C-H bond functionalization has been reported. As for silafluorenes, ~~the only~~ two existing approaches ~~towards silafluorenes~~ involving a direct intramolecular aromatic C-H silylation process were based on Rh-catalyzed double activation of Si-H and C-H bonds[7d,7h] and sila-Friedel-Crafts reaction[8] respectively. ~~As for silaindenes, no synthetic method through direct C-H bond cleavage has been developed.~~ In continuing our research on main group elements-centered radicals,[9] we wanted to devise more general and efficient methods to synthesize these molecules. In this report, we describe a silyl radical-based strategy~~[10]~~ for silafluorenes and silaindenes via direct C-H bond cleavage of readily available arylsilanes without the aid of transition metals, acids or bases. During our preparation of this manuscript, such an approach was also disclosed by Leifert and Studer for synthesis of silafluorenes.[10]

Our hypothesis applying silyl radicals in the synthesis of silafluorenes was inspired by the recent development of intramolecular aromatic homolytic substitution reactions, especially the intramolecular radical cyclization reactions of biaryl frameworks.[11] For examples, radical phosphination[12] and acylation[13] on the aryl group was induced by simple radical generators to afford dibenzophospholes and fluorenones respectively.

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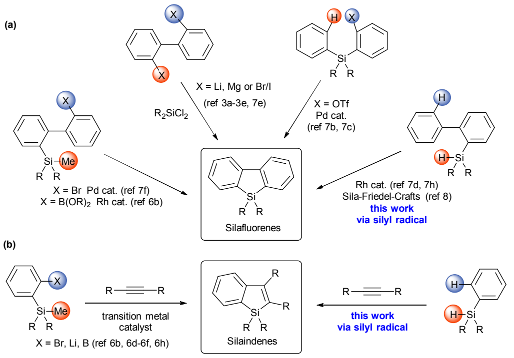
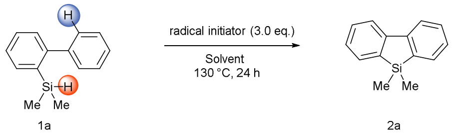


Scheme 1 General approaches to access silafluorenes and silaindenes

We initiated our studies by examining the reaction between biphenyl-2-hydrosilane **1a** as the silyl radical precursor and DTBP (di-*tert*-butyl peroxide) as a radical initiator in various solvents (Table 1). To our delight, the desired intramolecular homolytic aromatic silylation product, **2a**, could be obtained in 79% yield based on ^1H NMR analysis of the crude product when 1a was stirred with 3.0 equivalent of DTBP in benzene at 130 °C for 24 hours (entry 5). Using other solvents (e.g., MeCN or toluene) resulted in lower yields (entries 1-4). To further improve the yield, variant radical initiators were examined, however, all the tested radical initiators including BPO (benzoyl peroxide), AIBN (azodiisobutyronitrile) and TBHP (*tert*-butyl hydroperoxide) gave very low yields (entries 7-9).

The reaction was also performed under air atmosphere and a moderate yield (66%, entry 14) was obtained. Because some examples of base-promoted homolytic aromatic substitution (BHAS) process have been reported,[14] the effect of additive bases was briefly explored. In the present reaction, however, the added bases did not show significant beneficial effect (entries 10-13). Finally, an extensive screening of various solvents revealed trifluorotoluene to be the optimal solvent because of its higher boiling point, potentially lower toxicity and the resulting higher yield than benzene (entry 9).

Table 1. Optimization of Reaction Parameters[a]

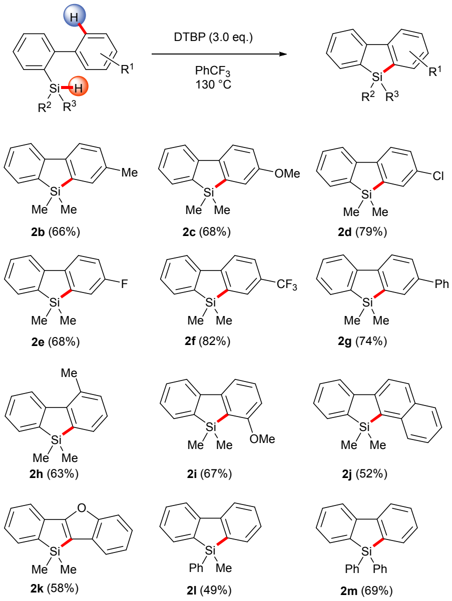


Entry	initiator	Solvent	Additive	Yield (%)[b]
1	DTBP	MeCN	-	46
2	DTBP	toluene	-	39
3	DTBP	DCE	-	36
4	DTBP	1.4-dioxane	-	57
5	DTBP	benzene	-	79
6	BPO	benzene	-	19
7	AIBN	benzene	-	trace
8	TBHP[c]	benzene	-	26
9	**DTBP**	**$PhCF_3$**	**-**	**84 (77)**[d]
10	DTBP	benzene	K_2CO_3 (3 eq.)	75
11	DTBP	benzene	*t*BuOLi(3 eq.)	64
12	DTBP	benzene	KOAc (3 eq.)	72
13	DTBP	benzene	K_3PO_4 (3 eq.)	60
14	DTBP	benzene	-	66[e]

[a] Reaction conditions: biphenyl-2-yldimethylsilane (0.1 mmol), radical initiator (0.3 mmol), additive (if necessary), solvent (0.5 ml) under N_2 atomosphere. [b] Yields based on ^1H NMR analysis of the crude products with 1,3,5-trimethoxybenzene added as an internal standard. [c] 70% solvent in H_2O. [d] Isolated yield shown in parenthesis. [e] the reaction was performed under air.

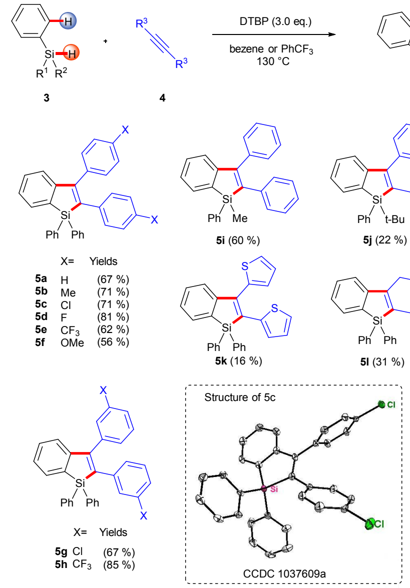
With the optimized condition in hand, the homolytic aromatic silylation method was applied for various 2-hydrosilyl biaryls. Biphenylhydrosilanes bearing electron-withdrawing and -donating groups at the 4'-position all gave desired silafluorenes in good yields (Scheme 2, **2b**-**2g**). A methyl group at the 2'-position was tolerated and the corresponding silafluorene derivative 2h was obtained in 63% yield. In this case, 9,10-dihydro-9-silaphenanthrene, which had been the major product of the Rh-catalyzed pathway[7d] due to intramolecular silylation on the methyl group, was not observed. When a biarylhydrosilane bearing a 3'-methoxy group (**1i**) was used as the substrate, the radical silylation occurred selectively at the more hindered position to produce **2i**, presumably governed by electronic effect. This regioselectivity was in sharp contrast with transition metal-catalyzed C-H activation wherein reactions usually take place at the least hindered position; therefore the present method is complementary in preparation of this type of silafluorenes. Furthermore, π-extended silafluorenes **2g**, **2j** and **2k** which may impart unusual electronic properties on the molecules could be obtained by this method. Finally, the substituents on the silicon center were also variable, thus single or double phenyl substituted silanes were converted to the corresponding products under the same conditions (**2l** and **2m**).

Radical cascade reactions are well known as powerful methods to enable quick access to complex compounds containing polycyclic frameworks.[15] In this context, intermolecular annulation of an arene-containing radical species with an alkyne might form highly substituted arene-fused rings in a concise fashion.[16] In fact, the selenium-centered radical has been reported to undergo this type of reaction to form a benzoselenophene as the minor product in a radical 1,2-addition process of $(PhSe)_2$ onto an alkyne.[17] More recently, benzophosphole oxides were elegantly accessed via this strategy.[18] It is known that silyl radicals can add to alkynes to form a new Si-C bond and a vinyl radical intermediate in radical hydrosilylation reactions,[10, 19] we therefore questioned whether silaindenes (benzosiloles) might be synthesized in a similar manner. Thus arylhydrosilanes, as silyl radical precursors, would intermolecularly react with alkynes to generate the vinyl radical intermediates that may be intramolecularly intercepted by the appendant aryl groups. Because many arylhydrosilanes are readily available, this approach would represent a more practical method in preparation of silaindenes than the previous ones which necessitate ortho-halogenated or -metalated arylsilanes (Scheme 1b).

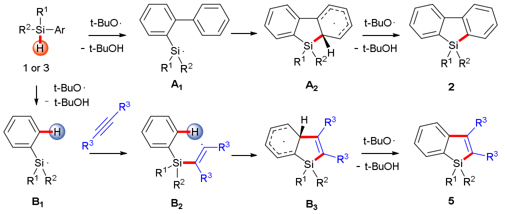


Scheme 2 Silafluorene synthesis via intramolecular homolytic aromatic silylation reaction

In practice, we first used commercially available triphenylhydrosilane (Ph_3SiH, **3a**) and 1,2-diphenylacetylene as the substrates and simply transplanted the reaction conditions of the above intramolecular silylation reaction (Scheme 3). Pleasingly, the corresponding silaindene **5a** could be isolated in 67% yield. Based on this success, we further examined the scope and limitations of this intermolecular radical annulation reaction. Diarylacetylenes containing electron-donating and electron-withdrawing groups are all viable reaction partners, leading to multiaryl-substituted silaindenes in moderate to good yields (**5a**-**5h**). Notably, these 1,1,2,3-tetraaryl silaindenes, which had not been synthesized via any previously existing methods, could be obtained via the current reaction in just one step from simple building blocks. A dithiophen-2-yl-acetylene and a dialkylacetylene were also used in the same condition but gave low yields of the desired products (**5k**, **5l**). When one of the substituents on the silyl group varied from phenyl to a methyl, the corresponding silaindene **5i** was obtained in 60% yield. A more hindered *tert*-butyl group on the silicon center could also be used, although with decreased yield (**5j**).



Scheme 3 Silaindenes synthesis via intermolecular radical annulation



Scheme 4 Reaction mechanism

On the basis of the established silyl radical chemistry[10] and other aromatic homolytic substitution[11] and radical cascade reactions,[15] we propose two possible reaction pathways as shown in Scheme 4. In both pathways, silyl radical is generated through homolytic Si-H bond cleavage. For the formation of silafluorenes, the intramolecular addition of the silyl radical onto the proximal arene generates the cyclohexadienyl radical **A2**. Hydrogen elimination of **A2** assisted by *tert*-butoxyl radical will give the rearomatized final product **2**. For silaindenes, the addition of the silyl radical across the alkyne triple bond generates the highly reactive alkenyl radical **B2** which then undergo intramolecular addition onto the phenyl moiety, forming another cyclohexadienyl radical **B3**. This radical eventually leads to silaindene **5**, again by *tert*-butoxyl radical mediated hydrogen abstraction.

In conclusion, we have developed a direct and efficient strategy employing aryl silyl radical intermediates towards the synthesis of silafluorenes and silaindenes. These reactions start from readily available arylhydrosilanes, proceed in a transition metal, base or acid-free system and furnish the products via direct Si-H and C-H cleavage pathways in one step. These synthetic methods are complementary to the existing ones towards benzosilole derivatives. Further extension and application of these reactions are underway in our laboratory.

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Electronic Supplementary Information (ESI) available: [Materials including experimental procedures, copies of ^{1}H and ^{13}C NMR spectra of all new products and crystallographic data for 5c]. See DOI: 10.1039/b000000x/

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20 CCDC 1037609 (5c) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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