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9-Silafluorenes via Base-Promoted Homolytic Aromatic Substitution (BHAS) – The Electron as a Catalyst

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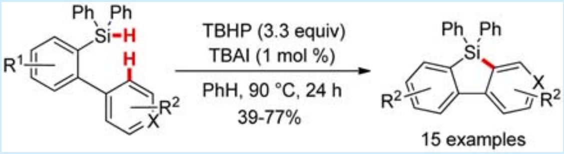
Supporting Information

ABSTRACT: Transition-metal-free intramolecular radical silylation of 2-diphenylsilylbiaryls via base-promoted homolytic aromatic substitution (BHAS) to give 9-silafluorenes is reported. 2-Diphenylsilylbiaryls are readily prepared, and cross dehydrogenative silylation occurs with *tert*-butylhydroperoxide (TBHP) as a cheap stoichiometric oxidant in the presence of a small amount of tetrabutylammonium iodide (TBAI) as an initiator. These cyclizations are catalyzed by the electron.



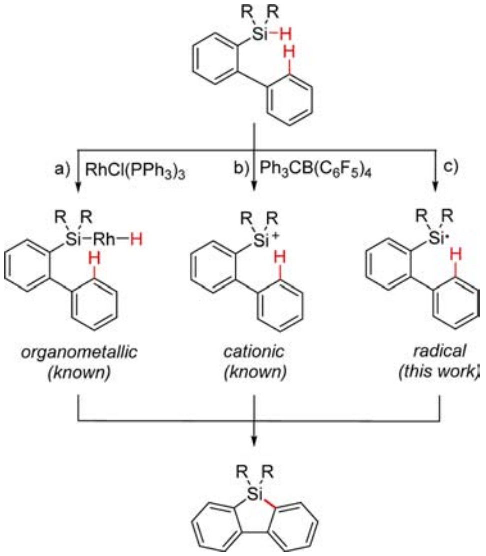
In the past few years, silicon derivatives in which the silicon atom is integrated into a π-system have gained increased attention due to their interesting physical properties. As members of this class of compounds, 9-silafluorenes, that are silicon bridged biaryls, have gained particular attention due to their highly valued use in functional organic materials.[1] For example, they have been integrated into OLEDs,[2] OFETs,[3] photovoltaic cells,[4] and fluorescent sensors.[5]

There are several reported synthetic routes toward 9-silafluorenes.[1,6] Shimizu et al. used C–C-bond formation in 2-(arylsilyl)aryl triflates as the key step for construction of the biaryl moiety via palladium catalysis.[7] It is also possible to access 9-silafluorenes via iridium-catalyzed [2 + 2 + 2]-cyclizations starting from diynes.[8] Furthermore, these interesting silyl derivatives have been successfully prepared from 2,2′-dihalogenated biaryls by metal–halogen exchange and subsequent cyclization with dihalosilanes[9] or via palladium-catalyzed silylation with dihydrosilanes.[10] The target compounds can also be obtained via palladium-[11] or rhodium-catalyzed[12] demethylative silylation of 2-methylsilyl-2′-bromo- or 2′-boronobiaryls, respectively.

In contrast to the intensively investigated transformations of doubly prefunctionalized substrates, to our knowledge only two processes that are a rhodium-catalyzed cyclization[13] (Scheme 1a) and a sila-Friedel–Crafts type reaction[14] (Scheme 1b) describing cross dehydrogenative cyclization starting with 2-biarylsilanes to give 9-silafluorenes are known in the literature. As compared to the above-discussed procedures which use doubly prefunctionalized precursors, an advantage of these two latter reactions is the ready access of the starting 2-biarylsilanes from 2-bromobiaryls.[13a] However, as a drawback of the Rh-version the price of the expensive catalyst has to be considered. We therefore regard the development of metal-free variants as important. Moreover, regarding the cationic metal-free sila-Friedel–Crafts reaction, the reactive trityl cation which is used as a stoichiometric reagent restricts the scope of that method.[14]

Motivated by recent results in radical fluorenone synthesis[15] we decided to develop an efficient new method for transition-metal-free preparation of 9-silafluorenes via radical chemistry by using readily accessible 2-biarylsilanes as precursors (Scheme 1c).

Scheme 1. A 9-Silafluorene from a 2-Biarylsilane



There are several options for the clean generation of silyl radicals from silanes, and various reactions involving silyl radicals have been developed.[16] Silyl radicals are known to add to alkenes,[17] and also homolytic aromatic substitutions with Si-radicals have been reported, albeit these latter reactions occur with lower efficiency.[18] Mareš and Chvalovský reported the synthesis of 9,9-dimethyl-9-silafluorene from the corresponding silane by a homolytic aromatic substitution via pyrolysis at around 600 °C.[18a] However, the silafluorene was only formed in traces.

We decided to use cheap and commercial *tert*-butylhydroperoxide (TBHP) in combination with TBAI as an initiator[19,15b]

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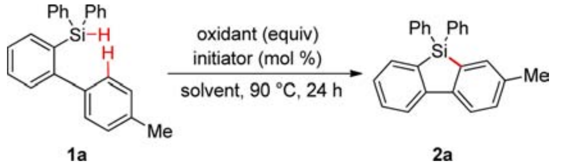
for generation of silyl radicals.[20] An obvious problem in this approach is the competing oxidation of the intermediately generated silyl radical by the *tert*-butylperoxyl radical to the corresponding silanol derivative.[21]

For reaction optimization the *para*-methylbiphenyl **1a** was used as a model substrate. Preparation of **1a** and all other silylated biphenyls is described in the Supporting Information (SI). Reactions were carried out in benzene at 90 °C in a sealed tube for 24 h, and different initiators (1 mol %) were tested. With iron(II) and iron(III) salts only low yields of the targeted silafluorene **2a** were obtained (Table 1, entries 1−3). By using copper(II) chloride the yield was increased (53%) (Table 1, entry 4), but CuOAc showed a lower initiator efficiency (39%) (Table 1, entry 5). Interestingly, CuI led to an improved yield of the desired 9-silafluorene (66%) (Table 1, entry 6). We assumed that the iodide anion in this salt supports initiation, which was proven by using TBAI (Table 1, entry 7). A similar yield as that for the CuI-initiated process was achieved with TBAI upon using a slightly higher amount of TBHP (65%) (Table 1, entry 8). Further increasing the amount of oxidant did not provide a better result (Table 1, entries 9, 10). Considering the green chemistry aspect, we decided to further optimize following the metal-free variant (Table 1, entry 8).

Table 1. Reaction Optimization Using 1a as a Substrate



entry	oxidant (equiv)	initiator (mol %)	solvent	yield (%)[a]
1	TBHP (2.2)	$FeCp_2$ (1.0)	benzene	34
2	TBHP (2.2)	$FeCl_3$ (1.0)	benzene	37
3	TBHP (2.2)	$Fe(acac)_2$ (1.0)	benzene	28
4	TBHP (2.2)	$CuCl_2$ (1.0)	benzene	53
5	TBHP (2.2)	CuOAc (1.0)	benzene	39
6	TBHP (2.2)	CuI (1.0)	benzene	66
7	TBHP (2.2)	TBAI (1.0)	benzene	55
8	TBHP (3.3)	TBAI (1.0)	benzene	65
9	TBHP (4.4)	TBAI (1.0)	benzene	62
10	TBHP (5.5)	TBAI (1.0)	benzene	58
11	TBHP (3.3)	TBAI (1.0)	MeCN	19
12	TBHP (3.3)	TBAI (1.0)	MTBE	26
13	TBHP (3.3)	TBAI (1.0)	DMA	traces
14	TBHP (3.3)	TBAI (1.0)	DMSO	11
15	TBHP (3.3)	TBAI (0.4)	benzene	46
16	TBHP (3.3)	TBAI (0.8)	benzene	63
17	TBHP (3.3)	TBAI (1.5)	benzene	62
18	TBHP (3.3)	TBAI (2.0)	benzene	59
19	TBHP (3.3)	TBAI (5.0)	benzene	42
20	TBPB (2.2)	TBAI (1.0)	benzene	33
21	CHP (3.3)	TBAI (1.0)	benzene	51
22	TBHP (3.3)	TBAI (1.0)	benzene	13[b]
23	TBHP (3.3)	TBAI (1.0)	benzene	51[c]

[a] Determined by ^1H NMR using CH_2Br_2 as an internal standard. [b] Addition of KOH (20 mol %). [c] Addition of PivOH (20 mol %).

Other solvents such as acetonitrile, *tert*-butylmethyl ether, dimethylformamide, and dimethyl sulfoxide (Table 1, entries 11−14) and varying the amount of initiator did not lead to improved yields (Table 1, entries 15−19). Using *tert*-butyl peroxybenzoate (TBPB) and cumylhydroperoxide (CHP) as oxidants (Table 1, entries 20 and 21) or adding potassium hydroxide or pivalic acid as additives (Table 1, entries 22 and 23) did not show any beneficial effects.

With the optimized conditions identified (entry 8), we investigated the scope and limitation of the intramolecular cross dehydrogenative silylation (Figure 1). With the unsubstituted silafluorene **2b** a slightly higher isolated yield (66%) was obtained as compared to **2a**. The yield further improved by switching to the *tert*-butyl substituted congener **1c** to afford silafluorene **2c** in 71% yield. Fluorinated biphenyl derivatives showed similar yields (**2d**−**f**). Regioselectivity was moderate for the *meta*-fluoro system **1e** to give **2e** and **2e**′ as a 2.5:1 mixture of isomers. In agreement with earlier reports on similar BHAS, the *ortho*-isomer was formed as a major product.[15b,22d] Since the sterically slightly more hindered isomer was formed as the major compound, we assume regioselectivity to be steered by electronic effects. Assignment of the major regioisomer to structure **2e** is based on NMR spectroscopy. Biphenyls bearing

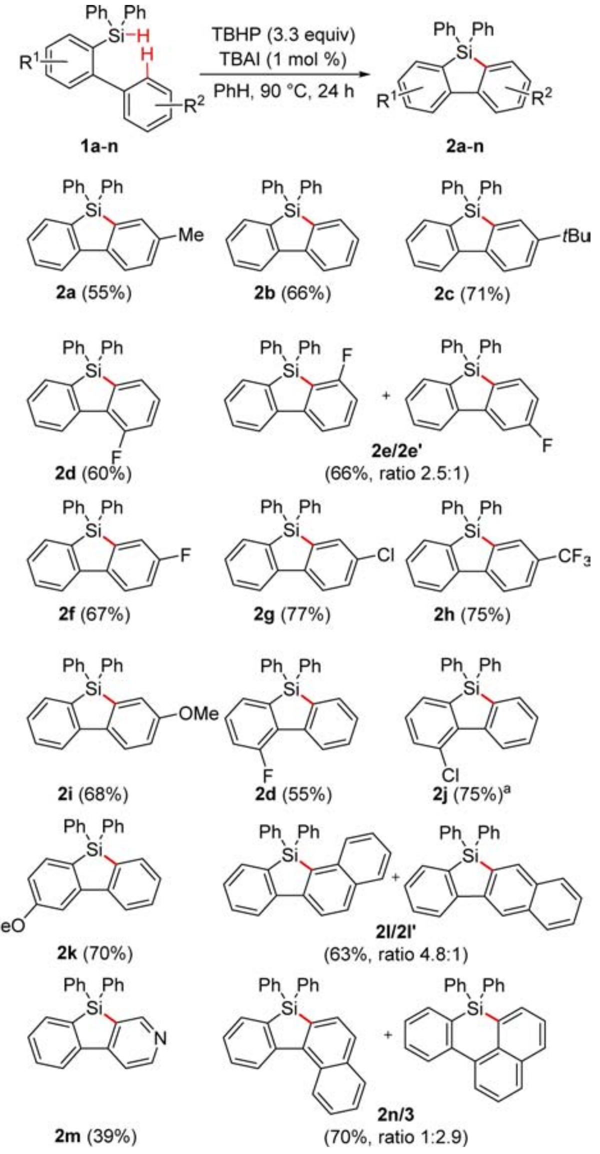


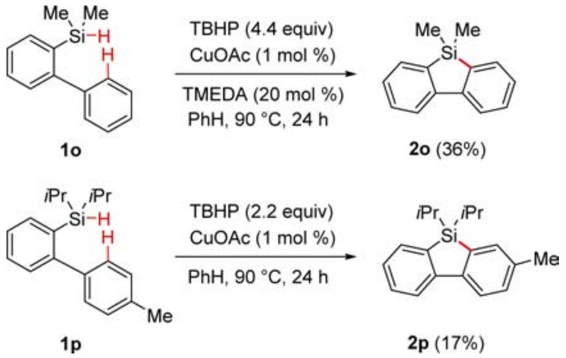
Figure 1. Various silafluorenes **2a**−**n** prepared (isolated yields). [a] Isolated as an inseparable mixture with starting silane **1j**.

other electron-withdrawing groups at the *para*-position, such as chloride and trifluoromethyl, afforded the corresponding products **2g** and **2h** in 77% and 75% isolated yield, respectively. The reaction also worked well for the electron-richer methoxy derivative (see **2i**, 68%).

We next investigated biphenyls **1d′** and **1j−k** which carry additional substituents at the arene moiety containing the diphenylsilyl group. An electron-withdrawing group at the 6-position is tolerated: **2d** and **2j** were obtained in moderate to good yields (55% and 75%). Biphenyl **1k** with a methoxy group in the 5-position provided silafluorene **2k** in 70% yield. Cyclization on a pyridine ring was less efficient, as shown for the preparation of **2m** which was obtained in 39% yield. The lower yield is likely due to the fact that pyridines show higher reactivity toward homolytic aromatic substitution at the 2- and 4-position.[23] Cyclization on naphthalene ring systems did not proceed regioselectively. In accordance with previous reports,[22] for the 2-naphthyl derivative **1l**, regioisomer **2l** was formed as the major product (**2l**/**2l′** = 4.8:1).[24] By using the 1-naphthyl congener **1n**, we found formation of the six-membered ring to give **3** to be favored over cyclization to the silafluorene **2n** (**2n**/**3** = 1:2.9)

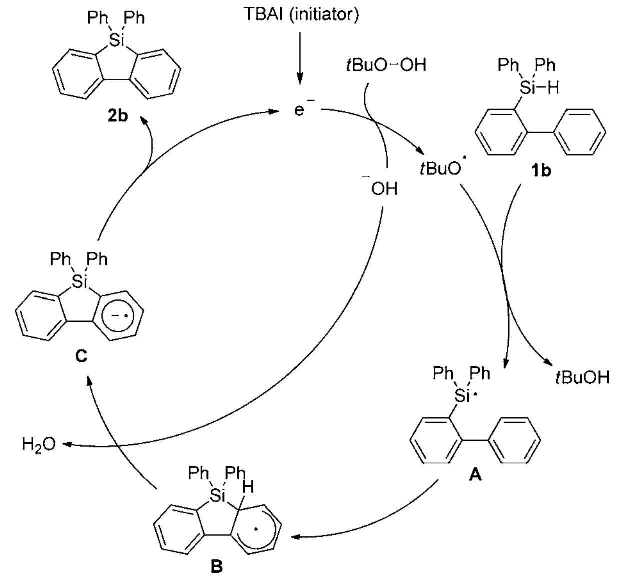
Finally, we tested whether the two Si-phenyl substituents can be replaced by alkyl groups. To this end, silanes **1o** and **1p** were prepared (see SI). A significantly lower NMR yield (25%) was obtained under standard metal-free conditions for the dimethyl derivative **1o** to give **2o**. A slightly improved yield (36%) for this reaction was achieved by using CuOAc (1 mol %) as a catalyst in the presence of tetramethylethylenediamine (TMEDA, Scheme 2).[25] An even lower yield was obtained with the sterically more hindered isopropyl derivative **1p** to afford **2p** by using the metal-free protocol (21%, NMR yield), and also for the Cu-catalyzed process the yield was not satisfactory (17% isolated).

Scheme 2. Cyclization of Bisalkyl-Substituted Silanes



The suggested mechanism for the silylative cross dehydrogenative coupling is presented in Scheme 3. We assume that TBAI acts as an initiator and not as a catalyst.[26,27a] In the initiation step, single electron transfer (SET) from the iodide to TBHP provides the *tert*-butoxyl radical along with the hydroxyl anion. The *tert*-butoxyl radical then abstracts the H atom from the silane **1b** to give the corresponding Si-centered radical **A** which cyclizes to cyclohexadienyl radical **B**.[28] The acidic proton[15b,22b] in **B** gets deprotonated by the hydroxyl anion to give the radical anion **C** which is a good single electron reducing agent. Formal liberation of an electron from **C** eventually provides product **2b** thereby closing the catalytic cycle, revealing that the electron acts as catalyst in this process.[27]

Scheme 3. Suggested Mechanism



In summary, we have presented a novel and environmentally benign method for the preparation of 9-silafluorenes from easily accessible biaryldiphenylsilanes with TBHP as a cheap and commercially available reagent and TBAI as an initiator. These reactions occur via intramolecular base-promoted homolytic aromatic substitution (BHAS). The novel process represents a further example of a reaction following the "Electron is a Catalyst" concept.[27a] 9-Silafluorenes are important compounds with potential applications as components in organic materials[2−5] which are now accessible via this inexpensive and metal-free approach.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and characterization data for the starting material and products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(24) In the silyl radical addition eventually leading to the major regioisomer **2m**, the cyclohexadienyl radical is likely better stabilized since two resonance structures can be drawn without destroying the aromaticity of the second arene moiety of the naphthalene core. For the regioisomeric cyclohexadienyl radical only one resonance structure keeping the arene resonance of the second ring intact can be drawn.

(25) The Cu-free variant delivered large amounts of silyl radical oxidation product (silanol). This is likely due to the fact that the silyl radical is sterically less shielded as compared to the diphenylsilyl radicals. This side reaction could be better suppressed with the Cu-protocol. We assume that the silanol derives from trapping of the Si-radical with the rather long-lived *tert*-butylperoxyl radical and that in the Cu-version concentration of the peroxyl radical is lower.

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(28) It is also possible that the *tert*-butoxyl radical abstracts an H atom from TBHP to give the *tert*-butylperoxyl radical which then abstracts the H-atom from the silane.