C–H Silylation

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A Catalytic S_EAr Approach to Dibenzosiloles Functionalized at Both Benzene Cores**

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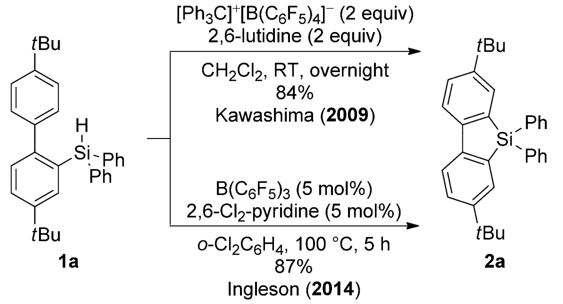
Dedicated to Professor Paul Knochel on the occasion of his 60th birthday

Abstract: *A general procedure for the catalytic preparation of dibenzosiloles functionalized at one or both benzene rings starting from readily available ortho-silylated biphenyls is reported. This method provides rapid access to silole building blocks substituted with chlorine atoms at both phenylene groups, thereby allowing catalytic access to directly polymerizable dibenzosiloles. Moreover, it is shown that, despite the involvement of highly electrophilic intermediates, a considerable range of Lewis-basic, for example, oxygen- and nitrogen-containing, functional groups is tolerated. The mechanism of this intramolecular electrophilic aromatic substitution (S_EAr) proceeds through a sulfur-stabilized silicon cation, generated catalytically from the hydrosilane precursor.*

Siloles and their benzannulated congeners continue to attract considerable attention.[1–3] These members of the metallole family distinguish themselves from their all-carbon analogues in their unique electronic structure, and hence are valuable building blocks for π-conjugated conducting polymers. Elegant procedures for the catalytic synthesis of siloles fused to two benzene rings have been reported, including palladium-catalyzed C–H/C–OTf,[4] C–I/Si–H,[5] and Si–Me/C–Br coupling reactions,[6] as well as iridium- and rhodium-catalyzed [2+2+2] cycloadditions of silicon-tethered diynes with alkynes.[7,8] Recently, ring closures starting from *ortho*-silylated biphenyls **1** to dibenzosiloles **2** were established. These approaches are particularly attractive because of the convenient availability of the starting materials, thereby allowing rapid access to functionalized silole motifs. Three conceptually different methods for this intramolecular formation of the C–Si bond were developed:[9] transition-metal-catalyzed C–H/Si–H coupling,[10] homolytic aromatic substitution involving silicon-centered radicals,[11,12] and electrophilic aromatic substitution (S_EAr) with stabilized silicon cations.[13,14]

The last pathway relies on the generation of a silicon electrophile that is subsequently attacked by the proximal aromatic ring. The idea traces back to the work of Kawashima and co-workers, where heterolytic cleavage of the Si–H bond by hydride abstraction with excess $[Ph_3C]^+[B(C_6F_5)_4]^-$ yields a silylium ion (**1a**→**2a**; Scheme 1). A stoichiometric amount of base is required to absorb the strong acid formed during the deprotonation of the Wheland intermediate.[13] The same transformation was achieved by Curless and Ingleson by Si–H bond activation with the strong Lewis acid $B(C_6F_5)_3$ in the presence of a catalytic amount of base.[14]



Scheme 1. Syntheses of dibenzosiloles by Friedel–Crafts-type reactions.

The variety of catalytic transformations to construct dibenzosiloles is impressive, but these methods have rarely been applied to the synthesis of polymerizable systems functionalized at both benzene cores.[15,16] However, such motifs are highly relevant for making polymeric materials by cross-coupling reactions.[17,18] We therefore set out to elaborate an S_EAr-based procedure that allows rapid synthesis of benzannulated silole building blocks with functional groups at both phenylene groups (**1**→**2**; Scheme 2, top left). We had shown before that cationic Ru–S complexes **3**[19] (Scheme 2, top right) cleave the Si–H bond of hydrosilanes R_3SiH (with R = alkyl and aryl) into a sulfur-stabilized silicon cation and a hydride.[20,21] This catalytic generation of a silicon electrophile was then used in the intermolecular S_EAr of indoles.[20] Conversely, benzenes failed to react even when decorated with an electron-donating group. We nevertheless envisioned the application of this activation mode to the intramolecular S_EAr reaction of benzenes, namely to the ring closure of **1** to **2** catalyzed by **3**. The catalytic cycle (Scheme 2, bottom) would start with activation[21] of the Si–H bond by **3** to give the sulfur-stabilized silicon cation (**1**→**4**) followed by the planned S_EAr reaction to form the Wheland intermediate (**4**→**5**) along

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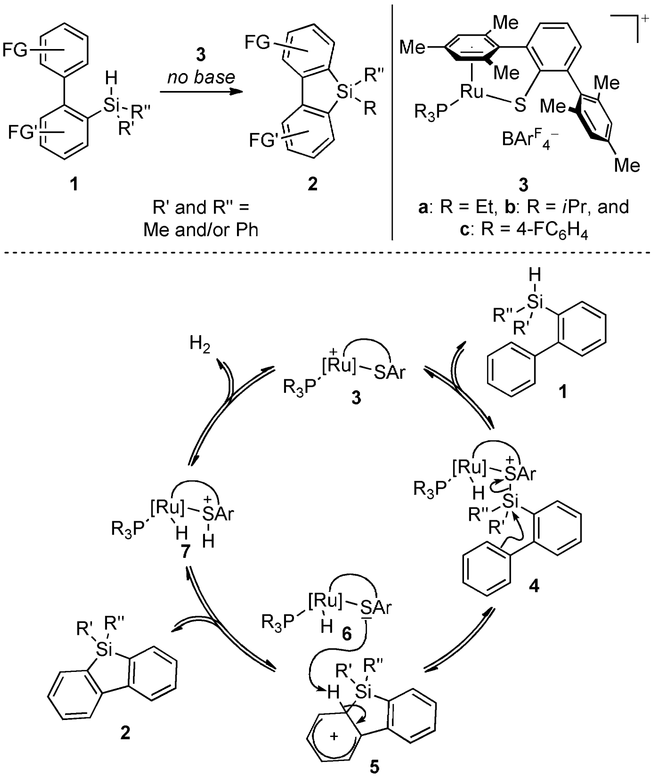
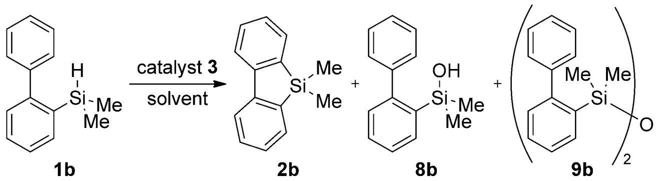


Scheme 2. S_EAr-based C–H silylation (top left; FG = functional group), catalyst **3** with $BAr^F_4{}^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (top right), and proposed catalytic cycle with simplified catalyst structure (bottom; $BAr^F_4{}^-$ counterion omitted for clarity).

Table 1: Optimization of the Friedel–Crafts-type C–H bond silylation.



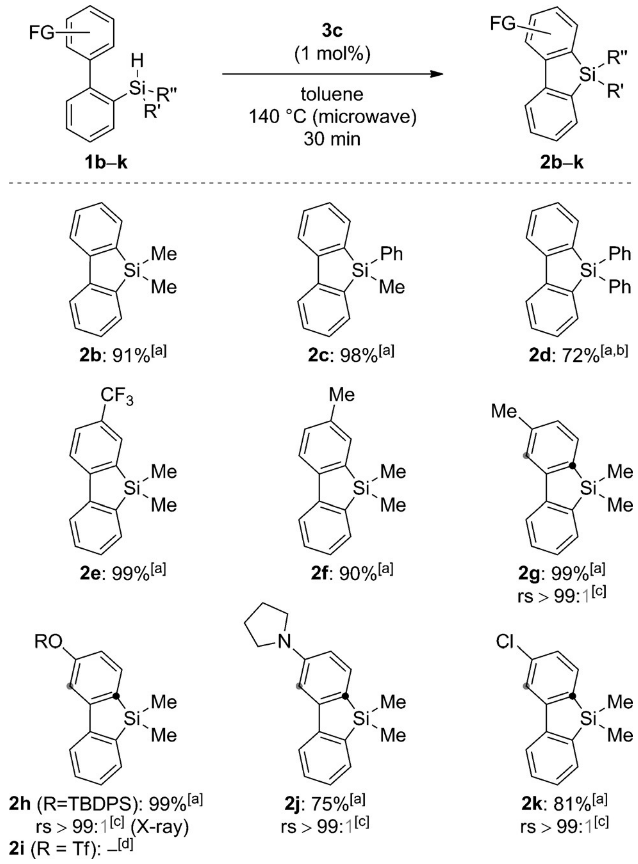
Entry	Catalyst	Solvent	T [°C]	t [h]	Ratio[a] 2b	8b	9b	Conv. [%][b]
1[c]	**3a** (2 mol%)	C_6H_5Cl	90	19	41	2	54	97
2[d]	**3a** (2 mol%)	C_6H_5Cl	120	22	12	8	1	21
3[e]	**3a** (1 mol%)	toluene	140	0.25	20	3	2	25
4[e]	**3b** (1 mol%)	toluene	140	0.25	8	1	2	11
5[e]	**3c** (1 mol%)	**toluene**	**140**	**0.25**	**92**	**2**	**6**	**>99**
6[e]	**3c** (1 mol%)	C_6H_5Cl	140	0.25	90	2	4	96
7[e]	**3c** (1 mol%)	toluene	120	0.25	87	6	3	96

[a] Determined by GLC analysis; ratio based on integration of baseline-separated peaks. [b] Determined by GLC analysis with reference to starting material. [c] Reactions were performed on a 0.1 mmol scale in Schlenk tubes (15 mL). [d] Reactions were performed on a 0.05 mmol scale in sealed pressure tubes (2 mL). [e] Reactions were performed on a 0.2 mmol scale in 35 mL vessels with microwave heating.

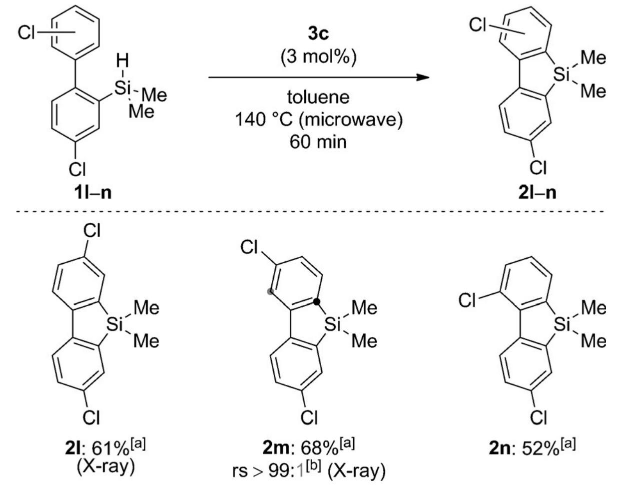
with ruthenium hydride **6**. The hydride would then abstract a proton from **5**,[22] thereby releasing the desired dibenzosilole (**5**→**2**). Dihydrogen adduct **7** finally liberates dihydrogen as the sole by-product, thereby shifting the equilibrium to **3**.

We began with identification of the optimal reaction setup using **1b** as a model substrate and employing complex **3a** with an electron-donating triethylphosphine ligand as the catalyst (Table 1). With chlorobenzene as solvent,[23] nearly full conversion of **1b** was detected by GLC analysis after maintaining the reaction at 90 °C for 19 h. However, the main product was not the expected dibenzosilole **2b** but disiloxane **9b** along with traces of silanol **8b** (Table 1, entry 1). These undesired (by-)products were formed from traces of water despite the use of Schlenk techniques. To exclude water more effectively, this and further reactions were repeated in sealed pressure tubes. This measure indeed suppressed side reactions, and little **8b** and **9b** were formed, but conversion of **1b** into **2b** dramatically slowed down even at 120 °C (Table 1, entry 2). We attribute this observation to the inability of adduct **7** to release dihydrogen and reform catalyst **3**, namely, dihydrogen inhibits the catalysis (Scheme 2, bottom). We concluded that unsealed vessels would be essential to achieve reasonable reaction rates, but this does not go hand in hand with the demand for the rigorous exclusion of moisture. After extensive experimentation, this problem was overcome by microwave heating.[24] An impressive rate acceleration allowed us to use an open reaction vessel (see the Supporting Information for a detailed procedure), which finally resulted in selective conversion of **1b** into **2b** within minutes rather than hours. The catalytic activity of **3a** and, likewise, **3b** with bulkier triisopropylphosphine as ligand was moderate (Table 1, entries 3 and 4). Another significant improvement was seen when switching from an electron-rich to an electron-poor phosphine ligand in **3**. Full conversion was obtained at 140 °C in 15 min when catalyst **3c** was used in either toluene or chlorobenzene (Table 1, entries 5 and 6). A slightly lower temperature led to a minor decrease in yield (Table 1, entry 7). It is noteworthy that catalyst **3c** does not perform better than **3a** in the sealed vessel (not shown).

Having established an effective procedure for the Friedel–Crafts-type C–H bond silylation, we investigated its scope (Scheme 3). Model substrate **1b** afforded **2b** in 91 % yield of the isolated product. Exchanging one methyl group on the silicon atom for a phenyl group (**1c**) resulted in an even higher yield of **2c**. Interestingly, no conversion was observed with the bulkier substrate **1d** under the optimized setup. The use of the less-reactive although sterically less-hindered catalyst **3a** led to isolation of the desired **2d** in 72 % yield. Next, we explored the functional-group tolerance of the reaction. Substrates with a trifluoromethyl group (**1e**) as well as a methyl group (**1f**) in the 4′-position smoothly underwent cyclization, thereby affording **2e** and **2f** in 99 % and 90 % yield, respectively. Substrate **1g** with a methyl group in the 3′-position could potentially form two regioisomeric siloles, but **2g** was formed in quantitative yield exclusively.[25] A frequent drawback of reactions involving silicon electrophiles is their



Scheme 3. Substrate scope of the Friedel–Crafts-type C–H bond silylation for the synthesis of monofunctionalized dibenzosiloles with different substituents at the silicon atom. rs = regioselectivity; TBDPS = *tert*-butyldiphenylsilyl; Tf = trifluoromethanesulfonyl. [a] Reactions were performed on a 0.2 mmol scale. Yields of isolated products after purification by flash chromatography on silica gel. [b] With **3a** (5 mol%) and 60 min reaction time. [c] The other regioisomer was not detected by GLC or NMR analysis. [d] Low conversion. With **3c** (5 mol%) and 60 min reaction time, a complex mixture was obtained.

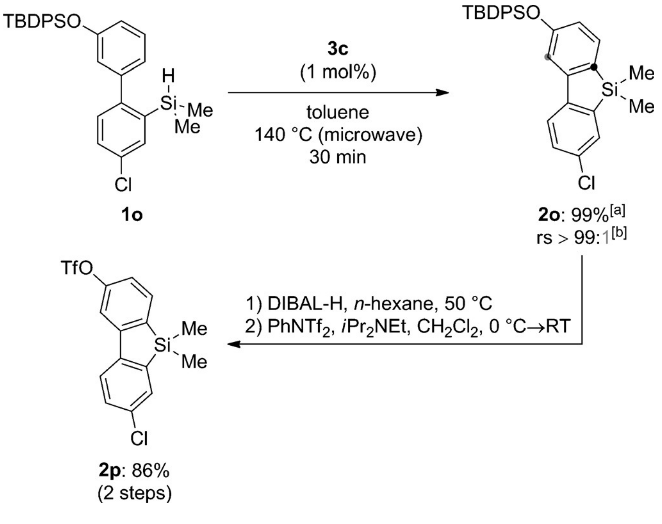


Scheme 4. Substrate scope of the Friedel–Crafts-type C–H bond silylation for the synthesis of difunctionalized silole monomers. [a] Reactions were performed on a 0.2 mmol scale. Yields of isolated products after purification by flash chromatography on silica gel. [b] The other regioisomer was not detected by GLC or NMR analysis.

incompatibility with oxygen donors. It is, therefore, remarkable that substrate **1h** with a silicon-protected hydroxy group converted cleanly into **2h** in 99% yield of the isolated product, again with complete regiocontrol. Conversely, precursor **1i** with a triflate group that would directly allow for subsequent cross-coupling reactions showed lower conversion. Apart from oxygen-containing Lewis bases, nitrogen functionalities were also tolerated, thus affording **2j** from **1j** in 75% yield as a single regioisomer. Moreover, chloro-substituted **1k** was successfully transformed into **2k**.

Dichloro-substituted dibenzosiloles are known to be relevant building blocks for the construction of π-extended structures,[18] but the catalytic synthesis of these molecules is unprecedented. A set of representative dichloro-substituted cyclization precursors (**1l**—**n**; Scheme 4) was subjected to the optimized procedure. These substrates showed lower reactivity, but full conversion was achieved with slightly higher catalyst loading (3 instead of 1 mol%) and prolonged reaction times (60 instead of 30 min). The C_{2h}-symmetric **2l** was isolated in good yield from the reaction of **1l**, and the unsymmetrically substituted **1m** was again converted regioselectively into **2m**. Sterically hindered **1n** with a chlorine substituent in the 2′-position also underwent ring closure to afford **2n**. The yields of such challenging transformations were decent throughout.

Finally, we developed a route to an orthogonally difunctionalized silole monomer that opens the door to more sophisticated polymeric structures through site-selective cross-coupling reactions. Precursor **1o** was subjected to the standard procedure and smoothly cyclized to afford **2o** as a single regioisomer in quantitative yield (Scheme 5). Dibenzosilole **2o** was then further transformed into the new silole motif **2p** in two routine steps.



Scheme 5. Synthesis of an orthogonally difunctionalized silole monomer. DIBAL-H = diisobutylaluminum hydride. [a] Reaction was performed on a 0.2 mmol scale. Yield of isolated products after purification by flash chromatography on silica gel. [b] The other regioisomer was not detected by GLC or NMR analysis.

In summary, we have reported here a powerful method for rapid access to mono- and difunctionalized dibenzosiloles through an intramolecular electrophilic aromatic substitution (S_EAr) involving a catalytically generated silicon electrophile. We showed that microwave heating significantly accelerates the reaction, thereby allowing us to perform this air- and moisture-sensitive transformation in an open vessel. With this reaction setup, the desired products were isolated in up to 99% yield within minutes. In addition, this procedure represents the first catalytic synthesis of dibenzosiloles with halogenation at both benzene cores, and hence will prove useful for developing novel π-conjugated conducting polymers.

Keywords: electrophilic substitution · homogeneous catalysis · microwave chemistry · regioselectivity · Si–H bond activation

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