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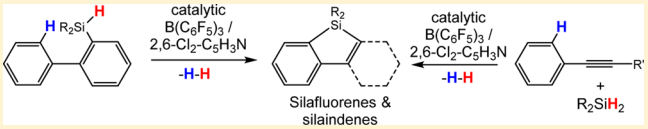
$B(C_6F_5)_3$-Catalyzed Synthesis of Benzofused-Siloles

Liam D. Curless and Michael J. Ingleson*

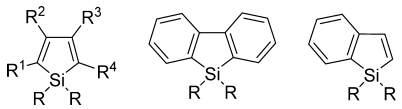
School of Chemistry, University of Manchester, Manchester, M13 9PL, U.K.

Supporting Information

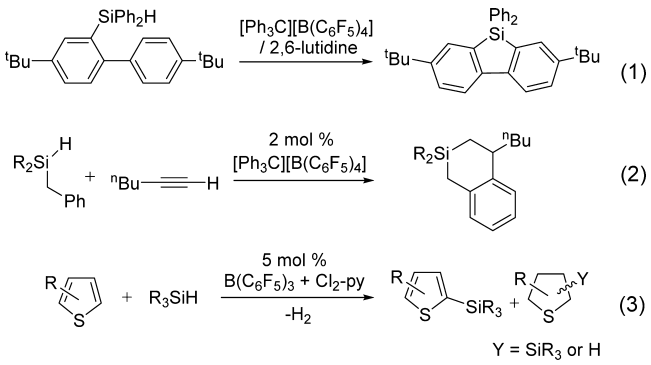
ABSTRACT: The dehydrosilylation of 2-(SiR_2H)-biphenyls catalyzed by $B(C_6F_5)_3$ and a weak base forms silafluorenes with H_2 as the only byproduct. Attempts to extend this approach to synthesize siloles derived from 2,2′-bithiophenes and *N*-Me-2-Ph-indole resulted in competing reactivity, including protodesilylation. $B(C_6F_5)_3$ also catalyzed the one-pot, two-step formation of silaindenes from aryl-alkynes by alkyne *trans*-hydrosilylation, followed by an intramolecular Sila-Friedel–Crafts reaction facilitated by a weak base.



Siloles, **1**, are five-membered, 4π electron heterocycles, and benzofused derivatives, **2** (silafluorenes) and **3** (silaindenes), are privileged moieties in organic electronics. Compounds containing **2** and **3** have been utilized in light emitting materials, field effect transistors, and photovoltaics due to their desirable optical and electronic properties.[1−5] The most established route to benzofused-siloles relies upon the combination of organo-lithium or magnesium reagents with R_2SiCl_2.[6] However, recent years have witnessed the development of multiple transition-metal-catalyzed approaches to **2**[7] and **3**.[8]



A conceptually different pathway to siloles, pioneered by Kawashima and co-workers,[9] utilizes an intramolecular Sila-Friedel–Crafts reaction. Hydride abstraction using stoichiometric trityl salt (Ph_3C^+) generates a silicenium cation (or a functional equivalent) that is attacked by a proximal aryl group to form the silole in the presence of 2,6-lutidine to sequester the protic byproduct from S_EAr (eq 1). Recently, the same



group extended this approach by reacting silicenium cations with alkynes to form β-silyl vinyl cations that undergo intramolecular S_EAr to afford six-membered silacycles.[10] Significantly, this could be operated catalytically in trityl salt, with additional silane acting as a hydride donor to form the saturated cyclized product and regenerating $[R_2BnSi{\cdot}(arene)]^+$ (eq 2). We were interested in developing catalytic routes to **2** and **3** by developing a S_EAr methodology using catalytic $B(C_6F_5)_3$ (BCF) to activate silanes (via $(C_6F_5)_3B$-(μ-H)-SiR_3)[11] and 2,6-dichloropyridine (Cl_2-py) to facilitate deprotonation of the silylated arenium cation.[12] We hypothesized that the competitive reduction that occurs alongside the intermolecular S_EAr of thiophenes using catalytic BCF/Cl_2-py (eq 3) would be disfavored with biphenyl-silyl derivatives due to the increased energetic drive from rearomatization of the arenium cation relative to the thiophenium cation. Herein is reported a catalytic (in BCF) intramolecular S_EAr route to silafluorenes and to silaindenes, the latter preceded by a catalytic (in BCF) alkyne *trans*-hydrosilylation.

Silafluorene Synthesis. The addition of stoichiometric BCF and Cl_2-py to 2-($SiPh_2H$)-biphenyl, **4a** (Figure 1), in CH_2Cl_2 at 20 °C resulted in the slow growth of new aromatic resonances (by ^1H NMR spectroscopy). Heating to 60 °C for 18 h in a sealed tube led to the full conversion of **4a** to a single new compound. Multinuclear NMR spectroscopy and X-ray crystallography (see the Supporting Information) confirmed

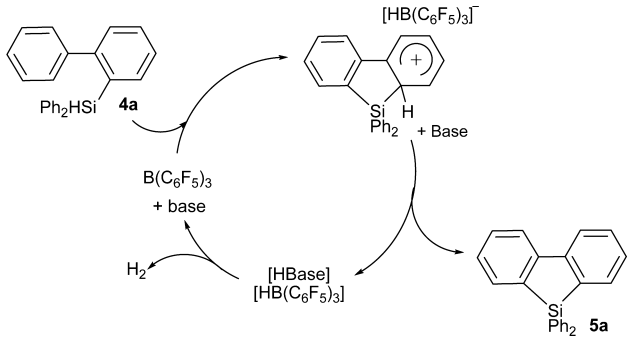


Figure 1. Catalytic (in BCF and Cl_2-py) formation of silafluorenes.

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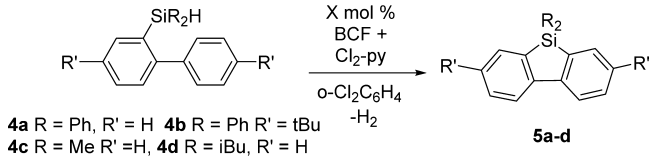
Table 1. Dehydrosilylation of Silylated Biphenyls with BCF



4a R = Ph, R' = H **4b** R = Ph R' = tBu
4c R = Me R' =H, **4d** R = iBu, R' = H

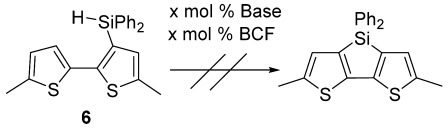
5a-d

entry	silane	BCF (mol %)	Cl_2-py (mol %)	*t* (h)	*T* (°C)	**5** (%)[a]
1[b]	**4a**	100	100	18	60	99
2	**4a**	10	10	24	100	99
3	**4a**	5	5	96	100	99 (90)
4	**4a**	10	0	168	100	50
5	**4b**	5	5	5	100	99 (87)
6[b]	**4c**	100	100	120	60	50[c]
7	**4d**	5	5	96	100	96 (79)

[a]Yields based on conversion of **4** determined by ^{1}H NMR spectroscopy, isolated yields in parentheses. [b]Run in CH_2Cl_2 in a sealed tube. [c]Complete consumption of **4c** occurs, forming **5c** and other products derived from silicon substituent scrambling (by NMR spectroscopy and GC MS).

that this was the desired silole, **5a**. When the reaction was repeated using 10 mol % BCF and Cl_2-py, full conversion to **5a** required 24 h at 100 °C in *ortho*-dichlorobenzene (*o*-DCB, Table 1, entry 2). At 5 mol % BCF/Cl_2-py loadings, full conversion to the silole required 96 h at 100 °C (entry 3). Previously, we have shown that BCF catalyzes the electrophilic silylation of heteroarenes in the absence of a base.[12] However, when **4a** and BCF (10 mol %) were heated to 100 °C in *o*-DCB, only 50% conversion of **4a** to **5a** was observed even after 7 days (entry 4), with unreacted **4a** still present. No diphenylsilane or biphenyl was observed in this reaction (by NMR spectroscopy), consistent with the arenium intermediate reacting directly with $[HBCF]^-$ and not with another equivalent of **4a** (which would generate **5a** and an equivalent of protonated **4a**[HBCF], ultimately leading to the protodesilylation products biphenyl, Ph_2SiH_2, and BCF). Thus, Cl_2-py is facilitating a key step in the catalytic cycle, presumably deprotonation of the arenium cation. Catalytic dehydrosilylation was also effective for 4,4′-^{t}Bu$_2$-2-($SiPh_2H$)-biphenyl (entry 5). Attempts to apply these catalytic S_EAr conditions to dimethyl substituted biphenylsilane, **4c**, led to two new methyl resonances in the ^{1}H NMR spectrum. Multinuclear NMR spectroscopy and GC-MS confirmed that the desired silole had formed along with products arising from substituent scrambling on silicon (entry 6). Related silane substituent scrambling has been reported mediated by silicon cations.[13] Isobutyl substituents on silicon provide sufficient steric bulk to prevent the substituent scrambling;[13b] therefore, clean formation of the dialkyl substituted silole, **5d**, was achieved on addition of 5 mol % of both BCF and Cl_2-py (entry 7).

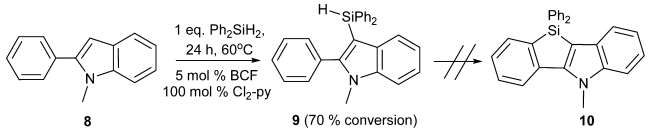
Attempted Synthesis of Heteroaromatic Ring Fused Siloles. The extension of catalytic S_EAr to form dithienosiloles would be particularly desirable due to the prevalence of this structure in compounds used for organic electronic applications.[14] The combination of 5,5′-Me$_2$-3-($SiPh_2H$)-2,2′-bithiophene, **6** (eq 4), with stoichiometric BCF and Cl_2-py in *o*-DCB



6 (4)

at 100 °C formed one major new product by ^{29}Si{^{1}H} NMR spectroscopy (at −21.4 ppm), which frustrated all attempts at isolation (only 5,5′-Me$_2$-bithiophene, **7**, was isolable from these reactions). Multiple aliphatic resonances were also observed (by ^{1}H NMR spectroscopy), again indicating competitive hydrogenation/hydrosilylation;[12] however, these were only present as extremely minor components in the reaction mixture. Attempts to cyclize **6** using catalytic BCF led to a more complex reaction mixture with four species now observed in the ^{29}Si{^{1}H} NMR spectrum with **7** and new aliphatic species also present (by ^{1}H NMR spectroscopy). The repeated formation of **7** is attributed to highly Brønsted acidic species (e.g., $[H(Cl_2\text{-py})]^+$) presumably formed as byproducts from S_EAr protodesilylating **6**. A series of stronger bases (relative to Cl_2-py) were investigated as these form weaker conjugate acids and thus may preclude protodesilylation. However, these did not result in any improved outcome (see the Supporting Information). Two H^+ scavenging methods were also investigated to improve the cyclization of **6**: (i) the addition of a sacrificial substrate that is rapidly reduced by the combination of $[H(Cl_2\text{-py})]^+$ and $[BCF\text{-}H]^-$ and (ii) in place of Cl_2-py, the use of a bulky strong base in stoichiometric quantities that, on protonation, has sufficient hydride ion affinity to abstract hydride from $[BCF\text{-}H]^-$, regenerating BCF.[15] However, neither of these approaches enabled formation of the dithienosilole due to undesired side reactions (see the Supporting Information).

The sequential intermolecular/intramolecular dehydrosilylation of 2-aryl-indoles would represent a simple route to heteroaromatic ring fused siloles such as **10** (Figure 2).



8 **9** (70 % conversion) **10**

Figure 2. Attempted double dehydrosilylation of 2-phenyl-*N*-methylindole with Ph_2SiH_2.

Intermolecular electrophilic dehydrosilylation of *N*-Me-indole with tertiary silanes has been previously reported catalyzed by a cationic ruthenium(II) complex,[16] and subsequently by BCF/Cl_2-py. However, the latter catalytic system proceeded with competing reduction to the indoline.[12] A phenyl group at the C2 position of *N*-Me-indole should inhibit reduction by increasing the steric bulk around C2, preventing H^- transfer

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from $[BCF-H]^-$ to the iminium cation (formed on electrophilic attack at C3 of *N*-Me-indole). Initial dehydrosilylation of 2-Ph-*N*-methyl-indole, **8**, was investigated with Ph_3SiH and stoichiometric BCF and Cl_2-py. After 48 h at 60 °C in CH_2Cl_2, 64% of **8** had been dehydrosilylated. Importantly, there was no evidence for formation of any indoline products (by ^1H NMR spectroscopy). With no reduced products observed using Ph_3SiH, the double-dehydrosilylation of **8** was attempted with Ph_2SiH_2 to form silole **10** (Figure 2). At 5 mol % BCF loading and stoichiometric Cl_2-py (required for shorter reaction times) after 24 h at 60 °C, there was a 70% conversion to compound **9**, with no further reactivity observed at longer reaction times. Under these conditions, there was no evidence for a second dehydrosilylation to form **10** (by ^1H and ^{29}Si NMR spectroscopy). Analysis of the ^{11}B and ^{19}F NMR spectra showed that BCF had been completely converted to $[BCF-H]^-$. The formation of $[BCF-H]^-$ is attributed to a small amount of indole reduction to the indoline, which will subsequently activate H_2 in a FLP with BCF to form [protonated indoline][BCF-H]. Minor resonances in the aliphatic region of the ^1H NMR spectrum are observed, consistent with indoline formation. The reaction of **8** with Ph_2SiH_2 catalyzed by BCF/Cl_2-py was repeated, but with 1 equiv of 1,1-diphenylethene (DPE) to sequester H_2; however, DPE undergoes preferential hydrosilylation.

Catalytic Silaindene Synthesis. Following the catalytic formation of the dibenzofused siloles, the formation of silaindenes was explored. This requires an initial alkyne hydrosilylation by a secondary silane, followed by an intramolecular dehydrosilylation (Figure 3, left). The geometry of

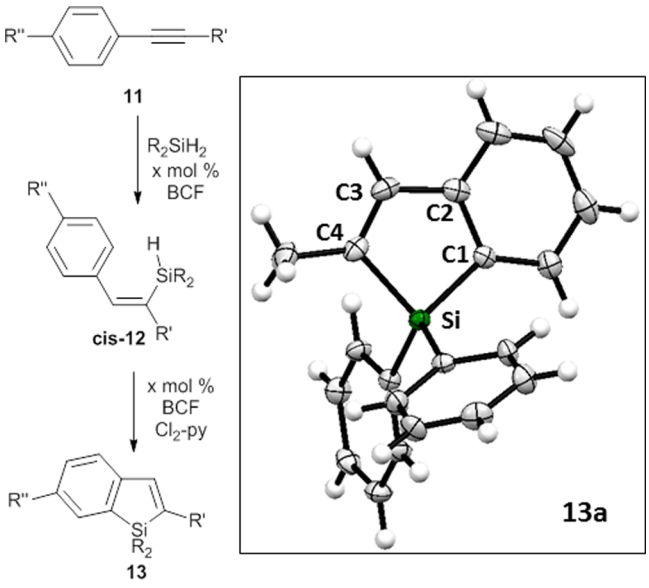

Figure 3. BCF-catalyzed synthesis of silaindenes. Right: the crystal structure of silaindene, **13a** (thermal ellipsoids at 50% probability).

the vinyl silane intermediate is key for subsequent cyclization, with *trans*-hydrosilylation of the alkyne essential to provide a *cis* arrangement of arene and silane. *Trans*-hydrosilylation of alkynes has limited precedence, but is known using FLP methodologies.[17] 1-Phenyl-1-propyne, **11a**, was added to 1 equiv of diphenylsilane and BCF in CH_2Cl_2. Encouragingly, after 5 h at 20 °C, all **11a** was consumed and there was an 84% conversion (by ^1H NMR spectroscopy) to the desired *cis*-vinylsilane, *cis*-**12a**, derived from *trans*-hydrosilylation (confirmed by NOESY; see the Supporting Information). The only other product (accounting for the remaining 16% of material) corresponded to the undesired *trans* isomer from *cis*-hydrosilylation. Addition of Cl_2-py (1 equiv) to this reaction mixture and heating to 60 °C for 72 h resulted in the slow growth of new resonances in the ^1H and $^{29}Si\{^1H\}$ NMR spectra, consistent with the silaindene **13a**. X-ray crystallography confirmed the formation of **13a** (Figure 3, inset), which forms in an overall 84% conversion based on 1-phenyl-1-propyne (Table 2, entry 1).

The formation of **13a** was repeated under catalytic conditions with a 5% BCF loading. The hydrosilylation of **11a** again gave approximately 85:15 *trans:cis* hydrosilylation after 5 h heating at 60 °C in CH_2Cl_2 in a sealed tube. The ring-closing step was extremely slow with catalytic loadings of BCF and Cl_2-py, with 3 days heating at 60 °C in CH_2Cl_2 yielding only a 23% conversion to silaindene **13a** (entry 2). Repeating in *o*-DCB and heating to 100 °C led to no improvement in conversion (entry 3); instead, decomposition of BCF occurs at this temperature with the $^{11}B/^{19}F$ NMR spectra showing multiple 3- and 4-coordinate BCF derived species. The reaction was also repeated in CH_2Cl_2 at 60 °C with 5 mol % BCF and stoichiometric Cl_2-py, which led to an increase in the rate of the electrophilic dehydrosilylation step (entry 4). Adding Cl_2-py prior to the initial hydrosilylation step was also possible, leading to **13a** in moderate overall conversion (entry 5). Attempts to expand the scope of this reaction were extremely limited. While 1-phenyl-1-butyne reacted successfully and more rapidly to form **13b** (entry 6), attempts with a range of other alkynes, including terminal alkynes, diaryl and bromo-substituted internal alkynes, all failed with none of these substrates undergoing any significant hydrosilylation with BCF and Ph_2SiH_2 (see the Supporting Information). The hydrosilylation of 1-(4-bromophenyl)-1-propyne with Ph_2SiH_2 and catalytic BCF did proceed (entry 7), but no subsequent cyclization was observed, attributed to the lower nucleophilicity of the bromo-substituted arene. Silaindene formation was also attempted using di-*tert*-butylsilane; however, no hydrosilylation of **11a** was observed presumably due to steric bulk at the silicon center preventing attack from the alkyne nucleophile on the BCF-(μ-H)-SiR_3 species. The less bulky silane di-*iso*-propylsilane was also used, and while hydrosilylation did occur slowly, the ^{19}F NMR spectrum showed that BCF degraded under these conditions to produce multiple compounds. Because of the catalyst decomposing, the hydrosilylation only proceeded to 35% in 24 h (entry 8). With BCF-catalyzed alkyne *trans*-hydrosilylation using 2° silanes limited in alkyne scope, alternative *trans*-hydrosilylation routes were investigated to no avail. For example, the *trans*-hydrosilylation of alkynes with catalytic $AlCl_3$ has been previously reported using tertiary silanes;[18] however, attempts to extend this procedure to secondary silanes predominantly resulted in the recovery of starting materials at varied loadings of $AlCl_3$ up to stoichiometric (relative to the alkyne) and for prolonged reaction times at a range of temperatures. An analogous route to germole formation was also explored, with *trans*-hydrogermylation of alkynes using catalytic BCF reported with tertiary germanes.[19] However, attempts to hydrogermylate 1-phenyl-1-propyne using Ph_2GeH_2 in CH_2Cl_2, benzene, and *o*-DCB led to no alkyne hydrogermylation, with BCF decomposition observed.

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Table 2. One-Pot Hydrosilylation/Dehydrosilylation of Alkynes To Form Silaindenes (see Figure 3 for Labeling)[a]

entry	11	R′	R″	silane	solvent	BCF (mol %)	t (h)	T (°C)	*cis*-12 (%)[b]	*trans*-12 (%)[b]	Cl_2-py (mol %)	t (h)	T (°C)	13 (%)[b]
1	**11a**	Me	H	Ph_2SiH_2	CH_2Cl_2	100	5	20	84	16	100	72	60	84
2	**11a**	Me	H	Ph_2SiH_2	CH_2Cl_2	5	5	60	85	15	5	48	60	23
3	**11a**	Me	H	Ph_2SiH_2	*o*-DCB	5	5	60	84	16	5	30	100	17
4	**11a**	Me	H	Ph_2SiH_2	CH_2Cl_2	5	4	60	84	16	100	72	60	70
5[c]	**11a**	Me	H	Ph_2SiH_2	CH_2Cl_2	5					100	72	60	50
6	**11b**	Et	H	Ph_2SiH_2	CH_2Cl_2	5	2	60	75	25	100	24	60	75
7	**11c**	Me	Br	Ph_2SiH_2	CH_2Cl_2	5	48	60	89	0	100	48	60	0
8	**11a**	Me	H	$^iPr_2SiH_2$	CH_2Cl_2	5	24	60	35					

[a]All reactions performed in sealed tubes. [b]Conversion based on **11** determined by ^1H NMR spectroscopy. [c]In one pot with both BCF and Cl_2-py added at the start of the reaction

In conclusion, a catalytic (in $B(C_6F_5)_3$) intramolecular Sila-Friedel–Crafts route to silafluorene compounds has been developed, which only produces H_2 as byproduct. A metal-free approach to silaindenes from alkynes has also been achieved by a BCF-catalyzed one-pot hydrosilylation/dehydrosilylation pathway. Both reactions are limited in scope due to (i) competing protodesilylation/reduction of heteroaromatic species, (ii) *trans*-hydrosilylation only proceeding for select alkynes, and (iii) BCF being insufficiently robust in the presence of highly electrophilic Lewis acids and/or strong Brønsted acids.

EXPERIMENTAL SECTION

General Comments. Unless otherwise stated, all manipulations were carried out using standard Schlenk techniques under argon, or in a glovebox under an atmosphere of argon (<0.1 ppm of O_2/H_2O). Unless otherwise indicated, solvents were distilled from appropriate drying agents: Ether (NaK), *n*-hexane (NaK), dichloromethane (CaH_2), and *o*-dichlorobenzene (CaH_2). Ether, *o*-dichlorobenzene, and dichloromethane were stored over activated 3 Å molecular sieves, while *n*-hexane was stored over a potassium mirror. All other compounds (excluding $B(C_6F_5)_3$) were purchased from commercial sources and used as received. Solvents for column chromatography were of technical grade and used without further purification. Column chromatography was performed on silica gel (230–400 mesh). NMR spectra were recorded on Bruker AvanceIII-400, Bruker AvanceII-500, or Bruker Ascend-400 spectrometers. Chemical shifts are reported as dimensionless δ values and are frequency referenced relative to residual protio impurities in the NMR solvents for ^1H and $^{13}C\{^1H\}$, respectively, while ^{11}B, ^{19}F, and ^{29}Si shifts are referenced relative to external BF_3-etherate, hexafluorobenzene, and tetramethylsilane, respectively. Coupling constants *J* are given in hertz (Hz) as positive values regardless of their real individual signs. High-resolution mass spectra (HRMS) were recorded on a Waters QTOF mass spectrometer. GCMS analysis was performed on an Agilent Technologies 7890A GC system equipped with an Agilent Technologies 5975C inert XL EI/CI MSD with a triple axis detector. The column employed was an Agilent J&W HP-5 ms ((5%-phenyl)-methylpolysiloxane) of dimensions: length, 30 m; internal diameter, 0.250 mm; film, 0.25 μm. Microanalysis was performed at the University of Manchester microanalytical service. An INEPT (Insensitive Nuclei Enhanced by Polarization Transfer) experiment was utilized to improve the sensitivity of ^{29}Si NMR experiments.

Procedure for Drying $B(C_6F_5)_3$. $B(C_6F_5)_3$ was stirred with excess Et_3SiH (5 equiv) in pentane for 72 h at ambient temperature. Solvent was removed and $B(C_6F_5)_3$ was dried in vacuo to give a dry white powder, which was pure by ^{11}B and $^{19}F\{^1H\}$ NMR spectroscopy.

General Procedure 1: The Synthesis of 2-(Dialkyl/Arylsilyl)-biphenyls. To a solution of 2-bromobiphenyl (2 mL, 11.6 mmol) and TMEDA (1.9 mL, 12.76 mmol), in diethyl ether (20 mL) was added *n*-butyl-lithium (8 mL, 1.6 M in hexane) dropwise at −78 °C, and the mixture was stirred for 5 h. To this solution was added diaryl/alkylchlorosilane (1.1 equiv) dropwise at −78 °C, and the mixture was stirred for 1 h. The reaction mixture was left to warm to ambient temperature and stirred for 24 h. The product was extracted with ether and washed with sodium hydrogen carbonate (aq.) and water. The organic layer was dried over magnesium sulfate. The solvent was removed under vacuum and purified by flash column chromatography.

4a 2-(Diphenylsilyl)biphenyl. Synthesized according to general procedure 1, starting with 2.3 mL of diphenylchlorosilane. The solvent was removed under vacuum and purified by flash column chromatography, where the eluent was hexane:ethyl acetate (4:1). This gave the title compound, **4a** (2.2 g), as a white solid in 57% yield. ^1H NMR ($CDCl_3$ 400 MHz) δ 7.54 (d, $^3J_{HH}$ 7.3 Hz, 1H), 7.48 (dt, $^3J_{HH}$ 1.3 Hz, $^3J_{HH}$ 7.9 Hz, 1H), 7.45–7.43 (m, 4H), 7.40–7.29 (m, 8H), 7.25–7.18 (m, 5H), 5.16 (s, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$ 100 MHz) δ 150.2, 143.1, 137.1, 135.7, 134.3, 132.3, 129.7, 129.5, 129.4, 129.3, 127.8, 127.7, 127.0, 126.4 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$ 80 MHz) δ −21.2 ppm. HRMS Found: 336.1329 *m*/*z* (expected for M^+ 336.1329). Elemental analysis expected C 85.70%, H 5.95%, Found: C 85.62%, H 6.39%.

4b Bis(4,4′-di-*tert*-butylbiphenyl-2-yl)silane.[9] Synthesized according to general procedure 1, starting with 2.3 mL of diphenylchlorosilane. The solvent was removed under vacuum and purified by flash column chromatography, where the eluent was pentane:CH_2Cl_2 (10:1). This gave the title compound, **4b** (2.6 g), as a white crystalline solid in 75% yield. ^1H and $^{13}C\{^1H\}$ data in accordance with the literature.[9] $^{29}Si\{^1H\}$ NMR ($CDCl_3$ 80 MHz) δ −20.76 ppm.

4c 2-(Dimethylsilyl)biphenyl. Synthesized according to general procedure 1, starting with 1.55 mL of dimethylchlorosilane. The solvent was removed under vacuum and purified by flash column chromatography, where the eluent was hexane. This gave the title compound, **4c** (1.8 g), as a colorless oil in 75% yield. ^1H and $^{13}C\{^1H\}$ NMR data were found to be in accordance with previously reported literature data.[20] $^{29}Si\{^1H\}$ NMR ($CDCl_3$ 80 MHz) δ −17.9 ppm.

4d 2-(Di-*iso*-butylsilyl)biphenyl. Synthesized according to general procedure 1, starting with 2 mL of di-*iso*-butylchlorosilane. The solvent was removed under vacuum and purified by flash column chromatography, where the eluent was pentane:CH_2Cl_2 (10:1). This gave the title compound, **4d** (2.3 g), as a colorless oil in 69% yield. ^1H NMR ($CDCl_3$ 400 MHz) δ 7.71 (d, $^3J_{HH}$ 7.3 Hz, 1H), 7.47–7.32 (M, 8H), 4.31 (quintet, $^3J_{HH}$ 3.8 Hz, 1H, Si-*H*), 1.66 (septet, $^3J_{HH}$ 6.8 Hz, 2H), 0.89 (2 overlapped doublets, $^3J_{HH}$ 6.3 Hz, 12H), 0.65–0.52 (m, 4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 100 MHz) δ 149.4, 143.8, 136.2, 134.9, 129.3, 129.2, 128.9, 127.7, 127.1, 126.3, 26.0, 25.4, 25.3, 23.8 ppm. $^{29}Si\{^1H\}$ NMR ($CDCl_3$ 80 MHz) δ −13.07 ppm. HRMS Found: 296.1945 *m*/*z* (expected for M^+ 296.1955). Elemental analysis expected C 81.01%, H 9.52%, Found: C 81.42%, H 9.63%.

5a 9,9-Diphenyl-9-silafluorene.[21] In an oven-dried J. Youngs tap fitted Schlenk tube, 131 mg of 2-(diphenylsilyl)biphenyl was added to a solution of BCF (10 mg, 5 mol %) in anhydrous *o*-DCB. This solution was agitated for 5 min before the addition of Cl_2-py (3 mg, 5 mol %) and then sealed and heated to 100 °C for 96 h. The solution was passed through a plug of silica and then dried under vacuum. Further purification by flash column chromatography (eluent: CH_2Cl_2) and drying gave 117 mg of **5a** as a white solid (90% isolated yield). ^1H NMR ($CDCl_3$ 400 MHz) δ 7.94 (d, $^3J_{HH}$ 7.9 Hz, 2H), 7.84 (d, $^3J_{HH}$ 6.6 Hz, 2H), 7.72–7.70 (m, 4H), 7.52 (td, $^3J_{HH}$ 7.6 Hz, 1.3

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Hz, 2H), 7.45 (tt, $^3J_{HH}$ 6.3 Hz, 1.3 Hz, 2H), 7.40−7.34 (m, 6H). ^{13}C {^1H} NMR ($CDCl_3$ 100 MHz) δ 148.8, 135.9, 135.5, 134.0, 132.7, 130.7, 130.1, 128.1, 127.8, 121.2 ppm. ^{29}Si {^1H} NMR ($CDCl_3$ 80 MHz) δ −12.7 ppm. HRMS Found: 335.1245 *m/z* (expected for M^+ 335.1251). Elemental analysis expected C 85.85%, H 5.78%, Found: C 85.19%, H 5.42%.

5b 2,7-Di-*tert*-butyl-9,9-diphenyl-9-silafluorene. In an oven-dried J. Youngs tap fitted Schlenk tube, 86 mg of bis(4,4′-di-*tert*-butylbiphenyl-2-yl)silane was added to a solution of BCF (10 mg, 5 mol %) in anhydrous *o*-DCB. This solution was agitated for 5 min before the addition of Cl_2-py (3 mg 5 mol %) and then sealed and heated to 100 °C for 96 h. The solution was passed through a plug of silica and then dried under vacuum. Further purification by flash column chromatography (eluent: pentane) and drying gave 74 mg of **5b** as a white powder (87% isolated yield). ^1H and ^{13}C {^1H} data in accordance with the literature.[9] ^{29}Si{^1H} NMR ($CDCl_3$ 80 MHz) δ −11.5 ppm.

5d 9,9-Di-*iso*-butyl-9-silafluorene. In an oven-dried J. Youngs tap fitted Schlenk tube, 1 mL of 2-(di-*iso*-butylsilyl)biphenyl was added to a solution of BCF (86 mg, 5 mol %) in anhydrous *o*-DCB. This solution was agitated for 5 min before the addition of Cl_2-py (25 mg 5 mol %) and then sealed and heated to 100 °C for 96 h. The solution was passed through a plug of silica and then dried under vacuum. Further purification by flash column chromatography (eluent: pentane) and drying gave 78 mg of **5d** as a colorless oil (79% isolated yield). ^1H NMR (CD_2Cl_2 400 MHz) δ 7.84 (d, $^3J_{HH}$ 7.8 Hz, 2H), 7.66 (d, $^3J_{HH}$ 7.0 Hz, 2H), 7.42 (t, $^3J_{HH}$ 7.8 Hz, 2H), 7.26 (t, $^3J_{HH}$ 7.3 Hz, 2H), 1.71 (septet, $^3J_{HH}$ 6.5 Hz, 2H), 0.98 (d, $^3J_{HH}$ 7.0 Hz, 4H), 0.81 (d, $^3J_{HH}$ 6.5 Hz, 12H). ^{13}C {^1H} NMR (CD_2Cl_2 100 MHz) δ 148.7, 139.1, 134.0, 130.5, 127.8, 121.4, 26.5, 25.8, 24.3 ppm. ^{29}Si {^1H} NMR (CD_2Cl_2 80 MHz) δ 1.36 ppm. HRMS Found: 294.1800 *m/z*, (expected for M^+ 294.1798).

13a 2-Methyl-1,1-diphenyl-1-silaindene. In an oven-dried J. Youngs tap fitted Schlenk tube, 73 μL of diphenyl silane was added to a solution of BCF (10 mg, 5 mol %) and 49 μL of 1-phenyl-1-propyne in anhydrous CH_2Cl_2. This solution was then sealed and heated to 60 °C for 4 h. One equivalent of Cl_2-py (58 mg) was added to the reaction mixture before being sealed and heated for a further 72 h at 60 °C. Preparative TLC with an eluent of hexane:CH_2Cl_2 (9:1) lead to several bands. Taking the top two-thirds of the top band gave ca. 82% of the 1,1-diphenyl-2-methyl-1-silaindene (**13a**) and 18% of the *cis*- and *trans*-vinylsilane mixture (**12a**). ^1H NMR (CD_2Cl_2 400 MHz) δ 7.62−7.60 (m, 5H), 7.46−7.33 (m, 7H), 7.27−7.23 (m, 1H), 7.19 (t, $^3J_{HH}$ 7.3 Hz, 1H), 7.13 (s, br, 1H), 2.16 (d, $^4J_{HH}$ 1.3 Hz, 3H). ^{13}C {^1H} NMR ($CDCl_3$ 100 MHz) δ 145.6, 135.7, 135.4, 134.3, 133.1, 132.3, 130.0, 128.2, 127.8, 126.3, 18.0 ppm. ^{29}Si {^1H} NMR (CD_2Cl_2 80 MHz) δ −9.16 ppm. HRMS Found: 298.1165 *m/z*, (expected for M^+ 298.1172).

13b 2-Ethyl-1,1-diphenyl-1-silaindene. In an oven-dried J. Youngs tap fitted Schlenk tube, 73 μL of diphenyl silane was added to a solution of BCF (10 mg, 5 mol %) and 56 μL of 1-phenyl-1-butyne in anhydrous CH_2Cl_2. This solution was then sealed and heated to 60 °C for 2 h. One equivalent of Cl_2-py (58 mg) was added to the reaction mixture before being sealed and heated for a further 24 h at 60 °C. Preparative TLC with an eluent of hexane:CH_2Cl_2 (9:1) lead to several bands. Taking the top two-thirds of the top band gave 89% of the 1,1-diphenyl-2-ethyl-1-silaindene (**13b**) and 11% of the *cis*- and *trans*-vinylsilane. ^1H NMR ($CDCl_3$ 400 MHz) δ 7.64−7.62 (m, 4H), 7.59 (d, $^3J_{HH}$ 7.6 Hz, 1H), 7.45−7.33 (m, 7H), 7.26 (d, $^3J_{HH}$ 7.6 Hz, 1H), 7.18 (dt, $^4J_{HH}$ 1.0 Hz, $^3J_{HH}$ 7.6 Hz, 1H), 7.13 (t, $^4J_{HH}$ 1.0 Hz, 1H), 2.56 (dq, $^4J_{HH}$ 1.8 Hz, $^3J_{HH}$ 7.3 Hz, 2H), 1.11 (t, $^3J_{HH}$ 7.6 Hz, 3H). ^{13}C {^1H} NMR ($CDCl_3$ 100 MHz) δ 150.3, 148.2, 143.2, 135.4, 135.2, 133.0, 132.5, 130.3, 130.0, 128.1, 126.3, 124.6, 25.5, 13.8 ppm. ^{29}Si {^1H} NMR ($CDCl_3$ 0 MHz) δ −9.11 ppm. HRMS Found: 312.1329 *m/z*, (expected for M^+ 312.1338).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Full experimental details for all reactions and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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