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Brønsted Acid-Promoted Formation of Stabilized Silylium Ions for Catalytic Friedel–Crafts C–H Silylation

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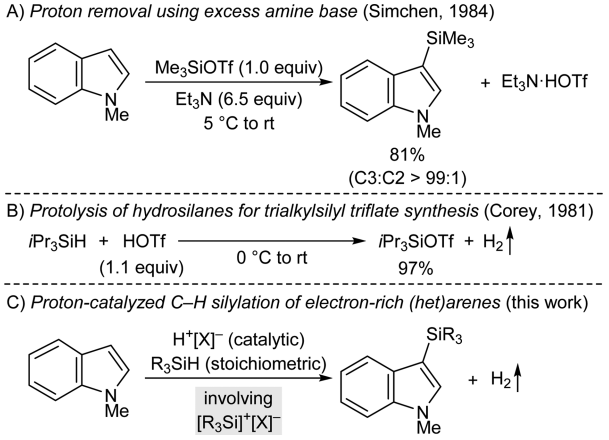
Supporting Information

ABSTRACT: A counterintuitive approach to electrophilic aromatic substitution with silicon electrophiles is disclosed. A strong Brønsted acid that would usually promote the reverse reaction, i.e., protodesilylation, was found to initiate the C–H silylation of electron-rich (hetero)arenes with hydrosilanes. Protonation of the hydrosilane followed by liberation of dihydrogen is key to success, fulfilling two purposes: to generate the stabilized silylium ion and to remove the proton released from the Wheland intermediate.

Electrophilic aromatic substitution (S_EAr) is a valuable method for the C–H functionalization of arenes. By exploiting the electrophilicity of Me_3SiOTf, Frick and Simchen accomplished a highly regioselective C–H silylation of indoles and pyrroles three decades ago (Scheme 1A).[1] To overcome competing protodesilylation, i.e., the reverse reaction, excess base had to be added to absorb the released protons. According to a straightforward procedure reported by Corey et al., such $Alkyl_3SiOTf$ are accessible from the reaction between $Alkyl_3SiH$ and TfOH (Scheme 1B).[2,3] It is notable that the hydride and proton are removed from the reaction in the form of dihydrogen. Inspired by Corey's work, we imagined that Brønsted acids with weakly coordinating counteranions $[X]^-$ could promote the catalytic formation of stabilized silicon cations from hydrosilanes.[4,5] The thus-generated silicon electrophiles could then participate in situ in the Friedel–Crafts C–H silylation of electron-rich (hetero)arenes (Scheme 1C).[1,6−8] Owing to the proton removal as dihydrogen, we expected this catalytic system to suppress protodesilylation.

Scheme 1. Merger of Electrophilic C–H Silylation and Brønsted Acid-Promoted Formation of Silicon Cations



To test our hypothesis, we investigated the stoichiometric formation of the silicon electrophile using Brønsted acid. Due to facile cleavage of the phenyl group (= protodesilylation) rather than loss of the hydride, the reaction of Me_2PhSiH (**1a**) with TfOH leads to HMe_2SiOTf but not to $Me_2PhSiOTf$ (eq 1).[9] We thus envisioned using a substantially weaker but still strong acid to avoid dephenylation. Accordingly, Brookhart's acid $[H(OEt_2)_2]^+[BAr^F{}_4]^-$ (**2**)[10] was employed to generate the corresponding ether-stabilized silicon cation.[11] D–H gas immediately evolved from the reaction after treatment of deuterium-labeled Me_2PhSiD (**1a**-d_1) with **2** (eq 2), indicating smooth proton transfer with gas evolution and coordination of Et_2O as driving forces. The formation of D–H was verified by a triplet at δ 4.44 ppm with a diagnostic coupling constant of ^1J = 42.6 Hz in the ^{1}H NMR spectrum. No cleavage of the phenyl group was observed. Instead, we obtained a biphasic system that usually indicates clathrate formation of the solvent and the newly generated silicon cation.[12] Identification of that cation by ^{29}Si NMR spectroscopy was however hampered by dynamic exchange between reversibly bound Et_2O[11a] and the benzene solvent, apparent from significant line broadening in the ^{1}H NMR spectrum. By replacing C_6D_6 with 1,2-$Cl_2C_6D_4$ as solvent, we were then able to detect $[Me_2PhSi(OEt_2)]^+[BAr^F{}_4]^-$ (**3a**) by ^{1}H/^{29}Si HMQC measurements and clearly establish the formation of the desired silyloxonium ion (eq 3 and Figure 1). The ^{29}Si NMR spectrum showed a characteristic signal at δ 53.2 ppm. In turn, the combination of TfOH and Et_2O in 1:2 ratio did not evolve any gas on addition to Me_2PhSiH but led to slow dephenylation.

Our group recently introduced catalytic electrophilic C–H silylations[6] of electron-rich arenes such as indoles and anilines based on cooperative Si–H bond activation[7b] and Lewis-acid catalysis,[7d] respectively. With the present work, we now aim at the development of a complementary process promoted by Brønsted acid **2**[13] (Table 1). Good yield and excellent regioselectivity were obtained using 1.0 mol % of Brookhart's acid **2** in the reaction between 1-methylindole (**4a**) and hydrosilane **1a** (**4a** → **5aa**, entry 1).[14,15] No reaction was seen in the absence of $[H(OEt_2)_2]^+[BAr^F{}_4]^-$ (**2**), and $Na^+[BAr^F{}_4]^-$ alone did not promote this transformation (entries 2 and 3). A gradual increase of the catalyst loading from 1.0 to 4.0 mol % led to diminished yields (entries 4 and 5). This unusual trend is

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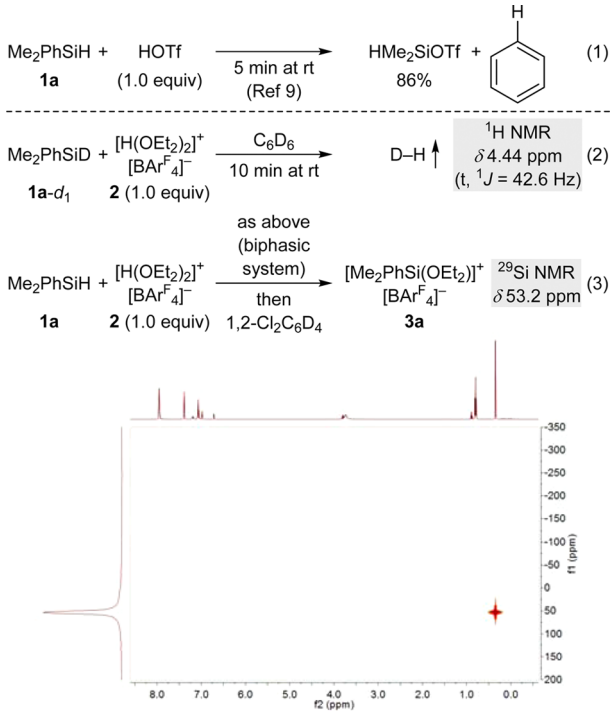
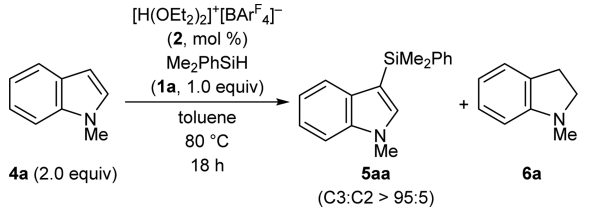


Figure 1. $^{1}H/^{29}Si$ HMQC spectrum of $[Me_2PhSi(OEt_2)]^+[BAr^F_4]^-$ (**3a**) recorded in 1,2-$Cl_2C_6D_4$ at room temperature.

Table 1. Optimization of the C3 Silylation of Indole[a]



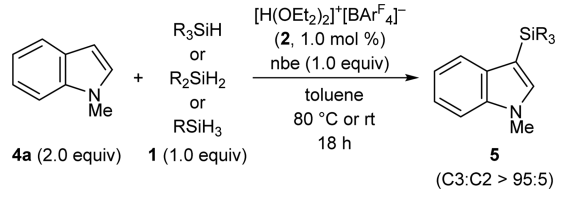
entry	**2** (mol %)	nbe (equiv)	yield (%)[b]
1	1.0	—	70
2	—	—	no reaction
3	—[c]	—	no reaction
4	2.0	—	77
5	4.0	—	53
6	2.0	0.50	85
7	2.0	1.0	95
8	1.0	1.0	97

[a]All reactions were performed on a 0.20 mmol scale (based on the hydrosilane) using double the amount of the indole (0.40 mmol, 2.0 equiv) as well as the indicated amount of catalyst **2** and norbornene in toluene (0.10 mL) at 80 °C for 18 h. [b]Based on hydrosilane and determined by ^{1}H NMR spectroscopy or GLC analysis using 1,3,5-trimethoxybenzene as internal standard. [c]$NaBAr^F_4$ (1.0 mol %) added instead of $[H(OEt_2)_2]^+[BAr^F_4]^-$ (**2**).

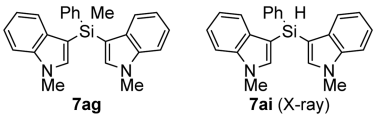
understood as the result of protodesilylation prevalent at higher proton concentrations.[1] It also emphasizes that proton release and removal, i.e., dihydrogen release, must be well balanced to overcome this intrinsic problem. To our delight, the addition of norbornene (nbe) as a proton scavenger[16] dramatically improved the yield to near-quantitative (entries 6–8). We note here that 1-methylindoline (**6a**) always formed as the byproduct, which is why these reactions were performed with the hydrosilane as the limiting reagent. Importantly, the silylated indole **5aa** (major) and the indoline **6a** (minor) did not form in equimolar ratio (for an explanation, see Scheme 4).

Next, we examined the hydrosilane scope (Table 2). With Me_2PhSiH (**1a**) the isolated yield was essentially quantitative,

Table 2. Screening of Hydrosilanes in the Indole Silylation[a]



entry	hydrosilane	T (°C)	yield (%)[b]
1	Me_2PhSiH (**1a**)	80	96 (**5aa**)
2	$MePh_2SiH$ (**1b**)	rt	93 (**5ab**)
3	Ph_3SiH (**1c**)	80	8[c] (**5ac**)
4	Et_3SiH (**1d**)	80	7[c] (**5ad**)
5	$(EtO)_2MeSiH$ (**1e**)	80	0[d] (**5ae**)
6	Ph_2SiH_2 (**1f**)	rt	96 (**5af**)
7	$MePhSiH_2$ (**1g**)	rt	73[e] (**7ag**)
8	Et_2SiH_2 (**1h**)	rt	61[c,f] (**5ah**)
9	$PhSiH_3$ (**1i**)	rt	74[e] (**7ai**)



[a]All reactions were performed on a 0.20 mmol scale (based on **1**) using double the amount of the indole (0.40 mmol, 2.0 equiv), $[H(OEt_2)_2]^+[BAr^F_4]^-$ (**2**, 1.0 mol %), and norbornene (1.0 equiv) in toluene (0.10 mL) at the indicated temperature for 18 h. [b]Isolated yield after flash chromatography on silica gel. [c]Determined by ^{1}H NMR spectroscopy using CH_2Br_2 as internal standard. [d]$(EtO)_3SiMe$ and $[(EtO)_2MeSi]_2O$ detected by GLC-MS analysis. [e]3-fold excess of the indole (0.60 mmol) used to obtain the bis(indol-3-yl)-substituted silane exclusively. [f]Indole used as the limiting reagent (0.20 mmol) together with hydrosilane **1h** (0.40 mmol); trace amounts of the corresponding bis(indol-3-yl)-substituted silane observed by GLC-MS analysis.

and the reaction proceeded smoothly with $MePh_2SiH$ (**1b**) even at room temperature (entries 1 and 2). Probably due to steric hindrance, low conversion was observed for Ph_3SiH (**1c**) and, likewise, for Et_3SiH (**1d**) (entries 3 and 4). The protocol was not compatible with $(EtO)_2MeSiH$ (**1e**) as a result of silylated oxonium ion formation[11b] (entry 5). Dihydrosilanes **1f**–**1h** also served as efficient coupling partners (entries 6–8). Monosubstitution was observed exclusively with Ph_2SiH_2 (**1f**) at room temperature (entry 6), but using a 3-fold excess of the indole, $MePhSiH_2$ (**1g**) underwent 2-fold C–H silylation to afford the bis(indol-3-yl)-substituted silane **7ag** (entry 7). Selective monosubstitution was achieved with Et_2SiH_2 (**1h**) when using the indole as the limiting reagent (entry 8). Again, bis(indol-3-yl)-substituted silane **7ai** formed from trihydrosilane $PhSiH_3$ (**1i**) (entry 9); the molecular structure of **7ai** was confirmed by X-ray diffraction (see the Supporting Information for details).

Given the potential for further derivatization, Ph_2SiH_2 (**1f**) was used to study the scope of the regioselective C–H silylation of heteroarenes (Scheme 2). The isolated yield for 1-methylindole was 96% (**4a** → **5af**), and slightly higher

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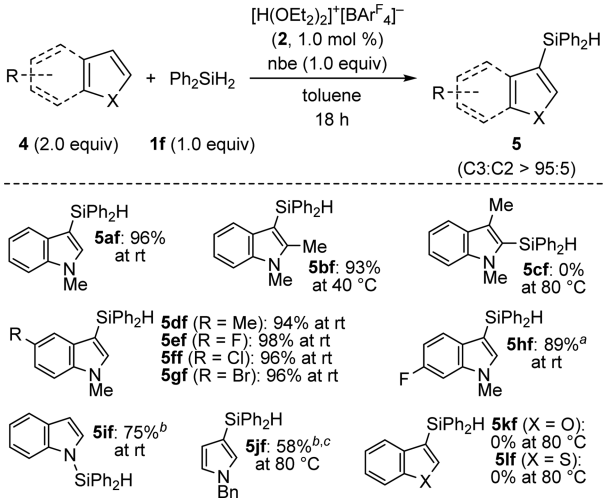
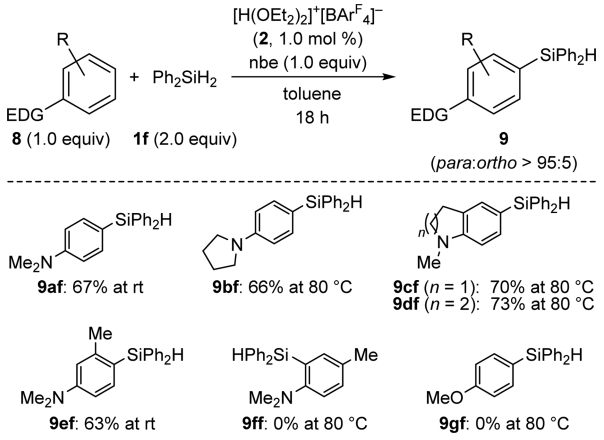
Scheme 2. Regioselective C−H Silylation of Heteroarenes



[a]Along with <10% of the corresponding C3-silylated indoline. [b]Determined by ^{1}H NMR spectroscopy using CH_2Br_2 as internal standard. [c]C3:C2 = 87:13.

Scheme 3. Regioselective Silylation of Aniline Derivatives and Attempted Silylation of Anisole[a]



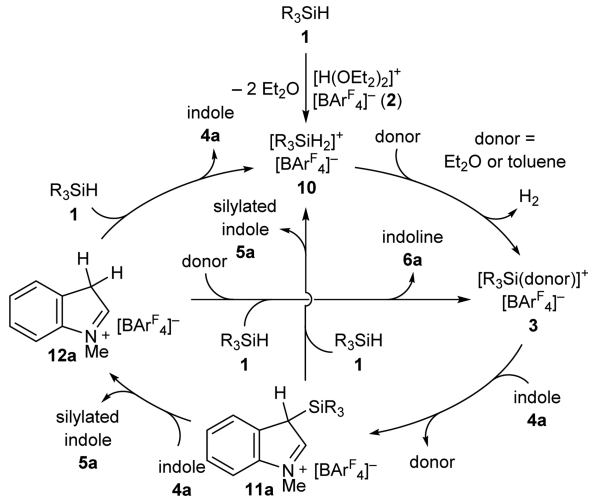
[a]EDG = electron-donating group.

temperature was required to obtain 93% yield for 1,2-dimethylindole (**4b** → **5bf**). Conversely, 1,3-dimethylindole did not react (**4c** not to **5cf**), furnishing proof of an S_EAr mechanism with the more nucleophilic indole C3 position blocked by a methyl group. 1,5-Dimethylindole underwent the C3-selective S_EAr at room temperature in high yield (**4d** → **5df**) as did the 5-halogenated 1-methylindoles (**4e**−**4g** → **5ef**−**5gf**); no dehalogenation was detected. These reactions were highly regioselective (C3:C2 > 95:5) as was the C−H silylation of 6-fluoro-substituted 1-methylindole (**4h** → **5hf**). Dehydrogenative Si−N coupling occurred with unprotected indole (**4i** → **5if**),[17] and no further reaction at C3 was found. Moderate yield (58%) and regioselectivity (C3:C2 = 87:13) were achieved with the more challenging pyrrole substrate (**4j** → **5jf**). This catalytic system was not able to facilitate the C−H silylation of benzofuran (**4k**) and benzothiophene (**4l**). To demonstrate the practicability of this protocol, a gram-scale synthesis of a C3-silylated indole using $MePh_2SiH$ (**1b**) was performed (**4a** → **5ab**, cf. Table 2, entry 2). With just 0.5 mol % loading of $[H(OEt_2)_2]^+[BAr^F_4]^-$ (**2**), the reaction on a 5.0 mmol scale furnished 1.6 g of silylated indole **5ab** in 95% isolated yield.

We then turned toward aniline derivatives as promising electron-rich arenes in the Brønsted acid-promoted silylation with hydrosilanes (Scheme 3).[7d,e] As aniline reduction was not observed with this setup, we returned to using the more conventional substrate-to-reagent ratio; a 2-fold excess of the hydrosilane was required to reach high yields. The addition of nbe was also crucial.[16] Indeed, *N*,*N*-dimethylaniline and *N*-phenylpyrrolidine reacted highly regioselectively in good yields at room temperature and 80 °C, respectively (**8a** → **9af** and **8b** → **9bf**). The success of this silylation relies heavily on the electronic property of substituents on the aniline as *ortho*-fluoro-substituted congeners did not react (not shown). Alkylation in the *ortho* position to the electron-donating amino group as in 1-methylindoline and 1-methyl-1,2,3,4-tetrahydroquinoline was tolerated (**8c** → **9cf** and **8d** → **9df**). The *meta*-substituted derivative also participated in similar yield, maintaining excellent *para* selectivity (**8e** → **9ef**), whereas the *para*-substituted isomer was unreactive (**8f** not to **9ff**). No silylation occurred in the reaction with anisole (**8g**).

On the basis of the literature precedence[2,18,20] and our own observations, we propose the following dominating catalytic cycle[16] for the Brønsted acid-promoted S_EAr with an in situ-generated silicon electrophile (Scheme 4). Brookhart's acid **2** is

Scheme 4. Proposed Catalytic Cycle of the Brønsted Acid-Promoted Electrophilic Indole Silylation



sufficiently strong to protonate the hydrosilane to form a pentacoordinate siliconium ion (**1** → **10**).[3,19] That transient intermediate will release dihydrogen[18] to afford the donor-stabilized silylium ion $[R_3Si(donor)]^+[BAr^F_4]^-$ (**10** → **3**). Et_2O introduced with $[H(OEt_2)_2]^+[BAr^F_4]^-$ (**2**) is likely to act as the stabilizing donor (cf. eq 3 and Figure 1) but the toluene solvent[12] will assume this role[18b] if ether cleavage occurs in the course of the reaction. The cationic silicon electrophile **3** is then attacked by the nucleophilic indole (**4a** → **11a**). The resulting Wheland complex is a strong Brønsted acid with the weakly coordinating $[BAr^F_4]^-$ counteranion, and direct protonation of another hydrosilane molecule closes the catalytic cycle (**1** → **10**) concomitant with formation of the C3-silylated indole (**11a** → **5a**).[20,21]

Formation of the indoline byproduct **6a** is rationalized by competing silylium-ion catalysis. Proton transfer from intermediate **11a** to the indole substrate **4a** used in excess not only

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liberates the C3-silylated indole **5a** but also arrives at another Wheland complex **12a**. This step was NMR spectroscopically corroborated by the reaction of **4a** with an independently prepared sample of **11a**. Iminium ion **12a** then accepts a hydride from hydrosilane **1** to yield indoline **6a** as well as donor-stabilized silylium ion **3**; quantitative deuterium incorporation at C2 of **6a** was seen when using Me_2PhSiD (**1a**-d_1). This reduction pathway will not occur with the aniline substrates (not shown).

To recap, we disclosed here a counterintuitive C−H silylation of electron-rich (hetero)arenes passing through an S_EAr mechanism. The transformation is initiated by Brønsted acid-mediated generation of a highly electrophilic silicon cation from hydrosilanes. Protonation of the hydrosilane leads to loss of dihydrogen and release of the stabilized silylium ions. The Wheland intermediate then largely maintains the catalytic cycle as the proton source. No protodesilylation is observed when the amount of acid is well balanced. This protocol is a practical and straightforward way for the installation of silicon groups on arenes, thereby complementing existing transition-metal and Lewis-acid catalysis.[6]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b04878.

Experimental procedures and data (PDF)
Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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