Lewis Acid Catalysis

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Friedel–Crafts-Type Intermolecular C–H Silylation of Electron-Rich Arenes Initiated by Base-Metal Salts

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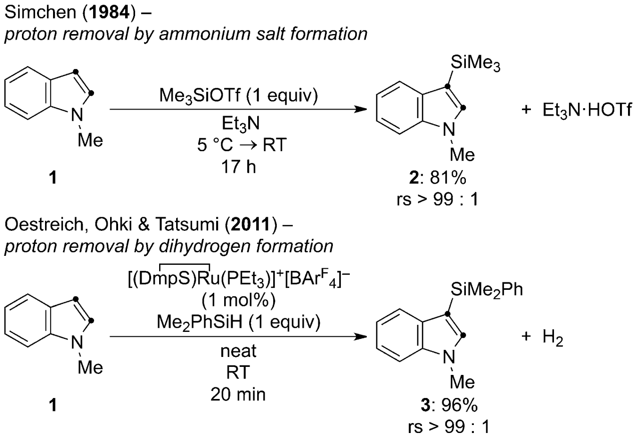
***Abstract:** An electrophilic aromatic substitution (S_EAr) with a catalytically generated silicon electrophile is reported. Essentially any commercially available base-metal salt acts as an initiator/catalyst when activated with $NaBAr^F_4$. The thus-generated Lewis acid then promotes the S_EAr of electron-rich arenes with hydrosilanes but not halosilanes. This new C–H silylation was optimized for $FeCl_2/NaBAr^F_4$, affording good yields at catalyst loadings as low as 0.5 mol %. The procedure is exceedingly straightforward and comes close to typical Friedel–Crafts methods, where no added base is needed to absorb the released protons.*

The installation of silicon groups at arenes by electrophilic aromatic substitution (S_EAr) was identified as an important synthetic goal nearly four decades ago.[1] However, this seemingly straightforward challenge has not lost its relevance because, then as now, there have been no practical solutions reported.[2,3] The key issue is that the Brønsted acid released in S_EAr rapidly triggers the reverse reaction, known as protodesilylation. Hence, protons must be absorbed irreversibly from this equilibrium. This was achieved by using neutral Me_3SiOTf and Et_3N as solvent in the C3-selective silylation of indoles and pyrroles (e.g., **1**→**2**; Scheme 1, top).[4] Recent variations employing Ph_3SiH activated by stoichiometric $[Ph_3C]^+[B(C_6F_5)_4]^-$ or catalytic $B(C_6F_5)_3$ (not shown) also require the addition of a base.[5] An alternative approach involves catalytic generation of the silicon electrophile by cooperative Si–H bond activation of hydrosilanes at the Ru–S bond of tethered cationic complexes.[6] After transfer of the silicon cation from the $[S–Si]^+$ site to the nucleophilic heterocycle, the sulfur atom acts as an internal base, eventually forming dihydrogen (e.g., **1**→**3**; Scheme 1, bottom).[7] These transformations have essentially remained the only examples of intermolecular electrophilic C–H silylation.[8–10] We demonstrate in this work that activated base-metal salts are also capable of initiating or catalyzing the silylation of arene C–H bonds with hydrosilanes but not chlorosilanes. The new procedure almost resembles the Friedel–Crafts reaction in its classical sense, with no addition of base required.[11]



Scheme 1. C–H silylation of electron-rich heterocycles by S_EAr. Ar^F = 3,5-bis(trifluoromethyl)phenyl, Dmp = 2,6-dimesitylphenyl, rs = regioselectivity, Tf = trifluoromethanesulfonyl.

We selected the electrophilic silylation of electron-rich *N*,*N*-dimethylaniline as a model reaction (**4**→**5**; Table 1). The Lewis acid $FeCl_2$ was used as the catalyst, and the halosilanes $Me_2PhSiCl$ and Me_2PhSiI, as well as the hydrosilane Me_2PhSiH were chosen as the silylating agents. As expected, treatment of **4** in the presence of $FeCl_2$ (5 mol %) with excess (5 equiv) of either of these reagents at 100 °C for prolonged reaction times did not show any conversion (Table 1, entries 1–3). To boost the Lewis acidity of $FeCl_2$, we decided to add equimolar amounts of $NaBAr^F_4$, based on the catalyst employed. This usually brings in the weakly coordinating tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion as a replacement for the chloride ligand. This technique is often used to transform well-defined neutral metal complexes into cationic ones, but we are not aware of examples of its application to conventional metal salts. We hoped to form "$[FeCl]^+[BAr^F_4]^-$", although the actual structure, in other words, its degree of aggregation or composition, is likely to be more complicated. The additive had no or little effect on the reactions with the halosilanes but changed the outcome with the hydrosilane dramatically (entries 4–6). The $FeCl_2/NaBAr^F_4$ catalyst system afforded **5** regioselectively with 87 % conversion in 70 % yield. $NaBAr^F_4$ alone did not promote the C–H silylation (entries 7–9).[12] We repeated the reactions of the halosilanes with 2,6-lutidine as a proton scavenger (entries 10 and 11). While the reaction with the chlorosilane was again unsuccessful, the iodosilane indeed reacted, converting **4** into **5** with 65 % conversion. Control experiments with $FeCl_2$/2,6-lutidine or 2,6-lutidine alone confirmed that $NaBAr^F_4$ as an additive is necessary (entries 12–14). This outcome corroborates the fact that

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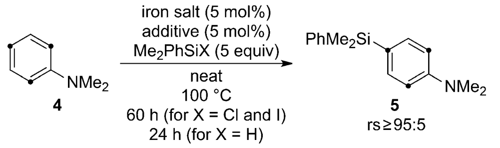
Table 1: Development of the Friedel–Crafts-type intermolecular C–H silylation catalyzed by iron Lewis acids.[a]



Entry	Iron salt	Additive	X	*T* [°C]	rs[b]	Conv. [%][c]
1	$\mathrm{FeCl_2}$	–	Cl	100	–	no conv.
2	$\mathrm{FeCl_2}$	–	I	100	–	trace
3	$\mathrm{FeCl_2}$	–	H	100	–	no conv.
4	$\mathrm{FeCl_2}$	$\mathrm{NaBAr^F_4}$	Cl	100	–	no conv.
5	$\mathrm{FeCl_2}$	$\mathrm{NaBAr^F_4}$	I	100	–	trace
6	**$\mathrm{FeCl_2}$[d]**	**$\mathrm{NaBAr^F_4}$**	**H**	**100**	**97:3**	**87 (70)**[e]
7	–	$\mathrm{NaBAr^F_4}$	Cl	100	–	no conv.[f]
8	–	$\mathrm{NaBAr^F_4}$	I	100	–	no conv.[f]
9	–	$\mathrm{NaBAr^F_4}$	H	100	–	no conv.
10	$\mathrm{FeCl_2}$	$\mathrm{NaBAr^F_4}$/ 2,6-lutidine[g]	Cl	100	–	no conv.
11	$\mathrm{FeCl_2}$	$\mathrm{NaBAr^F_4}$/ 2,6-lutidine[g]	I	100	$>$99:1	65
12	$\mathrm{FeCl_2}$	2,6-lutidine[g]	Cl	100	–	no conv.
13	$\mathrm{FeCl_2}$	2,6-lutidine[g]	I	100	–	trace
14	–	2,6-lutidine[g]	I	100	–	trace
15	$\mathrm{FeBr_2}$	$\mathrm{NaBAr^F_4}$	H	100	98:2	90
16	$\mathrm{Fe(OAc)_2}$	$\mathrm{NaBAr^F_4}$	H	100	$>$99:1	35
17	$\mathrm{FeCl_3}$	$\mathrm{NaBAr^F_4}$	H	100	97:3	83
18	$\mathrm{FeCl_2}$	$\mathrm{AgSbF_6}$	H	100	–	no conv.
19	$\mathrm{FeCl_2}$	$\mathrm{NaBAr^F_4}$	H	60	$>$99:1	70
20	$\mathrm{FeCl_2}$	$\mathrm{NaBAr^F_4}$	H	140	96:4	88
21	**$\mathrm{FeCl_2}$**	**$\mathrm{NaBAr^F_4}$**	**H**	**MW**[h]	**97:3**	**95 (78)**[e]
22[i]	$\mathrm{FeCl_2}$	$\mathrm{NaBAr^F_4}$	H	100	95:5	90 (58)[e]

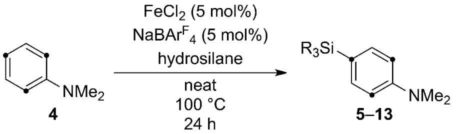
[a] Reactions were performed on a 0.1 mmol scale in a sealed tube. [b] *para*:*ortho* ratio determined by GLC analysis. [c] Determined by GLC analysis with tetracosane as internal standard. [d] Exactly the same result was obtained with anhydrous $\mathrm{FeCl_2}$ (99.99 %): 83 % conv., rs = 98:2. [e] Yield after purification by flash chromatography on silica gel. [f] Addition of 2,6-lutidine (1.0 equiv) did not make any difference. [g] 1.0 equiv. [h] Reaction was performed with microwave (MW) heating at 140 °C for 2 h. [i] Reaction was performed in an open flask.

protons and the reverse reaction caused by them cannot be ignored (see Scheme 1, top).[4,5] Other iron(II) and iron(III) salts were also effective, and those with halide counteranions were superior (entries 15–17). This is likely due to the ability of $\mathrm{NaBAr^F_4}$ to preferentially abstract halide anions. The use of $\mathrm{AgSbF_6}$ instead of $\mathrm{NaBAr^F_4}$ was not successful (entry 18).[13]

Further optimization of the catalyst system revealed that the use of 10 mol % of $\mathrm{FeCl_2/NaBAr^F_4}$ and 10 mol % $\mathrm{NaBAr^F_4}$ at 5.0 mol % $\mathrm{FeCl_2}$ had little effect. A more pronounced influence was seen when the reaction was run in a solvent; conversion dropped to 60 % in toluene (1 M). The conversion remained nearly unchanged in a temperature window from 60 to 140 °C (Table 1, entry 6 vs. entries 19 and 20). However, microwave heating to 140 °C resulted in substantial rate acceleration, reaching 95 % conversion within 2 h (entry 21). If desired, it is possible to perform the $\mathrm{S_EAr}$ in an open flask without exclusion of air and moisture (entry 22). To demonstrate the preparative utility on larger scale (2 mmol), we repeated the reaction at 100 °C for 60 h (entry 6) and 140 °C (MW) for 2 h (entry 21) at a catalyst loading as low as 0.5 mol % and with less hydrosilane (3 equiv); the yield was 72 % in both cases.

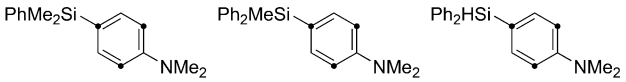
The new method is moderately general with regard to the hydrosilane (Table 2). As verified for the $\mathrm{FeCl_2/NaBAr^F_4}$ catalyst system, an aryl substituent at the silicon atom of the hydrosilane is required, and equally high conversions were achieved with mono-, di-, and trihydrosilanes (Table 2, entries 1, 2, 8, and 9); $\mathrm{Ph_3SiH}$ seems to be too sterically hindered (entry 3). Representative results with yields are summarized in Figure 1 (**4**→**5**, **6**, or **12**). Hydrosilanes solely decorated with alkyl, alkoxy, and/or silyloxy substituents did not react at all (entries 4–7).

Table 2: Screening of suitable hydrosilanes.[a]



Entry	Hydrosilane (equiv)	Aniline	rs[b]	Conv. [%][c]
1	$\mathrm{Me_2PhSiH}$ (5)	**5**	97:3	87
2	$\mathrm{MePh_2SiH}$ (5)	**6**	99:1	83
3	$\mathrm{Ph_3SiH}$ (5)	**7**	$>$99:1	30
4	$\mathrm{Et_3SiH}$ (5)	**8**	–	no conv.
5	$\mathrm{EtMe_2SiH}$ (5)	**9**	–	no conv.
6	$\mathrm{(EtO)_3SiH}$ (5)	**10**	–	no conv.
7	$\mathrm{(Me_3SiO)_2MeSiH}$ (5)	**11**	–	no conv.
8	$\mathrm{Ph_2SiH_2}$ (2)	**12**	98:2	85
9	$\mathrm{PhSiH_3}$ (1)	**13**	–[d]	80

[a] Reactions were performed on a 0.1 mmol scale in a sealed tube. [b] *para*:*ortho* ratio determined by GLC analysis. [c] Determined by GLC analysis with tetracosane as internal standard. [d] Mixture of mono- and disubstituted silanes obtained.



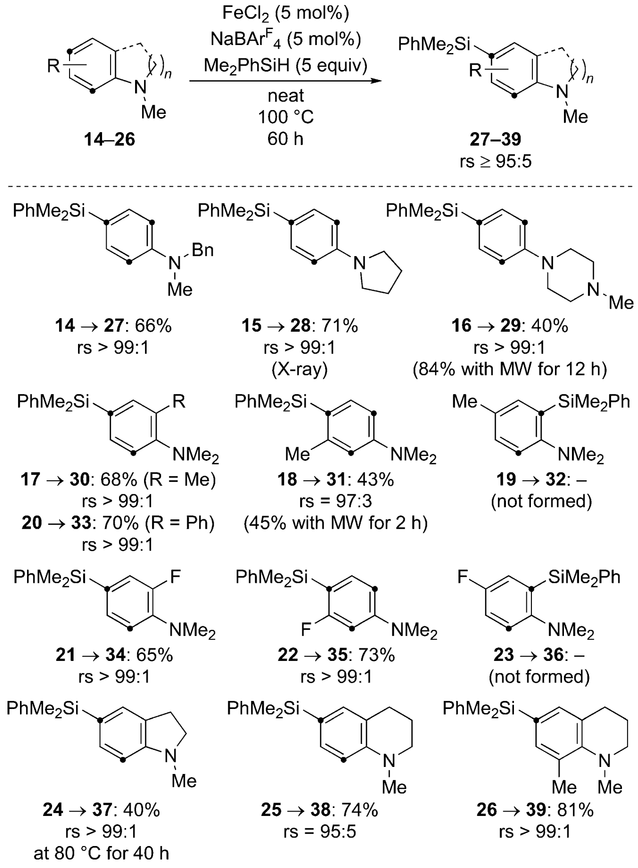
4 → **5**: 70% (78% with MW for 2 h)

4 → **6**: 69%

4 → **12**: 62%

Figure 1. C–H silylation of *N*,*N*-dimethylaniline with phenyl-substituted hydrosilanes (see Table 2).

The optimized conditions (see Table 1, entries 6 and 21) were then applied to the *N*,*N*-dialkyl-substituted anilines **14**–**23**, as well as to indoline **24** and the 1,2,3,4-tetrahydroquinolines **25** and **26** (Scheme 2). We routinely ran the reactions at 100 °C for 60 h but microwave heating at 140 °C for 12 h or less was also employed in selected cases. Yields were generally good for *ortho*- and *meta*-substituted substrates, and regioselectivity in favor of *para* substitution was excellent throughout. However, neither a methyl nor a fluoro group in the aniline *para* position, as in **19** and **23**, steered the reaction toward the *ortho* positions. In contrast to the successful use of fluorinated anilines, the related chlorinated and brominated anilines did participate in the C–H silylation but significant dehalogenation occurred (see the Supporting Information for details). As expected from the result with *ortho*-methyl-substituted **17**, cyclic compounds **24**–**26** also furnished the C5- and C6-silylated heterocycles in useful yields. The lower yield

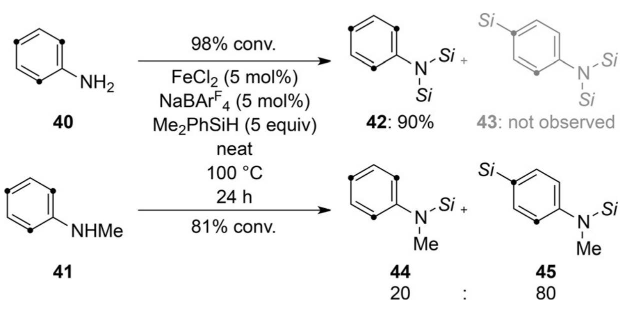


Scheme 2. Reaction scope I: Acyclic and cyclic *N*,*N*-disubstituted aniline derivatives.

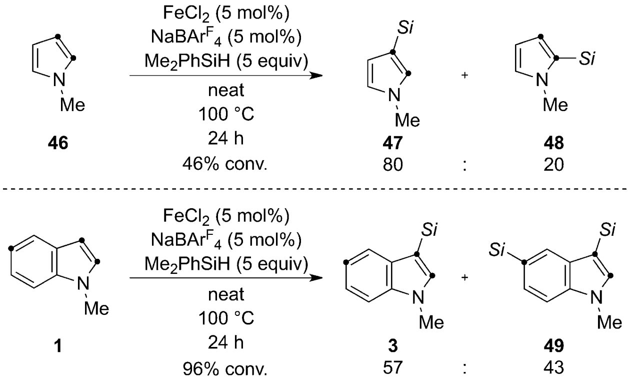
obtained for indoline **24** is due to indoline-to-indole oxidation, which is why this reaction demanded milder temperatures.

Free NH groups as in the anilines **40** and **41** underwent (two-fold) dehydrogenative Si–N couplings[14,15] prior to the planned S_EAr reaction (**40**→**42** but not **43** and **41**→**44** and **45**; Scheme 3). However, the resulting *N*,*N*-bissilylated aniline **42** is not sufficiently nucleophilic anymore, and **43** was not detected. Conversely, aniline **44**, which has one silyl group at the nitrogen atom, is not fully deactivated, and the C–H silylation did furnish **45** with good conversion.

Activated heterocycles such as N-substituted pyrroles and indoles are the preferred substrates for electrophilic C–H silylation (see Scheme 1).[4,5b,7,9] And indeed, pyrrole **46** reacted with moderate efficiency to afford regioisomeric **47** and **48** in an 80:20 ratio (Scheme 4, top). Indole **1** was converted into the expected C3-silylated indole **3** but also formed **49**, with the C–H bond at C5 additionally silylated (Scheme 4, bottom).[16] This stands in contrast to existing literature precedence,[4,5b,7,9] and is likely the result of reversible indole-to-indoline reduction, where the transient indoline undergoes *para*-selective C–H silylation (see **24**→**37**; Scheme 2, 80 °C instead of 100 °C to suppress competing indoline-to-indole oxidation).



Scheme 3. Reaction scope II: C–H silylation in the presence of free NH group(s). *Si* = $SiMe_2Ph$.



Scheme 4. Reaction scope III: Pyrroles and indoles. *Si* = $SiMe_2Ph$.

We were intrigued by the fact that the rather simple combination of an iron(II) or iron(III) salt with $NaBAr^F_4$ brings about an otherwise difficult S_EAr with an in situ generated silicon electrophile. We then tested various commercially available di- and trivalent metal chlorides and triflates and were surprised to find that all of them catalyzed the C–H silylation of *N*,*N*-dimethylaniline with $NaBAr^F_4$ as an additive (**4**→**5**; Figure 2).

The finding that such a broad range of metal salts together with $NaBAr^F_4$ is catalytically active raises the question of whether the same catalyst is released from these combinations. Our initial assumption was that $NaBAr^F_4$ generates a cationic Lewis acid catalyst by chloride or triflate abstraction from the metal salt. It is, however, known that the $BAr^F_4{}^-$ anion is not necessarily stable toward certain noble-metal cations, and C–B bond cleavage concomitant with attachment of an Ar^F group to the metal center is well documented.[17] Such transmetalation could also come into play here and liberate tris[3,5-bis(trifluoromethyl)phenyl]borane,[18] yet another potential catalyst for the present S_EAr.[19] We analyzed the action of $FeCl_2$ on $NaBAr^F_4$ by ^1H, ^{11}B, and ^{19}F NMR spectroscopy at room and elevated temperatures but could not detect any free BAr^F_3 in the resulting complex mixtures. At this stage, the true nature of the catalyst, either

$Sc(OTf)_3$ 68% conv. rs = 97:3	$CoCl_2$ 87% conv. rs = 98:2	$NiCl_2$ 74% conv. rs = 97:3	$CuCl_2$ 55% conv. rs = 95:5	$Zn(OTf)_2$ 88% conv. rs = 97:3	$AlCl_3$ 77% conv. rs = 98:2
$Y(OTf)_3$ 46% conv. rs = 98:2	$CeCl_3$ 72% conv. rs = 96:4	$Sm(OTf)_3$ 74% conv. rs = 99:1		$ZnCl_2$ 79% conv. rs > 99:1	$InCl_3$ 88% conv. rs = 98:2

Figure 2. Testing other metal salts in the C–H silylation of *N*,*N*-dimethylaniline [**4**→**5**: metal chloride or triflate (5 mol%), $NaBAr^F_4$ (5 mol%), neat, 100 °C, 24 h].

an in situ formed Ar^F-substituted base metal[17] or a boron Lewis acid, cannot be formulated.[20] The mechanism of the generation of the silicon electrophile as well as an overall analysis are the subject of ongoing investigations.

The present intermolecular C–H silylation by S_EAr complements the existing state of the art defined by noble-metal-[21] and KO*t*Bu-catalyzed[22] procedures.[8] The use of a base-metal salt together with $NaBAr^F_4$ and a hydrosilane rather than the more obvious chlorosilane is key to success. No base is required to absorb the proton released from the Wheland intermediate, which is why the new method is close to classic Friedel–Crafts reactions.

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Keywords: C–H activation · electrophilic substitution · hydrosilanes · Lewis acids · Si–H activation

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[20] $[Ph_3C]^+[B(C_6F_5)_4]^-$ (5 mol %) with and without 2,6-lutidine (1.0 equiv) yielded less than 10 % conversion in our model reaction **4**→**5**.[5a,10a] We therefore exclude hidden catalysis by silicon cations or hydronium ions.

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