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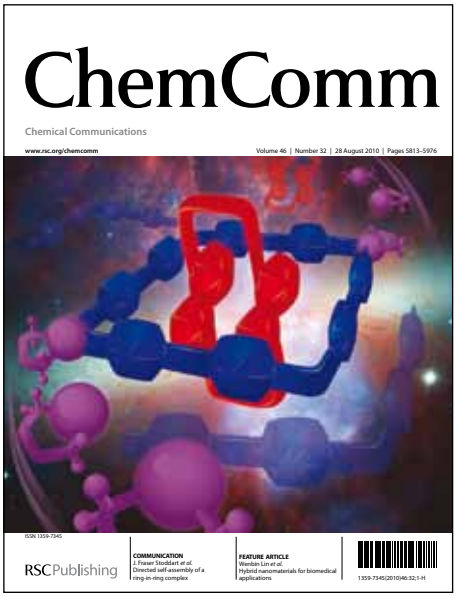

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ARTICLE TYPE

E-H (E = R_3Si or H) bond activation by $B(C_6F_5)_3$ and heteroarenes; competitive dehydrosilylation, hydrosilylation and hydrogenation.

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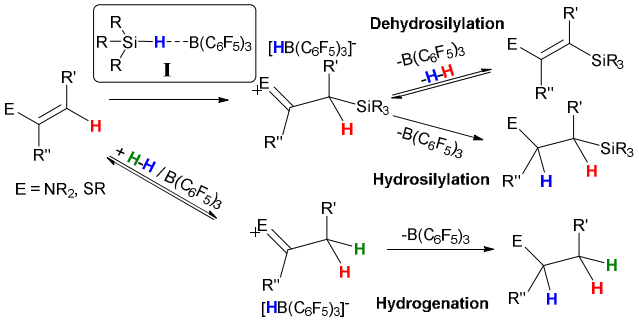
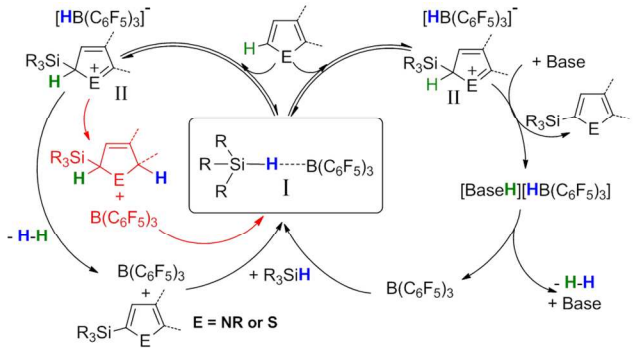
In the presence of $B(C_6F_5)_3$ five-membered heteroarenes undergo dehydrosilylation and hydrosilylation with silanes. The former, favoured on addition of a weak base, produces H_2 as a by-product making the process catalytic in $B(C_6F_5)_3$ but also enabling competitive heteroarene hydrogenation.

The activation of H_2 and silanes by boron Lewis acids and a nucleophile is developing into a powerful metal-free approach to hydrogenate, hydrosilylate and dehydrosilylate a range of substrates.[1, 2] $B(C_6F_5)_3$, and its derivatives, are the Lewis acids of choice combining considerable electrophilicity with sufficient bulk to 'frustrate' Lewis adduct formation.[2] $B(C_6F_5)_3$ activates R_3Si-H via species **I** (Scheme 1),[3] with subsequent transfer of R_3Si^+ to a nucleophile.[4] To date the combination of **I** with a nucleophile forms products from either hydrosilylation (e.g, with ketones) or dehydrosilylation (e.g., with alcohols).[4] However, with substrates such as heteroarenes and heteroatom substituted alkenes these outcomes are not necessarily mutually exclusive. Indeed, Oestreich *et al.*, have shown that both the hydrosilylation and the dehydrosilylation of enolizable carbonyl compounds is possible with a related silicon cation.[5, 6] Furthermore, the generation of H_2 from dehydrosilylation permits frustrated Lewis pair (FLP) mediated hydrogenation as an additional, potentially competitive, reaction pathway (Scheme 1, bottom).[2]



Scheme 1. Dehydro- / hydro-silylation and hydrogenation with $B(C_6F_5)_3$.

We were interested in determining how **I** reacts with nucleophilic heteroarenes, particularly as related silicon cations have been recently demonstrated to exclusively dehydrosilylate arenes.[7 - 9] Whilst $B(C_6F_5)_3$ reacts with highly nucleophilic arenes such as *N*-alkyl-indoles this occurs only extremely slowly.[10] As many heteroarenes actually have lower nucleophilicities than R_3SiH[11] compound **I** will form in their presence. Nucleophilic attack on **I** by a heteroarene will initially generate [R_3Si-arenium][$HB(C_6F_5)_3$], **II**, with multiple outcomes then possible. Herein we report a study into these competing pathways which include: (i) dehydrosilylation by the direct reaction of $[HB(C_6F_5)_3]^-$ with arenium cation **II** (Scheme 2, left), or by base catalysis where a Lewis base deprotonates the arenium cation **II** before dehydrocoupling with $[HB(C_6F_5)_3]^-$ (Scheme 2, right).[2] (ii) Hydrosilylation by hydride transfer from $[HB(C_6F_5)_3]^-$ to [R_3Si-arenium]$^+$ (Scheme 2, red), and (iii) hydrogenation. These processes are all catalytic in $B(C_6F_5)_3$, but turnover is limited by competing deactivation pathways that have also been elucidated.



Scheme 2. Dehydro- / hydro- (red) silylation catalysed by $B(C_6F_5)_3$.

Studies commenced with 2-methylthiophene (2-MT) and Ph_3SiH. 2-MT is less nucleophilic than Ph_3SiH and does not react with $B(C_6F_5)_3$. The combination of equimolar Ph_3SiH, $B(C_6F_5)_3$ and 2-MT produced 2-Me-5-(Ph_3Si)-thiophene, **2** (Table 1, entry 1). However, aliphatic 2-MT derived species were observed and unreacted 2-MT remained despite consumption of all Ph_3SiH, indicating a non-stoichiometric reaction. $B(C_6F_5)_3$ remained the dominant borane species (by ^{11}B and ^{19}F NMR spectroscopy), therefore an additional 4 equivalents of Ph_3SiH and 2-MT were added. This produced further equivalents of **2** indicating a catalytic process. Throughout, the aliphatic region of the ^1H NMR spectrum was complex but contained three doublets corresponding to three 2-Me groups (collectively termed **3**) each representing a different substituted tetrahydrothiophene derived from hydrosilylation.[12] At no point were vinylic resonances of substituted dihydrothiophene intermediates observed.

The ability of base to increase the proportion of **2** formed by facilitating the deprotonation of the arenium cation was next

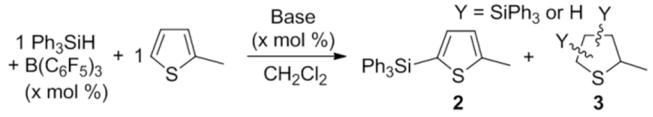


Table 1: Stoichiometric and catalytic electrophilic silylation of 2-MT.

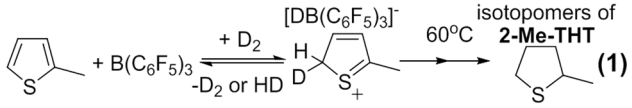
Entry	Base	$B(C_6F_5)_3$ / Base (mol %)	Time (h)	Temp. (°C)	2 (%)[a]	3 (%)[a]
1	-	100/0	42	20	34	31
2	$^tBu_2$-py	100/100	72	20	39	10
3	Cl_2-py	100/100	24	20	51	33
4	Cl_2-py	20/20	24	60	56	34
5	Cl_2-py	5/5	24	60	42	18
6	Cl_2-py	5/100	36	60	51	27
7[b]	Cl_2-py	5/5	24	60	46	32
8[c]	Cl_2-py	100/100	24	60	0	0

[a] = yields based on conversion of 2-MT by ^{1}H NMR spectroscopy, remaining material is 2-MT. [b] = with 1.5 equivalents of Ph_3SiH. [c] = in the presence of 1 eq. of tetrahydrothiophene.

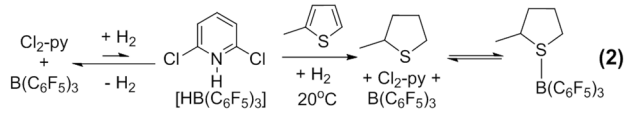
investigated. Addition of 2,6-ditertbutylpyridine ($^tBu_2$-py, entry 2) increased the ratio of **2** relative to **3**. However, to be catalytic the resultant $[H(amine)][HB(C_6F_5)_3]$ has to evolve H_2, a reaction requiring a weakly nucleophilic amine to be energetically favoured.[2] This precludes $^tBu_2$-py and 2,6-lutidine, the latter the optimal base in stoichiometric Sila-Friedel Crafts reactions.[9] As the steric bulk of the base strongly effects the barrier to deprotonation of silylated arenium cations isosteric bases to 2,6-lutidine were explored.[8, 9] Using 2,6-dichloropyridine (Cl_2-py) as a suitably weak base the amount of **2** produced (relative to **3**) increased (entry 3). Replacing CH_2Cl_2 with benzene resulted in no silylation (24 h, 20°C). In contrast, the silylation of carbonyl moieties with $B(C_6F_5)_3$ / R_3SiH is more rapid in non-polar solvents than in CH_2Cl_2 which obviated ionic intermediates.[3a] The necessity for polar solvents for heteroarene silylation implies the formation of unobserved ionic species, for example **II** (scheme 1). The silylation of 2-MT with various silanes using $B(C_6F_5)_3$ / Cl_2-py was also explored, but Ph_3SiH produced the highest amount of **2** relative to **3**, with less dehydrosilylation observed on decreasing silane steric bulk.[12]

Catalytic loadings of $B(C_6F_5)_3$ / Cl_2-py required heating for reasonable reaction times (entries 4 - 5) and led to similar ratios of **2** : **3**. Attempts with excess Cl_2-py did not significantly improve the selectivity for **2** (entry 6). Full consumption of 2-MT was not achieved even at longer times and using 1.5 eq. of Ph_3SiH (entry 5 vs 7), suggesting catalyst deactivation. During catalysis one new boron containing species gradually increased in intensity (by ^{11}B NMR spectroscopy) and moved progressively upfield to a limiting δ of -5 ppm. We surmised that aliphatic sulfides, **3**, were forming $R_2S{\rightarrow}B(C_6F_5)_3$ species retarding the catalysis. Indeed, equimolar tetrahydrothiophene and $B(C_6F_5)_3$ produced ^{11}B and ^{19}F NMR spectra comparable to those at the end of the catalytic runs.[12] Importantly, this mixture was inactive in silylation (entry 8), thus **3** may be an effective catalyst poison.

It was noteworthy that the overall conversion in reactions with Cl_2-py (e.g., entries 3 and 4) would be greater than 100 % based on Ph_3SiH if all the 2-MT derived aliphatic products were from the double hydrosilylation of 2-MT. As H_2 is the by-product from dehydrosilylation this results in competitive hydrogenation thus products from; (i) hydrosilylation and hydrogenation of 2-MT and (ii) the hydrogenation of 2-MT to 2-methyl-tetrahydrothiophene (2-Me-THT) dominate.[12] Related alkene and heteroarene hydrogenation by FLPs has been reported.[13, 14] To determine what components in the reaction mixture are activating H_2 equimolar $B(C_6F_5)_3$ / 2-MT was placed under D_2 (4 atm.) in the absence of Cl_2-py. At 20°C no reduction occurred but deuterium incorporation into the alpha position of 2-MT was observed indicating reversible activation of dihydrogen. On heating to 60°C aliphatic resonances were now also observed in the ^{2}H NMR spectrum indicating 2-MT reduction to partially deuterated isotopomers of 2-Me-THT (eq. 1).[12] $B(C_6F_5)_3$ / 2-MT is a rare example of a FLP in which a carbon nucleophile (2-MT) is activating dihydrogen.[14, 15] The reduction of 2-MT with $B(C_6F_5)_3$ in the presence of Cl_2-py was more facile, with 66 %



conversion of 2-MT to 2-Me-THT at only 20°C (16 h, 4 atm. H_2, eq. 2) indicating that Cl_2-py / $B(C_6F_5)_3$ is more effective for 2-MT hydrogenation, analogous to the high reduction activity of FLPs with other weak bases.[16] Complete reduction of 2-MT at 20°C is retarded by coordination of 2-Me-THT to $B(C_6F_5)_3$.[12] The necessity for Cl_2-py for 2-MT reduction at 20°C is consistent with the complete absence of 2-Me-THT in base free reactions (Table 1 entry 1, by NMR spectroscopy).[12] As previous reactions were performed in a closed system the H_2 concentration increases as dehydrosilylation proceeds enabling competitive hydrogenation. Silylation with $B(C_6F_5)_3$ / Cl_2-py performed in a tube sealed under vacuum (to minimise build up of dissolved H_2) produced no 2-Me-THT, but whilst there was a relative increase in **2**, aliphatic species (from hydrosilylation) were still present.[12]



The product distribution in the silylation of other heteroarenes using Ph_3SiH / $B(C_6F_5)_3$ / Cl_2-py was also explored. Thiophene, 2,2′-bithiophene and thieno-[3,2,*b*]-thiophene all resulted in no reaction at 20°C presumably due to reduced arene nucleophilicity relative to 2-MT. 2-^{t}Bu-thiophene, 2-BT, was amenable to stoichiometric and catalytic electrophilic silylation which occurs with concomitant hydrogenation (Table 2, entries 1-2). Electrophilic silylation via **I** could be extended to 5-membered *N*-heterocycles. Whilst *N*-TIPS protected pyrrole and indole were amenable to silylation, hydrogenation was again competitive (entries 3 and 4), although no hydrosilylation was observed in either case. Hydrogenation products were confirmed by independent reduction under 4 atm. H_2 (e.g., entry 5). Catalytic (in $B(C_6F_5)_3$) reductions were limited as (i) the hydrogenation of *N*-TIPS-indole produces a better Brønsted base, *N*-TIPS-indoline, that cleaves H_2 with $B(C_6F_5)_3$ to form [*N*-H-*N*-TIPS-indolinium][$HB(C_6F_5)_3$] thus sequestering $B(C_6F_5)_3$ and preventing turnover, (ii) the catalytic hydrogenation of ^{t}Bu-thiophene was retarded by coordination of 2-^{t}Bu-tetrahydrothiophene to $B(C_6F_5)_3$ (entry 6).[12]

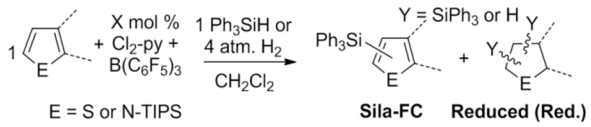
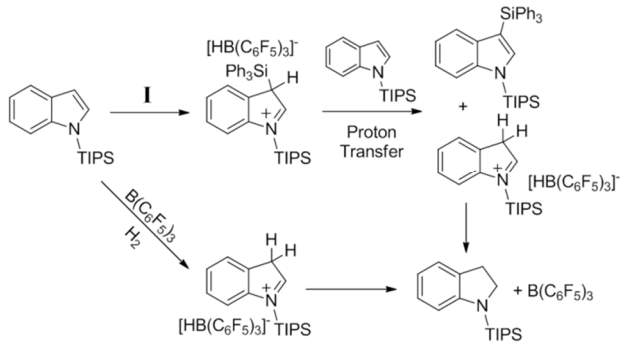


Table 2: Electrophilic functionalisation of select heteroarenes.

Entry	Substrate	Y-H	$B(C_6F_5)_3$ / Cl_2-py (mol %)	t (h)	T (°C)	Sila-FC[a] (%)	Red.[a] (%)
1	2-BT	Si-H	100/100	18	20	54	32
2	2-BT	Si-H	5/5	24	60	70	17
3	*N*-TIPS pyrrole	Si-H	100/100	48	20	42	45
4	*N*-TIPS-indole	Si-H	100/100	24	20	59	19[b]
5	*N*-TIPS-indole	H-H	100/100	16	20	-	80[b]
6	2-BT	H-H	100/100	24	20	-	80[c]
7	*N*-TIPS-indole	Si-H	100/0	24	20	30	21[b]
8	*N*-TIPS-indole	H-H	100/0	24	20	-	16[b]
9	*N*-TIPS-indole	H-H	100/0	24+24	20+60	-	35[b]

[a] = Conversion by consumption of the substrate and growth of products as determined by ^{1}H NMR spectroscopy, unreacted starting material also present. [b] = combined conversion to the indoline and protonated indoline. [c] = acid induced ^{t}Bu migration results in multiple reduction products.

The dehydrosilylation of *N*-TIPS-indole without Cl_2-py led to increased proportions of the reduction product, *N*-TIPS-indoline, (entry 7 Vs 4) analogous to 2-MT reactivity. Furthermore, in the absence of Cl_2-py the FLP hydrogenation of *N*-TIPS-indole with $B(C_6F_5)_3$ also proceeds confirming that *N*-TIPS indole is also a viable carbon nucleophile for FLP H_2 activation (entries 8 and 9).[12] It is noteworthy that there is less reduction of *N*-TIPS-indole at 20°C under H_2 than there is during silylation (entry 7 Vs 8) thus another reduction mechanism must be operating in silylation. Reduction presumably proceeds by silylation of *N*-TIPS-indole followed by proton transfer to another molecule of *N*-TIPS-indole, as observed in electrophilic borylations,[17] and finally reduction to *N*-TIPS-indoline by hydride transfer (Scheme 3).



Scheme 3. Reduction of *N*-TIPS-indole by competing mechanisms.

In conclusion, R_3Si-H-$B(C_6F_5)_3$, **I**, still forms in the presence of activated heteroarenes, which for the first time are shown to be viable nucleophiles towards **I**. Catalytic silylation pathways are demonstrated, but the competitive activation of Si-H and H-H bonds by boron Lewis acids / weak nucleophiles leads to multiple products. Furthermore, the formation of aliphatic R_2S species from thiophene hydrosilylation / hydrogenation inhibits catalyst turnover by coordination to $B(C_6F_5)_3$. Finally, the hydrogenation of both 2-MT and *N*-TIPS-indole with only $B(C_6F_5)_3$ / H_2 confirms both these heteroarenes are carbon nucleophiles capable of activating H_2 in a FLP. This suggests that many other arenes will be viable as carbon nucleophiles for H_2 cleavage in a FLP.

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† Electronic Supplementary Information (ESI) available: Experimental procedures and characterisation. See DOI: 10.1039/b000000x/

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