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Mono(hydrosilylation) of N-Heterocycles Catalyzed by $B(C_6F_5)_3$ and Silylium Ion

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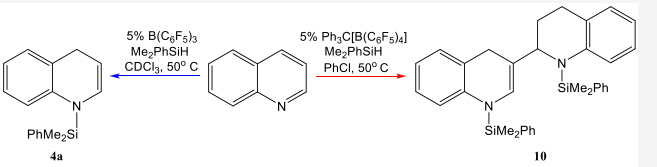
ABSTRACT: Catalytic hydrosilylations of various N-heterocycles mediated by silylium ion and electrophilic borane catalysts are reported. The reactions proceed via intermediate silylquinolinium ions that give rise to a variety of reduced and coupling products. Generally, highly selective 1,4-regioselectivity is observed.

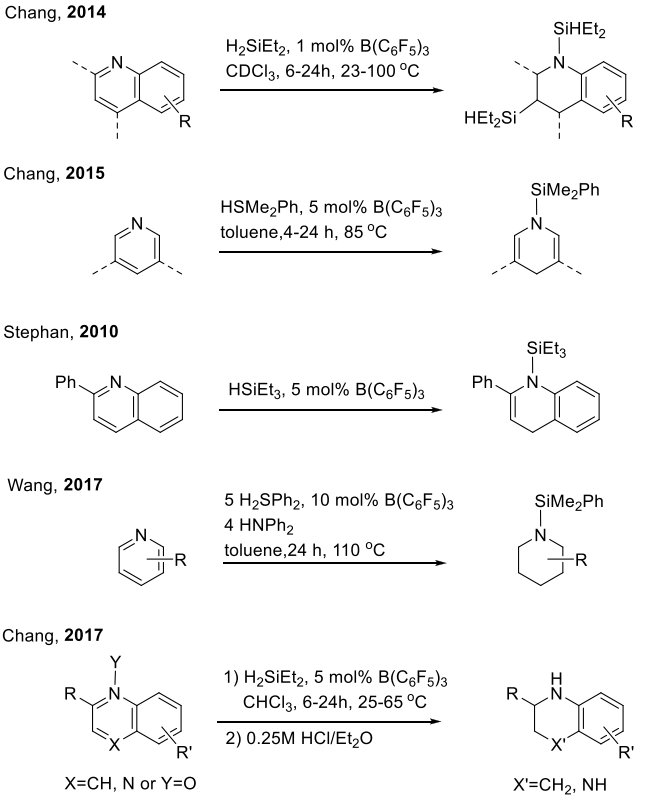


INTRODUCTION

Reduced aromatic N-heterocycles are important building blocks in a variety of agrochemical and pharmaceutical products[1] and also find applications in material science and synthetic chemistry.[2] The application of silanes and boranes in the reduction of heteroaromatics has become very popular over the past decade[3] because it allows for chemo- and regioselective reductions and avoids the harsh conditions typically required for catalytic hydrogenation.[4] Silanes are particularly attractive as reducing reagents because they are usually air stable and commercially available and allow for easy experimental setups. In 2011, our group reported the first instance of catalytic chemo- and regioselective 1,4-hydrosilylation of pyridines catalyzed by the cationic ruthenium complex $[Cp(^iPr_3P)Ru(NCCH_3)_2)]^+$.[5] Mechanistic studies showed that the unique activity and selectivity of this system was provided through the realization of unconventional ionic hydrosilylation mechanism.[6] An improved catalytic system based on Ru−S cooperativity was developed by Oestreich and co-workers,[7] and selective 1,2-hydrosilylation catalyzed by iridium was reported by the Chang group.[8]

A major advance of the field was accomplished by the realization of main-group catalysis,[9] such as 1,2-hydrosilylation catalyzed by $[NacNacCa(THF)(\mu\text{-}H)_2]$ reported by Harder and co-workers[10] and zinc-catalyzed 1,2-selective reduction developed in our laboratory.[11] In this regard, the use of bulky electrophilic boranes, such $B(C_6F_5)_3$, as catalyst in hydrosilylation has received significant attention.[12] In particular, Chang and co-workers reported borane-catalyzed double hydrosilylation of a range of quinolines, benzoquinolines, and isoquinolines to give 3-silyl-substituted tetrahydro products with a saturated N-ring (Scheme 1).[13] It was suggested that the reaction proceeds via the initial rate-limiting 1,4-hydrosilylation followed by a more facile 2,3-addition of silane to the double bond. As is the case for other borane-catalyzed hydrosilylations, the active species is produced by borane activation of the silane to give the polarized adduct $(F_5C_6)_3B{\leftarrow}H{-}SiR_3$[14,15] that transfers the silylium ion to the substrate

Scheme 1. Previous Examples of Borane-Catalyzed Hydrosilylation of Pyridines



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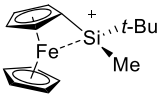
followed by hydride transfer from the borate $[(F_5C_6)_3BH]^-$.[12] The Chang group then found that under slightly different conditions double hydrosilylation of 3-substituted pyridines and 1,4-monohydrosilylation of some 3,5-disubstituted pyridines is also possible (Scheme 1).[16] The single example of quinoline 1,4-hydrosilylation was described by Stephan and co-workers.[17] Wang et al. reported that in the presence of a proton donor, such as Ph_2NH, the borane-catalyzed reduction proceeds to furnish tetrahydroquinoline and piperidine derivatives,[18] and the Chang group further revealed borane-catalyzed reduction of quinolines, quinoxalines, and quinoline *N*-oxides to tetrahydro derivatives in the absence of a proton donor.[19]

Since the generation of a silylium ion, R_3Si^+, is intrinsically linked to the proposed mechanism, we became interested if the use of a silylium ion as a catalyst would lead to the same catalytic outcome. We took into account that R_3Si^+ is isolobal with the borane $(F_5C_6)_3B$ but is more electrophilic.[20] The application of silylium ions in catalysis is much more limited in comparison with that of boranes and is primarily focused on C−F bond activation and Lewis acid catalysis, such as the Diels−Alder reaction.[20] The literature on silylium ion catalyzed hydrosilylation is particularly scarce. In 1999, Lambert and co-workers reported on the hydrosilylation of 1,1-diphenylethylene using an excess of Et_3SiH and 2 mol % of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**1**) that serves as an initiator of a silylium ion.[21] The scope of this catalysis has gradually grown to include reductions of CO_2, CO, carbonyls, indoles, and imines.[22,23] In 2013, Oestreich and co-workers reported catalytic hydrosilylation of N-tosylated aldimines mediated by the silylium ion **2**, which was generated from the reaction of the ferrocenylsilane $FcSi^tBu_2H$ and trityl cation.[22b] Here we report the catalytic mono(hydrosilylation) of various N-heterocycles using two different Lewis acids: a silylium ion and $B(C_6F_5)_3$.



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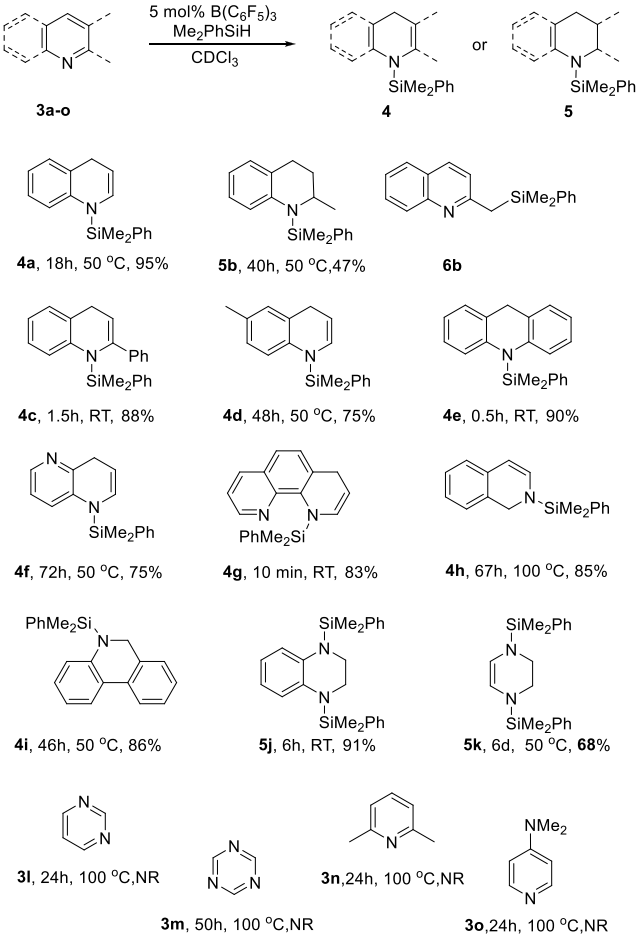
RESULTS AND DISCUSSION

We commenced our research by revisiting the $B(C_6F_5)_3$/silane system in an attempt to extend the scope of selective mono(hydrosilylation) of annulated pyridines **3** (Scheme 2). To this end, equimolar amounts of silane $HSiMe_2Ph$ and substrate were mixed in $CDCl_3$ followed by the addition of the borane $B(C_6F_5)_3$ (5%). Consistent with Chang's observations, minor amounts of tetrahydroquinoline products were detected in each reaction trial. Quinoline was reduced selectively to 1,4-dihydroquinoline in 95% yield after 18 h at 50 °C in $CDCl_3$. Interestingly, the quinaldine **3b** gave an equimolar mixture of two products that were identified by NMR as the tetrahydroquinaldine **5b** and the unexpected Me-silylated quinaldine **6b**. In particular, the newly formed silylmethylene unit of **6b** gives rise to a singlet in ^1H NMR at 2.93 ppm (2H) that correlates in HMBC with the quinaldine ^{13}C NMR C2 signal at 161.3 ppm and the $SiMe_2$ signal at −3.2 ppm. The reduced ring of **5b** shows a unique C2 methine peak at 3.77 ppm coupled in COSY with the methyl resonance at 1.27 ppm (d, J_{H-H} = 6.7 Hz) as well as to two diastereotopic C3 methylene signals at 1.98 and 1.93 ppm. The methylene

Scheme 2. Monohydrosilylation of Pyridines Catalyzed by $B(C_6F_5)_3$ (NMR Yields)[a]



[a]A 1% load of $B(C_6F_5)_3$ was used for substrates **3e−g**.

protons at the 4-position are seen as multiplets at 2.95 and 2.81 ppm. Blocking the 2-position with the phenyl group, such as in 2-phenylquinoline **3c**, leads to the expected 1,4-reduced derivative **4c**,[17] characterized by the benzylic methylene signal at 3.42 ppm (d, J_{H-H} = 4.8 Hz, 2H) and the enamine signal at 5.43 ppm (t, J_{H-H} = 4.8 Hz, 1H). The unactivated methyl group of 6-methylquinoline **3d** is not compromised, so that this substrate also reacts with 1,4-regioselectivity. Likewise, acridine, 1,5-naphthyridine, and 1,10-phenanthroline all gave the corresponding 1,4-dihydro products.[5,6a,7a] The regioselectivity of reduction for 1,5-naphthyridine was established by a nuclear Overhauser effect (NOE) experiment. Namely, the excitation of the methylene protons at 3.75 ppm revealed that they are not proximal to the silicon-bound methyl groups (3.75 ppm). In contrast, isoquinoline **3h** was 1,2-hydrosilylated and phenanthridine **3i** was reduced at the central ring C=N bond, as expected. Quinoxaline **3j** easily reacted at both C=N bonds, consuming 2 equiv of Me_2PhSiH. In contrast, of single-ring systems, such as pyrazine, pyrimidine, 1,3,5-triazine, 2,6-lutidine, and *N*,*N*-dimethylaminopyridine, only pyrazine was reduced to *N*,*N*-disilyltetrahydropyrazine **5k** and the others did not react even after 24 h at 100 °C.

To gain insight into the mechanism of reduction of quinaldine, we performed a labeling experiment with Me_2PhSiD. Deuterium incorporation was observed exclusively

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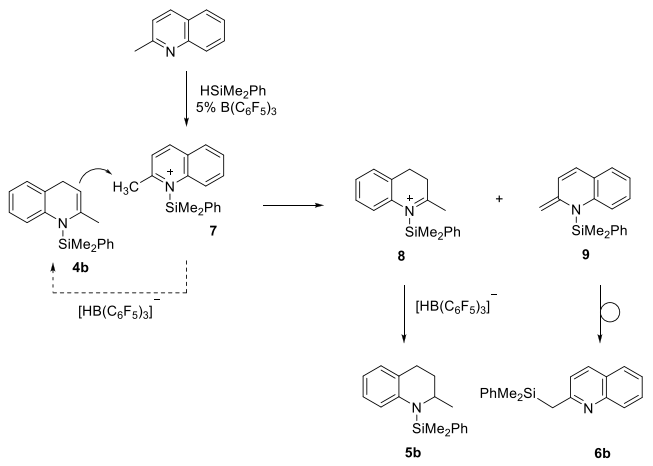
at the 2- and 4-positions of $\mathbf{5b_D}$ but not the 3-position. This observation led to the mechanistic proposal shown in Scheme 3. Once a significant amount of 1,4-hydrosilylated quinaldine

Scheme 3. Proposed Mechanism for the Formation of 5b and 6

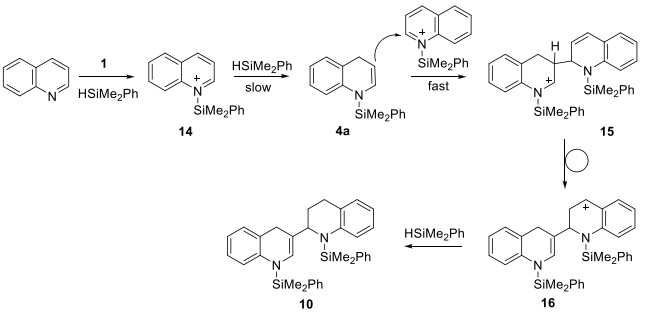


4b is produced, it starts to compete with the borate $[HB(C_6F_5)_3]^-$ for the quinaldinium ion **7**. That is, we propose that enamine **4b** manages to abstract a proton from the methyl group of **7** acidified by the positive charge on nitrogen. This proton transfer generates the N-silylated iminium ion **8** (from **4b**) and the dearomatized species **9**. The cation **8** is finally quenched in the reaction with $[HB(C_6F_5)_3]^-$, whereas **9** undergoes a [1,3]-sigmatropic silyl shift to regenerate the aromatic structure of the final Me-silylated quinaldine **6b**.[24]

Having established the scope of the borane-catalyzed monohydrosilylation, we turned our attention to silylium ion catalysis. Addition of 5 mol % of **1** to an equimolar mixture of quinoline and Et_3SiH results in zero conversion after 48 h at room temperature. To understand this lack of reactivity, a stoichiometric reaction with 100% **1** was carried out and the reaction progress was monitored by $^1H-^{29}Si$ HSQC spectroscopy. The $^1H-^{29}Si$ HSQC spectrum from the initial mixture of Et_3SiH and **1** in chlorobenzene displayed a ^{29}Si resonance at 126.9 ppm, supporting the formation of a chlorobenzene-stabilized silylium ion.[25] The subsequent addition of quinoline showed the formation of a silicon-bound quinolinium ion (51.5 ppm).[26] After the addition of a second equivalent of Et_3SiH, the ^{29}Si NMR spectrum remained unchanged except for the appearance of another resonance (9.20 ppm) corresponding to free Et_3SiH. These observations suggested that Et_3SiH was not sufficiently hydridic to transfer the hydride to the quinolinium ion.

Equipped with the understanding that a silane with a stronger hydride donor ability was required, we opted to use Me_2PhSiH. Although the computational estimation of the hydride ability showed that Me_2PhSiH is only a marginally better hydride donor than Et_3SiH (by 1 kcal/mol),[27] it was found to affect the reduction of the silyl quinolinium Ion to *N*-dimethylphenylsilyl-1,2,3,4-tetrahydroquinoline (**5a**) with 38% conversion after 24 h at 50 °C. In an attempted catalytic setup, a stoichiometric mixture of quinoline and Me_2PhSiH in chlorobenzene was charged with 5 mol % of **1** and heated to 50 °C for 53 h. Unexpectedly, the major product was identified to be the result of coupling of two reduced quinoline molecules that was assigned as the product of C3/C2′ coupling, compound **10** (Scheme 4). The identity of this product is

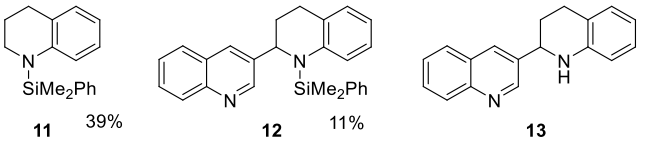
Scheme 4. Possible Mechanism for the Formation of 10



proposed on the basis of $^1H-^1H$ COSY, $^1H-^{13}C$ HSQC, $^1H-^{13}C$ HMBC, and DEPT 135 NMR spectra in PhCl. In particular, the methylene group of the dihydropyridine ring gives rise to two doublets at 3.43 and 3.13 pm (J_{H-H} = 19.1 Hz), whereas the unique olefin proton gives rise to a singlet at 6.27 ppm. Both of these signals correlate with the olefinic ^{13}C NMR signal at 141.4 ppm of the C3 carbon of dihydropyridine and with the C2′ signal of tetrahydropyridine (56.4 ppm) at the ring juncture. The latter signal correlates with the methine signal at 4.04 ppm of the tetrahydroquinoline. The connection of two rings was further confirmed by the observation of a four-bond correlation in COSY between the dihydropyridine olefin signal at 6.27 ppm and the tetrahydroquinoline methine signal at 4.04 ppm. The regioselectivity of coupling as C3/C2′ was established with the help of NOE experiments, which showed the proximity of the methine peak to two lower field signals due to the diastereotopic methyl groups of $SiMe_2Ph$ and the proximity to the olefinic signal of the dihydroquinoline ring. The methylene group of the dihydroquinoline moiety has NOE on the proton in the 5-position but not the $SiMe_3$ groups, thus confirming the 1,4-regioselectivity of reduction.

The other two products of this reductive coupling process were tetrahydroquinoline **11** (Chart 1) and a partially

Chart 1. Byproducts in 1-Catalyzed Hydrosilylation of Quinoline



aromatized version of **10**, compound **12**, featuring a quinoline moiety C3/C2′-coupled to tetrahydroquinoline.[28] Treatment of the reaction mixture with methanol followed by oxidation in air resulted in the single product **13** having a rearomatized quinoline ring. The ^1H NMR spectrum of the reaction mixture in $CDCl_3$ shows signals of re-formed aromatic protons at 8.92 ppm (2-position) and 8.45 ppm (4-position) coupled to each other with $^4J_{H-H}$ = 1.4 Hz. The unique methine proton of the tetrahydroquinoline ring gives rise to a resonance at 4.75 ppm (dd, $^3J_{H-H}$ = 8.6 Hz, $^3J_{H-H}$ = 3.5 Hz) coupled to the diasteretopic methylene signals at 2.24 and 2.11 ppm. These signals can be unequivocally assigned to the C2′ and C3′ positions, respectively, in the tetrahydroquinoline ring. The

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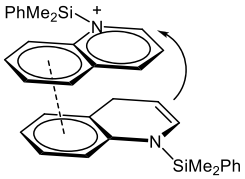
diastereotopic methylene in the C4′ position gives rise to multiplets at 2.95 and 2.75 ppm. HSQC and HMBC spectra further corroborate the notion that the main component of this mixture is the C3/C2′-coupled 2-(quinolinyl-3)-tetrahydroquinoline.

It is interesting that monitoring the reduction process with 1 equiv of silane did not reveal any significant amount of the expected 4-dihydroquinoline. However, when the reaction was carried out in the presence of excess silane (8−12 equiv), the initially observed products, formed already at room temperature, were 4-dihydroquinoline and the tetrahydroquinoline (in a 1.8 ratio). Then, as the reaction proceeded upon heating, the amount of dihydroquinoline increased quickly and reached a maximum of 26% at about 65% conversion, whereas the amount of tetrahydroquinoline increased much more slowly to 8% (at 65% conversion). Kinetic measurements in the presence of excess silane showed that the reaction is first order in quinoline and reaches saturation at about 9 equiv of $HSiMe_2Ph$.

These observations and the formation of **10** can be rationalized by the mechanistic proposal shown in Scheme 4. The reaction starts with the silylium ion transfer to the substrate to give an N-silylated quinolinium ion (**14**), which is then slowly reduced by silane to a 1,4-hydrosilylated quinoline (**4a**). Once a significant amount of **4a** is generated, it can effectively attack the ion **14** to form the carbocation **15** stabilized by α-nitrogen: i.e., an iminium ion. Proton transfer from the 3-position to the C3 carbon of the 1,2-dihydroquinoline ring generates the cation **16** that is ultimately reduced by silane, thus closing the catalytic cycle. Like the chemistry shown in Scheme 3, this suggests that the enamine **4a** is more nucleophilic/basic than the Si−H bond of Me_2PhSiH, which likely relates to the stability of the immediate cationic product, the iminium vs silylium ion, respectively. However, using excess silane changes the relative rates of the initial reduction versus coupling and leads to accumulation of a significant amount of 1,4-dihydroquinoline.

The possible rationale for the formation of C3/C2′ instead of the expected C3/C4′ coupling product is that the regioselectivity of attack is driven by stacking interactions between the electron-rich C-ring of enamine **4a** and the electron-poor C-ring of the quinolinium ion **14** as shown in Chart 2. These donor−acceptor interactions and the

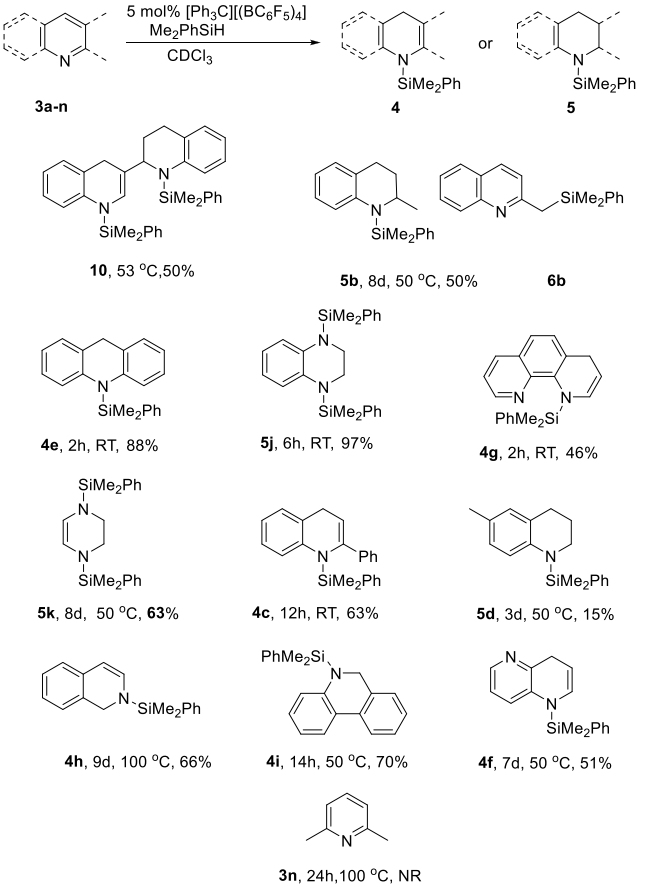
Chart 2. Stacking Interactions between Enamine 4a and Quinolinium Ion 14



minimization of steric repulsion between the bulky silyl groups dictate that the C3 position of **4a** be placed below the C2′ position of **14**.

The scope of the silylium ion catalysis was then studied (Scheme 5). Quinaldine gave the same two major products **5b** and **6b** as in the case of borane catalysis. This result was expected because the silane is an even weaker reducing reagent than borate $[HB(C_6F_5)_3]^-$ and cannot compete with enamine **4b** for the imidazolium salt **7**. Acridine, quinoxaline, and 1,10-

Scheme 5. Monohydrosilylation of Pyridines Catalyzed by $[Ph_3C]^+[B(C_6F_5)_4]^-$ (NMR Yields)



phenanthroline were reduced relatively quickly at room temperature. Acridine was reduced at the C9 position, and 1,10-phenanthroline underwent reduction at the C4 position. Quinoxaline again was reduced at both C=N bonds to give **5j**. Likewise, pyrazine, the only single-ring N-heterocycle which was successfully reduced by this method, was bis-(hydrosilylated). 2-Phenylquinoline was reduced at the C4 position[17] but required a slightly longer time of 12 h. 6-Methylquinoline reacted to give a mixture of products, indicated by several overlapping methyl signals in the ^1H NMR spectrum of the reaction mixture, with the major product being the N-silylated 1,2,3,4-tetrahydro-6-methylquinoline **5d**. Isoquinoline and phenanthridine were both reduced at the carbon adjacent to the nitrogen in the heterocycle. Isoquinoline required a longer reaction time and an increased temperature of 100 °C. In contrast, the standard conditions were sufficient for the reduction of phenanthridine. Similar to the case for borane catalysis, 1,5-naphthyridine was 1,4-hydrosilylated over several days while 2,6-lutidine remained unreactive after 24 h at 100 °C.

CONCLUSIONS

The isolobal, highly Lewis acidic borane and silylium ion catalysts effect the selective monohydrosilylation of six-membered aromatic N-heterocycles that is substrate-dependent. In most cases, 1,4-regioselective reduction was observed for both catalysts. For quinaldine, however, we observed both the reduction to tetrahydroquinaldine **5b** and an unusual

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silylation of the methyl group, which was explained by concurrent deprotonation of the *N*-silyl-quinaldinium intermediate by the first reduction product, 1,4-dihydroquinaldine. As expected, isoquinoline and phenanthridine were 1,2-hydrosilylated, whereas quinoxaline and pyrazine were double-hydrosilylated to their 1,2,3,4-tetrahydro derivatives. The biggest difference between the borane and silylium ion catalysis is that the latter mediates the unexpected formation of a C3/C2′ coupling product for the quinoline reduction, which can be rationalized in terms of the diminished reducing ability of the silane HMe_2SiPh in comparison with the borate $[HB(C_6F_5)_3]^-$, which leads to a more efficient attack of an enamine product on the *N*-silyl-quinolinium intermediate.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00697.

Experimental details (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

■ ABBREVIATIONS

NMR, nuclear magnetic resonance; COSY, correlation spectroscopy; DEPT, distortionless enhancement by polarization transfer; HSQC, heteronuclear single quantum coherence; HMBC, heteronuclear multiple bond correlation

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