A base-free, catalytic protocol for the dehydrogenative Si–N coupling of weakly nucleophilic N–H groups of heteroarenes or aryl-substituted amines with equimolar amounts of hydrosilanes is reported. Cooperative Si–H bond activation at a Ru–S bond generates a silicon electrophile that forms a Si–N bond prior to the N–H deprotonation by an intermediate Ru–H complex, only releasing H₂.

The formation of Si–N bonds is relevant to various areas of synthetic chemistry.¹ N–H bond silylation is one way to temporarily protect amino groups,² in particular the N–H group in indoles and pyrroles.³ Their silylated derivatives are prevalent building blocks for the construction of heteroarene-based complex molecules. The Si–N bond is relatively labile though, and N-silylated anilines have been employed as silylating agents themselves.⁴ The transition metal-catalysed synthesis of oligo-⁵ or polysilazanes⁶ is another significant application of Si–N coupling.

A silicon group is usually introduced at the nitrogen atom by a deprotonation/silylation sequence using a strong base and a halosilane.⁷ The formation of stoichiometric amounts of salt is an issue in this approach. The direct coupling of N–H and Si–H bonds is an attractive alternative that, ideally, generates dihydrogen as the sole by-product. Several dehydrogenative Si–N couplings are known today⁸ but generality and control of the chemoselectivity remain challenging. The latter was recently accomplished by Sadow et al.⁹a and Cui et al.⁹b in the direct catalytic mono-coupling of R₃SiH₄–n (with n = 1 and 2). Parallel to these current developments, progress has also been made toward the elusive dehydrogenative Si–N coupling of heteroarenes.¹⁰ The methods reported by Tsuchimoto et al.¹⁰b and Mizuno et al.¹⁰c are broadly applicable and robust but require the addition of an external base (stoichiometric and catalytic, respectively) and a nitrile solvent as a H₂ acceptor. We disclose herein a base- and H₂ acceptor-free protocol for the catalytic dehydrogenative Si–N coupling of both N–H group-containing heteroarenes and aryl-substituted amines that follows an unusual silylation/deprotonation sequence. Our laboratory, in collaboration with Ohki and Tatsumi, introduced the cooperative activation of Si–H bonds at the polar Ru–S bond¹¹ of the coordinatively unsaturated, tethered ruthenium complex 1¹² (left, Fig. 1). The heterolytic splitting of the Si–H bond (in analogy to H₂ activation¹³) results in the formation of a Ru–H complex and a silicon electrophile, a sulfur-stabilized silicon cation (right, Fig. 1). This catalytic entry into the chemistry of silicon cations has already allowed for the development of a regioselective Friedel–Crafts-type indole silylation¹⁴ and a chemoselective, dehydrogenative silylation of enolizable carbonyl compounds.¹⁵ The same reaction setup applied to weakly nucleophilic N–H groups now results in Si–N bond formation together with liberation of H₂.

Our investigation began with the N-silylation of indole (2) using Me₂PhSiH (3a) that we had used in our earlier C₃-silylation of N-protected indoles¹¹ (Scheme 1). For an equimolar mixture of indole and silane, full conversion was reached after 1 h at 60 °C using 1 mol% of 1. The expected N-silylated indole 4a was, however, contaminated with substantial amounts of the cognate indoline 5a in a ratio of 76 : 24. This ratio improved with prolonged reaction times in favour of the protected indole, e.g., 92 : 8 after 12 h.

We have shown before that 1 is capable of (reversible) indoline-to-indole dehydrogenation.¹¹
We then turned our attention to the screening of different triorganosilanes \(3\) in the dehydrogenative Si–N coupling of \(3\)-methylindole\(^1\) as well as pyrrole (6–9, Table 1). For the indole, sterically less demanding silanes \(3\)-a–\(3\)-c afforded excellent isolated yields whereas \(3\)-d and \(3\)-e did not react even at higher temperature (columns 3–5). For pyrrole, similar observations were made, yet requiring higher temperature and excess pyrrole (columns 6–8). It is somewhat unfortunate that \(i\)Pr\(_3\) SiH (3e) is not activated by catalyst \(1\) for steric reasons because the \(i\)Pr\(_3\) Si group is a commonly used protective group for these heteroarenes. By using an excess of \(3\)-a (10 equiv.), we examined the possibility of double silylation, that is N-silylation and subsequent Friedel–Crafts C-3-silylation of indole and pyrrole (2 \(\rightarrow\) 10a and 7 \(\rightarrow\) 11a, Scheme 2). Upon prolonging the reaction time (18 h instead of 1 h), doubly silylated 10a (along with 5a) and 11a were formed in high yields.

These findings are in accordance with previous results for N-protected indoles.\(^1\)

We next examined the scope of the indole motif, substituted and unsubstituted at the C-3 atom (12–16, Table 2, entries 1–5). All of them underwent clean Si–N coupling in good to excellent yields. Aside from pyrrole and indole, carbazole also participated in this dehydrogenative N-silylation (17, Table 2, entry 6). These results compare well with the reports by Tsuchimoto \(et\ al.\)^{10b} and Mizuno \(et\ al.\)^{10c} (vide supra). The fact that these heteroarenes are sufficiently nucleophilic encouraged us to also test aryl-substituted amines with enhanced nucleophilicity (24–30, Table 3, entries 1–7). Indole, essentially an aniline derivative, was dramatically more reactive than indole, yielding complete conversion in \(n\)-hexane after 5 min at ambient temperature (entry 1); indole-to-indole oxidation only occurs at elevated temperatures (cf. Scheme 1).\(^11\) Various substituted anilines displayed the same reactivity (Table 3, entries 2–7). It is worthy of note that the CF\(_3\) group in 29 remains intact under these conditions.\(^16\)

The chemoselectivity of our catalytic Si–N coupling was probed in the selective monoamination of dihydrosilane

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**Table 1** Screening of different triorganosilanes

<table>
<thead>
<tr>
<th>Entry</th>
<th>(\text{Si–H})</th>
<th>3-Methylindole (6)</th>
<th>Pyrrole (7)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. (°C)</td>
<td>Product Yield(^b) (%)</td>
<td>Temp. (°C)</td>
</tr>
<tr>
<td>1</td>
<td>Me(_2)PhSiH (3a)</td>
<td>60</td>
<td>8a</td>
</tr>
<tr>
<td>2</td>
<td>MePh2SiH (3b)</td>
<td>60</td>
<td>8b</td>
</tr>
<tr>
<td>3(^c)</td>
<td>EtMe2SiH (3c)</td>
<td>60</td>
<td>8c</td>
</tr>
<tr>
<td>4</td>
<td>Et(_3)SiH (3d)</td>
<td>90</td>
<td>8d</td>
</tr>
<tr>
<td>5</td>
<td>iPr(_3)SiH (3e)</td>
<td>90</td>
<td>8e</td>
</tr>
</tbody>
</table>

\(^{a}\) Conversion was monitored by GLC analysis and is based on the consumption of 3. \(^{b}\) Isolated yield after catalyst removal by filtration through a short plug of deactivated silica gel. \(^{c}\) Volatile at elevated temperatures, used in toluene (0.5 M). \(^{d}\) No reaction.

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**Scheme 2** Probing double silylation of indole and pyrrole.
Ph$_3$SiH$_2$ (3f) and aniline (26 → 32f, Scheme 3). With 1 equiv. of 26 at room temperature, only one Si–H bond of 3f was cross-coupled. With subsequent addition of another equivalent of 26 at elevated temperature, the remaining Si–H bonds also underwent the cross-coupling (26 → 37f, Scheme 3).

To summarize, we accomplished an efficient protocol for the base-free dehydrogenative Si–N coupling of monohydrosilanes and weakly to moderately nucleophilic N–H groups. Pyrroles, indoles and carbazoles fall into the former and anilines into the latter category. Alkyl-substituted amines are not compatible with coordinatively unsaturated complex 1, thwarting Si–H bond activation due to amine coordination (for a tentative mechanism, see the ESI†). Moreover, selective mono-coupling of a dihydrosilane and exactly 1.0 equiv. of aniline is feasible. This research was supported by the Deutsche Forschungsgemeinschaft (International Research Training Group Münster–Nagoya, GRK 1143, with predoctoral fellowships to C.D.F.K., 2011–2012 and H.F.T.K., 2007–2010) and the Deutsche Akademische Austauschdienst (Forschungsstipendium A/12/71607 to N.A., 2012). M.O. is indebted to the Einstein Foundation (Berlin) for an endowed professorship.

Notes and references

15 Used to prevent its reduction (cf. Scheme 1) and possible double silylation (cf. Scheme 2).
16 Another version of 1 is also able to catalyse the hydrodefluorination of 29: T. Stahl, H. F. T. Klare and M. Oestreich, J. Am. Chem. Soc., DOI: 10.1021/ja311398j.