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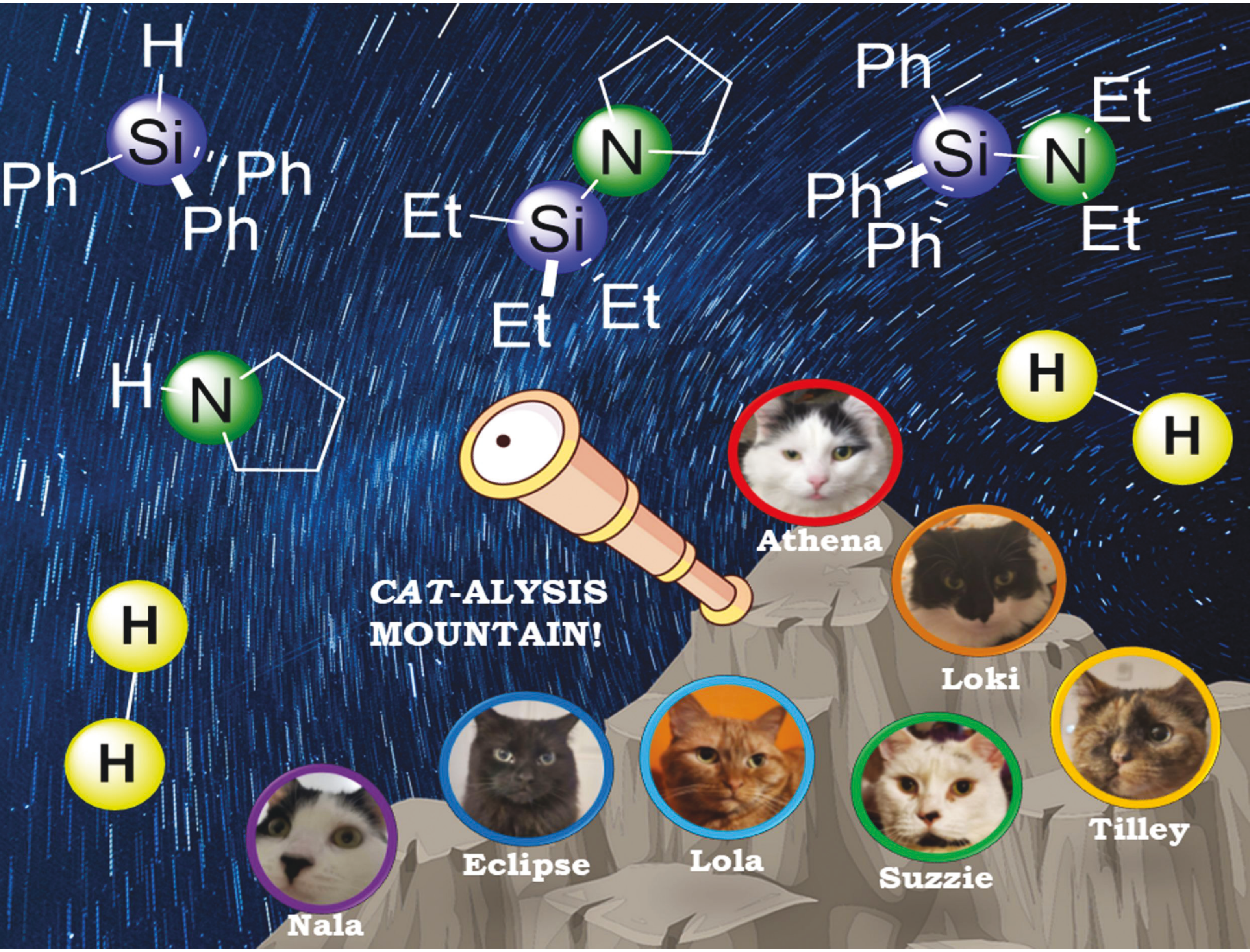

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Commercially available organolithium compounds as effective, simple precatalysts for silicon–nitrogen heterodehydrocoupling†

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A family of commercially available organolithium compounds were found to effectively catalyze the heterodehydrocoupling of silanes and amines under ambient conditions. Ubiquitous *n*BuLi (**1**) was utilized as the benchmark catalyst, where an array of primary, secondary, and tertiary arylsilanes were coupled to electron-donating amines, affording aminosilanes in high conversions with short reaction times. Preliminary mechanistic analysis is consistent with a nucleophilic-type system that involves the formation of a hypervalent silicon intermediate. This work underscores the accessibility of Si–N heterodehydrocoupling, with organolithium reagents emerging as some of the most straightforward and cost-effective precatalysts for this transformation.

Introduction

The field of silicon–nitrogen (*i.e.*, Si–N) heterodehydrocoupling has exploded. The sheer scope of precatalysts that facilitate this transformation has rapidly expanded with examples throughout the periodic table.[1–4] In general, dehydrocoupling has emerged as a versatile method to form main group (*i.e.*, p-block) products through catalysis.[2,5,6] This method is green and atom-economical, producing H_2 as the sole byproduct.[7] Liberated H_2 drastically simplifies purification and acts as the thermodynamic driving force in these reactions. Beyond a synthetic methodology to make main group substrates, heterodehydrocoupling has also been utilized in transfer and tandem hydrogenation reactions.[8]

Heterodehydrocoupling of silanes and amines is poised to emerge as a complementary method to form Si–N bonds.[1–4] Established applications for aminosilanes and silylamines include transition-metal, lanthanide and main group ligands,[9] silylating agents,[10,11] and as protecting groups in synthetic chemistry (Fig. 1, top).[12,13] In recent years, aminosilanes have been employed as chemical vapor deposition (CVD)[14] and ceramic[14,15] precursors (Fig. 1, bottom). Likewise, the synthesis of chiral Si–N products through heterodehydrocoupling has recently been reported.[16–18] The abundance of silane precursors from the Müller–Rochow process, as well as the air- and moisture-stability of many arylsilanes, further enhances the attractiveness of Si–N heterodehydrocoupling for synthetic applications.

Unfortunately, the full synthetic utility of heterodehydrocoupling has yet to be realized, and achieving this requires the

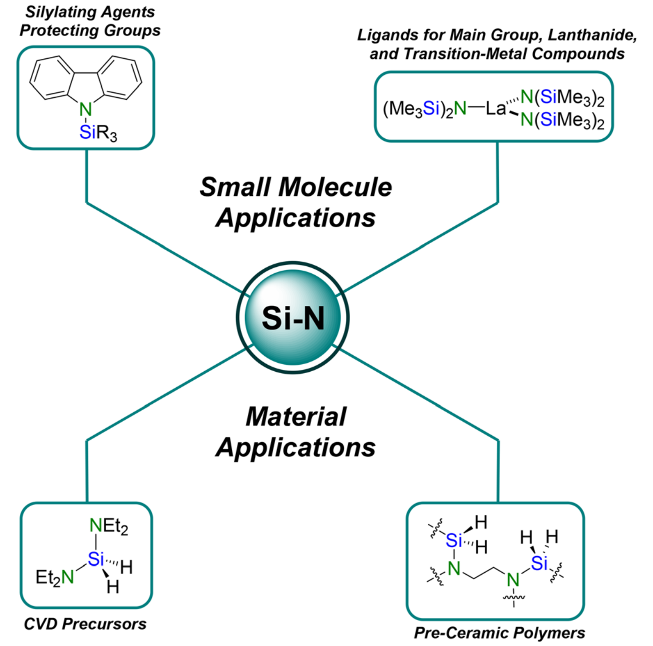

Fig. 1 Applications of small molecules, polymers, and materials with Si–N bonds.[14,15,19–21]

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discovery of accessible precatalysts that are highly active under ambient or otherwise mild conditions. Interestingly, Si–N heterodehydrocoupling catalysts enjoy a taste of mechanistic ubiquity (Fig. 2). For instance, most reported systems utilize precatalysts that enhance the nucleophilicity of amine to react with silane. Notably, nucleophilic mechanisms can be achieved with elements across the periodic table.[2] It was therefore hypothesized that the ubiquity of nucleophiles could be the key to generalizing heterodehydrocoupling with accessible, highly active catalysts.

Organolithium compounds are attractive precatalysts for Si–N heterodehydrocoupling, due to their commonplace use in synthetic laboratories. Weinmann and Müller utilized *n*BuLi (**1**) to couple simple amines such as NH_3 and $MeNH_2$ to borane-containing primary and secondary silanes, forming preceramic SiBCN polymers (Scheme 1).[28] That initial discovery provided context to reinvestigate **1** and related organolithium compounds under the hypothesis that these are accessible catalysts that would enable routine use of Si–N heterodehydrocoupling in synthesis. As such, optimal mild conditions for efficient catalysis were explored. Such exploration has established a robust substrate scope for these catalysts, and preliminary mechanistic study indeed validates the notion that a simple and accessible catalyst would be realized on the back of nucleophilic reactivity. Overall, the use of organolithium reagents as precatalysts has emerged as a robust method to form Si–N bonds through heterodehydrocoupling.

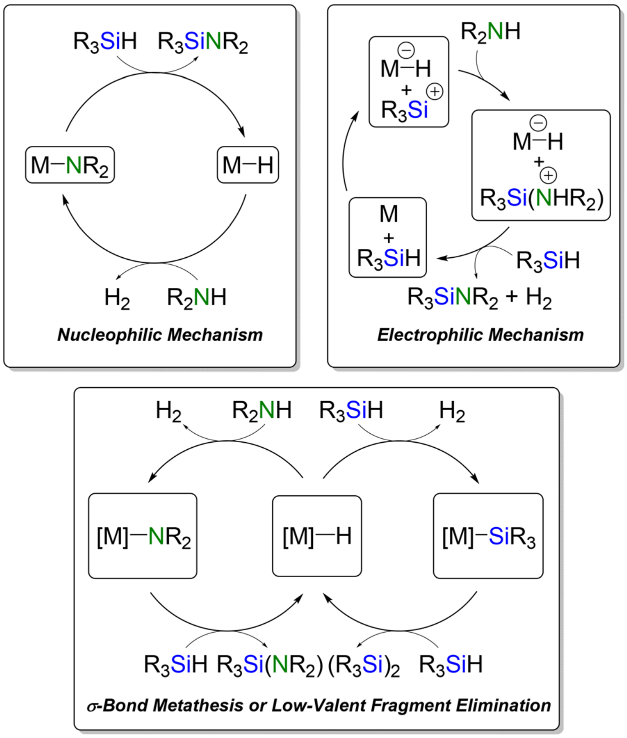
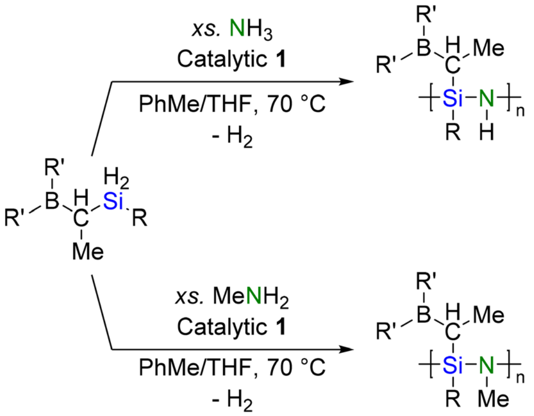


Fig. 2 General catalytic cycles for reported systems of Si–N heterodehydrocoupling ([M] = d^0 metal, while M is general towards rare-earth, transition metal, and main group compounds).[8,22–27]



Scheme 1 Heterodehydropolymerization of borane-modified silanes with either NH_3 or $MeNH_2$ using **1** as reported by Weinmann and Müller.[28]

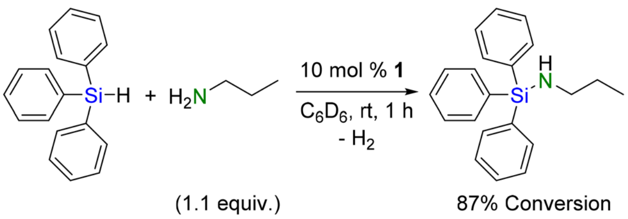
Results and discussion

Discovery and optimization

This study initially aimed to expand and improve upon recent advances in iron-catalysed Si–N heterodehydrocoupling through *in situ* activation with organolithium activators,[24,29] however, control reactions quickly demonstrated the utility of these activators as precatalysts. For instance, the reaction between Ph_3SiH and 1.1 equiv. of *n*$PrNH_2$ with 10 mol % *n*BuLi (**1**) furnished $Ph_3Si(NH$*n*$Pr)$ in 87% conversion after 1 h at ambient temperature (Scheme 2).

The reactivity of this system with tertiary arylsilanes is substantial. Other systems that couple Ph_3SiH with amines are generally limited to s- and f-block precatalysts like $(hmpa)_3Ca(\eta^2\text{-}Ph_2CNPh)$,[30] group I[31] and II[32] $M[N(SiMe_3)_2]_x$ compounds, alkyl and amido barium complexes with supporting iminoanilido ligands,[23] and $(thf)_2La[N(SiMe_3)_2]_3$.[33] This reactivity also exceeds that reported by Weinmann and Müller, who did not explore the coupling of amines with arylsilanes with **1**.[28] Notably, compound **1** is one of the few examples of a readily available precatalyst for this transformation.

Deprotonation of amine by **1** to form a nucleophilic lithium amido intermediate likely contributes to the versatile reactivity of this system. As such, this methodology may be generalized to any organolithium reagent. In the exploratory reaction between Ph_3SiH and 1.1 equiv. of *n*$PrNH_2$, the corresponding aminosilane $Ph_3Si(NH$*n*$Pr)$ was formed in 80% conversion or greater with



Scheme 2 Heterodehydrocoupling of Ph_3SiH and 1.1 equiv. of *n*$PrNH_2$ catalysed by **1**.

Table 1 Screening of commercially available organolithium reagents for Si–N coupling[a]

Entry	Cmpd.	R	%[b] (1 h)	%[b] (24 h)
1a	**1**	*n*Bu	89[c]	91
1b	**2**	*s*Bu	90	94
1c	**3**	*t*Bu	80	83
1d	**4**	Me	86	92
1e	**5**	Et	85	89
1f[d]	**6**	Me_3SiCH_2	82	86
1g	**7**	Ph	86	88

[a] Conditions: Ph_3SiH (3.7×10^{-1} mmol, 1.0 equiv.), nPrNH$_2$ (4.2 mmol $\times 10^{-1}$ mmol, 1.1 equiv.), and RLi (3.7×10^{-2} mmol, 10.0 mol %, as a solution in commercial solvent) in 0.5 mL of benzene-d_6 at ambient temperature in a PTFE-valved J-Young type NMR tube. [b] Reactions were run in triplicate and the averages were taken for 1 h and 24 h intervals. Conversions were measured *via* ^{1}H NMR spectroscopy by integration of residual Ph_3SiH *vs.* $Ph_3Si(NH\textit{n}Pr)$. [c] The slight disparity in conversions between Table 1 and Scheme 2 is due to a change in concentration. [d] Me_3SiCH_2Li was utilized as a solid for catalysis, rather than as a stock solution.

every tested organolithium compound (Table 1). The results of these reactions indeed confirm that the identity of organolithium precatalyst is irrelevant, suggesting that catalysis is operating through the same bond forming intermediate. Subsequent reactions focused solely on **1** as a precatalyst, given its relative ease of handling and ubiquity in synthetic laboratories.

Subsequent efforts were aimed at optimizing the conversion of Ph_3SiH to aminosilane, with the target being quantitative conversion within 1 h at ambient temperature. Notably, the benchmark amine was changed to *i*PrNH$_2$, as these reaction conditions proved to be more general than those used for *n*PrNH$_2$. Excess silane (Table 2, entry 2a) had the most deleterious effect on conversion, affording $Ph_3Si(NHiPr)$ in 61% conversion after 1 h. Conversely, excess amine concentration favoured rapid formation of aminosilane. It was found that 2.0 equiv. of *i*PrNH$_2$ were necessary to produce $Ph_3Si(NHiPr)$ quantitatively after 1 h at ambient temperature. Ultimately, this methodology was applied to the rest of the substrate scope, including expanding to the general formulation of 2.0 equiv. of amine per Si–H bond in silane substrate.

Substrate scope

The primary silane $PhSiH_3$ is often a starting point for Si–N heterodehydrocoupling with electron-rich amines such as *n*PrNH$_2$. These substrates help gauge the efficiency of a precatalyst towards this transformation, due to the enhanced hydricity of aminosilane Si–H bonds.[34] Reaction of $PhSiH_3$ and *n*PrNH$_2$ with **1** afforded the desired tris(aminosilane), PhSi(NH*n*Pr)$_3$, in 66% conversion after 1 h at ambient temperature (Table 3, entry 3a). The efficiency of this system is comparable to that of $(thf)_2La[N(SiMe_3)_2]_3$, which accomplished the coupling of $PhSiH_3$ with 3.0 equiv. of *n*PrNH$_2$ to afford PhSi(NH*n*Pr)$_3$ in 45–60% conversion in 10 min at ambient temperature.[33] In both instances, competitive formation of silylamines is observed. Notably, Sadow and coworkers isolated PhSi(NH*n*Pr)$_3$ in 99% yield when using (To^M)MgMe, a precatalyst that likely inhibits competing silylamine reactions.[22]

Table 2 Optimization conditions of the reaction between Ph_3SiH and *i*PrNH$_2$ with **1**[a]

Entry	Ph_3SiH (equiv.)	*i*PrNH$_2$ (equiv.)	% (1 h)
2a	1.1	1.0	61[b]
2b	1.0	1.1	81
2c	1.0	1.5	83
2d	1.0	2.0	100

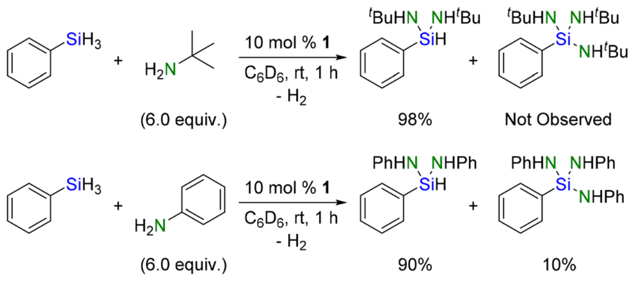
[a] Conditions: **1** in 0.5 mL of benzene-d_6. Conversions were measured *via* ^{1}H NMR spectroscopy by integrating residual Ph_3SiH *vs.* $Ph_3Si(NHiPr)$. [b] Conversions were measured by ^{1}H NMR spectroscopy after 1 h, determined by integration of $Ph_3Si(NHiPr)$ peak against the 0.4 M C_6Me_6 standard.

Table 3 Scope of Si–N heterodehydrocoupling between $PhSiH_3$ and amines with **1**[a]

Entry	Silane	Amine	Product	%[b]
3a	$PhSiH_3$	*n*PrNH$_2$	PhSi(NH*n*Pr)$_3$	66
3b	$PhSiH_3$	*i*PrNH$_2$	PhSi(NHiPr)$_3$	85
3c	$PhSiH_3$	*t*BuNH$_2$	PhSiH(NH*t*Bu)$_2$	98
3d	$PhSiH_3$	$PhNH_2$	$PhSiH(NHPh)_2$	90
			$PhSi(NHPh)_3$	10
3e	$PhSiH_3$	Et_2NH	$PhSiH_2(NEt_2)$	48
			$PhSiH(NEt_2)_2$	52
3f[c]	$PhSiH_3$	PyNH	$PhSi(NPy)_3$	100

[a] Conditions: $PhSiH_3$ (3.7×10^{-1} mmol, 1.0 equiv.), amine (22.6×10^{-1} mmol, 6.0 equiv.), and **1** (3.7×10^{-2} mmol, 10.0 mol %, stock solution in hexanes) in 0.5 mL of benzene-d_6 at ambient temperature in a PTFE-valved J-Young type NMR tube. [b] Conversions were measured by ^{1}H NMR spectroscopy after 1 h by integrating residual silane *vs.* product. [c] Conversion was measured after 0.5 h.

Byproduct formation is minimized with bulkier, non-linear amines. For instance, reaction between $PhSiH_3$ and *i*PrNH$_2$ afforded the tris(aminosilane) PhSi(NHiPr)$_3$ in 85% conversion (Table 3, entry 3b), as assessed by the appearance of a septet centered at $\delta = 3.24$ in the ^{1}H NMR spectrum and a resonance at $\delta = -37.20$ in the ^{29}Si{^{1}H} NMR spectrum. Three additional resonances consistent with *i*Pr groups were observed in the ^{1}H NMR spectrum that likely arise from the competing silylamine pathway. The reaction between $PhSiH_3$ and *t*BuNH$_2$ affords PhSiH(NH*t*Bu)$_2$ in 98% conversion after 1 h (Table 3, entry 3c; Scheme 3, top). No evidence for the tris(aminosilane) product, PhSi(NH*t*Bu)$_3$, was observed by ^{1}H NMR spectroscopy, and this



Scheme 3 Divergent reactivity between *t*BuNH$_2$ and PhNH$_2$ with $PhSiH_3$ catalysed by **1**.

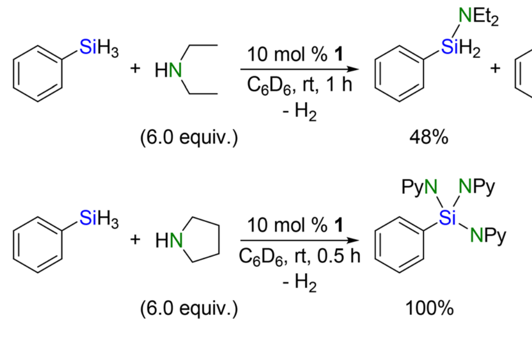
product has notably not been reported to be produced *via* heterodehydrocoupling. Nevertheless, competing silylamine production appears to be inhibited by the increased substitution on the primary amine.

The selective formation of certain aminosilane products from primary silanes was not observed using **1**. For instance, the reaction of PhSiH$_3$ and 2.0 equiv. of *i*PrNH$_2$ afforded a complex mixture of Si–H products appearing between δ = 5.00 and δ = 6.00 in the ^{1}H NMR spectrum. The selective formation of substituted aminosilane products remains a critical challenge in the field of Si–N heterodehydrocoupling. Recent reports suggest that lanthanide[35,36] and transition-metal[37] compounds with NHC ligands may offer an effective strategy to selectively form aminosilanes.

The role of amine basicity became evident in the reaction between PhSiH$_3$ and aniline (PhNH$_2$) with **1**. After 1 h, the bis- and tris(aminosilane) products PhSiH(NHPh)$_2$ and PhSi(NHPh)$_3$ were formed in 90% and 10% conversion, respectively (Table 3, entry 3d; Scheme 3, bottom). The diminished conversions of PhNH$_2$ compared to electron-donating amines has occurred in previously reported systems,[22,29,33] which has been attributed to the decreased basicity of M-NHPh intermediates.

Coupling of PhSiH$_3$ was extended to secondary amines (Scheme 4). Treatment of a solution of PhSiH$_3$ and Et$_2$NH with catalytic **1** produced a mixture of PhSiH$_2$(NEt$_2$) and PhSiH(NEt$_2$)$_2$ in 48% and 52% conversions, respectively (Table 3, entry 3e; Scheme 4, top). Like reactions with *t*BuNH$_2$, no evidence of the tris(aminosilane) product was observed by ^{1}H NMR spectroscopy. These results suggest that certain tris(aminosilane) products may be inaccessible through heterodehydrocoupling.

Conversely, reaction between PhSiH$_3$ and pyrrolidine (PyNH) produced PhSi(NPy)$_3$ in quantitative conversion after only 0.5 h at ambient temperature (Table 3, entry 3f; Scheme 4, bottom). Notably, extremely vigorous gas evolution occurred, which ceased within a few minutes. The divergent results between Et$_2$NH and PyNH indicates that the steric profile of the reagent may play a role in this reactivity, rather than just the basicity of the conjugate base. Results from the reaction between PhSiH$_3$ and PhNH$_2$ buttress this hypothesis, where the tris(aminosilane) PhSi(NHPh)$_3$ is formed in measurable quantities despite PhNH$_2$ being less basic than Et$_2$NH.



Scheme 4 Divergent reactivity between PhSiH$_3$ and secondary amines catalysed by **1**.

The effectiveness of **1** does not waver with increasing substitution on silane. For instance, reactions of PhMeSiH$_2$ with either *n*PrNH$_2$ or *i*PrNH$_2$ produced the corresponding bis(aminosilane) products in nearly quantitative conversions (Table 4, entries 4a and 4b, respectively). The production of silylamine byproducts appears to be minimized by the increased substitution on silane. These high conversions follow in the reaction between PhMeSiH$_2$ and *t*BuNH$_2$, which furnishes the mono(aminosilane) product PhMeSiH(NH*t*Bu) in 96% conversion (Table 4, entry 4c). Notably, reactions of PhNH$_2$ and secondary silanes begin to stagnate under standard conditions where mono(aminosilane) PhMeSiH(NHPh) is produced in 53% conversion (Table 4, entry 4d). However, PhMeSiH$_2$ is a versatile substrate where reactions with either Et$_2$NH and PyNH proceed quantitatively to the mono- and bis(aminosilane) products, respectively (Table 4, entries 4e and 4f, respectively).

Reactions with Ph$_2$SiH$_2$ largely proceed in a similar manner to those with PhMeSiH$_2$ with select differences. For instance, reactions of Ph$_2$SiH$_2$ with *n*PrNH$_2$ and *i*PrNH$_2$ produced bis(aminosilane) products in high conversions (Table 4, entries 4g and 4h, respectively). Utilizing *t*BuNH$_2$ affords both the mono(aminosilane) and bis(aminosilane) products Ph$_2$SiH(NH*t*Bu) and Ph$_2$Si(NH*t*Bu)$_2$ in 95% and 4% conversion, respectively (Table 4, entry 4i). This observation stands in contrast to reactions with PhMeSiH$_2$ and *t*BuNH$_2$ (Table 4, entry 4c) which exclusively produces the mono(aminosilane) product PhMeSiH(NH*t*Bu), but would appear to be consistent with the difference in steric profiles of these substrates. Mono- and bis(aminosilane) products Ph$_2$SiH(NHPh) and Ph$_2$Si(NHPh)$_2$ are produced in 99% and 1% conversions, respectively, from the reaction of Ph$_2$SiH$_2$ and PhNH$_2$ (Table 4, entry 4j). Reactions between Ph$_2$SiH$_2$ and Et$_2$NH struggle, producing Ph$_2$SiH(NEt$_2$) in 69% conversion (Table 4, entry 4k). Consistent with previous experiments, the fully substituted bis(aminosilane) Ph$_2$Si

Table 4 Scope of Si–N heterodehydrocoupling between secondary silanes and amines with **1** [a]

Entry	Silane	Amine	Product	% [b]
4a	PhMeSiH$_2$	*n*PrNH$_2$	PhMeSi(NH*n*Pr)$_2$	95
4b	PhMeSiH$_2$	*i*PrNH$_2$	PhMeSi(NHiPr)$_2$	100
4c	PhMeSiH$_2$	*t*BuNH$_2$	PhMeSiH(NH*t*Bu)	96
4d	PhMeSiH$_2$	PhNH$_2$	PhMeSiH(NHPh)	53
4e	PhMeSiH$_2$	Et$_2$NH	PhMeSiH(NEt$_2$)	100
4f[c]	PhMeSiH$_2$	PyNH	PhMeSi(NPy)$_2$	100
4g	Ph$_2$SiH$_2$	*n*PrNH$_2$	Ph$_2$Si(NH*n*Pr)$_2$	99
4h	Ph$_2$SiH$_2$	*i*PrNH$_2$	Ph$_2$Si(NHiPr)$_2$	100
4i	Ph$_2$SiH$_2$	*t*BuNH$_2$	Ph$_2$SiH(NH*t*Bu)	95
			Ph$_2$Si(NH*t*Bu)$_2$	4
4j	Ph$_2$SiH$_2$	PhNH$_2$	Ph$_2$SiH(NHPh)	99
			Ph$_2$Si(NHPh)$_2$	1
4k	Ph$_2$SiH$_2$	Et$_2$NH	Ph$_2$SiH(NEt$_2$)	69
4l[c]	Ph$_2$SiH$_2$	PyNH	Ph$_2$Si(NPy)$_2$	100

[a] Conditions: R$_2$SiH$_2$ (3.7 × 10^{-1} mmol, 1.0 equiv.), amine (15.0 × 10^{-1} mmol, 4.0 equiv.), and **1** (3.7 × 10^{-2} mmol, 10.0 mol %, stock solution in hexanes) in 0.5 mL of benzene-d_6 at ambient temperature in a PTFE-valved J-Young type NMR tube. [b] Conversions were measured by ^{1}H NMR spectroscopy after 1 h, by integrating residual silane *vs.* product. [c] Conversions were measured after 0.5 h.

$(NPy)_2$ is produced quantitatively in reactions between Ph_2SiH_2 and PyNH (Table 4, entry 4l).

Several trends emerge from the reactions between either $PhMeSiH_2$ or Ph_2SiH_2. Reactions between Ph_2SiH_2 and $PhNH_2$ proceed to higher conversions of the mono(aminosilane) product than reactions with $PhMeSiH_2$. This disparity highlights the difference in reactivity of secondary silanes with aryl- and alkyl groups. Steric effects are also evident for amines. For example, reactions of $PhMeSiH_2$ with *t*$BuNH_2$ and Et_2NH only produce the mono(aminosilane) product, despite high amine concentrations (Table 4, entries 4c and 4e, respectively).

Notably, increased substitution on silane frequently hampers high conversions to aminosilane products, which is not apparent in this study with **1**. Tertiary silanes such as $PhMe_2SiH$, Ph_2MeSiH, and Ph_3SiH were accessible substrates in catalysis with **1**. Linear amines such as *n*$PrNH_2$ and *i*$PrNH_2$ reacted smoothly with $PhMe_2SiH$ to afford the mono(aminosilane) products within 1 h at ambient temperature (Table 5, entries 5a and 5b, respectively). These results are consistent with less encumbered arylsilanes (Tables 3 and 4), further buttressing the supposition that substitution on silane directly impacts the production of silylamine byproducts. Aniline is completely unreactive towards $PhMe_2SiH$ under these conditions (Table 5, entry 5c), while Et_2NH affords $PhMe_2Si(NEt_2)$ in 48% conversion (Table 5, entry 5d). As with previous examples, $PhMe_2SiH$ reacts with PyNH rapidly and quantitatively to produce $PhMe_2Si(NPy)$ (Table 5, entry 5e).

Interestingly, Ph_3SiH emerged as a versatile coupling substrate in the presence of **1**, indicating the utility of this catalysis in protecting group chemistry. Simple amines such as *n*$PrNH_2$ and *i*$PrNH_2$ were coupled quantitatively to Ph_3SiH within 1 h at ambient temperature (Table 5, entries 5h and 5i, respectively), while reactions with *t*$BuNH_2$ afforded the mono (aminosilane) product $Ph_3Si(NH$*t*$Bu)$ in 80% conversion (Table 5, entry 5k). Notably, catalysis was not inhibited by increased chain-length on amines, quantitatively affording the corresponding aminosilane products from *n*$BuNH_2$, *n*$PeNH_2$, and *n*$HeNH_2$ (Table 5, entries 5j, 5l, and 5m, respectively). Aminosilane product $Ph_3Si(NH$*n*$Pe)$ has previously been furnished through catalysis with azametallacyclopropane $(hmpa)_3M(\eta^2\text{-}Ph_2CNPh)$ (M = Ca,[30] Yb[38]), while aminosilane products $Ph_3Si(NH$*n*$Bu)$ and $Ph_3Si(NH$*n*$He)$ have only been synthesized in stoichiometric reactions (Scheme 5).[39] Aniline is unreactive towards Ph_3SiH (Table 5, entry 5n). Reaction of Ph_3SiH and Et_2NH affords mono(aminosilane) $Ph_3Si(NEt_2)$ in 88% conversion (Table 5, entry 5o), which is significantly more effective than in reactions with $PhMe_2SiH$ (Table 5, entry 5d).

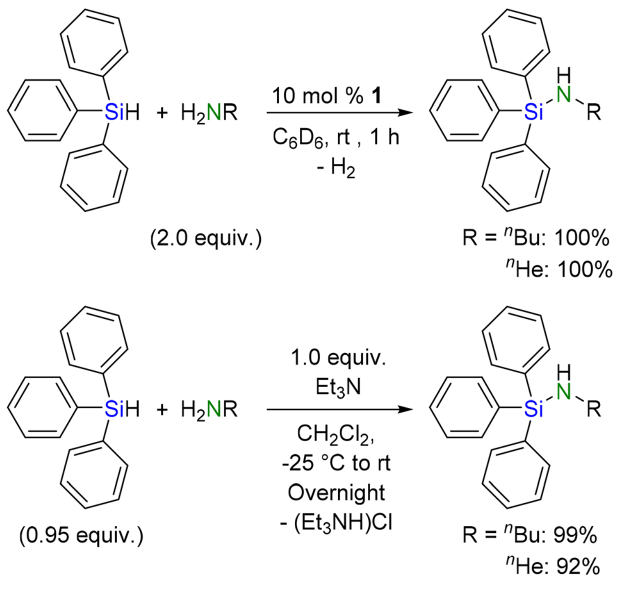
Finally, reaction of Ph_3SiH and PyNH affords $Ph_3Si(NPy)$ in quantitative conversion (Table 5, entry 5p). This high reactivity is consistent with known group I and II precatalysts. For instance, $(thf)_3Ba[CH(SiMe_3)_2]_2$ (Fig. 3, top left) affords $Ph_3Si(NPy)$ from equimolar Ph_3SiH and PyNH after only 5 min at 25 °C.[40] Group I $KN(SiMe_3)_2$ affords $Ph_3Si(NPy)$ quantitatively after 12 h under neat conditions (Fig. 3, bottom left),[31] while group II $M[N(SiMe_3)_2]_2$ (M = Mg, Ca, Sr) precatalysts consistently afford $Ph_3Si(NPy)$ in >90% conversion.[32] Recently, Schmidt and Rina utilized $La(DMBA)_3$ to furnish $Ph_3Si(NPy)$ in quantitative conversion after 16–20 h at 50 °C in pyridine (Fig. 3, top right).[41] The disproportionate reactivity of PyNH toward all silane substrates tested was motivation for not utilizing it as the model amine substrate in optimization reactions and mechanistic studies.[23,31,40]

Catalysis with **1** could also be extended to Et_3SiH. Reaction of Et_3SiH with 2.0 equiv. of PyNH in the presence of **1** furnished $Et_3Si(NPy)$ in 93% conversion after just 0.5 h at ambient temperature (Scheme 6).

Table 5 Scope of Si–N heterodehydrocoupling between tertiary silanes and amines with **1**[a]

Entry	Silane	Amine	Product	(%)[b]
5a	$PhMe_2SiH$	*n*$PrNH_2$	$PhMe_2Si(NH$*n*$Pr)$	100
5b	$PhMe_2SiH$	*i*$PrNH_2$	$PhMe_2Si(NHiPr)$	100
5c	$PhMe_2SiH$	$PhNH_2$	$PhMe_2Si(NHPh)$	0
5d	$PhMe_2SiH$	Et_2NH	$PhMe_2Si(NEt_2)$	48
5e[c]	$PhMe_2SiH$	PyNH	$PhMe_2Si(NPy)$	100[c]
5f	Ph_2MeSiH	*n*$PrNH_2$	$Ph_2MeSi(NH$*n*$Pr)$	100
5g	Ph_2MeSiH	Et_2NH	$Ph_2MeSi(NEt_2)_2$	57
5h	Ph_3SiH	*n*$PrNH_2$	$Ph_3Si(NH$*n*$Pr)$	100
5i	Ph_3SiH	*i*$PrNH_2$	$Ph_3Si(NHiPr)$	100
5j	Ph_3SiH	*n*$BuNH_2$	$Ph_3Si(NH$*n*$Bu)$	100
5k	Ph_3SiH	*t*$BuNH_2$	$Ph_3Si(NH$*t*$Bu)$	80
5l	Ph_3SIH	*n*$PeNH_2$	$Ph_3Si(NH$*n*$Pe)$	100
5m	Ph_3SiH	*n*$HeNH_2$	$Ph_3Si(NH$*n*$He)$	100
5n	Ph_3SiH	$PhNH_2$	$Ph_3Si(NHPh)$	0
5o	Ph_3SiH	Et_2NH	$Ph_3Si(NEt_2)$	88
5p[c]	Ph_3SiH	PyNH	$Ph_3Si(NPy)$	100

[a] Conditions: R_3SiH (3.7×10^{-1} mmol, 1.0 equiv.), amine (7.5×10^{-1} mmol, 2.0 equiv.), and **1** (3.7×10^{-2} mmol, 10.0 mol %, stock solution in hexanes) in 0.5 mL of benzene-d_6 at ambient temperature in a PTFE-valved J-Young type NMR tube. [b] Conversions were measured by ^{1}H NMR spectroscopy after 1 h, by integrating residual silane *vs.* product. [c] Conversions were measured after 0.5 h.



Scheme 5 Comparison of the stoichiometric and catalytic reactions of Ph_3SiH with *n*$BuNH_2$ or *n*$HeNH_2$.[39]

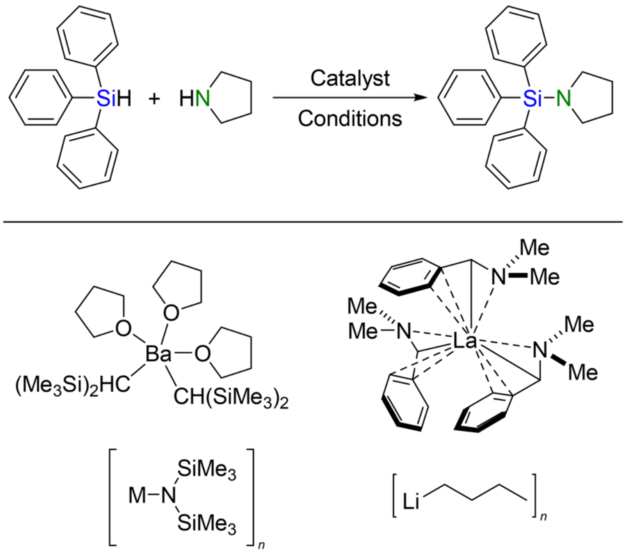
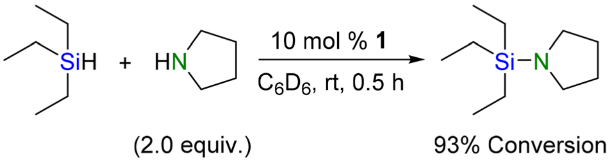


Fig. 3 Heterodehydrocoupling of Ph_3SiH and PyNH catalysed by s- and f-block precatalysts.[23,31,41]

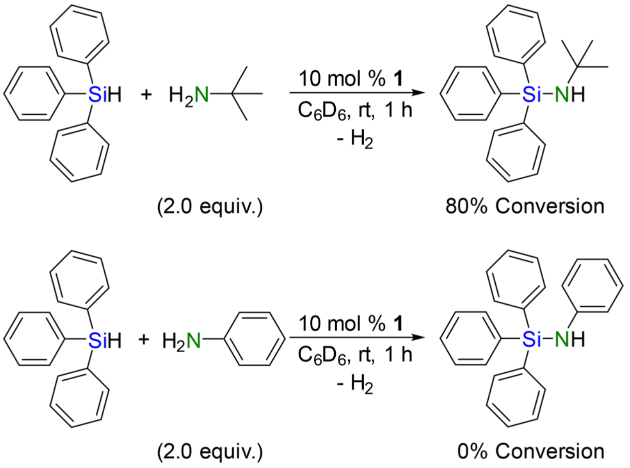


Scheme 6 Heterodehydrocoupling of Et_3SiH and PyNH catalysed by **1**.

This reactivity is comparable to $(thf)_3Ba[CH(SiMe_3)_2]_2$, which coupled equimolar Et_3SiH and PyNH to afford $Et_3Si(NPy)$ in 93% conversion after 2 h at 60 °C.[31] Catalysis with **1** continues to show its utility in protecting group chemistry. Heterodehydrocoupling of alkylsilanes and electron-deficient amines (*i.e.*, Ph_2NH, $PhNH_2$) is readily accomplished by Lewis acids.[8,20,42] However, that reactivity is not easily extended to electron-rich, linear amines, likely due to catalyst inhibition by coordination of these amines to the Lewis acid catalyst. The high reactivity of PyNH in the presence of **1** evidently contributes to the high conversions to $Et_3Si(NPy)$, as this activity is not easily extended to less reactive amines.

Mechanistic insight

Preliminary observations are consistent with nucleophilic attack of a M-NR_2 intermediate on silane. For instance, amine basicity appears to drive catalysis, which is illustrated by the relative reactivities of either $tBuNH_2$ or $PhNH_2$ with Ph_3SiH (Scheme 7).



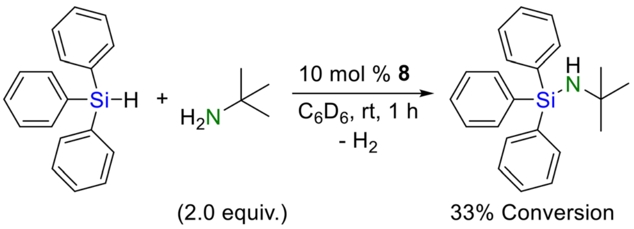
Scheme 7 Comparison of conversions in the reactions between $tBuNH_2$ or $PhNH_2$ with Ph_3SiH catalysed by **1**.

These results are consistent with the formation of a nucleophilic Li-NR_2 intermediate that enhances amine basicity during catalysis. To test this supposition, *t*BuNHLi (**8**) was isolated[43] and employed as a catalyst under otherwise standard reaction conditions. After 1 h at ambient temperatures, the aminosilane $Ph_3Si(NHtBu)$ was produced in 33% conversion (Scheme 8).

These results may be counterintuitive given that **8** is a theoretical "on-cycle" intermediate, but this may allude to the complex nature of the nucleophilic intermediate stemming from **1**. For instance, lithium amides adopt a wide range of oligomeric structures in non-polar solutions like benzene-d_6.[44] However, monomeric and dimeric lithium amides are possible in the presence of coordinating species like amines. As **8** was first isolated and then solubilized in benzene-d_6, it may retain its octameric structure and thus lead to slower catalysis compared to **1**. These observations notably highlight the importance of excess amine during this catalysis.

The formation of **8** is observable *via* ^1H NMR spectroscopy. Under standard reaction conditions, **1** quantitatively converts to **8** in the presence of excess $tBuNH_2$. The analogous reaction between Ph_3SiH and 10 mol % **1** does not result in the formation of observable products by NMR spectroscopy. These results suggest that Ph_3SiLi is not operant during catalysis, which is supported by the lack of characteristic colour changes throughout catalysis with **1–8**.[45] The absence of Ph_3SiLi is further supported by the fact that group II $MSiR_3$ compounds are known to be inactive for Si–N heterodehydrocoupling.[23]

Several additional observations discount competing mechanisms. Catalysis is not inhibited by high amine concentration, which is inconsistent with σ-bond metathesis.[46,47] A σ-bond



Scheme 8 Heterodehydrocoupling of Ph_3SiH and $tBuNH_2$ catalysed by **8**.

metathesis pathway would allow for disilane products that are not observed.[25,26,48] The lack of disilane products also suggests that low-valent silicon reactivity (*i.e.*, silylene elimination) is not involved.[46,49] Compound **1**'s lack of reactivity with Et_3SiH and Ph_2NH suggests that catalysis is not operating through an electrophilic mechanism (Scheme 9), which is generally observed for Lewis acid catalysts that generate transient silylium intermediates.[8,20,42] Finally, the selective formation of aminosilanes from primary and secondary silanes, and the lack of an EPR signal during catalysis, discounts a radical mechanism.

To further substantiate a nucleophilic mechanism, Hammett analysis was conducted to gauge the impact of electronic effects on the turnover-limiting step. Standard reaction conditions were applied in these competition experiments, reacting 2.0 equiv. of tBuNH$_2$ with 0.5 equiv. of Ph_3SiH and 0.5 equiv. of (p-X-C_6H_4)Ph_2SiH with catalytic **1** at ambient temperatures in benzene-d_6. Rate-acceleration with electron-withdrawing substituents on silane was observed, and a sizeable, positive slope ($\rho > 1.6$) demonstrated a build-up of negative charge in the turnover-limiting step (Fig. 4).

Analogous correlations ($\rho = 2.0$) were obtained between (p-X-C_6H_4)Ph_2SiH and PyNH mediated by barium precatalysts.[23] Similarly, Sadow's report with (To^M)MgNHtBu demonstrated rate-acceleration ($\rho = 1.4$) in reactions with p-substituted (p-X-C_6H_4)PhSiH$_2$ substrates.[22] Both studies attribute these results to the formation of a transient, hypervalent silicon intermediate. Indeed, results obtained from Fig. 4 support a mechanism that involves nucleophilic attack of amide on silane.

Consistent with previous reports,[2] we suggest a nucleophilic mechanism involving **1** (Scheme 10). Deprotonation of amine by **1** forms lithiated amido **9** and liberates butane. Intermediate **9** attacks silane to form hypervalent **10**, consistent with Hammett competition experiments (Fig. 4). Aminosilane is formed and a hydride equivalent reacts with amine to liberate H_2 and reform **9**.

Currently, the molecularity of mechanistic intermediates is not well understood. The inferior conversions to Ph_3Si(NHtBu) when using **8** (Scheme 8) suggest that discrete **8** is not the true nucleophilic intermediate. Similarly, the involvement of discrete LiH is unlikely, due to its poor solubility in non-polar solvents such as benzene-d_6. Group I MH compounds have been utilized for heterodehydrocoupling,[31,50] although these compounds do not reveal mechanism insight beyond the initiation step. Critically, the use of MH is often conducted in coordinating solvents such as THF. The need to use excess amine to push catalysis forward may indicate a critical, coordinative effect amine has on catalysis. However, suspected aggregated intermediates were not unveiled by either ^1H–$^{29}Si\{^1H\}$ HSQC and DOSY NMR during catalysis.

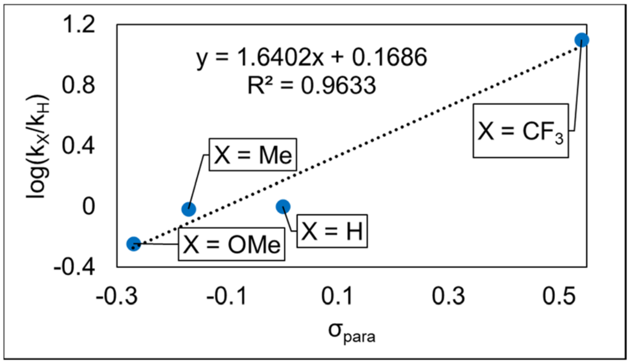
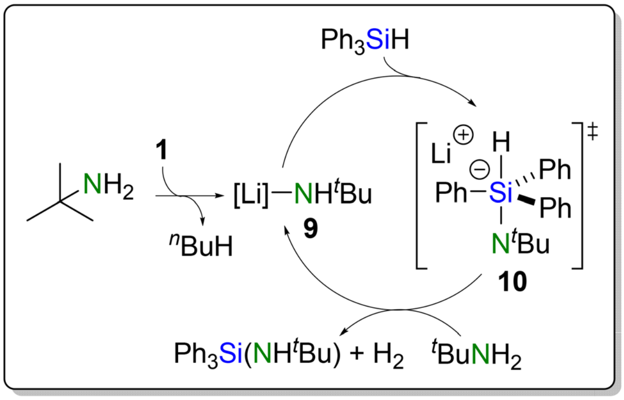
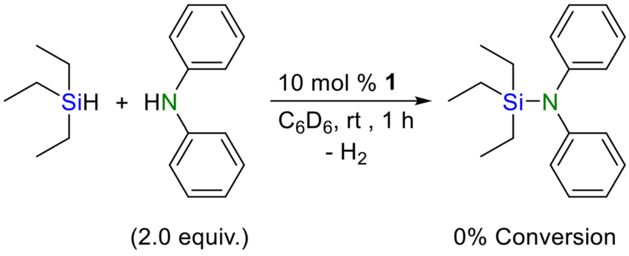


Fig. 4 Hammett correlation by competition experiments between tBuNH$_2$ and (p-X-C_6H_4)Ph_2SiH with **1**.



Scheme 10 Proposed catalytic cycle using **1** as a precatalyst to couple tBuNH$_2$ and Ph_3SiH. Brackets around lithium indicate a non-discrete intermediate.



Scheme 9 Unsuccessful reaction between Et_3SiH and Ph_2NH in the presence of **1**.

Conclusions

A deeper exploration of organolithium compounds has yielded a general and highly active protocol for the catalytic coupling of silanes and amines. This expands upon Weinmann and Müller's report of **1**-catalysed Si–N heterodehydrocoupling.[28] Using standard conditions that allowed conversion to compare reactions, it was found that primary, secondary, and tertiary silanes were all viable substrates with both primary and secondary amines. Alkyl amines were generally more reactive, as anticipated in a nucleophilic mechanism, while $PhNH_2$ was less reactive towards silane substrates. The compatibility of

Ph_3SiH and Et_3SiH with these conditions indicates that alkyl lithium reagents may be a viable method for protecting group chemistry *via* heterodehydrocoupling, although more extensive studies are required in this area. Nevertheless, the reactivity of these alkyl lithium reagents is similar to, rivals, or exceeds most reported catalysts, making these the most widely accessible, and therefore convenient, catalysts for this reaction.

Observations of the reactivity patterns and a Hammett analysis are most consistent with a nucleophilic mechanism, where other common reaction types are either directly or implicitly eliminated. Deprotonated amide is a valid precatalyst, but these lithium reagents give superior performance properties in the catalysis and are therefore recommended.

The catalyst activity observed under mild conditions with common reagents indicates that routine syntheses of aminosilanes would be accomplished with the protocols reported herein, though modification for a particular substrate set would be advisable. In any reaction with even limited turnover, revised conditions are likely to afford high conversions. Considering the substrate scope explored in this study, the activity of organolithium reagents as catalysts suggests that further expansion is possible. Overall, these results demonstrate that heterodehydrocoupling can be a viable synthetic strategy for Si–N bond formation using organolithium precatalysts.

Experimental methods

All manipulations were conducted under a positive pressure of N_2 in either an M. Braun glovebox or using standard Schlenk techniques. Dry, oxygen-free solvents, reagents, and solid support were used throughout experimentation and stored inside the glovebox. Solvents such as *n*-pentane, hexanes, and toluene were degassed with argon, dried by passing through columns of activated alumina and Q5, dispensed, and subsequently stored over 3 Å molecular sieves. Tetrahydrofuran (THF) was dried over sodium/benzophenone, and subsequently distilled and stored in a PTFE-sealed Strauss flask. Benzene-d_6 (C_6D_6) was distilled from calcium hydride (CaH_2) and stored over activated 3 Å molecular sieves for at least 48 h. Solid support such as Celite and 3 Å molecular sieves were dried between 160–180 °C under dynamic vacuum for at least 1 d.

Organolithium reagents were obtained from chemical vendors as solutions: methyl lithium (MeLi) in 1,2-dimethoxyethane, ethyl lithium (EtLi) in dibutyl ether, trimethylsilylmethyl lithium (Me_3SiCH_2Li) in pentane, *normal*-butyl lithium (*n*BuLi) in hexanes, *secondary*-butyl lithium (*s*BuLi) in cyclohexane, *tertiary*-butyl lithium (*t*BuLi) in pentane, and phenyl lithium (PhLi) in dibutyl ether. For catalysis, these solutions were filtered through Celite inside the glovebox, titrated thrice with *N*-benzylbenzamide in 2–3 mL of THF, and stored at −40 °C. Although stocks solutions were subsequently used without further purification, for consistent results, the molarities of **1**–**7** were determined at regular intervals. Me_3SiCH_2Li was isolated as a solid by filtering the received pentane solution through Celite inside the glovebox and recrystallizing from minimal pentane at −40 °C. Amines were distilled under dynamic N_2 from CaH_2 and stored over 3Å molecular sieves. $PhSiH_3$ was distilled under dynamic N_2, while $PhMeSiH_2$, Ph_2SiH_2, and $PhMe_2SiH$ were distilled under dynamic vacuum. $PhMe_2SiH$ and Ph_2MeSiH were transferred directly into the glovebox and stored over 3Å molecular sieves. Ph_3SiH was recrystallized from hexanes at −40 °C. Hexamethylbenzene (C_6Me_6) was sublimed at 150 °C under dynamic vacuum. Substituted tertiary silanes (p-X-C_6H_4)Ph_2SiH were prepared according to literature reports.[23]

Glassware was cleaned by sequential washings of base (5% KOH/10% ^{i}PrOH/85% deionized H_2O), acid (10% HNO_3/90% deionized H_2O), and water. Glassware was oven dried at 140 °C for at least 1 h, which was either transferred to the antechamber of an M. Braun glovebox or placed under dynamic vacuum connected to a Schlenk line. Catalytic reactions were conducted in PTFE-valved J-Young-type NMR tubes, which were cleaned and dried by the methods mentioned above.

Nuclear magnetic resonance (NMR) spectra were recorded at 25 °C on either a Varian 500 MHz spectrometer or a Bruker AXR 500 MHz spectrometer. Electron paramagnetic resonance (EPR) measurements were collected at ambient temperature on a Bruker EMXplus Spectrometer.

Author contributions

Methodology, experimentation, data acquisition, and data analysis were conducted by M. B. R., while conceptualization and writing were conducted by both M. B. R. and R. W. Additional experimentation, data acquisition, and data analysis conducted by C. E. B. and D. R. J. J. Funding was secured by M. B. R., D. R. J. J., and R. W. Additional edits and proof reading was conducted by all authors. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors have no conflicts of interest to declare.

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