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## ARTICLE

# Commercially Available Organolithium Compounds as Effective, Simple Precatalysts for Silicon–Nitrogen Heterodehydrocoupling

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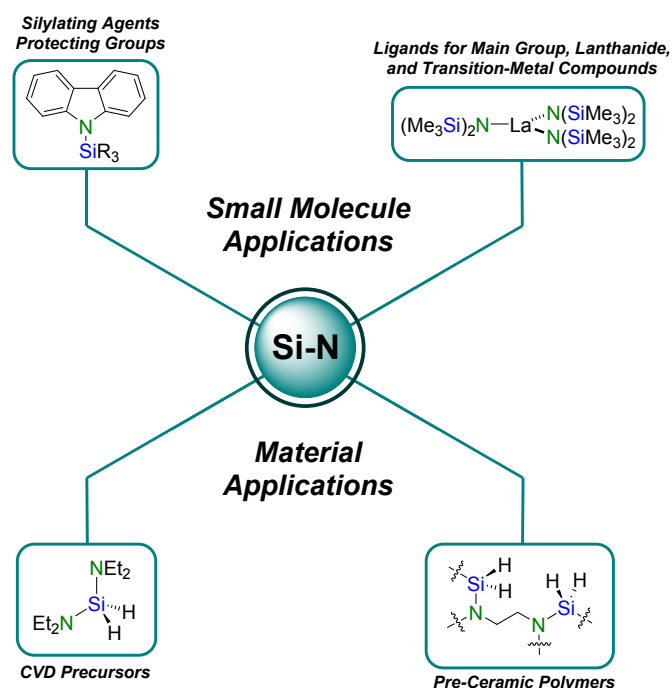
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A family of commercially available organolithium compounds were found to effectively catalyze the heterodehydrocoupling of silanes and amines under ambient conditions. Ubiquitous <sup>n</sup>BuLi (**1**) was utilized as the benchmark catalyst, where 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 using 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.<sup>1–4</sup> In general, dehydrocoupling has emerged as a versatile method to form main group (i.e., *p*-block) products through catalysis.<sup>2,5,6</sup> This method is green and atom-economical, producing H<sub>2</sub> as the sole byproduct.<sup>7</sup> Liberated H<sub>2</sub> drastically simplifies purification and acts 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.<sup>8</sup>

Heterodehydrocoupling of silanes and amines is poised to emerge as a complementary method to form Si–N bonds.<sup>1–4</sup> Established applications for aminosilanes and silylamines include transition-metal, lanthanide and main group ligands,<sup>9</sup> silylating agents,<sup>10,11</sup> and as protecting groups in synthetic chemistry (Figure 1, *top*).<sup>12,13</sup> In recent years, aminosilanes have been employed as chemical vapor deposition (CVD)<sup>14</sup> and ceramic<sup>14,15</sup> precursors (Figure 1, *bottom*). Likewise, the synthesis of chiral Si–N products through heterodehydrocoupling has recently been reported.<sup>16–18</sup> 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.



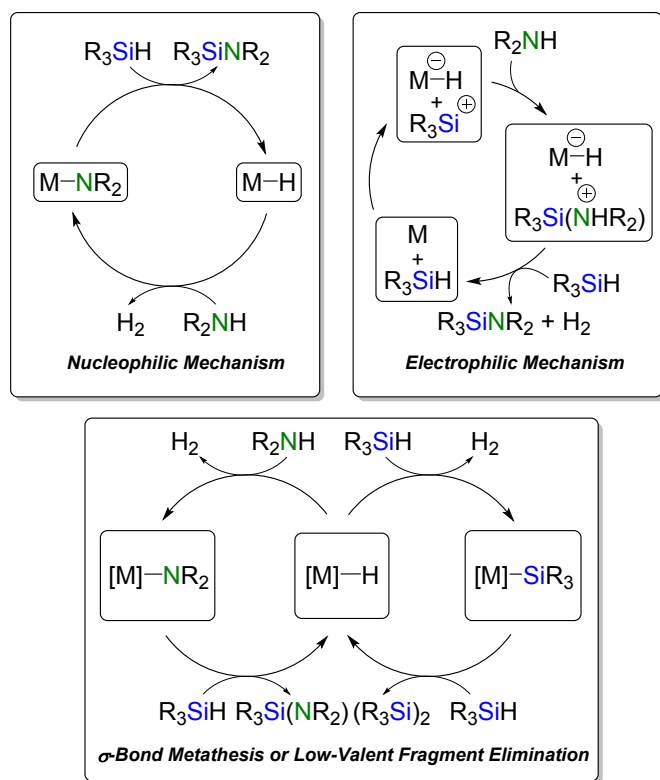
**Figure 1.** Applications of small molecules, polymers, and materials with Si–N bonds.<sup>14,15,19–21</sup>

Unfortunately, the full synthetic utility of heterodehydrocoupling has yet to be realized, and achieving this requires expansion of accessible precatalysts that are highly active under ambient or otherwise mild conditions. Interestingly, Si–N heterodehydrocoupling catalysts enjoy a taste of mechanistic ubiquity (Figure 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.<sup>2</sup> It was therefore hypothesized that the ubiquity of nucleophiles could be the key to generalizing heterodehydrocoupling by expanding accessible, highly active catalysts.

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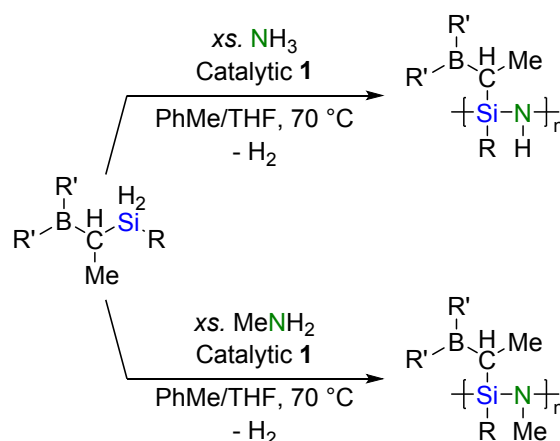
<sup>†</sup> Footnotes relating to the title and/or authors should appear here.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



**Figure 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).<sup>8, 22-27</sup>

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  $\text{NH}_3$  and  $\text{MeNH}_2$  to borane-containing primary and secondary silanes, forming preceramic SiBCN polymers (Scheme 1).<sup>28</sup> 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.

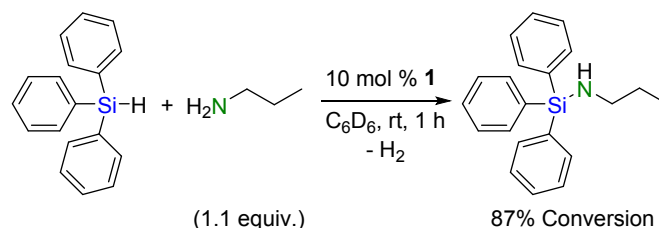


**Scheme 1.** Heterodehydrocoupling of borane-modified silanes with either  $\text{NH}_3$  or  $\text{MeNH}_2$  using **1** as reported by Weinmann and Müller.<sup>28</sup>

## 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,<sup>24, 29</sup> however, control reactions quickly demonstrated the utility of these activators as precatalysts. For instance, the reaction between  $\text{Ph}_3\text{SiH}$  and 1.1 equiv. of  $n\text{PrNH}_2$  with 10 mol %  $n\text{BuLi}$  (**1**) furnished  $\text{Ph}_3\text{Si}(\text{NH}n\text{Pr})$  in 87% conversion after 1 h at ambient temperature (Scheme 2).



**Scheme 2.** Heterodehydrocoupling of  $\text{Ph}_3\text{SiH}$  and 1.1 equiv. of  $n\text{PrNH}_2$  catalysed by **1**.

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

**Table 1.** Screening of commercially available organolithium reagents for Si–N coupling.<sup>[a]</sup>

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

<sup>[a]</sup>Conditions: Ph<sub>3</sub>SiH (3.7 × 10<sup>−1</sup> mmol, 1.0 equiv.), *n*PrNH<sub>2</sub> (4.2 mmol × 10<sup>−1</sup> mmol, 1.1 equiv.), and RLi (3.7 × 10<sup>−2</sup> mmol, 10.0 mol %, as a solution in commercial solvent) in 0.5 mL of benzene-*d*<sub>6</sub> at ambient temperature in a PTFE-valved J-Young type NMR tube. <sup>[b]</sup>Reactions were run in triplicate and the averages were taken for 1 h and 24 h intervals. Conversions were measured via <sup>1</sup>H NMR spectroscopy by integration of residual Ph<sub>3</sub>SiH vs Ph<sub>3</sub>Si(NH*n*Pr). <sup>[c]</sup>The slight disparity in conversions between Table 1 and Scheme 2 is due to a change in concentration. <sup>[d]</sup>Me<sub>3</sub>SiCH<sub>2</sub>Li was utilized as a solid for catalysis, rather than as a stock solution.

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<sub>3</sub>SiH and 1.1 equiv. of *n*PrNH<sub>2</sub>, the corresponding aminosilane Ph<sub>3</sub>Si(NH*n*Pr) was formed in 80% conversion or greater with every tested organolithium compound (Table 1). The results of these reactions indeed confirm that the identity of organolithium precatalyst was 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.

**Table 2.** Optimization conditions of the reaction between Ph<sub>3</sub>SiH and *i*PrNH<sub>2</sub> with **1**.<sup>[a]</sup>

Entry	Ph <sub>3</sub> SiH (equiv.)	<i>i</i> PrNH <sub>2</sub> (equiv.)	% (1 h)
2a	1.1	1.0	61 <sup>[b]</sup>
2b	1.0	1.1	81
2c	1.0	1.5	83
2d	1.0	2.0	100

<sup>[a]</sup>Conditions: **1** in 0.5 mL of benzene-*d*<sub>6</sub>. Conversions were measured via <sup>1</sup>H NMR spectroscopy by integrating residual Ph<sub>3</sub>SiH vs Ph<sub>3</sub>Si(NH*i*Pr).

<sup>[b]</sup>Conversions were measured by <sup>1</sup>H NMR spectroscopy after 1 h, determined by integration of Ph<sub>3</sub>Si(NH*i*Pr) peak against the 0.4 M C<sub>6</sub>Me<sub>6</sub> standard.

Subsequent efforts were aimed at optimizing the conversion of Ph<sub>3</sub>SiH to aminosilane, with the target being quantitative conversion within 1 h at ambient temperature. Notably, the benchmark amine was changed to *i*PrNH<sub>2</sub>, as these reaction conditions proved to be more general than those used for *n*PrNH<sub>2</sub>. Excess silane (Table 2, Entry 2a) had the most deleterious effect on conversion, affording

Ph<sub>3</sub>Si(NH*i*Pr) 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<sub>2</sub> were necessary to produce Ph<sub>3</sub>Si(NH*i*Pr) 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

**Table 3.** Scope of Si–N heterodehydrocoupling between Ph<sub>3</sub>SiH<sub>3</sub> and amines with **1**.<sup>[a]</sup>

Entry	Silane	Amine	Product	% <sup>[b]</sup>
3a	PhSiH <sub>3</sub>	<i>n</i> PrNH <sub>2</sub>	PhSi(NH <i>n</i> Pr) <sub>3</sub>	66
3b	PhSiH <sub>3</sub>	<i>i</i> PrNH <sub>2</sub>	PhSi(NH <i>i</i> Pr) <sub>3</sub>	85
3c	PhSiH <sub>3</sub>	<i>t</i> BuNH <sub>2</sub>	PhSiH(NH <i>t</i> Bu) <sub>2</sub>	98
3d	PhSiH <sub>3</sub>	PhNH <sub>2</sub>	PhSiH <sub>2</sub> (NHPh) PhSiH(NHPh) <sub>2</sub>	90 10
3e	PhSiH <sub>3</sub>	Et <sub>2</sub> NH	PhSiH <sub>2</sub> (NEt <sub>2</sub> ) PhSiH(NEt <sub>2</sub> ) <sub>2</sub>	48 52
3f <sup>[c]</sup>	PhSiH <sub>3</sub>	PyNH	PhSi(NPy) <sub>3</sub>	100

<sup>[a]</sup>Conditions: PhSiH<sub>3</sub> (3.7 × 10<sup>−1</sup> mmol, 1.0 equiv.), amine (22.6 × 10<sup>−1</sup> mmol, 6.0 equiv.), and **1** (3.7 × 10<sup>−2</sup> mmol, 10.0 mol %, stock solution in hexanes) in 0.5 mL of benzene-*d*<sub>6</sub> at ambient temperature in a PTFE-valved J-Young type NMR tube. <sup>[b]</sup>Conversions were measured by <sup>1</sup>H NMR spectroscopy after 1 h by integrating residual silane vs. product.

<sup>[c]</sup>Conversion was measured after 0.5 h.

The primary silane PhSiH<sub>3</sub> is often a starting point for Si–N heterodehydrocoupling with electron-rich amines such as *n*PrNH<sub>2</sub>. These substrates help gauge the efficiency of a precatalyst towards this transformation, due to the enhanced hydricity of aminosilane Si–H bonds.<sup>34</sup> Reaction of PhSiH<sub>3</sub> and *n*PrNH<sub>2</sub> with **1** afforded the desired tris(aminosilane), PhSi(NH*n*Pr)<sub>3</sub>, in 66% conversion after 1 h at ambient temperature (Table 3, Entry 3a). The efficiency of this system is comparable to that of (thf)<sub>2</sub>La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>, which accomplished the coupling of PhSiH<sub>3</sub> with 3.0 equiv. of *n*PrNH<sub>2</sub> to afford PhSi(NH*n*Pr)<sub>3</sub> in 45–60% conversion in 10 min at ambient temperature.<sup>33</sup> In both instances, competitive formation of silylamines is observed. Notably, Sadow and coworkers isolated PhSi(NH*n*Pr)<sub>3</sub> in 99% yield when using (To<sup>M</sup>)MgMe, a precatalyst that likely inhibits competing silylamine reactions.<sup>22</sup>

Byproduct formation is minimized with bulkier, non-linear amines. For instance, reaction between PhSiH<sub>3</sub> and *i*PrNH<sub>2</sub> afforded the tris(aminosilane) PhSi(NH*i*Pr)<sub>3</sub> in 85% conversion (Table 3, Entry 3b), as assessed by the appearance of a septet centered at δ = 3.24 in the <sup>1</sup>H NMR spectrum and a resonance at δ = −37.20 in the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum. Three additional resonances consistent with *i*Pr groups were observed in the <sup>1</sup>H NMR spectrum that likely arise from the competing silylamine pathway. The reaction between PhSiH<sub>3</sub> and *t*BuNH<sub>2</sub> affords PhSiH(NH*t*Bu)<sub>2</sub> in 98% conversion after 1 h (Table 3, Entry 3c; Scheme 3, top). No evidence for the tris(aminosilane) product, PhSi(NH*t*Bu)<sub>3</sub>, was observed by <sup>1</sup>H NMR spectroscopy, and this product has notably not been reported to be produced via

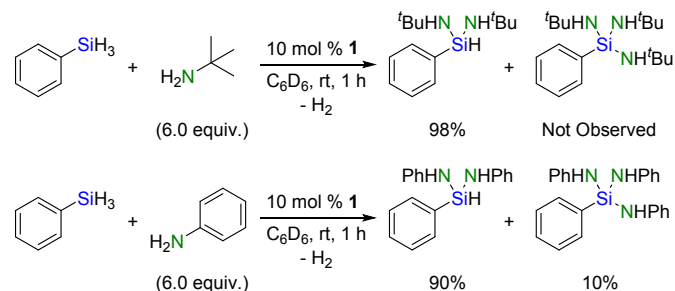
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heterodehydrocoupling. Nevertheless, competing silylamine production appears to be inhibited by the increased substitution on the primary amine.

The selective formation of certain aminosilane products from primary silanes was not observed using **1**. For instance, the reaction of  $\text{PhSiH}_3$  and 2.0 equiv. of  $\text{PrNH}_2$  afforded a complex mixture of Si–H products appearing between  $\delta = 5.00$  and  $\delta = 6.00$  in the  $^1\text{H}$  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<sup>35, 36</sup> and transition-metal<sup>37</sup> compounds with NHC ligands may offer an effective strategy to selectively form aminosilanes.

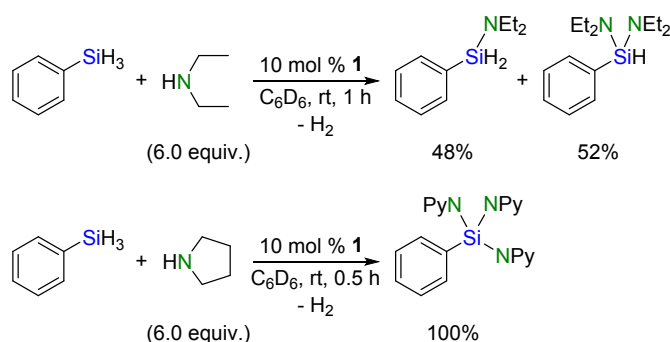
The role of amine basicity became evident in the reaction between  $\text{PhSiH}_3$  and aniline ( $\text{PhNH}_2$ ) with **1**. After 1 h, the bis- and tris(aminosilane) products  $\text{PhSiH}(\text{NHPh})_2$  and  $\text{PhSi}(\text{NHPh})_3$  were formed in 90% and 10% conversion, respectively (Table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



**Scheme 3.** Divergent reactivity between  $t\text{BuNH}_2$  and  $\text{PhNH}_2$  with  $\text{PhSiH}_3$  catalysed by **1**.

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

Conversely, reaction between  $\text{PhSiH}_3$  and pyrrolidine ( $\text{PyNH}$ ) produced  $\text{PhSi}(\text{NPy})_3$  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  $\text{Et}_2\text{NH}$  and  $\text{PyNH}$  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  $\text{PhSiH}_3$  and  $\text{PhNH}_2$  buttress this hypothesis, where the tris(aminosilane)  $\text{PhSi}(\text{NHPh})_3$  is formed in measurable quantities despite  $\text{PhNH}_2$  being less basic than  $\text{Et}_2\text{NH}$ .



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

**Table 4.** Scope of Si–N heterodehydrocoupling between secondary silanes and amines with **1**.<sup>[a]</sup>

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

<sup>[a]</sup>Conditions:  $\text{R}_2\text{SiH}_2$  ( $3.7 \times 10^{-1}$  mmol, 1.0 equiv.), amine ( $15.0 \times 10^{-1}$  mmol, 4.0 equiv.), and **1** ( $3.7 \times 10^{-2}$  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.

<sup>[b]</sup>Conversions were measured by  $^1\text{H}$  NMR spectroscopy after 1 h, by integrating residual silane vs. product. <sup>[c]</sup>Conversions were measured after 0.5 h.

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

conversion (Table 4, Entry 4d). However,  $\text{PhMeSiH}_2$  is a versatile substrate where reactions with either  $\text{Et}_2\text{NH}$  and  $\text{PyNH}$  proceed quantitatively to the mono- and bis(aminosilane) products, respectively (Table 4, Entries 4e and 4f, respectively).

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

Several trends emerge from the reactions between either  $\text{PhMeSiH}_2$  or  $\text{Ph}_2\text{SiH}_2$ . Reactions between  $\text{Ph}_2\text{SiH}_2$  and  $\text{PhNH}_2$  proceed to higher conversions of the mono(aminosilane) product than reactions with  $\text{PhMeSiH}_2$ . 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  $\text{PhMeSiH}_2$  with  $t\text{BuNH}_2$  and  $\text{Et}_2\text{NH}$  only produce the mono(aminosilane) product, despite high amine concentrations (Table 4, Entry 4c and 4e, respectively).

**Table 5.** Scope of Si–N heterodehydrocoupling between tertiary silanes and amines with **1**<sup>[a]</sup>

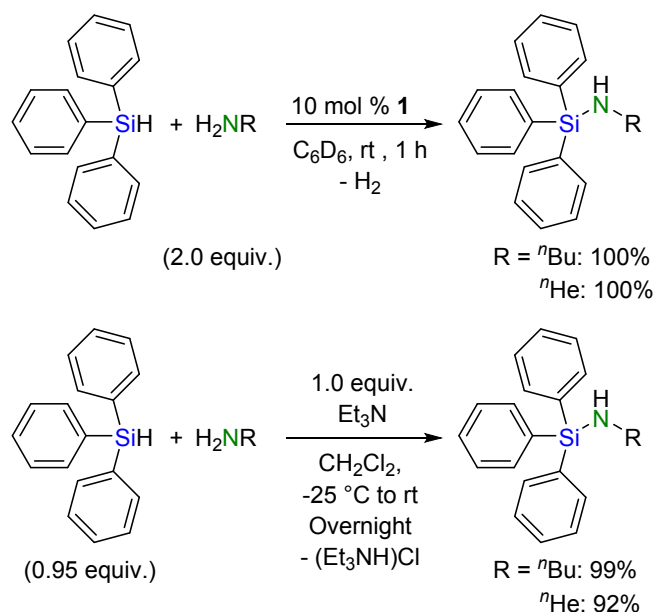
Entry	Silane	Amine	Product	(%) <sup>[b]</sup>
5a	$\text{PhMe}_2\text{SiH}$	$n\text{PrNH}_2$	$\text{PhMe}_2\text{Si}(\text{NH}n\text{Pr})$	100
5b	$\text{PhMe}_2\text{SiH}$	$i\text{PrNH}_2$	$\text{PhMe}_2\text{Si}(\text{NH}i\text{Pr})$	100
5c	$\text{PhMe}_2\text{SiH}$	$\text{PhNH}_2$	$\text{PhMe}_2\text{Si}(\text{NHPh})$	0
5d	$\text{PhMe}_2\text{SiH}$	$\text{Et}_2\text{NH}$	$\text{PhMe}_2\text{Si}(\text{NEt}_2)$	48
5e	$\text{PhMe}_2\text{SiH}$	$\text{PyNH}$	$\text{PhMe}_2\text{Si}(\text{NPy})$	100
5f	$\text{Ph}_2\text{MeSiH}$	$n\text{PrNH}_2$	$\text{Ph}_2\text{MeSi}(\text{NH}n\text{Pr})$	100
5g	$\text{Ph}_2\text{MeSiH}$	$\text{Et}_2\text{NH}$	$\text{Ph}_2\text{MeSi}(\text{NEt}_2)_2$	57
5h	$\text{Ph}_3\text{SiH}$	$n\text{PrNH}_2$	$\text{Ph}_3\text{Si}(\text{NH}n\text{Pr})$	100
5i	$\text{Ph}_3\text{SiH}$	$i\text{PrNH}_2$	$\text{Ph}_3\text{Si}(\text{NH}i\text{Pr})$	100
5j	$\text{Ph}_3\text{SiH}$	$n\text{BuNH}_2$	$\text{Ph}_3\text{Si}(\text{NH}n\text{Bu})$	100
5k	$\text{Ph}_3\text{SiH}$	$t\text{BuNH}_2$	$\text{Ph}_3\text{Si}(\text{NH}t\text{Bu})$	80
5l	$\text{Ph}_3\text{SiH}$	$n\text{PeNH}_2$	$\text{Ph}_3\text{Si}(\text{NH}n\text{Pe})$	100
5m	$\text{Ph}_3\text{SiH}$	$n\text{HeNH}_2$	$\text{Ph}_3\text{Si}(\text{NH}n\text{He})$	100

5n	$\text{Ph}_3\text{SiH}$	$\text{PhNH}_2$	$\text{Ph}_3\text{Si}(\text{NHPh})$	0
5o	$\text{Ph}_3\text{SiH}$	$\text{Et}_2\text{NH}$	$\text{Ph}_3\text{Si}(\text{NEt}_2)$	88
5p	$\text{Ph}_3\text{SiH}$	$\text{PyNH}$	$\text{Ph}_3\text{Si}(\text{NPy})$	100

<sup>[a]</sup>Conditions:  $\text{R}_3\text{SiH}$  ( $3.7 \times 10^{-1}$  mmol, 1.0 equiv.), amine ( $7.5 \times 10^{-1}$  mmol, 2.0 equiv.), and **1** ( $3.7 \times 10^{-2}$  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. <sup>[b]</sup>Conversions were measured by  $^1\text{H}$  NMR spectroscopy after 1 h, by integrating residual silane vs. product. <sup>[c]</sup>Conversions were measured after 0.5 h.

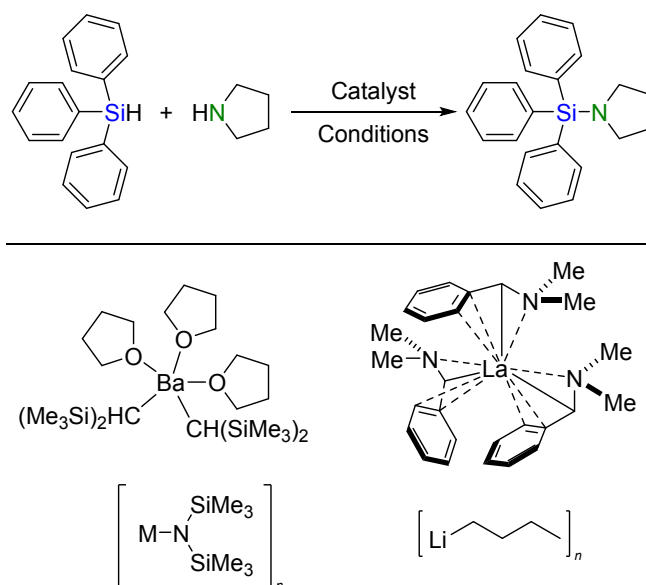
Notably, increased substitution on silane frequently hampers high conversions to aminosilane products, which is not apparent in this study with **1**. Tertiary silanes such as  $\text{PhMe}_2\text{SiH}$ ,  $\text{Ph}_2\text{MeSiH}$ , and  $\text{Ph}_3\text{SiH}$  were accessible substrates in catalysis with **1**. Linear amines such as  $n\text{PrNH}_2$  and  $i\text{PrNH}_2$  reacted smoothly with  $\text{PhMe}_2\text{SiH}$  to afford the mono(aminosilane) products within 1 h at ambient temperature (Table 5, Entry 5a and 5b, respectively). These results are consistent with less encumbered arylsilanes (Table 3 and 4), further buttressing the supposition that substitution on silane directly impacts the production of silylamine byproducts. Aniline is completely unreactive towards  $\text{PhMe}_2\text{SiH}$  under these conditions (Table 5, Entry 5c), while  $\text{Et}_2\text{NH}$  affords  $\text{PhMe}_2\text{Si}(\text{NEt}_2)$  in 48% conversion (Table 5, Entry 5d). As with previous examples,  $\text{PhMe}_2\text{SiH}$  reacts with  $\text{PyNH}$  rapidly and quantitatively to produce  $\text{PhMe}_2\text{Si}(\text{NPy})$  (Table 5, Entry 5e).

Interestingly,  $\text{Ph}_3\text{SiH}$  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  $n\text{PrNH}_2$  and  $i\text{PrNH}_2$  were coupled quantitatively to  $\text{Ph}_3\text{SiH}$  within 1 h at ambient temperature (Table 5, Entries 5h and 5i, respectively), while reactions with  $t\text{BuNH}_2$  afforded the mono(aminosilane) product  $\text{Ph}_3\text{Si}(\text{NH}t\text{Bu})$  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  $n\text{BuNH}_2$ ,  $n\text{PeNH}_2$ , and  $n\text{HeNH}_2$  (Table 5, Entries 5j, 5l, and 5m, respectively). Aminosilane product  $\text{Ph}_3\text{Si}(\text{NH}n\text{Pe})$  has previously been furnished through catalysis with azametallacyclopropane  $(\text{hmpa})_3\text{M}(\eta^2\text{-Ph}_2\text{CNPh})$  ( $\text{M} = \text{Ca}^{30}$ ,  $\text{Yb}^{38}$ ), while aminosilane products  $\text{Ph}_3\text{Si}(\text{NH}n\text{Bu})$  and  $\text{Ph}_3\text{Si}(\text{NH}n\text{He})$  have only been synthesized in stoichiometric reactions (Scheme 5).<sup>39</sup> Aniline is unreactive towards  $\text{Ph}_3\text{SiH}$  (Table 5, Entry 5n). Reaction of  $\text{Ph}_3\text{SiH}$  and  $\text{Et}_2\text{NH}$  affords mono(aminosilane)  $\text{Ph}_3\text{Si}(\text{NEt}_2)$  in 88% conversion (Table 5, Entry 5o), which is significantly more effective than in reactions with  $\text{PhMe}_2\text{SiH}$  (48%, Table 5, Entry 5d).



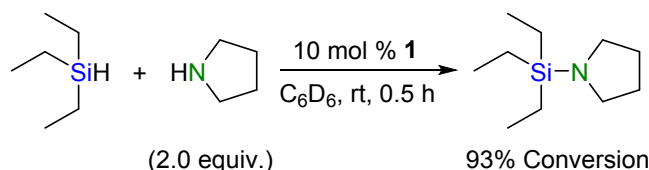
**Scheme 5.** Comparison of the stoichiometric and catalytic reactions of  $\text{Ph}_3\text{SiH}$  with  $n\text{BuNH}_2$  or  $n\text{HeNH}_2$ .<sup>39</sup>

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



**Figure 3.** Heterodehydrocoupling of  $\text{Ph}_3\text{SiH}$  and  $\text{PyNH}$  catalysed by s- and f-block precatalysts.<sup>23, 31, 41</sup>

Catalysis with **1** could also be extended to  $\text{Et}_3\text{SiH}$ . Reaction of  $\text{Et}_3\text{SiH}$  with 2.0 equiv. of  $\text{PyNH}$  in the presence of **1** furnished  $\text{Et}_3\text{Si(NPy)}$  in 93% conversion after just 0.5 h at ambient temperature (Scheme 6).



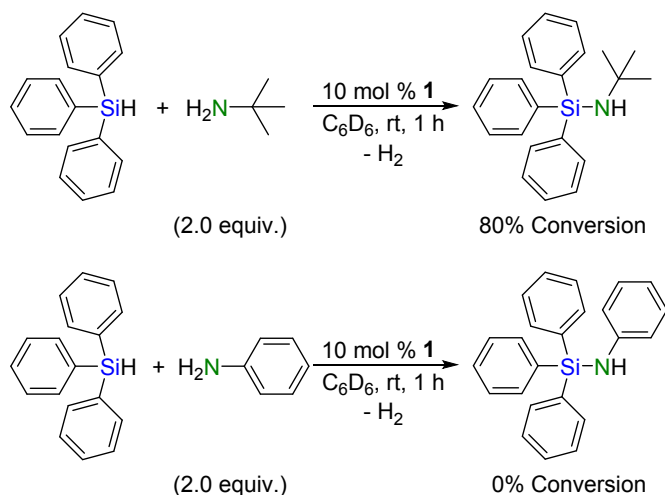
**Scheme 6.** Heterodehydrocoupling of  $\text{Et}_3\text{SiH}$  and  $\text{PyNH}$  catalysed by **1**.

This reactivity is comparable to  $(\text{thf})_3\text{Ba}[\text{CH}(\text{SiMe}_3)_2]_2$ , which coupled equimolar  $\text{Et}_3\text{SiH}$  and  $\text{PyNH}$  to afford  $\text{Et}_3\text{Si(NPy)}$  in 93% conversion after 2 h at  $60^\circ\text{C}$ .<sup>31</sup> Catalysis with **1** continues to show its utility in protecting group chemistry. Heterodehydrocoupling of alkylsilanes and electron-deficient amines (i.e.,  $\text{Ph}_2\text{NH}$ ,  $\text{PhNH}_2$ ) is readily accomplished by Lewis acids.<sup>8, 20, 42</sup> 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  $\text{PyNH}$  in the presence of **1** evidently contributes to the high conversions to  $\text{Et}_3\text{Si(NPy)}$ , as this activity is not easily extended to less reactive amines.

### Mechanistic Insight

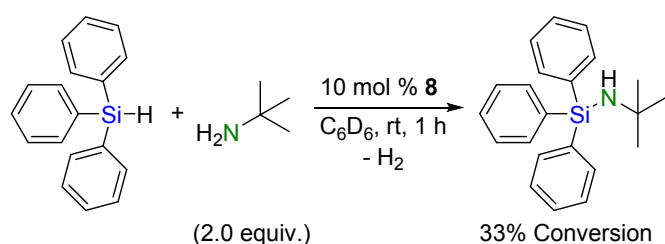
Preliminary observations are consistent with nucleophilic attack of a  $\text{M-NR}_2$  intermediate on silane. For instance, amine basicity appears to drive catalysis, which is illustrated by the relative reactivities of either  $t\text{BuNH}_2$  or  $\text{PhNH}_2$  with  $\text{Ph}_3\text{SiH}$  (Scheme 7).





**Scheme 7.** Comparison of conversions in the reactions between  $\text{tBuNH}_2$  or  $\text{PhNH}_2$  with  $\text{Ph}_3\text{SiH}$  catalysed by **1**.

These results are consistent with the formation of a nucleophilic  $\text{Li-NR}_2$  intermediate that enhances amine basicity during catalysis. To test this supposition,  $\text{tBuNHLi}$  (**8**) was isolated<sup>43</sup> and employed as a catalyst under otherwise standard reaction conditions. After 1 h at ambient temperatures, the aminosilane  $\text{Ph}_3\text{Si}(\text{NHtBu})$  was produced in 33% conversion (Scheme 8).

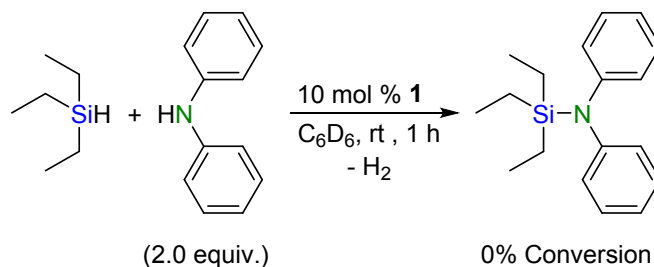


**Scheme 8.** Heterodehydrocoupling of  $\text{Ph}_3\text{SiH}$  and  $\text{tBuNH}_2$  catalysed by **8**.

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- $d_6$ .<sup>44</sup> 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.

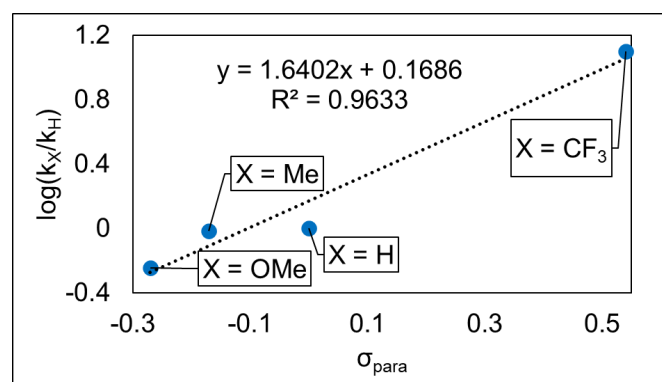
The formation of **8** is observable via  $^1\text{H}$  NMR spectroscopy. Under standard reaction conditions, **1** quantitatively converts to **8** in the presence of excess  $\text{tBuNH}_2$ . The analogous reaction between  $\text{Ph}_3\text{SiH}$  and 10 mol % **1** does not result in the formation of observable products by NMR spectroscopy. These results suggest that  $\text{Ph}_3\text{SiLi}$  is not operant during catalysis, which is supported by the lack of characteristic colour changes throughout catalysis with **1-8**.<sup>45</sup> The absence of  $\text{Ph}_3\text{SiLi}$  is further supported by the fact that group II  $\text{MSiR}_3$  compounds are known to be inactive for Si–N heterodehydrocoupling.<sup>23</sup>

Several additional observations discount competing mechanisms. Catalysis is not inhibited by high amine concentration, which is inconsistent with  $\sigma$ -bond metathesis.<sup>46, 47</sup> A  $\sigma$ -bond metathesis pathway would allow for disilane products that are not observed.<sup>25, 26, 48</sup> The lack of disilane products also suggests that low-valent silicon reactivity (i.e., silylene elimination) is not involved.<sup>46, 49</sup> Compound **1**'s lack of reactivity with  $\text{Et}_3\text{SiH}$  and  $\text{Ph}_2\text{NH}$  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.<sup>8, 20, 42</sup> Finally, the selective formation of aminosilanes from primary and secondary silanes, and the lack of an EPR signal during catalysis, discounts a radical mechanism.



**Scheme 9.** Unsuccessful reaction between  $\text{Et}_3\text{SiH}$  and  $\text{Ph}_2\text{NH}$  in the presence of **1**.

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  $\text{tBuNH}_2$  with 0.5 equiv. of  $\text{Ph}_3\text{SiH}$  and 0.5 equiv. of ( $p$ -X- $\text{C}_6\text{H}_4$ ) $\text{Ph}_2\text{SiH}$  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 (Figure 4).

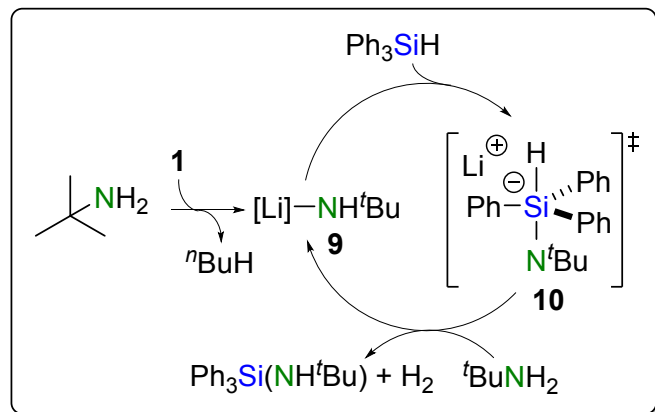


**Figure 4.** Hammett correlation by competition experiments between  $\text{tBuNH}_2$  and ( $p$ -X- $\text{C}_6\text{H}_4$ ) $\text{Ph}_2\text{SiH}$  with **1**.

Analogous correlations ( $\rho = 2.0$ ) were obtained between ( $p$ -X- $\text{C}_6\text{H}_4$ ) $\text{Ph}_2\text{SiH}$  and  $\text{PyNH}$  mediated by barium precatalysts.<sup>23</sup> Similarly, Sadow's report with  $(\text{To}^M)\text{MgNH}^t\text{Bu}$  demonstrated rate-acceleration ( $\rho = 1.4$ ) in reactions with  $p$ -substituted ( $p$ -X- $\text{C}_6\text{H}_4$ ) $\text{PhSiH}_2$  substrates.<sup>22</sup> Both studies attribute these results to the formation of a transient, hypervalent silicon intermediate. Indeed, results obtained from Figure 4 support a mechanism that involves nucleophilic attack of amide on silane.



Consistent with previous reports,<sup>2</sup> 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 (Figure 4). Aminosilane is formed and a hydride equivalent reacts with amine to liberate H<sub>2</sub> and reform **9**.



**Scheme 10.** Proposed catalytic cycle using **1** as a precatalyst to couple tBuNH<sub>2</sub> and Ph<sub>3</sub>SiH. Brackets around lithium indicate a non-discrete intermediate.

Currently, the molecularity of mechanistic intermediates is not well understood. The inferior conversions to Ph<sub>3</sub>Si(NH<sup>t</sup>Bu) 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*<sub>6</sub>. Group I MH compounds have been utilized for heterodehydrocoupling,<sup>31, 50</sup> 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 <sup>1</sup>H-<sup>29</sup>Si{<sup>1</sup>H} HSQC and DOSY NMR during catalysis.

## Conclusions

A deeper exploration of organolithium compounds has yielded a general and highly active protocol for catalytic coupling of silanes and amines. This expands upon Weinmann and Müller's report of **1**-catalysed Si–N heterodehydrocoupling.<sup>28</sup> 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<sub>2</sub> was less reactive towards silane substrates. The compatibility of Ph<sub>3</sub>SiH and Et<sub>3</sub>SiH 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 the routine synthetic strategy for Si–N bond formation using organolithium precatalysts.

## Experimental Methods

All manipulations were conducted under a positive pressure of N<sub>2</sub> 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 1 L PTFE-sealed Strauss flask. Benzene-*d*<sub>6</sub> (C<sub>6</sub>D<sub>6</sub>) was distilled from calcium hydride (CaH<sub>2</sub>) 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<sub>3</sub>SiCH<sub>2</sub>Li) 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 and 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<sub>3</sub>SiCH<sub>2</sub>Li 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<sub>2</sub> from CaH<sub>2</sub> and stored over 3 Å molecular sieves. PhSiH<sub>3</sub> was distilled under dynamic N<sub>2</sub>, while PhMeSiH<sub>2</sub>, Ph<sub>2</sub>SiH<sub>2</sub>, and PhMe<sub>2</sub>SiH were distilled under dynamic vacuum. PhMe<sub>2</sub>SiH and Ph<sub>2</sub>MeSiH were transferred directly into the glovebox and stored over 3 Å molecular sieves. Ph<sub>3</sub>SiH was recrystallized from hexanes at -40 °C. Hexamethylbenzene (C<sub>6</sub>Me<sub>6</sub>) was sublimed at 150 °C under dynamic

vacuum. Substituted tertiary silanes ( $p$ -X-C<sub>6</sub>H<sub>4</sub>)Ph<sub>2</sub>SiH were prepared according to literature reports.<sup>23</sup>

Glassware was cleaned by sequential washings of base (5 % KOH/10 % *i*-PrOH/85 % DI H<sub>2</sub>O), acid (10 % HNO<sub>3</sub>/90 % DI H<sub>2</sub>O), 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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## Notes and references

- Kuciński, K.; Hreczycho, G., Catalytic Formation of Silicon–Heteroatom (N, P, O, S) Bonds. *ChemCatChem* **2017**, *9* (11), 1868–1885.
- Reuter, M. B.; Hageman, K.; Waterman, R., Silicon–Nitrogen Bond Formation via Heterodehydrocoupling and Catalytic N-Silylation. *Chem. Eur. J.* **2021**, *27* (10), 3251–3261.
- Verma, V.; Koperniku, A.; Edwards, P. M.; Schafer, L. L., N-Silylamines in catalysis: synthesis and reactivity. *Chem. Commun.* **2022**, *58* (66), 9174–9189.
- Leland, B. E.; Mondal, J.; Trovitch, R. J., Sustainable preparation of aminosilane monomers, oligomers, and polymers through Si–N

- dehydrocoupling catalysis. *Chem. Commun.* **2023**, *59* (25), 3665–3684.
- Melen, R. L., Dehydrocoupling routes to element–element bonds catalysed by main group compounds. *Chem. Soc. Rev.* **2016**, *45* (4), 775–788.
- Reuter, M. B.; Seth, D. M.; Javier-Jiménez, D. R.; Finfer, E. J.; Beretta, E. A.; Waterman, R., Recent advances in catalytic pnictogen bond forming reactions via dehydrocoupling and hydrofunctionalization. *Chem. Commun.* **2023**, *59* (10), 1258–1273.
- Waterman, R., Mechanisms of metal-catalyzed dehydrocoupling reactions. *Chem. Soc. Rev.* **2013**, *42* (13), 5629–5641.
- Pérez, M.; Caputo, C. B.; Dobrovetsky, R.; Stephan, D. W., Metal-free transfer hydrogenation of olefins via dehydrocoupling catalysis. *PNAS* **2014**, *111* (30), 10917–10921.
- Coles, M. P., The role of the bis-trimethylsilylamido ligand, [N{SiMe<sub>3</sub>}<sub>2</sub>]<sup>–</sup>, in main group chemistry. Part 1: Structural chemistry of the s-block elements. *Coord. Chem. Rev.* **2015**, *297–298*, 2–23.
- Tanabe, Y.; Murakami, M.; Kitaichi, K.; Yoshida, Y., Mild, effective and selective method for the silylation of alcohols using silazanes promoted by catalytic tetrabutylammonium fluoride. *Tetrahedron Lett.* **1994**, *35* (45), 8409–8412.
- Tanabe, Y.; Misaki, T.; Kurihara, M.; Iida, A.; Nishii, Y., Silazanes/catalytic bases: mild, powerful and chemoselective agents for the preparation of enol silyl ethers from ketones and aldehydes. *Chem. Commun.* **2002**, (15), 1628–1629.
- Dhanak, D.; Reese, C. B., Studies in the protection of pyrrole and indole derivatives. *J. Chem. Soc., Perkin Trans.* **1986**, (0), 2181–2186.
- Jolicœur, B.; Chapman, E. E.; Thompson, A.; Lubell, W. D., Pyrrole protection. *Tetrahedron* **2006**, *62* (50), 11531–11563.
- Nguyen, T. T.; Mukhopadhyay, T. K.; MacMillan, S. N.; Janicke, M. T.; Trovitch, R. J., Synthesis of Aminosilane Chemical Vapor Deposition Precursors and Polycarbosilazanes through Manganese-Catalyzed Si–N Dehydrocoupling. *ACS Sustain. Chem. Eng.* **2022**, *10* (13), 4218–4226.
- Morris, L. J.; Whittell, G. R.; Eloi, J.-C.; Mahon, M. F.; Marken, F.; Manners, I.; Hill, M. S., Ferrocene-Containing Polycarbosilazanes via the Alkaline-Earth-Catalyzed Dehydrocoupling of Silanes and Amines. *Organometallics* **2019**, *38* (19), 3629–3648.
- Li, N.; Guan, B.-T., Yttrium–Benzyl Complexes Bearing Chiral Iminophosphonamide Ligands: Synthesis and Application in Catalytic Asymmetric Amine–Silane Dehydrocoupling Reactions. *Adv. Synth. Catal.* **2017**, *359* (20), 3526–3531.
- Li, N.; Guan, B.-T., A Dialkyl Calcium Carbene Adduct: Synthesis, Structure, and Catalytic Cross-Dehydrocoupling of Silanes with Amines. *Eur. J. Inorg. Chem.* **2019**, *2019* (16), 2231–2235.
- Liu, M.-M.; Xu, Y.; He, C., Catalytic Asymmetric Dehydrogenative Si–H/N–H Coupling: Synthesis of Silicon–Stereogenic Silazanes. *J. Am. Chem. Soc.* **2023**, *145* (21), 11727–11734.
- Zhai, W.; Li, B.; Wang, B., Ru<sub>3</sub>(CO)<sub>12</sub>-catalyzed dehydrogenative SiN coupling of indoles with hydrosilanes without additive. *Tetrahedron* **2018**, *74* (11), 1123–1128.
- Greb, L.; Tamke, S.; Paradies, J., Catalytic metal-free Si–N cross-dehydrocoupling. *Chem. Commun.* **2014**, *50* (18), 2318–2320.
- Bellini, C.; Orione, C.; Carpentier, J.-F.; Sarazin, Y., Tailored Cyclic and Linear Polycarbosilazanes by Barium-Catalyzed N–H/H–Si Dehydrocoupling Reactions. *Angew. Chem. Int. Ed.* **2016**, *55* (11), 3744–3748.
- Dunne, J. F.; Neal, S. R.; Engelkemier, J.; Ellern, A.; Sadow, A. D., Tris(oxazolinyl)boratomagnesium-Catalyzed Cross-Dehydrocoupling of Organosilanes with Amines, Hydrazine, and Ammonia. *J. Am. Chem. Soc.* **2011**, *133* (42), 16782–16785.

23. Bellini, C.; Carpentier, J.-F.; Tobisch, S.; Sarazin, Y., Barium-Mediated Cross-Dehydrocoupling of Hydrosilanes with Amines: A Theoretical and Experimental Approach. *Angew. Chem. Int. Ed.* **2015**, *54* (26), 7679-7683.
24. Gasperini, D.; King, A. K.; Coles, N. T.; Mahon, M. F.; Webster, R. L., Seeking Heteroatom-Rich Compounds: Synthetic and Mechanistic Studies into Iron Catalyzed Dehydrocoupling of Silanes. *ACS Catal.* **2020**, *10* (11), 6102-6112.
25. Liu, H. Q.; Harrod, J. F., Dehydrocoupling of ammonia and silanes catalyzed by dimethyltitanocene. *Organometallics* **1992**, *11* (2), 822-827.
26. He, J.; Liu, H. Q.; Harrod, J. F.; Hynes, R., Dehydrocoupling reactions of organosilanes with hydrazines. *Organometallics* **1994**, *13* (1), 336-343.
27. Erickson, K. A.; Cibuzar, M. P.; Mucha, N. T.; Waterman, R., Catalytic N-Si coupling as a vehicle for silane dehydrocoupling via  $\alpha$ -silylene elimination. *Dalton Trans.* **2018**, *47* (7), 2138-2142.
28. Weinmann, M.; Nast, S.; Berger, F.; Kaiser, G.; Müller, K.; Aldinger, F., Dehydrocoupling of tris(hydridosilyl)boranes with ammonia or amines: a novel route to Si-B-C-N preceramic polymers. *Appl. Organomet. Chem.* **2001**, *15* (10), 867-878.
29. Reuter, M. B.; Cibuzar, M. P.; Hammerton, J.; Waterman, R., Photoactivated silicon-oxygen and silicon-nitrogen heterodehydrocoupling with a commercially available iron compound. *Dalton Trans.* **2020**, *49* (9), 2972-2978.
30. Buch, F.; Harder, S., The Azametallacyclopropane  $\text{Ca}(\eta^2\text{-Ph}_2\text{CNPh})(\text{hmpa})_3$ : A Calcium Alternative to a Versatile Ytterbium(II) Catalyst. *Organometallics* **2007**, *26* (21), 5132-5135.
31. Anga, S.; Sarazin, Y.; Carpentier, J.-F.; Panda, T. K., Alkali-Metal-Catalyzed Cross-Dehydrogenative Couplings of Hydrosilanes with Amines. *ChemCatChem* **2016**, *8* (7), 1373-1378.
32. Hill, M. S.; Liptrot, D. J.; MacDougall, D. J.; Mahon, M. F.; Robinson, T. P., Hetero-dehydrocoupling of silanes and amines by heavier alkaline earth catalysis. *Chem. Sci.* **2013**, *4* (11), 4212-4222.
33. Cibuzar, M. P.; Waterman, R., Si-N Heterodehydrocoupling with a Lanthanide Compound. *Organometallics* **2018**, *37* (23), 4395-4401.
34. Wang, J. X.; Dash, A. K.; Berthet, J. C.; Ephritikhine, M.; Eisen, M. S., Dehydrocoupling reactions of amines with silanes catalyzed by  $[(\text{Et}_2\text{N})_3\text{U}][\text{BPh}_4]$ . *J. Organomet. Chem.* **2000**, *610* (1), 49-57.
35. Xie, W.; Hu, H.; Cui, C.,  $[(\text{NHC})\text{Yb}(\text{N}(\text{SiMe}_3)_2)_2]$ -Catalyzed Cross-Dehydrogenative Coupling of Silanes with Amines. *Angew. Chem. Int. Ed.* **2012**, *51* (44), 11141-11144.
36. Pindwal, A.; Ellern, A.; Sadow, A. D., Homoleptic Divalent Dialkyl Lanthanide-Catalyzed Cross-Dehydrocoupling of Silanes and Amines. *Organometallics* **2016**, *35* (11), 1674-1683.
37. Harinath, A.; Karmakar, H.; Kisan, D. A.; Nayek, H. P.; Panda, T. K., NHC-Zn alkyl catalyzed cross-dehydrocoupling of amines and silanes. *Organic & Biomolecular Chemistry* **2023**, *21* (20), 4237-4244.
38. Takaki, K.; Kamata, T.; Miura, Y.; Shishido, T.; Takehira, K., Dehydrogenative Silylation of Amines and Hydrosilylation of Imines Catalyzed by Ytterbium-Imine Complexes. *J. Org. Chem.* **1999**, *64* (11), 3891-3895.
39. Xu, M.; Kooij, B.; Wang, T.; Lin, J. H.; Qu, Z.-W.; Grimme, S.; Stephan, D. W., Facile Synthesis of Cyanide and Isocyanides from CO. *Angew. Chem. Int. Ed.* **2021**, *60* (31), 16965-16969.
40. Bellini, C.; Dorcet, V.; Carpentier, J.-F.; Tobisch, S.; Sarazin, Y., Alkaline-Earth-Catalysed Cross-Dehydrocoupling of Amines and Hydrosilanes: Reactivity Trends, Scope and Mechanism. *Chem. Eur. J.* **2016**, *22* (13), 4564-4583.
41. Rina, Y. A.; Schmidt, J. A. R., Heterodehydrocoupling of Silanes and Amines Catalyzed by a Simple Lanthanum-Based Complex. *Organometallics* **2022**, *41* (21), 2974-2984.
42. Mehta, M.; Goicoechea, J. M., Nitrenium Salts in Lewis Acid Catalysis. *Angew. Chem. Int. Ed.* **2020**, *59* (7), 2715-2719.
43. Barnett, N. D. R.; Clegg, W.; Horsburgh, L.; Lindsay, D. M.; Liu, Q.-Y.; Mackenzie, F. M.; Mulvey, R. E.; Williard, P. G., Novel octameric structure of the lithium primary amide  $[\{\text{ButN}(\text{H})\text{Li}\}_8]$  and its implication for the directed synthesis of heterometallic imide cages. *Chem. Commun.* **1996**, (20), 2321-2322.
44. Reich, H. J., Role of Organolithium Aggregates and Mixed Aggregates in Organolithium Mechanisms. *Chem. Rev.* **2013**, *113* (9), 7130-7178.
45. Mallick, S.; Xu, P.; Würthwein, E.-U.; Studer, A., Silyldefluorination of Fluoroarenes by Concerted Nucleophilic Aromatic Substitution. *Angew. Chem. Int. Ed.* **2019**, *58* (1), 283-287.
46. Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E.,  $\sigma$ -Bond metathesis for carbon-hydrogen bonds of hydrocarbons and Sc-R (R = H, alkyl, aryl) bonds of permethylscandocene derivatives. Evidence for noninvolvement of the  $\pi$  system in electrophilic activation of aromatic and vinylic C-H bonds. *J. Am. Chem. Soc.* **1987**, *109* (1), 203-219.
47. Waterman, R.,  $\sigma$ -Bond Metathesis: A 30-Year Retrospective. *Organometallics* **2013**, *32* (24), 7249-7263.
48. Aitken, C.; Harrod, J. F.; Gill, U. S., Structural studies of oligosilanes produced by catalytic dehydrogenative coupling of primary organosilanes. *Can. J. Chem.* **1987**, *65* (8), 1804-1809.
49. Watson, P. L.; Parshall, G. W., Organolanthanides in catalysis. *Acc. Chem. Res.* **1985**, *18* (2), 51-56.
50. SEYFERTH, D.; WISEMAN, G. H., High-Yield Synthesis of  $\text{Si}_3\text{N}_4/\text{SiC}$  Ceramic Materials by Pyrolysis of a Novel Polyorganosilazane. *J. Am. Ceram. Soc.* **1984**, *67* (7), C-132-C-133.