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Si−N Heterodehydrocoupling with a Lanthanide Compound

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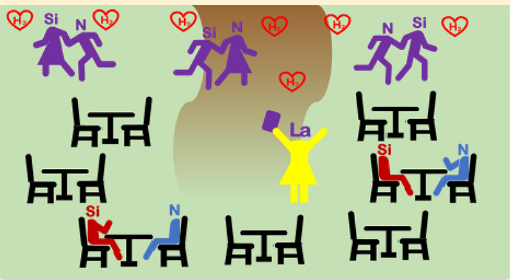
Supporting Information

ABSTRACT: [La{N(SiMe$_3$)$_2$}$_3$THF$_2$] (**1**) is an effective precatalyst for the heterodehydrocoupling of silanes and amines. Coupling of primary and secondary amines with aryl silanes was achieved with a loading of 0.8 mol % of [La{N(SiMe$_3$)$_2$}$_3$THF$_2$]. With primary amines, generation of tertiary and sometimes quaternary silamines was facile, often requiring only a few hours to reach completion, including new silamines Ph$_3$Si(^{n}PrNH) and Ph$_3$Si(^{i}PrNH). Secondary amines were also available for heterodehydrocoupling, though they generally required longer reaction times and, in some instances, higher reaction temperatures. This work expands upon the utility of *f*-block complexes in heterodehydrocoupling catalysis.



INTRODUCTION

Catalysis is a critical step in sustainable processes, but the relative abundance of the catalyst is a key factor in its overall utility.[1] A common approach for reducing the demand for precious metals in catalysis is to replace them with base metals. This methodology has met with some success, but significant challenges, including achieving comparable turnover metrics with similar catalyst loadings, remain. In fewer cases, rare earth metals have been used instead of base metals. Despite being labeled as rare earth elements, some lanthanides, lanthanum, cerium, and neodymium, for example, are more abundant in the earth's crust than some base metals such as cobalt.[2,3] Unsurprisingly, exploration of lanthanide-based catalysis has been an exciting area of growth.[4]

Organolanthanides have been shown to be viable catalysts for a variety of transformations with some critical advances in alkene polymerization,[5−10] but main group relevant transformations including dehydrocoupling[11] and heterofunctionalization[12−16] have been reported, as well. In 1999, Takaki and co-workers first demonstrated heterodehydrocoupling of silanes with amines using [Yb(η^2-Ph$_2$CNAr)(hmpa)$_n$] (Ar = 2, 6-diisopropylphenyl, hmpa = hexamethylphosphoramide), focusing on quaternary silamines from tertiary silanes.[17] In 2012, Cui and co-workers demonstrated that a different ytterbium catalyst, [IMesYb{N(SiMe$_3$)$_2$}$_2$] (IMes = 1,3-dimesitylimidazol-2-ylidene), could successfully heterodehydrocouple primary and secondary silanes with amines.[18] Sadow has expanded upon Si−N coupling with lanthanides, reporting that [Ln{C(SiHMe$_2$)$_3$}$_2$Im*t*Bu] (Ln = Yb, Sm; Im*t*Bu = 1,3-di-*tert*-butylimidazol-2-ylidene) are also active catalysts for this transformation.[19] To date, however, there are no reports of more abundant lanthanides catalyzing the heterodehydrocoupling of silanes and amines.

Silamines are utilized as mild, sterically hindered bases,[20] protecting groups for silanes[21−23] and amines,[24,25] and silylating reagents.[26−29] Polysilazanes are precursors for silicon-nitride-based ceramics.[30,31] Silamines are also important ligands in coordination chemistry.[32,33] Heterodehydrocoupling is an attractive avenue for silamine preparation versus salt metathesis because the H$_2$ byproduct is easily separated and simplifies workup. However, selectivity in dehydrocoupling is also challenging as an excess of amine is required. Recently, improved selectivity has been achieved with dehydrocoupling catalysts, though it remains challenging without designer ligands.[34,35] Overall, dehydrocoupling is a potentially more atom economic process for the generation of silamines, which argues for its continued study.

The primary aim of this work was an investigation of a more earth-abundant, simple lanthanum compound for this transformation. Due in part to commercial availability, the lanthanum(III) derivative, [La{N(SiMe$_3$)$_2$}$_3$], became the focus of this study, which has shown excellent activity in different main group bond-forming transformations.[14,36]

RESULTS AND DISCUSSION

Treatment of lanthanum trichloride with 3 equiv of lithium bis(trimethylsilyl)amide in THF for 6 h at ambient temperature affords the five-coordinate compound, [La{N(SiMe$_3$)$_2$}$_3$THF$_2$] (**1**; eq 1), as a colorless powder upon sublimation. Alternatively, **1** can be prepared by dissolving commercially available La{N(SiMe$_3$)$_2$}$_3$ in THF followed by removal of solvent under reduced pressure. The THF-solvated species has increased solubility in a variety of organic solvents,

$$\mathrm{LaCl_3 + 3\ Li{-}N(SiMe_3)_2} \xrightarrow[\substack{-\ 3\ \mathrm{LiCl}\\ 25\ ^\circ\mathrm{C}}]{\mathrm{THF}} \underset{\mathbf{1}}{\mathrm{La[N(SiMe_3)_2]_3THF_2}} \qquad (1)$$

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including benzene-d_6 and thus was the preferred complex for this study.

Compound **1** was tested as a Si−N heterodehydrocoupling catalyst. Treatment of a 3:1 mixture of *n*-propylamine and phenylsilane with 5 mol % of **1** at 25 °C resulted in immediate effervescence of H_2. In fewer than 10 min, $PhSi(^nPrNH)_3$ was produced, but additional ill-defined byproducts were also present. Reducing the catalyst loading to 0.8 mol % and increasing the amine/silane ratio to 4:1 increased the conversion to the desired product to 85% with only a slight increase in reaction time (Table 1). Further increasing the amine/silane ratio had no significant impact on yield.

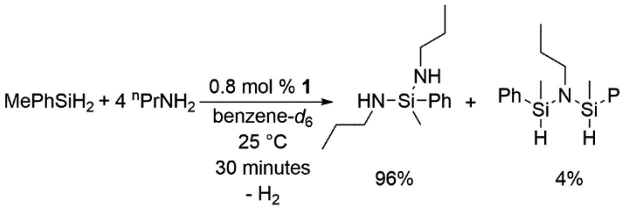
Table 1. Coupling of Silanes with *n*-Propylamine Catalyzed by $[La\{N(SiMe_3)_2\}_3THF_2]$ (1)[a]

entry	silane	equiv[b]	product	conversion
1[c]	$PhSiH_3$	3	$PhSi(^nPrNH)_3$	40−50
2	$PhSiH_3$	4	$PhSi(^nPrNH)_3$	85
3	$MePhSiH_2$	4	$MePhSi(^nPrNH)_2$	96
4	Ph_2SiH_2	4	$Ph_2Si(^nPrNH)_2$	100
5[d]	Ph_3SiH	2	$Ph_3Si(^nPrNH)$	100

[a] Conditions: 0.8 mol % of **1** at 25 °C in benzene-d_6 solution. Products were characterized by ^1H, ^{29}Si, and ^1H−^{29}Si HSQC NMR spectroscopy. Conversion determined by integration of ^1H NMR spectra. [b] Equivalents of amine per equivalent of silane. [c] 5 mol % of **1**. [d] t = 60 °C.

Secondary silanes were also effective substrates. Reaction of a 4:1 mixture of *n*-propylamine and methylphenylsilane with 0.8 mol % of **1** provided the quaternary silane, $MePhSi(^nPrNH)_2$, in 96% conversion, as measured by ^1H NMR spectroscopy (Scheme 1). Trace amounts of a byproduct were observed in the ^1H and ^1H−^{29}Si HSQC NMR spectra at δ 5.19 and δ −12.6, respectively. Although we cannot provide definitive data, this product is most consistent with $^nPrN(MePhSiH)_2$ based on Sadow's reported preparation of $^iPrN(MePhSiH)_2$ by magnesium-catalyzed reaction of 2 equiv of methylphenylsilane with isopropylamine.[34] Increasing the amine/silane ratio continued to provide the quaternary silane with the same byproduct. However, treatment of a 4:1 solution of *n*-propylamine and diphenylsilane with 0.8 mol % of **1** produced the expected product, $Ph_2Si(^nPrNH)_2$, quantitatively, according to NMR spectroscopy.

Scheme 1. Dehydrocoupling of Methylphenylsilane and *n*-Propylamine by 1 (Table 1, entry 2)



$$PhSiH_3 + 4\ ^nPrNH_2 \xrightarrow[\substack{\text{benzene-}d_6 \\ 25\ °C \\ 10\ \text{minutes} \\ -H_2}]{0.8\ \text{mol}\ \%\ \mathbf{1}} PhSi(^nPrNH)_3 \quad 85\ \% \qquad (2)$$

Tertiary silanes were the most challenging substrates for this system. Reaction of 2:1 mixture of *n*-propylamine and triphenylsilane with 0.8 mol % of **1** at ambient temperature affords $Ph_3Si(^nPrNH)$ over a period of 24 h. Conducting this reaction at 60 °C, however, gave complete conversion in less than 3 h. These initial reactions prompted a broader investigation, and a family of silanes and amine substrates were screened based on their appearance in previous studies.[18,19,34,37−40]

More sterically encumbering amine substrates, isopropylamine, aniline, and *tert*-butylamine, were tested (Table 2). Similar to the *n*-propylamine reactions, optimal conversions with isopropylamine required an increased amine/silane ratio. Reactions with aniline and *tert*-butylamine with phenylsilane required a slight excess of amine to achieve quantitative conversions. For secondary silanes, reaction at 60 °C provided optimal product formation in less than 2 h. In reactions with aniline, clean formation of the tertiary and quaternary silane products was possible from secondary silane substrates, depending only on reaction times.

Due to the steric pressure around silicon, quaternary silamines have been challenging to make by dehydrocoupling. A 2:1 mixture of isopropylamine with triphenylsilane in the presence of 0.8 mol % of **1** at 60 °C gives $Ph_3Si(^iPrNH)$ quantitatively in 1.5 h (Table 2, entry 4). Under the same conditions, the analogous reaction with *n*-propylamine and triphenylsilane gave $Ph_3Si(^nPrNH)$ quantitatively in 2.75 h (Table 1, entry 4; eq 3). To the best of our knowledge, this is the first time $Ph_3Si(^nPrNH)$ and $Ph_3Si(^iPrNH)$ have been synthesized by any method. Both aniline and *tert*-butylamine reacted with triphenylsilane but required forcing conditions. Increased catalyst loading (4 mol % of **1**), temperature (90 °C), and reaction times (36−48 h) were needed for even minimal conversions. Although NMR spectra demonstrated consumption of silane in all cases, low conversions thwarted product identification. Ultimately, coupling with triphenylsilane was largely dependent on the identity of the amine.

$$Ph_3SiH + 2\ ^xPrNH_2 \xrightarrow[\substack{\text{benzene-}d_6 \\ 60\ °C \\ -H_2}]{0.8\ \text{mol}\ \%\ \mathbf{1}} Ph_3Si(^xPrNH) \quad 100\ \% \qquad (3)$$

^{n}Pr, t = 2.75 hours; ^{i}Pr, t = 1.5 hours

Generation of a quaternary silamine from a primary or secondary silane is also possible. By slightly increasing the amine/silane ratio to 4:1 and heating the reaction to 90 °C, reaction of aniline and phenylsilane in the presence of 0.8 mol % of **1** provides quantitative conversion to $PhSi(PhNH)_3$ (Table 2, entry 6). Due to the increased steric pressure of aniline over isopropylamine, the reactions with secondary silanes take considerably longer. $MePhSi(PhNH)_2$ and $PhSi(PhNH)_3$ have been synthesized before but not by heterodehydrocoupling.[41,42]

Reactivity with secondary amines was also largely dependent on the identity of the amine. Diethylamine was readily coupled with primary and secondary silanes (Table 3). Use of a bulkier amine, bis(trimethylsilyl)amine, required up to 24 h reaction time for complete conversion under the conditions tested (Table 3). Coupling of tertiary silanes with secondary amines was not achieved under conditions screened. In reactions between secondary silanes and bis(trimethylsilyl)amine, even

Table 2. Coupling of Silanes with More Sterically Encumbered Amines by **1**[a]

entry	silane	amine	equiv[b]	temp (°C)	product	conversion[c]	time (h)
1	$PhSiH_3$	$^iPrNH_2$	6	25	$PhSi(^iPrNH)_3$	90[d]	0.5
2	$MePhSiH_2$	$^iPrNH_2$	4	25	$MePhSi(^iPrNH)_2$	100	0.5
3	Ph_2SiH_2	$^iPrNH_2$	4	25	$Ph_2Si(^iPrNH)_2$	100	0.5
4	Ph_3SiH	$^iPrNH_2$	2	60	$Ph_3Si(^iPrNH)$	100	1.5
5	$PhSiH_3$	$PhNH_2$	3.1	25	$Ph(PhNH)_2SiH$	100	0.5
6	$PhSiH_3$	$PhNH_2$	4	90	$PhSi(PhNH)_3$	100	24
7	$MePhSiH_2$	$PhNH_2$	2.1	60	$MePh(PhNH)SiH$	100	3
8	$MePhSiH_2$	$PhNH_2$	2.1	60	$MePhSi(PhNH)_2$	76	36
9	Ph_2SiH_2	$PhNH_2$	2.1	60	$Ph_2(PhNH)SiH$	100	1.5
10	Ph_2SiH_2	$PhNH_2$	2.1	60	$Ph_2Si(PhNH)_2$	100	72
11	$PhSiH_3$	$^tBuNH_2$	3.1	25	$Ph(^tBuNH)_2SiH$	100	1.5
12	$MePhSiH_2$	$^tBuNH_2$	2.1	60	$MePh(^tBuNH)SiH$	100	3
13	Ph_2SiH_2	$^tBuNH_2$	2.1	60	$Ph_2(^tBuNH)SiH$	100	1.5

[a] Conditions: 0.8 mol % of **1** at *T* °C in benzene-d_6 solution. Products were characterized by ^1H, ^{29}Si, and $^1H-^{29}Si$ HSQC NMR spectroscopy. [b] Equivalents of amine per equivalent of silane. [c] For conversions less than 100%, reactions were not complete (i.e., no byproducts observed). [d] Mixture of several silamines.

Table 3. Coupling of Silanes and Secondary Amines by **1**[a]

entry	silane	amine	equiv[b]	temp (°C)	product	conversion	time (h)
1	$PhSiH_3$	Et_2NH	3.1	60	$Ph(Et_2N)SiH_2$	97	0.5
2	$PhSiH_3$	Et_2NH	3.1	60	$Ph(Et_2N)_2SiH$	97	24
3	$MePhSiH_2$	Et_2NH	2.1	90	$MePh(Et_2N)SiH$	100	1.5
4	Ph_2SiH_2	Et_2NH	2.1	90	$Ph_2(Et_2N)SiH$	100	1.5
5[c]	Ph_3SiH	Et_2NH	1.1	90	none	0	72
6	$PhSiH_3$	$HN(SiMe_3)_2$	3.1	90	$Ph\{N(SiMe_3)_2\}SiH_2$	100	24
7[c]	$MePhSiH_2$	$HN(SiMe_3)_2$	2.1	90	none	0	24
8[c]	Ph_2SiH_2	$HN(SiMe_3)_2$	2.1	90	none	0	24
9[c]	Ph_3SiH	$HN(SiMe_3)_2$	1.1	90	none	0	24

[a] Conditions: 0.8 mol % of **1** at *T* °C in benzene-d_6 solution. Products were characterized by ^1H, ^{29}Si, and $^1H-^{29}Si$ HSQC NMR spectroscopy. Conversion was determined by integration of ^1H NMR spectra. [b] Equivalents of amine per equivalent of silane. [c] 4 mol % of **1**.

after extended reaction times (24 h or longer), increased catalyst loading (4%), and higher temperatures (90 °C), no consumption of starting materials was observed. Based on these trends, the decrease of reactivity with bis(trimethylsilyl)-amine is likely a result of increased steric crowding at nitrogen or decreased basicity/nucleophilicity compared to diethylamine.

Competitive dehydrocoupling of the bis(trimethylsilyl)-amide ligands on **1** and less sterically hindered amines was not observed except for the reaction of diethylamine and phenylsilane. In this reaction, approximately 2% conversion to $Ph\{N(SiMe_3)_2\}SiH_2$ was observed.[18] Neither $MePh\{N(SiMe_3)_2\}SiH$ nor $Ph_2\{N(SiMe_3)_2\}SiH$ were observed in the reaction between methylphenylsilane or diphenylsilane with diethylamine, respectively.[43] In addition, there are no cases in which bis(trimethylsilyl)amine was coupled with silamine products.

It is likely that the mechanism of dehydrocoupling with **1** is similar to that which Sadow and co-workers proposed for $[To^MMgMe]$ (To^M = tris(4,4-dimethyl-2-oxazolinyl)-phenylborate).[34] The observation of bis(trimethylsilyl)amine in all reactions by NMR spectroscopy suggests in situ amide exchange at **1** that affords the presumed active catalyst, $N(SiMe_3)_{3-x}(RNH)_xLa(THF)_z$ (z = 0−2). It is also possible that one or both THF molecules may dissociate in this step. It is difficult to differentiate bound versus free THF in this system by ^1H NMR spectroscopy. Then Si−N bond formation, by either amine attack at silicon or σ-bond metathesis, ensues to generate a hydride intermediate. A Ln−H bond would be primed to react with another equivalent of the amine to regenerate the catalyst. The difference between reactions of methylphenyl and diphenylsilane provides some insight into the mechanism of the Si−N bond-forming step. Despite being more sterically crowded, the reaction time to completion for more electrophilic diphenylsilane with aniline and *tert*-butylamine was shorter than that with methylphenylsilane (NB: This reaction time is, at best, merely a proxy for relative rate; Table 2, entries 7, 9, 13, and 14). As such, these observations give a preliminary indication that nucleophilic amide attack on silicon followed by rapid *β*-hydride transfer to lanthanum may be more likely than σ-bond metathesis.

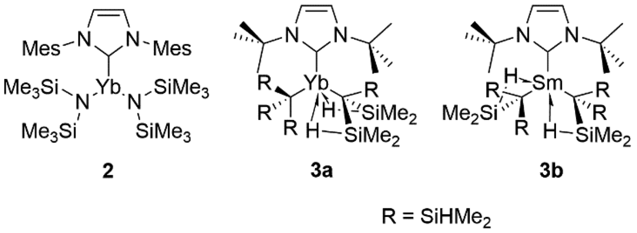
To better compare the activity of **1** to that of the other lanthanide catalysts, turnover number (TON) and turnover frequency (TOF) were calculated. Turnover frequency was calculated using total reaction time. We acknowledge that total reaction time, rather than initial rate, significantly underestimates the activity, but these data are available, providing a benchmark to compare catalysts.[44] A second feature to consider in the dehydrocoupling of silanes with amines is selectivity. As a result, two different TOFs were calculated. The first is the traditional calculation:

$$\mathrm{TOF} = \frac{\text{mols product}}{(\text{mols catalyst}) \times (\text{reaction time})} \tag{4}$$

This calculation describes the turnover frequency of the reaction as it relates to selectivity for a given product. In this calculation, moles of product are defined as only the primary reaction product. A second turnover frequency, TOF^{SiN}, was calculated to approximate the total Si−N coupling events for each catalyst, which approximates overall activity. This is calculated by

$$TOF^{SiN} = \frac{(\text{mols product}) \times (\text{Si−N bonds formed})}{(\text{mols catalyst}) \times (\text{reaction time}} \quad (5)$$

The TOF^{SiN} value speaks to the Si−N coupling potential of each reaction. Naturally, this term somewhat underappreciates the ability of these catalysts to selectively make certain silamines, which is a general goal of this catalysis. It is critical to note that these terms are highly related, essentially rephrasing the same activity values, but these do allow for a comparison between activity and selectivity. With these two terms, however, some general comparative statements can be made about lanthanide-based amine−silane heterodehydrocoupling catalysts (Figure 1).



2 **3a** **3b**

R = $SiHMe_2$

Figure 1. Lanthanide-based Si−N heterodehydrocoupling catalysts.

Compound **1** and the reported lanthanide-based catalysts, Cui's [IMesYb{N($SiMe_3$)$_2$}$_2$] catalyst (**2**)[18] and Sadow's [Ln{C($SiHMe_2$)$_3$}$_2$Im*t*Bu] (Ln = Yb (**3a**), Sm (**3b**)) catalysts,[19] demonstrate excellent reactivity in the coupling of silanes with isopropylamine (Table 4). For the generation of $PhSi(^iPrNH)_3$, it is evident that **1** is the most active catalyst, nearly doubling the TOF and TOF^{SiN} as compared to the next most active catalyst. Compared to **3a** and **3b**, **2** is more active for coupling secondary silanes with amines. In the reaction between diphenylsilane and isopropylamine, the monoaddition product, $Ph_2(^iPrNH)SiH$, is generated by **2**, **3a**, and **3b** with TOFs of 20, <1, and <1, respectively. The double-addition product, $Ph_2Si(^iPrNH)_2$, is generated by **1** with a TOF of 250, an order of magnitude greater than that of **2**. Though high TOF is desirable, selectivity is also of high utility. When the ratio of amine to silane approaches unity, selectivity decreases for **1** (vide supra). The TOFs may be lower for **2**, **3a**, and **3b**, but they are more selective and therefore continue to have utility in a variety of applications.

Table 4. TON and TOFs of Lanthanum-Based Si−N Heterodehydrocoupling Catalysts with $^iPrNH_2$

entry	silane	catalyst	product	TON	TOF[a]	TOF^{SiN} [a]
1	$PhSiH_3$	**1**[b]	$PhSiR_3$	337.5	225	675
2	$PhSiH_3$	**2**[c]	$PhSiR_3$	59.4	3.3	10
3	$PhSiH_3$	**3a**[c]	$PhSiR_3$	37.8	126	378
4	Ph_2SiH_2	**1**[b]	Ph_2SiR_2	250	250	500
5	Ph_2SiH_2	**2**[c]	Ph_2RSiH	20	20	20
6	Ph_2SiH_2	**3a**[c]	Ph_2RSiH	8.7	<1	<1
7	Ph_2SiH_2	**3b**[c]	Ph_2RSiH	8.8	<1	<1

[a] Per hour, **2**,[18] **3a**,**b**.[19] [b] Catalyst loading = 0.8 mol %. [c] Catalyst loading = 5 mol %.

Similar trends exist with more sterically encumbered primary and secondary amines (Table 5). In bulkier systems, reactions catalyzed by **2** are complete in approximately the same amount of time as that for **1**. Again, the reason for the large differences in TOF and TOF^{SiN} is catalyst loading. Cui and co-workers catalyze reactions with 5 mol % of **2**, whereas **1** can be utilized with loadings less than 1 mol %. The result is approximately a 5-fold increase in TOF and TOF^{SiN} for **1** versus **2**. Analyzing TOF and TOF^{SiN} becomes further convoluted when reaction conditions change. Appropriate TOF and TOF^{SiN} comparisons for reactions of diethylamine with phenylsilane or diphenylsilane are difficult because the reaction temperatures are different for all catalysts. Overall, **1** has generally high TOF and TOF^{SiN} with mild reaction conditions.

There are several possible explanations why **1** is an active catalyst. Many d^0 metal complexes have demonstrated the capacity to be Si−N heterodehydrocoupling catalysts.[34,45−52] The decreased electronegativity of these catalysts is likely an important contributor in their reactivity. This trend is similar in the *f*-block, where La and Yb are among the least electronegative elements. One potential difference among these compounds are the carbene ligands common to compounds **2** and **3**, whereas **1** lacks such strongly electron-donating ligands. The relative donation to the metal could be an important factor in either N−H bond activation or N−Si bond formation. Similarly, the oxidation state of these catalysts likely has a large effect on reactivity. Compounds **2** and **3** are in the +2 oxidation state, whereas **1** is in its +3 oxidation state. Similar to having more donating ligands, a decreased oxidation state may slow N−H activation to regenerate the active catalyst. An alternative rationale for increased activity of **1** could be the potential difference in the number of active sites. Up to three bis(trimethylsilyl)amido ligands could be labilized at **1**. Presuming the ancillary ligand of **2** and **3** does not dissociate, there would only be up to two actives sites. Further investigation of these differences may yield design features for future catalysts.

In summary, **1**, which is easily obtained in a one-step synthesis or by addition of THF to commercial [La{N($SiMe_3$)$_2$}$_3$], is perhaps the most active lanthanide-based precatalyst for the heterodehydrocoupling of amines and silanes. With catalyst loadings below 1 mol %, dehydrocoupling was efficient in most cases. Coupling silanes with propylamines occurred on the minute time scale, though sometimes yield was lowered due to generation of poorly identified products. Generating quaternary silamines from triphenylsilane with propylamines was also achieved for the first time. Reactivity with bulkier amines was also facile, making tertiary silamines readily. In some cases, even new silamines were generated. Lastly, less sterically bulky secondary amines were readily transformed into silamines in the presence of **1** and primary and secondary silanes.

■ EXPERIMENTAL SECTION

General Information. All manipulations were performed under a nitrogen atmosphere with dry, oxygen-free solvents using an M. Braun glovebox or standard Schlenk techniques. Benzene-d_6 was purchased from Cambridge Isotope Laboratory and then degassed and dried over NaK alloy. Tetrahydrofuran was dried over sodium and vacuum transferred. NMR spectra were recorded with a Bruker AXR 500 MHz or Varian 500 MHz spectrometer. Reported ^1H NMR resonances are

Table 5. Coupling of Amines with $PhSiH_3$ and Ph_2SiH_2

entry	catalyst	loading (mol %)	amine	product	TON	TOF[a]	TOF^{SiN} [a]
1	**1**	0.8	$^tBuNH_2$	$Ph(^tBuNH)_2SiH$	250	83	167
2	**2**	5	$^tBuNH_2$	$Ph(^tBuNH)_2SiH$	40	20	40
3	**3a**	5	$^tBuNH_2$	$Ph(^tBuNH)_2SiH$	36.8	1.2	2
4[b]	**1**	0.8	$^tBuNH_2$	$Ph_2(^tBuNH)SiH$	125	83	83
5	**2**	5	$^tBuNH_2$	$Ph_2(^tBuNH)SiH$	20	20	20
6	**3a**	10	$^tBuNH_2$	$Ph_2(^tBuNH)SiH$	8.7	<1	<1
7[b]	**1**	0.8	Et_2NH	$Ph(Et_2N)SiH_2$	121	242	243
8	**2**	5	Et_2NH	$Ph(Et_2N)_2SiH$	40	20	40
9	**3a**	5	Et_2NH	$Ph(Et_2N)_2SiH$	32.8	1	2
10	**3b**	5	Et_2NH	$Ph(Et_2N)_2SiH$	32.4	1	2
11[c]	**1**	0.8	Et_2NH	$Ph_2(Et_2N)SiH$	125	83	83
12	**2**	5	Et_2NH	$Ph_2(Et_2N)SiH$	20	20	20
13	**3a**	5	Et_2NH	$Ph_2(Et_2N)SiH$	8.2	<1	<1

[a] Per hour, **2**,[18] **3a**,**b**.[19] [b] Reaction performed at 60 °C. [c] Reaction performed at 90 °C.

referenced to the residual solvent resonance (benzene-d_6 = δ 7.16). ESI-mass spectra were collected on an AB-Sciex 4000 QTrap Hybrid triple quadrupole/linear ion trap mass spectrometer. IR data were collected on a Bruker Alpha FTIR spectrometer as neat samples. Phenylsilane (Oakwood Chemicals), methylphenylsilane (Sigma-Aldrich), diphenylsilane (Acros Organics), and triphenylsilane (Gelest) were used as received. *N*-Propylamine (Sigma-Aldrich), isopropylamine (Alfa Aesar), *tert*-butylamine (Alfa Aesar), aniline (Sigma-Aldrich), and diethylamine (Acros Organics) were dried by being stirred over calcium hydride followed by distillation. Bis(trimethylsilyl)amine (Acros Organics) was used as received.

[La{N(SiMe$_3$)$_2$}$_3$THF$_2$][53] *(**1**).* Over 20 min, lithium bis(trimethylsilyl)amide (4.092 g, 24.45 mmol) in 25 mL of THF was slowly added to $LaCl_3$ (2.000 g, 8.15 mmol) in 25 mL of THF. The reaction was stirred for 6 h. Solvent was removed, and the residue was extracted with hexanes. Removal of solvent and vacuum sublimation at 80−90 °C provided the product as a colorless powder in 60% yield (3.735 g, 4.89 mmol). ^1H NMR (benzene-d_6, 500 MHz): δ 3.64 (m, 8H), 1.26 (m, 8H), 0.37 (s, 54H).

Catalysis Experiments. All reactions were conducted using a J-Young type polytetrafluoroethylene-valved NMR tube in benzene-d_6 solution. Upon obtaining an initial ^1H NMR spectrum, the reaction mixture was placed in an oil bath at the listed temperature. All NMR spectra were collected at 25 °C.

General Method for Heterodehydrocoupling Reactions. In a N_2-filled drybox, appropriate amounts of an amine and silane were measured and mixed in ca. 0.5 mL of benzene-d_6. This solution was then pipetted into a vial containing **1**. The solution was quickly transferred into a J-Young-type polytetrafluoroethylene-valved NMR tube. An initial NMR spectrum was collected, and then the sample was placed in an oil bath at the listed temperature. The reaction was monitored by NMR spectroscopy until reactivity had ceased.

Preparation of Ph$_3$Si(^{n}PrNH). *n*-Propylamine (38.1 mg, 0.644 mmol) and triphenylsilane (83.9 mg, 0.322 mmol) in 0.5 mL of benzene-d_6 were added to **1** (2 mg, 2.6×10^{-3} mmol). The reaction was then heated at 60 °C. Over 2.75 h, $Ph_3Si(^nPrNH)$ was produced in 100% yield. Volatile materials were removed under reduced pressure, and the resultant colorless residue was dissolved in hexanes. The hexanes solution was filtered through a bed of Celite and concentrated until the first signs of precipitation. The hexanes solution was warmed until all solid was dissolved. The solution was then cooled to −20 °C for 24 h. The resulting colorless precipitate was isolated by decanting the hexanes solution and washing with minimal, cold hexanes. $Ph_3Si(^nPrNH)$ was isolated as a white solid in 96% yield. ^1H NMR (benzene-d_6, 500 MHz): δ 7.72 (m, 6 H), 7.22 (m, 9 H), 2.85 (q, 2 H), 1.31 (sextet, 2 H), 0.99 (br, 1 H), 0.71 (t, 3 H). ^{13}C NMR (benzene-d_6, 126 MHz): δ 136.5, 136.0, 129.8, 128.1, 44.8, 27.8, 11.4. ^{29}Si NMR (benzene-d_6, 99 MHz): δ 16.48. IR (neat, cm^{-1}): 3402, 3066, 2954, 2922, 2852, 1427, 1396, 1110, 1008, 830, 736, 698, 521, 498. MS (ESI): 318.2.

Preparation of Ph$_3$Si(^{i}PrNH). Isopropylamine (38.1 mg, 0.644 mmol) and triphenylsilane (83.9 mg, 0.322 mmol) in 0.5 mL of benzene-d_6 were added to **1** (2 mg, 2.6×10^{-3} mmol). The reaction was heated at 60 °C. Over 1.5 h, $Ph_3Si(^iPrNH)$ was observed in 100% yield. Volatiles were removed, and the residue was dissolved in hexanes. The hexanes solution was filtered through a bed of Celite and concentrated until the first signs of precipitation. The hexanes solution was warmed until all solids redissolved. The solution was then cooled to −20° for 24 h. The resulting colorless precipitate was isolated by decanting the hexanes solution and washing with minimal, cold hexanes. $Ph_3Si(^iPrNH)$ was isolated as a white solid in 93% yield. ^1H NMR (benzene-d_6, 500 MHz): δ 7.72 (m, 6H), 7.22 (m, 9H), 3.14 (m, 1H), 0.96 (d, 6H), 0.92 (br, 1H). ^{13}C NMR (benzene-d_6, 126 MHz): δ 136.8, 136.0, 129.7, 128.1, 43.9, 27.8. ^{29}Si NMR (benzene-d_6, 99 MHz): δ −17.86. IR (neat, cm^{-1}): 3387, 3065, 2955, 2924, 2863, 1427, 1379, 1165, 1111, 1017, 871, 739, 699, 523, 497. MS (ESI): 318.2.

Preparation of MePhSi(PhNH)$_2$. Dichloromethylphenylsilane (0.511g, 2.67 mmol) and aniline (1.0 g, 10.7 mmol) were stirred in 15 mL of diethyl ether for 24 h. The diethyl ether solution was filtered through a bed of Celite and concentrated until the first signs of precipitation. The hexanes solution was warmed until solids redissolved. The solution was then cooled to −20 °C for 24 h. The resulting colorless precipitate was isolated by decanting the hexanes solution and washing with minimal, cold hexanes. $MePhSi(PhNH)_2$ was isolated as colorless block crystals in 47% yield. ^1H NMR (benzene-d_6, 500 MHz): δ 7.61 (m, 2H), 7.16 (m, 3H), 7.05 (m, 4H), 6.73 (m, 2H), 6.69 (m, 4H), 3.52 (s, 2H), 0.45 (s, 3H). ^{13}C NMR (benzene-d_6, 126 MHz): δ 146.3, 136.2, 134.4, 130.5, 129.6, 128.5, 119.2, 117.4. ^{29}Si NMR (benzene-d_6, 99 MHz): δ −19.80. IR (neat, cm^{-1}): 3375, 3041, 1599,1497, 1376, 1284, 1114, 902, 751, 692, 471. MS (ESI): 305.2.

Preparation of PhSi(PhNH)$_3$. Phenylsilane (113.3 mg, 1.005 mmol) and aniline (389.9 mg, 4.19 mmol) in 0.5 mL of benzene-d_6 were added to **1** (8 mg, 1.05×10^{-2} mmol). The reaction was heated at 90 °C for 24 h. Solvent was removed, and the colorless solid was washed with pentane. $PhSi(PhNH)_3$ was collected as a colorless solid in 86% yield. ^1H NMR (benzene-d_6, 500 MHz): δ 7.78 (m, 2H), 7.13 (m, 1H), 7.08 (m, 2h), 7.02 (m, 6H), 6.74 (m, 9H), 3.84 (s, 3H). ^{13}C NMR (benzene-d_6, 126 MHz): δ 145.5, 134.9, 134.0, 130.9, 129.6, 128.6, 119.7, 117.6. ^{29}Si NMR (benzene-d_6, 99 MHz): δ −41.47. IR (neat, cm^{-1}): 3371, 3042, 1599, 1496, 1475, 1383, 1280, 1118, 905, 890, 752, 692, 490, 464. MS (ESI): 382.2.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.8b00372.

Experimental details, characterization data and reaction spectra are included (PDF)

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The authors declare no competing financial interest.

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