Group I Alkoxides and Amylates as Highly Efficient Silicon–Nitrogen Heterodehydrocoupling Precatalysts for the Synthesis of Aminosilanes

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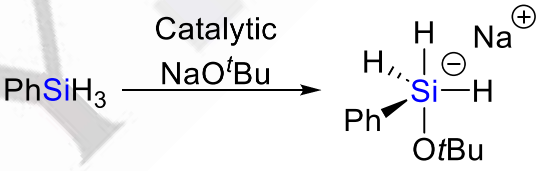
We dedicate this work, an effort solely in main group chemistry, to Evamarie Hey-Hawkins, Dietrich Gudat, Hansjörg Grützmacher, Manfred Scheer, Rainer Streubel, and Werner Uhl with deep admiration and respect, on the occasion of their respective retirements.

Abstract: Group I alkoxides are highly active precatalysts in the heterodehydrocoupling of silanes and amines to afford aminosilane products. The broadly soluble and commercially available KO^{t}Amyl was utilized as the benchmark precatalyst for this transformation. Challenging substrates such as anilines were found to readily couple primary, secondary, and tertiary silanes in high conversions (> 90%) after only 2 h at 40 °C. Traditionally challenging silanes such as Ph$_3$SiH were also easily coupled to simple primary and secondary amines under mild conditions, with reactivity that rivals many rare earth and transition-metal catalysts for this transformation. Preliminary evidence suggests the formation of hypercoordinated intermediates, but radicals were detected under catalytic conditions, indicating a mechanism that is rare for Si–N bond formation.

Introduction

Simplicity in catalyst design is emerging as a critical criteria for accessible silicon–nitrogen (i.e., Si–N) heterodehydrocoupling.[1] Although heterodehydrocoupling has advanced remarkably in the overall field of catalytic Si–N bond formation,[1][2] an overlooked and under-investigated aspect of this transformation is accessibility and applicability to synthetic chemists. For instance, while abundant metal catalysts have driven the field lately,[3] many of these compounds can be synthetically demanding and only offer limited activity. On the other hand, commercially available reagents have become increasingly popular to elicit this reactivity, which is buttressed by the high activity of these compounds.[4] Indeed, commercially available reagents may offer a fundamental opportunity to make Si–N heterodehydrocoupling more accessible to synthetic chemists, in a manner that previous systems have thus far failed to accomplish.

In particular, group I alkoxides have emerged as critical components in main group bond forming catalysis with silanes.[5] In these transformations, it has been proposed that alkoxide interacts with silane to form a hypercoordinated silicon intermediate (Scheme 1).[5b, 6] The increased hydricity of these intermediates can activate acatalytic metal chlorides and form active metal hydrides, or react with substrates directly. Arguably the most important advantage of utilizing alkoxides is the ability to access new reactivity with commercially available silanes. For Si–N, this reactivity could help enhance established nucleophilic chemistry.



Scheme 1. Formation of hypercoordinated silicon intermediates from PhSiH$_3$ and NaO^{t}Bu, as proposed by Thomas and co-workers.[5b]

An examination by Tuttle and Murphy explored the efficacy of KO^{t}Bu as a catalyst in Si–N heterodehydrocoupling (Figure 1).[4e] In their study, four amines were coupled to Et$_3$SiH in modest yields. Forcing conditions were necessary to achieve these yields, which included neat conditions, elevated temperatures, and high catalyst loadings.

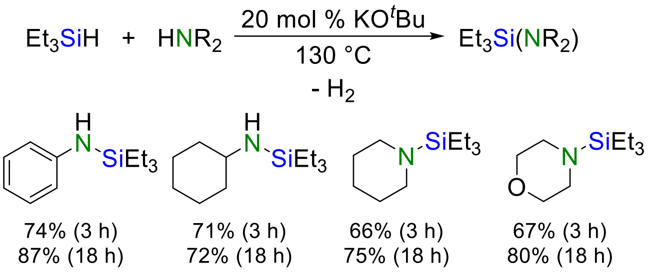


Figure 1. Scope and efficiency of KO^{t}Bu-catalyzed Si–N heterodehydrocoupling of aryl and cyclic amines with Et$_3$SiH as reported by Tuttle and Murphy.[4e]

The results of Tuttle and Murphy's study suggested that coupling silanes and amines was a challenging strategy with group I alkoxides as precatalysts. Nevertheless, these results do not necessarily discount their efficacy as activators to metal chloride compounds. We became interested in exploring iron(II) chloride precursors, given the limited scope of iron examples with this transformation.[3k, 4f] As a result, the operant hypothesis was that catalytically-active iron(II) species could be generated and employed as reactive intermediates for Si–N heterodehydrocoupling. What emerged was a protocol that elicits high conversions of aminosilanes using group I alkoxides and amylates (Figure 2).

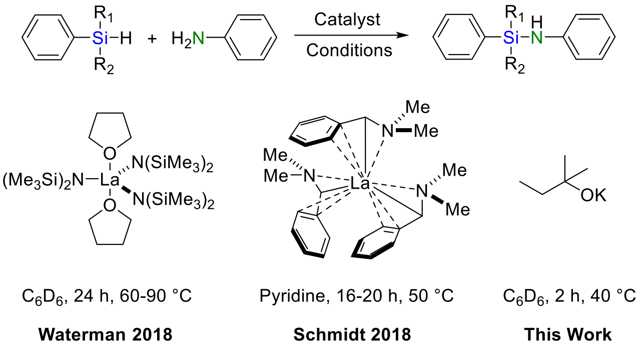
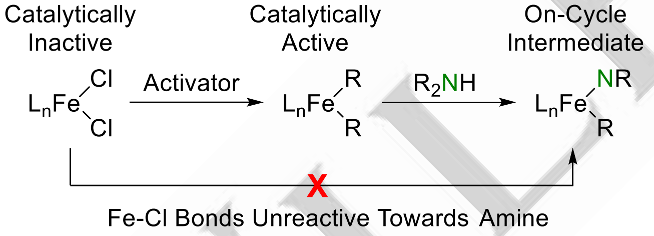


Figure 2. Catalysts and conditions for the catalytic formation of aniline-substituted aminosilanes through heterodehydrocoupling.[7]

Results and Discussion

Discovery

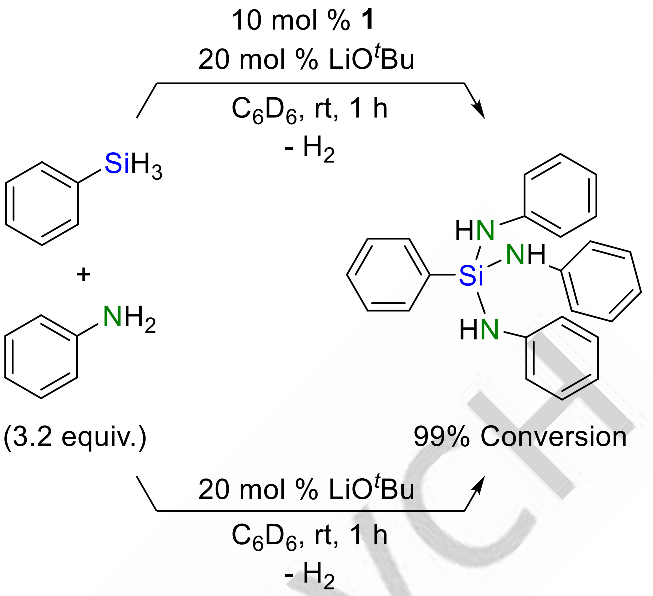
Several iron(II) compounds (i.e., L$_n$FeCl$_2$) were targeted as precursors, which were to be reacted with 2.0 equiv. of an activator to form catalytically-active intermediates (Scheme 2). Iron complex [DipN=C(Me)–(Me)C=NDip]FeCl$_2$ (**1**) was chosen as the initial starting point, given its versatile performance in main group catalysis with activators.[8]



Scheme 2. General strategy for *in situ* activation of iron(II) precursors.

The choice of activator became a critical consideration. For instance, the groups of Carpentier and Panda demonstrated that group I amides promoted Si–N heterodehydrocoupling.[4b] Similarly, organolithium reagents were found to catalyze this transformation on their own.[4i, 9] Importantly, organolithium reagents have a propensity to reduce certain iron(II) chloride compounds, which further complicates their use as activators.[10] Instead, group I alkoxides were targeted for this transformation, owing to their discovery as mild activators.[5b]

As a final consideration, simple amines such as ^{n}PrNH$_2$ are frequently utilized in probing reactions, but reactivity with ^{n}PrNH$_2$ is generally not representative of a greater set of amine substrates due to its ease of activation. Aniline (PhNH$_2$) was instead chosen because it is a challenging substrate to couple with silanes.[1]



Scheme 3. Comparison of co-catalytic L$_n$FeCl$_2$ and LiO^{t}Bu or solely LiO^{t}Bu in the reaction of PhSiH$_3$ and 3.2 equiv. of PhNH$_2$.

In the reaction between PhSiH$_3$ and 3.2 equiv. of PhNH$_2$ with 10 mol % of **1** and 20 mol % of LiO^{t}Bu, the tris(aminosilane) product PhSi(NHPh)$_3$ was produced in 99% conversion as measured by ^{1}H NMR spectroscopy (Scheme 3, *top*). However, control reactions quickly demonstrated that iron was not necessary for this reactivity, where 20 mol % of LiO^{t}Bu affords PhSi(NHPh)$_3$ in 99% conversion (Scheme 3, *bottom*). The iron is either a superfluous additive or the co-catalytic system has identical reactivity as the alkoxide. In light of the wide availability of alcohols and alkoxides, iron was abandoned. The study then focused on group I alkoxides as precatalysts for this transformation. This was doubly intriguing given the prior reports of KO^{t}Bu reactivity.[4e]

Table 1. Initial exploration of scope and efficiency of selected group I methoxide and *tert*-butoxide compounds in the reaction of PhSiH$_3$ and PhNH$_2$.[a]

Entry	Catalyst	PhSiH$_2$(NHPh) (%)[b]	PhSiH(NHPh)$_2$ (%)[b]	PhSi(NHPh)$_3$ (%)[b]
1	NaOMe	3	0	0
2[c]	LiO^{t}Bu	16	70	2
3	NaO^{t}Bu	0	4	96
4	KO^{t}Bu	0	1	99

[a]Conditions: PhSiH$_3$ (1.0 equiv.), PhNH$_2$ (3.09 equiv.), and catalyst (10.0 mol %) in 0.5 mL of benzene-*d*$_6$ for 1 h at ambient temperature in a PTFE-valved J-Young type NMR tube. [b]Aminosilane conversions were measured by ^{1}H NMR spectroscopy by integrating residual silane vs. product. [c]Incomplete conversion from PhSiH$_3$.

Initial efforts sought to optimize the reaction between PhSiH$_3$ and PhNH$_2$ by testing a small set of group I methoxide and *tert*-butoxide compounds as precatalysts. Reactions using NaOMe were the least efficient, which afforded $PhSiH_2(NHPh)$ in only 3% conversion after 1 h at ambient temperature (Table 1, Entry 1). Increased reactivity with LiO^tBu was observed, albeit to incomplete conversion from $PhSiH_3$ (Table 1, Entry 2). Heavier cations such as sodium and potassium produced higher conversions of bis- and tris(aminosilane) products (Table 1, Entry 3 and 4). These results followed the initial pattern of unprecedented reactivity with $PhNH_2$ in this reaction.

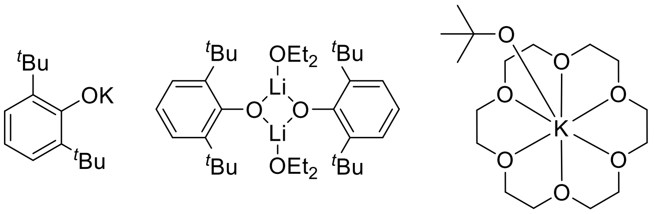


Figure 3. Several broadly soluble sources of phenoxide and *tert*-butoxide which were tested for Si–N heterodehydrocoupling.

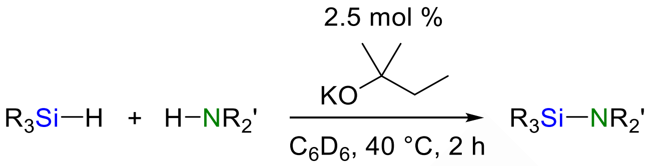
Group I alkoxides are soluble in a limited range of organic solvents. Therefore, several candidate precatalysts were explored in an effort to generalize this transformation. However, phenoxides such as $KO(2,6\text{-}^tBu\text{-}C_6H_3)$ (Figure 3, *left*) and $[Li(et_2o)(2,6\text{-}^tBu\text{-}C_6H_3O)]_2$ (Figure 3, *center*) were inactive for this transformation. The crown ether *tert*-butoxide complex [K(18-crown-6)(O^tBu)] (Figure 3, *right*) was also pursued. However, this compound was challenging to isolate and purify and ultimately could not be tested for catalysis.[11]

The commercially available KO^tAmyl proved to be a more accessible alternative to previous examples. Reactions with KO^tAmyl proceeded to higher conversions than with KO^tBu, and conditions could be tuned to significantly reduce catalyst loading without a significant loss in activity. Moreover, KO^tAmyl exhibits good solubility in a range of organic solvents. These factors determined the selection of KO^tAmyl as the benchmark precatalyst. Optimal conditions to achieve nearly complete conversion in a reaction of $PhSiH_3$ and $PhNH_2$ were 2 h at 40 °C with 2.5 mol % KO^tAmyl (*vide infra*). These were then leveraged as standard conditions for further catalytic reactions, acknowledging that some systems may be optimized further.

Scope of Catalysis

While the use of $PhNH_2$ in Si–N heterodehydrocoupling was unique and exciting, the first test for this catalyst system was to confirm this catalyst was indeed general to an appropriate range of silanes and amines for general synthetic utility. Thus, a suite of common substrates in this catalysis were tested for heterodehydrocoupling with catalytic KO^tAmyl under standard conditions as described (Table 2). The initial tests sample primary, secondary, and tertiary silanes as well as primary and secondary amines with both aromatic and aliphatic substituents.

Table 2. Scope and efficiency of KO^tAmyl as precatalyst with a set of silanes and amines to assess heterodehydrocoupling reactivity.[a]



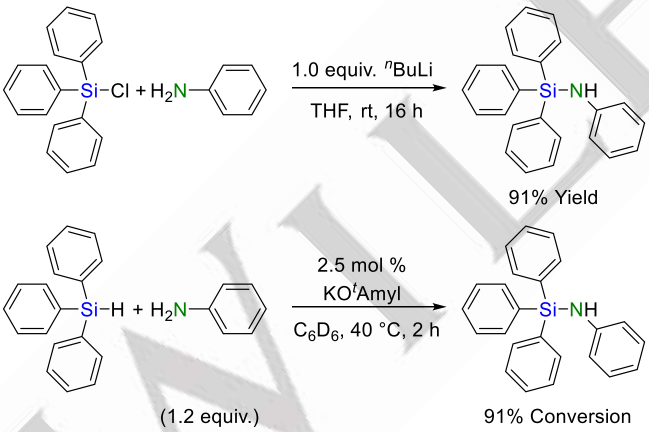
Entry	Silane	Amine	Product(s)	%[b]
1	$PhSiH_3$	$PhNH_2$	$PhSi(NHPh)_3$	97
2	$PhSiH_3$	$p\text{-F-}C_6H_4NH_2$	$PhSi(NHC_6H_4\text{-}p\text{-F})_3$	99
3	$PhSiH_3$	$p\text{-}^tBu\text{-}C_6H_4NH_2$	$PhSi(NHC_6H_4\text{-}p\text{-}^tBu)_3$	98
4	$PhMeSiH_2$	$PhNH_2$	$PhMeSi(NHPh)_2$	99
5	Ph_2SiH_2	$PhNH_2$	$Ph_2Si(NHPh)_2$	99
6	$PhMe_2SiH$	$^nPrNH_2$	$PhMe_2Si(NH^nPr)$	98
7	Ph_3SiH	$^nPrNH_2$	$Ph_3Si(NH^nPr)$	100
8	Ph_3SiH	$^iPrNH_2$	$Ph_3Si(NH^iPr)$	94
9	Ph_3SiH	$^nPeNH_2$	$Ph_3Si(NH^nPe)$	100
10	Ph_3SiH	$^nHeNH_2$	$Ph_3Si(NH^nHe)$	100
11	Ph_3SiH	$PhNH_2$	$Ph_3Si(NHPh)$	91
12	Ph_3SiH	Ph_2NH	$Ph_3Si(NPh_2)$	0
13	Ph_3SiH	Et_2NH	$Ph_3Si(NEt_2)$	92
14	Ph_3SiH	PyNH	$Ph_3Si(NPy)$	100
15	Ph_3SiH	AzNH	$Ph_3Si(NAz)$	0
16	Ph_3SiH	KeNH	$Ph_3Si(NKe)$	0
17	Et_3SiH	Ph_2NH	$Et_3Si(NPh_2)$	0

[a] Conditions: silane (1.0 equiv.), amine (1.2-3.2 equiv.), and catalyst (2.5 mol %, 0.5 M in benzene-d_6) in 0.5 mL of benzene-d_6 for 2 h at 40 °C in a PTFE-valved J-Young type NMR tube. [b] Aminosilane conversions were measured by ^1H NMR spectroscopy by integrating residual silane vs. product. PyNH = pyrrolidine; AzNH = azole, pyrrole; KeNH = ketole, indole.

Reaction of $PhSiH_3$ with 3.2 equiv. of $PhNH_2$ in the presence of 2.5 mol % of KO^tAmyl produces $PhSi(NHPh)_3$ in 97% conversion after 2 h at 40 °C (Table 2, Entry 1). Although many systems are capable of coupling $PhSiH_3$ and $PhNH_2$, fewer than a handful are capable of producing $PhSi(NHPh)_3$. Previous examples to afford $PhSi(NHPh)_3$ include $(thf)_2La[N(SiMe_3)_2]_3$ and $La(DMBA)_3$ (DMBA = *N,N*-dimethylbenzylamine).[7] Thus for $PhNH_2$, heterodehydrocoupling between $PhSiH_3$ and $PhNH_2$ with KO^tAmyl is the most efficient and cost-effective method to date, which is accomplished in low-loadings, under mild temperatures, and in short reaction times. It therefore became important to extend this catalysis to other substrates.

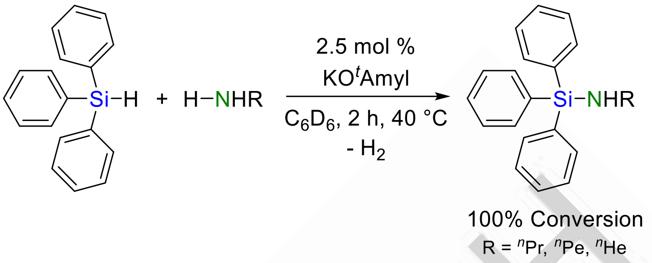
Selected *para*-substituted anilines were explored as coupling substrates to $PhSiH_3$ in the presence of KO^{t}Amyl to probe electronic effects at the amine, which are often telling of a nucleophilic-type mechanism.[1b] The reaction between $PhSiH_3$ and 3.2 equiv. of *p*-F-$C_6H_4NH_2$ affords $PhSi(NHC_6H_4$-*p*-$F)_3$ in 99% conversion (Table 2, Entry 2), which is supported by the presence of diagnostic aryl C–H resonances in the ^1H NMR spectrum and a major product resonance in $^{19}F\{^1H\}$ NMR spectrum. Reactions with *p*-^{t}Bu-$C_6H_4NH_2$ likewise produce $PhSi(NHC_6H_4$-*p*-$^tBu)_3$ in 98% conversion (Table 2, Entry 3). These electronically diverse substrates give similar conversion under standard conditions, which is inconsistent with a nucleophilic mechanism. Notably, initial exploration in the reaction between $^nOcSiH_3$ and $PhNH_2$ indicates that this catalyst may be general for primary silanes with both alkyl and aryl groups. Moreover, catalysis with KO^{t}Amyl greatly enhances the accessibility for aminosilane with substituted aniline groups, which was previously only accessible through heterodehydrocoupling with Schmidt's $La(DMBA)_3$.[7b]

Reactivity with $PhNH_2$ does not diminish with increased substitution on silane. This observation is exemplified in the reactions of $PhNH_2$ with either $PhMeSiH_2$ or Ph_2SiH_2 to afford the respective bis(aminosilane) products in 99% conversion (Table 2, Entry 4 and 5). Heterodehydrocoupling between Ph_3SiH and $PhNH_2$ was also successful, producing $Ph_3Si(NHPh)$ in 91% conversion (Table 2, Entry 11). Notably, traditional nucleophilic systems struggle to couple these two substrates.[1b] Thus far, no reported system has produced $Ph_3Si(NHPh)$ in high conversion (Scheme 4).



Scheme 4. Comparison of the stoichiometric and catalytic reactions to afford $Ph_3Si(NHPh)$.[12]

Primary and secondary alkyl amines were accessible substrates with tertiary silanes. Reaction of either $PhMe_2SiH$ or Ph_3SiH with $^nPrNH_2$ under standard conditions produces the mono(aminosilane) products $PhMe_2Si(NH^nPr)$ and $Ph_3Si(NH^nPr)$ in 98% or 100% conversion, respectively, as measured by ^1H NMR spectroscopy (Table 2, Entry 6 and 7). Changing the substitution on amine appears to have limited impact on the catalysis. For example, reaction of Ph_3SiH and $^iPrNH_2$ affords $Ph_3Si(NH^iPr)$ in 94% conversion under standard conditions (Table 2, Entry 8). Likewise, increased chain length on amine also demonstrated little effect on the catalysis (Scheme 5), where reaction of Ph_3SiH with each $^nPeNH_2$ and $^nHeNH_2$ affords $Ph_3Si(NH^nPe)$ and $Ph_3Si(NH^nHe)$, respectively, in quantitative conversion (Table 2, Entry 9 and 10).



Scheme 5. Effect of chain length in heterodehydrocoupling reactions with Ph_3SiH.

Both Et_2NH and pyrrolidine (PyNH) were rapidly coupled to Ph_3SiH, affording the corresponding aminosilanes in high or quantitative conversions (Table 2, Entry 13 and 14). The high activity of KO^{t}Amyl with Ph_3SiH encouraged us to explore aryl amines for protecting group chemistry. However, attempts to couple pyrrole (AzNH) and indole (KeNH) to Ph_3SiH were unsuccessful (Table 2, Entry 15 and 16), largely due to precipitation of solids upon addition of precatalyst.

Several substrates were inaccessible under these conditions. For instance, reactions between alkyl amines and primary or secondary silanes afforded mixtures of Si–N containing products. Reactions with either Ph_3SiH (Table 2, Entry 12) or Et_3SiH (Table 2, 17) with Ph_2NH did not successfully form aminosilane products. These results do not conform to known nucleophilic or electrophilic mechanisms.[1b]

Instead, these violations in reactivity trends could be preliminary evidence for the involvement of radicals. For instance, C–H silylation mediated by KO^{t}Bu implicated radical intermediates, where a mixture of KO^{t}Bu and Et_3SiH was shown to be EPR active.[5a] In this study, standard catalytic reactions involving KO^{t}Amyl were also found to be EPR active. Two distinct peaks are observed during catalysis, which also appear in the stoichiometric reactions between Ph_3SiH and KO^{t}Amyl. The analogous catalytic reaction with $^tBuNH_2$ reveals hyperfine splitting, which is tentatively assigned to a nitrogen-centered radical. Notably, however, attempts to trap suspected radical intermediates with TEMPO during catalysis have thus far been unsuccessful. Ongoing efforts are underway to determine the identity of these reactive intermediates.

Overall, the involvement of radical intermediates helps to explain the lack of selectivity related to coupling primary and secondary silanes with alkyl amines, as well as the high overall activity with tertiary silanes. This is exemplified is reactions between Ph_3SiH and $PhNH_2$, where classic nucleophilic systems often fail.[7] While dehydrocoupling mechanisms through radical intermediates are known,[13] to the best of our knowledge, this appears to be the first reported instance for Si–N heterodehydrocoupling.

Table 3. Scope and efficiency of simple radical initiators in the heterodehydrocoupling of Ph_3SiH and $PhNH_2$.[a]

Entry	Initiator	Conversion (%, 2 h)[b]	Conversion (%, 24 h)[b]
1	AIBN	0	0
2	ABCN	0	0
3	DMPA	0	0

[a]Conditions: Ph_3SiH (1.0 equiv.), $PhNH_2$ (1.1 equiv.), and initiator (2.5 mol %, 0.5 M in benzene-d_6) in 0.5 mL of benzene-d_6 at 40 °C in a PTFE-valved J-Young type NMR tube. [b]Conversions were measured by ^1H NMR spectroscopy by integrating residual silane vs. product. AIBN = 2,2'-azobis(2-methylpropionitrile); ABCN = 1,1'-azobis(cyclohexanecarbonitrile); DMPA = 2,2-dimethoxy-2-phenylacetophenone.

Finally, to test the generality in generating radical intermediates for this reaction, we explored simpler radical initiators as catalysts to couple Ph_3SiH and $PhNH_2$ at 40 °C in benzene-d_6 (Table 3). Every tested compound failed to produce the expected aminosilane $Ph_3Si(NHPh)$ after 2 and 24 h, which highlights the unique reactivity of group I alkoxides and amylates in this chemistry.

Conclusion

Group I alkoxides were reinvestigated as precatalysts for Si–N heterodehydrocoupling. The planned study anticipated alkoxide activators in iron catalysis, but initial results demonstrated unexpectedly high activity of these alkoxides in the absence of iron. A range of salts are active, however, the commercially available derivative, KO^{t}Amyl, gives the highest activity.

These catalysts are convenient for aniline substrates, which are very poorly represented by conventional nucleophilic catalysts.[1b] Additionally, these compounds are active for tertiary silanes, and can even couple tertiary silanes with aniline. While much of this activity is known for many compounds across the periodic table, this high activity with aniline substrates has only been reported using lanthanum compounds.[7]

Unusually high activity comes with an unusual mechanism, with respect to prior reports of Si–N heterodehydrocoupling catalysts.[1a, 1b, 1d] Despite a strong history in the literature of alkoxides reacting with organosilanes to afford meta-stable hypercoordinated compounds, a nucleophilic mechanism appears not to be the operant pathway. Observation of these reactions by EPR spectroscopy provide evidence for the generation of radicals under catalytic conditions. Conventional radical reagents fail to afford the same reactivity under these conditions, indicating this is a more complex mechanism than mere generation of radicals, which is under further investigation. This study compliments the on-going success of EPR spectroscopy to detect radical reactivity under catalytic conditions where traditional radical traps give complex or indeterminant reactivity.[14] As such, KO^{t}Amyl now competes with simple organolithium reagents as the best catalyst for routine use in Si–N coupling catalysis.[4i] Most importantly, KO^{t}Amyl and alkoxide precatalysts are some of the most readily accessible reagents for Si–N heterodehydrocoupling.

Experimental

All manipulations were conducted under a positive pressure of nitrogen (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 alumina and Q5, and subsequently stored over 3Å 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 freeze-pump-thawed thrice and stored over activated 3Å molecular sieves for at least 48 h prior to use. Celite and 3Å molecular sieves were dried between 180-200 °C under dynamic vacuum for at least 1 d.

Iron compound **1** was isolated and purified according to literature proceedings.[8a] Sodium methoxide was used as received without further purification. Group I metal *tert*-butoxides (i.e., MO^{t}Bu; M = Li, Na, K) were generally sublimed under dynamic vacuum. For catalysis, the sublimed solids were further filtered through Celite in anhydrous THF inside the glovebox to remove residual impurities, with the purified products being isolated as fluffy white solids after prolonged drying under dynamic vacuum. Potassium *tert*-amylate (KO^{t}Amyl, 25 % w/w in toluene) was isolated as a solid by removing toluene and excess alcohol under dynamic vacuum between 100-120 °C. Catalytic quality KO^{t}Amyl was filtered through Celite in anhydrous hexanes, recrystallized from minimal hexanes at -40 °C overnight, filtered, washed with minimal cold hexanes, and dried under dynamic vacuum to afford a white solid. 2,2'-azobis(2-methylpropionitrile) (AIBN) was dissolved in boiling methanol and recrystallized at -20 °C overnight. 1,1'-azobis(cyclohexanecarbonitrile) (ABCN) was dissolved in boiling ethanol and recrystallized at -20 °C overnight. 2,2-dimethoxy-2-phenylacetophenone (DMPA) was dissolved in boiling methanol and recrystallized at -20 °C; the compound is light-sensitive and thus this procedure was done in the dark (i.e., reaction glassware was wrapped in aluminium foil). Solid anilines were sublimed under dynamic vacuum, and subsequently recrystallized from anhydrous THF in the glovebox. Liquid anilines were dried over barium oxide and fractionally distilled under dynamic vacuum. Liquid amines were distilled under dynamic N_2 from calcium hydride and stored over 3Å molecular sieves. $PhSiH_3$ and $PhMeSiH_2$ were distilled under dynamic N_2 and stored over 3Å molecular sieves. Ph_2SiH_2 was distilled under dynamic vacuum and stored over 3Å molecular sieves. $PhMe_2SiH$ and Ph_2MeSiH were received, transferred to 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.

Glassware was cleaned by sequential washings of base (15 % saturated aqueaous KOH solution, 85% ^{i}PrOH), acid (10 % HNO_3, 90 % H_2O), and deionized 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-sealed J-Young NMR tubes, which were cleaned and dried by the methods mentioned above. Reactions were heated to 40 °C in silicone oil baths, which were heated by an external hot plate and the temperature measured by a thermometer.

Nuclear Magnetic Resonance (NMR) spectra were recorded at 25 °C on either a Varian 500 MHz spectrometer or a Bruker AXR 500 MHz spectrometer. Chemical shifts (δ) are reported in parts per million (ppm). ^{1}H NMR spectra were referenced to an internal standard of C_6Me_6 (δ = 2.13 ppm). Multiplicities are reported as the following: singlet (s), broad singlet (brs), doublet (d), triplet (t), quartet (q), pentet (p), doublet of doublet (dd), or multiplet (m). Coupling constants, *J*, are reported in Hertz (Hz).

Electron paramagnetic resonance (EPR) measurements were collected at ambient temperature on a Bruker EMXplus Spectrometer. Reactions were run in either quartz or borosilicate PTFE-sealed J-Young NMR tubes. Conditions for EPR acquisition are provided in Section S4.

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 was conducted by D.R.J.J. and C.E.B. 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.

Supporting Information

The authors have cited additional references within the Supporting Information.[15]

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Keywords: silanes • amines • alkoxides • amylates • heterodehydrocoupling

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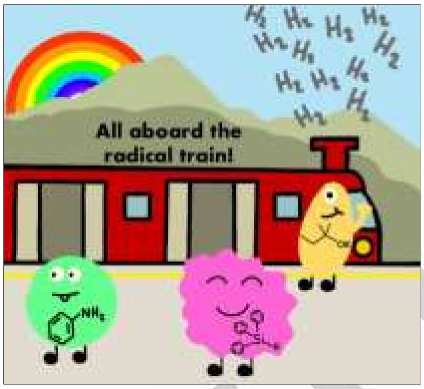

TOC Text: All aboard! Group I alkoxides and amylates efficiently catalyze the heterodehydrocoupling of challenging silane and amine substrates under mild conditions! This represents one of the most straightforward and accessible methods to form aminosilanes through heterodehydrocoupling! This train is now leaving the station – don't miss it!

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