Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Grignard Reagents as Simple Precatalysts for the Dehydrocoupling of Amines and Silanes

Claire E. Bushey,[a] Diego R. Javier-Jiménez,[a] Matthew B. Reuter,[a] and Rory Waterman[a,*]

Methyl magnesium bromide is a precatalyst for the dehydrocoupling of silanes and amines to produce aminosilane products under mild conditions. As a commercially available Grignard reagent, this precatalyst represents a simplification over previous magnesium-containing catalysts for Si–N bond formation while displaying similar activity to other magnesium-based catalysts. This observation is consistent with the hypothesis that competitive Schlenk equilibrium can be addressed by not using an ancillary ligand. While the activity of MeMgBr is lower than some reported catalysts, including other commercially available precatalysts, unique selectivity was observed for MeMgBr that may allow for directed synthesis of aminosilane products. This work continues to increase the accessibility of Si–N heterodehydrocoupling through a growing family of commercially available precatalysts that balance activity and selectivity.

Introduction

Silicon–nitrogen (i.e., Si–N) heterodehydrocoupling is a facile way to produce aminosilanes that play an important role as materials precursors for both chemical vapor deposition and ceramics.[1,2] Further application of aminosilanes and silylamines include uses as ligands, silylating agents, and protecting groups.[3-5] While many of these compound are made by stoichiometric dehydrohalogenation, heterodehydrocoupling has become an attractive route in comparison to stoichiometric processes due to the high atom economy and limited waste produced as a result of the catalytic reaction. The hydrogen gas formed in dehydrocoupling is an environmentally benign and non-toxic byproduct, which simultaneously simplifies product purification and provides a driving thermodynamic force for the desired transformation.[6] Hydrogen is a key commodity chemical, and an economy of dehydrocoupling and hydrogen collection is an attractive idea, more so than disposing of salt waste. It is important to underscore that the generation of gas in a reaction, and hydrogen gas in particular, represents particular risks. Appropriate caution and controls are needed.

In recent years, Si–N dehydrocoupling has been explored with a wide range of compounds across the periodic table.[7-13] That approach has yielded highly active precatalysts including the barium compound $Ba[CH(SiMe_3)_2]_2(THF)_3$, which has reported TOF up to 3600 h^{-1} and the platinum(II) compound $[Pt(I^tBu')(I^tBu)][BAr^F{}_4]$ (I^tBu = 1,3-di-*tert*-butylimidazolylidene; I^tBu' = cyclometalated I^tBu; $BAr^F{}_4$ = $B(3,5\text{-}CF_3)_2C_6H_3)_4^-$).[14,15] Notably, $[Pt(I^tBu')(I^tBu)][BAr^F{}_4]$ not only has part-per-million catalyst loading allowing for high TON and TOF values but also demonstrates good selectivity for the less activated aminosilane products, with conversions greater than 90%.[15] This feature, selectivity for the less activated aminosilane product, was also identified with amido calcium(II) compounds supported by Schiff base ligands, albeit with more modest activity than measured for $[Pt(I^tBu')(I^tBu)][BAr^F{}_4]$.[16]

These and related successes in identifying active precatalysts for Si–N bond formation have created new challenges for this transformation. In particular, there is now a drive to consider the selectivity of products when multiple Si–H and N–H bonds are available, which would require catalysts that are not necessarily the most active for the dehydrocoupling of these substrates.[9,10] The second challenge is the discovery of a 'second' generation of catalysts that are more accessible to researchers who may use this transformation infrequently. For those teams, catalysts that are simple, readily available, and inexpensive are ideal. We have sought to address this particular challenge through exploration of candidate precatalysts that are commercially available and routine reagents in many synthetic chemistry and materials laboratories, an effort that has yield some success with active precatalysts.[17,18] Armed with these initial hits and facing the challenge of selectivity, we continued to explore of precatalyst candidates with the same governing aims of ease of access and abundance.

Magnesium compounds are established precatalysts for this transformation, and these are known as molecular compounds with various ancillary ligands. These compounds include To^MMgMe (To^M = tris(4,4-dimethyl-2-oxazoliny)phenylborate), $IMesMg(Mes)[N(SiMe_3)_2]$, magnesocenophanes, and *ansa*-half-sandwich magnesium complexes and have been shown to be active catalysts with some selectivity in Si–N heterodehydrocoupling reactions.[19-22] For example, $IMesMg(Mes)[N(SiMe_3)_2]$ gave between 80–100% product conversion for both primary and secondary silanes with a variety of amines, though high heating was required depending

---

[a] Department of Chemistry, Discovery Hall, University of Vermont, Burlington, VT 05405, USA. E-mail: rory.waterman@uvm.edu

Supplementary Information available: Full experimental details and spectra. See DOI: 10.1039/x0xx00000x

on the substrates used.[22] Good selectivity was demonstrated both by the tendency to form the less substituted aminosilane and the rarity of mixtures of different products. Similarly, To^{M}MgMe gave high product conversion for most substrates, and the detailed mechanistic study of this catalyst greatly informs understanding of most Si–N dehydrocoupling catalysts.[21] Furthermore, selectivity for specific aminosilane products was high for this catalyst although specific adjustment of the silane to amine ratio was required.[21] Magnesocenophanes were less consistent in reactivity with variable activity and selectivity depending on both the substrates and catalyst ligands.[20] *Ansa*-half-sandwich magnesium complexes, in comparison, gave exclusively the mono(aminosilane) product with modest to high activity depending on the substrates.[19]

Recognizing the value of these contributions with magnesium compounds, we have returned to this metal with two hypotheses. First, promoting heterodehydrocoupling over other methodologies to prepare Si–N bonds in chemical and materials synthesis requires a library of accessible catalysts, and simple organomagnesium compounds (i.e., Grignards) are ideal candidates as readily available examples. Second, the Schlenk equilibrium will undercut most efforts to use traditional ligands on group 2 metals, which indicates that precatalysts with no designer ligands are likely to exhibit similar activity to those with ligands.[23,24] This issue was partially addressed by Hill and coworkers examining $Mg[N(SiMe_3)_2]_2$ as a precatalyst for this transformation, demonstrating success and providing motivation for this work.[25] In this study, we partially address both hypotheses through an investigation of MeMgBr, a representative Grignard reagent, as precatalyst for the heterodehydrocoupling of amines and silanes. While MeMgBr is modestly active for Si–N dehydrocoupling, demonstrating comparable activity to previous reports, the increased selectivity to the less substituted aminosilane products were observed with MeMgBr allowing access to products previously inaccessible through other commercially available precatalysts.[17,18]

Results and Discussion

This study focuses on methyl magnesium bromide (MeMgBr), which is widely available from commercial suppliers, typically as a THF or etherate solution. As with prior investigations of alkyl lithium and potassium alkoxide reagents,[17,18] a key consideration was identifying a commercially available compound that is routine in many synthetic laboratories. Rather than considering heavier aliphatic Grignards or aryls Grignards, MeMgBr is particularly attractive for the ease of separating the byproduct conjugate base (methane) and inorganic salts.

The reactivity of MeMgBr was initially screened in two key reactions using 5 mol % loading. The first was a 1:1 molar ratio of Ph_3SiH and $PhNH_2$ at ambient temperature in which no conversion was observed over a period of 24 h. The second was a reaction of 1.0 equiv. of $PhSiH_3$ and 3.2 equiv. of $^tBuNH_2$, also at ambient temperature. The second reaction afforded 37% of the mono(aminosilane) product after 1 h. These screening data demonstrated that $^tBuNH_2$ was viable for optimization of reactions conditions. This substrate exhibits greater steric bulk than the more common $^nPrNH_2$, making it a more challenging but a better representative substrate for a wide range of amines.

Developing reaction conditions

In the optimization reactions presented in Table 1, $PhSiH_3$ was treated with varying equivalents of $^tBuNH_2$ and 5 mol % of MeMgBr in benzene-d_6 solution. Because initial conversions were modest over convenient time periods, reactions at 40 °C were also performed. Conversion to both $PhSiH(NH^tBu)_2$ and $PhSiH_2(NH^tBu)$ was observed by ^1H NMR spectroscopy, and conversion was measured by integration of the residual $PhSiH_3$ peak vs. combined integration of the $PhSiH(NH^tBu)_2$ and $PhSiH_2(NH^tBu)$ against the internal standard. Calculation of the ratio of mono- to bis(aminosilane) products was performed by relative integration of methyl resonances for the respective products.

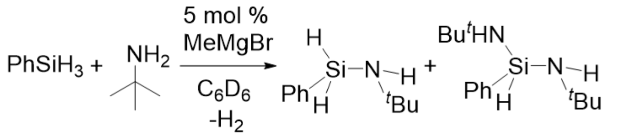


Table 1 Optimization of conditions for the reaction of $PhSiH_3$ and $^tBuNH_2$ with MeMgBr[a]

Entry	$^tBuNH_2$[b]	Products	1 h	2 h	4 h
1a	3.2	$PhSiH(NH^tBu)_2$	4	5	8
		$PhSiH_2(NH^tBu)$	96	95	92
1b[c]	3.2	$PhSiH(NH^tBu)_2$	7	21	47
		$PhSiH_2(NH^tBu)$	93	79	53
1c	6.0	$PhSiH(NH^tBu)_2$	9	12	20
		$PhSiH_2(NH^tBu)$	91	88	80
1d[c]	6.0	$PhSiH(NH^tBu)_2$	22	NA	NA
		$PhSiH_2(NH^tBu)$	78	NA	NA

[a] Measured by integration of ^1H NMR spectra in benzene-d_6 solution at ambient temperature with 5 mol % of MeMgBr. [b] Relative equivalent of amine to silane. [c] Reaction conducted at 40 °C.

After 1 h, there was nearly quantitative conversion to the mono(aminosilane) product regardless of optimization conditions. Indeed, the simplest conditions with ambient temperature and 3.2 equiv. of amine consumed just over 1.0 equiv. of Si–H bonds (entry 1a, Table 1). Due to the conversion to the mono(aminosilane) being facile, further optimization was then based on the conversion to the bis(aminosilane) product, which occurred relatively slowly. As expected, both excess amine and increased temperature provided more rapid conversion to the bis(aminosilane) product, with heating having a more significant effect on conversion. This qualitative observation is an initial indicator of a nucleophilic mechanism in which the Grignard deprotonates amine to then attack silane, consistent with Sadow's study of magnesium compounds for this transformation.[21]

The key observation from these optimization reactions is that MeMgBr can afford selectivity not seen by KO^{t}Amyl or ^{n}BuLi.[17,18] At ambient temperature (entries 1a and 1c), conversions were quite high, and large excesses of amine failed to give significant quantities of multiple Si–H bond activation products unless both excessive concentrations (6 equiv.) of amine and elevated temperatures were used (entry 1d, Table 1). This observation is interesting because the relative rate of Si–H bond activation appears to be relatively high as evidenced by high conversions at ambient temperature (entries 1a and 1c, Table 1).

The optimization process yielded standard conditions of 1:6 silane to amine ratio treated with 5 mol % of MeMgBr at ambient temperature for 1 h, used for the duration of this work. These conditions are similar to that for ^{n}BuLi, but this investigation uses a 50% lower catalyst loading of 5 mol %.[18] In comparison to other magnesium precatalysts, Sadow's work with To^{M}MgMe used different silane to amine ratios which required individual optimization based on substrate to afford selective product formation and conversion was measured after 24 h, rather after 1 h with MeMgBr.[21] *Ansa*-half-sandwich magnesium complexes used near identical reactions conditions with the exception of silane to amine ratios which were 1:1 rather than excess of amine.[19] In studies with magnesocenophanes, similar to To^{M}MgMe, conversion was measured after 24 h with heating to 60 °C.[20] In this study, heating was demonstrated to push the reaction forward, but it was hypothesized that better selectivity would be achieved for more reactive amines at lower temperature so reactions were performed at ambient temperature.

Substrate Scope

The amine substrate scope for this reaction was first explored using a variety of primary and secondary amines (Table 2). Primary silanes such as $PhSiH_3$ are more facile substrates in this reaction as compared to secondary or tertiary silanes, where steric bulk often limits conversion.[12] Additionally, a primary silane substrate allows for up to three Si–H bond activation events, and this substrate was used to identify trends in product selectivity, which appears to be an advantage of MeMgBr as a precatalyst.

In all examples with aliphatic amine substrates, conversions of no less than 70% were measured after 1 h under standard conditions (Table 2). This activity is comparable to that seen for ^{n}BuLi and simple lanthanide precatalysts but distinctly less than those compounds.[18,26,27] Nevertheless, the Grignard does continue to exhibit enhanced selectivity as compared to the aforementioned precatalysts, which give silylamine byproducts. Such byproducts are not observed in these reactions. Other magnesium precatalysts exhibit somewhat variable behavior in comparison. For example, magnesocenophane precatalysts reported by Schäfer are much less active, but this is a particular feature of these compounds with primary silane substrates.[20] For To^{M}MgMe, quantitative conversions were measured after 24 h. Based on optimization data (*vide supra*), it is anticipated that MeMgBr would continue to convert substrate at longer reaction times, which suggests activity is comparable to To^{M}MgMe. As an example, for the coupling of $PhSiH_3$ and $^tBuNH_2$, where MeMgBr gave 91% conversion to $PhSiH_2(NH^tBu)$ after 1 h (entry 2b, Table 2), To^{M}MgMe gave 99% conversion to $PhSiH_2(NH^tBu)$ after 24 h.[21] While the activity of MeMgBr may not standout significantly from more complex magnesium precatalysts, the absence of ancillary ligands or additional preparation to use MeMgBr is an important consideration for other investigators to consider this catalyst for routine use. Indeed, reactivity here is highly comparable to $Mg[N(SiMe_3)_2]_2$, and the main difference is that Grignard reagents are often already available in most laboratories as commercial solutions of routine use.[25] This data provides additional support to our assertion that dehydrocoupling reactions can be achieved with simpler catalysts than previously reported, namely those routinely available in synthetic laboratories.

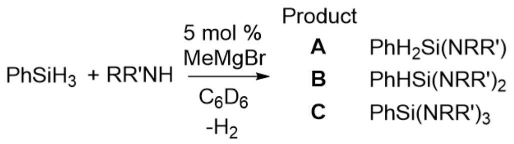


Table 2 Dehydrocoupling of primary and secondary amines with $PhSiH_3$ with MeMgBr[a]

Entry	Amine	Percent of products[b]		
		A	B	C
2a[c]	$^nBuNH_2$	-	-	98
2b	$^tBuNH_2$	91	9	-
2c	$^sBuNH_2$	-	-	70
2d	$^nHeNH_2$	-	-	98
2e	$^iPrNH_2$	-	-	70
2f	Et_2NH	44	56	-
2g	PyNH	-	100	-
2h	$PhNH_2$	-	-	-

[a] Conditions: $PhSiH_3$ (3.4×10^{-1} mmol, 1.0 equiv.), amine (2.02 mmol, 6.0 equiv.), and MeMgBr (1.68×10^{-2} mmol, 5.0 mol %, stock solution in THF) in 0.5 mL of benzene-*d*$_6$ with C_6Me_6 as an internal standard at ambient temperature in a PFTE-valved J-Young type NMR tube. [b] Conversion was measured at 1 h by integration of residual silane vs. product by ^1H NMR spectroscopy. [c] Conversion measured after 0.5 h.

Anime basicity appears to play an important role in reactivity. For example, aniline, a traditionally challenging substrate in this kind of catalysis, showed no reactivity under the standard conditions (entry 2h, Table 2). This observation is implicit of a nucleophilic mechanism, which is common in Si–N heterodehydrocoupling catalysis.[7]

Steric factors are also important in the selectivity of these reactions. The bulkiest two substrates, $^tBuNH_2$ and Et_2NH, afforded mixtures of products based on gradual substitution (entries 2b and 2f, Table 2). However, neither substrate gave the fully substituted, $PhSi(NRR')_3$, product under standard conditions. The slightly less encumbered $^{i}PrNH_2$ only afforded the fully substituted product $PhSi(NH^{i}Pr)_3$, though the conversion was at an apparently reduced relative rate as compared to other substrates (entry 2e). These data would suggest that there may be conditions to select for products like $PhSi(NHR)H_2$ under MeMgBr catalysis, but optimal conditions are substrate dependent. Exploration of such conditions are clearly based on product need and not a focus of this study. Aliphatic chain length appeared to have no significant effects on reactivity as both entries 2a and 2d gave 98% conversion to the tris(aminosilane) product after 1 h.

The behavior of secondary amines is slightly variable. Where Et_2NH gave a mixture of mono(aminosilane) and bis(aminosilane) products (entry 2f), pyrrolidine (PyNH) gave exclusively the bis(aminosilane) in quantitative conversion (entry 2f). This difference appears to be attributable to the steric constraints of Et_2NH, but it is interesting that no excess reaction to the tris(aminosilane) was seen with PyNH, despite the conditions (6.0 equiv. of pyrrolidine). The pyrrolidine reaction demonstrates the potential selectivity of MeMgBr, noting that ^{n}BuLi-catalyzed dehydrocoupling with this substrate proceeded rapidly to the tris(aminosilane) product.[18]

Interestingly, the mixtures of products in reactions with Et_2NH seen herein echo those reported for $Mg[N(SiMe_3)_2]_2$.[25] In that study, greater selectivity was achieved with a bulkier substrate, $(SiMe_3)_2NH$,[25] while in this instance, pyrrolidine was adequate to provide product selectivity.

The reactivity of MeMgBr was then examined with secondary silanes using both primary and secondary amines (Table 3). The increased substitution on the silane and corresponding increased steric bulk likely led to the reduced activity, but further examples of uniquely high selectivity were also noted. In most cases, there was complete consumption of silane substrate within 1 h, except in reactions with the most sterically encumbered amines, $^{t}BuNH_2$ and Et_2NH, which gave conversions of 27–60% (entries 3b, 3d, 3f, and 3f, Table 3). Prior reactions indicate that substrate-optimized conditions would likely give quantitative conversion.

In comparison with other commercially available precatalysts such as ^{n}BuLi, the activity of MeMgBr is somewhat lower.[18] However, MeMgBr exhibits greater selectivity for the less activated aminosilane products. Furthermore, activity as well as selectivity were akin to that seen for $Mg[N(SiMe_3)_2]_2$ excepting that $MePhSiH_2$ was not used in Hill's report.[25] Examination of other magnesium compounds with secondary silanes shows similar selectivity trends of formation of the mono(aminosilane) product. The *ansa*-half-sandwich magnesium compounds have similar reactivity as MeMgBr after 1 h[19] (entries 3b and 3c), while magnesocenophane precatalysts show a range of reactivity dependent on both the specific precatalyst and substrates.[20] This reactivity ranges from formation of $Ph_2SiH(NH^{t}Bu)$ in 94% conversion after 24 h at 60 °C to formation of the same product in 27% conversion with the only difference being magnesocenophane precatalyst.[20] Furthermore, the most active precatalyst is not consistent, as the best precatalyst for Ph_2SiH_2 and $^{t}BuNH_2$ is the worst precatalyst for $PhSiH_3$ and $^{t}BuNH_2$.[20] Sadow's work with To^{M}MgMe shows better reactivity with secondary silanes than MeMgBr giving 89% or greater yield for alkyl amines and secondary silanes although the commercial availability of our example lends itself to better accessibility of these reactions and products.[21]

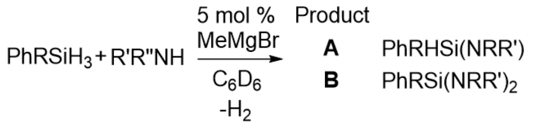


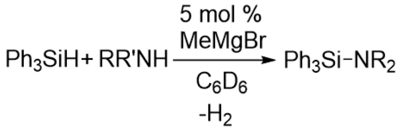
Table 3 Dehydrocoupling of secondary silanes with amines catalyzed by MeMgBr[a]

Entry	Silane	Amine	Percent of products[b]	
			A	B
3a	Ph_2SiH_2	$^{n}BuNH_2$	20	80
3b	Ph_2SiH_2	$^{t}BuNH_2$	50	-
3c	Ph_2SiH_2	PyNH	100	-
3d	Ph_2SiH_2	Et_2NH	27	-
3e	$PhMeSiH_2$	$^{n}BuNH_2$	45	55
3f	$PhMeSiH_2$	$^{t}BuNH_2$	29	-
3g	$PhMeSiH_2$	PyNH	100	-
3h	$PhMeSiH_2$	Et_2NH	60	-

[a]Conditions: R_2SiH_2 (3.4×10^{-1} mmol, 1.0 equiv.), amine (1.34 mmol, 4.0 equiv.), and MeMgBr (1.68×10^{-2} mmol, 5.0 mol %, stock solution in THF) in 0.5 mL of benzene-*d*$_6$ with C_6Me_6 as an internal standard at ambient temperature in a PFTE-valved J-Young type NMR tube. [b]Conversion was measured at 1 h by integration of residual silane vs. product by ^{1}H NMR spectroscopy.

Steric factors continue to play an important role in selectivity. Less encumbered amines (entries 3a and 3e) afforded a mixture of products, but reactions of secondary silanes with bulkier amines such as Et_2NH and $^{t}BuNH_2$ afforded a single product, respectively (Table 3, entries 3b, 3d, 3f, and 3h). Pyrrolidine, which showed selective formation of the bis(aminosilane) with $PhSiH_3$, gave similarly selective product formation to the mono(aminosilane) for both Ph_2SiH_2 and $PhMeSiH_2$ with quantitative conversion under standard conditions (entries 3c and 3g, Table 3). The selectivity seen with MeMgBr allows for easy access to aminosilane products previously inaccessible through commercially available precatalysts.[17, 18]

Further expansion of the substrate scope to tertiary silanes showed a pronounced decrease in activity. For these reactions, extended reaction times and elevated temperatures were necessary for appreciable conversions in any substrate pair examined.



$$Ph_3SiH + RR'NH \xrightarrow[C_6D_6 \\ -H_2]{5\ mol\ \%\\ MeMgBr} Ph_3Si{-}NR_2$$

Table 4 Scope of Si–N heterodehydrocoupling between Ph_3SiH and amines with MeMgBr[a]

Entry	Amine	1 h[b]	4 h[b]	20 h[b,c]
4a	$^tBuNH_2$	0	0	0
4b	$^nBuNH_2$	0	1	63
4c	PyNH	0	9	51

[a]Conditions: Ph_3SiH (3.4×10^{-1} mmol, 1.0 equiv.), amine (6.7×10^{-1} mmol, 2.0 equiv.), and MeMgBr (1.68×10^{-2} mmol, 5.0 mol %, stock solution in THF) in 0.5 mL of benzene-d_6 at ambient temperature in a PFTE-valved J-Young type NMR tube. [b]Conversion was measured by integration of residual silane vs. product by ^1H NMR spectroscopy at time noted. [c]Reaction performed at 40 °C.

Amines that showed good reactivity with $PhSiH_3$ such as $^nBuNH_2$ and PyNH showed little reactivity after 4 h at ambient temperature, affording only reliably detectable product as measured by ^1H NMR spectroscopy. Heating these reactions at 40 ° C for 20 h gave greater product conversion to 63% and 51%, respectively, but these conditions failed to realize the comparable reactivity with other commercially available catalysts, KO^{t}Amyl or ^{n}BuLi.[17,18] The more sterically encumbered substrate $^tBuNH_2$ showed no conversion under the conditions used.

Mechanistic considerations

Throughout this study, results with MeMgBr have implied that the amine substrate is being deprotonated and attacks the silane substrate, consistent with detailed mechanistic study of To^{M}MgMe,[21] a so-called nucleophilic mechanism. This supposition is supported by the formation of methane during catalytic reactions herein, as observed by ^1H NMR spectrosocpy ($\sim\delta = 0.17$), and by deprotonation of amine in a stoichiometric reaction between $^nBuNH_2$ and MeMgBr in a benzene-d_6 solution. It would be anticipated that silane would be relatively inert towards MeMgBr in a nucleophilic mechanism.[7] A stoichiometric reaction of $PhSiH_3$ and MeMgBr in a benzene-d_6 solution did provide evidence of partial silane alkylation to afford $PhMeSiH_2$. However, no catalytic reactions provide evidence of this reactivity, suggesting that the relative rate of alkylation is greater than that of silane dehydrocoupling. The final consideration is that related reagents give similar conversions. For example, MesMgBr affords a similar conversion, and Me_2Mg gives lower conversion, both for the reaction of $PhSiH_3$ and $^nBuNH_2$ in comparison to MeMgBr under standard conditions. The latter observation is attributed to the lower nucleophilicity of dialkyl magnesium compounds relative to Grignard reagents.

Conclusions

Commercially available MeMgBr was explored as a precatalyst for Si–N bond formation under the hypothesis that this reagent would give at least similar activity to more complex magnesium catalysts that have been reported. This hypothesis is part of a larger goal of screening and identifying reagents that will make this kind of catalysis broadly accessible to synthetic chemists and materials researchers. Overall, MeMgBr is a modestly active and easy to use precatalyst for this reaction, showing particular success with primary silanes and aliphatic amines. Consistent with our initial hypothesis, an increase in selectivity was observed characterized by limited formation of byproducts common in reactions with linear amines and primary silanes along with the formation of the less substituted aminosilane product when using bulkier amines and more substituted silanes. Reactions with pyrrolidine showed particular success with quantitative conversions and perfect selectivity to the less substituted aminosilane product under mild conditions. This precatalyst, however, quickly becomes limited by steric bulk, and reactions with tertiary silanes are ineffective without forcing conditions. Reactivity patterns for MeMgBr are consistent with a nucleophilic mechanism such as that proposed for other magnesium compounds, like To^{M}MgMe.[21] This study helps to expand the scope of commercially available precatalysts as well as establishing reactivity patterns that give end users choice in product selectivity.

Experimental Methods

All manipulations were conducted under a positive pressure of purified nitrogen gas in either an M. Braun glovebox or by standard Schlenk techniques. Dry, oxygen-free solvents, reagents, and molecular sieves were used and stored in a glovebox. Benzene-d_6 was subjected to three freeze-pump-thaw cycles and stored over activated 3Å molecular sieves for at least 48 h prior to use. Molecular sieves (3Å) were dried between 180–200 °C under dynamic vacuum for at least 1 d.

Methyl magnesium bromide and 2-mesitylmagnesium bromide (MesMgBr) were obtained from chemical vendors as solutions in tetrahydrofuran (THF). Dimethylmagnesium was synthesized according to a modified literature procedure followed by filtration.[28] For catalysis, this reagent was titrated thrice with I_2 and 0.5 M LiCl in THF solution to determine concentration. Amines were distilled under dynamic N_2 from CaH_2 and stored over 3Å molecular sieves. $PhSiH_3$ was distilled under dynamic N_2 and stored over 3Å molecular sieves while Ph_2SiH_2 and $PhMeSiH_2$ were distilled under dynamic vacuum and stored over 3Å molecular sieves. Ph_3SiH was recrystallized from hexanes solution at –40 °C. Hexamethylbenzene (C_6Me_6) was sublimed at 150 °C under dynamic vacuum.

Glassware was cleaned by sequential washings of base (5% KOH/10% ^{i}PrOH/85% H_2O), acid (10% HNO_3/90% H_2O), and deionized water. Glassware was then oven dried at 140 °C for at least 1 h, followed by either transfer to the antechamber of an M. Braun glovebox or placed under dynamic vacuum through a Schlenk line. Catalysis reactions were conducted in PTFE-sealed

J-Young NMR tubes that were cleaned and dried by the methods mentioned above. Nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature on 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).

General catalysis protocol

SAFETY NOTE: While these reactions are moderately active, appropriate controls for reactions generating gas and, in particular, a flammable gas such as hydrogen should be used.

In a glovebox, a 20 mL scintillation vial was charged with 0.5 mL of benzene-d_6, followed by 50 µL of a 0.4 M C_6Me_6 solution in benzene-d_6, silane, amine, and catalyst in the molar amounts specified. The solution was quickly transferred to a PTFE-valved J-Young NMR tube via a glass pipette. The reaction was then removed from the glovebox, monitored as specified, and left to react at ambient temperature unless otherwise specified.

Author contributions

Methodology, experimentation, data acquisition, and data analysis were conducted by C.E.B., while conceptualization and writing were conducted by both C.E.B. and R.W. Additional experimentation, data acquisition, and data analysis was conducted by D.R.J.J. and additional data analysis conducted by M.B.R. Funding was secured by 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.

Data availability

Original data can be obtained on request from the authors and is posted at time of publication to www.uvm.edu/~waterman.

Acknowledgements

This work was supported by the U.S. National Science Foundation through CHE-2348198 and CHE-2101766 (to R.W.). C.E.B. thanks the University of Vermont Department of Chemistry for summer research funding and the University of Vermont College of Arts and Sciences for a Ronald Suiter Prize.

Notes and references

1. T. T. Nguyen, T. K. Mukhopadhyay, S. N. MacMillan, M. T. Janicke and R. J. Trovitch, *ACS Sustain. Chem. Eng.*, 2022, **10**, 4218-4226.
2. L. J. Morris, G. R. Whittell, J.-C. Eloi, M. F. Mahon, F. Marken, I. Manners and M. S. Hill, *Organometallics*, 2019, **38**, 3629-3648.
3. Y. Tanabe, T. Misaki, M. Kurihara, A. Iida and Y. Nishii, *Chem. Commun.*, 2002, 1628-1629.
4. D. Dhanak and C. B. Reese, *J. Chem. Soc. Perkin Trans.*, 1986, 2181-2186.
5. M. P. Coles, *Coord. Chem. Rev.*, 2015, **297-298**, 2-23.
6. R. Waterman, *Chem. Soc. Rev.*, 2013, **42**, 5629-5641.
7. M. B. Reuter, K. Hageman and R. Waterman, *Chem. Eur. J.*, 2021, **27**, 3251-3261.
8. M. B. Reuter, D. M. Seth, D. R. Javier-Jiménez, E. J. Finfer, E. A. Beretta and R. Waterman, *Chem. Commun.*, 2023, **59**, 1258-1273.
9. V. Verma, A. Koperniku, P. M. Edwards and L. L. Schafer, *Chem. Commun.*, 2022, **58**, 9174-9189.
10. B. E. Leland, J. Mondal and R. J. Trovitch, *Chem. Commun.*, 2023, **59**, 3665-3684.
11. K. Kuciński and G. Hreczycho, *ChemCatChem*, 2017, **9**, 1868-1885.
12. R. L. Melen, *Chem. Soc. Rev.*, 2016, **45**, 775-788.
13. E. M. Leitao, T. Jurca and I. Manners, *Nat. Chem.*, 2013, **5**, 817-829.
14. C. Bellini, V. Dorcet, J.-F. Carpentier, S. Tobisch and Y. Sarazin, *Chem. Eur. J.*, 2016, **22**, 4564-4583.
15. P. Ríos, M. Roselló-Merino, O. Rivada-Wheelaghan, J. Borge, J. López-Serrano and S. Conejero, *Chem. Commun.*, 2018, **54**, 619-622.
16. N. V. Forosenko, I. V. Basalov, A. V. Cherkasov, G. K. Fukin, E. S. Shubina and A. A. Trifonov, *Dalton Trans.*, 2018, **47**, 12570-12581.
17. M. B. Reuter, D. R. Javier-Jiménez, C. E. Bushey and R. Waterman, *Chem. Eur. J.*, 2023, **29**, e202302618.
18. M. B. Reuter, C. E. Bushey, D. R. Javier-Jiménez and R. Waterman, *Dalton Transactions*, 2023, **52**, 13497-13506.
19. L. Wirtz, K. Y. Ghulam, B. Morgenstern and A. Schäfer, *ChemCatChem*, 2022, **14**, e202201007.
20. L. Wirtz, J. Lambert, B. Morgenstern and A. Schäfer, *Organometallics*, 2021, **40**, 2108-2117.
21. J. F. Dunne, S. R. Neal, J. Engelkemier, A. Ellern and A. D. Sadow, *J. Am. Chem. Soc.*, 2011, **133**, 16782-16785.
22. A. Baishya, T. Peddarao and S. Nembenna, *Dalton Trans.*, 2017, **46**, 5880-5887.
23. P. Schüler, S. Sengupta, S. Krieck and M. Westerhausen, *Chem. Eur. J.*, 2023, **29**, e202300833.
24. D. Seyferth, *Organometallics*, 2009, **28**, 1598-1605.
25. M. S. Hill, D. J. Liptrot, D. J. MacDougall, M. F. Mahon and T. P. Robinson, *Chemical Science*, 2013, **4**, 4212-4222.
26. M. P. Cibuzar and R. Waterman, *Organometallics*, 2018, **37**, 4395-4401.
27. Y. A. Rina and J. A. R. Schmidt, *Organometallics*, 2022, **41**, 2974-2984.
28. D. Tobia, J. Baranski and B. Rickborn, *The Journal of Organic Chemistry*, 1989, **54**, 4253-4256.