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Stoichiometric and catalytic Si–N bond formation using the p-block base Al(NMe₂)₃†‡

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The aluminium amide $Al(NMe_2)_3$ acts as a stoichiometric or catalytic reagent in dehydrogenic Si–N bond formation using amines and silanes. Although of limited substrate scope, this represents the first p-block metal catalytic system for N–H/Si–H dehydrocoupling. The observed catalytic rate law for the formation of aminosilane products in a model study of one of the catalytic reactions suggests a mechanism involving the silane component in the deprotonation of the amine (possibly in the form of a hypervalent silicon hydride).

1. Introduction

Catalytic bond-forming reactions using organotransition metal complexes are a central area of modern research. Of particular interest in recent decades has been the use of single-site transition metal catalysts in a growing range of dehydrogenic main group element-element bond-forming reactions (eqn (1)). Primary motivations in this area are the potential to produce novel types of inorganic polymers and materials, as well as possible applications in reversible hydrogen storage. Like conventional organometallic catalysis, however, this new field of 'inorganometallic' catalysis is dominated by precious metals (such as palladium and rhodium). For this reason, there has most recently been a drive to assess the use of more Earthabundant main group metals in place of transition metals. Although less active than transition metal catalysts, the main group counterparts are capable of catalysing a comparable range of element-element bond-forming reactions, most widely studied being homonuclear P-H/P-H1 and heteronuclear B-H/N-H2 coupling. However, completely novel N-H/N-H coupling into N-N bonds has also been observed using main group reagents, for which there are few analogous transition metal reactions.³

 $E-H + H-E' \rightarrow E-E' + H-H \tag{1}$

$$R_2NH + R'_3SiCl \rightarrow R_2N-SiR'_3 + HCl$$
(2)

$$R_2NH + R'_3SiH \rightarrow R_2N-SiR'_3 + H_2$$
(3)

broad range of synthetic organic and materials applications.^{4,5} Aminosilane compounds have traditionally been synthesised via aminolysis, a process that generates HCl as a side product (eqn (2)). Efforts to provide an alternative route to Si-N bonds using N-H/Si-H dehydrocoupling reactions (eqn (3)) have largely involved catalysts such as (Ph₃P)RhCl,⁶ Cu(1)Cl,⁷ $(NHC)Yb[N(SiMe_3)_2]_2^8$ (NHC = N-heterocyclic carbene) and [(Et₂N)U][BPh₄].⁹ Apart from the applications of non-metal based Frustrated Lewis Pairs (FLPs),¹⁰ main group catalysed Si-N coupling has so far focused on s-block metal reagents. Harder and coworkers first showed that the Ca^{II} complex $Ca(\eta^{3}-Ph_{2}CNPh)(hmpa)_{3}$ (hmpa = hexamethylphosphoramide) can catalyse the dehydrogenic formation of Si-N bonds,¹¹ in an analogous way to the Yb^{II} complex reported previously.¹² Other alkaline metal complexes were later shown to be active as dehydrocoupling pre-catalysts, notably Mg(TO^M) [TO^M = tris-(4,4-dimethyl-2-oxazolinyl)phenylborate)] by Sadow and coworkers¹³ and M{N(SiMe₃)₂}₂ (M = Mg, Ca, Sr) by Hill *et al.*¹⁴

Interest in Si-N bonded compounds has stemmed from a

Sadow proposed the mechanism shown in Scheme 1 for his Mg-based catalyst, which has been assumed to be widely applicable to many Si–N dehydrocoupling systems.¹³ The active catalyst is thought to be a metal hydride ([M]-H), similar to that proposed in catalytic N–H/Si–H dehydrocoupling using $[(Et_2N)U][BPh_4]$.⁹ Like the proposed mechanism of amineborane dehydrogenation,¹⁵ the next step is the protonolysis reaction of the amine (R₂NH) with the metal hydride catalyst. The formation of the N-centre, leading to the formation of a hypervalent nucleophilic silicon intermediate *via* attack of the N-atom of the amide onto R'₃SiH. Subsequent β-H elimination regenerates the metal hydride catalyst and gives the aminosilane product. The overall mechanism is supported by the insight that nucleophilic species activate Si–N bond formation.¹⁶

Despite general consensus concerning the overall details of the mechanism of N-H/Si-H coupling using s-block catalysts,



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[‡]Electronic supplementary information (ESI) available: Full 1-D and 2-D NMR characterisation of compounds obtained from catalytic and stoichiometric redactions involving **A** (see Table 1 of the text), full kinetic studies of the reaction of Et₂NH with PhSiH₃, steady-state analysis of metal-hydride and hypervalent silicon hydride mechanisms. See DOI: 10.1039/c5dt00662g



Scheme 1 Proposed mechanism for N–H/Si–H dehydrocoupling.

there still remains some debate. In particular, recent studies by Hill have suggested that sigma-bond metathesis may be a key component of the catalytic cycle.¹⁴ In addition, the determination of the rate laws governing these reactions has so far provided only modest support for the mechanism shown in Scheme 1. Hill has shown that the rate of consumption of the amine using $M{N(SiMe_3)_2}$ (M = Mg, Ca) is first order in amine and catalyst, but zero order in silane (eqn (4)).¹⁴ This rate law is entirely consistent with a mechanism involving deprotonation of the amine by an intermediate hydride as a key step (as illustrated in Scheme 1). However, an apparent change in the mechanism is suggested by the observation of a different rate law for the consumption of the amine for M = Sr, which is dependent on the silane and amine. Harder has shown that the overall rate of formation of the aminosilane products using his catalyst is zero order in amine and first order in catalyst and silane (eqn (5)).¹¹ The observation that the same rate law governs the rate of depletion of silane in Sadow's system led to the important conclusion that the turnover-limiting step involves the interaction of the catalyst with the silane and that the amine itself is not involved in the transition state.13

$$\frac{-d[\text{amine}]}{dt} = k[\text{cat}][\text{amine}] \tag{4}$$

$$\frac{+d[\text{aminosilane}]}{dt} = k[\text{cat}][\text{silane}]$$
(5)

In this paper we report the first p-block metal catalysed N–H/Si–H dehydrocoupling reactions using the pre-catalyst $Al(NMe_2)_3$ (A), and compare its substrate scope and activity to the previously reported alkaline earth metal systems. Detailed exploration of the reaction kinetics allows us to suggest a new mechanism for this type of dehydrocoupling reaction, implicating a hypervalent silicon hydride in the key protonolysis step. Taken together with previously reported investigations,

our studies indicate that at least two mechanisms can be followed, a *metal hydride* mechanism and a *silyl* mechanism, which may explain some of the major contradictions between the previous established kinetic data.

Results and discussion

2.1 Activity and scope of pre-catalyst A

A range of reactions between various silanes and amines using $Al(NMe_2)_3$ (A) as the pre-catalyst (Scheme 2) were monitored by examining the Si-H protons of the silane precursors and aminosilane products in the ¹H NMR spectra, with the unambiguous assignment of the products being made with the aid of 2D NMR experiments (see ESI 1-4[‡]). Preliminary studies aimed to assess the optimum catalytic loading, substrate stoichiometry and temperature were performed to allow sufficiently fast reactions to be monitored. For this purpose the dehydrocoupling reaction of Et₂NH with PhSiH₃ in toluene was used as a model system. It was found that the use of less than 10 mol% of A and/or less than a 1:2 ratio of the silane to amine at room temperature led to slow reaction and a large induction period before H₂ evolution was observed (ca. 15 min). A similar induction period has been seen for the dehydrogenation of amineboranes using A, and corresponds to the time needed for significant concentration of the active catalyst to build up in the reaction.¹⁵ Apart from gas evolution from the reaction, the formation of H₂ was confirmed by the presence of a singlet at δ 4.5 ppm in a sealed Young's tap NMR tube.¹⁷ On the basis of these preliminary studies a minimum catalyst loading of 10 mol%, excess of amine and temperature of 70 °C were used for most of the further studies of the substrate scope.

Table 1 shows the optimum conditions used and the products formed in catalytic and stoichiometric reactions investigated in the current work. As shown in entry 1, pre-catalyst A is most active for the reaction between PhSiH₃ and BnNH₂ (Bn = benzyl). This reaction was the only one investigated for which a rapid reaction occurs at room temperature, being complete in 24 h using a 10 mol% loading of A and a 3:1 ratio of BnNH₂: PhSiH₃. Similarly to previously reported studies of Group 2 catalysts, the use of a 1:1 precursor ratio gave an intractable mixture of products in this case.¹⁴ Using a 3:1 ratio of reactants, the only organically-soluble product is the bis-substituted aminosilane (BnNH)₂SiHPh (1) (²⁹Si NMR δ –25.0 ppm; see also ESI[‡]). In addition, an unidentified white insoluble power is also produced, which has been observed previously in alkali metal catalysed reactions using the same substrates.14



Scheme 2 General silicon-nitrogen dehydrocoupling scheme.

Table 1 Al(NMe₂)₃ catalysed silicon-nitrogen dehydrocoupling

Entry	Silane	Amine	Catalyst loading	Products	Conversion
1	PhSiH ₂	BnNH ₂ ^{<i>a</i>}	10 mol%	(BnNH) ₂ SiHPh	94%
2	5	$Et_2 NH^{\tilde{b}}$	10 mol%	$PhSiH_2NEt_2 + PhSiH(NMe_2)(NEt_2)$	93%
3		ⁱ PrNH ₂ ^c	30 mol%	$PhSiH(iPrNH)_2 + PhSiH(NMe_2)(iPrNH) + PhSiH_2(NMe_2) (trace)$	85%
4		^t BuNH ₂ ^c	30 mol%	$PhSiH(^{t}BuNH)(NMe_{2}) + PhSiH(NMe_{2})_{2} + PhSiH_{2}(NMe_{2})$	33%
5		$PhNH_2$		No reaction	
6		ⁱ Pr ₂ NH		No reaction	
7		HMDS		No reaction	
8	Ph_2SiH_2	Et_2NH	100 mol%	$Ph_2SiH(NMe_2)$	Stoichiometric
9	^t Bu ₂ SiH ₂	Et_2NH	10 mol%	No reaction	

^{*a*} Using 1:3 molar ratio of silane to amine at 25 °C. ^{*b*} Using 1:2 molar ratio of silane to amine at 70 °C. ^{*c*} Using 1:1.5 molar ratio of silane to amine at 70 °C.

The catalytic reaction of PhSiH₃ and Et₂NH proceeds slowly at room temperature using a 10 mol% loading of A and a 1:2 ratio of silane to amine (ca. 7 days). However, at 70 °C it is complete in 24 h (entry 2). In contrast to the reaction involving BnNH₂, two products PhSiH₂(NEt₂) (2a) (70%) and PhSiH- $(NMe_2)(NEt_2)$ (2b) (23%), are formed. The first (2a) is the expected product of 1:1 N-H/Si-H coupling, while the unexpected product 2b can be traced to the initial inductive phase of the reaction in which pre-catalyst A reacts with PhSiH₃ to form a metal hydride intermediate and the byproduct PhSiH₂(NMe₂) (which then couples with Et₂NH, Scheme 3). Support for this come from NMR spectroscopic study of a 1:1 mixture of PhSiH₃ with A in d₈-toluene which, after immediate evolution of H2 gas, gives a mixture of the mono- and di-substituted products PhSiH₂(NMe₂) and PhSiH- $(NMe_2)_2$ (ESI 5a[‡]). This reaction also leads to the replacement of the resonance for A (δ = 110 ppm, br) in the room-temperature ²⁷Al NMR spectrum by a new species (δ 130 ppm, br) (ESI 5b[‡]), which is also present throughout *in situ* studies of the catalytic reactions of Et₂NH with PhSiH₃.

Fig. 1 summarizes selected NMR spectroscopic data on the product mixture of **2a** and **2b** produced in the catalytic reaction (Table 1, entry 2). PhSiH(NMe₂)(NEt₂) (**2b**) was identified through a series of NMR experiments. The short-range (¹*J*_{Si-H} = 202 Hz) ²⁹Si⁻¹H heteronuclear single quantum coherence (HSQC) spectrum (Fig. 1b) shows a cross-peak correlating the doublet ²⁹Si resonance at δ –18 ppm (Fig. 1c) with a the ¹H-singlet for the Si-H proton at δ 5.04 ppm. Additional cross peaks were observed in the long-range ²⁹Si⁻¹H HSQC spectrum between the ²⁹Si resonance and the ¹H-singlet for the



Scheme 3 Formation of the unexpected product 2b.



Fig. 1 (a) ¹H NMR spectra of the reaction between PhSiH₃ (1 equiv.) and Et₂NH (2 equiv.) catalysed by A (10 mol%), showing the formation of PhSiH₂NMe₂ (2a) PhSiH(NMe₂)(NEt₂) (2b), (b) ²⁹Si-¹H HSQC short-range spectrum correlating the diagnostic ¹H signal for the Si-H proton at δ = 5.04 ppm with the ²⁹Si resonance at δ = -18 ppm in PhSiH(NMe₂)(NEt₂). (2b), (c) proton coupled ²⁹Si NMR spectrum showing doublet of the product PhSiH(NMe₂)(NEt₂) (2b), and (d) ²⁹Si-¹H HSQC long-range spectrum correlating the silicon resonance at δ = -18 ppm with the ¹H resonances at δ = 2.56 (s, NMe₂) and 2.90 ppm (q, NEt₂) in PhSiH(NMe₂)-(NEt₂) (2b). All spectra were acquired at ambient temperature and in d₈-toluene.

Me-groups of Me₂N (δ 2.56 ppm) and the ¹H-quartet for the two CH₂-groups of Et₂N (δ 2.90 ppm) (Fig. 1d).

Similar products to **2b**, resulting from catalyst-activation and containing Me_2N -groups, are also formed in the reactions of PhSiH₃ with ⁱPrNH₂ and ^{*t*}BuNH₂ (Table 1, entries 3 and 4). The proportion of these by-products increases with increased steric bulk of the amine substituent so that for ⁱPrNH₂ the final product mixture after 24 h at 70 °C using a 30 mol% loading of **A** is composed of PhSiH(ⁱPrNH)₂ (30%), PhSiH-(NMe₂)(ⁱPrNH) (54%) and a trace amount of PhSiH₂(NMe₂). For ^{*t*}BuNH₂, all of the products contain Me₂N-substitution. In experiments investigating the effects of changing the catalyst loading on product distribution in the reaction of PhSiH₃ with Et₂NH it was found that the ratio of the product (**2a**) to the by-product (**2b**) increases markedly with increased catalyst

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Paper

60%

Ratios of Product Formation



Fig. 2 Kinetic plot showing the product distribution of 2a and 2b from the reaction of $PhSiH_3$ and Et_2NH varying the loading of the precatalyst A.

loading (Fig. 2). It is worth noting that no such products arising from ligand-redistribution of the pre-catalyst were observed in the previously reported studies of Group 2 systems.^{11,13,14} The absence of such by-products presumably reflects the nature and steric demands of the ligands present in the pre-catalysts. For example, the activation stage of M{N-(SiMe_3)_2}_2 (M = Mg, Ca, Sr)^{14} would give the bulky amine (Me_3Si)_2NH (see Scheme 4) which is less reactive than Me_2NH. Supporting this view, we have found that the reaction of Et_2NH with PhSiH₃ with (ⁱPr_2N)_3Al in place of Al(NMe_2)_3 (A) gives **2a** as the exclusive product (with none of the analogous compound to **2b** being observed).

Looking at the remaining reactions involving $PhSiH_3$ and Ph_2SiH_2 (Table 1, entries 5–9), it is clear that the activity of pre-catalyst **A** is severely limited by the nature of the amine and, in particular, the steric demands of the amine and silane precursors. The inability of **A** to couple $PhNH_2$ with $PhSiH_3$ (entry 5) may be due to the acidity of the higher amine, causing catalyst decomposition or deactivation. Harder and Sadow also report a lack of or reduced activity using aniline derivatives and Group 2 catalysts.^{11,13} This, however, contrasts with work by Hill who found that acidic aniline compounds increased the reactivity of the catalyst.¹² The strong steric influence on reactivity is seen in the inability of **A** to couple more bulky secondary amines with PhSiH₃ at 70 °C using a 10 mol% loading (entries 6 and 7) and the lack of activity under these

conditions in the coupling of Et_2NH and the secondary silane Ph_2SiH_2 (entry 9). It is noteworthy that increasing the catalyst loading to 100 mol% leads entirely to stoichiometric reaction of **A** with Ph_2SiH_2 (entry 8), *via* the same mechanism as that discussed above in Scheme 4.

Direct comparison of the activity and substrate scope of pre-catalyst A with previously reported Group 2 N-H/Si-H dehydrocoupling systems is difficult because only limited turnover frequency data is available and the fact that only a few of the coupling reactions reported are directly comparable with the current study. In respect to rate of conversion, pre-catalyst A is clearly less active than Sadows catalyst $Mg(TO^{M})$, which will couple primary amines and silanes at room temperature using a 5 mol% loading in 24 h. It can be noted, however, that only the coupling of primary amines and silanes was explored in this previous case. Although the substrate scope of Hill's catalytic system involving $M{N(SiMe_3)_2}_2$ (M = Mg, Ca, Sr) is greater than that of A, being able to couple a broader range of secondary amines and silanes, the time taken to obtain product conversion is difficult to compare with the previously reported study.¹⁴ Our overall conclusions are that, although A is competent at coupling less sterically demanding amines and silanes, its use in catalysis is limited by side reactions. Nonetheless, this is the first p-block metal based prototype and there is clearly scope for catalyst development in this area, particularly in respect to variation of the steric bulk of the amide ligands present in the pre-catalyst.

2.2 Kinetic studies of the reaction of Et₂NH with PhSiH₃ using pre-catalyst A

We next turned to a detailed investigation of the mechanism of the dehydrocoupling reaction involving **A**, noting the rate laws previously determined for N–H/Si–H dehydrocoupling using Group 2 reagents.^{11,13,14} For this purpose, we focused on the coupling reactions of Et₂NH with PhSiH₃ using **A**. In preliminary studies we showed that **A** does not react significantly with Et₂NH at 25–70 °C in toluene, suggesting that this simple reaction is part of the catalytic cycle or catalyst activation.

The rates of formation of the combined aminosilane products **2a** and **2b** in toluene at 80 °C were monitored as a function of catalyst loading (Fig. 3), silane concentration (Fig. 4)



Scheme 4 Outline of a mechanism involving a hypervalent silicon hydride as the protonolysis source.



Fig. 3 Kinetic plots for the reaction of $PhSiH_3$ and Et_2NH (1:2 equivalents) at 80 °C in toluene varying concentrations of the pre-catalyst A.



Fig. 4 Kinetic plot for the reaction of $PhSiH_3$ and Et_2NH using 10 mol% of A in toluene varying the concentration of $PhSiH_3$.

and amine concentration (Fig. 5), using the ¹H NMR spectroscopic Si–H resonances. It is clear from inspection of the raw data alone that the reaction rate is independent of the concentration of amine, within experimental error (see the duplicate data for the 3:1 molar ratio reaction of Et_2NH with PhSiH₃ in Fig. 5).

Fig. 6a and 6b show plots of the initial rates verses pre-catalyst loading and silane concentration, derived from the data presented in Fig. 3 and 4, respectively. To a very good approximation the initial rate at a given concentration of pre-catalyst or silane is equal to the rate of formation of the mono-substituted product **2a**, since the rate of formation of di-substituted **2b** is negligible at the beginning of the reaction (as it requires **2a** as a precursor). It can be seen from this analysis that the rate law for the formation of the aminosilane products is the same as that previously obtained by Harder (eqn (5)), being first order in silane and pre-catalyst but zero order in amine. Further analysis also reveals that the rate law for the consumption of silane is first order in silane and catalyst but zero order in amine (the same rate law as determined by Sadow¹³) (ESI 6‡).

If the aluminium hydride was the protonolysis source in the mechanism (as in Scheme 1) then the rate law would be eqn (6) (see steady-state analysis ESI 7a[‡]). The same rate law would also operate *even* if the attack of the N-atom of the metal amide ([M]-NR₂) onto the silane (R'₃SiH) (Scheme 1) is



Fig. 5 Kinetic plot showing reaction of $PhSiH_3$ and Et_2NH using 10 mol% of A in toluene varying the concentration of amine.



Fig. 6 (a) Initial rates of reaction vs. pre-catalyst loading for the 1:2 reaction of PhSiH₃ with Et₂NH, and (b) initial rates vs. silane concentration with 10 mol% loading of pre-catalyst. The straight lines drawn are the best-fit ones.

assumed to be the rate-determining step (ESI 7b^{\ddagger}), as proposed by Sadow.^{13,18}

$$\frac{+d[\text{aminosilane}]}{dt} = k[\text{cat}][\text{amine}]$$
(6)

The observed rate law therefore does not appear to be fully consistent with the mechanism shown in Scheme 1. However, one possibility is that the silane is intimately involved in the protonolysis step. Such a mechanism is outlined in Scheme 4 in which a hypervalent silicon hydride is involved. Steady-state analysis (see ESI 8^+) suggests that the participation of such a species as the protonolysis source would result in eqn (5) as the rate law (the experimentally observed rate law for the reaction investigated in the current work using pre-catalyst **A**). Significantly, this proposed mechanism is also consistent with the previous conclusion that the turnover-limiting step involves the interaction of the catalyst ([M]-H) with the silane.¹³

The rate of reaction of intermediate metal hydrides with amines is likely to be a key factor influencing which mechanism dominates [*i.e.*, metal-hydride (Scheme 1) *vs.* hypervalent silicon hydride (Scheme 4)]. This is potentially the cause of the change in mechanism suggested previously by the kinetics of N–H/Si–H coupling moving from $M{N(SiMe_3)_2}_2$ (M = Mg, Ca) (eqn (4) being the rate equation) to $Sr{N(SiMe_3)_2}_2$ (having a rate equation that is partially dependent on the silane concentration).¹⁴ It is well known that the reaction rates of aluminium hydrides with amines can be slow,¹⁹ potentially making H-transfer to silicon more viable than deprotonation of the amine. It can be noted also that the hypervalent silicon hydride anion $[PhSiH_4]^-$ has been implicated as an intermediate in a previous study of the hydrosilylation of alkenes using alkaline earth metal catalysts.²⁰ Also highly relevant to the current study, the switch between a metal hydride and hypervalent silicon hydride mechanism in this previous case is apparently highly dependent on metal–H bond polarity.²⁰

3. Conclusions

We have shown for the first time that a p-block metal based pre-catalyst [Al(NMe₂)₃ (A)] can be employed in N–H/Si–H dehydrocoupling reactions. Clearly, however, the substrate scope of A is limited generally to the least sterically demanding primary amines and silanes. One obvious problem with the use of A is the production of by-products resulting from Me₂Ngroup transfer to the silane. Reduction in coupling rate and increase in the proportion of these by-products occur with more sterically-encumbered amines and silanes. The observation that Me₂N-group transfer can be suppressed by increasing the steric bulk of the amido group present in the precatalyst [as seen for Al(NⁱPr₂)₃] may be important in the development of more selective reagents in this area.

Our measurements of the reaction kinetics of the coupling reaction of Et_2NH with $PhSiH_3$ using **A** are consistent with Harder's previous report using $Ca(\eta^3-Ph_2CNPh)(hmpa)_3$. From these measurements we have suggested that the dependence of the rate equation on the silane concentration may be due to the intimate involvement of the silane in the deprotonation of the amine (potentially in the form of a hypervalent silicon hydride).

4. Experimental section

All chemicals (the silanes PhSiH₃ and Ph₂SiH₂, and the amines BnNH₂, Et₂NH, PhNH₂, ^tBuNH₂, ⁱPrNH₂, ⁱPr₂NH, HMDS) were acquired from Aldrich. Amines were dried by distillation over CaH2 and stored under dry, O-free N2. The precatalyst $Al(NMe_2)_3$ (A) was prepared by the literature method from AlCl₃ and LiNMe₂.²¹ D₈-toluene was dried using a sodium mirror. Most NMR-scale reactions were performed in Young's tap thin-walled 528PP NMR tubes using a Bruker Avance B8-500 MHz spectrometer. For safety, however, kinetic experiments investigating the variation of Et₂NH concentration in its reaction with PhSiH₃ were undertaken in medium-walled Young's tap NMR tubes (i.e., a significant pressure is developed at 80 °C, especially using a large excess of the volatile amine). In order to test that the rate of reactions were not affected if undertaken in a sealed system, a background experiment was initially performed following the rate of formation of the aminosilane products (2a and 2b) of the 2:1 reaction of Et2NH with PhSiH3 at 80 °C in toluene, with and without venting of the H₂ formed as the reaction proceeded. The



Fig. 7 Comparison of overall rate of formation of aminosilanes 2a and 2b in the reaction of Et_2NH with PhSiH₃ using 10 mol% A at 70 °C in toluene, vented (to allow the H₂ generated to escape) and unvented (in a sealed NMR tube).

results show that the formation of H_2 in a sealed NMR tube has no effect on the rate (Fig. 7). Therefore all further studies were undertaken in sealed NMR tubes.

The following data refer to the entries given in Table 1 of the text;

Entry 1 – PhSiH₃ (0.07 ml, 0.60 mmol) followed by BnNH₂ (0.21 ml, 1.80 mmol) was added to an NMR tube containing Al (NMe₂)₃ (10 mg, 0.06 mmol) in d₈-toluene (0.7 ml). Gas evolution was observed immediately. After 24 hours an insoluble white precipitate was formed and (BnNH)₂SiHPh (1) was observed by NMR spectroscopy. ¹H NMR (+25 °C, 500 MHz), δ /ppm = 1.24 (s, 2H N*H*), 3.96 (m, 4H C*H*₂), 5.22 (s, 1H, Si*H*), 7.06–7.24 (m, 10H, *Bn*), 7.26 (m, 3H, *Ph*), 7.67 (m, 2H, *Ph*). ²⁹Si NMR (+25 °C, 99 MHz), δ /ppm = -25.0 (d).

Entry 2 – PhSiH₃ (0.07 ml, 0.60 mmol) followed by Et₂NH (0.10 ml, 1.20 mmol) was added to a solution of Al(NMe₂)₃ (10 mg, 0.06 mmol) in d₈-toluene (0.7 ml). The NMR tube was heated to 70 °C and hydrogen evolution was observed. After 24 hours two products PhSiH₂NEt₂ (**2a**) and PhSiH(NMe₂)-(NEt₂) (**2b**) are observed in 70% and 23% yield, respectively (the remainder was unreacted PhSiH₃). **2a**: ¹H NMR (+25 °C, 500 MHz), δ /ppm = 0.99 (t, 6H NCH₂CH₃), 2.84 (q, 4H NCH₂CH₃), 5.08 (s, 2H, SiH₂), 7.21 (m 3H, *Ph*), 7.59 (m, 2H, *Ph*). ²⁹Si NMR (+25 °C, 99 MHz), δ /ppm = -25.0 (t). **2b**: ¹H NMR (500 MHz), δ /ppm = 0.99 (t, 6H, NCH₂CH₃), 2.56 (s, 6H, NCH₃) 2.90 (q, 4H NCH₂CH₃), 5.04 (s, 1H, SiH), 7.24 (m, 3H, *Ph*), 7.62 (m, 2H, *Ph*). ²⁹Si NMR (25 °C, 99 MHz) δ /ppm = -18.0 (d).

Entry 3 – PhSiH₃ (0.07 ml, 0.60 mmol) followed by ⁱPrNH₂ (0.08 ml, 0.90 mmol) was added to an NMR tube containing toluene-d₈ (0.7 ml). The tube was charged with Al(NMe₂)₃ (30 mg, 0.18 mmol) and gas evolution was observed immediately. After 24 hours PhSiH(ⁱPrNH)₂ (**3a**) and PhSiH(ⁱPrNH)-(NMe₂) (**3b**) were observed in 31% and 54% conversion, respectively (the remainder is unreacted PhSiH₃).

3a: ¹H NMR (+25 °C, 500 MHz), δ /ppm = 0.66 (d, J = 7.5 Hz, 2H, NH, br) 0.99 (dd, J = 6.4 Hz, 1.7 Hz, 12H, (CH₃)₂CH, 3.14–3.24 (m, 2H (CH₃)₂CH), 5.10 (t, 2.1 Hz, 1H, SiH), 7.18–7.21 (m, Ph) 7.63–7.65 (m, Ph). ²⁹Si NMR (+25 °C, 99 MHz), δ /ppm = -31.0. 3b: ¹H NMR (+25 °C, 500 MHz), δ/ppm = 0.72 (d, *J* = 6 Hz 2H, N*H*, br), 1.02 (d *J* = 6.4 Hz 6H (C*H*₃)₂CH), 3.08–3.12 (m, 1H (CH₃)₂C*H*), 5.04 (d *J* = 2.2 Hz, 1H, Si*H*), 7.18–7.21 (m, Ph) 7.55–7.56 (m, Ph). ²⁹Si NMR (+25 °C, 99 MHz), δ/ppm = –24.0.

Entry 4 – PhSiH₃ (0.07 ml, 0.60 mmol) followed by ^tBuNH₂ (0.10 ml, 0.90 mmol) was added to an NMR tube containing d₈-toluene (0.7 ml). The tube was charged with Al(NMe₂)₃ (30 mg, 0.18 mmol) and gas evolution was observed immediately. After 24 hours an PhSiH(^tBuNH)(NMe₂) (4a), PhSiH-(NMe₂)₂ (4b) and PhSiH₂(NMe₂) (4c) were observed in 17%, 11% and 5% conversion, respectively (the remainder is unreacted PhSiH₃).

4a: ¹H NMR (+25 °C 500 MHz), δ/ppm = 1.03 (NH), 1.15 (s, 9H, N^tBu) 2.55 (s, 6H, NMe₂), 5.13 (d, J = 3 Hz, 1H, SiH), 7.16–7.20 (m, Ph), 7.50–7.58 (m, Ph). ²⁹Si NMR (+25 °C, 99 MHz), δ/ppm = -28.0. 4b: ¹H NMR (+25 °C 500 MHz), δ/ppm = 2.49, (s, 12H, NMe₂), 4.97, (s, 1H, SiH₂), 7.16–7.20 (m, Ph) 7.50–7.58 (m,Ph). ²⁹Si NMR (+25 °C, 99 MHz) δ/ppm = -17. 4c: ¹H NMR (+25 °C, 500 MHz), δ/ppm = 2.43 (s, 6H, NMe₂) 4.99 (s, 2H, SiH₂) 7.16–7.20 (m, Ph), 7.50–7.58 (m,Ph). ²⁹Si NMR (+25 °C, 99 MHz). ²⁹Si NMR (+25 °C, 99 MHz), δ/ppm = -22.0.

Entry 8 – Ph₂SiH₂ (0.06 ml, 0.30 mmol) followed by Et₂NH (0.10 ml, 1.20 mmol) were added to a solution of Al(NMe₂)₃ (5 mg, 0.03 mmol) in d₈-toluene (0.7 ml). Gas evolution was observed upon addition and the NMR tube was heated to 70 °C. Full conversion to Ph₂SiHNMe₂ (8) was observed. ¹H NMR (+25 °C 500 MHz), δ /ppm = 2.54 (s, 6H) 5.44 (s, 1H) 7.21 (m, 6H) 7.58 (m, 4H). ²⁹Si NMR (+25 °C, 99 MHz) δ /ppm = -12.0.

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