

Yttrium-Catalyzed Amine–Silane Dehydrocoupling: Extended Reaction Scope with a Phosphorous-Based Ligand

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ABSTRACT:

The scope of the catalytic dehydrocoupling of primary and secondary amines with phenylsilanes has been investigated using $[Y\{N(SiMe_3)_2\}_3]$ and a four-coordinate analogue bearing a cyclometallated phosphonium methylide ligand. Inclusion of the phosphorous-based ligand on yttrium results in increased substrate scope compared to the tris(amide) analogue. While reversible C–H bond activation of the cyclometallated ligand was observed in stoichiometric experiments, D-labelling experiments and DFT calculations suggest that reversible ligand activation is not involved in silazane formation under catalytic conditions. We suggest that the extended reaction scope with the four-coordinate yttrium phosphonium methylide complex

relative to the three-coordinate yttrium (tris)amide complex is a result of differences in the ease of amine inhibition of catalysis.

Introduction

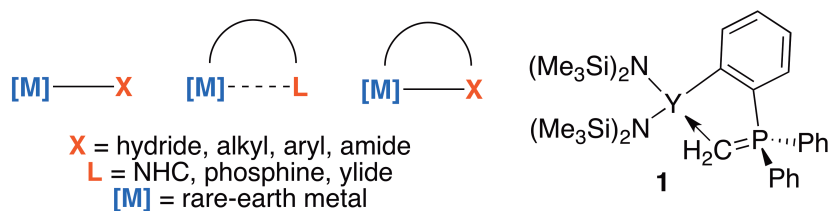
The dehydrocoupling of amines and silanes to form silazanes is a reaction that has received considerable attention over the last five years.¹ While early investigations into silazanes focused on the formation of polysilazanes and their pyrolysis to form silicon nitride (Si₃N₄),² in recent years the Si–N moiety has found extensive use as a protecting group in organic synthesis or as part of kinetically stabilizing ligands in coordination chemistry.^{3–4} Catalysts based upon elements from across the periodic table have been reported to effect the cross dehydrocoupling of amines and silanes. Although catalysts incorporating Pt,⁵ Rh,⁶ Ru,⁷ Ti,⁸ Cu⁹ and U¹⁰ along with those based on Lewis acids¹¹ and Lewis bases¹² have been known for some time, recently amide and alkyl complexes of the s-block and rare-earth elements have emerged as highly efficient and inexpensive mediators of this reaction.

For example, in 2007 Harder and co-workers reported that the dehydrocoupling of amines and silanes could be efficiently catalyzed by $[(\eta^2\text{-Ph}_2\text{CNPh})\text{M}(\text{HMPA})_3]$ (M = Ca, Yb).^{13a} Sadow and co-workers demonstrated improved reaction selectivity and scope through use of the magnesium complex $[\{\text{To}^{\text{M}}\}\text{MgMe}]$ (To^{M} = tris(4,4-dimethyl-2-oxazolinyl)phenylborate).^{13b} *Bis*(amide) and *bis*(alkyl) complexes of Ca, Sr, Ba and the related divalent lanthanide Yb, including $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (M = Ca, Sr, Ba) and $[(\text{IMes})\text{Yb}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) have been reported as catalysts for Si–N bond formation by the groups of Hill, Cui and Carpentier.^{13–14} The turnover frequency and turnover number for one

of the most active barium catalysts $[\text{Ba}\{\text{CH}(\text{SiMe}_3)_2\}_2(\text{THF})_3]$ reach 3600 h^{-1} and 396 respectively for the dehydrocoupling of pyrrolidine and triphenylsilane.^{13d} Divergent mechanistic arguments have materialized from these studies. Depending on the catalyst, it has been proposed that Si–N bond formation occurs through either a concerted σ -bond metathesis step between M–N and Si–H bonds or by nucleophilic attack of the nitrogen atom of a metal amide onto the electrophilic Si center to generate a hypervalent silicate intermediate that then decomposes through β -hydride elimination.¹³⁻¹⁴

We recently introduced the cyclometallated complex **1**. This complex incorporates the three elements of ligand design outlined in Figure 1 – namely appended X- and L-type ligands along with reactive σ -bonded substituents.¹⁵ Here we show that **1** is a highly effective catalyst for the dehydrocoupling of amines and silanes. The inclusion of the phosphonium methylene ligand on yttrium results in an increase in the scope and efficiency of catalysis relative to the parent *tris*(amide) complex $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (**2**).

Figure 1. Catalyst design for small molecule activation with rare-earth metals.



Substrate activation through a reversible reaction of a chelating ligand has long been considered in the organometallic chemistry of the rare-earth elements. For example, the potential for cyclopentadienyl systems to undergo reversible ligand activation has been appreciated since

the early studies of Watson, Bercaw and others on the addition of H–H and C–H and bonds to $[(Cp^*)_2M(Me)]$ ($M = Lu, Sc$).¹⁶⁻¹⁸ This observation of ligand-based reactivity is not limited to tuck-in complexes or related species bearing appended X-type ligands: In 2010, Arnold and Turner reported the 1,2-addition of E–X ($E = Si, Sn, P, B$; $X = Cl, N_3$) bonds across the M–C bond of *N*-heterocyclic carbene adducts of scandium, yttrium, cerium and uranium, along with elimination and subsequent carbon–heteroatom and nitrogen–heteroatom bond formation from isolated zwitterionic intermediates.¹⁹ Parallels may be drawn with Frustrated Lewis Pairs based on zirconium and yttrium reported by Wass and co-workers.²⁰ Broadly both systems could be classified as a reactive metal with an appended L-type ligand (Figure 1).

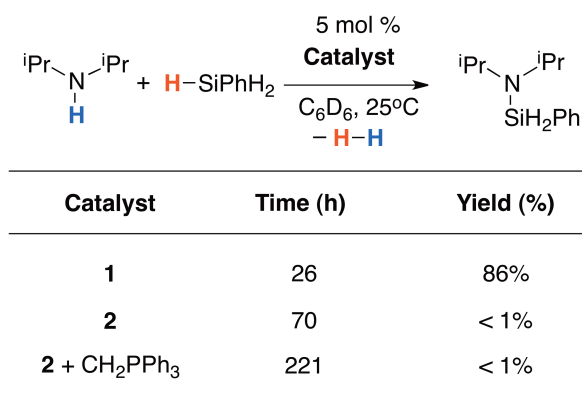
As part of the current contribution, we have investigated the potential of **1** to react with substrates by reversible ligand activation under both stoichiometric and catalytic conditions. Although substrate activation by participation of *both* the appended L- and X-type ligands is possible under stoichiometric conditions, through the isolation of catalytic intermediates, D-labelling experiments, inhibition experiments and DFT calculations, we conclude that reversible ligand activation is not involved in silazane formation under catalytic conditions. The extended reaction scope of catalyst **1** with respect to catalyst **2** is rationalised through a mechanism in which amine inhibition is more significant for the 3-coordinate tris(amide) **2** than the four-coordinate complex **1**.

Results

Reaction Scope

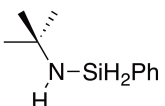
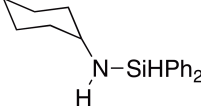
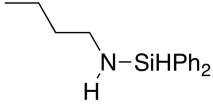
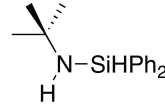
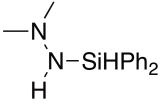
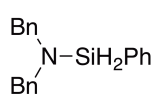
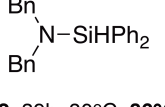
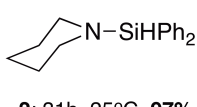
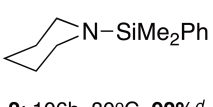
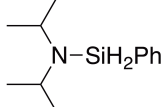
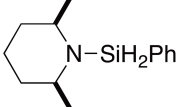
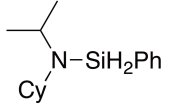
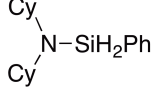
The selective dehydrocoupling of $i\text{Pr}_2\text{NH}$ and PhSiH_3 may be catalyzed by 5 mol% $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_3]$ (**2**) producing $i\text{Pr}_2\text{NSiH}_2\text{Ph}$ in 93% conversion after 164 h at 80 °C in C_6D_6 .⁷⁻⁸ Upon modification of the precatalyst to **1**, preparations proceed to high conversion within 24 h at 25 °C. Control experiments with **2** or mixtures of **2** and Ph_3PCH_2 revealed only trace formation of $i\text{Pr}_2\text{NSiH}_2\text{Ph}$ after weeks at 25 °C.

Scheme 1. The catalytic dehydrocoupling of di-*iso*-propylamine with phenylsilane.



Based on this observation we investigated **1** and **2** as catalysts for the cross dehydrocoupling of a series of amines and silanes. The catalysts are selective for the 1:1 reaction of a number of primary and secondary amines with a series of organosilanes. The reaction scope along with a comparison of the two precatalysts is presented in Table 1. The products have been characterized by ^1H , ^{29}Si , ^{15}N , ^{13}C NMR spectroscopy (see supporting information).

Table 1. Reaction scope of amine–silane dehydrocoupling catalyzed by **1** or **2**.

$ \begin{array}{c} \text{R}^1 \\ \\ \text{N}-\text{H} \\ \\ \text{R}^2 \end{array} + \text{H}-\text{SiR}_3 \xrightarrow[\text{C}_6\text{D}_6, \text{ time, temp.}]{10 \text{ mol } \% \text{ Cat}} \begin{array}{c} \text{R}^1 \\ \\ \text{N}-\text{SiR}_3 \\ \\ \text{R}^2 \end{array} + \text{H}-\text{H} $		
 2: 19h, 25°C, 99% ^a 1: 1h, 25°C, 99%	 2: 0.5h, 25°C, 95% ^b 1: 0.25h, 25°C, 98%	 2: 0.5h, 25°C, 99% 1: 0.5h, 25°C, 99%
 2: 1h, 80 °C, 99% 1: 1h, 80°C, 99%	 2: 46h, 25°C, 64% 1: 96h, 25°C, 63%	 2: 2.5 h, 80°C, 98% ^c 1: 6.5h, 80°C, 98%
 2: 39h, 80°C, 86% 1: 39h, 80°C, 86%	 2: 31h, 25°C, 97% 1: 5h, 25°C, 99%	 2: 106h, 80°C, 92% ^d 1: 19h, 80°C, 99%
 2: 262h, 25°C, 0% 1: 44h, 25°C, 95%	 2: 288h, 80°C, 52% ^e 1: 3h, 80°C, 98%	 2: 288h, 80°C, 55% ^f 1: 4h, 80°C, 99%
 2: 271h, 80°C, 88% ^g 1: 1h, 80°C, 93%		

Reactions conducted with a 1:1 mixture of silane:amine. Yields recorded by ¹H NMR spectroscopy against hexamethylbenzene or ferrocene as an internal standard. ^a57% after 2h, ^b83% after 0.25h, ^c80% after 2.5 h ^d60% after 19h, ^e17% after 21h, ^f22% after 19h, ^g12% after 19h.

Catalysts **1** and **2** show comparable activities for the addition of primary amines and unhindered secondary amines to phenylsilane and diphenylsilane. For example, comparison of the initial rates of the reaction of piperidine with diphenylsilane reveals a near identical activity for both catalysts with no observable induction period for either (Supporting information, Figure S1-2). A handful of catalytic systems are known to be competent for the dehydrocoupling of sterically demanding secondary amines with silanes.¹³⁻¹⁴ It is for these substrates that stark differences are noted for catalysts **1** and **2**. While **1** rapidly dehydrocouples dicyclohexylamine, 2,6-dimethylpiperidine and *iso*-propylcyclohexylamine with phenylsilane either at 25 °C or within a few hours at 80 °C, catalyst **2** is either inactive or requires more than a week at 80 °C to reach moderate to acceptable yields of the corresponding silazanes.

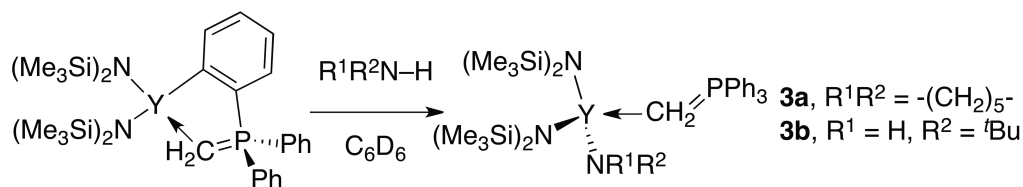
Catalyst Resting States

The *J*-coupling between ⁸⁹Y and ³¹P nuclei observed in NMR offers a useful spectroscopic handle to investigate the catalytic resting states. Monitoring catalytic preparations by ³¹P{¹H} and ¹H NMR allowed the identification of two distinct regimes that are dependent on the amine employed. For sterically unhindered primary amines such as N,N-dimethylhydrazine, n-butylamine and cyclohexylamine (**Regime 1, Table 1, top**), free CH₂PPh₃ and varying amounts HN(SiMe₃)₂ are observed by ³¹P and ¹H NMR spectroscopy within the first 15 minutes of the reaction, suggesting facile protonolysis and displacement of the ylide from the coordination sphere of catalyst. Similarly, for piperidine and *tert*-butylamine, **1** is consumed within the first

point of analysis, in this case generating the corresponding triphenylphosphonium methyllide adducts **3a** and **3b** (Scheme 2).

A stoichiometric reaction between **1** and piperidine in C₆D₆ resulted in clean formation of the *in situ* observed product. The reaction still occurs rapidly when **2**, Ph₃PCH₂ and excess amine (1.2 equiv.) are dissolved in C₆D₆. Scale up gave **3a** and **3b** as crystalline solids in 50% and 69% yields respectively (Scheme 2). The ¹H NMR spectrum of both **3a** and **3b** show a distinct sharp doublet of doublets for the methyllide hydrogens (**3a**, δ = 1.20 ppm, ²J_{31P-1H} = 17.6Hz, ²J_{89Y-1H} = 2.4Hz; **3b**, δ = 1.13 ppm, ²J_{31P-1H} = 17.6Hz, ²J_{89Y-1H} = 2.4Hz). For **3b** the N–H resonance can be seen as a doublet at δ 2.18 ppm (1H, ²J_{89Y-1H} = 2.4Hz). The coupling to ⁸⁹Y was confirmed by running a ¹H{³¹P} experiment. A single phosphorus environment was detected in each case (**3a**, δ = + 32.4 ppm, ²J_{89Y-31P} = 5.0Hz; **3b**, δ = + 32.5 ppm, ²J_{89Y-31P} = 4.9Hz). Single crystal X-ray diffraction experiments confirmed the structures. The Y–C bond lengths in **3a** (2.5441(18) Å), **3b** (2.531(2) Å), and **2•CH₂PPh₃** (2.554(3)Å) (*vide infra*) are within experimental error of one another.

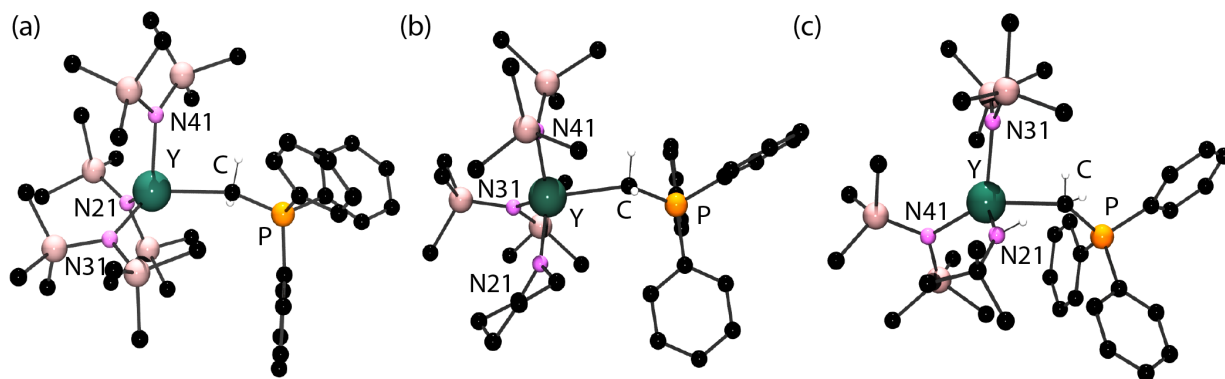
Scheme 2. Synthesis of catalyst resting states **3a** and **3b**



Complex **3a** proved kinetically competent for the dehydrocoupling of piperidine and diphenylsilane at a similar initial rate to **1** and **2**. Similarly **3b** was found to be catalytically

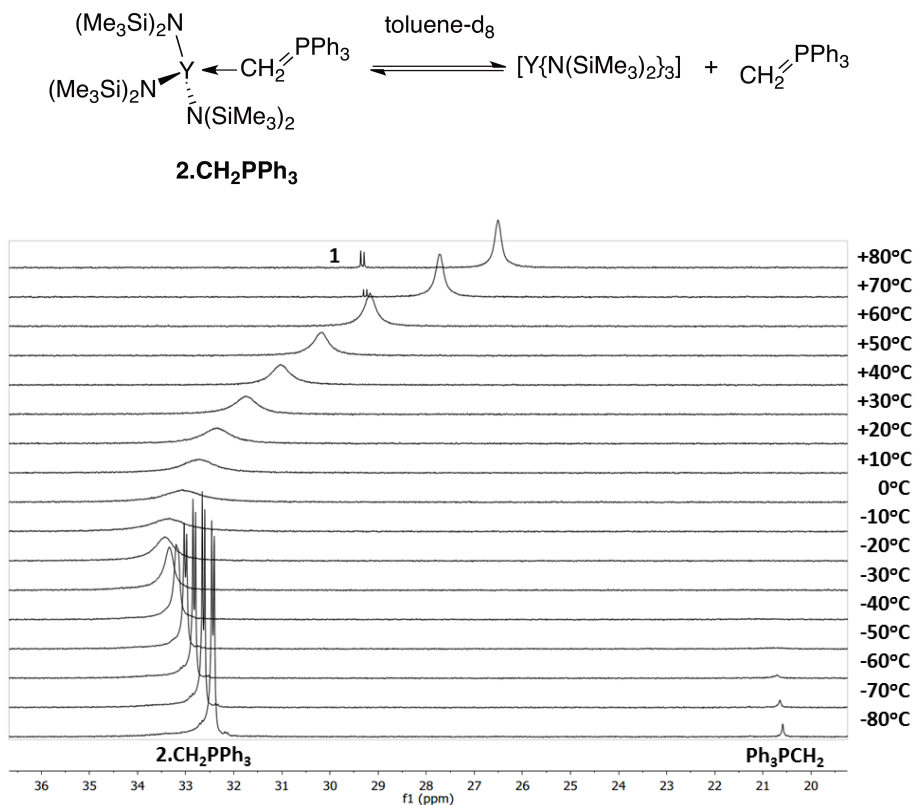
competent for the reaction of phenylsilane and *tert*-butylamine giving the corresponding silazane in 99% yield after 1h at 25 °C. Based on this observation and the data presented in Table 1, we propose that for the addition of 1° amines and unhindered 2° amines to arylsilanes a common catalyst may be generated. Complexes **1**, **2** and **3a/b** give rise to similar species under catalytic conditions. Hence, protonolysis of **2** with a single equiv. of amine yields observable intermediates **3a-b** that may lose an equivalent of ylide and generate similar species to those derived from **1** under catalytic conditions.

Figure 2. The crystal structures of (a) **2•CH₂PPh₃**, (b) **3a** and (c) **3b**. Selected bond angles (°) and bond lengths (Å): **2•CH₂PPh₃**: Y–N(21) 2.246(2), Y–N(41) 2.274(2), Y–N(31) 2.277(2), Y–C 2.554(3), C–P 1.739(3). **3a**: Y–C 2.5441(18), P–C 1.7366(17), Y–N(21) 2.1781(15), Y–N(31) 2.2810(14), Y–N(41) 2.676(14), Y–C–P 141.33(10); **3b**: Y–C 2.531(2), P–C 1.730(2), Y–N 2.158(2), Y–N 2.273(2), Y–N 2.2633(19), Y–C–P 144.39(14).



During preparations of **1** we identified the ylide adduct **2•CH₂PPh₃** ($\delta = +30.5$ ppm, C₆D₆) as an intermediate. Consistent with the hypothesis outline above, VT NMR studies on isolated samples of **2•CH₂PPh₃** in toluene-d⁸ demonstrated that ylide coordination is reversible, with the equilibrium lying towards **2** + CH₂PPh₃ at higher temperatures (Figure 3).

Figure 3. $^{31}\text{P}\{^1\text{H}\}$ NMR stackplot for a 39 mM C_7D_8 solution of **2**• CH_2PPh_3 between -80°C and $+80^\circ\text{C}$.

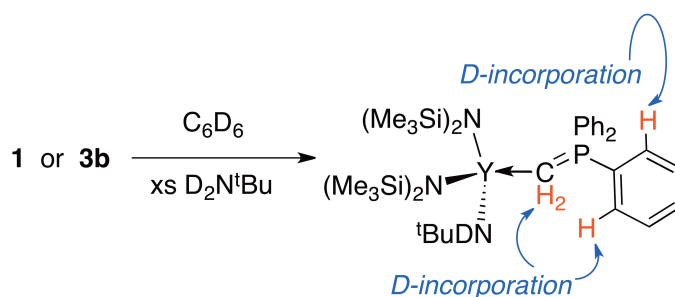


In contrast when hindered secondary amines are employed as substrates (*Regime 2, Table 1, bottom*), ring opening of the P-based ligand of **1** or displacement of the ylide from yttrium is not observed. For di-*iso*-propylamine, dicyclohexylamine, *iso*-propylcyclohexylamine and *cis*-2,6-dimethylpiperidine, **1** ($\delta = +28.3$ ppm) is observed as the catalyst resting state throughout the reaction. It is for these substrates that a significant difference between the activity of **1** and **2** is recorded in catalytic silazane formation (Table 1).

Reversible Ligand Activation under Stoichiometric Conditions

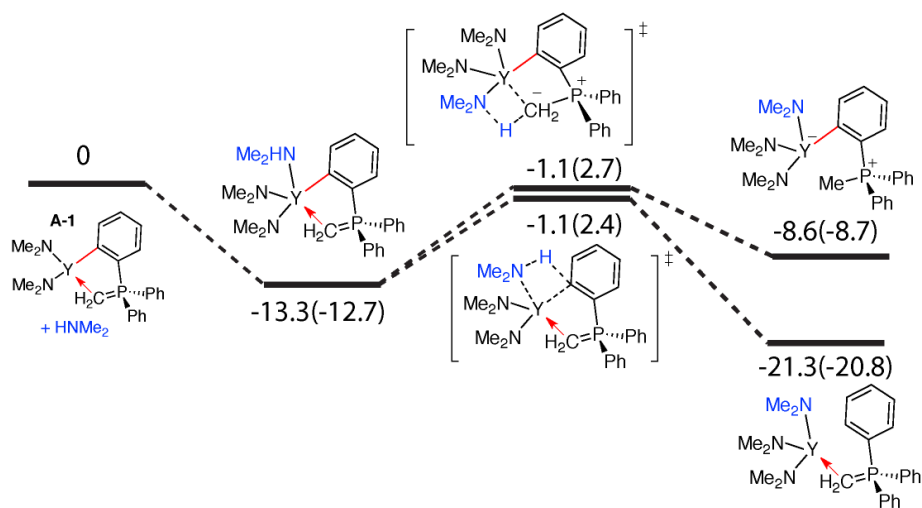
In order to probe whether the reaction of **1** with amines could be reversible, a series of deuterium labeling experiments were conducted. The reaction of ${}^t\text{BuND}_2$ with either **1** or **3b** resulted in significant D-incorporation into the C–H bonds of *both* the methylene position and the aryl ring as evidenced by ${}^1\text{H}$ and ${}^2\text{H}$ NMR spectroscopy (Scheme 3). A similar labelling experiment in which **1** was reacted with excess ${}^i\text{Pr}_2\text{ND}$ neither led to ring opening of the phosphonium methylene ligand nor resulted in significant D-incorporation into the aryl ring. This experiment is consistent with the observation of **1** as a catalytic resting state during the dehydrocoupling of ${}^i\text{Pr}_2\text{NH}$ with PhSiH_3 . In both labelling experiments D-incorporation was observed into the methylene position, and control experiments in which triphenylphosphonium methylene was reacted with ${}^t\text{BuND}_2$ show facile H/D exchange between the N–D and C–H groups. A such little mechanistic information can be gained from D-incorporation into the methylene position of complexes **1** and **3b**.

Scheme 3. Deuterium isotope tracer experiments



The experiments were supported by DFT calculations using a sterically unhindered model. The addition of the N–H bond of dimethylamine across the Y–C_{ylide} and aryl Y–C_{Aryl} bonds of **A-1** (a model of **1** in which the –N(SiMe₃)₂ ligands have been replaced with NMe₂) are represented in Figure 3. Both reactions were found to occur by an energetically accessible σ -bond metathesis transition state, but the former reaction is not only less exergonic than the latter but also expected to be reversible based on the energy of transition state for the microscopic reverse, amine elimination (Figure 3).

Figure 3. DFT calculations of the potential energy surfaces for addition of Me₂NH to **A-1**. Electronic energies with solvent corrected (PCM, benzene) energies from single-point calculations in parantheses. Values in kcal mol⁻¹.



While we have not extended this model to more sterically demanding substrates, for hindered secondary amines the D-labelling experiments show no conclusive evidence for the addition of the amine across the aryl Y–C_{Aryl} position. Here **1** is likely to be both kinetically and thermodynamically stable with respect to the ring opened products.

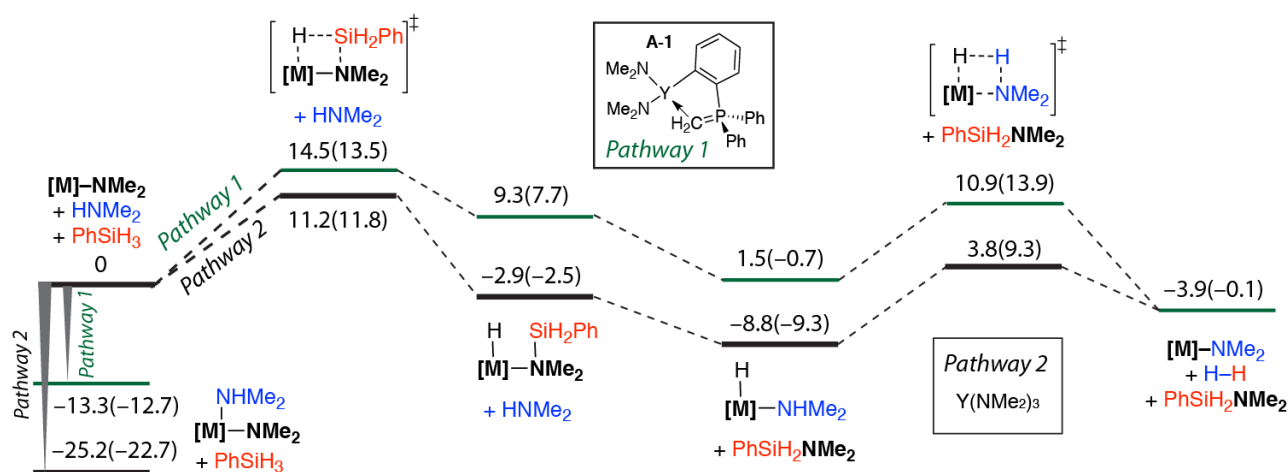
Proposed Catalytic Mechanism

To summarise the stoichiometric experiments and observations under catalytic conditions, during reactions of primary or sterically unhindered secondary amines with **1** the ylide is readily displaced from the coordination sphere of yttrium. Complexes of the form $[Y(NR_2)_3(CH_2PPh_3)]$ are a potential intermediates in this reaction. In the cases where these adducts are isolable, evidence for the reversible addition of the N–H bond of the amine across *both* the Y–C_{Aryl} and Y–C_{ylide} positions of the phosphonium methyllide ligand has been gathered. For sterically hindered secondary amines, no data to support the displacement of the ylide from **1** or reversible ligand activation under either stoichiometric or catalytic conditions were collected.

In order to gain more insight into catalysis and to explore possible explanations for the difference between catalysts **1** and **2**, a series of DFT calculations were conducted. The potential energy surfaces for a series of reaction mechanisms for the addition of PhSiH₃ to Me₂NH were calculated for $[Y(NMe_2)_3]$ and **A-1** by DFT methods. To further exclude a role of ligand activation in catalysis, the conventional σ -bond metathesis pathways were compared against amine activation by addition across *both* the C_{ylide} and C_{Aryl} ligands of **A-1**. Despite repeated attempts to optimise silicate structures there was no evidence to suggest that yttrium silicates play a role in low energy reaction pathways. The calculated intermediates and diamond-like transition states conform to geometries that are well established in rare-earth chemistry (see supporting information).²¹

The lowest energy reaction pathways occur for the addition of the amine across the Y–N bond of $[Y(NMe_2)_3]$ and the Y–N bond of **A-1** (Figure 5). While feasible reaction pathways were located for silazane formation involving amine activation using the X- or L-type ligand of **A-1**, in this model system these pathways incorporate transition states that are considerably higher in energy than those represented in Figure 5 (see supporting information). These findings suggest that reversible ligand activation is not a satisfactory explanation for the improved catalytic performance of **1** over **2**.

Figure 5. DFT calculations of the potential energy surface for amine-silane dehydrocoupling. *Pathway 1* catalyzed by **A-1** and *pathway 2* catalyzed by $[Y(NMe_2)_3]$. Electronic energies with solvent corrected (PCM, benzene) energies from single-point calculations on optimised structures in parentheses. Values in kcal mol⁻¹.



Consistent with these theoretical data, additional deuterium labelling experiments in which **3b**, iBuND_2 and $PhSiH_3$ were mixed in a 1:10:10 ratio or **1**, iPr_2ND and $PhSiH_3$ were mixed in a

1:10:10 ratio did not lead to significant D-incorporation into the *ortho*-position of the aryl group of ligand. Hence, under catalytic conditions reversible activation of the phosphonium methyllide ligand by substrate addition across the Y–C_{Aryl} bond is not significant.

The DFT studies suggest that catalytic reactions should suffer from amine inhibition, with the effect being more significant for the 3-coordinate precatalyst **2** than for the 4-coordinate precatalyst **1**.²² *Pathway 2* would be expected to suffer from strong catalyst inhibition due to a significant stabilization of the system upon amine coordination to [Y(NMe₂)₃]. Amine coordination would be expected to raise the overall activation energy to Si–N bond formation due to the need for a dissociative step prior to entering into the catalytic manifold. In contrast, *pathway 1* is weakly inhibited and amine coordination to **A-1** is thermodynamically less favorable than for [Y(NMe₂)₃].²³

Although the suitability of the computational model is limited due to the reduced size of the alkyl groups on amine and amide moieties relative to the real system, inhibition experiments in which catalytic or stoichiometric quantities of HN(SiMe)₂ were added to the reaction of ⁱPr₂NH with PhSiH₃ catalyzed by **1**, slowed the reaction but failed to prevent silazane formation. Under the same conditions, complex **2** shows no activity for amine silane dehydrocoupling (see supporting information, Figure S5).

Although we cannot unambiguously rule out a role of the phosphorous-based ligand in supporting or solubilising yttrium hydride clusters, we suggest that the significant difference between **1** and **2** in catalysis is a reflection of the strength of amine binding to the precatalyst and the degree of catalyst inhibition. The difference between the two catalyst systems is borne out for the most sterically hindered amines; those which would be expected to show the largest sensitivity to the steric environment at yttrium and those for which **1** is observed as a resting state through out the reaction.¹³

Conclusions

In summary, the cyclometallated complex **1** is an effective catalyst for the dehydrogenative coupling of amines and silanes. For the addition of a series of sterically demanding secondary amines to phenylsilane, this catalyst is dramatically more effective than $[Y\{N(SiMe_3)_2\}_3]$. While reversible activation of the cyclometallated ligand has been observed in stoichiometric experiments with amines, D-labelling experiments and DFT calculations suggest that reversible ligand activation is not involved in silazane formation under catalytic conditions.

Experimental

General procedure, exemplified for *Bn₂SiH₂Ph*: In a glovebox, dibenzylamine (22.4 μ L, 0.12 mmol), phenylsilane (14.4 μ L, 0.12 mmol) and the internal standard were dissolved in C₆D₆ (450 μ L) and transferred to a Youngs tap NMR tube. The tube was removed from the glovebox, a

baseline ^1H NMR spectrum recorded and the tube returned to the glovebox before the addition of **3** (10 mol%) in C_6D_6 (150 μL). The reaction was monitored *in situ* by ^1H and ^{31}P NMR spectroscopy and gave 99 % yield after 3.5 h at 25 $^\circ\text{C}$. ^1H NMR (400 MHz, C_6D_6) δ 3.85 (s, 4H), 5.35 (s, 2H), 7.05 – 7.19 (m, 13H), 7.62 – 7.64 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ 51.2, 126.8, 128.1, 128.2, 128.3, 130.1, 134.3, 135.1, 139.8; ^{15}N NMR (51 MHz, C_6D_6) δ +24.1; ^{29}Si NMR (99MHz, C_6D_6) δ -20.0 .

*Synthesis of **2**• CH_2PPh_3 :* In a glovebox, $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ (460 mg, 0.81 mmol) and Ph_3PCH_2 (0.22 g, 0.81 mmol) were weighed out separately and transferred to a schlenk. The schlenk was sealed, removed from the box and attached to a vacuum line where dry diethyl ether (5 mL) was added under a purge of argon. The mixture was agitated and left to stand for 1 h at 25 $^\circ\text{C}$. The solution was removed under vacuum and the product extracted into n-hexane (5 mL). The solution was filtered, reduced in volume and stored at -20 $^\circ\text{C}$ to produce yellow crystals. The crystals were isolated through filtration and dried under vacuum to give **2**• CH_2PPh_3 (404 mg, 0.48 mmol, 59 %); ^1H (400 MHz, C_6D_6 , 298 K) δ 0.45 (s, 54H), 1.23 (br d, 2H, $^2J^{31\text{P}-^1\text{H}} = 13.6$ Hz), 7.00-7.05 (m, 9H), 7.52-7.61 (m, 6H); ^{13}C NMR (101 MHz, C_6D_6 , 298 K) δ 6.5, 8.5 (br), 129.0 (d, $J^{31\text{P}-^{13}\text{C}} = 11.7$ Hz), 132.4, 133.0 (d, $J^{31\text{P}-^{13}\text{C}} = 9.7$ Hz); ^{31}P (162 MHz, C_6D_6 , 298K) δ + 30.5; Elemental analysis calculated for $\text{C}_{37}\text{H}_{71}\text{N}_3\text{PSi}_6\text{Y} = \text{C}: 52.51\%$, $\text{H}: 8.46\%$, $\text{N}: 4.96\%$ Found = $\text{C}: 52.31$, $\text{H}: 8.45$, $\text{N}: 4.98$.

*Synthesis of **3a**:* In a glovebox, $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ (400 mg, 0.70 mmol) and Ph_3PCH_2 (194 mg, 0.70 mmol) were weighed into a 20 ml scintillation vial. Dry diethyl ether (5 mL) was added, followed by piperidine (83 μL , 0.84 mmol, 1.2 equiv.). The mixture was agitated and left to stand for 2 h at 25 $^\circ\text{C}$. The volatiles were removed under vacuum and the product extracted into n-hexane (5 mL). The solution was filtered, reduced in volume and stored at -20 $^\circ\text{C}$ to produce pale yellow crystals. The crystals were isolated through filtration and dried under vacuum to give **3a** (269 mg, 0.35 mmol, 50 %); ^1H (400 MHz, C_6D_6 , 298 K) δ 0.47 (s, 36H), 1.20 (dd, 2H, $^2J^{31\text{P}-^1\text{H}} = 17.6$ Hz, $^2J^{89\text{Y}-^1\text{H}} = 2.8$ Hz), 1.52 – 1.58 (m, 4H), 1.67 – 1.72 (m, 2H), 3.36 (m, 4H), 7.01 - 7.03 (m, 9H), 7.45 - 7.50 (m, 6H); ^{13}C NMR (101 MHz, C_6D_6 , 298 K) δ 5.8, 9.1 (dd, $^1J^{31\text{P}-^{13}\text{C}} = ^1J^{89\text{Y}-^{13}\text{C}}$

= 31.4 Hz), 27.0, 29.3, 51.9, 127.7, 128.0, 129.4 (d, $J^{31\text{P}-^{13}\text{C}} = 11.8$ Hz), 132.6 (d, $J^{31\text{P}-^{13}\text{C}} = 2.4$ Hz), 132.9 (d, $J^{31\text{P}-^{13}\text{C}} = 9.7$ Hz); ^{31}P (162 MHz, C_6D_6 , 298K) δ + 32.4 (d, $^2J^{31\text{P}-^{89}\text{Y}} = 5.2$ Hz); Elemental analysis calculated for $\text{C}_{36}\text{H}_{62}\text{N}_3\text{PSi}_4\text{Y}$ = C: 56.22%, H: 8.13%, N: 5.46% Found = C: 56.56%, H: 8.24%, N: 5.40%.

Synthesis of **3b:** In a glovebox, $[\text{Y}\{\text{N}(\text{SiMe}_3)_2\}_2]_2$ (150 g, 0.26 mmol) and Ph_3PCH_2 (73 mg, 0.26 mmol) were weighed into a 20 ml scintillation vial. Dry diethyl ether (5 mL) was added, followed by n -butylamine (33 μl , 0.32 mmol, 1.2 equiv.). The mixture was agitated and left to stand for 2 h at 25 °C. The volatiles were removed under vacuum and the product extracted into n -hexane (5 mL). The solution was filtered, reduced in volume and stored at -20 °C to produce pale yellow crystals. The crystals were isolated through filtration and dried under vacuum to give **3b** (138 mg, 0.18 mmol, 69 %); ^1H (400 MHz, C_6D_6 , 298 K) δ 0.46 (s, 36H), 1.13 (dd, 2H, $^2J^{31\text{P}-^1\text{H}} = 17.6$ Hz, $^2J^{89\text{Y}-^1\text{H}} = 2.4$ Hz), 1.37 (s, 9H), 2.18 (d, 1H, $^2J^{89\text{Y}-^1\text{H}} = 2.4$ Hz) 7.01-7.04 (m, 9H), 7.52-7.58 (m, 6H); ^{13}C NMR (101 MHz, C_6D_6 , 298 K) δ 6.0, 9.0 (dd, $^1J^{31\text{P}-^{13}\text{C}} = ^1J^{89\text{Y}-^{13}\text{C}} = 30.5$ Hz), 36.2, 129.3 (d, $J^{31\text{P}-^{13}\text{C}} = 11.8$ Hz), 132.6 (d, $J^{31\text{P}-^{13}\text{C}} = 2.4$ Hz), 133.0 (d, $J^{31\text{P}-^{13}\text{C}} = 9.7$ Hz); ^{31}P (162 MHz, C_6D_6 , 298K) δ + 32.5 (d, $^2J^{31\text{P}-^{89}\text{Y}} = 4.9$ Hz). Due to the air-sensitive nature of this compound repeated attempts to obtain satisfactory elemental analysis failed.

DFT studies: Calculations were conducted in Gaussian09. All minima were confirmed by frequency calculations and where applicable solid-state data were used as an input for the atom coordinates. Geometry optimizations were performed using the hybrid Becke three-parameter functional with Lee-Yang-Parr correlation (B3LYP). A hybrid 6,31G+(d,p) (C, H, N, Si, P) and LanL2DZ (Y) basis set was used. A (benzene) solvent correction was applied by calculating single point energies of the optimized structures employing the polarization continuum model in Gaussian 09.

ASSOCIATED CONTENT

Supporting Information. Full experimental and computational details, and crystallographic data is available free of charge via the Internet at <http://pubs.acs.org>.

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22. The effect of excess amine on the dielectric constant of the solvent, or explicit amine solvation of the yttrium center by one or more molecules of amine was not explored at every stage of the catalytic cycle,
23. While inhibition of *pathway 2* could also occur by protonolysis and ring opening of the cyclometallated ylide with the amine (supporting information). Based on the observation of **1** as a resting state throughout the reaction with these substrates, we propose that this reaction is disfavored for sterically hindered 2° amines.

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