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# Barium-Mediated Cross-Dehydrocoupling of Hydrosilanes with Amines – A Complementary Approach by Theory and Experiment

Clément Bellini,<sup>[a]</sup> Jean-François Carpentier,<sup>\*[a]</sup> Sven Tobisch,<sup>\*[b]</sup> and Yann Sarazin<sup>\*[a]</sup>

Dedication ((optional))

**Abstract:** Complexes of the alkaline-earths, and most prominently barium, are very active and productive precatalysts (TON = 396, TOF up to 3600 h<sup>-1</sup>; Ca < Sr < Ba) for N–H/H–Si cross-dehydrocoupling, with excellent chemoselectivity in the reaction of (di)amines with (di)hydrosilanes. Experimental and DFT investigations revealed that the reactions proceed via nucleophilic attack of a metal-amide at the incoming silane and subsequent turnover-limiting H-transfer to the metal center.

Silazanes are valuable compounds used as ligands in coordination chemistry,<sup>[1]</sup> and as bases,<sup>[2]</sup> O–Si silylating agents<sup>[3]</sup> or protecting groups for amines, indoles and anilines in organic synthesis.<sup>[4]</sup> In addition, oligo- and polysilazanes constitute excellent precursors of Si<sub>3</sub>N<sub>4</sub> ceramics.<sup>[5]</sup> Historical protocols for the production of silazanes involving metalation of amines with alkali bases or aminolysis of chlorosilanes,<sup>[4a,6]</sup> which generate stoichiometric amounts of salts or HCl by-products, are being replaced by more efficacious procedures. Although dependent on efficient routes and ready access to a broad range of hydrosilanes, the catalyzed N–H / H–Si cross-dehydrocoupling (CDC) of hydrosilanes and HNR<sup>1</sup>R<sup>2</sup> amines (R<sup>1</sup>, R<sup>2</sup> = H, alkyl, aryl), with H<sub>2</sub> being the sole by-product, is a very effective catalytic process. While this catalysis was at first dominated by simple alkali hydrides<sup>[5a,5d]</sup> or middle and late transition metal species,<sup>[4b–c,4e,5b,7]</sup> some breakthroughs have now been achieved using borane organocatalysts<sup>[4f,8]</sup> or complexes built on ions of oxophilic metals, e.g. Al<sup>3+</sup>,<sup>[9]</sup> Yb<sup>2+</sup>,<sup>[10]</sup> U<sup>4+</sup>,<sup>[11]</sup> Zn<sup>2+</sup>,<sup>[12]</sup> and Ae<sup>2+</sup> (Ae = alkaline-earth),<sup>[10b,13]</sup> However, high catalytic activity and selectivity, e.g. in the coupling of primary/secondary hydrosilanes with primary amines or ammonia, remain challenging.

The Ae compounds known to catalyze the construction of N–Si bonds are very effective. Notably, Sadow's tris(oxazolonyl)-borato (To<sup>M</sup>) magnesium precatalyst couples primary amines, ammonia or hydrazine with phenyl-substituted hydrosilanes.<sup>[13a]</sup> Hill has shown that the versatile Ae{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (Ae = Mg, Ca,

Sr) operate under mild conditions, with the calcium precatalyst outperforming its magnesium and strontium congeners.<sup>[13b]</sup> As often in Ae-mediated catalysis,<sup>[14]</sup> several subtleties linked to the size and charge density of the Ae metal under consideration were revealed upon mechanistic investigations. However, the larger barium was left out of these studies, and to date no Ba precatalyst is known for the CDC of amines and hydrosilanes. We report here that highly active and selective barium complexes surpass their Ca and Sr analogues in the catalysis of N–H/H–Si CDC reactions involving a variety of substrates; the main mechanistic features are delineated by combining experimental data and DFT computations.

A first screening evidenced that the readily prepared bis(amido) compounds Ae{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>•(THF)<sub>x</sub> (x = 0 for Ae = Mg, 1; x = 2 for Ae = Ca, 2; Sr, 3; Ba, 4) and their derivatives bearing an iminoanilido ligand {N^N}Ae{N(SiMe<sub>3</sub>)<sub>2</sub>}•(THF)<sub>x</sub> (Ae = Ca, x = 1, 5; Sr, x = 2, 6; Ba, x = 2, 7; {N^N} = [ArN(σ-C<sub>6</sub>H<sub>4</sub>)C(H)=NAr]– with Ar = 2,6-*i*Pr-C<sub>6</sub>H<sub>3</sub>)<sup>[14f]</sup> all catalyze the CDC of pyrrolidine and triphenylsilane at 25 °C, with a metal loading as low as 0.25 mol-% (Table 1). The Ba alkyl complexes Ba{CH(SiMe<sub>3</sub>)<sub>2</sub>}•(THF)<sub>3</sub> (**8**) and {N^N}Ba{CH(SiMe<sub>3</sub>)<sub>2</sub>}•(THF)<sub>2</sub> (**9**),<sup>[14g]</sup> which require more synthetic efforts, also proved very effective.

Key trends for the Ae-mediated CDC coupling of amines and hydrosilanes, which need to be used as purified and dry substrates, emerge from Table 1: (i) For both families of precatalysts, the catalytic activity increases with metal size, electropositivity and polarizability according to Mg << Ca < Sr < Ba; barium is the metal of choice for this catalysis.<sup>[15]</sup> The most active precatalysts are **4** and **8**, which fully convert the substrates within 15 min to display a unique combination of productivity (TON = 396) and activity (TOF up to 3600 h<sup>-1</sup>); (ii) The simple bis(amido) and bis(alkyl) Ba precatalysts (**4** and **8**) perform better than their derivatives incorporating the bulky iminoanilide (**7** and **9**), and hence the use of ancillary ligands is not mandatory; (iii) The [Ba] alkyl precatalysts are more active than their amido derivatives.<sup>[16]</sup> The superiority of [Ba] alkyl precatalysts *vis-à-vis* amido ones can be attributed to the greater basicity of the alkyl group, resulting in the formation of a far larger amount of [Ba] pyrrolido species which are likely catalytically active species (*vide infra*).<sup>[17]</sup> Along this line, the stoichiometric reaction of pyrrolidine (HN(CH<sub>2</sub>)<sub>4</sub>) with **9** yields a pyrrolido barium compound upon release of CH<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>, whereas **7** reacts to give the bis(pyrrolidine) adduct {N^N}Ae{N(SiMe<sub>3</sub>)<sub>2</sub>}•[HN(CH<sub>2</sub>)<sub>4</sub>]<sub>2</sub> upon displacement of the THF molecules, without any evidence for aminolysis of the [Ba]–N(SiMe<sub>3</sub>)<sub>2</sub> bond. Moreover, the NMR-scale reaction (C<sub>6</sub>D<sub>6</sub>, 25 °C) of two equiv of pyrrolidine with **8** releases CH<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub> quantitatively, whereas with **4** the evolution of free HN(SiMe<sub>3</sub>)<sub>2</sub> cannot be detected.

The Ba precatalysts **4** and **8** were used to probe substrate scope, employing in particular substrates with multiple reactive

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sites, e.g.  $\text{HR}_2\text{Si}^{\wedge\wedge}\text{SiR}_2\text{H}$ ,  $\text{R}_x\text{SiH}_{4-x}$  ( $x \geq 2$ ) and/or primary amines, for which chemoselectivity is a key aspect. Representative examples are collated in Figure 1.

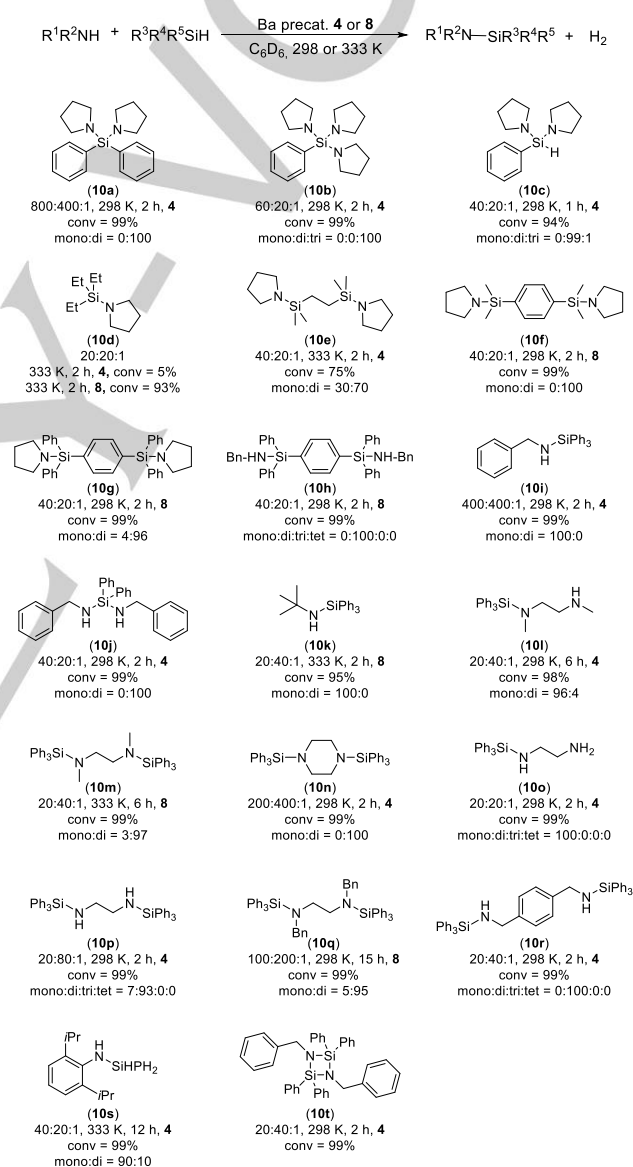
**Table 1.** Alkaline-earth catalyzed cross-dehydrocoupling of pyrrolidine and triphenylsilane<sup>[a]</sup>

Entry	Precatalyst	Time [min]	Conv. [%] <sup>[b]</sup>	TOF [ $\text{h}^{-1}$ ] <sup>[c]</sup>
1	1	15×60	2	0.5
2	2	15×60	72	19
3	3	15×60	99	26
4	4	5	53	2544
5	4	15	99	1584
6	5	15×60	42	11
7	6	15×60	74	20
8	7	15	32	512
9	7	2×60	94	188
10	8	5	75	3600
11	8	15	99	1584
12	9	15	54	864

[a] Reactions carried out at 298 K in  $\text{C}_6\text{D}_6$  (0.5 mL), with [pyrrolidine]<sub>0</sub>/[Ph<sub>3</sub>SiH]<sub>0</sub>/[precatalyst]<sub>0</sub> = 400:400:1 and [Ae]<sub>0</sub> = 10.0 mM; reactions times were not optimized. [b] Conversion of Ph<sub>3</sub>SiH determined by <sup>1</sup>H NMR spectroscopy. [c] Turnover frequency.

The reactions were carried out in  $\text{C}_6\text{D}_6$ , but experiments showed that identical results were obtained in the more polar  $\text{C}_6\text{D}_5\text{Cl}$  and mixtures of  $\text{C}_6\text{D}_6$  and 1,2- $\text{F}_2\text{-C}_6\text{H}_4$ . The choice of the precatalyst (**4** vs. **8**) was dictated by the selectivity that was sought, and/or by the reactivity of the substrates. Overall, the catalytic activities and chemoselectivity are excellent. Like Ph<sub>3</sub>SiH, mono- and diarylhydrosilanes react readily with pyrrolidine (**10a–10c**); the reaction of PhSiH<sub>3</sub> with pyrrolidine (HN(CH<sub>2</sub>)<sub>4</sub>) can be selectively oriented towards PhSi(N(CH<sub>2</sub>)<sub>4</sub>)<sub>3</sub> (**10b**) or PhSiH(N(CH<sub>2</sub>)<sub>4</sub>)<sub>2</sub> (**10c**). By comparison, the reactions with trialkylhydrosilanes are sluggish (**10d–10e**) and require forcing conditions. The presence of one or more aromatic rings thus improves reactions rates. This holds also true for  $\text{HR}_2\text{Si}^{\wedge\wedge}\text{SiR}_2\text{H}$ : **10f**, **10g** and even **10h** (where benzylamine replaced pyrrolidine) can be readily obtained with high selectivities. Benzylamine is a reactive substrate, and the syntheses of BnNHSiPh<sub>3</sub> (**10i**) and Ph<sub>2</sub>Si(NHBn)<sub>2</sub> (**10j**) are achieved quantitatively and selectively, even with high substrate loading for **10i**. On the other hand, bulky (*t*BuNH<sub>2</sub>, for **10k**) or poorly nucleophilic (anilines, for **10s**) amines are less reactive: even if they are selective towards the mono-coupled silazanes, the reactions necessitate careful control of more forcing experimental conditions. HN(SiMe<sub>3</sub>)<sub>2</sub> and Ph<sub>3</sub>CNH<sub>2</sub> showed no or limited reactivity.<sup>[18]</sup> Diamines are valuable substrates. Even at low precatalyst loading, the reactions of piperazine or BnNHCH<sub>2</sub>CH<sub>2</sub>NHBn with Ph<sub>3</sub>SiH afford the di-coupled products **10n** and **10q**, respectively. The catalyzed reaction of Ph<sub>3</sub>SiH and *N,N'*-dimethylethylenediamine can conveniently be directed towards the mono- or the di-coupled products **10l** and **10m**,

respectively, by tuning of the experimental conditions. Besides, depending solely on the initial ratio of the substrates, the reaction of ethylenediamine and Ph<sub>3</sub>SiH affords either the mono- or the di-coupled products (**10o** and **10p**, respectively); coupling occurs only once on each N atom, and irrespective of the initial contents in Ph<sub>3</sub>SiH, further dehydrocoupling giving (Ph<sub>3</sub>Si)<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NH(SiPh<sub>3</sub>) is not observed. Similarly, the reaction of *p*-xylylenediamine and Ph<sub>3</sub>SiH only generates the *N,N'*-disilazane **10r**. Interestingly, further reaction of **10j** (20 equiv) with Ph<sub>2</sub>SiH<sub>2</sub> (40 equiv) affords the four-member cycle **10t**. Overall, the combination of activity, productivity and chemoselectivity displayed by the barium compounds **4** and **8** to produce the silazanes **10a–10t**, many of which are accessed by CDC processes for the first time, is unique.



**Figure 1.** Barium-catalyzed coupling of amines and silanes. Reactions carried out in  $\text{C}_6\text{D}_6$ , using precatalysts **4** or **8**. For each product (**10a–10r**) are indicated the [amine]<sub>0</sub>/[silane]<sub>0</sub>/[precatalyst]<sub>0</sub> contents, reaction temperature and time, precatalyst, conversion of the substrates and chemoselectivity between mono-, di-, tri- and tetra-silazane products.

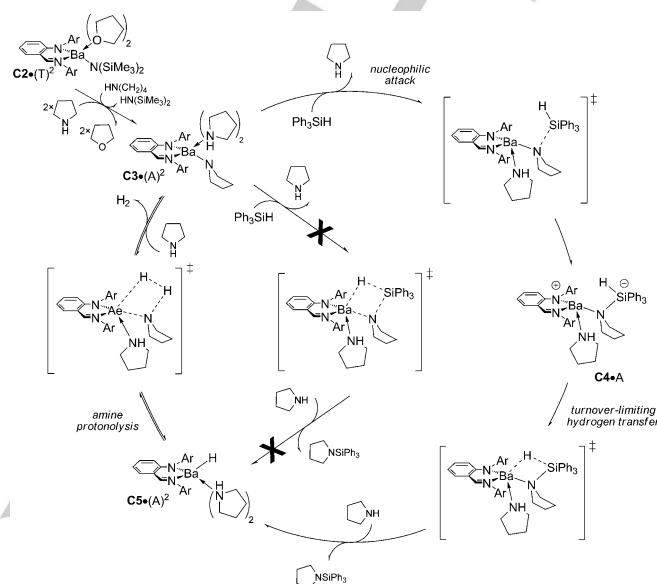
Kinetic analysis of the benchmark coupling of pyrrolidine and triphenylsilane catalyzed by **7** – a slower Ba precatalyst which lends itself well to kinetic monitoring – was performed in C<sub>6</sub>D<sub>6</sub> at 298 K; details are provided in the Supporting information. The catalyzed reaction proceeded with first-order kinetics in [**7**] over a 15-fold concentration range. Further experiments using a 21-fold excess of silane vs. HN(CH<sub>2</sub>)<sub>4</sub> indicated a partial zeroth kinetic order in [HN(CH<sub>2</sub>)<sub>4</sub>]; partial first order in [Ph<sub>3</sub>SiH] was deduced from the reverse experiments. The second-order kinetic rate law hence obeys  $-d[\text{Ph}_3\text{SiH}]/dt = k[\text{Ba}]^1 \cdot [\text{Ph}_3\text{SiH}]^1 \cdot [\text{HN}(\text{CH}_2)_4]^0$ , with  $k = 4.801(13) \cdot 10^{-3} \text{ M}^{-1} \cdot \text{s}^{-1}$ . It matches that found by Sadow for his Mg complex<sup>[13a]</sup> but differs from those reported by Hill for his amido precatalysts.<sup>[13b]</sup> A primary kinetic isotope effect (KIE) of  $k_{\text{H}}/k_{\text{D}} = 7.8(1)$  was measured for the coupling of Ph<sub>3</sub>SiD and HN(CH<sub>2</sub>)<sub>4</sub>,<sup>[19]</sup> whereas none was found in the catalyzed reaction of Ph<sub>3</sub>SiH and DN(CH<sub>2</sub>)<sub>4</sub> ( $k_{\text{H}}/k_{\text{D}} = 1.1(1)$ ). These measurements are consistent with the kinetic rate law and indicate Si–H bond breaking to be a key event in the rate-determining step. The activation parameters for this reaction were derived from Arrhenius and Eyring analyses:  $E_{\text{a}} = 16.2(23) \text{ kcal} \cdot \text{mol}^{-1}$ ,  $\Delta H^{\ddagger} = 15.6(23) \text{ kcal} \cdot \text{mol}^{-1}$  and  $\Delta S^{\ddagger} = -13.3(7.5) \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ , i.e.  $\Delta G_{298}^{\ddagger} = 19.6(1) \text{ kcal} \cdot \text{mol}^{-1}$  at 298 K. The negative value of  $\Delta S^{\ddagger}$  indicates an associative mechanism, but it is small compared to those reported for other Mg–Sr precatalysts;<sup>[13]</sup> this is possibly to be related to the very large size of the Ba<sup>2+</sup> ion ( $r_{\text{ionic}} = 1.38 \text{ \AA}$ ), which may induce a less constrained arrangement for the transition state.

Electronic effects were assessed by changing the substituent at the *para* position of one of the aromatic rings in the organosilane. The data for the CDC of HN(CH<sub>2</sub>)<sub>4</sub> with Ph<sub>2</sub>(*p*-X-C<sub>6</sub>H<sub>4</sub>)SiH catalyzed by **7** under standard conditions, where X is either OMe, Me, H, F or CF<sub>3</sub>, showed that the reaction rate increased substantially for electron-withdrawing *p*-substituents, and varied according to X = OMe < Me < H < F < CF<sub>3</sub>. Hammett analysis of the linear plot  $\ln(k_{\text{H}}/k_{\text{X}}) = \rho(X) \cdot \rho$  revealed a large, positive slope of  $\rho = 2.0(10)$ , an evidence that electron-withdrawing para groups help lower the activation barrier and accelerate the reaction rate through stabilization of a developing negative charge.

On the basis of these kinetic data, the generation of silazane products (**P**) can be envisioned proceeding through stepwise or concerted pathways to furnish a [Ba] hydride intermediate, which is transformed back into the barium pyrrolide compound thereafter (Scheme 1). In an attempt to further inform our understanding, the CDC of pyrrolidine ( $\equiv$  **A**) and Ph<sub>3</sub>SiH ( $\equiv$  **S**) by {N^N}Ba{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF)<sub>2</sub> (**7**, denoted thereafter as **C2**·(T)<sub>2</sub>) has been subjected to thorough computational examination. We have studied various mechanistic pathways conceivable for either a [Ba]-pyrrolide or -silyl representing the catalytically competent compound with the aid of a reliable DFT methodology (dispersion-corrected B97-D3 in conjunction with basis sets of triple- $\zeta$  quality and a sound treatment of bulk solvent effects), which has been demonstrated before to reliably map the energy landscape of Ae-mediated hydroamination.<sup>[14h,i]</sup> It enables us to exclude all but one mechanistic pathways, involving nucleophilic attack of the amido at the silane and subsequent hydrogen transfer to the Ba center, which accounts for all the key features observed.

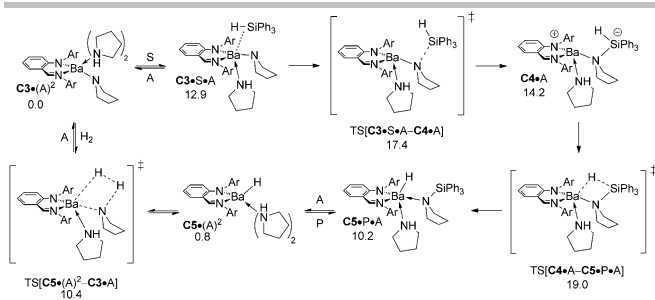
Scheme 1 depicts the mechanistic pathway that prevails for CDC of amines with silanes by the iminoanilide barium-silazanido precatalyst **7** ( $\equiv$  **C2**·(T)<sub>2</sub>). The initial conversion of **C2**·(T)<sub>2</sub> into the {N^N}Ba-pyrrolide compound, which is predominantly present as bis-amine adduct **C3**·(A)<sub>2</sub> and shows further-

more no propensity toward dimer formation, is sufficiently facile kinetically, as revealed by a recent computational study of the hydroamination of styrene catalyzed by **7**.<sup>[14h]</sup> As far as catalytically competent silane adducted species (**C3**·S·(A)<sup>n</sup>) are concerned, a single adducted pyrrolidine molecule stabilizes **C3**·S greatly, whilst the presence of the rather bulky Ph<sub>3</sub>SiH prevents the {N^N}Ba center to accommodate a second amine molecule.



**Scheme 1.** Proposed mechanism for cross-dehydrocoupling of amines and silanes mediated by an iminoanilide barium silazanido precatalyst.

The energetically prevalent mechanism (Figure 2) sees the initial nucleophilic attack of the barium amido to the silane to furnish a transient silicate intermediate **C4** to be followed by hydrogen transfer to barium, hence affording {N^N}Ba hydride **C5** with the release of the silazane product (**P**). The most accessible pathway commencing from **C3**·S·(A)<sup>n</sup>, featuring an only loosely associated silane molecule, benefits from the participation of one associated pyrrolidine spectator molecule on both kinetic and thermodynamic grounds. The initial N–Si bond-forming nucleophilic attack of the barium-pyrrolide is seen to be kinetically affordable ( $\Delta G^{\ddagger} = 17.4 \text{ kcal} \cdot \text{mol}^{-1}$  relative to **C3**·(A)<sub>2</sub>, Figure 2). It is linked to the energetically more demanding hydrogen transfer to barium ( $\Delta G^{\ddagger} = 19.0 \text{ kcal} \cdot \text{mol}^{-1}$  relative to **C3**·(A)<sub>2</sub>), via a transient metastable silicate intermediate, featuring a five-coordinate silicon center. Figure 2 reveals that the silazane **P** is likely displaced readily at the bis-amine adducted {N^N}Ba hydride (**C5**·(A)<sub>2</sub>) by incoming amine. The stepwise **C3**·(A)<sub>2</sub> → **C3**·S·A → **C4**·A → **C5**·P·A → **C5**·(A)<sub>2</sub> formation of the silazane product is virtually thermoneutral, with the second slow hydrogen transfer to Ba dictating the kinetics of this transformation.



**Figure 2.** Prevalent mechanistic pathway for cross-dehydrocoupling of pyrrolidine and triphenylsilane by an iminoanilide barium-pyrrolide catalyst complex.

It is worth noting that all our attempts to localize a low-energy TS structure describing Ba–N/Si–H  $\sigma$ -bond-breaking metathesis, hence describing a concerted process analogue (cf. Scheme 1), have been unsuccessful. It can thus be concluded with some level of confidence that such process would require a much higher, insurmountable barrier to overcome and is thus unlikely to have any relevance for catalyst turnover.

The ensuing protonolysis of the pyrrolidine by the  $\{N^*N\}$ Ba-hydride converts **C5** back into the catalytically competent  $\{N^*N\}$ Ba-pyrrolide complex for another catalyst turnover through the release of one equiv of H<sub>2</sub>. Similar to what has been found for the stepwise silazane formation, another adducted amine spectator molecule facilitates the process. Pyrrolidine **C5**\*(A)<sub>2</sub> (+A)  $\rightarrow$  **C3**\*(A)<sub>2</sub> + H<sub>2</sub> protonolysis is kinetically easy ( $\Delta G^\ddagger = 11.2$  kcal.mol<sup>-1</sup> relative to **C5**\*(A)<sub>2</sub>, Figure 1) and almost thermoneutral. Hence,  $\{N^*N\}$ Ba-hydride (**C5**\*(A)<sub>2</sub>) and -pyrrolide (**C3**\*(A)<sub>2</sub>) compounds can be expected to readily interconvert, participating in a mobile equilibrium.

Our collective experimental and computational approach provided compelling evidence in support of the prevailing mechanism to be a stepwise pathway (cf. Scheme 1) comprising of N–Si bond forming nucleophilic attack of the barium-pyrrolide at the silane and subsequent turnover-limiting hydrogen transfer to the Ba center, to be linked to kinetically easy amine protonolysis, for cross-dehydrocoupling of amines and organosilanes in the presence of a catalytically competent iminoanilide barium-amide and barium-alkyl compounds. The turnover-limiting hydrogen transfer accounts for the substantial primary KIE and rate acceleration observed for an electron-withdrawing silane *para*-substituent; its DFT-derived barrier satisfactorily matches empirically determined Eyring parameters. A similar mechanism has been proposed for To<sup>M</sup>-magnesium catalysts,<sup>[13a]</sup> but where nucleophilic attack is turnover limiting.<sup>[19]</sup>

In conclusion, barium precatalysts, especially simple homoleptic dialkyls, exhibit unique activities and selectivities towards a broad variety of substrates in the cross-dehydrocoupling of amines and silanes; key mechanistic features have been delineated. We are now implementing this catalysis to synthesize polymeric materials, and to produce dissymmetric polysilazanes by multiple sequential CDC of different primary diamines and dihydrosilanes.

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**Keywords:** barium and alkaline earths • DFT • cross-dehydrocoupling • amines/hydrosilanes • mechanisms

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- [15] This finding contrasts with Hill's report on Ae{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> CDC precatalysts, for which activity increased with Ae = Mg < Sr < Ca, ref. [13b]. Under our experimental conditions ([Ph<sub>3</sub>SiH]<sub>0</sub>/[HN(CH<sub>2</sub>)<sub>4</sub>]<sub>0</sub>/[Ae]<sub>0</sub> = 400:400:1, 298 K, C<sub>6</sub>D<sub>6</sub>), we found that Ae{N(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub> (Ae = Ca–Ba) and their THF adducts **2–4** featured almost identical catalytic activities.
- [16] When Ph<sub>3</sub>SiH was replaced at 333 K by the far less reactive Et<sub>3</sub>SiH under otherwise identical conditions, **8** and **4** achieved respectively 93% and 5% conversion of the substrates.
- [17] Ba(SiPh<sub>3</sub>)<sub>2</sub>\*(THF)<sub>3</sub>, obtained in THF from BaI<sub>2</sub> and KSiPh<sub>3</sub>, does not catalyze the reaction of Ph<sub>3</sub>SiH and pyrrolidine.
- [18] The reactions of HN(SiMe<sub>3</sub>)<sub>2</sub> (20 equiv vs. **4**) or Ph<sub>3</sub>CNH<sub>2</sub> (20 equiv vs. **8**) with Ph<sub>3</sub>SiH (20 equiv) at 333 K gave respectively 0% and 24% con-

version. The absence of reactivity of  $\text{HN}(\text{SiMe}_3)_2$  with the bulky triphenylsilane was reported for  $\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2$ , ref. [13b].

- [19] By contrast, no significant KIE was found for the reaction between  $\{\text{To}^{\text{M}}\}\text{MgNHtBu}$  and  $\text{PhMeSiD}_2$  at 0 °C:  $k_{\text{H}}/k_{\text{D}} = 1.0(2)$ , ref. [13a].

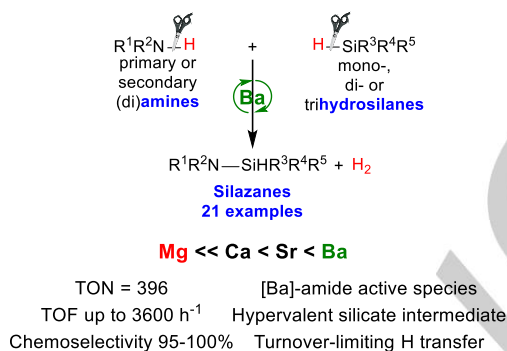
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## Entry for the Table of Contents

## COMMUNICATION

Barium and alkalino-earth complexes are very active, productive and chemoselective precatalysts (TON = 396, TOF up to 3600 h<sup>-1</sup>; Ca < Sr < Ba) for the N–H/H–Si cross-dehydrocoupling of (di)amines with (di)hydrosilanes. The mechanisms have been elucidated by combining DFT and experimental data.

## BARIUM catalyzed CROSS DEHYDROCOUPLING



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Barium-mediated cross-dehydrocoupling of hydrosilanes with amines – A complementary approach by theory and experiment