Synthetic Methods

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Barium-Mediated Cross-Dehydrocoupling of Hydrosilanes with Amines: A Theoretical and Experimental Approach**

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Abstract: *Alkaline-earth (most prominently barium) complexes of the type* $[Ae\{N(SiMe_3)_2\}_2\cdot(THF)_x]$ *and* $[\{N^\wedge N\}Ae\{N(SiMe_3)_2\}\cdot(THF)_x]$ *are very active and productive precatalysts (TON = 396, TOF up to 3600* h^{-1}*; 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 by nucleophilic attack of a metal amide at the incoming silane and subsequent turnover-limiting hydrogen transfer to the metal center.*

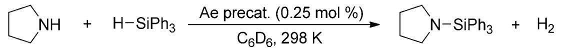
Silazanides are valuable compounds used as ligands in coordination chemistry,[1] as bases,[2] O−Si silylating agents,[3] or protecting groups in organic synthesis.[4] In addition, oligo- and polysilazanes constitute excellent precursors of Si_3N_4 ceramics.[5] Historical protocols for the production of silazanes involving metalation of amines or aminolysis of chlorosilanes,[6] which generate stoichiometric amounts of salts or HCl by-products, are being replaced by catalyzed reactions. Although dependent on ready access to a broad range of hydrosilanes, the catalyzed N−H/H−Si cross-dehydrocoupling (CDC) of hydrosilanes and HNR^1R^2 amines (R^1, R^2 = H, alkyl, aryl), with H_2 being the sole by-product, is an effective catalytic process. While this catalysis was at first dominated by simple alkali hydrides[5a,d] or middle- and late-transition-metal species,[4a,b,5b,7] some breakthroughs have now been achieved using borane organocatalysts[4d,8] or complexes built on ions of oxophilic metals, for example, Al^{3+},[9] Yb^{2+},[10] U^{4+},[11] Zn^{2+},[12] and Ae^{2+} (Ae = alkaline earth).[10b,13] However, high catalytic activity and selectivity, for example, 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 promising. Notably, Sadow's tris(oxazolinyl)borato (To^M) magnesium precatalyst couples either primary amines, ammonia, or hydrazine with phenyl-substituted hydrosilanes.[13a] Hill et al. have shown that $[Ae\{N(SiMe_3)_2\}_2]$ (Ae = Mg, Ca, Sr) operates under mild reaction conditions, with the Ca precatalyst outperforming its Mg and Sr congeners.[13b] As is often found in Ae-mediated catalysis,[14] several subtleties linked to the size and charge density of the Ae metal under consideration were revealed upon investigating the mechanism. However, no precatalyst of the larger Ba is known to date for the CDC of amines and hydrosilanes. We report herein that highly active and selective Ba complexes surpass their Ca and Sr analogues in the catalysis of N−H/H−Si CDC reactions. The main mechanistic features are delineated by combining experimental data and DFT computations.

The bis(amido) compounds $[Ae\{N(SiMe_3)_2\}_2\cdot(THF)_x]$ (x = 0 for Ae = Mg, **1**; x = 2 for Ae = Ca, **2**; Sr, **3**; Ba, **4**) and their derivatives bearing an iminoanilido ligand $[\{N^\wedge N\}Ae\{N(SiMe_3)_2\}\cdot(THF)_x]$ (Ae = Ca, x = 1, **5**; Sr, x = 2, **6**; Ba, x = 2, **7**; $\{N^\wedge N\}^- = [ArN(o\text{-}C_6H_4)C(H)=NAr]^-$ with Ar = 2,6-$iPr_2C_6H_3$)[14d] all catalyze the CDC of pyrrolidine and triphenylsilane at 25 °C, with a metal loading as low as 0.25 mol% (Table 1). The synthetically more demanding barium alkyl complexes $[Ba\{CH(SiMe_3)_2\}_2\cdot(THF)_3]$ (**8**) and $[\{N^\wedge N\}Ba\{CH(SiMe_3)_2\}\cdot(THF)_2]$ (**9**)[14e] also proved very effective.

Key trends for the Ae-mediated CDC coupling of amines and hydrosilanes, which must be used as purified, dry substrates, emerge from Table 1 1) For both families of

Table 1: Alkaline-earth-catalyzed cross-dehydrocoupling of pyrrolidine and triphenylsilane.[a]



Entry	Precatalyst	t [min]	Conv. [%][b]	TOF [h^{-1}][c]
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 at 298 K in C_6D_6 (0.5 mL), with $[HN(CH_2)_4]_0/[Ph_3SiH]_0/[precatalyst]_0$ = 400:400:1 and $[Ae]_0$ = 10.0 mM; reactions times not optimized. [b] Conversion of Ph_3SiH determined by ^1H NMR spectroscopy. [c] Turnover frequency.

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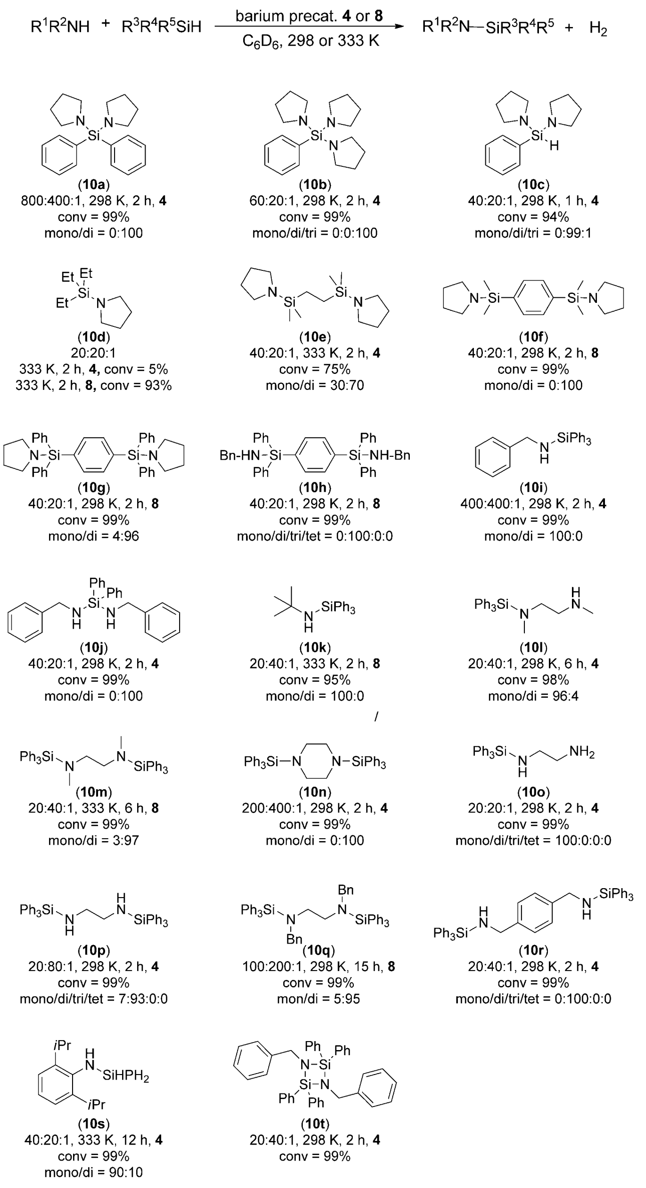
precatalysts, the catalytic activity increases with metal size, electropositivity, and polarizability according to Mg ≪ Ca < Sr < Ba; barium is the metal of choice for this catalysis.[15] The most active precatalysts are **4** and **8**, which fully convert the substrates within 15 minutes and displayed a unique combination of productivity (TON = 396) and activity (TOF up to 3600 h^{-1}). 2) The simple bis(amido) and bis(alkyl) barium precatalysts **4** and **8**, respectively, perform better than their derivatives incorporating the bulky iminoanilide (**7** and **9**), and hence the use of ancillary ligands is not mandatory. 3) The barium alkyl precatalysts are more active than their amido derivatives.[16] The superiority of barium alkyl precatalysts as opposed to amido ones is attributed to the greater basicity of the alkyl group, thus resulting in the formation of a larger amount of barium pyrrolido species which are thought to be the catalytically active species.[17] Along these line, the stoichiometric reaction of pyrrolidine [HN(CH$_2$)$_4$] with **9** yields a barium pyrrolido compound upon release of CH$_2$(SiMe$_3$)$_2$, whereas **7** reacts to give [{N^N}Ae{N(SiMe$_3$)$_2$}·{HN(CH$_2$)$_4$}$_2$] upon displacement of THF, without evidence for aminolysis of the Ba–N(SiMe$_3$)$_2$ bond. Moreover, the NMR-scale reaction (C$_6$D$_6$, 25 °C) of two equivalents of pyrrolidine with **8** releases CH$_2$(SiMe$_3$)$_2$ quantitatively, whereas with **4** the evolution of free HN(SiMe$_3$)$_2$ cannot be detected.

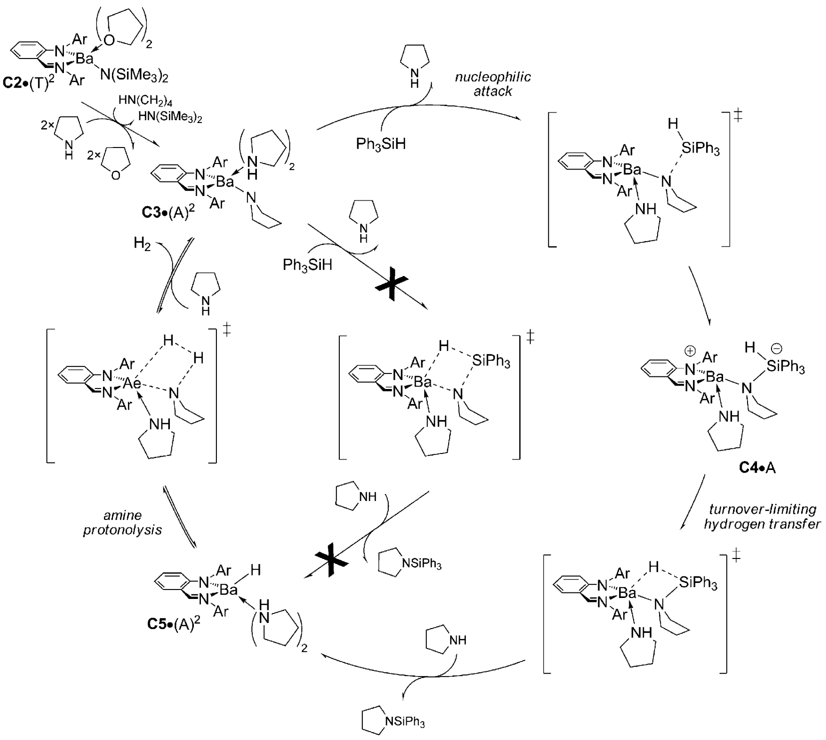
The substrate scope was probed with the barium precatalysts **4** and **8**, by employing, in particular, substrates with multiple reactive sites. For example, HR$_2$Si^^^SiR$_2$H, H$_x$SiR$_{4-x}$ ($x \geq 2$), and/or primary amines, for which chemoselectivity is a key aspect (Scheme 1).

The reactions were carried out in C$_6$D$_6$, but identical results were obtained in C$_6$D$_5$Cl and mixtures of C$_6$D$_6$ and 1,2-F$_2$-C$_6$H$_4$. The choice of the precatalyst (**4** versus **8**) was dictated by the selectivity that was sought and by the reactivity of the substrates. Like Ph$_3$SiH, mono- and diarylhydrosilanes react readily with pyrrolidine (**10 a–c**). The reaction of PhSiH$_3$ with HN(CH$_2$)$_4$ can be selectively oriented towards PhSi{N(CH$_2$)$_4$}$_3$ (**10 b**) or PhSiH{N(CH$_2$)$_4$}$_2$ (**10 c**). By comparison, the reactions with trialkylhydrosilanes are sluggish (**10 d**,**e**); the presence of aromatic ring(s) thus improves reactions rates. This reactivity is also true for HR$_2$Si^^^SiR$_2$H: **10 f**, **10 g**, and even **10 h** [where BnNH$_2$ replaced HN(CH$_2$)$_4$] can be obtained with high selectivities. BnNH$_2$ is a reactive substrate, and the syntheses of BnNHSiPh$_3$ (**10 i**) and Ph$_2$Si(NHBn)$_2$ (**10 j**) are achieved quantitatively and selectively, even with high substrate loading for **10 i**. In contrast, bulky (*t*BuNH$_2$, for **10 k**) or poorly nucleophilic (anilines, for **10 s**) amines are less reactive: even if they are selective towards the monocoupled silazanes, the reactions necessitate careful control of more forcing experimental conditions. HN(SiMe$_3$)$_2$ and Ph$_3$CNH$_2$ showed no or limited reactivity.[18] Diamines are valuable substrates. Even at low precatalyst loading, the reactions of piperazine or BnNHCH$_2$CH$_2$NHBn with Ph$_3$SiH afford the dicoupled products **10 n** and **10 q**, respectively. The catalyzed reaction of Ph$_3$SiH and *N*,*N'*-dimethylethylenediamine can be directed towards the mono- or the dicoupled products **10 l** and **10 m**, respectively, by tuning of the experimental conditions. Besides, depending solely on the initial ratio of substrates, the reaction of H$_2$NCH$_2$CH$_2$NH$_2$ and Ph$_3$SiH affords either the mono- or the dicoupled products (**10 o** and **10 p**, respectively). Coupling occurs only once on each N atom, and further dehydrocoupling, giving (Ph$_3$Si)$_2$NCH$_2$CH$_2$NH(SiPh$_3$), is never observed. The reaction of *p*-xylylenediamine and Ph$_3$SiH only generates the *N*,*N'*-disilazane **10 r**. Further reaction of **10 j** (20 equiv) with Ph$_2$SiH$_2$ (40 equiv) affords the four-membered cycle **10 t**. Overall, the combination of activity, productivity, and chemoselectivity displayed by the barium compounds **4** and **8** to produce the silazanes **10 a–t**, many of which are accessed by CDC processes for the first time, is unique.



Scheme 1. Barium-catalyzed CDC of amines and silanes. Reactions in C$_6$D$_6$ using precatalysts **4** or **8**. For each product (**10 a–t**), the [amine]$_0$/[silane]$_0$/[precat]$_0$ content, reaction temperature and time, precatalyst, substrate conversion, and chemoselectivity between mono-, di-, tri-, and tetrasilazane products are given. The conversion and chemoselectivity were determined by NMR spectroscopy.

Kinetic analysis of the benchmark coupling of $HN(CH_2)_4$ and Ph_3SiH catalyzed by **7**, a slower barium precatalyst which lends itself well to kinetic monitoring, was performed in C_6D_6 at 298 K. The catalyzed reaction proceeded with first-order kinetics in [**7**] over a 15-fold concentration range. Additional experiments using a 21-fold excess of silane versus $HN(CH_2)_4$ indicated a partial zeroth order in $[HN(CH_2)_4]$, and a partial first-order in $[Ph_3SiH]$ was deduced from the reverse experiments. The second-order kinetic rate law thus obeys $-d[Ph_3SiH]/dt = k[Ba]^1[Ph_3SiH]^1[HN(CH_2)_4]^0$, with $k = 4.801(13)\times10^{-3}\,M^{-1}\,s^{-1}$. It matches that found by Sadow and co-workers for their magnesium complex[13a] but differs from those reported by Hill et al. for amido precatalysts.[13b] A primary kinetic isotope effect (KIE) of $k_H/k_D = 7.8(1)$ was measured for the coupling of Ph_3SiD and $HN(CH_2)_4$,[19] whereas none was found in the catalyzed reaction of Ph_3SiH and $DN(CH_2)_4$ $[k_H/k_D = 1.1(1)]$. 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: $E_a = 16.2\pm2.3$ kcal mol^{-1}, $\Delta H^{\neq} = 15.6\pm2.3$ kcal mol^{-1}, and $\Delta S^{\neq} = -13.3\pm0.7$ cal mol^{-1} K^{-1}, that is, $\Delta G_{298}{}^{\neq} = 19.6\pm0.1$ kcal mol^{-1} at 298 K. The value of $\Delta S^{\neq}$ indicates an associative mechanism, but it is small compared to those given for Mg and Sr precatalysts,[13] and may reflect that the large size of the Ba^{2+} ion ($r_{ionic} = 1.38$ Å) induces a less constrained arrangement in the transition state.



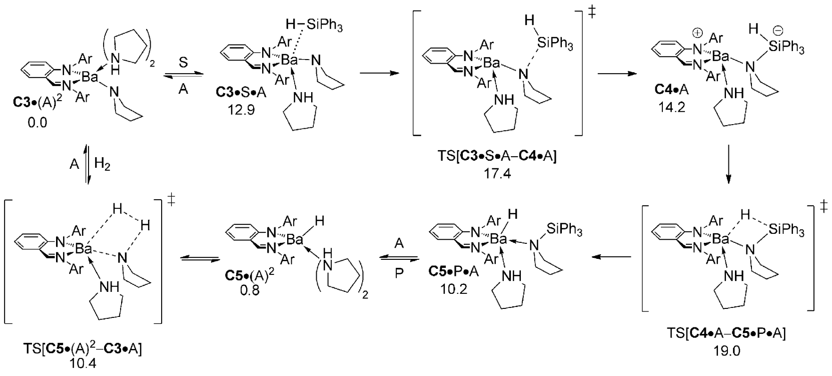
Scheme 2. Proposed mechanism for cross-dehydrocoupling of amines and silanes mediated by an iminoanilide barium silazanido precatalyst.

Electronic effects were assessed by changing the substituent at the *para* position of one of the aromatic rings in the hydrosilane. The data for the CDC of $HN(CH_2)_4$ with $Ph_2(p\text{-}X\text{-}C_6H_4)SiH$ catalyzed by **7** under standard reaction conditions, where X is either OMe, Me, H, F, or CF_3, showed that the reaction rate increased for electron-withdrawing *p*-substituents, and varied according to $X = OMe < Me < H < F < CF_3$. Hammett analysis of the linear plot $\ln(k_H/k_X) = \sigma_p(X)\rho$ revealed a large, positive slope of $\rho = 2.0\pm1.0$, evidence that electron-withdrawing groups at the *para* position lower the activation barrier through stabilization of a developing negative charge.

On the basis of these kinetic data, the generation of silazane products (**P**) can be envisioned to proceed through either stepwise or concerted pathways to furnish a barium hydrido intermediate, which is transformed into the barium pyrrolido compound thereafter (Scheme 2). In an attempt to further inform our understanding, the CDC of pyrrolidine (**A**) and Ph_3SiH (**S**) by $[\{N^\wedge N\}Ba\{N(SiMe_3)_2\}\cdot(THF)_2]$ (**7**, denoted thereafter as **C2**$\cdot(T)^2$) was subjected to thorough computational examination. We studied various mechanistic pathways conceivable for either a barium pyrrolide or barium 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-ζ quality and a sound treatment of bulk solvent effects), which has been demonstrated to reliably map the energy landscape of Ae-mediated hydroamination.[14f,g] It enables us to exclude all but one mechanistic pathway which involves nucleophilic attack of the amide at the silane and subsequent hydrogen transfer to the Ba center, and it accounts for all the key features observed.

Scheme 2 depicts the mechanistic pathway that prevails for CDC of amines with silanes by the iminoanilide barium silazanido precatalyst **7** ($\equiv$ **C2**$\cdot(T)^2$). The initial conversion of **C2**$\cdot(T)^2$ into the {N^N}barium pyrrolide compound, which is predominantly present as the bis(amine) adduct **C3**$\cdot(A)^2$ and shows no propensity toward dimer formation, is sufficiently facile kinetically, as revealed by a recent computational study of the hydroamination of styrene catalyzed by **7**.[14f] As far as catalytically competent silane adducted species (**C3**$\cdot$S$\cdot(A)^n$) are concerned, a single adducted pyrrolidine molecule stabilizes **C3**$\cdot$S greatly, whilst the presence of the rather bulky Ph_3SiH prevents the {N^N}Ba center from accommodating a second amine molecule.

The energetically prevalent mechanism (Scheme 3) involves the initial nucleophilic attack of the barium amido at the silane to furnish the transient silicate intermediate **C4**, with subsequent hydrogen transfer to barium, thus affording the {N^N}barium hydride **C5** with the release of the silazane product **P**. The most accessible pathway commencing from **C3**$\cdot$S$\cdot(A)^n$, featuring an only loosely associated silane molecule, benefits from the participation of one associated



Scheme 3. Prevalent mechanistic pathway for cross-dehydrocoupling of pyrrolidine and triphenylsilane by an iminoanilide barium pyrrolide catalyst complex.

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 ($\Delta G^{\neq} = 17.4\,\mathrm{kcal\,mol^{-1}}$ relative to **C3**·(A)^2). It is linked to the energetically more demanding hydrogen transfer to barium ($\Delta G^{\neq} = 19.0\,\mathrm{kcal\,mol^{-1}}$ relative to **C3**·(A)^2), via a transient metastable silicate intermediate featuring a five-coordinate silicon center. Scheme 3 reveals that **P** is likely displaced readily at the bis(amine) adducted {N^N}barium hydride (**C5**·(A)^2) by an incoming amine. The stepwise **C3**·(A)^2→**C3**·S·A→**C4**·A→**C5**·P·A→**C5**·(A)^2 formation of the silazane product is virtually thermoneutral, with the second slow hydrogen transfer to barium dictating the kinetics of this reaction.

All our attempts to localize a low-energy TS structure describing Ba–N/Si–H σ-bond-breaking metathesis, thus describing a concerted process analogue (see Scheme 2), have been unsuccessful. It can thus confidently be concluded that such a 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}barium hydride converts **C5** back into the catalytically competent {N^N}Ba pyrrolide complex for another catalyst turnover through the release of one equivalent of H_2. Similar to what has been found for the stepwise silazane formation, another adducted amine spectator molecule facilitates the process. The pyrrolidine **C5**·(A)^2 (+A)→**C3**·(A)^2 + H_2 protonolysis is kinetically easy ($\Delta G^{\neq} = 11.2\,\mathrm{kcal\,mol^{-1}}$ relative to **C5**·(A)^2; Scheme 3) and almost thermoneutral. Hence, the {N^N}barium hydride **C5**·(A)^2 and {N^N}barium pyrrolide **C3**·(A)^2 compounds can readily interconvert, thus participating in a mobile equilibrium.

In conclusion, barium precatalysts exhibit unique activities and selectivities towards a broad range of substrates in the cross-dehydrocoupling of amines and hydrosilanes. Our collective experimental and computational approach provide compelling evidence in support of the prevailing mechanism being a stepwise pathway comprising N–Si bond-forming nucleophilic attack of the barium pyrrolide at the silane and subsequent turnover-limiting hydrogen transfer to the Ba center. This step is linked to kinetically easy amine protonolysis for CDC of amines and organosilanes in the presence of 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 a silane having an electron-withdrawing group at the *para* position. Its DFT-derived barrier satisfactorily matches empirically determined Eyring parameters. A similar mechanism has been proposed for To^M magnesium catalysts,[13a] but where nucleophilic attack is turnover limiting.[19] We are now implementing this catalysis to obtain polymeric materials, and to produce dissymmetric polysilazanes by stepwise CDC of primary diamines and dihydrosilanes.

Keywords: amines · alkaline earth metals · barium · density functional calculations · reaction mechanisms

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[15] This finding contrasts with Hill's report on $[Ae\{N(SiMe_3)_2\}_2]$ CDC precatalysts, for which activity increased with $Ae = Mg < Sr < Ca$; Ref. [13b]. Under our experimental conditions ($[Ph_3SiH]_0/[HN(CH_2)_4]_0/[Ae]_0 = 400{:}400{:}1$, 298 K, C_6D_6), we found that $[Ae\{N(SiMe_3)_2\}_2]$ ($Ae = Ca$–Ba) and their THF adducts **2**–**4** behaved almost identically.

[16] When, other things being equal, Ph_3SiH was replaced at 333 K by the less reactive Et_3SiH, **8** and **4** gave respectively 93 and 5% conversion.

[17] $[Ba(SiPh_3)_2\cdot(THF)_3]$, obtained in THF from BaI_2 and $KSiPh_3$, does not catalyze the reaction of Ph_3SiH and pyrrolidine.

[18] The reactions of $HN(SiMe_3)_2$ (20 equiv vs. **4**) or Ph_3CNH_2 (20 equiv vs. **8**) with Ph_3SiH (20 equiv) at 333 K gave respectively 0 and 24% conversion. The absence of reactivity of $HN(SiMe_3)_2$ with Ph_3SiH was reported for $[Ae\{N(SiMe_3)_2\}_2]$; Ref. [13b].

[19] No significant KIE was found for the reaction between $\{To^M\}MgNHtBu$ and $PhMeSiD_2$ at 273 K: $k_H/k_D = 1.0(2)$; Ref. [13a].

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