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Cross-Coupling

Sequential Barium-Catalysed N–H/H–Si Dehydrogenative Cross-Couplings: Cyclodisilazanes versus Linear Oligosilazanes

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Abstract: Starting from Ph_3SiH, the barium precatalyst $Ba[CH(SiMe_3)_2]_2{\cdot}(THF)_3$ was used to produce the disilazane $Ph_3SiN(Bn)SiPh_2NHBn$ (**4**) by sequential N–H/H–Si dehydrogenative couplings with $BnNH_2$ and Ph_2SiH_2. Substrate scope was extended to other amines and hydrosilanes. This smooth protocol gives quantitative yields and full chemoselectivity. Compound **4** and the intermediates $Ph_3SiNHBn$ and $Ph_3SiN(Bn)SiHPh_2$ were structurally characterised. Further attempts at chain extension by dehydrocoupling of Ph_2SiH_2 with **4** instead resulted in cyclisation of this compound, forming the cyclodisilazane *c*-$(Ph_2Si\text{-}NBn)_2$ (**5**) which was crystallographically authenticated. The ring-closure mechanism leading to **5** upon release of C_6H_6 was determined by complementary experimental and theoretical (DFT) investigations. $Ba[CH(SiMe_3)_2]_2{\cdot}(THF)_3$ and **4** react to afford the reactive $Ba\{N(Bn)SiPh_2N(Bn)SiPh_3\}_2$, which was characterised in situ by NMR spectroscopy. Next, in a stepwise process, intramolecular nucleophilic attack of the metal-bound amide on the terminal silicon atom generates a five-coordinate silicate. It is followed by turnover-limiting β-C_6H_5 transfer to barium; this releases **5** and forms a transient [Ba]–Ph species, which undergoes aminolysis to regenerate [Ba]–$N(Bn)SiPh_2N(Bn)SiPh_3$. DFT computations reveal that the irreversible production of **5** through such a stepwise ring-closure mechanism is much more kinetically facile ($\Delta G^{\ddagger} = 26.2$ kcal mol^{-1}) than an alternative σ-metathesis pathway ($\Delta G^{\ddagger} = 48.2$ kcal mol^{-1}).

Introduction

Silazanes are common and versatile compounds containing N–Si bonds which can be used in coordination chemistry,[1] as bases,[2] silylating agents[3] or protecting groups for amines, indoles and anilines in organic synthesis.[4] Oligo- and polysilazanes are commonly prepared by alkali-mediated ring-opening polymerisation of cyclosilazanes following the Seyferth-Wiseman procedure.[5] Although readily implemented, this oligo/polymerisation method necessitates the synthesis of cyclosilazanes that are not easily characterised.[5,6] Alternative routes to oligo- and polysilazanes involve the dehydrocoupling of amines and hydrosilanes, which can be catalysed by a variety of complexes of late transition metals,[7] titanium,[8] or the older polycondensation by ammonolysis and aminolysis reactions.[6a,9] Polycarbosilazanes are related preceramics containing -(Si–C–N)$_n$- backbones; amorphous SiCN ceramics are useful for their corrosion resistance, high-temperature stability and long-term durability for applications as structural materials.[10] Polycarbosilazanes are commonly synthesised by aminolysis of dichlorosilanes with 1,2-ethylenediamine[11] or other diamines[12] upon release of ammonium chlorides as by-products. Original dendrimers were obtained in an iterative two-step strategy employing first Karstedt's catalyst for the hydrosilylation of tris(vinyldimethylsilyl)amine with chlorodimethylsilane, followed by treatment with alkali bis(vinyldimethylsilyl)amide.[13] Nevertheless, until recently, the most atom-efficient synthetic protocol relied on the cross-dehydrocoupling (CDC) of 1,4-bis(dimethylsilyl)benzene and ammonia catalysed by $Pd_2(dba)_3$, an attractive process even though the reaction requires 72 h to convert only a portion of 200 equiv of the comonomers.[14]

We have been keen on implementing alkaline earth complexes (Ae = Ca, Sr, Ba) in catalysed N–H/H–Si dehydrocoupling reactions, a clean route to the production of silazanes[15] and polycarbosilazanes.[16] We have shown that barium precatalysts display a unique combination of high activity and chemoselectivity in the couplings of a variety of amines, (di)hydrosilanes, α,ω-diamines and α,ω-di(hydrosilanes), which has enabled

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Supporting information, including general procedures, synthetic protocols, complete characterisation for all new compounds, crystallographic data, kinetic measurements and DFT calculations, as well as the ORCID number(s) for the author(s) of this article are available under http://dx.doi.org/10.1002/chem.201603191.

access to a range of silazanes and linear disilazanes. Other catalytic systems exist for these types of reactions. Some are built on middle and late transition metals, for example, Al_2O_3-supported palladium species and graphene-supported palladium nanoparticles,[17] $Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$ clusters,[7a–b,18] as well as discrete ruthenium,[4b,e] rhodium,[4c,7c] chromium[19] or copper complexes.[20] Precatalysts based on oxophilic metals such as titanium,[8,21] aluminium,[22] yttrium,[23] ytterbium(II),[24] uranium(IV),[25] zinc,[26] alkali metals[27] and alkaline earths,[15,28] for which σ-bond metathesis or Si-to-metal β-hydride transfer are key mechanistic features, have proved very effective of late.

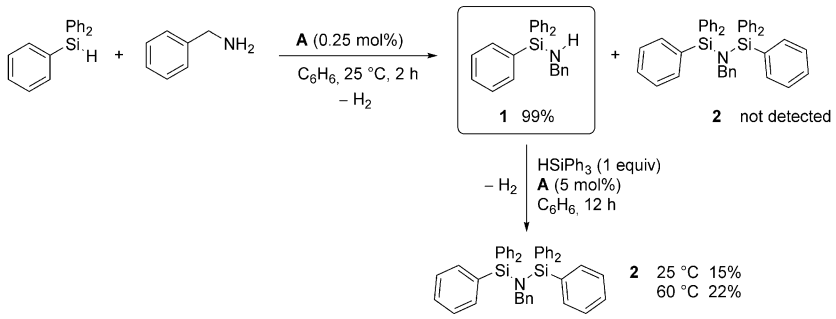
We report here the utilisation of $Ba[CH(SiMe_3)_2]_2{\cdot}(THF)_3$, a most efficient barium-based precatalyst for N–H/H–Si dehydrocouplings,[15] for the preparation of original compounds containing several silazanyl linkers. They are obtained by a controlled extension process upon sequential coupling of a variety dihydrosilazanes and diamines. It is shown how the same precatalyst can also readily lead to the ring-closing formation of 4-membered cyclodisilazanes. The results of DFT computations, aimed at probing the rival mechanistic pathways leading to cyclisation, are presented.

Results and Discussion

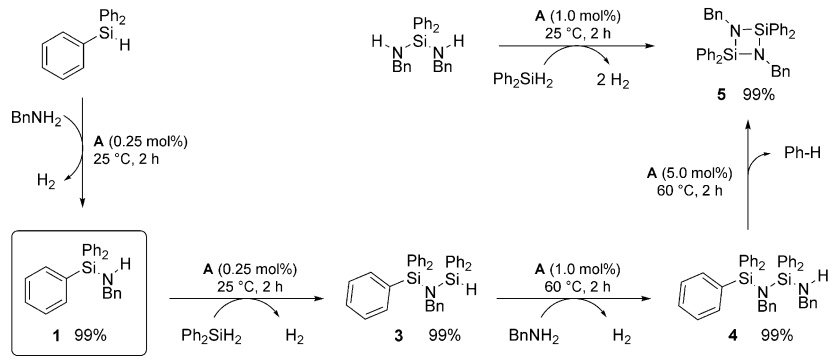
Initial reactivity studies

The barium precatalyst $Ba[CH(SiMe_3)_2]_2{\cdot}(THF)_3$ (**A**), which has recently proved very effective in N–H/H–Si CDC reactions,[15,16] was selected for the present study. It catalyses the coupling of triphenylsilane and benzylamine ($[Ph_3SiH]_0/[BnNH_2]_0/[\mathbf{A}]_0 = 400:400:1$, $[BnNH_2]_0 = 4.0$ M in benzene, Bn = benzyl) at 25 °C within 2 h to afford the known monocoupled product $Ph_3SiNHBn$ (**1**) with complete chemoselectivity. Single crystals of **1**, the starting material for the subsequent work described here, were obtained and its molecular solid-state structure was established. Under these experimental conditions, the formation of the di-coupled product, $(Ph_3Si)_2NBn$ (**2**), or that of cyclic disilazanes were not detected. Compound **2** could only be obtained in poor yields by coupling of Ph_3SiH with pre-isolated **1** (12 h, 25 °C, yield: 15%; 60 °C, yield: 22%); high precatalyst loading was required, typically $[Ph_3SiH]_0/[\mathbf{1}]_0/[\mathbf{A}]_0 = 20:20:1$, with $[\mathbf{1}]_0 = 0.20$ M in benzene (Scheme 1).[29] The difficulties encountered in obtaining **2** are reminiscent of the little propensity shown by R_3SiNHR' silazanes (R, R′ = aryl, alkyl) to engage in Ae-mediated cross-dehydrocoupling reactions with bulky hydrosilanes such as Ph_3SiH, and can probably be ascribed to excessive steric congestion.[15]

With a less cumbersome and more reactive hydrosilane, the coupling of high loadings of **1** with diphenylsilane (Ph_2SiH_2) catalysed by **A** ($[Ph_2SiH_2]_0/[\mathbf{1}]_0/[\mathbf{A}]_0 = 400:400:1$, $[\mathbf{1}]_0 = 4.00$ M in benzene) was quantitative within 2 h at 25 °C and afforded the asymmetric disilazane $Ph_3SiN(Bn)SiHPh_2$ (**3**) with complete selectivity (Scheme 2). This compound was isolated and dehydrocoupled with $BnNH_2$ ($[\mathbf{3}]_0/[BnNH_2]_0/[\mathbf{A}]_0 = 100:100:1$, $[BnNH_2]_0 = 1.0$ M in benzene) at 60 °C within 2 h, to give the linear product $Ph_3SiN(Bn)SiPh_2NHBn$ (**4**) quantitatively. See the Supporting Information for complete product characterisation.



Scheme 1. Synthesis of $Ph_3SiNHCH_2C_6H_5$ (**1**) catalysed by $Ba[CH(SiMe_3)_2]_2{\cdot}(THF)_3$ (**A**).[29]



Scheme 2. Stepwise syntheses of silazanes and (cyclo-)disilazanes catalysed by $Ba[CH(SiMe_3)_2]_2{\cdot}(THF)_3$ (**A**). All reactions were carried out in benzene.[29]

We tried to extend this stepwise chain growth to the production of longer molecules with the ambition to obtain oligo- and, ultimately, polycarbosilazanes. However, the attempted coupling of **4** with Ph_2SiH_2 (0.2 M for each substrate) did not yield the expected $Ph_3SiN(Bn)SiPh_2N(Bn)SiPh_2H$, but instead returned quantitatively the cyclodisilazane *c*-$(Ph_2Si{-}NBn)_2$ (**5**) and unreacted Ph_2SiH_2. The catalytic (5.0 mol% of **A**) formation of **5** upon cyclisation of **4** with concomitant release of benzene (vide infra) also occurs at higher substrate concentrations (2.0 M), or even in the absence of Ph_2SiH_2 under otherwise identical experimental conditions (60 °C, 2 h, $[\mathbf{4}]_0/[\mathbf{A}]_0 = 20{:}1$, $[\mathbf{4}]_0 = 0.2$ M).[30]

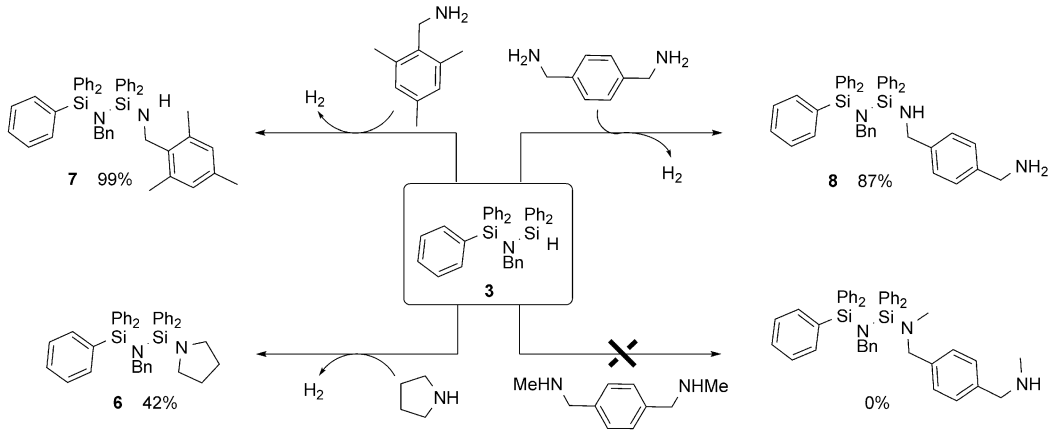
Overall, the multistep sequential Ba-promoted process forming **4** from triphenylsilane is unusual, as well as being highly effective and chemoselective. Like **1**, silazanes **3–5** were all isolated as colourless solids, and crystals were grown from concentrated pentane solutions. Their identities were established on the basis of the NMR spectroscopic (^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$), mass spectrometric and crystallographic data of the purified products. For these and the following related compounds, elemental analyses were often thwarted because of high silicon contents, but they were overall consistent with the proposed formulations.[31,32]

Reaction scope

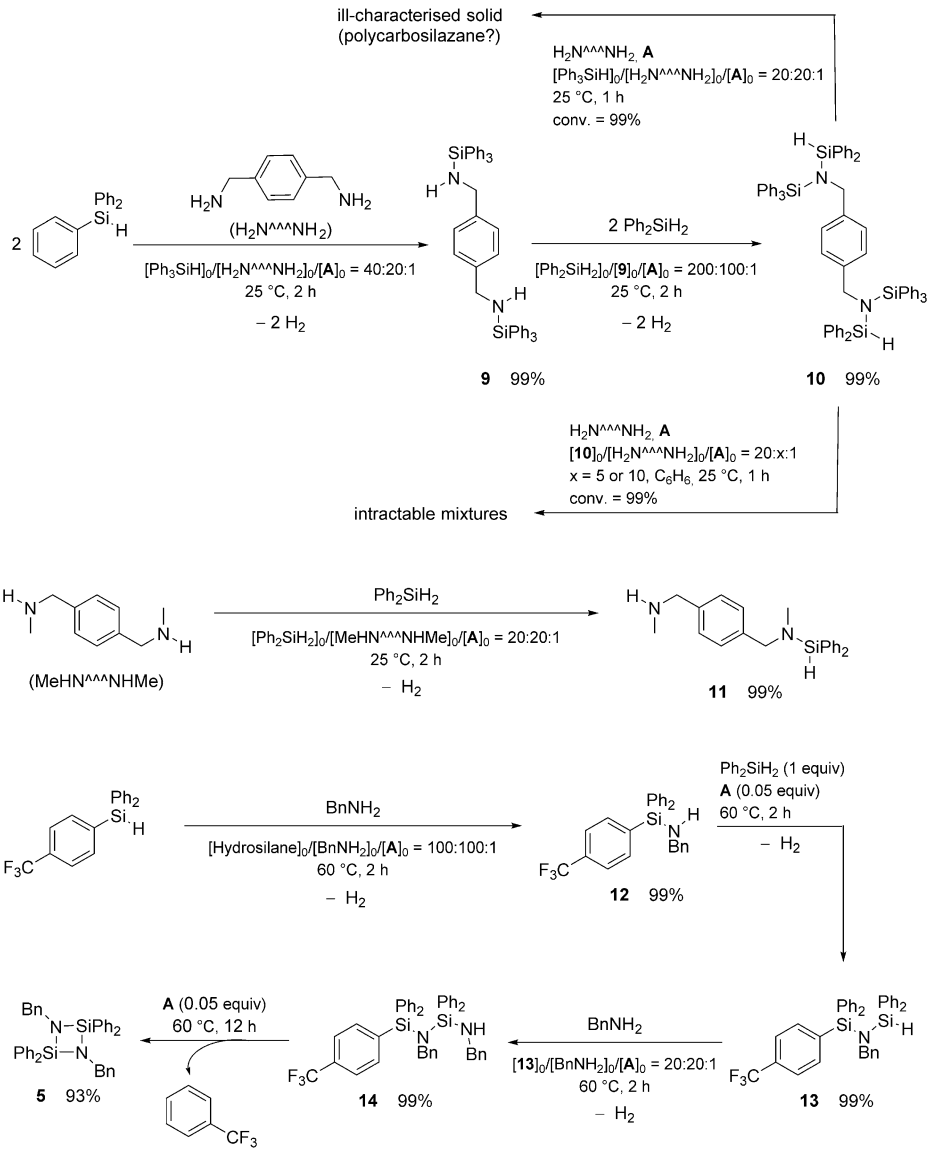
Starting from **3**, the method employed to obtain **4** by coupling with $BnNH_2$ was extended to other amines (Scheme 3). $Ph_3SiN(Bn)SiPh_2N(CH_2)_4$ (**6**) was obtained in a 42% unoptimised yield upon dehydrocoupling of **3** and pyrrolidine under mild conditions. The coupling of **3** with diamines or with primary amines is more pertinent. Instead of $BnNH_2$ leading to the formation of **4**, the CDC of **3** with $MesCH_2NH_2$ (Mes = mesityl) yielded $Ph_3SiN(Bn)SiPh_2NHMes$ (**7**) quantitatively. The coupling of **3** with 1,4-phenylenedimethanamine ($H_2N\text{^^^}NH_2$) afforded $Ph_3SiN(Bn)SiPh_2NHCH_2C_6H_4CH_2NH_2$ (**8**). Cyclisation and formation of a $[Si_2N_2]$ cyclic moiety giving a putative $[Si_2N_2]{-}CH_2C_6H_4CH_2NH_2$ species could perhaps occur in **8**. To prevent such scenario, 1,1′-(1,4-phenylene)bis(*N*-methylmethanamine) (MeHN^^^NHMe) incorporating two secondary amines with *N,N′*-dimethyl substituents was also tested in the coupling with **3**, but no conversion to $Ph_3SiN(Bn)SiPh_2N(Me)CH_2C_6H_4CH_2NHMe$ was detected. Similar observations were made previously in the couplings with Ph_3SiH upon going from $BnNH_2$, which is highly reactive, to the secondary amine Bn_2NH, which showed almost no reactivity.[15b] CDC reactions are thus greatly sensitive to steric effects.

Starting materials other than **1** and **3** are also amenable to couplings catalysed by **A** (Scheme 4). It has been shown that the coupling of 2 equiv of Ph_3SiH with 1,4-phenylenedimethanamine selectively affords $Ph_3SiNHCH_2C_6H_4CH_2NHSiPh_3$ (**9**).[15b] This precursor was further subjected to coupling with 2 equiv of Ph_2SiH_2. The reaction was quantitative (25 °C, 2 h, $[Ph_2SiH_2]_0/[\mathbf{9}]_0/[\mathbf{A}]_0 = 200{:}100{:}1$) and produced the bis(disilazane) $Ph_2HSi(Ph_3Si)NCH_2C_6H_4CH_2N(Ph_3Si)\text{-}SiHPh_2$ (**10**), which contains two hydrosilanyl functional groups in the α and ω positions. The subsequent coupling of the difunctional **10** with 1 equiv of $H_2N\text{^^^}NH_2$ at 25 °C for 1 h ($[\mathbf{10}]_0/[H_2N\text{^^^}NH_2]_0/[\mathbf{A}]_0 = 20{:}20{:}1$) yielded an insoluble white solid, probably a cross-linked polycarbosilazane resulting from dehydropolymerisation; the ^1H and ^{29}Si NMR data of this material could not interpreted. The reaction of **10** with 5 or 10 equiv of $H_2N\text{^^^}NH_2$ versus **A** ($[\mathbf{10}]_0/[H_2N\text{^^^}NH_2]_0/[\mathbf{A}]_0 = 20{:}X{:}1$) gave intractable mixtures. $HSiPh_2N(Me)CH_2C_6H_4CH_2NHMe$ (**11**) is a starting material for the grafting of either a dihydrosilane or an amine, on the -NHMe or the -NMeSiPh$_2$H tail-ends, respectively, or as a bifunctional AB monomer for dehydropolymerisation reactions to obtain high molecular polycarbosilazanes.[16] It can be obtained from the quantitative and chemoselective coupling of MeHN^^^NHMe with a single equivalent of Ph_2SiH_2 (Scheme 4).

Substituents can be introduced onto the amines, as in **7** (see Scheme 3), or alternatively in the hydrosilanes. For instance, (*p*-$CF_3C_6H_4$)$Ph_2SiNHBn$ (**12**) was prepared upon coupling of (*p*-$CF_3C_6H_4$)Ph_2SiH and $BnNH_2$ (Scheme 4). The coupling of **12** with Ph_2SiH_2 ($[Ph_2SiH_2]_0/[\mathbf{12}]_0/[\mathbf{A}]_0 = 20{:}20{:}1$) smoothly gave (*p*-$CF_3C_6H_4$)$Ph_2SiN(Bn)SiHPh_2$ (**13**), which could be further reacted with $BnNH_2$ to afford (*p*-$CF_3C_6H_4$)$Ph_2SiN(Bn)SiPh_2NHBn$ (**14**). In



Scheme 3. Synthesis of linear disilazanes catalysed by $Ba[CH(SiMe_3)_2]_2{\cdot}(THF)_3$ (**A**) starting from $Ph_3SiN(Bn)SiHPh_2$ (**3**). Experimental conditions: Precatalyst **A** (5.0 μmol), $[\mathbf{3}]_0/[\text{amine}]_0/[\mathbf{A}]_0 = 20{:}20{:}1$, $[\text{amine}]_0 = 0.2$ M in benzene, 60 °C, 2 h.[29]

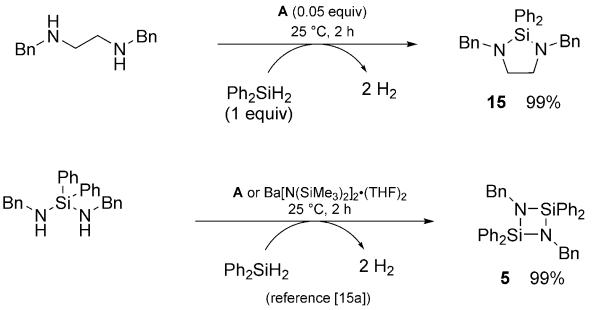


Scheme 4. Sequential grafting of various amines and hydrosilanes in CDC reactions catalysed by $Ba[CH(SiMe_3)_2]_2{\cdot}(THF)_3$ (**A**).[29] All reactions performed in benzene.

the way seen for the cyclisation from **4** to **5**, upon exposure to precatalyst **A** at 60 °C for 12 h, the linear **14** led to the formation of **5** by selective elimination of 1 equiv of $C_6H_5CF_3$, as established by ^1H and ^{19}F NMR spectroscopy. The mechanism proposed for the cyclisation, with formation of a transient pentavalent silicate and transfer of a partially negatively charged aromatic moiety to barium stabilised by *para* electron-withdrawing groups, accounts for the selectivity towards the elimination of *p*-$CF_3C_6H_5$ in the production of **5** from **14** (vide infra). This series of reactions also works for *p*-methyl-substituted arylhydrosilanes. However, they are more sluggish reagents, for example requiring heating for 12 h at 60 °C to afford (*p*-$CH_3C_6H_4)Ph_2SiN(Bn)SiPh_2NHBn$. Further cyclisation of this compound does not even reach 10% conversion (upon selective elimination of benzene, while the release of toluene is not detected) after heating for 12 h at 60 °C. In a rough empirical evaluation, the reaction rate therefore seems to increase when electronic density on the silicon atom decreases ($Me < H < CF_3$), and the proposed mechanism detailed in the following sections is consistent with this observation.

The formation of the cyclic product **5** upon elimination of an aromatic molecule, benzene in the case of **4** and trifluoromethylbenzene for **14**, is not the sole method for the preparation of cyclosilazanes. The coupling of $BnNHCH_2CH_2NHBn$ with Ph_2SiH_2 catalysed by **A** or even $Ba[N(SiMe_3)_2]_2{\cdot}(THF)_2$ takes place readily to give the corresponding 5-membered cycle **15**, *c*-$[Ph_2SiN(Bn)CH_2CH_2N(Bn)]$ (Scheme 5). Furthermore, compound **5** itself had previously been obtained by barium-mediated H_2-releasing dehydrocoupling of Ph_2SiH_2 with $BnNHSiPh_2NHBn$.[15a]

The peculiarity of the formation of **5** from **4** or **14** lies in the fact that it is formed not by cross-dehydrocoupling of an amine and hydrosilane with hydrogen evolution, but upon ring-forming, barium-catalysed Si–C bond cleavage with con-



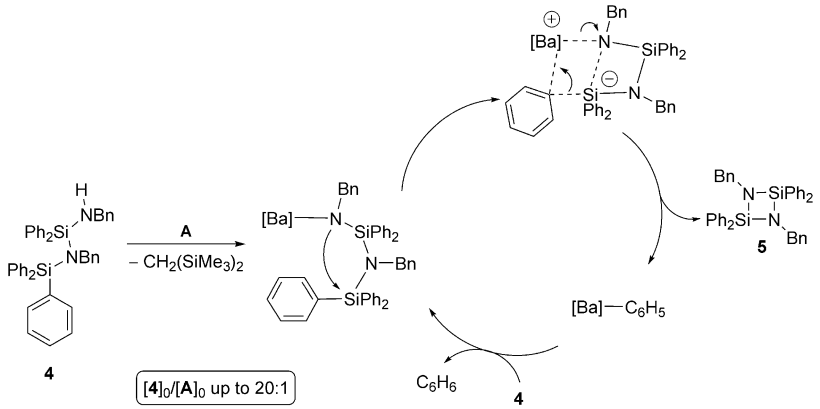
Scheme 5. Formation of cyclo(di)silazanes by barium-mediated CDC reactions.[29]

comitant elimination of one stoichiometric equivalent of aromatic by-product. Although not common, the rupture of Si–C bonds has already been documented under other circumstances. The cleavage of Si–C bonds under acidic conditions has long been known.[33] More recently, several cases of metal-promoted Si–C bond ruptures have been disclosed for both C_{sp^2} and C_{sp^3} carbon atoms. For instance, the lutetium hydride $[(C_5Me_5)_2Lu(\mu\text{-}H)]_2$ was reported to cleave the Si–C_{sp^2} bond in $PhSiH_3$ to generate benzene and cross-linked polysilanes $(SiH_x)_y$.[34] Nickel and palladium silyl pincer complexes can undergo structural rearrangements implicating reversible Si–C_{sp^3} and Si–C_{sp^2} bond activation.[35] The rhodium-catalysed coupling of 2-trimethylsilylphenylboronic acid with internal alkynes produces 2,3-disubstituted benzosilole derivatives.[36] $Rh(H)(CO)(PPh_3)_3$ triggers Si–C_R bond cleavage in $[o\text{-}(Ph_2P)C_6H_4]_2SiMeR$ (R = Ph, Me, Et); it was shown that the facility of bond activation increased with temperature and according to Si–Et < Si–Me < Si–Ph.[37] Perhaps more relevant to the present work, the stoichiometric conversion of Si–C_{aryl} σ-bonds into Si–heteroatom ones in the reactions of η^3-α-silabenzyl molybdenum and tungsten complexes with 2-substituted pyridines has been reported very recently.[38] The cleavage of Si–C bonds is also promoted by supercritical water[39] or by montmorillonite.[40]

The fact that **4** could be synthesised from **3** under catalytic conditions and without contamination by **5**, and that pure **4**, after isolation and re-dissolution in benzene in the presence of **A** (0.05 equiv, 60 °C, 2 h; see Scheme 2), cleanly and quantitatively yielded **5** in a catalysed process, suggests an intriguing reactivity pattern. We are unable at this time to propose a conclusive explanation for this phenomenon. One conceivable hypothesis is that during the formation of **4** by coupling of $BnNH_2$ and **3**, the catalyst resting state is under the form of a putative "$[Ba(NHBn)_2(S)_x]_n$" species, in which S is THF or $BnNH_2$.[41] This species may be insufficiently basic to deprotonate the newly-formed **4** present in the reaction mixture. In contrast, reaction of the pre-isolated, purified **4** with the highly basic barium bis(alkyl) **A** must produce a species akin to "$Ba[N(Bn)SiPh_2N(Bn)SiPh_3]_2\cdot(THF)_n$" (DFT computations favours $n = 0$, vide infra) by aminolysis and irreversible release of $CH_2(SiMe_3)_2$. The fact that the relatively less basic $Ba[N(SiMe_3)_2]_2\cdot(THF)_2$ fails entirely to react with **4** (only unreacted materials are returned) is congruent with this working hypothesis. In the absence of any reactive substrate other than **4**, if this new compound "$Ba[N(Bn)SiPh_2N(Bn)SiPh_3]_2\cdot(THF)_n$" evolves, it can only be towards the formation of the cyclodisilazane **5**. If so, this may for instance occur by nucleophilic attack of the N_{amide} atom onto the terminal Si atom creating a hypervalent silicate followed by β-C_6H_5 transfer to Ba, or perhaps by a less likely σ-metathetical pathway. Such processes should give rise to a transient [Ba]–Ph species, which is basic enough to deprotonate more incoming **4** and, in doing so, regenerate "$Ba[N(Bn)SiPh_2N(Bn)SiPh_3]\cdot(THF)_n$" and release benzene (Scheme 6).

Regarding the mechanism of the cyclisation reaction

The NMR-scale reaction of **A** with 2 equiv of **4** in [D_6]benzene (2 h, 25 °C) was examined by ^1H NMR spectroscopy (Figure 1). It generated preponderantly a new barium compound, the ^1H NMR data of which showed in particular two sharp singlets integrating for two hydrogens each at $\delta_{^1H}$ 4.59 and 4.13 ppm and corresponding to two types of $C_6H_5CH_2$ methylene hydrogens. This data agreed with the formulation $Ba[N(Bn)SiPh_2N(Bn)SiPh_3]_2$ (Figure 1). Quantitative release of $CH_2(SiMe_3)_2$ was also detected, together with the presence of **5** (about



Scheme 6. Possible stepwise mechanism involving a transient [Ba]–Ph species for the quantitative synthesis of *c*-$(Ph_2SiNBn)_2$ (**5**) starting from $Ph_3SiN(Bn)SiPh_2NHBn$ (**4**) and catalysed by $Ba[CH(SiMe_3)_2]_2\cdot(THF)_3$ (**A**).

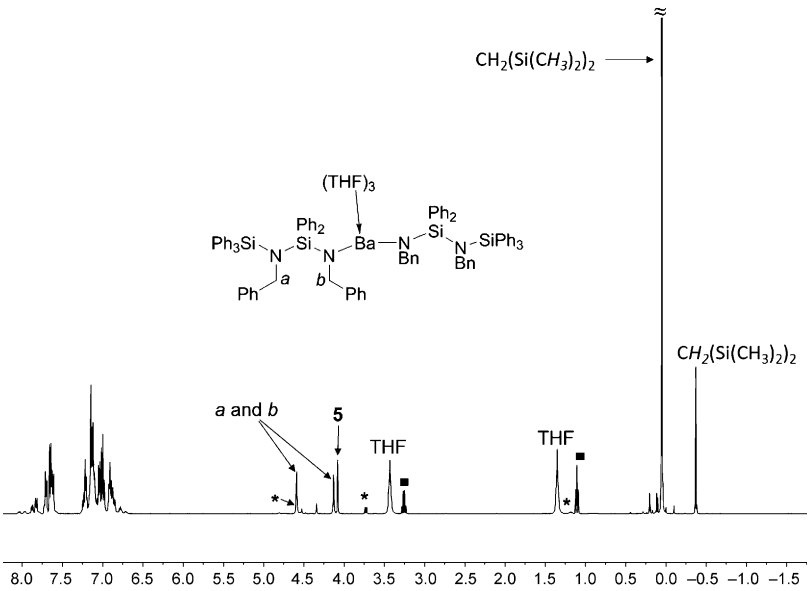
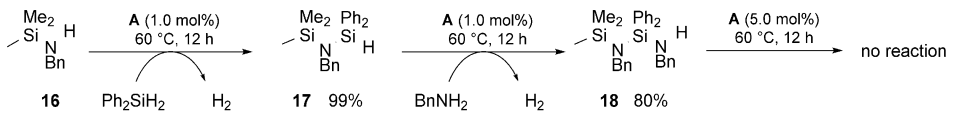


Figure 1. ^{1}H NMR spectrum ([D$_6$]benzene, 25 °C, 400.1 MHz) of the NMR-scale reaction of Ba[CH(SiMe$_3$)$_2$]$_2$·(THF)$_3$ (**A**) with 2 equiv of Ph$_3$SiN(Bn)SiPh$_2$NHBn (**4**), showing the quantitative release of CH$_2$(SiMe$_3$)$_2$ and formation of a minor amount of *c*-(Ph$_2$SiNBn)$_2$ (**5**). * = unreacted **4**. ■ = residual Et$_2$O.

40 %, diagnostic singlet at $\delta_{^1H}$ 4.08 ppm) and minute amounts of unreacted **4**. The preparation of an authentic sample of this complex by reacting **A** with 2.0 equiv of **4** showed that the THF molecules did not remain metal-bound. The ^{1}H NMR data of the product obtained after work-up was consistent with that given in Figure 1, except for the fact that no resonance for THF was detectable. These data confirm that Ba[N(Bn)-SiPh$_2$N(Bn)SiPh$_3$]$_2$ can be made, but also that it is unstable at room temperature. It spontaneously evolves in solution to generate **5** in increasing amounts over the course of 6 h, and also partly decomposes to release **4** together with unidentified barium species.

The formation of **5** upon addition of 20 equiv of **4** to **A** in [D$_8$]toluene at 60 °C, that is, under catalytic conditions, was monitored spectroscopically over the course of several hours. Gradual but eventual quantitative formation of **5**, together with the release of benzene could be visualised (sharp singlet resonances at $\delta_{^1H}$ 7.13 ppm and $\delta_{^{13}C}$ 128.53 ppm) concomitantly with the consumption of **4**. The kinetic rate law exhibits partial first order in both catalyst and substrate concentrations. The value of the observed rate constant, $k_{obs,H} = 1.98 \pm 0.1 \times 10^{-5}$ s^{-1}, was determined from the semi-logarithmic plot of conversion versus reaction time. No primary kinetic isotope effect (KIE) was seen (the cyclisation of Ph$_3$SiN(Bn)SiPh$_2$NDBn also proceeded with $k_{obs,D} = 2.00 \pm 0.1 \times 10^{-5}$ s^{-1}, $k_{obs,H}/k_{obs,D} = 0.99 \pm 0.1$), indicating that the rupture of the N–H bond is not a key component of the turnover-limiting step. The activation parameters $\Delta H^{\ddagger} = 20.6 \pm 0.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -9.5 \pm 0.1$ cal mol^{-1} K^{-1} ($\Delta G^{\ddagger} = 23.4 \pm 0.1$ kcal mol^{-1} at 298 K) were extracted by Eyring analysis of kinetic data recorded in the temperature range 328–353 K (five data points). The cyclisation **4**→**5** upon exclusive elimination of C$_6$H$_5$CF$_3$ from **14** proceeds with $k_{obs} = 5.16 \pm 0.1 \times 10^{-5}$ s^{-1}. Enhancement of the cyclisation rate upon addition of an electron-withdrawing group in the *para* position of one of the aryl rings on the silicon atom that undergoes ring-closure, is consistent with the existence of a negative charge developing on this Si atom in the transition state. Finally, the formation of (C$_6$D$_5$)$_3$SiN(Bn)SiPh$_2$NHBn (or its (C$_6$D$_5$)$_x$(Ph)$_{3-x}$SiN(Bn)Si(C$_6$D$_5$)$_{x'}$(Ph)$_{2-x'}$NHBn precursors) is not detected when the benzene-releasing transformation **4**→**5** is carried out in [D$_6$]benzene over several hours, revealing that this ring-closing process is irreversible. Considered collectively, these observations are compatible with a mechanism such as that described in Scheme 6.

Importantly, no ring-closure takes place when Me$_3$SiN(Bn)SiPh$_2$NHBn (**18**), with alkyl instead of aryl substituents on the tail-end silicon atom, is heated in [D$_6$]benzene for 12 h at 60 °C in the presence of 5.0 mol % of **A**. The compound remains unreacted throughout the course of the experiment, with no evolution detected spectroscopically. The release of benzene in the cyclisation process from **4** to **5** (instead of an alkane from **18**) seems to be a key driving force, or at least one can safely conclude that for this process, Si–C$_{sp^2}$ bonds are more likely to undergo activation than Si–C$_{sp^3}$ bonds. Compound **18** had first been isolated after the two-step sequential procedure (Scheme 7) involving the coupling of the known



Scheme 7. Catalytic synthesis of Me$_3$SiN(Bn)SiPh$_2$NHBn (**18**).

$Me_3SiNHBn$ (**16**) with Ph_2SiH_2 to afford $Me_3SiN(Bn)SiHPh_2$ (**17**), followed by coupling with $BnNH_2$.[42]

The benzene-releasing cyclisation from **4** to **5** is not specific to barium precatalysts; it is also catalysed by, for instance, $Ca[CH(SiMe_3)_2]_2{\cdot}(THF)_2$ (**B**), the calcium analogue of **A**. In a control experiment performed under otherwise identical experimental conditions ($[\mathbf{4}]_0/[\text{precatalyst}]_0 = 20{:}1$, 60 °C in benzene, $[\text{precatalyst}]_0 = 10$ mM), **B** catalyses the reaction at a rate very comparable to that of **A**, $k_{obs} = 9.16 \pm 0.3 \times 10^{-6}\ s^{-1}$ and $1.98 \pm 0.1 \times 10^{-5}\ s^{-1}$, respectively. Eyring analyses in the temperature range 328–353 K (five data points) allowed for the calculation of the activation parameters for **B**, $\Delta H^{\neq} = 16.8 \pm 0.1$ kcal mol^{-1} and $\Delta S^{\neq} = -22.3 \pm 0.1$ cal mol^{-1} K^{-1}, with $\Delta G^{\neq} = 23.4 \pm 0.1$ kcal mol^{-1} at 298 K. This final value replicates that for **A**, but the respective enthalpic and entropic contributions are very different. Due to its much smaller size compared to barium (effective r_{ionic} for C.N. = 6: Ca^{2+}, 1.00 Å; Ba^{2+}, 1.38 Å), calcium has a greater entropic factor that becomes unfavourable as the temperature of the reaction is increased. The energy of activation determined by Arrhenius analysis is actually lower for the calcium precatalyst **B** ($E_a = 17.5 \pm 0.1$ kcal mol^{-1}; $R^2 = 0.9938$) than for the barium **A** ($E_a = 21.3 \pm 0.2$ kcal mol^{-1}; $R^2 = 0.9928$).

Computational investigations

A reliable state-of-the-art density functional theory (DFT) method has been employed to complement the mechanistic studies reported above with an aim to further enhance our understanding of mechanistic intricacies behind the generation of cyclodisilazanes. We have examined various mechanistic pathways conceivable for the conversion of disilazane **4** into the 4-membered cyclodisilazane **5** by the barium precatalyst **A** (denoted **C1**·(T)^3 hereafter). For the disilazane, the two silicon-bound phenyl spectator groups have been replaced by methyl ones ($\mathbf{4}_{Me}$) for the sole purpose of expediting computations, but no further simplifications of any kind have been imposed for any of the key species involved. The computational methodology employed (dispersion-corrected B97-D3 in conjunction with triple-ζ basis sets and a sound treatment of bulk solvent effects; see the computational methodology in the Supporting Information) adequately simulated the authentic reaction conditions and has been demonstrated before to reliably map the free-energy landscape of alkaline earth-mediated hydroelementation reactions.[15,43] This has allowed mechanistic conclusions with substantial predictive value to be drawn.

We started with an examination of the Ba–C alkyl bond aminolysis at starting material **C1**·(T)^3 (≡**A**) by $\mathbf{4}_{Me}$, thereby transforming **C1**·(T)^3 into the related $[Ba\{N(Bn)SiMe_2N(Bn)SiMe_2Ph\}_2]$ barium bis-amido compound **C2**, which is likely competent to trigger the $\mathbf{4}_{Me} \rightarrow \mathbf{5}_{Me}$ conversion. The activation of **C1**·(T)^3 entails that amine binds initially at barium. Several pathways, which are distinguished by the number of THF molecules to remain bound at barium, have been examined. The most accessible case (Figure S18) together with the complete account of all the studied pathways (Figure S17–S20) can be found in the Supporting Information. The energetically prevalent pathway for Ba–C alkyl bond aminolysis sees the first exchange of one THF for an amine molecule and evolves through a metathesis-type transition-state (TS) structure to deliver intermediate **CI2**·(T)^2·RSi featuring a barium-bound $H_2C(SiMe_3)_2$ moiety. Its rapid displacement by another amine molecule prepares for protonolytic cleavage of the second Ba–C alkyl bond through a similar metathesis-type TS structure that decays thereafter into **C2** with the rapid release of $H_2C(SiMe_3)_2$ and THF. The Ba–C alkyl bond protonolysis has an affordable barrier of 16.7 kcal mol^{-1} (for aminolysis of the first Ba–C bond, see Figure S18) to overcome and is driven by a huge thermodynamic force that amounts to 35.3 kcal mol^{-1}. Thus, one can safely conclude that barium bis-alkyl **C1**·(T)^3 is likely converted irreversibly in a quantitative fashion by $\mathbf{4}_{Me}$ into the competent barium bis-silazanyl amido compound **C2**.

It has been shown above that **4** exhibits a distinct reactivity pattern under varying experimental conditions, on the one hand, when generated under conditions of CDC catalysis (hence in the presence of benzylamine), or alternatively in the absence of any amine substrate other than **4**. Thus, we deemed it instructive to study the aminolysis of **C1**·(T)^3 by NH_2Bn and the conversion of the thus formed barium bis-benzylamido **C3** into **C2** as well. The sequential protonolytic displacement of a hydrocarbyl with an amido group by either $\mathbf{4}_{Me}$ or NH_2Bn, share structural features and similar energy profiles. For the less encumbered primary NH_2Bn, the most accessible pathway (see Figure S22, but also Figures S21, S23, S24 in the Supporting Information) proceeds after the initial displacement of all three THF molecules by amine with a moderate overall barrier of 7.5 kcal mol^{-1} to engage thereafter in the cleavage of the remaining Ba–C bond. This affords the NH_2Bn adduct **C3**·(Am)^3 of the barium bis-benzylamido compound. Overall, the conversion of starting material **C1**·(T)^3 in the presence of $\mathbf{4}_{Me}$ or NH_2Bn into the respective barium bis-amido compounds is found affordable kinetically and strongly downhill, driven by a thermodynamic force of comparable substantial amount.

For the experimental setup of CDC catalysis to be applied, the barium bis-benzylamido, which is predominantly present as amine adduct **C3**·(Am)^3, is likely representing the catalyst resting state.[15] Hence, under such conditions, **C3** needs first to be converted into **C2** to proceed along the various conceivable avenues that lead to the formation of the cyclodisilazane. Interestingly, the sequential exchange of benzylamido by silazanyl amido appears to be equally kinetically viable, featuring an overall activation energy of 11.3 kcal mol^{-1}. This barrier is linked to aminolysis of the first Ba–N amido bond, along the energetically prevalent pathway (see Figure S26 but also Figures S25, S27, S28 in the Supporting Information) that proceeds from the bis-silazane adduct **C3**·$(\mathbf{4}_{Me})^2$. However, the thermodynamic force associated with the overall transformation of **C3** into **C2** is found strikingly different to the findings for starting material **C1**·(T)^3. The huge negative reaction free energy predicted there is indicative of an irreversible and essentially quantitative conversion of **C1**·(T)^3 into the respective barium bis-amido compounds. This is in sharp contrast to the process here, which does not benefit from a massive thermodynamic driving force, but is rather thermoneutral with **C3**·(Am)$^3 \rightleftarrows$**C2** likely in a mobile equilibrium that does not favour **C2** over **C3**.

The benzylamido ligand is thus predicted to effect deprotonation of $\mathbf{4}_{Me}$ substantially less so than does the more basic hydrocarbyl ligand. The ineffectiveness of the protonolytic exchange of benzylamido by silazanyl amido at **C3**·(Am)[3] due to unfavourable thermodynamics limits the population of **C2** under conditions optimal for CDC catalysis. Given that **C2** cannot be expected to be present in appreciable amounts under such conditions, it explains why the formation of cyclodisilazane **5** could not be observed during catalytic experiments.

The barium bis-silazanyl amido compound **C2** is predicted to be predominantly present without amine or THF molecules directly bound to barium. It features a metal centre that is capable of accommodating THF molecules at moderate costs, whereas the propensity of $\mathbf{4}_{Me}$ to bind is substantially less pronounced.

Turning now to the plausible mechanistic proposal outlined in Scheme 6, it comprises N–Si bond-forming cyclisation at **C2** with β-C_6H_5 abstraction from the thus formed barium silicate **C4**. These processes could proceed through stepwise or metathesis-like pathways, to furnish a barium amido phenyl compound **C5** to which cyclodisilazane $\mathbf{5}_{Me}$ may be bound. Protonolytic cleavage of the Ba–C phenyl bond at **C5** by another molecule of $\mathbf{4}_{Me}$ would regenerate **C2** with release of 1 equiv of benzene.

Commencing from **C2**, the initial N–Si bond-forming cyclisation evolves through a TS structure that describes ring closure by nucleophilic attack of the metal-bound amido nitrogen at the terminal silicon within the vicinity of the barium centre at distances of around 2.41 and 2.67 Å (see Figure S29 in the Supporting Information) for the emerging N–Si and dative Ba–N bonds, respectively. The terminal phenyl group, featuring an already elongated Si–C linkage (1.94 Å) is suitably aligned towards the barium centre. Following the reaction path further, the TS structure decays into a metastable nucleophilic silicate intermediate **C4** with a five-coordinate silicon centre carrying a partial negative charge. The cyclisation has an activation barrier of 18.7 kcal mol^{-1} to overcome along the most accessible pathway (Figure 2), which does not see the participation of additional metal-bound amine molecules (see Figure S30), to afford the metastable high-energy barium silicate **C4**. It characterises C–N bond-forming ring closure to be kinetically affordable and reversible, with **C2**⇄**C4** in a mobile equilibrium that strongly favours **C2**. A metal-bound amine molecule appears to counterbalance to some extent the weakening of the Ba–N linkage in the TS structure and also the silicate intermediate. However, additional $\mathbf{4}_{Me}$ is found to not stabilise the key species involved (see Figure S30).

As already indicated by its profoundly elongated Si–Ph linkage (2.09 Å) together with a suitably towards barium oriented phenyl group, silicate **C4** shows a distinct aptitude to undergo β-C_6H_5 abstraction from the five-coordinate terminal silicon onto barium. It evolves through a TS structure with distances of approximately 2.83 and 2.75 Å for vanishing Si–C and emerging Ba–C phenyl bonds (see Figure S31), respectively, and generates the cyclodisilazane $\mathbf{5}_{Me}$ bound to barium silazanyl amido phenyl **C5**.

Focusing at first on the intrinsic reactivity, an additionally associated $\mathbf{4}_{Me}$ molecule is seen facilitating the process on both kinetic and thermodynamic grounds (see Figures 3 and S32 in the Supporting Information). Phenyl transfer along the favourable **C4**·$\mathbf{4}_{Me}$→**C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$ pathway features a rather modest intrinsic activation barrier ($\Delta G^{\ddagger}_{int}$ = 9.0 kcal mol^{-1}, relative to **C4**·$\mathbf{4}_{Me}$,) and is virtually thermoneutral (ΔG_{int} = 0.9 kcal mol^{-1}, relative to **C4**·$\mathbf{4}_{Me}$). Hence, as far as intrinsic reactivity is concerned, phenyl transfer is found to proceed more rapidly than preceding cyclisation, with **C4**·$\mathbf{4}_{Me}$ and **C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$ expected to participate in a mobile equilibrium, but without a distinct ther-

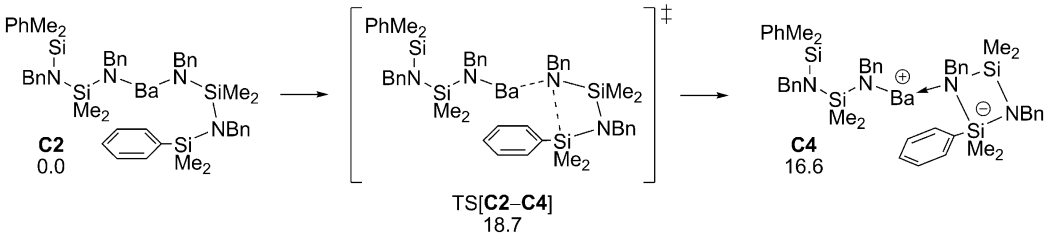


Figure 2. N–Si bond-forming cyclisation at barium bis-silazanyl amido **C2**. Energies are given in kcal mol^{-1} relative to {**C2** + n × $\mathbf{4}_{Me}$}.

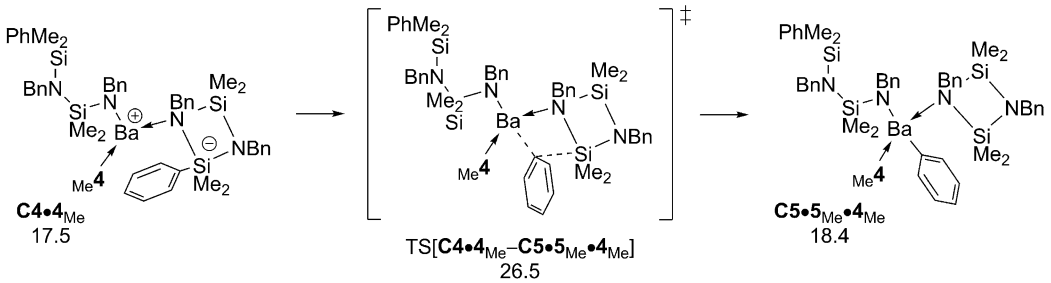


Figure 3. β-C_6H_5 transfer onto the metal centre at barium silicate **C4**. Energies are given in kcal mol^{-1} relative to {**C2** + n × $\mathbf{4}_{Me}$}.

modynamic preference for either side. However, the unfavourable thermodynamic profile of the **C2**⇄**C4** ring closure (together with $\mathbf{4}_{Me}$ complexation at **C4**) markedly favours **C2** over **C4**·$\mathbf{4}_{Me}$, which renders the second phenyl transfer of the stepwise **C2**⇄**C4**(+$\mathbf{4}_{Me}$)⇄**C4**·$\mathbf{4}_{Me}$⇄**C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$ more kinetically demanding.

As already mentioned above, Ba–N/Si–C σ-bond breaking metathesis commencing from **C2** describes the concerted analogue to the thus far studied stepwise generation of **C5** (see the Supporting Information for more details). The protonolytic cleavage of the Ba–C phenyl bond at **C5** by another molecule of $\mathbf{4}_{Me}$ regenerates barium bis-silazanyl amido **C2**, which is accompanied by the release of benzene. The process commencing from the mono-amine adduct **C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$ evolves through a metathesis-type TS structure (see Figure S33 in the Supporting Information). This TS decays through facile liberation of benzene initially into a $\mathbf{5}_{Me}$ adduct of **C2**, from which $\mathbf{5}_{Me}$ is readily released. The protonolytic expulsion of the phenyl ligand is seen to be astonishingly kinetically facile, featuring an intrinsic barrier of 3.7 kcal mol^{-1} (relative to **C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$), and is strongly exergonic (Figure 4). The subsequent rapid release of the cyclodisilazane from **C2**·$\mathbf{5}_{Me}$ drives the overall aminolysis step even further downhill. Furthermore, **C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$ is likely showing a higher propensity towards undergoing forward protonolytic Ba–C phenyl bond cleavage rather than reverse Si–C bond-forming phenyl transfer. In light of the predicted kinetic gap of 4.4 kcal mol^{-1} ($\Delta\Delta G^{\ddagger}$ between **C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$→**C2**·$\mathbf{5}_{Me}$ + PhH and **C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$⇄**C4**·$\mathbf{4}_{Me}$) in favour of the forward protonolysis, **C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$ is likely a short-lived intermediate that converts into **C2**·$\mathbf{5}_{Me}$ almost immediately after it is generated. Hence, TS[**C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$–**C2**·$\mathbf{5}_{Me}$] of the favourable protonolysis pathway shown in Figure 4 does not define the highest point to be crossed along the minimum-energy pathway for generation of the cyclodisilazane. Instead, TS[**C4**·$\mathbf{4}_{Me}$–**C5**·$\mathbf{5}_{Me}$·$\mathbf{4}_{Me}$] for β-C_5H_6 transfer onto barium (Figure 3) represents the species of highest free energy.

Over the course of exploring the existence of alternative mechanistic avenues, we managed to successfully locate a multicentre TS structure that is linked to barium silicate **C4**·$\mathbf{4}_{Me}$ describing β-C_6H_5 transfer with concomitant $\mathbf{4}_{Me}$ amine-proton delivery onto phenyl. This all occurs outside of the immediate vicinity of the metal centre (see the Supporting Information for more details).

Overall, the reported computational examination of several mechanistic avenues rationalises the distinct reactivity pattern of disilazane **4** observed under varying experimental setups and defines the most accessible among the various examined pathways for its conversion into cyclodisilazane **5**. It involves: (1) kinetically affordable and reversible N–Si bond-forming cyclisation through nucleophilic attack of the barium silazanyl amido at the terminal silicon, (2) reversible β-C_6H_5 transfer onto the barium centre at the thus generated barium silicate and (3) rapid and strongly downhill Ba–C phenyl-bond aminolysis to regenerate the barium bis-silazanyl amido with concomitant release of benzene. The TS structure for β-C_6H_5 transfer represents the species of highest energy traversed along the identified minimum-energy pathway. The DFT-derived effective barrier of 26.2 kcal mol^{-1} for conversion of $\mathbf{4}_{Me}$ into $\mathbf{5}_{Me}$ mediated by barium precatalyst **A** compares favourably with experimentally determined Eyring parameters for the **4**→**5** transformation. The operative mechanism for the novel Ae-mediated conversion of disilazane **4** into cyclodisilazane **5** established here, through complementary kinetic analysis and DFT investigations, is consistent with all relevant process features. This includes the rate dependency observed upon varying concentrations of precatalyst and/or substrate,[44] the absence of a primary KIE to be detectable and the enhancement of the rate observed for disilazanes with a *para*-phenyl-substituted terminal silicon centre featuring electron-withdrawing groups.

Conclusions

The barium alkyl precatalyst $Ba[CH(SiMe_3)_2]_2{\cdot}(THF)_3$ enables the preparation of unusual silazanes of various sizes and compositions upon iterative dehydrocouplings of primary amine and secondary dihydrosilanes. Until now, molecules with Si–N–Si–N sequences of up to four backbone heteroatoms have been obtained in quantitative yields and complete chemoselectivity under mild conditions. We are hoping to extend this methodology of sequential dehydrocouplings to higher degrees, that is, for the syntheses of oligo- and polycarbosilazanes of increasing sizes and multiple compositions. For now, this ambition has been hampered by an unforeseen phenomenon of cyclisation leading to the formation of thermodynamically stable four-membered Si_2N_2 cyclodisilazanes such as *c*-$(Ph_2Si–NBn)_2$ (**5**). The main lines of the mechanism leading to the benzene-releasing cyclisation of $Ph_3SiN(Bn)SiPh_2NHBn$ (**4**) have been clearly delineated. The identified operative stepwise process involves the initial facile formation of a [Ba{N(Bn)-$SiPh_2N(Bn)SiPh_3$}$_2$] species, in which the intramolecular nucleo-

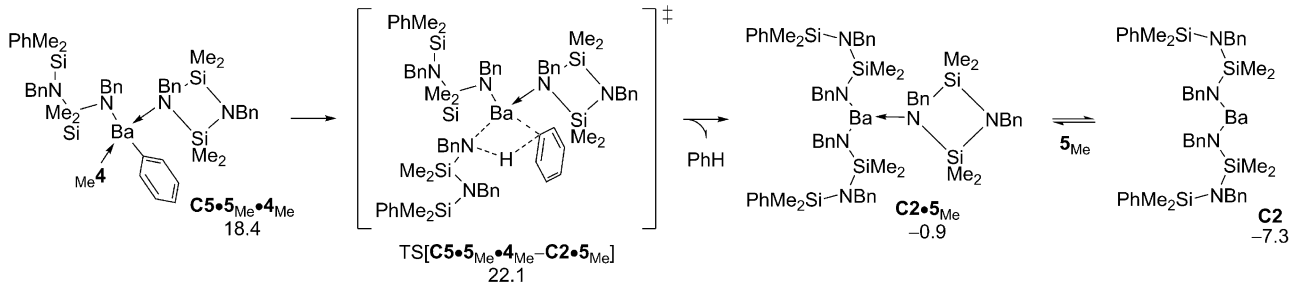


Figure 4. Ba–C phenyl-bond protonolysis at barium phenyl amido **C5**. Energies are given in kcal mol^{-1} relative to {**C2** + n × $\mathbf{4}_{Me}$}.

philic attack of the metal-bound amide onto the terminal silicon atom generating a five-coordinate silicate is followed by turnover-limiting β-C_6H_5 transfer to barium. This releases the cyclic disilazane *c*-$(Ph_2Si{-}NBn)_2$ and produces a transient [Ba]–Ph species which is irreversibly protonolysed by another $Ph_3SiN(Bn)SiPh_2NHBn$ molecule to regenerate the competent [Ba]–$N(Bn)SiPh_2N(Bn)SiPh_3$ species.

Regarding the synthesis of long chain linear polycarbosilazanes, we are now considering the introduction of substituents that, by their steric or electronic effects, will privilege chain growth over cyclisation. One other possibility is to employ hydrosilanes bearing aliphatic substituents only, since cyclisation is driven by the release of aromatic molecules, whereas it does not occur when the chain growth is initiated from, for instance, a trimethylsilanyl fragment. However, this must be evaluated in the light of the limited reactivity displayed elsewhere by alkylsilanes in N–H/H–Si dehydrocouplings.[15b] Optimising the conditions for the barium-mediated dehydropolymerisation[16] of $HSiPh_2N(Me)CH_2C_6H_4CH_2NHMe$ (and derivatives thereof), an α,ω-bifunctional monomer synthesised here (**11**) for the first time, is another option. Our efforts towards the preparation of polycarbosilazane preceramic polymers[10] will be reported in due course.

The formation of cyclodisilazanes also conveys significant interest, because they are valuable monomers for the synthesis of linear, high-molecular-weight polysilazanes.[5,6a] This method is by no means restricted to aromatic-substituted amines and hydrosilanes, but can be extended to many primary and secondary amines, thus opening access to the preparation of a broad range of such products. Even though methods for the preparation of cyclodisilazanes have been known for a number of years,[6a] including by cyclization of bis(methylamino)silanes with chlorosilanes[45] or pyrolysis of diaminodiorganosilanes,[46] none are as general and versatile as the barium-catalysed cyclisation process described here. In addition, it is easily implemented (even if, so far our attempts at carrying out one-pot, multi-step syntheses with a single load of precatalyst have been rewarded by limited success, possibly due to the high sensitivity of the catalytically active species), does not require harsh experimental conditions and is relatively atom efficient.

Experimental Section

Experimental procedures are given in the Supporting Information. CCDC 1435967 (**1**), 1435968 (**3**), 1435969 (**4**) and 1435970 (**5**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Keywords: barium · cyclisation · H–Si coupling · N–H coupling · sequential chain extension · silazanes

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[29] The conversions here and in the following sections are given for optimised reaction times and temperatures for reactions performed in NMR tubes. For large-scale syntheses followed to ensure complete conversion of the substrates, other conditions were used, as given in the experimental protocols. See the Supporting Information for details.

[30] It has been shown before that **5** could be prepared in a more principled fashion by dehydrocoupling of $BnNHSiPh_2NHBn$ with Ph_2SiH_2 catalysed by $Ba[N(SiMe_3)_2]_2{\cdot}(THF)_2$, see ref. [15a]. As a test, this same reaction catalysed by **A** gave full conversion to **5** under mild conditions ($[Ph_2SiH_2]_0/[BnNHSiPh_2NHBn]_0/[\mathbf{A}]_0 = 100:100:1$, $[BnNHSiPh_2NHBn]_0 =$ 1.0 M in benzene, 25 °C, 2 h).

[31] Because of the high contents in silicon resulting in the formation of non-pyrolysable silicon carbides, the results for the analysis of carbon contents were lower than expected in a number of occasions, see the Supporting Information.

[32] The ^{29}Si NMR spectra for **3** and **4** are characterised by two singlet resonances of equal intensities, at $\delta_{^{29}Si} = -9.87$ and -13.18 ppm for **3**, and at -11.19 and -15.97 ppm for **4**. A single resonance at -11.50 ppm is found in the ^{29}Si NMR spectrum of **5**. These values fall within the typical range of ^{29}Si chemical shifts expected for aryl-substituted silazanes.

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[41] Whereas barium amides are key reactive intermediates in Ba-catalysed N–H/H–Si CDC reactions, barium silyl species do not intervene in this catalytic cycle. See ref. [15].

[42] The otherwise commercially available $Me_3SiNHBn$ (**16**; CAS number 14856-79-2) was prepared by metathesis between Me_3SiCl and BnNHLi, because the CDC of amines with hydrosilanes bearing aliphatic alkyl groups is rather sluggish, see ref. [15].

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[44] The DFT-derived mechanistic scenario for generation of **5** from **4** in the presence of barium bis-alkyl precatalyst **A**, which sees the initial rapid and quantitative conversion of the barium bis-alkyl into the barium bis-silazanyl amido compound, competent of triggering **4**→**5** transformation to involve substrate-assisted β-C_6H_5 transfer onto barium as the most kinetically demanding step, conforms with the observed rate law, describing a first-order dependence on the concentration of both catalyst and substrate.

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FULL PAPER

Cross-Coupling

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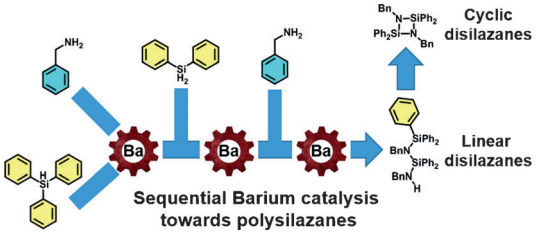
Sequential Barium-Catalysed N–H/H–Si Dehydrogenative Cross-Couplings: Cyclodisilazanes versus Linear Oligosilazanes



Power to barium: The barium complex $Ba[CH(SiMe_3)_2]_2{\cdot}(THF)_3$ catalyses the controlled, highly active and chemoselective formation of linear or cyclic "Si–N–Si–N" disilazanes upon sequential cross-dehydrocoupling of simple amines and hydrosilanes. The mechanistic pathways have been established by combination of experimental and computational data.