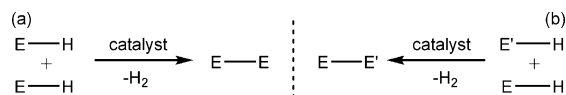


Beyond Dehydrocoupling: Group 2 Mediated Boron–Nitrogen Desilacoupling

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Abstract: The alkaline-earth element bis(trimethylsilyl)-amides, $[Ae\{N(SiMe_3)_2\}_2(thf)_2]$ [$Ae = Mg, Ca, Sr$], are effective precatalysts for boron–nitrogen bond formation through the desilacoupling of amines, $RR'NH$ ($R = \text{alkyl, aryl}$; $R' = H, \text{alkyl, aryl}$), and $pinBSiMe_2Ph$. This reactivity also yields a stoichiometric quantity of Me_2PhSiH and provides the first example of a catalytic main-group element–element coupling that is not dependent on the concurrent elimination of H_2 .

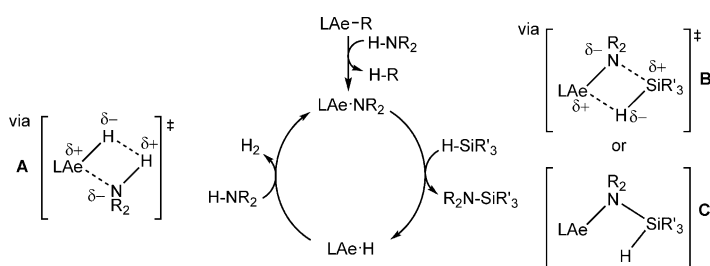
The selective catalytic formation of element–element bonds is of vital importance for the synthesis of both molecular and macromolecular entities. While a majority of attention will remain fixated on the construction of C–C and C–E ($E = p\text{-block element}$) bonds, there is growing interest in the development of catalytic routes to homonuclear E–E ($E = B, Si, Sn, P, As, \text{etc.}$) and heteronuclear E–E' (e.g. $E = B, E' = N$; $E = Si, E' = N, O$) linkages.^[1] Without exception, all of these latter advances have been achieved through the catalytic dehydrocoupling of E–H and E'–H or E–H and E'–H substrates with concomitant elimination of dihydrogen (Scheme 1). While such dehydrogenative methods will



Scheme 1. Catalyzed dehydrocoupling for the formation of a) homonuclear and b) heteronuclear main-group element–element bonds.

undoubtedly continue at the forefront of p-block cross-coupling, this chemistry is critically dependent on the availability of suitable E–H and E'–H substrates. For the heavier p-block elements in particular, this latter requirement is likely to impose a severe limitation on the ultimate scope of available reactivity. It is clear, therefore, that the construction of increasingly sophisticated p-block molecules and materials will be greatly facilitated by the development of alternative and more generalized protocols for the catalytic assembly of E–E and E–E' bonded species.

The use of catalytic reagents derived from the heavier alkaline-earth elements ($Ae = Mg, Ca, Sr, \text{and } Ba$) is attractive on account of their high terrestrial abundance and low toxicity.^[2] In the case of these elements, access to catalytic manifolds through E/E'–H oxidative addition steps commonly associated with many transition-metal-based catalyses is precluded by the stability of the 2+ oxidation state. Rather, successive small-molecule activation steps must be effected through σ -bond metathesis and related reaction processes, the efficacy of which is dictated by both the polarization and relative basicity of the substrates and catalytic intermediates. A case in point is provided by the group 2 catalyzed Si–H/H–N heterodehydrocoupling of hydrosilanes and amines, HNR^1R^2 ($R^1, R^2 = H, \text{alkyl, aryl}$; Scheme 2).^[3] The orientation of each dihydrogen- and silazane-producing metathesis transition state shown as **A** and **B** in Scheme 2 is dictated by the relative polarization of the hydridic Si–H and acidic N–H functions and the polarization of the substituent bonding to the highly electropositive alkaline-earth center. Two recent reports serve to highlight a further subtlety. Kinetic and computational analysis of reactions utilizing tris(oxazolinyl)-borato magnesium or anilidoimine barium reagents has deduced that the rate-determining step of the catalysis is best described as a nucleophilic attack on silane by a magnesium or barium amide. The silazane product and an alkaline-earth element hydride available for onward propagation of the catalysis then result from intramolecular β -hydride elimination within the consequent five-coordinate silicate intermediate (**C** in Scheme 2).^[3a,c] This reactivity may, thus, be



Scheme 2. Silazane formation by dehydrocoupling of silane Si–H and amine N–H bonds mediated by alkaline-earth elements.

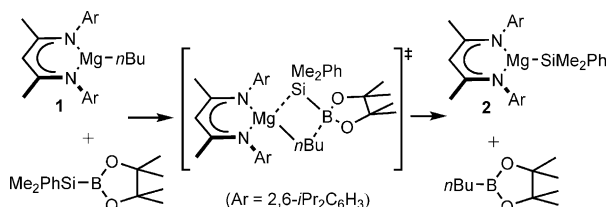
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rationalized as a result of both the hydridic character of the Si–H function and the ability of silicon to attain a hypervalent 5-coordinate geometry. More generally, these observations emphasize that the activation of any E–E' bond at a group 2 center is not only dependent on the bond polarity but also the aptitude of the less electronegative (or more Lewis acidic)

center to increase its coordination number. Herein, we extrapolate these design criteria to the selective activation of a silicon–boron bond which informs the first example of a catalytic p-block cross-metathesis that is not dependent on the elimination of dihydrogen.

The commercially available silylborane pinBSiMe₂Ph (pin = pinacolato) has an established pedigree in various copper-catalyzed silyl transfer protocols^[4] as well as in the more recent silylative cyclopropanation of allyl phosphates.^[5] In this latter case a silylpotassium species, generated in situ by reaction with KN(SiMe₃)₂, was suggested to be the active nucleophilic reagent. The combination of a Si–B bond which is negatively polarized toward silicon and a coordinatively unsaturated boron center suggested that pinBSiMe₂Ph would react with Ae–E bonds with high specificity and formation of the alkaline-earth element silyl species. This rationale was borne out by a reaction performed in toluene solution between the β-diketiminato magnesium *n*-butyl derivative (**1**) and an equimolar quantity of pinBSiMe₂Ph (Scheme 3).



Scheme 3. The synthetic route to compound **2**.

Analysis by ¹H NMR spectroscopy indicated that complete conversion to a single new magnesium species (**2**) had occurred after 12 h at room temperature while the corresponding ¹¹B NMR spectrum was consistent with consumption of pinBSiMe₂Ph and the formation of *n*BuBpin (δ = 37.0 ppm). The solution integrity of **2** as a β-diketiminato magnesium silyl species was clearly evident through the appearance of a single new resonance in the ²⁹Si-{¹H} NMR spectrum at δ = –25.3 ppm and correlations observed between the diastereotopic silyl methyl proton resonances at δ = 0.06 and 0.43 ppm and the doublet signals associated with the isopropyl methyl groups of the β-diketiminato ligand in the ¹H NOESY NMR spectrum.

The solid-state constitution of **2** was confirmed through a single-crystal X-ray diffraction analysis, the results of which are shown in Figure 1. Although **2** is the first example of a three-coordinate magnesium silyl to be structurally characterized, the Mg–Si [2.5897(8) Å] bond length is unremarkable, albeit at the low end of the previously observed range.^[6]

Having established the viability of this magnesium-centered Si–B metathesis reactivity, we envisaged its incorporation into the boron–nitrogen “desilacoupling” reaction shown in Scheme 4. This reaction is attractive as it enables the catalytic synthesis of useful aminoboranes, R₂NBpin.^[7] A stoichiometric reaction between **2** and Et₂NH monitored by ¹H NMR spectroscopy, however, appeared to provide the

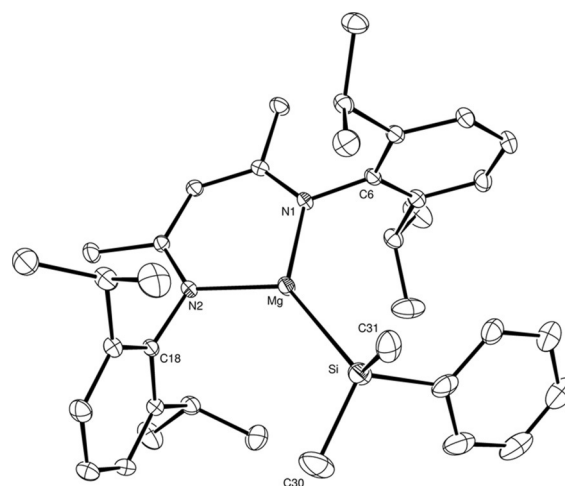
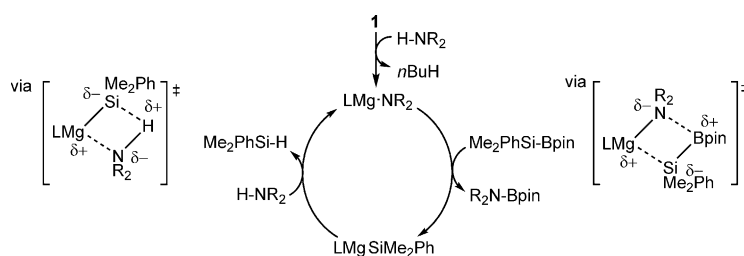


Figure 1. ORTEP representation (25 % thermal ellipsoids) of **2** with hydrogen atoms removed for clarity.^[9] Selected bond lengths [Å] and angles [°]: Mg–N2 2.0128(13), Mg–N1 2.0173(13), Mg–Si 2.5900(7), N2–Mg–N1 93.40(5), N2–Mg–Si 130.76(4), N1–Mg–Si 135.81(4).

adduct species **2**·Et₂NH and no evidence of triorganosilyl protonation was observed even after heating at 60 °C for 1 hour. Furthermore, an attempted catalytic reaction between equimolar (0.05 mmol) quantities of pinBSiMe₂Ph and Et₂NH in C₆D₆ with 5 mol % **1** provided only very limited evidence of Me₂PhSiH formation alongside multiple silicon-



Scheme 4. Hypothetical magnesium-catalyzed boron–nitrogen “desilacoupling” reaction.

and boron-containing products even after heating overnight at 60 °C.

Greater reactivity has typically been observed for many group 2 catalyzed processes through the use of calcium–rather than magnesium-based reagents.^[2] A further attempted catalytic reaction performed utilizing a 5 mol % loading of the β-diketiminato calcium amide [HC{(Me)CN-2,6-*i*Pr₂C₆H₃})₂Ca{N(SiMe₃)₂}(thf)] (**3**), however, provided similarly limited consumption of the Et₂NH coupling partner at room temperature. Heating of this latter reaction to 60 °C also provided no evidence of the desired heteronuclear coupling and yielded the previously reported pinacolborane redistribution product, (μ₂-pinacolato-*O,O'*)-bis(pinacolato-*O,O'*)diboron (B₂pin₃), as the only identifiable new species.^[8]

We reasoned that this apparently limited onward reactivity was a likely consequence of the sterically demanding

nature of the β -diketiminato supporting ligand. We, thus, turned our attention to the less sterically encumbered bis(trimethylsilyl)amido derivatives, $[\text{Ae}[\text{N}(\text{SiMe}_3)_2]_2(\text{thf})_2]$ [$\text{Ae} = \text{Mg}$ (**4**), Ca (**5**), Sr (**6**)], which we have previously demonstrated as highly competent catalysts for the dehydrocoupling of silanes and amines.^[3b] In this case an initial reaction performed between $\text{pinBSiMe}_2\text{Ph}$ and Et_2NH with 5 mol % **5** provided > 95 % conversion to the aminoborane product, Et_2NBpin , over 3 days at room temperature with no evidence of concurrent pinacolate redistribution to B_2pin_3 . The other products of the reaction were $\text{HN}(\text{SiMe}_3)_2$, produced at the immediate onset of the reaction through protonation of the precatalyst, and a stoichiometric quantity of Me_2PhSiH which was clearly evident from the appearance of septet (1H) and doublet (6H) ^1H NMR resonances centered at $\delta = 4.61$ and 0.21 ppm, respectively.

Encouraged by this catalytic boron–nitrogen desilacoupling, the scope of the reaction was investigated for all three bis(trimethylsilyl)amido precatalysts (**4–6**) with a range of mono- and diorganoamines and anilines at room temperature. The results of this study, shown in Table 1, highlight a general

Table 1: Boron–nitrogen desilacoupling catalyzed by compounds **4–6** (0.0025 mmol) with amine (0.05 mmol) and $\text{pinBSiMe}_2\text{Ph}$ (0.05 mmol) in C_6D_6 (0.5 mL).

Entry	Amine ^[c]	4		5		6	
		Conv. [%]	$t^{[d]}$	Conv. [%]	$t^{[d]}$	Conv. [%]	$t^{[d]}$
1	BnNH_2	42	3 d ^[b]	33	2 d ^[a]	80	1 d ^[a]
2	$t\text{BuNH}_2$	86	3 d ^[b]	99	1 d ^[a]	99	1 d ^[a]
3	PhNH_2	33	10 d ^[b]	78	2 d ^[a]	98	1 d ^[a]
4	DippNH ₂	10	10 d ^[b]	96	1 d ^[a]	97 ^[e]	1 d ^[a]
5	$\text{PhNH}(\text{Me})$	90	2 d ^[a]	99	1 d ^[a]	99	1 d ^[a]
6	Et_2NH	94	1 d ^[a]	95	3 d ^[a]	96	3 d ^[a]
7	$(\text{CH}_2)_5\text{NH}$	78	2 d ^[a]	99	1 d ^[a]	99	5 min ^[a]
8	$\text{O}(\text{CH}_2)_4\text{NH}$	71	5 d ^[b]	99	1 d ^[a]	99	5 min ^[a]
9	Ph_2NH	45	5 d ^[b]	99	2 d ^[a]	92	2 d ^[a]
10	$\text{HN}(\text{SiMe}_3)_2$	0	3 d ^[b]	0	3 d ^[b]	88	1 d ^[b]

[a] At room temperature. [b] At 60 °C. [c] Bn = benzyl, Dipp = 2,6-diisopropylphenyl. [d] d = days. [e] Product is DippN(Bpin)₂.

increase in catalytic activity with increasing ionic radius of the catalytic group 2 metal center. Although reactions with the magnesium precatalyst (**4**) were observed to proceed significantly more slowly and to display much greater variability dependent on the steric demands of the amine coupling partner, only for the extremely sterically hindered hexamethyldisilazane did the reaction shut down completely (Table 1, entry 10). The calcium- and strontium-based catalyses were significantly less sensitive to changes in steric encumbrance of the amine. Although no specific trend could be discerned across the range of alkyl and aryl substitution patterns, secondary alkyl amines were, in general, observed to react with greater efficacy than primary amines (Table 1, entries 6–8). The reactions ensued with good stoichiometric control and, among primary amine substrates, only the Sr-catalyzed

transformation of the more sterically encumbered aniline DippNH₂ displayed a preference for bis-borylation. In no case was any onward reactivity of the Me_2PhSiH by-product observed even with heating of the completed desilacoupling reactions to 100 °C.

The empirical trends discerned by inspection of Table 1 were further examined through a kinetic study performed on the reaction of $\text{Ph}(\text{Me})\text{NH}$ and $\text{pinBSiMe}_2\text{Ph}$. Reactions catalyzed by the magnesium species **4** were omitted as the catalysis was too slow to allow kinetic monitoring within practicable timeframes. In all experiments performed with **5** and **6**, precatalyst activation was observed to ensue through complete protonation of the bis(trimethylsilyl)amide residues. The reactions performed with 2–8 mol % **6** conformed to global first order kinetics and the resultant variation in k_{obs} indicated a second order rate dependence on **[6]**. In contrast, reactions utilizing a similar range of catalyst loadings of **5** provided notably linear second order rate plots and a first order dependence on changing catalyst concentration. Further experiments performed under pseudo first order conditions with a 20-fold excess of $\text{Ph}(\text{Me})\text{NH}$ for both systems allowed the formulation of the contrasting rate laws shown as Equations (1) and (2).

$$\text{Rate} = k[\mathbf{5}]^1[\text{Ph}(\text{Me})\text{NH}]^1[\text{pinBSiMe}_2\text{Ph}]^1 \quad (1)$$

$$\text{Rate} = k[\mathbf{6}]^2[\text{Ph}(\text{Me})\text{NH}]^0[\text{pinBSiMe}_2\text{Ph}]^1 \quad (2)$$

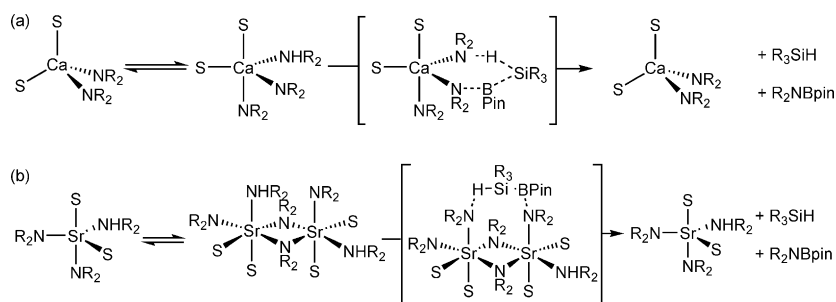
The activation parameters (Table 2), deduced through variable temperature Arrhenius and Eyring analyses, are similar for both systems and, we suggest, most likely reflect variations across the relevant Ae–N bond strengths. In both

Table 2: Activation parameters for the catalytic desilacoupling of *N*-methylaniline with $\text{pinBSiMe}_2\text{Ph}$ mediated by **5** and **6**.

	E_a [kJ mol ^{−1}]	$\Delta H^\ddagger$ [kJ mol ^{−1}]	$\Delta S^\ddagger$ [J mol ^{−1} K ^{−1}]	$\Delta G^\ddagger_{298}$ [kJ mol ^{−1}]
5	58.4(1)	55.8(1)	−113.0(4)	22.2
6	50.7(1)	48.2(1)	−144.2(3)	52.3

cases a significantly negative entropy of activation is consistent with the assembly of a highly ordered rate-determining transition state. We and others have previously highlighted the impact of entropic effects on the rate-determining kinetics of reactions catalyzed by group 2 reagents and these earlier data have typically been interpreted to reflect a looser substrate assembly about larger and less polarizing alkaline-earth element centers.^[3b,c,10]

Although a similar rationale could be applicable to the desilacoupling mechanism shown in Scheme 4, the low reactivity of **2** with amines and the dearth of any experimental evidence for alkaline-earth element silyl formation under catalytic conditions imply that organosilyl species such as **2** are unlikely to be kinetically competent. The comparable activation parameters summarized in Table 2, therefore, lead us to propose that the rate laws summarized as Equation (1)



Scheme 5. Proposed outer sphere Si-H and B-N bond forming processes catalyzed by a) calcium b) strontium bis(bis(trimethylsilyl)amide)s.

and (2) are more likely reflective of the basicity of the amine substrate and rapid but contrasting alkaline-earth element amide/amine pre-equilibration steps. The respective mono- and bimetallic outer sphere mechanisms illustrated in Scheme 5 are, thus, suggested to facilitate the, possibly concerted, formation of the resultant B-N and Si-H bonds. Although no precise structural information may be deduced, we suggest that the differing catalyst nuclearity inferred from the kinetic data is a direct consequence of increasing Ae radius and resultant decreasing cation charge density with increasing atomic weight.

In conclusion, we show that the readily accessible heavier alkaline-earth element amides [Ae{N(SiMe₃)₂}(thf)₂] [Ae = Mg, Ca, Sr] are competent reagents for the boron-nitrogen desilacoupling of amines and silylboranes. To the best of our knowledge, the reactivity described herein provides the first example of a non-dehydrogenative catalytic cross-coupling. Moreover, our observations suggest that such processes are likely to display even greater mechanistic diversity than initially anticipated. We suggest that this reactivity begins to lay a foundation for the development of a more generalized set of substrate design principles, which will greatly expand the scope of main-group-catalyzed reactivity.

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Keywords: calcium · dehydrocoupling · desilacoupling · magnesium · strontium

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