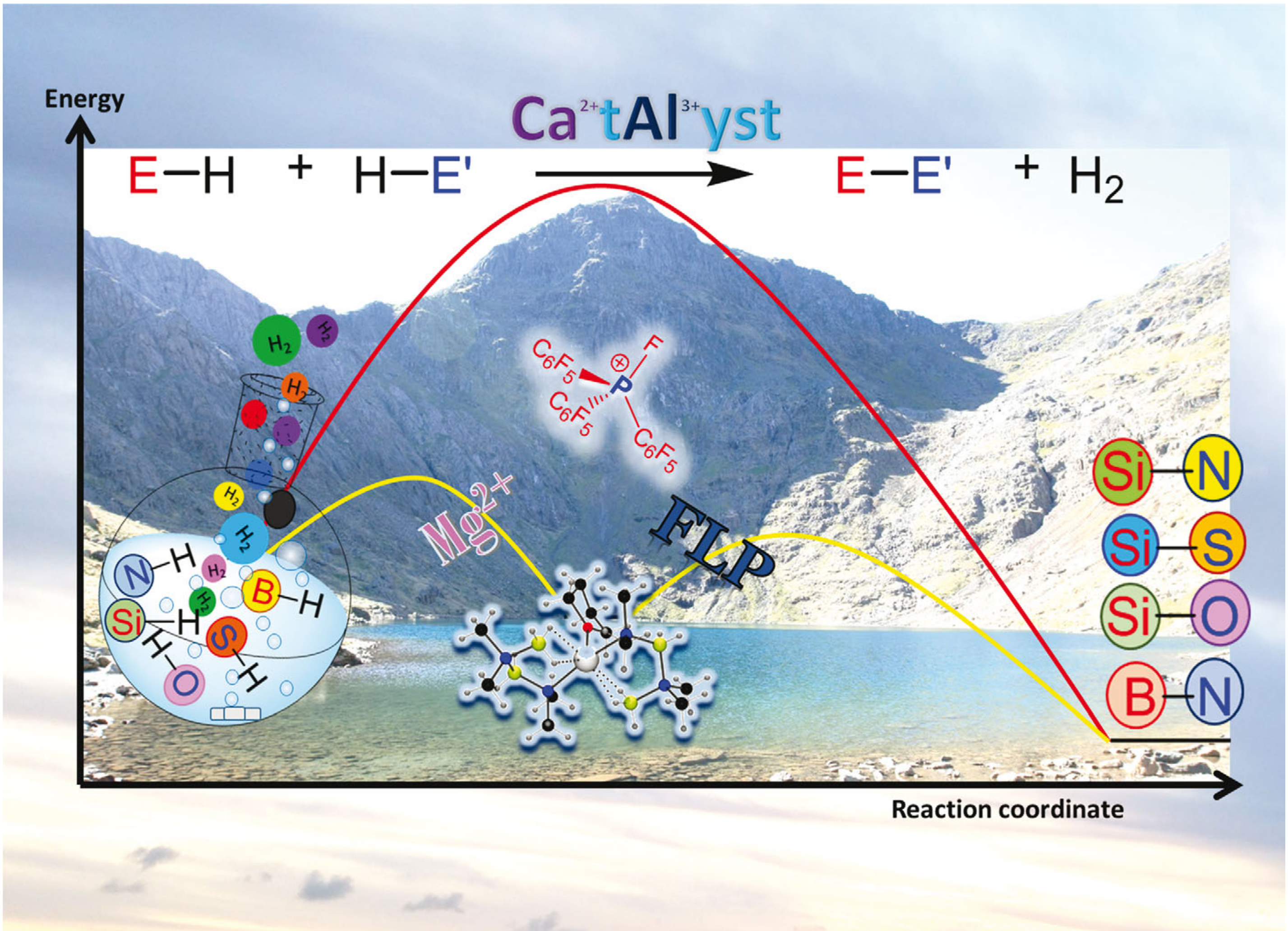

Featuring work from the research group of Rebecca Melen, Cardiff University, UK

Dehydrocoupling routes to element–element bonds catalysed by main group compounds

This tutorial review by Melen highlights recent advances in the use of main group catalysts in the formation of E–E bonds.

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Chem Soc Rev

TUTORIAL REVIEW

View Article Online
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Cite this: *Chem. Soc. Rev.*, 2016, **45**, 775

Received 2nd July 2015

DOI: 10.1039/c5cs00521c

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Dehydrocoupling routes to element–element bonds catalysed by main group compounds†

Rebecca L. Melen

Dehydrocoupling reactions, *i.e.* reactions involving elimination of H_2 between two E–H bonds, provide a clean route to E–E bonds within the main group. The products afforded from these reactions have applications in organic synthesis and materials chemistry, and in addition the H_2 released during these reactions can also be useful as an energy source. Previous methods for dehydrocoupling involve both thermal and transition metal catalysed routes but recent developments have shown that main group compounds can be used as catalysts in these reactions. This tutorial review will focus on the development of main group catalysed dehydrocoupling reactions as a route to heteronuclear element–element bonds.

Key learning points

(1) Introduction to main group element–element bonds and their applications
(2) Dehydrocoupling reactions as a route to element–element bonds
(3) Main group compounds in dehydrocoupling reactions
(4) Comparison of reactivity pathways and mechanistic aspects of different main group dehydrocoupling catalysts
(5) Future prospects of main group catalysed dehydrocoupling

1. Introduction to dehydrocoupling

Dehydrocoupling involves the formation of element–element (E–E) bonds with the concurrent loss of hydrogen gas. Dehydrocoupling reactions between two of the same elements (homo-dehydrocoupling) or two different elements (hetero-dehydrocoupling) provide a convenient and clean method to synthesise E–E and E–E′ bonds with the release of H_2 as the sole by-product (eqn (1)).

$$\text{E–E} + \text{H–E}' \rightarrow \text{E–E}' + H_2 \qquad (1)$$

Both E–E and E–E′ bond-forming reactions are central to the development of many areas of main group chemistry including inorganic rings, chains and polymers. These reactions offer significant advantages over previous methods of main-group E–E′ bond formation which were often difficult. Classical syntheses involved element-specific reductive coupling, high temperature condensation reactions or salt metathesis reactions.[1] Dehydrogenative coupling reactions have a wide range of important applications in terms of both the main group element products formed and the H_2 gas released. The E–E′ bonded products have found applications in both organic synthesis and materials chemistry, whereas the H_2 released during these reactions could be used as an energy source for a future Green Economy.[1] In this Tutorial Review ‘classical’ thermal dehydrocoupling reactions as a method for E–E and E–E′ bond formation will be introduced, followed by a review of recent developments in main-group catalysed dehydrocoupling reactions specifically in hetero-dehydrocoupling reactions. In particular a comparison of the similarities and differences in catalytic activity between main group elements will be addressed, focusing on important factors which appear necessary for efficient main group catalysts. The development of E–E and E–E′ bond-forming reactions is as important to main group chemists as C–C bond forming reactions are to organic chemists.

One of the classical approaches to form E–E bonds is the thermolysis of binary element hydrides, EH_n. In these cases the entropically favourable elimination of H_2 appears a significant driving force in E–E bond formation. As early as 1880 the complete decomposition of silane (SiH_4) at elevated temperatures (400 °C) was found to afford elemental Si and dihydrogen.[2] Indeed, the thermal decomposition of SiH_4 is an industrially important process and SiH_4 is now used as a source of ultra-high purity silicon *via* chemical vapor deposition.[3] However, the outcome of such dehydrocoupling reactions is often poorly defined.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5cs00521c

Whilst the ultimate product may be elemental E and dihydrogen, intermediate hydrides of formula E_xH_y can also be isolated under milder thermolysis conditions. In many cases a mixture of products can be observed in which the product distribution is sensitive to the temperature. For example, thermal decomposition of B_2H_6 is very complicated and leads to higher order boranes.[4] The pyrolysis above 100 °C is a stepwise process (eqn (2)) initially affording B_3H_7 and subsequently higher boranes such as B_4H_{10}, B_5H_9, B_5H_{11}, B_6H_{10}, B_6H_{12} and eventually yielding the more stable borane $B_{10}H_{14}$ along with polymeric BH boranes and higher order boranes. In these cases careful control of the reaction temperature, time and pressure is required to isolate the intermediate boranes in reasonable yields.[5]

$$B_2H_6 \rightleftharpoons 2BH_3$$

$$B_2H_6 + BH_3 \rightarrow B_3H_7 + H_2$$

$$B_3H_7 + BH_3 \rightleftharpoons B_4H_{10} \qquad (2)$$

The E–H bond cleavage occurring during pyrolysis broadly follows the strength of the E–H bond broken (Table 1).[1] Thus, whilst methane has to be heated in the range 800–1000 °C to generate carbon black and polycyclic hydrocarbons,[7] silane completely decomposes[2] at 400 °C and the thermal decomposition of germane to form elemental germanium and dihydrogen commences at just 280 °C.[8] The weakening of the E–H bond on descending group 14 is reflected in other groups of the periodic table due to poorer E–H covalency on descending the group through orbital size/energy mismatch.[1] Conversely there is a general increase in E–H bond energy from left to right across a period due to the increasing ionic contribution to bonding associated with the greater bond polarity. Both the strength and polarity of the E–H bond are important factors when considering E–H dehydrocoupling processes.[1] Similar pyrolytic decomposition reactions have been used in E–E′ bond formation and is well-illustrated by the formation of boron nitride from thermal decomposition of NH_3BH_3.[9] These thermal methods are energy intensive and, in some cases, may lead to a distribution of products rather than a well-defined single product. As a consequence approaches to generate single products or a single major product under mild conditions are highly desirable.[9] While metal-catalysed carbon–carbon bond forming reactions are an extremely important part of modern synthetic organic chemistry, the catalytic formation of main group element–element bonds represents a comparatively new and exciting area.[10] Catalytic E–E bond formation was first reported by Sneddon in 1984 in the formation of homonuclear B–B bonds when they successfully linked two polyhedral boron cages using $PtBr_2$ as a catalyst.[10] Subsequently catalytic E–E bond formation has become an area of specific interest with many reports of efficient transition metal catalysts with long lifetimes and good turnover frequencies in the formation of a wide range of homo- and hetero-nuclear E–E bonds under mild conditions.[1,9–11] Most catalytic reactions are currently considered the domain of transition metals however, in recent years there has been an evolution of main group catalysis. An alternative strategy to E–E and E–E′ bond formation is to use main-group catalysts and these are the focus of this review.

Rebecca L. Melen

Rebecca Melen studied for her MSc and PhD degrees at the University of Cambridge, completing her PhD in 2012 with Prof. Dominic Wright. Her research focused on dehydrocoupling reactions using main group compounds. Following Postdoctoral studies with Prof. Douglas Stephan in Toronto and with Prof. Lutz Gade in Heidelberg, she took up a position at Cardiff University in 2014. Her research interests include diverse aspects of main group reactivity and catalysis.

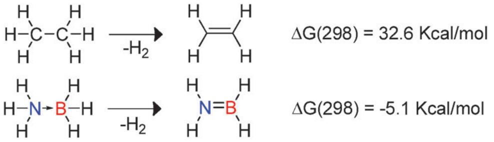
Table 1 Approximate diatomic E–H bond enthalpies (kJ mol^{-1})[6]

Group 13	Group 14	Group 15	Group 16	Group 17
B–H	C–H	N–H	O–H	F–H
389	411	386	456	565
Al–H	Si–H	P–H	S–H	Cl–H
285	318	321	364	432
Ga–H	Ge–H	As–H	Se–H	Br–H
<274	285	297	313	366
In–H	Sn–H	Sb–H	Te–H	I–H
243	264	257	270	298

2. Catalytic heteronuclear-dehydrocoupling

2.1 B–N bond formation

The use of hydrogen as a renewable, non-toxic and clean energy source in addition to its high energy density has attracted attention in recent years.[9] In this context amine-borane compounds may be effective hydrogen storage materials since they offer high hydrogen content by mass (*ca.* 20% by mass hydrogen for NH_3BH_3). Indeed there is now a substantial body of research describing efficient approaches to the catalytic hetero-dehydrocoupling reactions of amine-boranes as hydrogen sources.[1,9,10] These studies have also been driven by the interest in boron-nitrides such as hexagonal boron-nitride which has a range of applications in high temperature ceramics and as a lubricant *inter alia.*[1] As a consequence one of the most well-studied areas of dehydrocoupling is the dehydrogenation of amine-borane compounds. The differing electronegativities of B and N with respect to H within the donor–acceptor adduct $H_3N \rightarrow BH_3$ results in polarisation of both B–H and N–H bonds.[9] This polarity enables facile release of hydrogen with the dehydrogenation of NH_3BH_3 to generate $H_2N{=}BH_2$ being mildly exothermic and favourable on both entropic and enthalpic terms. This is in stark contrast to isoelectronic ethane for which dehydrogenation to form ethene is endothermic (Scheme 1).[9] As a consequence, although dehydrocoupling of NH_3BH_3 is thermodynamically



Scheme 1 Thermodynamics of dehydrogenation of ethane *versus* NH_3BH_3.

favoured at 298 K, much higher temperature are required for the dehydrogenation of ethane.[12]

Owing to the mild conditions and increased selectivity in catalysed dehydrocoupling reactions, a wide range of transition metal catalysts have been developed and employed in the dehydrogenation/dehydrocoupling of a diverse spectrum of primary (RNH_2BH_3) and secondary (R_2NHBH_3) amine-boranes to afford monomeric or dimeric products, borazines or polymeric B–N compounds depending on the substrate.[9] The synthesis of poly-amino-boranes has been explored to generate boron-nitrogen polymers which are analogues of polyolefins $[R_2NBR_2']_n$ which may have potential applications in the synthesis of carbon free ceramics.[1,9,10] There are currently many catalysts based upon transition metals which have been applied to amine-borane dehydrogenation reactions.[9] Of these, the platinum group metals appear to offer some of the best catalytic reactions to date and have been widely studied. However, complexes of first row transition metals (*e.g.* Fe, Cu) and early transition metals (*e.g.* Ti, Zr) have also been explored.[9] An important aspect of transition-metal catalysed dehydrocoupling appears to be associated with the Lewis acidic (or Lewis basic) character of the metal. For example a range of d^0 metals *e.g.* Ti, Zr have high Lewis acidity and have been shown to be effective in the dehydrocoupling of amine-boranes.[13] The diverse range of main group metals and oxidation states permit the Lewis acidity and basicity of as well as hard/soft character of the main group metal to be fine tuned. This opportunity to tune both Lewis acidity and basicity is at the heart of much of the renaissance in main group chemistry and has led to a range of both s- and p-block catalysts whose activities appear related to their Lewis acidity and/or the presence of strongly basic anions which are capable of deprotonating the amine-borane substrate.[13]

2.1.1 B–N bond formation using alkaline earth elements. An important discovery in B–N dehydrocoupling was the observation that the closed shell group 2 ions can catalyse dehydrocoupling reactions. The alkaline earth (Ae) systems employed have been based upon magnesium, calcium and strontium bearing alkyl, amido ligands or β-diketiminate ligands (Fig. 1).

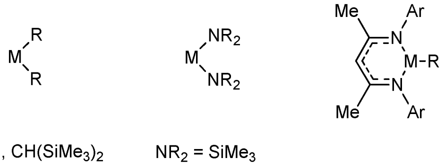


Fig. 1 Alkaline earth systems employed in dehydrocoupling reactions.

When Me_2NHBH_3 was reacted with $MgBu_2$ or $Mg[CH(SiMe_3)_2]_2(thf)_2$ in a 4 : 1 ratio, a stoichiometric dehydrocoupling reaction occurred to liberate H_2 and generate $Mg(NMe_2BH_2NMe_2BH_3)_2(thf)$ which was identified by multinuclear NMR and X-ray diffraction (Fig. 2, left).[14] The crystal structure reveals the B_2N_2 chain coordinates to the magnesium centre through an Mg–N bond and also *via* an agostic Mg···HB interaction. Heating this species to 60 °C resulted in the elimination of $[Me_2NBH_2]_2$ by an intramolecular σ-bond metathesis (δ-hydride elimination) presumably giving the magnesium hydride as a side-product.[14] The liberation of the dehydrocoupled dimer $[Me_2NBH_2]_2$ from the magnesium at elevated temperatures suggests the potential for a catalytic process. Whilst no direct evidence for Mg–H could be observed in this case, magnesium hydrides have been clearly identified elsewhere in this chemistry (*vide infra*).

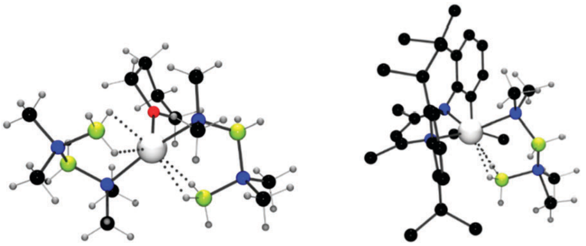
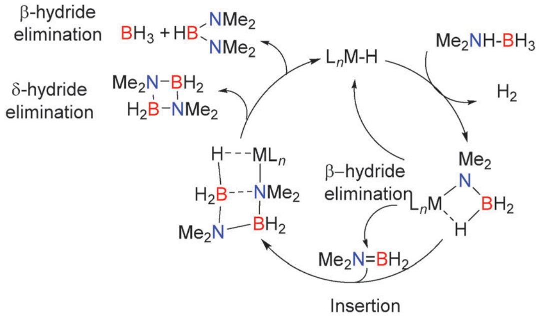


Fig. 2 X-ray structure of $Mg(NMe_2BH_2NMe_2BH_3)_2(thf)$ (left) and (Dipp-nacnac)$Mg(NMe_2BH_2NMe_2BH_3)$ (right) showing Mg···HB interactions.

In order to test the catalytic potential of these reactions 5 mol% $Mg[CH(SiMe_3)_2]_2(thf)_2$ was employed in the dehydrocoupling of Me_2NHBH_3 resulting in formation of the dimer $[Me_2NBH_2]_2$ after 72 h at 60 °C along with smaller quantities of $(Me_2N)_2BH$.[14] The proposed mechanism shown in Scheme 2 is supported by NMR data and the identification of intermediates including both Ae–NMe_2BH_3 and Ae–$NMe_2BH_2NMe_2BH_3$ complexes in this and closely-related reactions.

Evidence for the proposed mechanism involving β-hydride elimination and insertion steps was provided by the stoichiometric reactions of alkyl–strontium complexes with secondary amine-boranes to give $(Me_3Si)_2HC$-Sr-NR_2BH_3 (R = Me, $(CH_2)_2$) which could undergo stoichiometric β-hydride elimination and Sr–C insertion reactions to give $(Me_3Si)_2HC$-BH-NR_2.[15] Similarly the stoichiometric reactions of $M[N(SiMe_3)_2]_2$ (M = Mg, Ca, Sr, Ba) with Me_2NHBH_3 or $^iPr_2NHBH_3$ were investigated.[16] With the magnesium silylamide starting material the amino-boranes

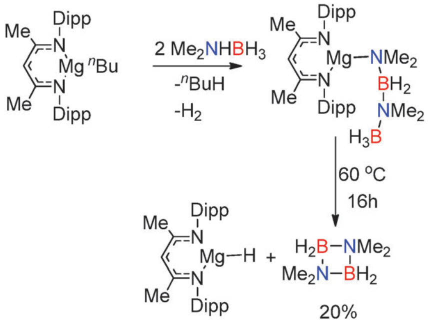


Scheme 2 Proposed mechanism for the catalytic dehydrocoupling of Me_2NHBH_3 group 2 metals.

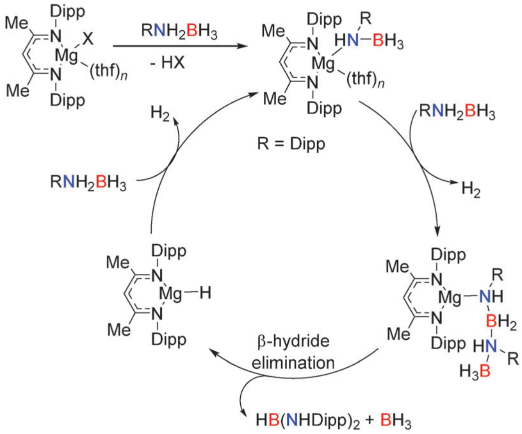
$Me_2N{=}BH_2$ or $^iPr_2N{=}BH_2$ are formed in high yields *via* δ-hydride elimination, whereas with calcium (depending upon the stoichiometry) the yields of the amino-boranes are much lower and with strontium and barium only the metal amido-borane complexes ($M–NMe_2BH_3$ or $M–N^iPr_2BH_3$) are formed with no evidence for β-hydride elimination.[16] Thus it would appear that the reactivity for the elimination is in the order Mg > Ca > Sr > Ba. Such behaviour might be usefully compared to the tendency of d-block alkyls to undergo β-hydride elimination reactions in which the migration appears favourable for more electropositive ('hard') metal ions and proceeds *via* an agostic M···H interaction.[17] Indeed, the dehydrogenation of $^iPr_2NHBH_3$ using 5 mol% $Mg[N(SiMe_3)_2]_2$ resulted in complete dehydrogenation to $^iPr_2N{=}BH_2$ after 1 h. Thus the most active catalysts appear to be those based on Mg.[16]

Replacement of the alkyl and amido ligands by the more strongly coordinating chelate nacnac type ligand affords more stable "heteroleptic" complexes,[18] though the presence of at least one strongly basic M–H, M–R or $M–NR_2$ group is necessary to assist the initial activation of the amine-borane substrate. The reaction of (Dipp-nacnac)Mg^nBu with two equivalents of Me_2NHBH_3 yielded the Mg-chain species (Dipp-nacnac)-$Mg(NMe_2BH_2NMe_2BH_3)$ which was structurally characterised and shows agostic Mg···HB interactions in the solid state (Fig. 2, right) similar to that for $Mg(NMe_2BH_2NMe_2BH_3)_2(thf)$ described above.[14] This compound was found to be more thermodynamically stable than $Mg(NMe_2BH_2NMe_2BH_3)_2(thf)$ and only underwent 20% conversion to $[Me_2NBH_2]_2$ at 60 °C after 16 h (Scheme 3). Significantly elimination of $[Me_2NBH_2]_2$ resulted in the formation of the dimeric magnesium hydride $[(Dipp\text{-}nacnac)MgH(thf)_2]_2$ which, in this case, could be observed by ^1H NMR spectroscopy, thus providing evidence of the formation of metal hydrides in these reactions.[14]

In the presence of more sterically demanding substrates, the outcome of the reaction appears somewhat modified. For example, the closely related bis(trimethylsilyl)amido derivative $[(Dipp\text{-}nacnac)MgN(SiMe_3)_2]_2$ reacts with the sterically encumbered $(Dipp)NH_2BH_3$ with the rapid evolution of hydrogen and formation of the di-amino-borane $HB[NH(Dipp)]_2$ rather than dimeric $[DippNHBH_2]_2$ (Scheme 4).[19] This reaction was found to be catalytic with a mechanism essentially the same as that described in Scheme 2: the reaction proceeds *via* a magnesium amido-borane intermediate $Mg\text{-}NH(Dipp)BH_3$ which reacts with the amine-borane $(Dipp)NH_2BH_3$ with release of H_2 to generate the chain species $Mg\text{-}NH(Dipp)BH_2NH(Dipp)BH_3$. This then undergoes a β-hydride elimination (rather than δ-hydride elimination) to give the symmetrical di-amino-borane product, $HB[NH(Dipp)]_2$ and BH_3, generating a magnesium hydride which can then react with the amine-borane releasing H_2 thereby regenerating the magnesium amido-borane and completing the catalytic cycle.[19] Thus a common catalytic cycle seems prevalent within this series of compounds; initial deprotonation of the N–H group of the RNH_2BH_3 substrate occurs *via* the strongly basic Mg–R or $Mg–NR_2$ group affording an $Ae–NHRBH_3$ complex. Addition of a second equivalent of substrate leads to elimination of H_2 and formation of $Ae–N(R)HBH_2NH(R)BH_3$ which then undergoes a δ-hydride elimination to generate the hydride Ae–H and release dimeric $[RNHBH_2]_2$ although β-hydride elimination can be a competing factor generating $HB(NHR)_2$. In the case of the bulky amine-borane $DippNH_2BH_3$ β-hydride elimination is preferable over δ-hydride elimination generating $HB[NH(Dipp)]_2$ as the product in this reaction. In both cases (β- or δ-hydride elimination) a magnesium hydride species forms which appears a sufficiently potent base to deprotonate another equivalent of amine-borane RNH_2BH_3 regenerating further $Ae–NHRBH_3$ thus allowing a catalytic reaction to take place.

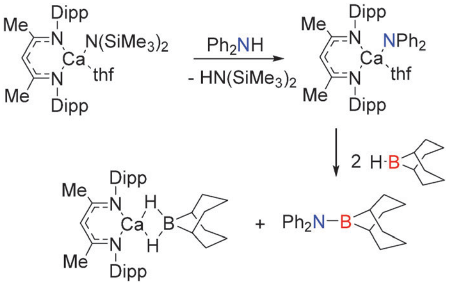


Scheme 3 Dehydrocoupling of Me_2NHBH_3 using $[(Dipp\text{-}nacnac)Mg^nBu]_2$.

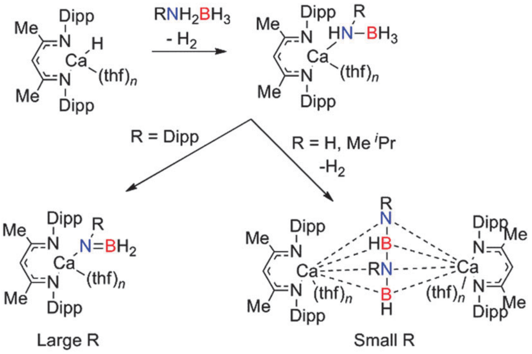


Scheme 4 Synthesis of the diaminoborane $HB[NH(Dipp)]_2$ using the pre-catalyst $[(Dipp\text{-}nacnac)MgN(SiMe_3)_2]_2$.

One of the first indications that the related calcium nacnac complexes may be used in B–N coupling was the report of the stoichiometric σ-bond metathesis reaction between a β-diketiminato calcium amide complex with 9-BBN to give the B–N product and a calcium borohydride complex (Scheme 5).[20] Here again the $Ae–NR_2$ group is used to deprotonate the secondary amine in the first step of the reaction. Similar stoichiometric reactions of $[(Dipp\text{-}nacnac)CaH(thf)]_2$ with NH_3BH_3, $MeNH_2BH_3$ or $^iPrNH_2BH_3$ have led to the isolation of calcium amido-borane intermediates which comprise an $NBNB^{2-}$ chain which is formed *via* a B–N coupling process with release of hydrogen (Scheme 6).[18,21] For the bulky substrate $DippNH_2BH_3$ formation of the $B_2N_2{}^{2-}$ chain is suppressed and the calcium complex, $Ae–N(R){=}BH_2$ is formed with release of H_2.[21] The isolation of this complex suggest that,



Scheme 5 Dehydrocoupling of 9-BBN and Ph_2NH using a β-diketiminato calcium amide.



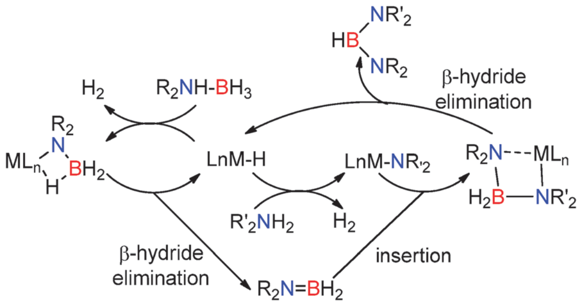
Scheme 6 Dehydrogenation of primary amine-boranes using a (Dipp-nacnac)CaH species.

for Ca, the kinetics of reaction with a further equivalent of RNH_2BH_3 is slow in relation to elimination of H_2 to form the bimetallic complex, whereas for Mg reaction with a further equivalent of substrate appears more favoured. Although [(Dipp-nacnac)-Ca-NH_2BH_3(thf)] was found to be thermally unstable,[18] [(Dipp-nacnac)Ca-NMe_2BH_3(thf)] demonstrated higher stability and at 80 °C underwent some decomposition to generate the monomeric amino-borane $Me_2N{=}BH_2$ and $(Me_2N)_2BH$ and the calcium hydride complex $[(\text{Dipp-nacnac})\text{CaH(thf)}_2]_2$.[14] These studies suggest that a β-hydride elimination/σ-bond metathesis reaction pathway is more prevalent for Ca than Mg which tended to undergo δ-hydride elimination.

In summary, NMR and crystallographic studies of the catalytic and stoichiometric dehydrocoupling of Me_2NHBH_3, together with the evidence of metal hydride intermediates in these systems enabled a general mechanism for the dehydrocoupling mechanism to be proposed (Scheme 2) which combines the aspects described for the mechanisms in Schemes 3–6. The amino-borane $Me_2N{=}BH_2$ is thought to be formed from the β-hydride elimination/σ-bond metathesis of the M–NMe_2BH_3 complex. The alkene-analogue $Me_2N{=}BH_2$ can then insert into the metal-bonded $[Me_2NBH_3]^-$ anion giving the metal-bonded $[NMe_2BH_2NMe_2BH_3]^-$ species. Subsequent δ-hydride elimination affords $[Me_2NBH_2]_2$ whereas β-hydride elimination generates $[(Me_2N)_2BH]$ (Scheme 2). The dehydrocoupling of the secondary amine-borane, pyrrolidine amine-borane $(CH_2)_4NHBH_3$ using both Ca and Mg-based catalysts proves instructive in this regard. When (Dipp-nacnac)$MgN(SiMe_3)_2$ was reacted with one or two equivalents of $(CH_2)_4NHBH_3$ then the compounds (Dipp-nacnac)$MgN(CH_2)_4BH_3$ and (Dipp-nacnac)-$MgN(CH_2)_4BH_2N(CH_2)_4BH_3$ were formed respectively, consistent with the rapid addition of a second equivalent of amine-borane over elimination of dihydrogen.[16] Heating the later compound to 60 °C resulted in the formation of the cyclic dimer product $[(CH_2)_4NBH_2]_2$ as shown by the presence of a triplet in the ^{11}B NMR spectrum at $\delta = 6.5$ ppm, and in the ^1H NMR spectrum a shift due to the potential magnesium hydride was observed suggesting a δ-hydride elimination, identical to that described in the catalytic cycle above for Me_2NHBH_3.[16] With the heavier calcium analogue [(Dipp-nacnac)$CaN(SiMe_3)_2$(thf)] dehydrocoupling of one equivalent of $(CH_2)_4NHBH_3$ gave the calcium amido-borane [(Dipp-nacnac)Ca-$N(CH_2)_4$-BH_3] however subsequent reaction with a second equivalent of amine-borane did not occur.[16] This is consistent with the observation that the calcium is less active in these processes than magnesium as [Ca]-NMe_2BH_3 also does not undergo β-hydride elimination or B–N coupling to form the Ca–NBNB chain.

The alkaline earth bis(trimethylsilyl)amides $M[N(SiMe_3)_2]_2$ (M = Mg, Ca) were later found to be active in the synthesis of unsymmetrical di-amino-boranes from the dehydrocoupling of amine-boranes (R_2NHBH_3) and amines ($R'NH_2$) to give $(R_2N)BH(NR_2')$.[22] These reactions are proposed to proceed *via* metal hydride intermediates which can react with the amine-borane to form the previously observed metal bonded amido-borane which then undergoes β-hydride elimination yielding the amino-borane $R_2N{=}BH_2$.[22] In addition to reaction of the metal hydride with the amine-borane, the metal hydride may also react with the amine resulting in deprotonation of the amine, releasing hydrogen and generating a metal amido species. This metal amido intermediate can then react with the amino-borane $R_2N{=}BH_2$ to give a metal bound di-amido-borate M–$NR_2'BH_2NR_2$. Subsequent β-hydride elimination from this species releases the neutral unsymmetrical di-amino-boranes $(R_2N)BH(NR_2')$ and regenerates the metal hydride (Scheme 7).[22] This methodology has significant advantages over previous synthetic approaches to prepare di-amino-boranes in which only symmetrical-di-amino-boranes $(R_2N)BH(NR_2')$ ($R{=}R'$) could be synthesised from redistribution reactions of tris(dialkylamino)boranes $[(R_2N)_3B]$ with B_2H_6.[23]

In summary, the catalytic dehydrocoupling of a range of amines and boranes has been achieved using alkaline earth



Scheme 7 Proposed mechanism for the group 2 catalysed dehydrocoupling of amines with amine-boranes.

alkyl/amido or β-diketiminate complexes with the catalytic activity in the order Mg > Ca > Sc, consistent with the stronger Lewis acidity/hardness of the smaller group 2 metals. Importantly, in common with transition metal catalytic systems, the β-hydride elimination metal hydrides are proposed as key intermediates in the reactions. Significantly this work showed that higher catalytic activity appears to result from increased charge density of the metal and therefore the use of the more positively charged Al^{3+} and Ga^{3+} complexes are anticipated to be more active in the dehydrogenic coupling of amine-boranes.

2.1.2 B–N bond formation using group 3 metals. The catalytic dehydrocoupling using group 13 elements containing basic $E–NR_2$ bonds has also been investigated and shows several similarities to the group 2 catalysts described above. In this regard, the dehydrocoupling of Me_2NHBH_3 with $Al(NMe_2)_3$ was explored.[24] The reaction of Me_2NHBH_3 with 8 mol% $Al(NMe_2)_3$ was followed by *in situ* ^{11}B NMR studies and showed the rapid formation of $(Me_2NBH_2)_2$ under ambient conditions in addition to small quantities of $(Me_2N)_2BH$ and a triplet at (δ = 1.87 ppm, $^1J_{BH}$ = 107 Hz) which was subsequently assigned to the hypervalent 5-coordinate Al^{III} hydride $[\{(Me_2N)_2BH_2\}_2AlH]$ (Fig. 3) which was isolated from the 1 : 1 stoichiometric reaction of $Al(NMe_2)_3$ with Me_2NHBH_3. The Al^{III} hydride was found to be a thermally stable catalyst for this reaction.[24]

Although the activity of the pre-catalyst $Al(NMe_2)_3$ is relatively low at room temperature (the 8 mol% loading in toluene gives a *ca.* 80% conversion after 5 days), the reaction is significantly faster at elevated temperatures. For example a 5 mol% loading of $Al(NMe_2)_3$ at 50 °C in toluene gives complete conversion after 48 h.[24] The reactivity at higher temperature is at the lower end of that observed for a range of transition metal catalysed systems.[9] DFT studies revealed that the complex $[\{(Me_2N)_2BH_2\}_2AlH]$ readily undergoes a β-hydride transfer from B to Al with a low activation energy ($\Delta G^{\ddagger} \sim +78.2$ kJ mol^{-1} at 298 K) with simultaneous elimination of $Me_2NBHNMe_2$ (identified in the ^{11}B NMR spectrum) which was energetically favourable ($\Delta G = -59.4$ kJ mol^{-1}) to form the four-coordinate aluminium dihydride $(Me_2NBH_2NMe_2)AlH_2$ which is the proposed active catalyst in this reaction.[25] Notably the aluminium dihydride is structurally related to other aluminium dihydrides such as $[^iPr_2NAlH_2]_2$ which have also been shown to be active in dehydrocoupling reactions (see below).[25] The reaction was observed to be first-order in the starting material. A mechanism involving dehydrogenation of Me_2NHBH_3 to give $Me_2N{=}BH_2$ followed by rapid dimerisation to give $(Me_2NBH_2)_2$ can be discounted since $Me_2N{=}BH_2$ is relatively stable in solution and was not detected in the ^{11}B NMR.[25] A general mechanism for the aluminium hydride catalysed dehydrocoupling can be envisaged which proceeds *via* the Al–H acting as a base to deprotonate the substrate (analogous to the alkaline earth chemistry), leading to the formation of a metal-bound $Me_2NBH_3^-$ species which can undergo dehydrocoupling with a second equivalent of substrate to form an aluminium coordinated $[Me_2NBH_2NMe_2BH_3]^-$ intermediate reminiscent of that seen for group 2 catalysts. Subsequent δ-hydride elimination regenerates the dihydride catalyst and releases the product $(Me_2NBH_2)_2$.[25]

The 2 : 1 stoichiometric reaction of the related amine-borane $^iPr_2NHBH_3$ with $Al(N^iPr_2)_3$ afforded the centrosymmetric dimeric aluminium dihydride $[H_2Al(\mu\text{-}N^iPr_2)]_2$. This catalyst once again exhibits the presence of a metal hydride which appears critical in these main-group catalysed dehydrocoupling reactions and notably $[^iPr_2NAlH_2]_2$ exhibits the same core structure as $(Me_2NBH_2NMe_2)AlH_2$ discussed above (by replacement of Al by B). This $[H_2Al(\mu\text{-}N^iPr_2)]_2$ complex was found to be a very active catalyst for the dehydrogenation of $^iPr_2NHBH_3$ to afford $^iPr_2N{=}BH_2$, *e.g.* a 0.5 mol% loading of crystalline $[H_2Al(\mu\text{-}N^iPr_2)]_2$ resulted in the dehydrogenation of $^iPr_2NHBH_3$ to $^iPr_2N{=}BH_2$ at 20 °C.[25] Although low concentrations of highly reactive monomeric $H_2AlN^iPr_2$ cannot be discounted, a mechanism based on a dimetallic aluminium catalyst $[H_2Al(\mu\text{-}N^iPr_2)]_2$ as the active catalyst is proposed (Scheme 8). Initial deprotonation of the protic N–H group by the basic Al–H hydride, releasing H_2 and generates the $[Al]–N^iPr_2–BH_3$ species. A subsequent β-hydride shift from boron to aluminium affords $^iPr_2N{=}BH_2$ and regenerates the catalyst.[25] This deprotonation/β-hydride elimination sequence is identical to that observed for group 2 metal catalysts in the dehydrocoupling of amine-boranes (Section 2.1.1). Since the $[H_2Al(\mu\text{-}N^iPr_2)]_2$ catalyst is prepared *in situ* from $^iPr_2NHBH_3$ and $Al(N^iPr_2)_3$ then $Al(N^iPr_2)_3$ can be used as a pre-catalyst. Thus a 10 mol% loading of $Al(N^iPr_2)_3$ resulted in complete conversion of $^iPr_2NHBH_3$ to $^iPr_2N{=}BH_2$ in 2 h at 60 °C, albeit with a relatively long induction period prior to release of H_2 gas. Similar to the dehydrocoupling of Me_2NHBH_3 the reaction was shown to be first order in substrate.[25] These are similar to the transition metal catalysts $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$ and Cp_2Ti which catalyse the same dehydrogenation reaction in 49% yield at 25 °C in 24 h using a 1 mol% catalyst or give quantitative yields in 1 h at 20 °C using a 2 mol% loading respectively.[13,25]

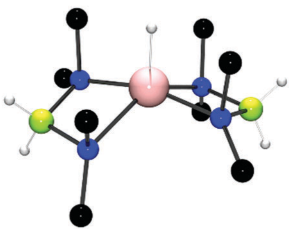
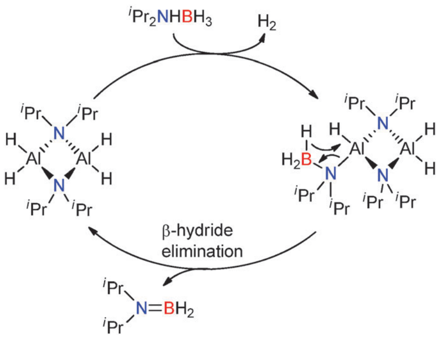


Fig. 3 The crystal structure of the Al^{III} hydride $[\{(Me_2N)_2BH_2\}_2AlH]$.



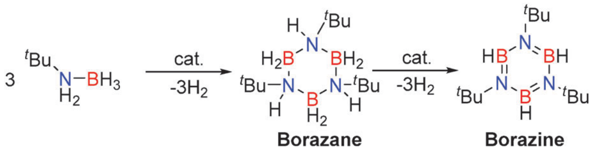
Scheme 8 Catalytic dehydrogenation of $^iPr_2NHBH_3$ using $[H_2Al(\mu\text{-}N^iPr_2)]_2$.

Further evidence for aluminium hydrides/dihydrides as the active catalyst is reflected in the observation that (i) $LiAlH_4$ catalyses the dehydrocoupling of Me_2NHBH_3, although the mechanism is much more complicated than that observed for $Al(NMe_2)_3$ and with substantially lower catalytic activity; (ii) a series of ^tBuO-substituted aluminium hydrides also catalyse the dehydrocoupling of amine-boranes at elevated temperatures with the dihydride $[^tBuOAlH_2]_2$ showing the highest activity.[26]

Replacement of Al^{III} by Ga^{III} was interesting given their identical formal charges and similarity of their radii (due to the d-block contraction) thereby offering potentially similar Lewis acidity. Their reactivity is reflected through a comparison of the ability of $E(NMe_2)_3$ (E = Al, Ga) to effect the dehydrocoupling of the primary amine-borane, $^tBuNH_2BH_3$. In these reactions up to two equivalents of hydrogen can be released per equivalent of starting material, offering the potential to form ring compounds such as borazanes $(^tBuNHBH_2)_3$ and borazines $(^tBuNBH)_3$ by elimination of either one or two equivalents of H_2 respectively, or formation of polymeric compounds such as $[-(R)N{=}B(H)-]_n$. Preparative scale reactions at reduced temperatures allowed the intermediate borazane (isoelectronic with cyclohexane derivatives) $[^tBuNHBH_2]_3$ to be isolated and structurally characterised.[25] Under ambient conditions (3 mol% $Al(NMe_2)_3$ or 5 mol% $Ga(NMe_2)_3$) further dehydrocoupling afforded the borazine $(^tBuNBH)_3$ in addition to an unidentified BN containing polymeric product.[25] This is similar to transition metal processes, such as with the catalyst $[Rh(1,5\text{-cod})(\mu\text{-Cl})]_2$, in which borazanes are intermediates *en route* to borazines in the dehydrocoupling of primary amine-boranes (Scheme 9).[13,27]

Notably gallium appeared to be more active than the corresponding aluminium complexes however precipitation of gallium metal during the reaction reflected a poorer catalyst lifetime. This appears to be due to reduced redox stability which resulted in precipitation of gallium metal during the reaction. Such redox instability was also observed in the reduction of tin(II) and arsenic(III) to either the metal or a Zintl phase during the homo-dehydrocoupling of phosphines.[13,25,28]

2.1.3 B–N bond formation using group 4 metals. Tin(II) compounds have also been examined in the catalytic dehydrogenation of amine-boranes. $Cp^*{}_2SnCl_2$ and Ph_2SnCl_2 were examined as pre-catalysts for the dehydrocoupling of Me_2NHBH_3 but were only found to be only slightly active giving 69% and 47% conversion in benzene at 65 °C using 10 mol% of the tin compound. $SnCl_2$ was also found to be a poor catalyst for the reaction giving only 23% conversion under the same conditions. The precipitation of metallic tin from these reactions accounts for the reduced activity of the tin catalyst relative to the aluminium analogues above. The tin catalysts were also found to be less selective than the aluminium compounds giving a variety of different products from the reaction including the dimer $[Me_2NBH_2]_2$, $Me_2NHBH_2NMe_2$, $H_2BNMe_2BH_3$, as well as other unidentified species (Table 2).[29]



Scheme 9 Dehydrocoupling of primary amine-boranes to give borazines *via* borazane intermediates.

Similar dehydrocoupling studies using $^tBuNH_2BH_3$ as a substrate with $Cp^*{}_2SnCl_2$ (10 mol%), Ph_2SnCl_2 (10 mol%) and $SnCl_2$ (5 mol%) were examined. After 4–5 days at 65 °C a range of dehydrocoupled products were obtained with 95%, 93% and 84% conversion respectively (Table 3).[29] Whilst these reactions showed significantly higher conversions than the corresponding dehydrocoupling reactions with secondary amine-boranes (Table 2), they were also markedly less selective than the aluminium catalysts affording a wide range of product distribution and surprisingly little borazine product. Notably the lack of borazine product may offer distinct advantages in the context of hydrogen storage since borazines are known to poison fuel cells.[9] It is interesting to note that whilst the Sn^{IV} catalysts gave quite a lot of the dehydrogenated $^tBuN(H){=}BH_2$ product, $SnCl_2$ only yielded $<5\%$ of this product, consistent with the harder more Lewis acidic Sn^{IV} centre favouring β-hydride elimination. It is less clear what the active catalyst(s) is/are during these reactions, though the intermediacy of tin-hydrides is likely based on studies on group 2 and 3 metals. For example, dehydrogenation of $^tBuNH_2BH_3$ most likely occurs *via* a β-hydride elimination from a tin amido-borane complex, affording the amino-borane $^tBuN(H){=}BH_2$ and generating a tin hydride (Scheme 10),[29] in a similar manner to that observed for the dehydrocoupling of $^iPr_2NHBH_3$ with $Al(N^iPr_2)_3$ and the dehydrocoupling of amine-boranes with group 2 catalysts.

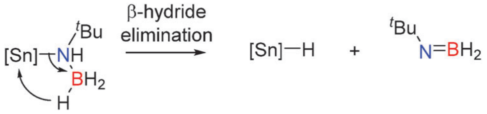
2.1.4 B–N bond formation using frustrated Lewis pairs. Frustrated Lewis pairs (FLPs) comprise sterically hindered Lewis and bases which are precluded from adduct formation upon steric grounds.[30] Aluminium–phosphorus FLPs have also been used in dehydrogenic bond forming reactions. Unlike the group 13-catalysed dehydrocoupling reactions (Section 2.1.2), no aluminium hydrides are formed from these Al/P-based FLPs during this catalytic cycle. The 9.3 mol% reaction of the FLP $Mes_2PC({=}C(H)Ph)Al^tBu_2$ with Me_2NHBH_3 at 45 °C in the melt resulted in rapid evolution of H_2 gas and formation of monomeric $Me_2N{=}BH_2$.[31] This subsequently dimerises to give

Table 2 Dehydrocoupling of Me_2NHBH_3 using tin catalysts

Catalyst	$[Me_2NBH_2]_2$ (%)	$Me_2NHBH_2NMe_2$ (%)	$H_2BNMe_2BH_3$ (%)	Other (%)
$Cp^*{}_2SnCl_2$	67	25	7	<5
Ph_2SnCl_2	18	32	16	34
$SnCl_2$	39	12	2	21

Table 3 Dehydrocoupling of $^tBuNH_2BH_3$ using tin catalysts

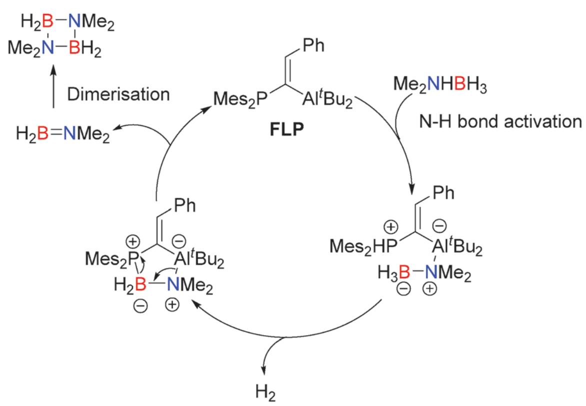
Catalyst	Polymers (%)	$(^tBuNBH)_3$ (%)	$^tBuNH{=}BH_2$ (%)	$^tBuNHB_2H_5$ (%)	Other (%)
$Cp^*{}_2SnCl_2$	20	0	16	26	30
Ph_2SnCl_2	41	8	23	23	30
$SnCl_2$	13	6	<5	33	41



Scheme 10 β-Hydride elimination from the tin amido-borane to give a tin hydride and $^tBuN(H){=}BH_2$.

the borazane $(Me_2NBH_2)_2$ in 71% yield after just 45 minutes when heating to 90 °C giving TONs of 7.6 and a TOF of 10.2 h^{-1}. A substantially lower 0.4 mol% loading of the FLP also proved effective giving 77% yield of the borazane with improved TON (198.3) but somewhat lower TOF (4.5 h^{-1}). The mechanism for the FLP reaction is different to the other aluminium catalysed reactions and does not appear to involve either aluminium hydride intermediates or an [Al]-bonded chain species. Moreover the reaction generates monomeric $Me_2N{=}BH_2$ which has never been observed in the other aluminium catalysed reactions, thereby mitigating against a similar mechanism. In this reaction initial N–H bond activation (and deprotonation) by the phosphine component of the FLP is proposed to form a phosphonium aluminate (Scheme 11), in a similar fashion to other E–H bond activation reactions of FLPs. This then undergoes dehydrogenation with one of the hydridic B–H bonds. Subsequent ring closure affords the amido-borane adduct of the FLP which can eliminate $Me_2N{=}BH_2$ (which can then dimerise to the borazane) and regenerate the catalyst.[31] Despite the different outcome of this reaction in relation to the Al-catalysed processes previously discussed, there are remarkable similarities with both catalyst types offering a Lewis-basic centre (P in this case *versus* hydride or R_2N^- for the main-group metal-catalysed reactions) and a Lewis acidic Al. Indeed the process is very similar to that observed for the dehydrocoupling of $^iPr_2NHBH_3$ using $[AlH_2(\mu\text{-}N^iPr_2)]_2$ (Scheme 8) and the proposed mechanism for dehydrocoupling of Me_2NHBH_3 with $Al(NMe_2)_3$ since, in all cases, the same initial N–H bond activation forming an aluminium amido-borane is observed.

A similar mechanism was proposed in the stoichiometric dehydrocoupling of Me_2NHBH_3 with the intermolecular FLP $B(C_6F_5)_3/^tBu_3P$.[32] In this reaction the Lewis acid/base pair are not geometrically constrained and the dimeric borazane $(Me_2NBH_2)_2$ was the major product in the reaction (rather than $Me_2N{=}BH_2$), alongside smaller quantities of di-amino-borane $HB(NMe_2)_2$. In a similar fashion to the aluminium/phosphorus FLP described above, monomeric $Me_2N{=}BH_2$ was also observed in small quantities in the ^{11}B NMR spectrum which was consumed over time to give the borazane dimer. Here a slightly different order of reaction steps is proposed in the mechanism in which $B(C_6F_5)_3$ first abstracts a hydride from the amine-borane Me_2NHBH_3 to give $[Me_2NHBH_2][(C_6F_5)_3B–H]$. Deprotonation of the protic N–H proton in the $[Me_2NHBH_2]^+$ cation by the phosphine generates the phosphonium cation $[^tBu_3P–H]^+$ and affords the monomer $Me_2N{=}BH_2$ which can then dimerise (Scheme 12). Indeed, the phosphonium borohydride $[^tBu_3PH][HB(C_6F_5)_3]$ was observed as a product in the reaction.[32]



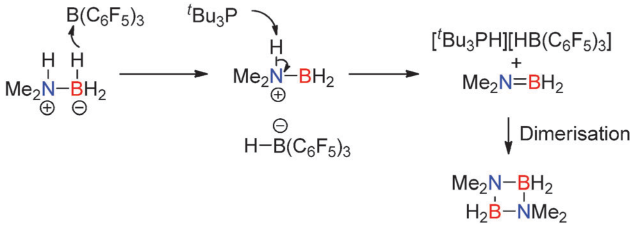
Scheme 11 FLP catalysed dehydrocoupling of Me_2NHBH_3.

2.2 B–P bond formation

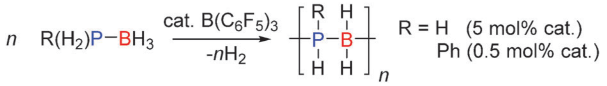
The dehydrocoupling of phosphine-boranes would be expected to be easier than amine-boranes due to the weaker P–H bond relative to the N–H bond. The strong Lewis acid $B(C_6F_5)_3$ was found to be a good catalyst for the dehydrocoupling of phosphine-boranes to form polymeric compounds. 0.5 mol% $B(C_6F_5)_3$ was found to catalyse the dehydrocoupling of $PhPH_2BH_3$ to form poly(phenylphosphino)boranes $[PhPH–BH_2]_n$ in quantitative yield after 3 days at 20 °C or after 3 h at 90 °C (Scheme 13).[33] In this reaction $B(C_6F_5)_3$ was found to be much more active than the transition metal Rh(I) catalyst (RhI) reported around the same time which afforded the polymer in 100% yield after 15 h at 110 °C using the same catalyst loading.[34] In addition the dehydrocoupling of phosphine-borane PH_3BH_3 was also achieved. PH_3 and BH_3 were bubbled into solution of $B(C_6F_5)_3$ (*ca.* 5 mol%) and the resulting solution heated to 70 °C. The ^{31}P and ^{11}B NMR spectra showed the formation of oligomeric and polymeric poly(phosphinoboranes) $H_3P(BH_2PH_2)_nBH_3$ species (Scheme 13). The mechanism likely follows that identified for other $B(C_6F_5)_3$ reactions in which the most hydridic E–H bond is activated by the Lewis acidic boron atom (Section 2.3).[33]

2.3 Si–E bond formation

Hetero-dehydrocoupling to form Si–E bonds has also been an area of significant interest given the diversity of applications of



Scheme 12 Stoichiometric dehydrocoupling of Me_2NHBH_3 with the intermolecular FLP $B(C_6F_5)_3/^tBu_3P$.



Scheme 13 Dehydrocoupling of phosphine-boranes using $B(C_6F_5)_3$.

compounds such as silicones and silazanes ranging from construction materials through to elastomers and medical applications (*vide infra*). In many of these cases the outcome of Si–E (E = N, O, S) bond forming reactions using Lewis acids is strongly dependent upon the coupling reaction since the lone pairs on amines, alcohols and thiols can act as efficient Lewis bases thereby shutting down catalyst activity: for example, with small sterically unencumbered primary alkyl alcohols (EtOH and ^{n}PrOH) catalyst 'poisoning' occurs due to the strongly Lewis basic nature of the lone pair on O which favours formation of strong adducts with the Lewis acid. However, for the less basic thiols, more weakly basic alcohols such as catechol (π-conjugation of the O–lone pair to the aromatic ring) or secondary amines (in which the steric bulk inhibits formation of a Lewis acid–base pair) reactivity is observed in which the rate of reaction was dependent upon the concentration of the oxygen-donor. Conversely the weaker nature of the B–S bond (compared to B–O) means that Lewis acid-catalysed reactions in the presence of thiols reveal a higher activity than the corresponding alcohol due to the poorer Lewis basic nature of sulfur resulting in more free borane for Si–H activation.

2.3.1 Si–O bond formation. The chemical inertness of the Si–O bond furnishes a range of chemically stable siloxanes (silicones) which occur in many aspects of everyday life; the inertness and oxygen permeability of polysiloxanes $(Me_2SiO)_n$ favours their use in medical applications ranging from contact lenses to surgical implants, whilst they are also used in building materials such as water-repellent silicone sealants *inter alia*.[35] Si–OC coupling has also gained interest for its applications in silicone-grafted ethers. Conventionally precious metal catalysts such as rhodium and platinum have been employed in the dehydrocoupling of alcohols with hydrosilanes. However, these catalysts suffer from the disadvantage that they are frequently intolerant to C═C or C≡C functional groups often resulting in sequential dehydrocoupling/hydrogenation reactions. However the strong Lewis acid $B(C_6F_5)_3$ has been found to be catalytically active in the dehydrocoupling of alcohols with silanes to form Si–O bonds and has the potential to support a wider range of substrates. These reactions were found to occur in high yields at room temperature using 2 mol% catalyst (eqn (3)).[36]

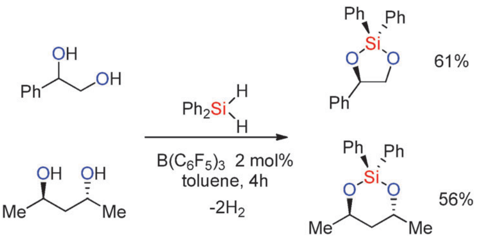
$$RO-H+H-SiR_3{}' \xrightarrow{\text{Catalyst}} RO-SiR_3{}'+H_2 \qquad (3)$$

The reaction times (a few hours to several days) reflect the potential of the alcohol to poison the Lewis-acid through (reversible) adduct formation. Thus primary aliphatic alcohols ROH gave the silylated product cleanly albeit with longer reaction times of *ca.* 1–6 days at room temperature although accelerated rates were observed when heating the reaction to 60 °C [thereby labilising the $ROH\cdot B(C_6F_5)_3$ adduct] or by using higher catalyst loadings (8 mol%).[36] With secondary and tertiary alcohols much faster reactions were observed with the products being formed in just 30 min to 1 h (see ESI,† Table S1). Reactions with dihydrosilanes were also possible and allowed for two dehydrocoupling reactions to occur for each silane molecule. Thus the reactions of a 1,2- or 1,3-diol with diphenylsilane resulted in elimination of two equivalents of dihydrogen and the formation of cyclic siloxanes in moderate yields (Scheme 14).[36]

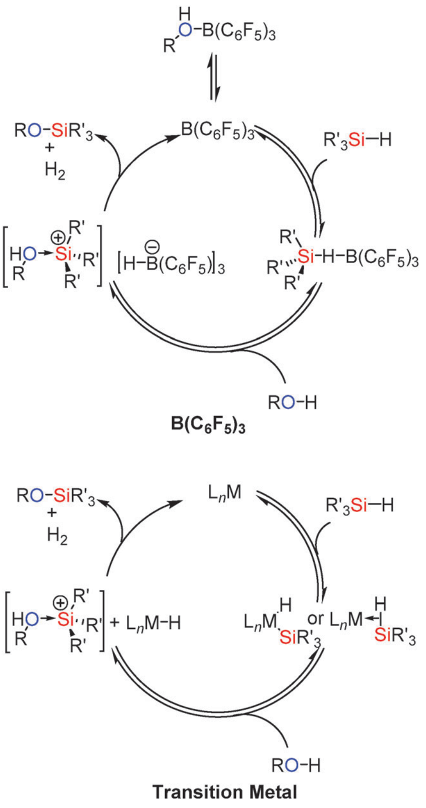
The mechanism for the reaction is thought to be related to that in the catalytic hydrosilation of carbonyls using $B(C_6F_5)_3$.[37] Thus the borane activates the silane Si–H bond *via* formation of a bridging hydride. Removal of electron density from the Si–H bond activates the Si to nucleophilic attack from the alcohol yielding $[R(H)O-SiR_3{}']^+$ and $[HB(C_6F_5)_3]^-$. This can then readily liberate H_2 to give the coupled product and regenerate $B(C_6F_5)_3$ (Scheme 15). Since the lone pairs on the alcohol (or other functional groups present) may interact with the catalyst, dissociation of the alcohol from the $[R(H)O-B(C_6F_5)_3]$ adduct to regenerate free $B(C_6F_5)_3$ is necessary before it can interact with the silane. Thus more basic and less sterically hindered primary alcohols react more slowly; an observation that has also been seen in some transition metal catalysed systems.[38] These mechanisms have been found to be similar to those observed for transition metal catalysed Si–O bond forming dehydrocoupling reactions in that Si–H bond activation occurs in the initial step of the reaction.[39] In the case of the transition metals this is *via* oxidative addition or by formation of a σ-complex[40] which is then activated to nucleophilic attack from the alcohol to give a trialkylsubstituted silylium cation as an alcohol adduct. This acidic species can then protonate the metal hydride [similar to the boron hydrido species $[(C_6F_5)_3B-H]^-$] eliminating H_2 and regenerating the catalyst (Scheme 15).[36]

$B(C_6F_5)_3$ has been employed in the synthesis of the Si–O containing polymers polyaryloxysilanes and siloxanes. The rapid dehydrocoupling of bis-phenols with dihydrosilanes was achieved using low catalyst loadings (0.1–0.025 mol%) to yield high molecular weight Si–O polymers and with higher catalyst loadings (2–5 mol%) lower molecular weight polymers were obtained (Scheme 16).[41]

The dehydrocoupling of phenols with the silane Et_3SiH using a phosphonium catalyst $[(C_6F_5)_3PF][B(C_6F_5)_4]$[42] (Scheme 17) has also been studied (see ESI,† Fig. S1 and Table S2). The phosphonium ion is a very strong phosphorus centred Lewis acid. Whilst $B(C_6F_5)_3$ described above owes its high Lewis activity to the presence of a vacant p-orbital in combination with three electron withdrawing C_6F_5 groups, the electrophilic phosphonium ion is highly electrophilic due to the presence of electron withdrawing groups in combination with the cationic charge resulting in a low lying P–F σ*-orbital. This catalyst leads to rapid quantitative

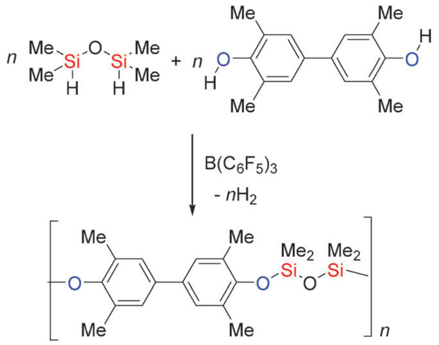


Scheme 14 Catalytic dehydrocoupling of 1,2- and 1,3-diols with diphenylsilane.



Scheme 15 Similarities between $B(C_6F_5)_3$ (top) and transition metal (bottom) catalysed Si–O coupling.

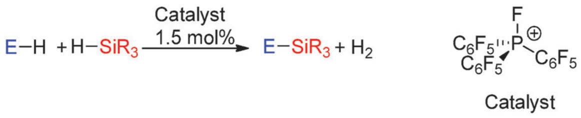
conversion to $ROSiEt_3$ products in just 2 h using C_6H_5OH or (o-Me)$_2C_6H_3OH$ and in 3 h using p-MeC_6H_4OH.[42] When the alcohol contains a strongly electron-withdrawing group, *e.g.* C_6F_5OH, then slower reaction rates are observed taking a day to reach completion. With the phenol p-$MeOC_6H_4OH$ demethylation and silylation of the methoxy group was observed in addition to the dehydrocoupling of the alcohol. In this reaction the former process could be prevented by adding one equivalent of the silane. Finally the dehydrocoupling of the carboxylic acid p-$C_8H_{17}(C_6H_4)CO_2H$ with Et_3SiH was also possible giving full conversion to the ester p-$C_8H_{17}(C_6H_4)CO_2$–$SiEt_3$ in less than one hour.[42] The mechanism follows that described in Section 2.3.3 for Si–N bond formation *via* dehydrocoupling in which a hypervalent trigonal bipyramidal phosphorus atom is postulated in Si–H bond activation.



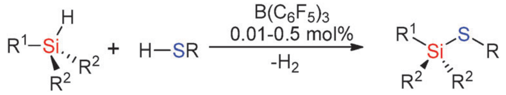
Scheme 16 Dehydrocoupling to generate Si–O containing polymers.

2.3.2 Si–S bond formation. The weaker basicity of the thiol RSH inhibits poisoning of the $B(C_6F_5)_3$ catalyst and even relatively unencumbered thiols such as ^{n}PrSH can be successfully used in hetero-dehydrocoupling reactions. For example reactions of RSH (R = ^{n}Pr, p-tol) with tertiary silanes using low $B(C_6F_5)_3$ loadings of 0.01–0.50 mol% gave quantitative yields of the product at room temperature in less than 75 min (Scheme 18).[43]

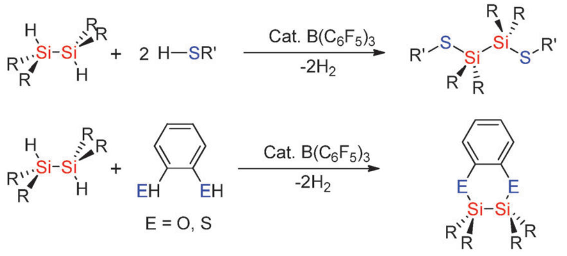
Selectivity for Si–X bond formation over Si–Si bond cleavage was observed in some cases in the hetero-dehydrocoupling reactions of disilanes with alcohols and thiols to form Si–O and Si–S bonds using catalytic amounts of $B(C_6F_5)_3$. Less sterically encumbered *sym*-dihydridodisilanes $[R_2SiH]_2$ also undergo dehydrocoupling reactions with thiols R′SH (R′ = ^{n}Pr, p-tol) using catalytic amounts of $B(C_6F_5)_3$ to give $[R_2SiSR']_2$ (Scheme 19).[43] In these reactions disilanes bearing smaller R-groups showed faster reactions with the bulky disilane $[^iPr_2SiH]_2$ showing no reactivity suggesting that a key step may be the activation of the Si–H bond by the Lewis acid catalyst. In the case of 1,2-benzene dithiol as the starting material an intermolecular reaction took place affording a $C_2S_2Si_2$ heterocyclic ring (Scheme 19).[43] These reactions were extremely fast, for example, the reaction of 1,2-benzenedithiol with $[Me_2SiH]_2$ using 0.004 mol% $B(C_6F_5)_3$ gave the product in just 30 minutes.[43] The hetero-dehydrocoupling of silanes with thiols also takes place in an analogous fashion to that between alcohols and silanes when using the fluorophosphonium catalyst, $[(C_6F_5)_3PF][B(C_6F_5)_4]$ (Scheme 17).[42] The formation of Si–S bonds from the dehydrocoupling of thiols with Et_3SiH generally



Scheme 17 Dehydrocoupling of alcohols and thiols with silanes using a phosphonium ion catalyst (the $[B(C_6F_5)_4]^-$ counterion is not shown).



Scheme 18 Dehydrocoupling of silanes with thiols.



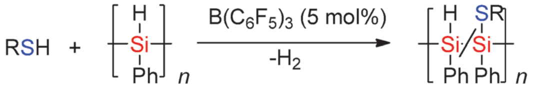
Scheme 19 Dehydrocoupling of dihydridodisilanes with thiols and alcohols.

formed the dehydrocoupled product quantitatively in less than one hour (see ESI,† Table S3). Importantly, the dehydrocoupling of thiols using the phosphonium catalyst was found to be faster than that for the dehydrocoupling with alcohols presumably due to the weaker S–H bond compared to O–H. As with the dehydrocoupling of the alcohol C_6F_5OH, the corresponding thiol C_6F_5SH also resulted in slightly slower reaction rates taking 1 week to reach completion at ambient temperatures but could be accelerated by heating the reaction to 100 °C to give complete conversion to $C_6F_5S–SiEt_3$ in 3 h.[42] Mechanistically, the hetero-dehydrocoupling of Si–H and E–H (E = N, O, S) is believed to occur *via* the same process which is discussed in Section 2.3.3 for Si–N bond formation.

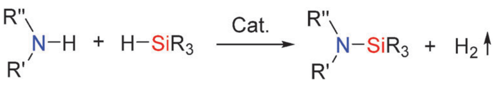
The Lewis acidic borane $B(C_6F_5)_3$ in the presence of thiols has been found to be selective in the Si–H bond cleavage of poly(phenyl)silane to generate thiol substituted polysilanes by dehydrocoupling reactions.[43] When poly(phenyl)silane and ^{n}PrSH or *p*-tolSH were mixed with a catalytic amount of $B(C_6F_5)_3$ (5 mol%), release of H_2 was observed resulting in solid polymers in which hetero-dehydrocoupling (to form Si–S bonds) occurred (Scheme 20). The degree of Si–H to Si–S dehydrocoupling in the polysilane polymer was estimated by NMR spectroscopy to be 15–40% with both $\nu_{Si–H}$ bands and $\nu_{Si–S}$ bands being observed in the IR spectrum.[44]

2.3.3 Si–N bond formation.

Si–N bonds are usually synthesised by the aminolysis of chlorosilanes.[45] However alternative methods such as dehydrocoupling which do not release HCl are of interest. The dehydrogenic Si–N coupling between hydrosilanes and anilines, carbazoles and indoles have all been catalysed using $B(C_6F_5)_3$ (Scheme 21, also see ESI,† Table S4).[46] Here too the potential for the N lone pair to coordinate to the Lewis acid catalyst can potentially prove problematic for less sterically hindered primary amines (*cf.* alcohols in Section 2.3.1) but $B(C_6F_5)_3$ appears active towards a wide range of amines. For example, in the dehydrocoupling of diphenylamines the 5 mol% and 1 mol% loading of $B(C_6F_5)_3$ in the dehydrocoupling of bis-(4-tolyl)amine with Ph_2MeSiH led to the formation of the dehydrocoupled product in 95% and 73% yield respectively.[46] Carbazoles have also been used as substrates giving the Si–N products in 83–97% yields using 1 mol% catalyst. In addition, a variety of silanes could be used in the reaction. Thus Et_3SiH or $(Me_2SiH)_2O$ could be used in the dehydrocoupling with carbazole or bis(4-tolyl)amine respectively. Silylation reactions of primary anilines including electron deficient anilines was also very effective at 60–70 °C to give the products in 88–97% yield.[46] The dehydrocoupling of diamine, pyrrole and indole derivatives were also examined. Whilst pyrroles were unreactive, diamines and indoles were active in the intermolecular heterodehydrocoupling with silanes. Indoles were selectively transformed into 1-silylated indoline products *via* a dehydrocoupling/hydrogenation reaction.[46]



Scheme 20 Hetero-dehydrocoupling to form Si–Si and Si–S bonds.

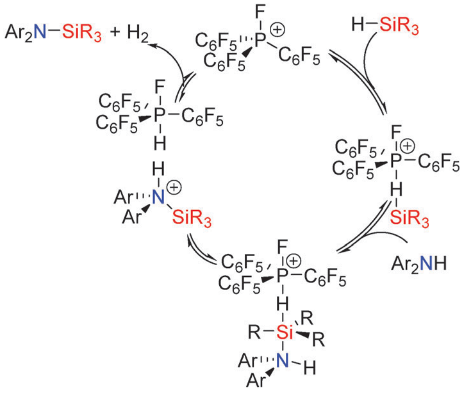


Scheme 21 Si–N coupling using $B(C_6F_5)_3$ or the fluorophosphonium catalyst $[(C_6F_5)_3PF][B(C_6F_5)_4]$.

The Si–N dehydrocoupling reactions performed using 1.5 mol% of the fluorophosphonium catalyst $[(C_6F_5)_3PF]^+$ described earlier (Section 2.3.1) were also performed (Scheme 21, also see ESI,† Table S5) and found to be dependent upon the silane used.[42] Thus, increased reaction times were necessary to give the products in appreciable yields when using bulky silanes such as Ph_3SiH or $PhMe_2SiH$ and, with even more sterically encumbered silanes (*e.g.* $^{i}Pr_3SiH$), no reaction was observed. The best results were therefore observed using the smaller silane Et_3SiH.[42]

The mechanism for the dehydrocoupling (Scheme 22) is proposed to be similar to that described for the Lewis acid $B(C_6F_5)_3$ and transition metals systems reported earlier and involves initial interaction of the Si–H bond with the fluorophosphonium $[(C_6F_5)_3PF]^+$ Lewis acid. This activates the Si–H bond to attack from the Lewis basic coupling partner (N, S, O) yielding a hypervalent silicon species containing hydridic (Si–$H^{\delta-}$) and protic (E–$H^{\delta+}$) hydrogen atoms which readily release H_2 generating the dehydrocoupled product and regenerating the catalyst.[42] This is consistent with the observation that sterically encumbered silanes were less effective in the reaction in which a hypervalent silicon species is formed. Additionally, small and/or basic amines (*e.g.* $^{i}Pr_2NH$ or aniline) are not as active in the dehydrocoupling reaction with Et_3SiH due to interaction of the Lewis basic amine with the catalyst in competition with the silane similar to that observed for $B(C_6F_5)_3$ with less sterically bulky alcohols or amines. This competitive process was supported by the observation that the reaction was accelerated when excess silane was added whilst addition of an excess of amine diminished the reaction rate.[42]

Group 2 catalysts have also been found to promote Si–N coupling. The azametallacyclopropane Ca(η^2-Ph_2CNPh)$(hmpa)_3$ was the first alkaline earth catalyst to be described in catalytic Si–N dehydrocoupling.[47] Subsequently more extensive studies

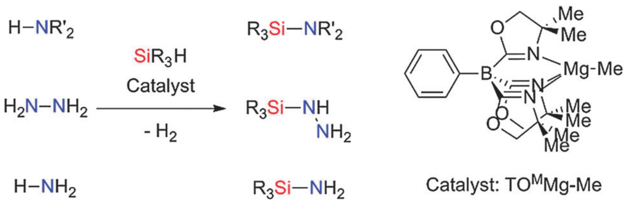


Scheme 22 Catalytic dehydrocoupling using phosphonium catalysts (the $[B(C_6F_5)_4]^-$ counterion is not shown).

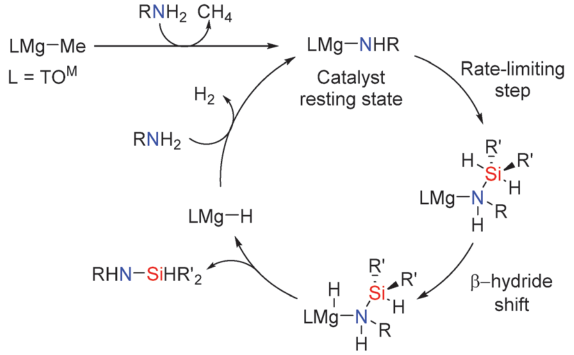
into the activity of alkaline earth pre-catalysts and the mechanisms of dehydrocoupling were made. For example, magnesium catalysts have also been found to be active in the formation of Si–N bonds *via* dehydrocoupling reactions.[48] The 4-coordinate magnesium pre-catalyst TO^MMgMe [TO^M = tris(4,4-dimethyl-2-oxazolinyl)phenylborate] (Scheme 23) was found to be active in the cross-dehydrocoupling of N–H and Si–H bonds to give Si–N bonded products with the release of hydrogen. Using 5 mol% catalyst the Si–N silazane product from the reactions between amines and silanes could be formed in high yields after 24 h at room temperature (see ESI,† Table S6).[48] The catalytic dehydrocoupling of hydrazine N_2H_4, with silanes (Et_3SiH, $(C_3H_5)Me_2SiH$ and $BnMe_2SiH$) was also possible giving the mono-silylhydrazines $R_3SiNHNH_2$. Whilst the reaction with $(C_3H_5)Me_2SiH$ goes to completion after 7 h to give $(C_3H_5)Me_2SiNHNH_2$ the reactions with Et_3SiH or $BnMe_2SiH$ were much slower.[48] Selective mono-silylation of ammonia was also possible (Scheme 23). This is interesting because the N–H proton is not acidic (pK_a of 41 in DMSO) and thus single N–H activation of ammonia is difficult. In addition, multiple silylation might also be expected since once one N–H bond is replaced by an N–Si bond the remaining N–H bonds become more acidic thereby rendering mono-silylation difficult and potentially resulting in multiple silylation reactions. In the reaction of ammonia with $BnMe_2SiH$ or $(C_3H_5)Me_2SiH$ using 5 mol% TO^MMgMe the mono-silylated products $BnMe_2SiNH_2$ and $(C_3H_5)Me_2SiNH_2$ were formed exclusively after 15 h and 5 h respectively.[48]

The mechanism for this reaction is shown in Scheme 24. The catalyst resting state in these reactions was observed to be the magnesium amide TO^MMgNHR (R = Pr, ^{i}Pr, Ph) which is formed rapidly upon reaction of the amine with the pre-catalyst TO^MMgMe. Mechanistic studies suggested that the reactions involve nucleophilic attack of the metal amide onto the silicon centre to form a five-coordinate silicon intermediate. This is the rate limiting step which is then followed by a β-hydride type transfer from the silicon atom to the magnesium centre (a similar process to that seen in the dehydrocoupling of amine boranes using aluminium hydrides described earlier). This then generates the metal hydride and the silazane product. This mechanism is consistent with the observation that more nucleophilic amines react faster in the rate determining step and secondly that changing the amine concentration had no effect on the rate of the reaction even at high amine concentrations showing a zeroth-order rate law in amine concentration.[48] The rate law for the reaction was found to be:

$$\text{Rate} = k[\text{amine}]^0[\text{cat}]^1[\text{silane}]^1$$



Scheme 23 Structure of the catalyst TO^MMgMe and Si–N coupling reactions.



Scheme 24 Proposed mechanism for magnesium catalysed Si–N bond formation.

Alkaline earth amido complexes $[M\{N(SiMe_3)_2\}_2]_2$ (M = Mg, Ca or Sr) were also found to be active in dehydrogenative Si–N bond formation when using a 5 mol% loading of the pre-catalyst.[49] These reactions were possible for a variety of amines with the calcium pre-catalysts being the more active than the strontium and magnesium counterpart, consistent with their enhanced Lewis acidity (high charge : radius ratio). The steric and electronic properties of the amine and silane were also found to be influential in the extent and rate of formation of the silazane product. In contrast to that found for the TO^MMgMe pre-catalyst described above, the rate of the dehydrocoupling reactions involving $PhMeSiH_2$ and $^tBuNH_2$ using $[M\{N(SiMe_3)_2\}_2]_2$ (M = Mg, Ca) were found to be dependent upon the concentration of amine and not the silane. The zero order dependence upon the concentration of silane suggests that in this case the silane plays no role in the rate-limiting step.[49] The reactions with magnesium and calcium could be described using the rate equation:

$$\text{Rate} = k[\text{amine}]^1[\text{cat}]^1[\text{silane}]^0$$

The strontium catalysts showed a different rate law being second order depending upon both the concentrations of amine and silane suggesting that perhaps Si–H/Mg–N σ-bond metathesis step to give a Sr–H bond is the rate determining step.[49]

$$\text{Rate} = k[\text{cat}]^2[\text{amine}]^1[\text{silane}]^1$$

Importantly, the order of the overall reaction, the method of activation of the pre-catalyst and the rate limiting step vary depending upon the alkaline earth metal used and are dependent upon the radius of the M^{2+} ion and the consequent charge density at the group 2 metal centre.

2.3.4 Si–C bond formation.

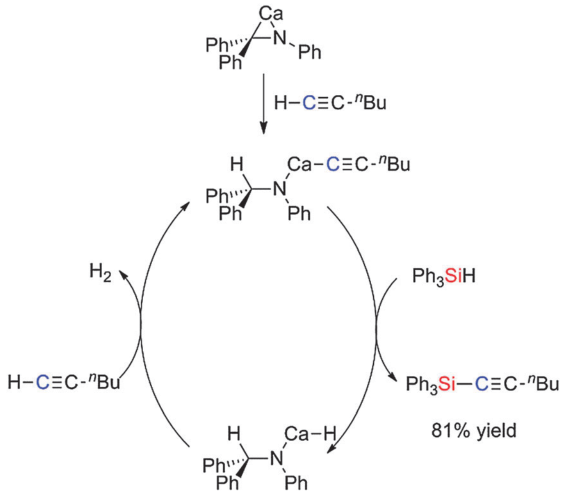
Si–C coupling between silanes and the terminal acetylene $C_4H_9C{\equiv}CH$ has been achieved using the azametallacyclopropane Ca(η^2-Ph_2CNPh)(hmpa)$_3$.[47] The reaction of 1-hexyne with Ph_3SiH yielded the expected product Ph_3Si–$C{\equiv}C$–C_4H_9 in 81% yield using a 5 mol% loading of the catalyst. With $Ph(Me)SiH_2$ a mixture of mono- and di-alkynyl products were formed with more of the mono-alkynyl product being formed with higher silane/alkyne ratios. The active catalyst in the reaction is formed from the reaction of the azametallacyclopropane with the terminal alkyne to form the calcium acetylide complex which can then react with the silane generating the calcium hydride species and the Si–C coupled product. Reaction of the Ca–H species with a molecule of alkyne regenerates the Ca–acetylide complex with release of hydrogen (Scheme 25).[47]

3. General mechanistic aspects of main group catalysed dehydrocoupling

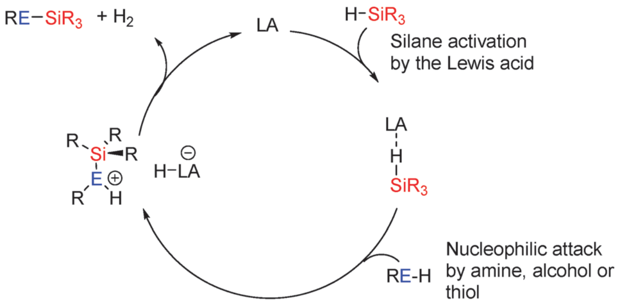
An examination of this varied group of dehydrocoupling processes discussed in Section 2 reveal a number of common features which lead to several generic catalytic cycles which we can separate into two categories: (i) Lewis-acid catalysed processes and (ii) s-block and p-block metal-catalysed reactions implementing Lewis acidic metals coupled to strongly basic substituents *e.g.* metal hydrides, metal-alkyls and metal-amides all of which have the potential to activate the substrate by deprotonation.

3.1 Main group Lewis-acid catalysed dehydrocoupling

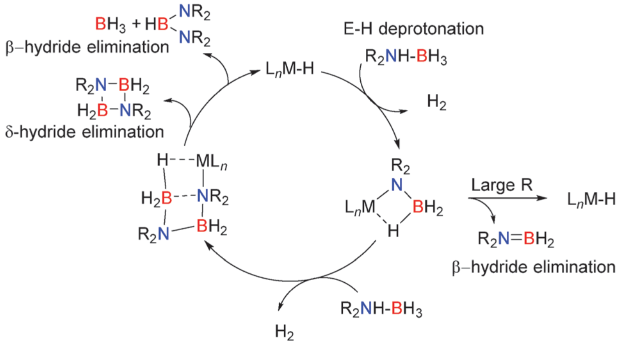
The most common Lewis-acid used in these reactions is $B(C_6F_5)_3$ which is a strong but sterically hindered Lewis acid. The $[(C_6F_5)_3PF]^+$ cation can also be considered Lewis acidic by virtue of the strongly electron-withdrawing perfluoroaryl groups and the potential for phosphorus to adopt a 5-coordinate hypervalent state. Both species can be deactivated in the presence of strong Lewis-bases (alcohols, amines, thiols) through Lewis acid/Lewis base adduct formation. However, the steric demands at the Lewis acidic B or P^+ centre typically make such adduct formation reversible particularly at elevated temperatures or, for sterically demanding substrates, impossible. These Lewis acidic centres appear to activate the E–H bonds bearing hydridic hydrogens (*e.g.* Si–H) making the heteroatom E itself more susceptible to nucleophilic attack by a lone pair on ROH, R_2NH, RSH *etc.* This is then followed by H_2 elimination to generate the E–E′ bond (Scheme 26).



Scheme 25 Si–C coupling using a calcium catalyst.



Scheme 26 General mechanism for Lewis acid catalysed dehydrocoupling.



Scheme 27 General mechanism for Lewis acid catalysed dehydrocoupling.

3.2 Basic s- and p-block Lewis-acid catalysed dehydrocoupling

Here the reaction chemistry appears somewhat different but common themes are already emerging in both alkaline earth and group 13 chemistry. Typically the catalyst contains one or more M–H, M–R or $M–NR_2$ groups which are strongly basic and deprotonate the E–H bonds bearing protic hydrogens *e.g.* N–H in the initial step of the reaction. In the case of amine-borane dehydrocoupling, sterically demanding groups on the substrate favour a close M···H–B contact which leads to formation of $R_2N{=}BH_2$ *via* a β-hydride elimination. For less sterically demanding groups, the larger angle accommodated at nitrogen disfavours β-hydride elimination and a bimolecular reaction becomes favoured in which the terminal boron atom becomes activated to nucleophilic attack and a chain growth process occurs to form $M–NR_2BH_2NR_2BH_3$. In most cases the resultant six-membered intermediate can be generated which then favours a δ-hydride elimination, regenerating the active metal-hydride catalyst (Scheme 27).

4. Conclusions

In the last two decades we have witnessed a remarkable revolution in the area of main group catalysed dehydrocoupling reactions including both s- and p-block metals as well as non-metal catalysed processes. In many cases these main group catalysts reveal remarkable selectivity in product formation, often affording a single major product. Whilst such reactivity initially appeared diverse, common themes are now becoming apparent in their reactivity and mechanistic pathways which should favour more tailored approaches to not only optimise catalyst activity but also control the outcome of such dehydrocoupling reactions.

Future work in the area of main group catalysis should focus on the development of new types of E–E′ bond-forming reactions and the optimisation of catalyst activity. With regard to the latter, unlike transition metal chemistry, it should be noted that there have been no previous systematic attempts to vary the ligand set in order to optimise activity of main group metal catalysts. As is already apparent from studies so far, changing the steric demands of the ligands in the pre-catalysts is one obvious way of modifying both the kinetics and selectivity. However, a further way of enhancing activity in the future is to control the Lewis acidity of the metal centres, and increase redox stability. This would lead to greater polarisation of metal-bonded intermediates and potentially longer catalyst life-times.

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