



Alkaline Earths as Main Group Reagents in Molecular Catalysis

Journal:	<i>Chemical Society Reviews</i>
Manuscript ID	CS-REV-11-2015-000880.R1
Article Type:	Review Article
Date Submitted by the Author:	12-Jan-2016
Complete List of Authors:	Hill, Michael; University of Bath, Chemistry Liptrot, David; University of Bath, Chemistry Weetman, Catherine; University of Bath, Chemistry

Alkaline Earths as Main Group Reagents in Molecular Catalysis

Michael S. Hill, David J. Liptrot and Catherine Weetman

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

Email: msh27@bath.ac.uk

Abstract

The past decade has witnessed some remarkable advances in our appreciation of the structural and reaction chemistry of the heavier alkaline earth (Ae = Mg, Ca, Sr, Ba) elements. Derived from complexes of these metals in their immutable +2 oxidation state, a broad and widely applicable catalytic chemistry has also emerged, driven by considerations of cost and inherent low toxicity. The considerable adjustments incurred to ionic radius and resultant cation charge density also provide reactivity with considerable mechanistic and kinetic variability as group 2 is descended. In an attempt to place these advances in the broader context of contemporary main group element chemistry, this review focusses on the developing state of the art in both multiple bond heterofunctionalisation and cross coupling catalysis. We review specific advances in alkene and alkyne hydroamination and hydrophosphination catalysis and related extensions of this reactivity that allow the synthesis of a wide variety of acyclic and heterocyclic small molecules. The use of heavier alkaline earth hydride derivatives as pre-catalysts and intermediates in multiple bond hydrogenation, hydrosilylation and hydroboration is also described along with the emergence of these and related reagents in a variety of dehydrocoupling processes that allow that facile catalytic construction of Si-C, Si-N and B-N bonds.

Introduction

Catalysis is central to the world's chemical industry and the mitigation of its energy demands. The importance of catalysis cannot be overstated with, for example, the chemical outputs from industrial catalytic processes accounting for ca. 20 % of the GDP of the United States. In common with the largest global industrial homogeneous catalytic process, the rhodium-catalysed hydroformylation of alkenes, a majority of current homogeneous catalysis is mediated through the reactivity of precious metals such as platinum, palladium, rhodium and iridium. These elements are expensive† and particularly sensitive to potential supply restrictions as a consequence of their geological scarcity. In response to these concerns, a growing international effort is being applied to the identification of alternative catalytic vectors derived from the lighter first row transition metals and the elements of the s- and p-blocks of the periodic table.

† For example, rhodium US\$ 1300 /troy oz, platinum US\$ 1600 /troy oz, iridium US\$ 1070 /troy oz versus magnesium US\$ 0.13 /troy oz and calcium US\$ 0.005 /troy oz.

Within the main group of elements the chemistry and reactivity of ‘frustrated’ Lewis pairs (FLPs) has attracted intense attention since Stephan’s initial report of heterolytic H₂ cleavage in 2007 and these systems continue to be applied to a growing suite of catalytic processes, in some cases competitive with established transition metal systems.¹ While the FLP concept has provided a topical strategy for the design and application of main group elements in synthesis and catalysis, the alkaline earth (Ae = Mg, Ca, Sr and Ba) metals of group 2, in the form of magnesium Grignard reagents, have been notable stoichiometric reagents for more than a century. Their development as catalytic reagents, however, is similarly recent and the broader development of the chemistry of these elements is highly attractive. Many of the group 2 metals are notable for their high relative abundance in the Earth’s crust,² resultant low cost and their environmentally benign nature. This suggests that a catalytic framework based on these metals could be sustainable, economical and green.

With some notable exceptions the chemistry of the group 2 metals is marked by their extremely stable +2 oxidation state.^{3,4} This redox inactivity precludes chemistry characteristic of many catalytic transition metals, which typically relies upon oxidation state variation for bond activation. Although all of the heavier group 2 congeners have a strong propensity to form their respective Ae²⁺ ions with a d⁰ electronic configuration, marked variations in the ionic radii of the ions are observed as the group is descended, with a concurrent increase in polarisability and electropositivity (Figure 1).

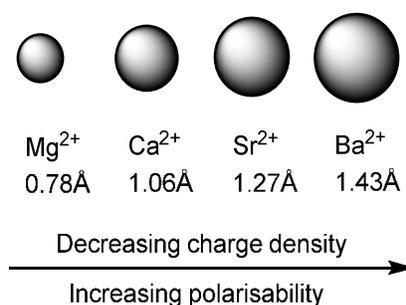
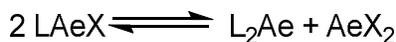


Figure 1: The variation of the ionic radii of group 2 Ae²⁺ ions.⁴

These intrinsic variations have profound consequences for the nature of metal to ligand bonding for group 2. Although a case for some degree of covalency may be made in ligand binding to magnesium, similar considerations are all but precluded for its heavier congeners, the bonding of which is dominated by non-directional ionic interactions. A consequent major challenge, therefore, is presented by the synthesis of well defined, heteroleptic heavier group 2 complexes owing to their propensity to undergo Schlenk-type equilibria (Scheme 1, where L = spectator ligand, X = reactive group).



Scheme 1: The Schlenk-type redistribution of group 2 Ae²⁺ complexes.

Redistribution of heteroleptic complexes often yields metal centres ligated by two large, stabilising ligands. Consequent approaches to spectator ligands for group 2 (Scheme 2) have focused on polydentate monoanionic frameworks encompassing hard donor sites and significant steric bulk to provide kinetic stability and suppress the Schlenk-like redistribution. Stabilising ligands include β -diketiminates (**1a-g**),⁵⁻¹⁰ borates (**7**),^{11,12} (bisimino)acenaphthenes,¹³ bisimidazolinates (**6**),¹⁴ aminotropiminates,^{15,16} triazenides¹⁷ and anilido-imines (**5a-c**)¹⁸ An alternative approach has foregone the requirement for a spectator ligand and has relied upon the use of homoleptic group 2 pre-catalysts including those incorporating bulky amides (**2a-d**, **3a-d**)^{19,20} and alkyls (**4a-d**).^{21,22} A range of well-known ligands and complex types relevant to this work are summarised in Figure 2.

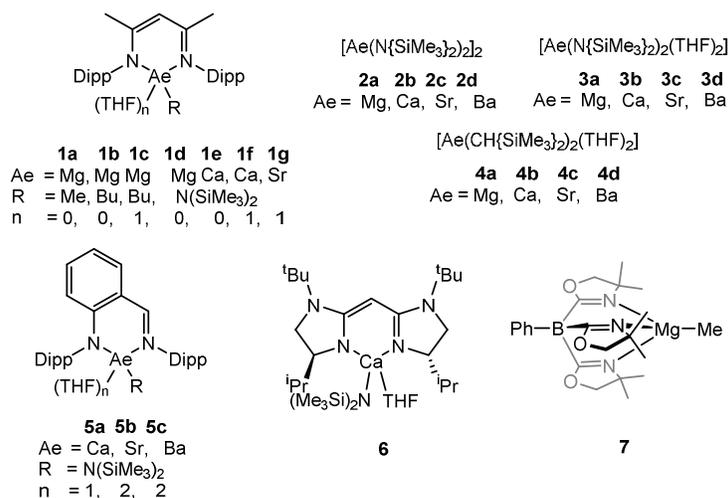
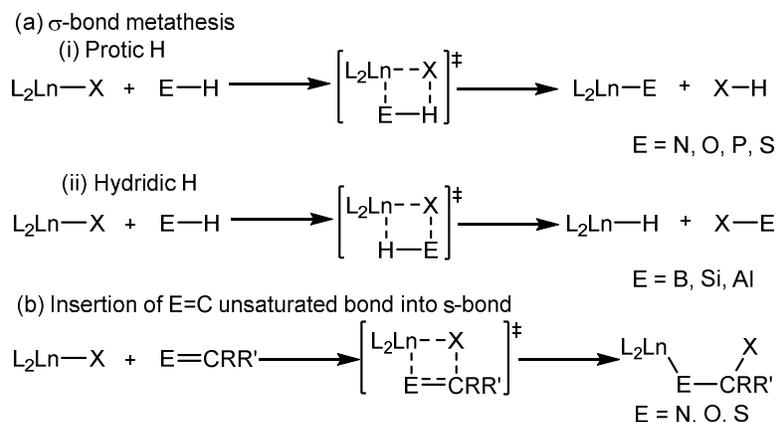


Figure 2: A range of pre-catalysts utilised in group 2-mediated catalysis (Dipp = 2,6-di-*iso*-propylphenyl).

The lanthanide analogy

The Ae²⁺ state of all the group 2 elements provides an effective d⁰ electronic configuration and analogies have, thus, been drawn with trivalent, redox inactive, d⁰ lanthanide (Ln) complexes of the form L₂LnX (L = spectator ligands, X = reactive group). Reactivity of the lanthanides is marked by two principal mechanistic steps, σ -bond metathesis and polarised insertion, which occur without any adjustment to the oxidation state of the metal. These steps are summarised in Scheme 2.²³



Scheme 2: The key steps in trivalent lanthanide mediated catalysis: (a) σ -bond metathesis with a (i) protic E-H bond (ii) hydridic E-H bond, (b) the insertion of an unsaturated bond into an Ln-X σ -bond.

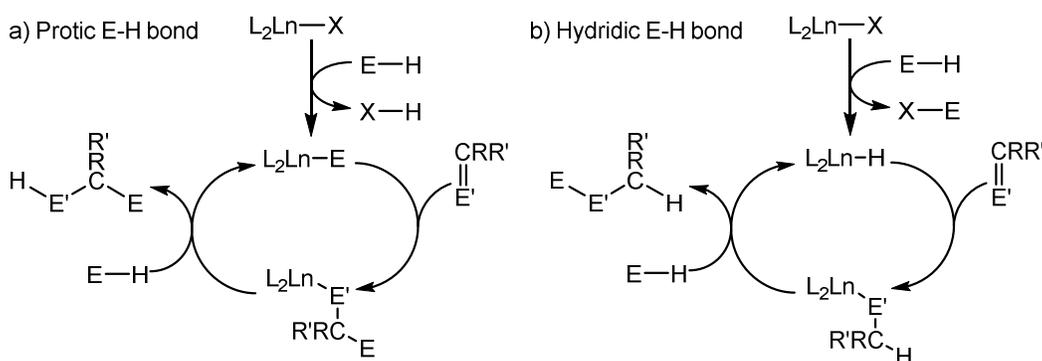


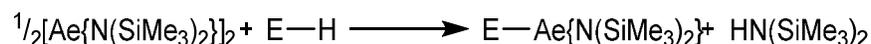
Figure 3: Catalytic cycles predicated upon the steps summarised in Scheme 2. (a) The addition of an E-H fragment to a C=E' moiety with polarization of the E-H bond yielding a protic hydrogen; (b) the addition of an E-H fragment to a C=E' unsaturated moiety with polarisation of the E-H bond yielding a hydridic hydrogen.

The reaction types illustrated in Scheme 2 may be combined to construct catalytic cycles (Figure 3) leading to the heterofunctionalisation of multiple bonds. The divergence in these catalytic cycles occurs as a result of the polarisation of the substrate E-H bond. As highlighted by Scheme 2, whilst protic E-H bonds engage in protonolysis to yield an Ln-E fragment, hydridic E-H bonds undergo a σ -bond metathesis to yield a lanthanide hydride. In the case of Figure 3(a), the former case is in operation wherein the Ln-E fragment undergoes an insertion of the unsaturated bond yielding a species of the form $\text{L}_2\text{LnEC}(\text{E})\text{RR}'$ which can undergo subsequent protonolysis with a further equivalent of the E-H bonded substrate. This reactivity typically provides the anti-Markovnikov product and another Ln-E fragment which is available for onward turnover. In contrast, when the E-H bond is hydridic (Figure 3(b)), the metal hydride L_2LnH is active for the insertion, yielding the intermediate $\text{L}_2\text{LnEC}(\text{H})\text{RR}'$ which undergoes a σ -bond metathesis with the E-H fragment to yield the

active L_2LnH species and the Markovnikov addition product. Exploitation of these cycles has yielded a wide variety of heterofunctionalisation reactions operant upon unsaturated moieties mediated by L_2LnX species, including hydroamination, hydroboration, hydrophosphination and hydroalkoxylation of alkenes alongside polymerisation of olefins.²⁴⁻⁵²

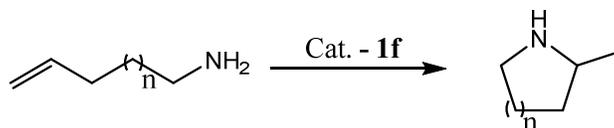
Catalysis with Ae^{2+} complexes

Hydroamination of alkenes and alkynes: Group 2 mediated Lewis acid catalysis has undergone a recent renaissance and there has also been significant interest in the utilisation of magnesium and calcium species for the ring opening polymerisation of cyclic esters such as ϵ -caprolactone and *rac*-lactide.⁵³ The majority of recent advances in the use of alkaline earth compounds in molecular catalysis have been derived from the viewpoint that the d^0 valence configuration of a Ae^{2+} centre will render it some level of 'lanthanide mimetic' character enabling the construction of catalytic cycles analogous to those shown in Figure 3. In terms of the historical development of the area, initial work focused upon the viability of group 2 protonolysis steps, (Scheme 2(a)(i)) to yield catalytically relevant species. To this end, the reactivity of alkaline earth amides and alkyls with alcohols, pyrroles, terminal alkynes, phosphines and C-H acidic heterocycles has been shown to yield alkoxide,⁵⁴⁻⁵⁶ pyrrolide,⁵⁷ acetylide,⁵⁸⁻⁶¹ phosphide⁶²⁻⁶⁵ and carbanion⁶⁶ fragments bound to a group 2 centre alongside the protonated basic residue. In the case of metal hexamethyldisilazides (**2a-d**), for example this is an amine, as summarised in Scheme 3.



Scheme 3: The protonolysis of a protic E-H bond by group 2 hexamethyldisilazides, yielding a new E-M bond and hexamethyldisilazane (Ae = Mg, Ca, Sr, Ba).

While such protonolysis reactions, particularly in organomagnesium chemistry are well preceded, work by Westerhausen and co-workers demonstrated that group 2 phosphides of the type $[Ae\{P(SiMe_3)_2\}_2(THF)_4]$ (Ae = Ca, Sr, Ba) readily underwent facile metallophosphination through insertion of 1,4-diphenylbutadiyne. Furthermore these compounds, and their amide analogues **2a-d** were shown to add readily across the C-N bond in benzonitrile.⁶⁷⁻⁷¹ Further evidence for the ability of group 2 complexes to mediate insertion chemistry was provided by the styrene polymerization activity shown by the group 2 benzyl complexes, such as $[Ae(DMAT)_2(THF)_2]$ (Ae = Ca, Sr, DMAT = 2-dimethylamino-2-trimethylsilylbenzyl), reported by Harder.⁷²⁻⁷⁵ Guided by this reactivity, initial reports of group-2-mediated molecular catalysis centred on the heterofunctionalisation of unsaturated C=C and C=E moieties, similar to the earlier reports of lanthanide mediated catalysis.



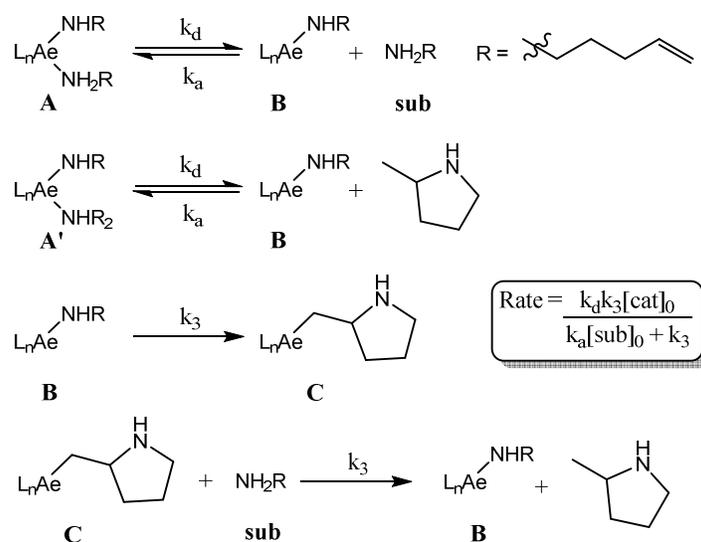
Scheme 4: The group 2-catalysed intramolecular hydroamination of aminoalkenes.

The first example of a well-defined molecular catalysis mediated by a group 2 centre was provided by intramolecular hydroamination of aminoalkenes and -alkynes (Scheme 4).⁷⁶ Although initial reports were concentrated on the use of Chisholm's β -diketiminato calcium amide (**1f**), this reactivity was found to be mediated by a much wider range of group 2 catalysts including **1a-g**,^{5,6,9} **2a-d**, and **3a-d**.^{8,9} Extensive mechanistic investigation into both the homoleptic group 2 bisamides **2a-d**, **3a-d** alongside the bisalkyls **4a-d** and β -diketiminato ligated magnesium, calcium and strontium centres **1a-g** has been subsequently undertaken by Hill and co-workers.

This reaction was found to give access to a wide range of nitrogen-containing heterocycles, including 5- and 6-membered rings in near quantitative yields under mild conditions. 7-membered rings are also accessible but only with specific pre-catalysts and in moderate yields. In all cases cyclisations are effected in concordance with Baldwin's rules⁷⁷ and both alkenes and alkynes consistently yielded the expected isomers. Substitution around the aminoalkene was generally found to decrease the rate of reaction, and terminal mono- or disubstitution often prevented the reaction completely. Furthermore, geminal substitution was found to be beneficial to the reaction rate, attributed to a Thorpe-Ingold effect through which a reduction of conformational freedom for these groups induces the adoption of more reactive conformations.⁷⁸ Synthesis of 5-membered rings proceeded faster than 6-membered rings which, in turn, proceeded faster than the far more problematic 7-membered rings. Consideration of the basicity of the β -diketiminato group 2 metal amides **1d-f** indicated that entry into the catalytic cycle occurs via protonolysis yielding hexamethyldisilazane. This step was found to be reversible and a dynamic equilibrium observed for both congeners which appear to be monomeric. On the other hand the protonolysis is irreversible for magnesium alkyl derivatives such as **1a-c**. These investigations yielded a range of soluble and stable group 2 metal amides which form exergonically, and could be subjected to both NMR and crystallographic characterisation, indicating the viability of a group 2 metal amide intermediate in these hydroamination reactions.

Kinetic analysis, initially undertaken with **1a** and **1f**, indicated a marked dependence of the rate of reaction on the identity of the group 2 metal centre. Calcium-catalysed intramolecular hydroamination was markedly faster than that catalysed by magnesium. Further studies focussed on magnesium owing to the accessibility of **1a** which undergoes an irreversible initiation yielding the active catalyst and inert methane.⁷ The reaction was found to be first order with respect to [pre-catalyst], suggesting the reaction occurs with a monomeric catalytic centre in solution. Although, a first order rate relationship to aminoalkene concentration was observed, the mechanism is significantly more complicated. A

range of proposed equilibria involving complexation and decomplexation of both the substrate and product amines, alongside the protonolysis and insertion steps yielded a rate law as shown in Scheme 5.

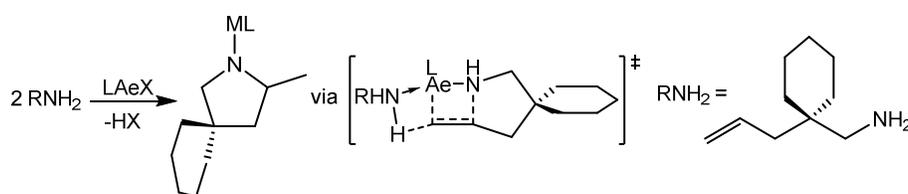


Scheme 5: The initial proposed model for hydroamination catalysis mediated by **1d-f**.

These data yielded a pair of catalytic manifolds involving irreversible or reversible catalyst initiation which were consistent with the elementary steps proposed by Marks in lanthanide catalysis and the initially proposed mechanism for group 2-catalysed heterofunctionalisation. On this basis the rate determining step was proposed to be occur through C-C multiple bond insertion via the polarised four-membered transition state shown in Scheme 2(b).⁸ Although thorough kinetic investigations were only undertaken into the magnesium β -diketiminato complex **1a**, it was proposed that the calcium complex **1f** performed analogously. Furthermore the pronounced observed Thorpe-Ingold effect, which is consistent across the various congeners, is far more easily explained by a C=C insertive rate-determining step.

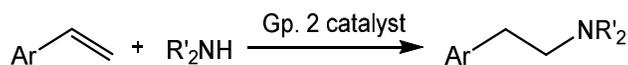
Arrhenius and Eyring analyses comparing the solvated β -diketiminato supported calcium and strontium amides **1f** and **1g** suggested a trend which reflects the variation in rate with a decreased free energy of activation (ΔG^\ddagger) for the calcium congener. Further studies of the group 2 bisamides **2a-d** and their THF adducts **3a-d** alongside the bisalkyls **4a-d** allowed a direct comparison of all the congeners from magnesium to barium.⁹ Most notably, barium proved to be an ineffective catalyst for intramolecular hydroamination resulting in a maximum of two turnovers followed by the formation of an unidentified, insoluble and inactive product. Arrhenius and Eyring analyses of these reactions indicated a marked dependence of the activation energy and free energy of activation values on the identity of the metal. More notable variations were deduced for the activation entropies (ΔS^\ddagger), with strontium amides providing consistently less negative values than calcium with a proportionate effect

on the free energy of activation. This entropy dominated free energy change of activation has emerged as a common theme for group 2 catalysis and has been attributed primarily to the larger size and more deformable coordination geometry of the Sr^{2+} cation, and its consequent ability to assemble less well-ordered transition states. A moderate kinetic isotope effect for *N*-deuteration was observed leading Hill and co-workers to postulate a modification to the previously suggested rate determining transition state in which a concerted C-N bond formation/protonolysis step occurs via a 6-membered two-substrate transition state as shown in Scheme 6. A similar deduction had also previously been proposed by Sadow and co-workers on the basis of stoichiometric experiments with an magnesium amidoalkene derivative of a tris(oxazolonyl) ligand.⁷⁹ In this latter case, C=C insertion into the Mg-N bond was only observed to ensue upon the addition of a further equivalent of the protic aminoalkene substrate.



Scheme 6: The 6-membered proton-assisted transition state proposed to account for the observed kinetic isotope effect during calcium-catalysed intramolecular hydroamination of amino alkenes.

Beyond these investigations into intramolecular hydroamination, a number of successful group 2 catalysts have been described for the more entropically demanding intermolecular hydroamination (Scheme 7). In this case, Hill and co-workers have utilised the group 2 bisamide (**2a-d**) and bisalkyl (**4a-d**) species are competent pre-catalysts for this reaction^{80,81} while the group of Sarazin has investigated the anilidoimine supported group 2 derivatives **5a-c**.¹⁸ Access to the catalytic manifold again occurs through protonolysis of the pre-catalyst while the regioselectivity of the initial addition is defined by the orientation of partial charges in the polarised transition state and hence the inherent polarity of the unsaturated substrate and metal-amide bond. Formation of the anti-Markovnikov product and return to the catalytic amide intermediate occurs via a protonolysis of a further equivalent of N-H bond. The Ca- and Sr-catalysed reactions are thus far restricted to the intermolecular hydroamination of styrene and its derivatives, dienes and diphenylacetylene, which proceed in moderate to good yields at ambient to mild conditions. Viable coupling partners include a wide range of cyclic and acyclic mono- and disubstituted amines.^{18,80}



Scheme 7: The intermolecular hydroamination of styrene.

Initial rate analysis of reactions performed with the group 2 bisamides **2a-d**, and di-*n*-butylmagnesium invoked a rate dependence was in the order Sr > Ca >> Ba > Mg.⁸¹ As a result of the extremely slow rate of conversion by both barium and magnesium pre-catalysts, no further analysis of these species was undertaken. The slow rates were attributed to the inability of the diffuse barium centre to sufficiently polarise the C=C bond and due to the reduced polarising ability of the far less polar Mg-N bond respectively. These investigations gave rise to a rate law for the intermolecular hydroamination of alkenes, as shown in Equation 1, where the second order rate dependence on [catalyst] was suggested to implicate a dimeric metal centre.

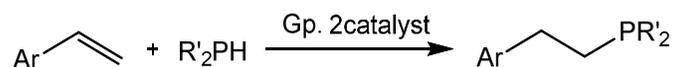
$$rate = k[amine]^1[alkene]^1[catalyst]^2 \quad (1)$$

Kinetic isotope studies yielded values for *N*-deuteroamines similar to those observed for the intramolecular hydroamination of aminoalkenes, which were again interpreted as suggestive of concerted C-N bond forming and protonolysis step, analogous to that shown in Scheme 6.

In contrast to the rate dependence observed for catalysis performed with **2a-b**, the barium congener was found to provide the highest activity in an assessment of the anilidoimine derivatives **5a-c**.¹⁸ Kinetic analysis suggested a rate law similar to that proposed for the metal bisamides although the likely monomeric constitution of the active catalyst, as a consequence of ligation, yielded a first order dependence on [catalyst]. Although the Sarazin group also postulated a proton-assisted 6-membered rate determining transition state involving concerted C-N bond formation and protonolysis, this deduction has been challenged by computational density functional theory (DFT) analysis of both the intra- and intermolecular variants of this reactivity performed by Tobisch.⁸² A detailed examination of various mechanistic scenarios concluded that the requisite multi-centred transition states required by the proton-assisted concerted NC/CH bond-forming pathway are energetically prohibitive in comparison to the kinetically less demanding sigma-insertive path.

Further group 2-mediated heterofunctionalisation catalyses

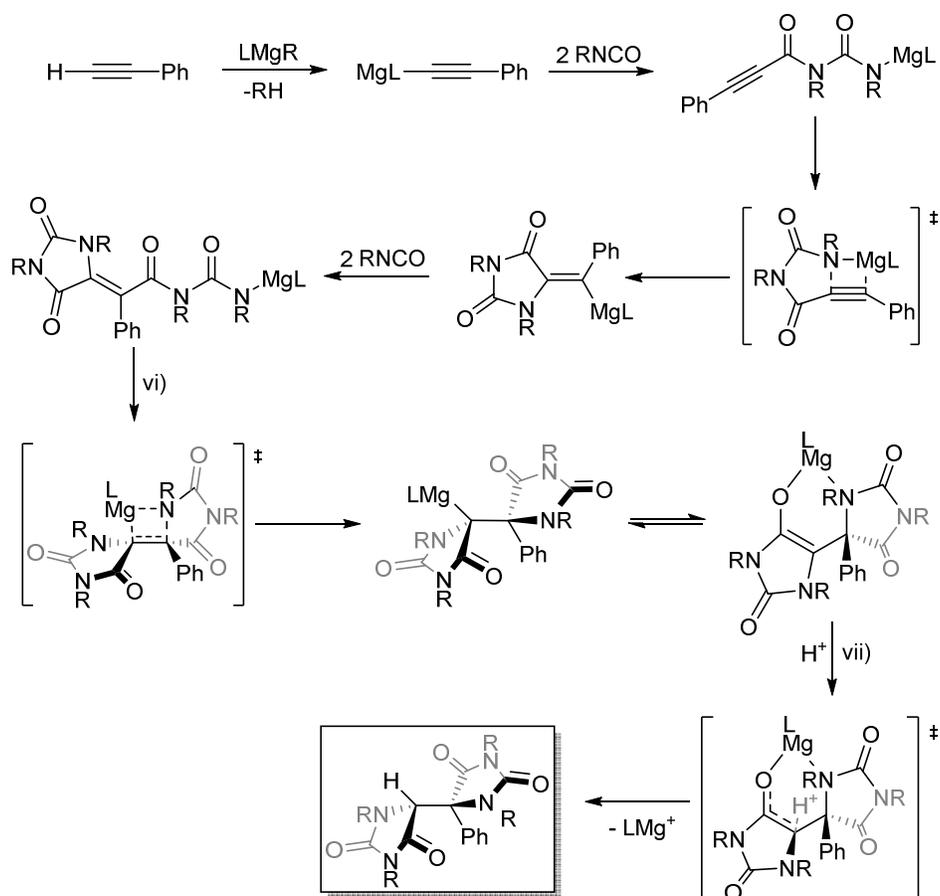
A wide range of combinations of further protic E-H and multiple C=E' bonds have also been reported as suitable substrates for group 2 catalysed heterofunctionalisation reactions. Hill and co-workers described the catalytic intermolecular hydrophosphination of alkenes utilising the β -diketiminato calcium complex **1f** as shown in Scheme 8.⁸³ Westerhausen and co-workers subsequently extended the scope of this reaction to alkynes utilising a homoleptic calcium phosphanide pre-catalyst⁸⁴ and the Sarazin group have described the hydrophosphination of alkenes catalysed by the same suite of heteroleptic calcium, strontium and barium amides employed in their studies of hydroamination. In this latter case, the order of reactivity was also found to be Ca < Sr < Ba and both the anilidoimine- and phenoxide-supported catalysts were shown to provide higher activity than their analogous β -diketiminato species.^{18, 85} Moving beyond the activation of P(III)-H bonds, the Sarazin group have also reported the hydrophosphonylation of ketones and aldehydes mediated by **3b-d**.⁸⁶



Scheme 8: The group 2-catalysed hydrophosphination of alkenes.

The scope of these reactions has been further expanded to unsaturated substrates beyond alkenes, alkynes and ketones. Extensive reports of carbodiimide heterofunctionalisation have been made, which include hydroamination^{87,88} and hydrophosphination⁸⁹ to provide the guanidine and phosphaguanidine species respectively.

Enabled by the ready deprotonation of terminal alkynes by group 2 amides (**3a-c**), the hydroacylenation of carbodiimides allowing the catalytic synthesis of propargylamidines is also readily achieved.^{90,91} Although a number of catalytic group 2-based transformations of isocyanates to isocyanurates⁹² and ureas^{93,94} have been described, attempted extension of this latter reactivity to the catalytic synthesis of propargylamides was unsuccessful. Rather, addition of a combination of an organoisocyanate and a terminal aryl alkyne to alkyl magnesium species resulted in a cascade of inter- and intramolecular insertion events to yield a unique series of bis(imidazolin-2,4-dione) molecules (Scheme 9).⁹⁵ While this stoichiometric reactivity could not be extended to a catalytic regime, the *in situ* formation of propargyl amidines by pre-catalysts **3a-c** and interception with RNCO, RNCS and CS₂ substrates has recently enabled the catalytic and atom-efficient one pot assembly of a wide variety of functionalised imidazolidine-2-ones and -thiones, 2-imino-imidazolidines and thiazolidine-2-thiones.^{96,97} In an interesting recent advance Harder and co-workers have suggested that the presence of the group 2 centre is unnecessary in the hydroamination of ArN=C=O and RN=C=NR (R = alkyl) by Ph₂NH. This study did, however, deduce that the presence of a metal cation is crucial in the intramolecular hydroamination of unactivated C=C bonds in H₂C=CHCH₂CPh₂CH₂NH₂ and, on this basis, implemented a simple hybrid catalyst consisting of a strong organic Schwesinger base and the salt CaI₂ to provide quantitative conversion to the pyrrolidine product at room temperature.⁹⁸



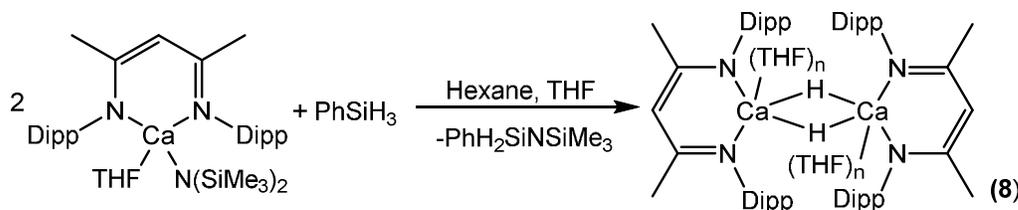
Scheme 9: Proposed stepwise mechanism yielding bis(imidazolin-2,4-dione)s via metallocarboration and metalloamination steps.⁹⁵

Alkaline Earth Hydrides and Reductive Heterofunctionalisation

Extension of this group 2 catalysed heterofunctionalisation chemistry to systems appropriate for the hydrogenation, hydrosilylation or hydroboration of multiply bonded substrates (i.e. analogous to the lanthanide-based reactivity illustrated in Figure 3b) naturally implicates the generation of alkaline earth hydride intermediates. This requirement has naturally resulted in a focus on the isolation of well-defined and isolable molecular hydrides. While this objective has yet to be achieved for strontium and barium, there has been significant recent progress leading to the isolation a variety of magnesium and strontium hydrido species.

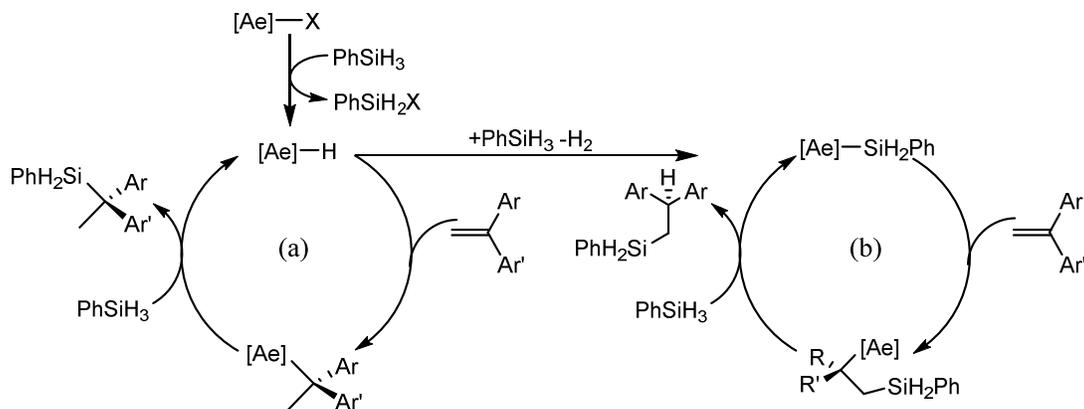
These studies were initiated by Harder's seminal report of a β -diketiminato-supported calcium hydride (**8**), the synthesis of which relied upon the σ -bond metathesis pathway illustrated in Scheme 10.⁹⁹ Subsequent reports by Jones and Stasch described a variety of similar β -diketiminato-supported magnesium hydrides,^{100,101} and the σ -bond metathesis route utilising phenylsilane has now yielded a variety of higher magnesium hydrides reported by the groups of Hill,¹⁰² Harder¹⁰³ and Okuda.¹⁰⁴ An

exploration of the stoichiometric reactivity of **8** with a variety of unsaturated substrates provided well-defined and predictable insertive behaviour and established a foundation for the catalytic implementation of heavier group 2 element hydrides (Scheme 11).¹⁰⁵⁻¹⁰⁸



Scheme 10: Synthesis of a β -diketiminato calcium hydride.⁹⁹

An initial report of the hydrosilylation of activated alkenes with range of calcium and strontium benzyl complexes of the form $[\text{Ae}(\text{DMAT})_2(\text{THF})_2]$ ($\text{Ae} = \text{Ca}$, (**9**) Sr , (**10**); $\text{DMAT} = 2$ -dimethylamino-2-trimethylsilylbenzyl) was provided by the Harder group.¹⁰⁹ Notably, the regioselectivity of the reaction was contingent upon metal identity and solvent, with a more polar solvent yielding a terminal silane. This led the authors to postulate two contrasting catalytic cycles, one consistent with that proposed for lanthanide catalysis (Figure 3b) and one which implicated a metal silyl formed via the deprotonation of silane by an incipient metal hydride (Scheme 11a and b respectively).



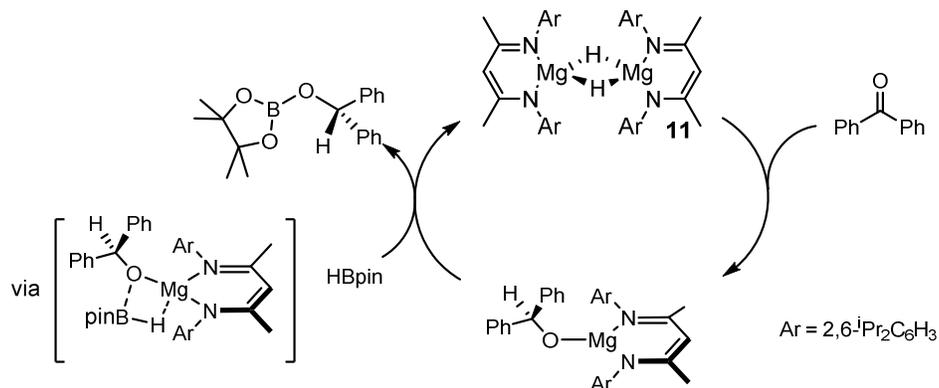
Scheme 11: The solvent dependent catalytic cycles proposed by Harder and co-workers for the hydrosilylation of activated alkenes.¹⁰⁹

Attempts to extend this reactivity to an asymmetric regime in the hydrosilylation of styrene utilising **6** were broadly unsuccessful, with enantiomeric excesses of only 5-10%.¹¹⁰ Okuda and co-workers extended this reactivity to a homoleptic calcium silyl, $[\text{Ca}(\text{SiPh}_3)_2(\text{THF})_4]$, which was found to mediate the hydrosilylation of α -phenyl- and α -methylstyrene with triphenylsilane and again proceeded with regioselectivity reflecting the intermediacy of a calcium silyl, lending further credence to Harder's mechanistic hypothesis.¹¹¹

Harder was then able to demonstrate that compounds **8** – **10** were able to catalyse the hydrogenation of diphenylethylene and styrene derivatives with conversions as high as >99% at pressures under 20 bar H₂ and at mild (<100°C) reaction temperatures.¹¹² This reactivity was again predicated on a sequence of metathesis and insertion reactions and is especially significant in requiring what is formally a heterolytic activation of H₂. This latter observation was emphasised by a subsequent computational density functional theory study of the hydrogenation of 1,1-diphenylethylene and myrcene catalysed by **8**, which inferred that the charge separation incurred during the H-H cleavage reaction was of a similar magnitude to that implicated during the heterolytic activation of dihydrogen by a typical frustrated Lewis pair.¹¹³

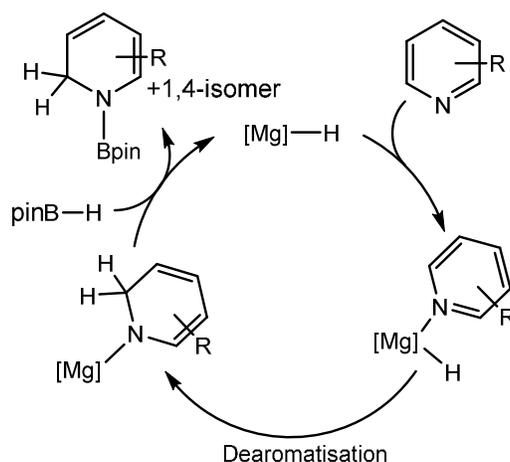
The Harder group then turned their attention to hydroboration of diphenylethylene with catecholborane utilising a range of organocalcium catalysts.¹¹⁴ Once again, reactivity which contrasted with that previously observed for the lanthanides was noted whereby (Ph₂CHCH₂)₃B rather than the expected Ph₂CHCH₂OBCat was produced. This activity was attributed to a calcium-hydride mediated decomposition of the catecholborane, yielding BH₃ and B₂Cat₃, leading to the suggestion that calcium catalyses the decomposition of HBcat.

Similar decomposition of HBcat in the presence of group 2 complexes was also noted by Hill and co-workers, leading them to turn their attention to the less electron withdrawing pinacol borane (HBpin). This latter borane provided efficient turnover with magnesium pre-catalyst (**1b**), via *in situ* generation of the magnesium hydride **11** for the hydroboration of aldehydes and ketones.¹¹⁵ Use of as little as 0.05 mol% of **1b** complete conversion of aldehydes to the fully reduced boron ester was observed in less than 1 hour. This extremely active catalyst also provided high reactivity for ketone hydroboration whilst use of 0.1 mol% of **1b** enabled complete conversion in 2 hours in a reaction which was proposed to ensue through the sequence of polarised insertion and metathesis events depicted in Scheme 12.



Scheme 12: Magnesium-catalysed hydroboration of aldehydes and ketones.

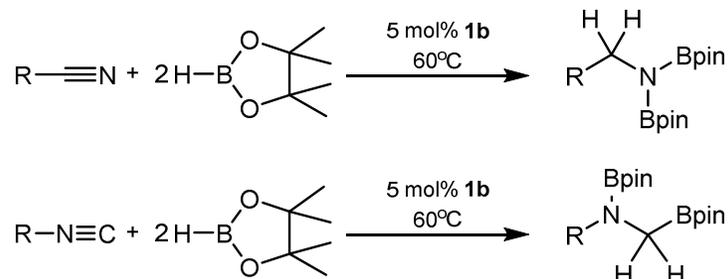
In a similar manner, the β -diketiminato magnesium *n*-butyl complex **1b** was described as an efficient pre-catalyst for the hydroboration of pyridines (Scheme 13), to provide a mixture of *N*-boryl-1,2- and 1,4-dihydropyridines.¹¹⁶ Kinetic studies of this reactivity have indicated that catalytic turnover is dependent on a pre-equilibrium involving dissociation of donor substrate molecules from the coordination sphere of the catalytic Mg centre.¹¹⁷ Harder has also shown that a bis(magnesium) hydride supported by a bis(β -diketiminato) ligand allows the stoichiometric dearomatisation of pyridines with a preference for 1,2-addition.¹¹⁸ Although extension of this stoichiometric reactivity to catalytic hydroboration of pyridines with HBpin provided efficient turnover, the regioselectivity observed in the stoichiometric reactions did not translate to the catalytic regime.



Scheme 13: Magnesium-catalysed hydroboration of pyridines

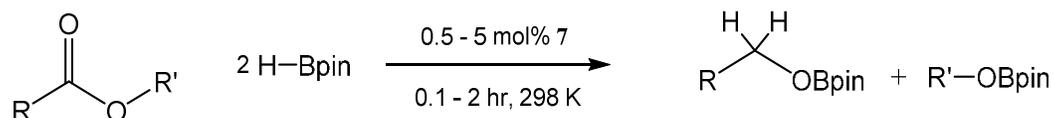
This hydroboration reactivity was extended to the unsaturated C=N bonds of a variety of aldimine and ketamine substrates.¹¹⁹ Reactions typically required 5 mol% (**1b**) and at room temperature near full conversion was observed in 2 hours for the aldehyde-derived imines. The bulkier ketone-derived imine substrates required mild heating (50 °C) and extended reaction times (up to 24 hours) to reach approximately 80% conversion. The reactions were observed to proceed through the intermediacy of well-defined magnesium amides, two examples of which were isolated and structurally characterised. Mechanistic investigations suggested that the catalytic rate determining process occurs at an isolated magnesium centre and requires the presence of two molecules of the imine substrate for effective turnover. This latter observation was rationalized as a requirement for the secondary substrate molecule to displace HBpin, most likely as a component of a borohydride anion, from the coordination sphere of the catalytic magnesium centre. A very recent extension of this work has provided the first examples of a main group catalysed bis-hydroboration of organic nitriles and isonitriles to provide regioisomeric bis-borylated primary and secondary amines respectively (Scheme 14).^{120,121} Although in both cases mechanistic analysis of catalysis derived from the β -diketiminato magnesium pre-catalyst **1b** was again broadly indicative of familiar polarised insertion and metathesis

events, differences observed across a broad range of substrate types could be traced to variations in the positions of several pre-equilibria and serves to highlight that homogeneous processes performed under heavier alkaline earth catalysis may yet demonstrate previously unappreciated mechanistic diversity.



Scheme 14: Magnesium-catalysed bis-hydroboration of organic nitriles (top) and isocyanides (bottom).

In related work Sadow and co-workers have reported the use of magnesium pre-catalyst, **7**, for the hydroboration of esters.¹²² With two equivalents of HBpin this was found to result in cleavage of the C-O bond to yield two alkoxyborane products in the presence of 0.5-5 mol% **7** at room temperature (Scheme 15).

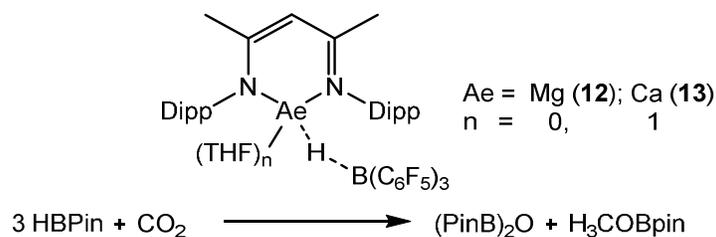


Scheme 15: The magnesium-catalysed hydroboration of esters

This system was also found to be tolerant to a variety of functional groups and conjugated olefins showing selectivity for the ester group over 1,4-addition. Compound **7** and was shown to react readily with HBpin to generate MeBpin and an unstable magnesium hydride species. It was also possible to isolate a derivative of the borohydride anion [H₂Bpin]⁻ through slow addition of **7** to 15 equivalents of HBpin. Addition of EtOAc to **7** resulted in the formation of the corresponding magnesium ethoxide with production of acetone through a series of insertion and β -ethoxide elimination reactions while kinetic studies of the hydroboration of EtOAc provided the rate law shown as Equation 2.

$$\text{Rate} = k'[\text{Mg}]^1[\text{EtOAc}]^{1/2}[\text{HBpin}]^0 \quad (2)$$

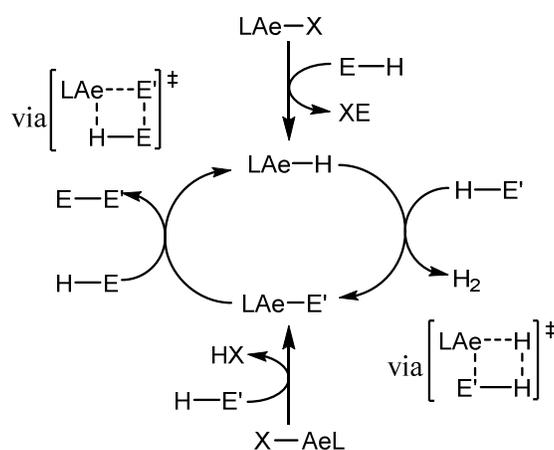
This rate law indicated that the σ -bond metathesis reaction is turnover limiting thus ruling out an insertion/ σ -bond metathesis pathway while the half-order dependence on [EtOAc] was interpreted to indicate a reversible interaction between the catalyst and the ester to give ester cleavage prior to the turnover-limiting step. Sadow and co-workers also provided evidence of the presence of a magnesium derivative of the [EtO(H)Bpin]⁻ anion from *in situ* monitoring of a series of catalytic reactions, which was identified as the catalytic resting state and shown to yield the borate ester products on addition of



Scheme 17: Group 2 catalysts (**12** and **13**) for the hydroboration of carbon dioxide.

Group 2-Mediated Cross-Metathesis and Dehydrocoupling

In addition to the preceding heterofunctionalisation reactivity, all of which requires the incorporation of at least one unsaturated substrate, catalytic group 2-centred reactions that are predicated entirely on σ -bond metathesis reactivity can be constructed to effect the cross metathesis of two dissimilar σ -bonds. A prototypical catalytic manifold based on a dehydrogenative coupling of E-H and E'-H bonds is shown in Scheme 18.

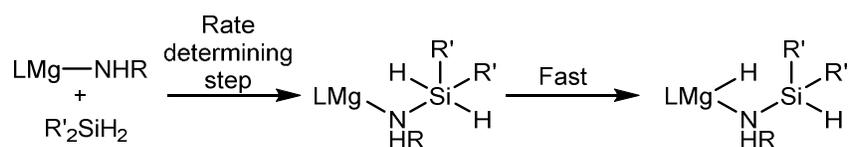


Scheme 18: Prototypical mechanism for group-2-catalysed dehydrogenative cross metathesis.

While a number of group 2-mediated cross metatheses have been reported, these are limited to reactions between E'-H protic and E-H hydridic moieties yielding E-E' bonds and dihydrogen in dehydrocouplings. Harder and co-workers reported a Si-C dehydrocoupling between a silane and terminal alkyne which proceeded in a catalytic fashion, alongside an initial report of Si-N dehydrocoupling between a range of silanes and amines.¹²⁸ More recently, Sadow and co-workers have performed a more in-depth investigation into the dehydrocoupling between silanes and amines mediated by the trisoxazolinyborate magnesium pre-catalyst **7**.¹²⁹ This reaction is postulated to occur via a manifold similar to that shown in Scheme 18 and allows access to a range of silazanes in excellent yields. Kinetic analysis yielded a rate law as shown in Equation 3.

$$\text{rate} = k[\text{amine}]^0[\text{silane}]^1[\text{catalyst}]^1 \quad (3)$$

A large, negative entropy of activation (ΔS^\ddagger) value was also determined, which was interpreted to represent a highly ordered transition state with catalyst and silane involved in the rate determining step. Kinetic isotope studies employing deuterated silane provided a small normal kinetic isotope effect ($\frac{k_H}{k_D} = 1.0(2)$) indicating the onset of limited Si-H bond cleavage in the rate determining transition state. A Hammett plot with a moderate positive slope was thought to suggest a transition state involving a five-coordinate silicon centre due to the stabilising effect of electron withdrawing substituents on this species. This observation was suggested to favour a limited degree of Si-H cleavage in the transition state, whereby increasingly electron-withdrawing aryl substituents would disfavour hydride transfer to magnesium. On this basis, Sadow postulated nucleophilic attack of the magnesium amide on silane as the rate determining step followed by a rapid hydride transfer reminiscent of β -hydride elimination to yield the product neutral silazane complexed to the metal centre as shown in Scheme 19.¹²⁹

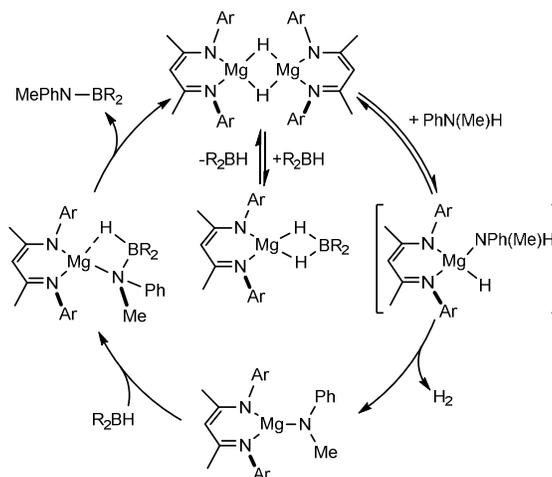


Scheme 19: The proposed mechanism of silicon-nitrogen dehydrocoupling proposed by Sadow and co-workers.

In a similar manner the homoleptic alkaline earth hexamethyldisilazides, $[\text{Ae}\{\text{N}(\text{SiMe}_3)_2\}_2]$ (**3a** – **3c**), have been demonstrated as active pre-catalysts for the cross-dehydrocoupling of Si-H and N-H bonds. Although reactions performed with all three pre-catalysts presented a number of common features, variations in overall reaction order, mode of pre-catalyst activation and the nature of the rate determining process were postulated to arise as a consequence of the marked change in Ae^{2+} radius and resultant charge density as group 2 is descended.¹³⁰ A recent application has also employed the anilido-imine species **5a** – **5c** as very active and productive pre-catalysts (TON=396, TOF up to 3600h(-1); Ca<Sr<Ba) for NH/HSi cross-dehydrocoupling, with excellent chemoselectivity in the reaction of (di)amines with (di)hydrosilanes. Experimental and DFT investigations again revealed that the reactions proceed by a process which is best described as a nucleophilic attack of a metal amide at the incoming silane and subsequent turnover-limiting hydrogen transfer to the metal centre.¹³¹

In a further recent advance, dehydrocoupling reactions between the borane substrates HBpin and 9-BBN and a range of amines and anilines have been shown to ensue under very mild conditions in the presence of compound **1b**. The facility of the reactions was suggested to be a function of the Lewis acidity of the borane substrate and to be dictated by resultant pre-equilibria between, and the relative stability of, magnesium hydride and borohydride intermediates during the course of the catalysis as shown in Scheme 20.¹³² In a manner reminiscent of the above described Si-N dehydrocoupling

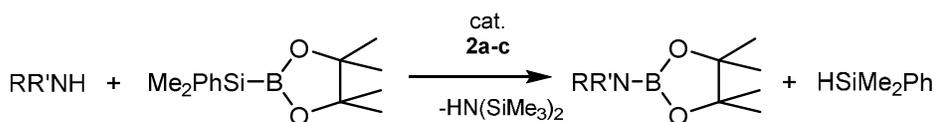
catalysis, regeneration of the catalytic magnesium hydride was proposed to occur via effective β -hydride elimination from the amidoborohydride intermediate.



Scheme 20: Proposed mechanism for Mg-catalyzed dehydrocoupling of amines and boranes.¹³²

Further related reactivity has been described by Hill with regards to phosphine oxides. Diarylphosphine oxides undergo both reduction and dehydrocoupling in the presence of phenylsilane mediated by **1f** and **2b**, to yield both the mixed P(III)-P(V) compound $\text{Ph}_2\text{P}(\text{O})\text{PPh}_2$ and its fully reduced counterpart Ph_2PPPh_2 . Triarylphosphine oxides were also shown to react with P-P coupling, which is postulated to occur via a P-C σ -bond metathesis.¹³³

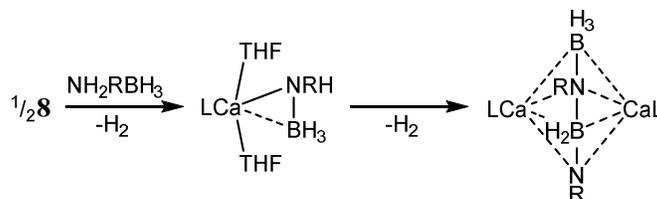
Although this latter observation suggests that not only X-H bonds but X-E bonds may be viable partners for cross metathesis, the ability to move ‘beyond dehydrocoupling’ for the group 2 catalysed cross-metathesis of sigma bonds has been demonstrated only very recently.¹³⁴ The alkaline earth bis(trimethylsilyl)amides **2a-c** are effective pre-catalysts for boron-nitrogen bond formation through the ‘desilacoupling’ of amines, $\text{RR}'\text{NH}$ ($\text{R} = \text{alkyl, aryl}$; $\text{R}' = \text{H, alkyl, aryl}$), and $\text{pinBSiMe}_2\text{Ph}$ (Scheme 21). This reactivity also yielded a stoichiometric quantity of Me_2PhSiH and provided the first example of a catalytic main group element-element coupling that is not dependent on the concurrent elimination of H_2 . Stoichiometric reactivity studies between the magnesium alkyl **1a** and $\text{pinBSiMe}_2\text{Ph}$ provided the corresponding magnesium silyl and $n\text{BuBpin}$ metathesis by-products. A kinetic investigation and the absence of any observable magnesium silyl formation during the course of the catalysis led the authors to suggest the operation of alternative outer sphere mechanisms.



Scheme 21: The alkaline earth-catalysed ‘desilacoupling’ of amines and boranes.¹³⁴

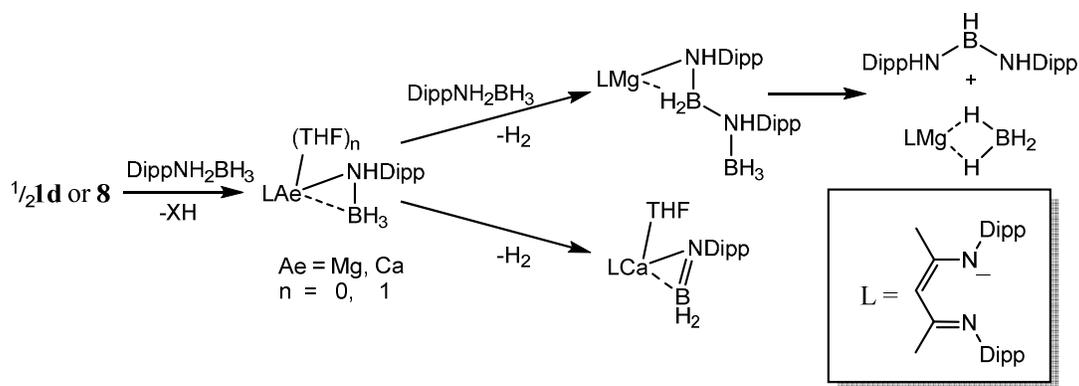
Alternative Mechanisms in Group 2-Mediated Reactivity

While the group 2-catalysed boron-nitrogen cross-coupling of dialkyl boranes or borane esters has only been described very recently,¹³⁵ the dehydrocoupling of amine-boranes, $R_nNH_{3-n}\cdot BH_3$ ($n = 0, 1, 2$) has been explored more extensively. Harder and co-workers' report of the reactivity of the β -diketiminato calcium hydride, **8**, with ammonia-borane yielded, initially, the ligated calcium amidoborane which, upon gentle heating, resulted in a B-N coupling, yielding a $[NH-BH_2-NH-BH_3]^{2-}$ dianion, bridging two β -diketiminato supported calcium centres, as summarised in Scheme 22.¹³⁶



Scheme 22: The dehydrogenative coupling of ammonia-borane and methylamine-borane mediated by compound **8** to yield a coupled diaminodiborane dianion reported by Harder and co-workers. ($R = H, Me$).

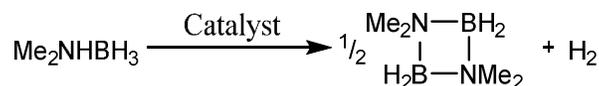
Similar reactivity, albeit at a slightly elevated temperature, was observed for methylamine-borane $MeNH_2\cdot BH_3$, and a further investigation into the far more sterically encumbered $DippNH_2\cdot BH_3$ yielded a deprotonated iminoborane coordinated to a β -diketiminato supported calcium centre. In contrast to this result, the lighter magnesium congener, utilising **1d**, yielded a di(amino)borane of the form $[DippNHBHNHDipp]$, under analogous reaction conditions Scheme 23.¹³⁷



Scheme 23: Congeneric variations in the dehydrogenation of $DippNH_2BH_3$ by **1d** or **8**.

Subsequent extensive catalytic and stoichiometric dehydrocoupling of secondary amine boranes, primarily $Me_2NH\cdot BH_3$, was investigated by Hill and co-workers. (Scheme 24).¹³⁸ Although the major boron-containing product of the catalysis was found to be the cyclic diborazane $[Me_2N-BH_2]_2$, stoichiometric investigations allowed the identification of not only amidoborane fragments bound to

group 2 centres, but also magnesium complexes (**14** and **15**) of the anion $[\text{NMe}_2\text{-BH}_2\text{-NMe}_2\text{-BH}_3]^-$ derived from the formal dehydrocoupling of two $\text{Me}_2\text{NH}\cdot\text{CH}_3$ substrate molecules (Figure 4).



Scheme 24: The dehydrogenative dimerisation of dimethylamine-borane extensively investigated by the Hill group.

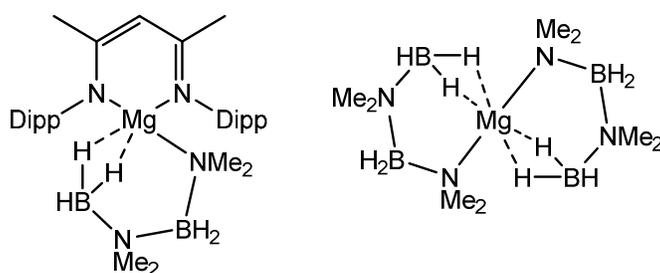
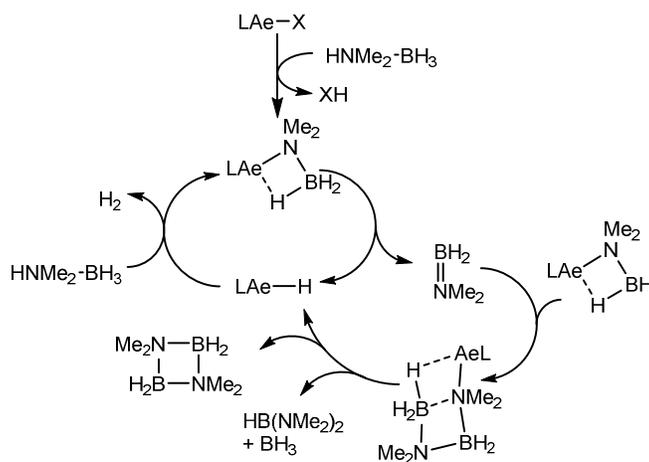


Figure 4: The crystallographically-characterised magnesium complexes **14** and **15** of a coupled diaminodiborane anion proposed by Hill and co-workers, to represent intermediates in the group 2 mediated dehydrogenative dimerisation of dimethylamine-borane.¹³⁸

Although this reaction and these intermediates could be accounted for by a σ -bond metathesis only pathway, further extensive NMR investigations in conjunction with these crystallographic investigations led this group to postulate the alternative catalytic manifold shown in Scheme 25.¹³⁸



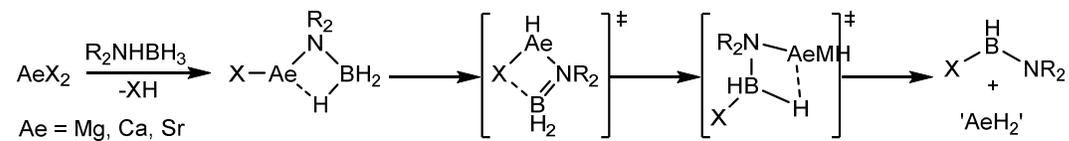
Scheme 25: The proposed mechanism of the group-2-catalysed dehydrocoupling of dimethylamine-borane.

In this mechanism an initial protonolysis yields a metal-amidoborane which undergoes a β -hydride elimination to yield a metal-hydride and an aminoborane moiety. This unsaturated fragment, which is isoelectronic to a C=C bond, then undergoes an insertion into an Ae-N bond of a metal-amidoborane. This process is analogous to the aforementioned polarised insertion reactivity prevalent in C=E heterofunctionalisation catalysis and provides a coupled metal-diamidodiborane analogous to compounds **14** and **15** which undergoes a subsequent δ -hydride elimination to yield the observed product and a metal hydride. As such this reaction involves an intramolecular B-N cross coupling to yield an initial π -bond and a subsequent B-N σ -bond and represents a hybrid of both the cross metathesis and insertion pathways.¹³⁸ Although extension of this work to pyrrolidine-borane indicated a generality to this mechanism, moving to the far bulkier secondary amine-borane, di-*iso*-propylamine-borane, yielded only the respective aminoborane, ${}^i\text{Pr}_2\text{N}=\text{BH}_2$, even under catalytic conditions as shown in Scheme 26. It was postulated that dehydrogenation of di-*iso*-propylamine borane ensues similarly by β -hydride elimination from an initially formed alkaline earth amidoborane derivative. The product aminoborane, ${}^i\text{Pr}_2\text{N}=\text{BH}_2$, however, is unable to undergo subsequent Ae-N insertion as a result of the greater steric demands of the *iso*-propyl substituents.



Scheme 26: The dehydrogenation of ${}^i\text{Pr}_2\text{NH}\cdot\text{BH}_3$ yielding an aminoborane which is incapable of dimerisation, and dihydrogen.

Further evidence for the intermediacy of unsaturated aminoborane units was provided by a subsequent report which noted the interception of a postulated *in situ* generated aminooborane by a Sr-X (X = NR₂, CH(SiMe₃)₂) bond to yield variously an unsymmetrical diaminoborane or aminoalkylborane in the case of **3c** and **4c** respectively. In each case an equivalent of 'SrH₂' was also formed which, in the case of amines, could be intercepted dehydrogenatively to yield amides and render the synthesis of diaminoboranes catalytic in alkaline earth dication utilising **3a** and **3b** as pre-catalysts (Scheme 27).¹³⁹



Scheme 27: The insertion reactivity of *in situ* generated aminoborane fragments into Ae-X bonds (X = R₂N, (Me₃Si)₂CH) to yield unsymmetrically substituted boranes and catalytically viable group 2 hydrides.

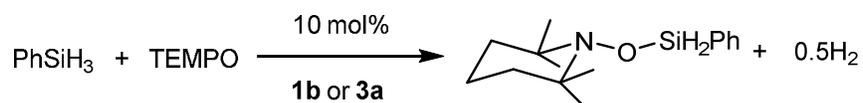
Most notable in this chemistry was the rate-dependence of amine borane dehydrocoupling upon metal identity, which was found to be contingent upon an increase in cation charge-density (Ba < Sr < Ca <

Mg) yielding increasingly efficient dehydrocoupling. Further mitigation for this hypothesis was provided by the observation that the even greater charge density of the Sc^{3+} ion provided a rate of catalytic dimethylamine borane dehydrocoupling well in excess of that of magnesium.¹⁴⁰

Conclusions and Future Perspectives

It is readily apparent that the utility of group 2-based species as potentially sustainable reagents in homogeneous catalysis has progressed enormously during the past decade. Despite the many advances described above, however, the scope and absolute activity of bond activation processes available remains relatively narrow in comparison to the vast breadth of transformations which may be catalysed by transition metal reagents. Furthermore, and notwithstanding the many and varied mechanistic deductions so far, a clear conceptual framework to facilitate the development of future s-block catalyst types is somewhat lacking. It is, thus, interesting to reflect on the advances made in parallel and related areas, with particular regard to catalytic and bond activation reactivity derived from what may be generically termed as main group species.

As highlighted in the introduction to this review, redox activity is a common feature of many transition metal catalysis. While a variety of single electron oxidative reactions of metal-metal bonded Mg(I) centres have been demonstrated by Jones and co-workers,^{3,141} these processes are confined to stoichiometric reductions as the regeneration of the magnesium(I) dimers under catalytic conditions is unlikely. In contrast it is interesting to note that many enzymes utilise redox inactive magnesium and calcium centres to modulate electron transfer processes through the use of biological structures analogous to non-innocent or redox active ligands.¹⁴² With these considerations in mind, Hill and co-workers have utilised the stable radical 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) to derive the first example of a single electron transfer with an s-block element in catalysis (Scheme 28).¹⁴³ In this case H_2 evolution was observed between an otherwise unreactive mixture of TEMPO and phenylsilane upon addition of a catalytic quantity of either compound **1b** or **3a**. The proposed mechanism is rationalised as a combination of Si-H/Mg-O metathesis and single electron oxidation of the as formed magnesium hydride. Although extensions to this approach are likely to require elements of more system-specific ligand design, the application of single electron transfer steps to more productive element-element bond forming reactions should provide a competitive area of future interest in s-block chemistry.



Scheme 28: Magnesium-catalysed coupling of silanes and TEMPO.

Oxidative addition reactions of small molecules such as dihydrogen to typical transition metals are commonly pictured to ensue through the assembly of a synergic HOMO/LUMO interaction of an unfilled metal d-orbital and the σ orbital of H_2 in conjunction with back donation from a filled metal orbital to $\sigma^*(H_2)$. In a similar manner Bertrand's singlet (alkyl)(amino)-carbenes (CAACs),¹⁴⁴ the amido(boryl)- amido(silyl)silyenes of Aldridge and Jones and Power's heavier group 13 and 14 systems are able to effect H_2 activation under very mild conditions.^{145,146} In such cases the facility of the activation is again viewed as resulting from the complementary engagement of the σ and σ^* orbitals of the H_2 substrate and the respective LUMO and HOMO of the formally low oxidation state triel- or tetrel-based molecules. Probably the highest profile main group systems for H_2 activation, however, have been provided by Stephan's 'frustrated' Lewis pairs (FLPs).¹ Although there has been some dispute over their precise mode of action, the most authoritative treatment of these systems also describes the assembly of the H_2 activation transition state as a result of cooperative $\sigma(H_2)$ donation to the Lewis acid component of the FLP and Lewis base donation to $\sigma^*(H_2)$.¹⁴⁷ In such cases substrate engagement results in effectively barrierless *heterolytic* H-H cleavage. Although orbitally unconstrained and non-directional, it is notable that similarly high levels of polarisation and charge separation are implicated during the small molecule activation steps mediated by the highly polar alkaline earth reagents described herein. The activation of H_2 by a Mg-X or Ca-X bond may be considered as a subset of the same reaction type in which heterolysis of the H-H bond is achieved through a $\sigma(H_2)$ interaction with the Lewis acidic Ae centre in concert with simultaneous, but heavily polarised, charge donation from the basic X substituent to the $\sigma^*(H_2)$ orbital.¹¹³ From this standpoint, and more generally, the σ -bond metathesis reactivity so generally associated with group 2-centred and FLP bond activation may be viewed as displaying a high degree of complementarity. It seems likely that future directions will be increasingly led by a similar cross-fertilisation of concepts from other areas. Furthermore, the greater unification of models for reactivity across the entire main group of elements may allow the eventual design of catalytic main group systems including the group 2 elements which are competitive with or even surpass the utility of transition metals.

References

1. D. W. Stephan, *J. Am. Chem. Soc.* 2015, **137**, 10018.
2. A. Yaroshevsky, *Geochem. Int.*, 2006, **44**, 48.
3. (a) S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 1754; (b) M. Westerhausen, *Angew. Chem., Int. Ed.*, 2008, **47**, 2185.
4. S. Krieck, H. Görls, L. Yu, M. Reiher and M. Westerhausen, *J. Am. Chem. Soc.*, 2009, **131**, 2977.
5. M. H. Chisholm, J. Gallucci and K. Phomphrai, *Chem. Commun.*, 2003, 48; M. H. Chisholm, J. C. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2004, **43**, 6717.

6. S. Sarish, S. Nembenna, S. Nagendran, H. W. Roesky, A. Pal, R. Herbst-Irmer, A. Ringe and J. Magull, *Inorg. Chem.*, 2008, **47**, 5971.
7. A. G. M. Barrett, I. J. Casely, M. R. Crimmin, M. S. Hill, J. R. Lachs, M. F. Mahon and P. A. Procopiu, *Inorg. Chem.*, 2009, **48**, 4445.
8. M. R. Crimmin, M. Arrowsmith, A. G. M. Barrett, I. J. Casely, M. S. Hill and P. A. Procopiu, *J. Am. Chem. Soc.*, 2009, **131**, 9670.
9. M. Arrowsmith, M. R. Crimmin, A. G. M. Barrett, M. S. Hill, G. Kociok-Köhn, P. A. Procopiu, *Organometallics*, 2011, **30**, 1493.
10. C. Jones, S. J. Bonyhady, S. Nembenna and A. Stasch, *Eur. J. Inorg. Chem.*, 2012, 2596.
11. J. F. Dunne, J. Su, A. Ellern and A. D. Sadow, *Organometallics*, 2008, **27**, 2399.
12. J. F. Dunne, S. R. Neal, J. Engelkemier, A. Ellern and A. D. Sadow, *J. Am. Chem. Soc.*, 2011, **133**, 16782.
13. M. Arrowsmith, M. S. Hill and G. Kociok-Köhn, *Organometallics*, 2011, **30**, 1291.
14. J. S. Wixey and B. D. Ward, *Dalton Trans.*, 2011, **40**, 7693.
15. S. Datta, P. W. Roesky and S. Blechert, *Organometallics*, 2007, **26**, 4392.
16. S. Datta, M. T. Gamer and P. W. Roesky, *Organometallics*, 2008, **27**, 1207.
17. A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, G. Kociok-Köhn and P. A. Procopiu, *Inorg. Chem.*, 2008, **47**, 7366.
18. B. Liu, T. Roisnel, J.-F. Carpentier and Y. Sarazin, *Angew. Chem., Int. Ed.*, 2012, **51**, 4943.
19. B. A. Vaartstra, J. C. Huffman, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1991, **30**, 121.
20. M. Westerhausen, M. Hartmann, N. Makropoulos, B. Wieneke, M. Wieneke, W. Schwarz and D. Stalke; *Z. Naturforsch., B: Chem. Sci.*, 1998, **53**, 117.
21. M. R. Crimmin, A. G. M. Barrett, M. S. Hill, D. J. MacDougall, M. F. Mahon and P. A. Procopiu, *Chem. Eur. J.*, 2008, **14**, 11292.
22. M. Arrowsmith, M. S. Hill and G. Kociok-Köhn, *Organometallics*, 2010, **29**, 4203.
23. For extensive reviews on this topic see: S. Hong and T. J. Marks, *Acc. Chem. Res.*, 2004, **37**, 673; A. Molander and J. A. C. Romero, *Chem. Rev.*, 2002, **102**, 2161.
24. Y. W. Li and T. J. Marks, *Organometallics*, 1996, **15**, 3770.
25. M. R. Gagné and T. J. Marks, *J. Am. Chem. Soc.*, 1989, **111**, 4108.
26. S. W. Hong, S. Tian, M. V. Metz and T. J. Marks, *J. Am. Chem. Soc.*, 2003, **125**, 14768.
27. S. D. Wobser, C. J. Stephenson, M. Delferro and T. J. Marks, *Organometallics*, 2013, **32**, 1317.
28. B. D. Stubbart and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 4253.
29. X. H. Yu, S. Seo and T. J. Marks, *J. Am. Chem. Soc.*, 2007, **129**, 7244.
30. A. Dzudza and T. J. Marks, *Organic Lett.*, 2009, **11**, 1523.
31. P. W. Roesky, U. Denninger, C. L. Stern and T. J. Marks, *Organometallics*, 1997, **16**, 4486.
32. A. Motta, I. L. Fragala and T. J. Marks, *Organometallics*, 2005, **24**, 4995.
33. A. M. Kawaoka, M. R. Douglass and T. J. Marks, *Organometallics*, 2003, **22**, 4630.

34. S. Y. Seo, X. H. Yu and T. J. Marks, *J. Am. Chem. Soc.*, 2009, **131**, 263.
35. S. Hong, A. M. Kawaoka and T. J. Marks, *J. Am. Chem. Soc.*, 2003, **125**, 15878.
36. M. R. Douglass, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 2001, **123**, 10221.
37. C. J. Weiss, S. D. Wobser and T. J. Marks, *Organometallics*, 2010, **29**, 6308.
38. A. Dzudza and T. J. Marks, *J. Org. Chem.*, 2008, **73**, 4004.
39. S. Seo and T. J. Marks, *Chem. Eur. J.*, 2010, **16**, 5148.
40. C. J. Weiss and T. J. Marks, *Dalton Trans.*, 2010, **39**, 6576.
41. A. M. Seyam, B. D. Stubbert, T. R. Jensen, J. J. O'Donnell, C. L. Stern and T. J. Marks, *Inorg. Chim. Acta*, 2004, **357**, 4029.
42. A. Motta, I. L. Fragala and T. J. Marks, *Organometallics*, 2006, **25**, 5533.
43. V. M. Arredondo, S. Tian, F. E. McDonald and T. J. Marks, *J. Am. Chem. Soc.*, 1999, **121**, 3633.
44. Y. W. Li and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 1757.
45. J. S. Ryu, T. J. Marks and F. E. McDonald, *J. Org. Chem.*, 2004, **69**, 1038.
46. A. M. Kawaoka and T. J. Marks, *J. Am. Chem. Soc.*, 2005, **127**, 6311.
47. J. S. Ryu, G. Y. Li and T. J. Marks, *J. Am. Chem. Soc.*, 2003, **125**, 12584.
48. X. H. Yu and T. J. Marks, *Organometallics*, 2007, **26**, 365.
49. L. Jia, X. M. Yang, A. M. Seyam, I. D. L. Albert, P. F. Fu, S. T. Yang and T. J. Marks, *J. Am. Chem. Soc.*, 1996, **118**, 7900.
50. S. Seo, X. H. Yu and T. J. Marks, *Tetrahedron Lett.*, 2013, **54**, 1828.
51. G. Jeske, H. Lauke, H. Mauermann, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8111.
52. G. Jeske, H. Lauke, H. Mauermann, P. N. Swepston, H. Schumann and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 8091.
53. For an in depth review see: J.-M. Begouin and M. Niggemann, *Chem. Eur. J.*, 2013, **19**, 8030 and references contained therein.
54. M. Westerhausen, S. Schneiderbauer, A. N. Kneifel, Y. Soltl, P. Mayer, H. Nöth, Z. Y. Zhong, P. J. Dijkstra and J. Feijen, *Eur. J. Inorg. Chem.*, 2003, 3432.
55. Y. Sarazin, R. H. Howard, D. L. Hughes, S. M. Humphrey and M. Bochmann, *Dalton Trans.*, 2006, 340.
56. M. G. Davidson, C. T. O'Hara, M. D. Jones, C. G. Keir, M. F. Mahon and G. Kociok-Köhn, *Inorg. Chem.*, 2007, **46**, 7686.
57. W. Vargas and K. Ruhlandt-Senge. *Eur. J. Inorg. Chem.*, 2003, 3472.
58. D. J. Burkey and T. P. Hanusa, *Organometallics*, 1996, **15**, 4971.
59. D. C. Green, U. Englich and K. Ruhlandt-Senge. *J. Chem. Ed.*, 1999, **38**, 354.
60. A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, S. L. Lomas, M. F. Mahon, P. A. Procopiu and K. Suntharalingam, *Organometallics*, 2008, **27**, 6300.

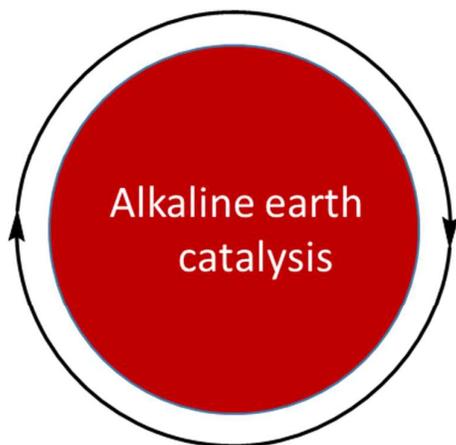
61. M. Westerhausen, M. H. Digeser, M. Krofta, N. Wiberg, H. Nöth, J. Knizek, W. Ponikwar and T. Seifert, *Eur. J. Inorg. Chem.*, 1999, 743.
62. A. G. Avent, M. R. Crimmin, M. S. Hill and P. B. Hitchcock, *Organometallics*, 2005, **24**, 1184.
63. M. Westerhausen, M. H. Digeser, B. Wieneke, H. Nöth and J. Knizek, *Eur. J. Inorg. Chem.*, 1998, 517.
64. M. Westerhausen, C. Birg, M. Krofta, P. Mayer, T. Seifert, H. Nöth, A. Pfitzner, T. Nilges and H. J. Deiseroth, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1073.
65. M. Westerhausen, M. H. Digeser, H. Nöth and J. Knizek, *Z. Anorg. Allg. Chem.*, 1998, **624**, 215.
66. S. E. Baillie, V. L. Blair, T. D. Bradley, W. Clegg, J. Cowan, R. W. Harrington, A. Hernan. R. Kennedy, Z. Livingstone and E. Hevia, *Chem. Sci.*, 2013, **4**, 1895.
67. M. Westerhausen, M. H. Digeser and W. Schwarz, *Inorg. Chem.*, 1997, **36**, 521.
68. M. Westerhausen, M. H. Digeser, H. Nöth, W. Ponikwar, T. Seifert and K. Polborn, *Inorg. Chem.*, 1999, **38**, 3207.
69. M. Westerhausen, M. H. Digeser, C. Guckel, H. Nöth, J. Knizek and W. Ponikwar, *Organometallics*, 1999, **18**, 2491.
70. M. Westerhausen, H. D. Hausen and W. Schwarz, *Z. Anorg. Allg. Chem.*, 1992, **618**, 121.
71. M. Westerhausen and H. D. Hausen, *Z. Anorg. Allg. Chem.*, 1992, **615**, 27.
72. A. Weeber, S. Harder, H. H. Brintzinger and K. Knoll, *Organometallics*, 2000, **19**, 1325.
73. F. Feil and S. Harder, *Organometallics*, 2000, **19**, 5010.
74. F. Feil and S. Harder, *Organometallics*, 2001, **20**, 4616.
75. S. Harder, F. Feil and A. Weeber, *Organometallics*, 2001, **20**, 1044.
76. M. R. Crimmin, I. J. Casely and M. S. Hill, *J. Am. Chem. Soc.*, 2005, **127**, 2042.
77. J. E. Baldwin, *J. Chem. Soc. Commun.*, 1976, 734.
78. M. E. Jung and G. Piizzi, *Chem. Rev.*, 2005, **105**, 1735.
79. J. F. Dunne, D. B. Fulton, A. Ellern and A. D. Sadow, *J. Am. Chem. Soc.*, 2010, **132**, 17680.
80. C. Brinkmann, A. G. M. Barrett, M. S. Hill and P. A. Procopiou, *J. Am. Chem. Soc.*, 2012, **134**, 2193.
81. A. G. M. Barrett, C. Brinkmann, M. R. Crimmin, M. S. Hill, P. Hunt and P. A. Procopiou, *J. Am. Chem. Soc.*, 2009, **131**, 12906.
82. (a) S. Tobisch, *Chem. Eur. J.*, 2011, **17**, 14979; (b) S. Tobisch, *Chem. Eur. J.*, 2014, **20**, 8988; (c) S. Tobisch, *Chem. Eur. J.*, 2015, **21**, 6765.
83. M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock and P. A. Procopiou, *Organometallics*, 2007, **26**, 2953.
84. T. M. A. Görls and M. Westerhausen, *Inorg. Chem. Commun.*, 2008, **11**, 1419.
85. B. Liu, T. Roisnel, J.-F. Carpentier and Y. Sarazin, *Chem. Eur. J.*, 2013, **19**, 2784.

86. B. Liu, J.-F. Carpentier and Y. Sarazin, *Chem. Eur. J.*, 2012, **18**, 13259.
87. J. R. Lachs, A. G. M. Barrett, M. R. Crimmin, G. Kociok-Köhn, M. S. Hill, M. F. Mahon and P. A. Procopiou, *Eur. J. Inorg. Chem.*, 2008, 4173.
88. A. Baishya, M. K. Barman, T. Peddaraao and S. Nembenna, *J. Organomet. Chem.*, 2014, **769**, 112.
89. M. R. Crimmin, A. G. M. Barrett, M. S. Hill, P. B. Hitchcock and P. A. Procopiou, *Organometallics*, 2008, **27**, 497.
90. A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, S. L. Lomas, M. F. Mahon and P. A. Procopiou, *Dalton Trans.*, 2010, **39**, 7393.
91. M. Arrowsmith, M. R. Crimmin, M. S. Hill, S. L. Lomas, M. S. Heng, P. B. Hitchcock and G. Kociok-Köhn, *Dalton Transactions*, 2014, **43**, 14249.
92. L. Orzechowski and S. Harder, *Organometallics*, 2007, **26**, 2144.
93. A. G. M. Barrett, T. C. Boorman, M. R. Crimmin, M. S. Hill, G. Kociok-Köhn and P. A. Procopiou, *Chem. Commun.*, 2008, 5206.
94. A. Hernan-Gomez, T. D. Bradley, A. R. Kennedy, Z. Livingstone, S. D. Robertson, and E. Hevia, *Chem. Commun.*, 2013, **49**, 8659.
95. D. J. Liptrot, M. S. Hill and M. F. Mahon, *Angew. Chem. Int. Ed.*, 2013, **52**, 5364.
96. M. Arrowsmith, W. M. S. Shepherd, M. S. Hill and G. Kociok-Köhn, *Chem. Commun.*, 2014, **50**, 12676.
97. M. Arrowsmith, M. S. Hill and G. Kociok-Köhn, *Chem. Eur. J.*, 2015, **21**, 10548.
98. J. Penafiel, L. Maron, and S. Harder, *Angew. Chem., Int. Ed.*, 2015, **54**, 201.
99. S. Harder and J. Brettar, *Angew. Chem., Int. Ed.*, 2006, **45**, 3474.
100. S. P. Green, C. Jones and A. Stasch, *Angew. Chem., Int. Ed.*, 2008, **47**, 9079.
101. S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards and G. J. McIntyre, *Chem. Eur. J.*, 2010, **16**, 938.
102. M. Arrowsmith, M. S. Hill, D. J. MacDougall, M. F. Mahon, *Angew. Chem., Int. Ed.* 2009, **48**, 4013.
103. (a) S. Harder, J. Spielmann, J. Intemann, H. Bandmann, *Angew. Chem., Int. Ed.*, 2011, **50**, 4156; (b) J. Intemann, J. Spielmann, P. Sirsch, S. Harder, *Chem. Eur. J.* 2013, **19**, 8478.
104. (a) P. Jochmann, J. P. Davin, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem.* 2012, **51**, 4452; (b) D. Martin, K. Beckerle, S. Schnitzler, T. P. Spaniol, L. Maron and J. Okuda, *Angew. Chem., Int. Ed.* 2015, **54**, 4115; (c) V. Leich, T. P. Spaniol and J. Okuda, *Inorg. Chem.*, 2015, **54**, 4927; (d) S. Schnitzler, T. P. Spaniol, L. Maron and J. Okuda, *Chem. Eur. J.*, 2015, **21**, 11330.
105. J. Spielmann and S. Harder, *Chem. Eur. J.*, 2007, **13**, 8928.
106. S. Harder, *Chem. Commun.*, 2012, **48**, 11165.

107. J. Spielmann and S. Harder, *Eur. J. Inorg. Chem.*, 2008, 1480.
108. J. Spielmann, G. Jansen, H. Bandmann and S. Harder, *Angew. Chem., Int. Ed.*, 2008, **47**, 6290.
109. F. Buch, H. Brettar and S. Harder, *Angew. Chem., Int. Ed.*, 2006, **45**, 2741.
110. F. Buch and S. Harder, *Z. Naturforsch., B: Chem. Sci.*, 2008, **63**, 169.
111. V. Leich, T. P. Spaniol, L. Maron and J. Okuda, *Chem. Commun.*, 2014, **50**, 2311.
112. S. Harder and J. Brettar, *Angew. Chem., Int. Ed.*, 2006, **45**, 3474.
113. G. Zeng and S. Li, *Inorg. Chem.*, **2010**, *49*, 336.
114. S. Harder and J. Spielmann, *J. Organomet. Chem.*, 2012, **698**, 7.
115. M. Arrowsmith, T. J. Hadlington, M. S. Hill and G. Kociok-Köhn, *Chemical Communications*, 2012, **48**, 4567.
116. M. Arrowsmith, M. S. Hill, T. Hadlington, G. Kociok-Köhn and C. Weetman, *Organometallics*, 2011, **30**, 5556.
117. C. Weetman, M. S. Hill and M. F. Mahon, *Polyhedron*, 2015, in press, doi:10.1016/j.poly.2015.08.018.
118. J. Intemann, M. Lutz and S. Harder, *Organometallics*, 2014, **33**, 5722.
119. M. Arrowsmith, M. S. Hill and G. Kociok-Köhn, *Chem.-Eur. J.*, 2013, **19**, 2776.
120. C. Weetman, M. S. Hill and M. F. Mahon, *Chem. Commun.*, 2015, **51**, 14477.
121. C. Weetman, M. D. Anker, M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. Liptrot and Mary F. Mahon, *Chem. Sci.*, 2015, in press, DOI: 10.1039/C5SC03114A.
122. D. Mukherjee, A. Ellern and A. D. Sadow, *Chem. Sci.*, 2014, **5**, 959.
123. N. L. Lampland, M. Hovey, D. Mukherjee and A. D. Sadow, *ACS Catalysis*, 2015, **5**, 4219.
124. N. L. Lampland, A. Pindwal, S. R. Neal, S. Schlauderaff, Arkady Ellern and A. D. Sadow, *Chem. Sci.* 2015, **6**, 6901.
125. (a) M. D. Anker, M. S. Hill, J. P. Lowe and M. F. Mahon, *Angew. Chem. Int. Ed.*, 2015, **54**, 10009; see also (b) R. Lalrempuia, C. E. Kefalidis, S. J. Bonyhady, B. Schwarze, L. Maron, A. Stasch and C. Jones, *J. Am. Chem. Soc.*, 2015, **137**, 8944.
126. M. D. Anker, M. Arrowsmith, P. Bellham, M. S. Hill, G. Kociok-Köhn, D. J. Liptrot, M. F. Mahon and C. Weetman, *Chem. Sci.*, 2014, **5**, 2826.
127. A. Berkefeld, W. E. Piers, M. Parvez, L. Castro, L. Maron and O. Eisenstein, *Chem. Sci.*, 2013, **4**, 2152.
128. F. Buch and S. Harder, *Organometallics*, 2007, **26**, 5132.
129. J. F. Dunne, S. R. Neal, J. Engelkemier, A. Ellern and A. D. Sadow, *J. Am. Chem. Soc.*, 2011, **133**, 16782.
130. M. S. Hill, D. J. Liptrot, D. J. MacDougall, M. F. Mahon and T. P. Robinson; *Chem. Sci.*; 2013, **4**, 4212.

131. C. Bellini, J.-F. Carpentier, S. Tobisch and Y. Sarazin, *Angew. Chem. Int. Ed.*, 2015, **54**, 7679.
132. D. J. Liptrot, M. S. Hill, M. F. Mahon and A. S. S. Wilson, *Angew. Chem. Int. Ed.*, 2015, **54**, 13362.
133. M. S. Hill, M. F. Mahon and T. P. Robinson, *Chem. Commun.*, 2010, **46**, 2498.
134. D. J. Liptrot, M. Arrowsmith, A. L. Colebatch, T. J. Hadlington, M. S. Hill, G. Kociok-Köhn and M. F. Mahon, *Angew. Chem. Int. Ed.*, 2015, in press, DOI: 10.1002/anie.201507004.
135. For an early example of stoichiometric calcium-centred B-N bond formation, see A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, P. A. Procopiou, *Organometallics* **2007**, *26*, 4076.
136. (a) J. Spielmann, G. Jansen, H. Bandmann and S. Harder, *Angew. Chem., Int. Ed.*, 2008, **47**, 6290; (b) Spielmann, D. F. J. Piesik and S. Harder, *Chem. Eur. J.*, 2010, **16**, 8307; (c) J. Spielmann and S. Harder, *Dalton Trans.*, 2011, **40**, 8314.
137. (a) J. Spielmann and S. Harder, *J. Am. Chem. Soc.*, 2009, **131**, 5064; (b) J. Spielmann, M. Bolte and S. Harder, *Chem. Commun.*, 2009, 6934.
138. (a) D. J. Liptrot, M. S. Hill, M. F. Mahon and D. J. MacDougall, *Chem. Eur. J.*, 2010, **16**, 8508; (b) M. S. Hill, M. Hodgson, D. J. Liptrot and M. F. Mahon, *Dalton Trans.*, 2011, **40**, 7783.
139. (a) P. Bellham, M. S. Hill, D. J. Liptrot, D. J. MacDougall and M. F. Mahon, *Chem. Commun.*, 2011, **47**, 9060; (b) P. Bellham, M. S. Hill, G. Kociok-Köhn and D. J. Liptrot, *Dalton Trans.*, 2013, **42**, 737; (c) P. Bellham, M. S. Hill, G. Kociok-Köhn and D. J. Liptrot, *Chem. Commun.*, 2013, **49**, 1960.
140. M. S. Hill, G. Kociok-Köhn and T. P. Robinson, *Chem. Commun.*, 2010, **46**, 7587.
141. (a) S. P. Green, C. Jones and A. Stasch, *Angew. Chem., Int. Ed.*, 2008, **47**, 9079. (b) J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards and G. J. McIntyre, *Chem. Eur. J.*, 2010, **16**, 938.
142. V. K. K. Praneeth, M. R. Ringenburg and T. R. Ward, *Angew. Chem., Int. Ed.*, 2012, **51**, 10228.
143. D. J. Liptrot, M. S. Hill and M. F. Mahon; *Angew. Chem., Int. Ed.*, 2014, **53**, 6224.
144. G. D. Frey, V. Lavallo, B. Donnadiou, W. W. Schoeller and G. Bertrand, *Science*, **2007**, *316*, 439.
145. A. V. Protchenko K. H. Birjkumar, A. D. Schwarz, D. Vidovic, C. Jones, N. Kaltsoyannis, P. Mountford and S. Aldridge, *J. Am. Chem. Soc.*, 2012, **134**, 6500.
146. G. H. Spikes, J. C. Fettinger and P. P. Power, *J. Am. Chem. Soc.*, 2005, **127**, 12232.
147. T. A. Rokob, I. Bakó, A. Stirling, A. Hamza and I. Pápai, *J. Am. Chem. Soc.*, 2013, **135**, 4425.

For Table of Contents:



Author biographies:

Mike Hill received his PhD from the University of Bath in 1994. After postdoctoral research at North Dakota State University with Professor David Atwood and a brief period in industry with Pilkington plc, he worked as a postdoctoral fellow with Professor Colin Eaborn FRS at the University of Sussex. He was awarded a Royal Society URF in 2000 before being appointed to a lectureship at Imperial College London in 2002. In 2007 he returned to Bath where he was promoted to Professor in 2011. His interests lie in the organometallic chemistry of the s- and p-block elements applied to homogeneous catalysis and materials fabrication.



David Liptrot received his MChem (Hons) in Chemistry with Industrial Training from the University of Bath in 2011 and remained there to undertake a PhD on group 2 catalysis in the laboratory of Professor Mike Hill. After completing this in 2014 he went on to work with Professor Roland Fischer (Graz University of Technology, Austria) and in 2015 took up his current position as a Lindemann Postdoctoral Fellow with Professor Philip Power FRS (University of California, Davis, USA). His research interests range from catalysis to inorganic polymers and he currently studies the application of dispersion effects to stabilise organometallic compounds.



Cath Weetman was an undergraduate at the University of Bath where she achieved MChem (Hons) with a year of Industrial Training in 2011. Her year in industry with SASOL Technology UK at the University St. Andrews inspired her choice of PhD project, with Professor Mike Hill in Bath, in the area of group 2-based hydroboration catalysis which she completed in 2015. In October 2015 she moved to the University of Edinburgh where she is currently a postdoctoral researcher studying the activation of small molecules by f-element complexes in the groups of Professor Polly Arnold and Professor Jason Love.