Ring-shaped phosphinoamido magnesium hydride complexes: syntheses, structures, reactivity and catalysis

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Dedicated to Prof. Herbert W. Roesky on the occasion of his 80th birthday

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A series of magnesium(II) complexes bearing the sterically demanding phosphinoamide ligand, $L^- = Ph_2PNDip^-$, Dip = 2,6-diisopropylphenyl, including heteroleptic magnesium alkyl and hydride complexes are described. The ligand geometry enforces various novel ring and cluster geometries for the heteroleptic compounds. We have studied the stoichiometric reactivity of $[(LMgH)_4]$ towards unsaturated substrates, and investigated catalytic hydroborations and hydrosilylations of ketones and pyridines. We found that hydroborations of two ketones using pinacolborane with various Mg precatalysts is very rapid at room temperature with very low catalyst loadings, and ketone hydrosilylation using phenylsilane is rapid at 70°C. Our studies point to an insertion/σ-bond metathesis catalytic cycle of an *in-situ* formed active "MgH_2" species.

Introduction

Metal hydrides and their complexes play a fundamental role in many applications including as hydride sources in synthesis and catalysis, and for hydrogen storage technologies.[1] Of the binary hydrogen compounds of the chemical elements, s-block metal hydrides are unique due to the highly electropositive nature of the Alkali and Alkaline Earth metals, and their electronegativity difference to hydrogen. Thus, these metal hydrides are generally classified as ionic or saline.[2,3] The s-block is furthermore home to highly earth abundant, non-toxic and even biocompatible metals such as Na, K, Mg and Ca, that offer a range of properties for future sustainable chemical applications.[4] A range of well-defined s-block metal hydride complexes have been reported in very recent years and these have already been successfully used in stoichiometric and catalytic transformations, and the hydrogen storage properties of some examples have been investigated.[2,3] The recent success in this area can be attributed to both the development of suitable synthetic strategies to generate s-block metal hydride fragments, and the design and use of stabilising ligand systems that prevent dismutation and other decomposition reactions of the formed complexes that can lead to the precipitation of insoluble saline metal hydrides. Generally, the ionic and flexible metal-ligand interactions in s-block metal coordination chemistry require ligand systems that suppress dismutation equilibria, for example, by employing chelating, bridging, and/or sterically demanding ligands.[2,3]

The majority of well-defined s-block metal hydride complexes has been prepared with magnesium, and these encompass complexes with sterically demanding β-diketiminates,[5] mixed s-block amido species,[6] and a variety of other carbon-, nitrogen- or oxygen-based ligand species,[7,8] as well as a few examples of related calcium hydride complexes.[9] They have been accessed either via hydride metathesis using magnesium alkyl or amido fragments with main group element hydride species (such as silanes, boranes or alanes), by β-hydrogen elimination, or via hydrogenation of dimeric magnesium(I) compounds with cyclohexadiene or alane complexes. The newly formed complexes show both interesting stoichiometric and catalytic reactivity.[2,10-13] For several catalytic applications, the active magnesium hydride catalyst was conveniently generated *in-situ* from stoichiometric hydride sources such as boranes and silanes.[2,10,11]

We have previously employed the simple, sterically demanding phosphinoamide ligand Ph$_2$PNDip$^-$ (Dip = 2,6-diisopropylphenyl), L$^-$, to obtain the well-defined and hydrocarbon-soluble lithium hydride complex [(LLi)$_4$(LiH)$_4$] and studied its properties and reactivity.[14] Herein we report the extension to magnesium hydride complexes with this ligand. We reasoned that the orientation of the donor atoms of the phosphinoamide ligand,[14,15] which typically favours bridging coordination modes, is similar to what we found for pyrazolate ligands,[16] and could favour the

formation of unprecedented cluster or ring complexes that potentially liberate reactive LMgH fragments for unusual stoichiometric and catalytic reactivity. In addition, the inclusion of the NMR-active phosphorus centre in the ligand system should allow further insights into the reactivity of the newly formed compounds.

Results and Discussion

Synthesis

To access suitable precursor molecules to phosphinoamido magnesium hydride complexes, we studied the reaction of the sterically demanding phosphinoamine[15] DipNHPPh$_2$, LH,[14b] with commercially available di-n-butyl magnesium in hydrocarbon solvents. The reaction of LH with Mg(nBu)$_2$ in a 2:1 molar ratio afforded one main product according to ^{1}H and ^{31}P{^{1}H} NMR spectroscopic studies. A good yield of the new complex [(L$_2$Mg)$_2$] **1** was isolated and the molecular structure of the complex was structurally characterised, see scheme 1 and Figure 1. The 1:1 molar reaction of LH with Mg(nBu)$_2$ on the other hand afforded a product mixture with a main species showing ^{1}H NMR spectroscopic resonances that suggest one Mg-bound nBu group per three phosphinoamide ligands, and a doublet and a triplet in the ^{31}P{^{1}H} NMR spectrum suggesting different phosphinoamido ligand environments in a 2:1 ratio that couple with each other. Work-up afforded the expected complex [L$_3$Mg$_2$(nBu)] **2** in a moderate isolated yield, that could be structurally characterised, see scheme 1 and Figure 1. From reactions with the 1:1 molar ratio, we furthermore obtained colourless crystals of the unusual magnesium ethyl complex [{(LMgEt)$_2$}$_6$] **3**, see Figure 1, in very low yield in one instance. Previous studies have shown that commercially available Mg(nBu)$_2$ can contain other organic substituents such as ethyl groups, and even significant quantities of aluminium.[17]

please insert Scheme 1 here

The homoleptic complex [(L$_2$Mg)$_2$] **1** crystallises with half a molecule in the asymmetric unit. Each Mg centre is in a planar, three-coordinate environment binding to one terminal κ^1-N phosphinoamide and to one P and N donor atom, respectively, of two μ-κ^2-P,N phosphinoamides. In [L$_3$Mg$_2$(nBu)] **2**·1.5 C$_5$H$_{12}$, Mg1 and Mg2 are bridged by two phosphinoamides with N,N'-coordination to Mg1 and P,P' coordination to Mg2 and a bridging nBu group. Mg2 is additionally coordinated by a terminal phosphinoamide ligand. In the solid state, Mg1 shows further short contacts to hydrogen atoms of one isopropyl group (shortest contact: Mg1···H40A of *ca.* 2.2 Å). Complex [{(LMgEt)$_2$}$_6$] **3**·7 C$_6$H$_{14}$, crystallised in the trigonal crystal system and is a large ring

3

system formed by six (LMgEt)$_2$ subunits. In the latter, an Mg$_2$ unit is bridged by two phosphinoamides and one ethyl group in a way that each Mg atom is P,N,C-coordinated. In addition, Mg2 binds to the carbon atom of a "terminal" ethyl group that is coordinated via short Mg$\cdots$H contacts to the Mg1' centre of the next Mg$_2$ subunit, forming the connective backbone of the (Mg$\cdots$Mg–CH$_2\cdots$)$_6$ ring system. It seems that the larger butyl group does not support a stable compound in the desired 1:1 phosphinoamide:butyl stoichiometry and forms [L$_3$Mg$_2$(nBu)] **2** instead, but the smaller ethyl group in [{(LMgEt)$_2$}$_6$] **3** does allow this composition. Furthermore, compounds **1-3** show that the preferred coordination mode of phosphinoamide ligands between two Mg centres under the given conditions (*e.g.* non-coordinating solvents) is a *cis*-like μ-κ^2-P,N coordination bridge, though terminal κ^1-N coordination is observed as well.

In deuterated benzene solution, the homoleptic complex [(L$_2$Mg)$_2$] **1** only shows one doublet and one septet for the protons of the isopropyl groups in its ^{1}H NMR spectrum and one singlet in its ^{31}P{^{1}H} NMR spectrum (56.4 ppm) supporting fast ligand exchange under these conditions, which can be expected for highly fluxional ionic s-block metal ion-ligand interactions. In deuterated THF, the compound shows two broad methyl and one broad methine resonances at room temperature that resolve to one broad methyl resonance and a sharp methine septet at 60°C in its ^{1}H NMR spectra (Figure S2-3). Complex [L$_3$Mg$_2$(nBu)] **2** shows broadened and overlapping resonances for the isopropyl groups in its ^{1}H NMR spectrum recorded in deuterated benzene, and a doublet (δ 29.8 ppm) and triplet (δ 42.7 ppm) in its ^{31}P{^{1}H} NMR spectrum with a $J_{\text{P-P}}$ coupling of 30.8 Hz. This supports the retention of the overall solid state connectivity of [L$_3$Mg$_2$(nBu)] **2** in solution, with two different phosphinoamide ligands in a ratio of 2:1.

please insert Figure 1 here

Because no convenient stable [{LMg(nBu)}$_n$] complex was formed as a precursor to desired [{LMgH}$_n$] complexes, we treated 1:1 mixtures of LH and Mg(nBu)$_2$ in *n*-hexane/heptane with phenylsilane under reflux or at 60°C for 16 h. These experiments afforded the structurally characterised mixed alkyl hydride complex [{L$_2$Mg$_2$(nBu)H}$_2$] **4** in good isolated yield, see scheme 1 and Figure 2. The 1:1 reactions of LH and Mg(nBu)$_2$ in toluene or deuterated benzene with phenylsilane at 70°C for 16 h afforded the tetrameric magnesium hydride complex [(LMgH)$_4$] **5**, see scheme 1 and Figure 2. Solution NMR studies show an almost quantitative conversion to **5**, and larger scale experiments afforded the isolated complex in moderate to good yield. In addition, the hexameric complex [(LMgH)$_6$] **6** could be structurally characterised from benzene in one case as a low yield by-product, see Figure 2. Similarly, related experiments with more than one molar equivalent of Mg(nBu)$_2$ per LH in various stoichiometries, followed by phenylsilane treatment at

elevated temperatures, also yielded [(LMgH)$_4$] **5** as the main product as judged by NMR spectroscopy and from lower isolated yields of **5** from these studies. Furthermore, isolated complex [{L$_2$Mg$_2$(*n*Bu)H}$_2$] **4** can be converted to [(LMgH)$_4$] **5** with phenylsilane at 80°C in benzene or toluene for 16 h in good yield producing the expected silane PhSiH$_2$(*n*Bu) as a by-product. We conducted similar experiments of isolated **2** with phenylsilane at 60°C for 16 h and found that [(LMgH)$_4$] **5** is also generated alongside PhSiH$_2$(*n*Bu) and a new Si- and P-containing compound, PhSiH$_2$(L) **7**, as judged by multinuclear NMR spectroscopy.[18] We then investigated the same reaction of phenylsilane with isolated [(L$_2$Mg)$_2$] **1** at 70°C in deuterated benzene and found that significant quantities of [(LMgH)$_4$] **5** alongside PhSiH$_2$(L) **7** are formed. After 30 h at 70°C, the reaction mixture shows only LSiH$_2$Ph **7** and [(LMgH)$_4$] **5** in a ratio of *ca.* 5:1. This observation is further evidence that magnesium hydride species can be generated from simple homoleptic magnesium(II) complexes and main group hydride sources, that can be responsible for stoichiometric or catalytic reactivity of these systems.

The mixed alkyl hydride complex [{L$_2$Mg$_2$(*n*Bu)H}$_2$] **4**·C$_6$H$_{14}$ crystallised with half a molecule in the asymmetric unit. In **4**, the four Mg atoms are in one plane and form a parallelogram that is similar to a distorted diamond. The four sides of the parallelogram are bridged by μ-κ^2-P,N-coordinated phosphinoamides with alternating N,P and P,N arrangement. The Mg centre (Mg1) on the acute corner of the parallelogram is *N,N′* coordinated by two bridging phosphinoamides and the Mg centre (Mg2) on the obtuse corner of the parallelogram is *P,P′* coordinated by two phosphinoamides. The two phosphinoamides (P1) that bridge the longer edges of the parallelogram lie in the Mg$_4$ plane, whereas the other two phosphinoamide ligands (P2) are located above and below the Mg$_4$ plane (*c.f.* the NMR discussion). The two *n*-butyl groups sit above and below the plane directly on the two edges of the shortest parallelogram sides which consequently have the shortest Mg1···Mg2 distances. The two hydride ligands form μ^3-bridges over Mg1,Mg2,Mg2' triangles on opposite sides of the Mg$_4$ plane that are not occupied by *n*Bu groups. The molecular structures of the hydride complexes [(LMgH)$_4$] **5** and [(LMgH)$_6$] **6** have many similar geometrical features. The Mg atoms for both compounds lie in one plane, respectively, and form a distorted square in **5** and a perfect hexagon in **6**. Phosphinoamide ligands bridge two Mg centres on the outside of each edge and alternatingly lie above or below the respective Mg$_n$ (n = 4 or 6) plane. The phosphinoamides are arranged around the (MgH)$_n$ core in a symmetrical, head-to-tail like fashion. Hydride ligands bridge between two Mg atoms and again alternate above and below the Mg$_n$ plane and are each opposite of bridging phosphinoamide positions. The hydride ligands in **5** sit directly above or below the edges of the distorted Mg$_4$ square, while those in **6** point somewhat towards the centre of the hexagon. Complex **5** is relatively symmetric showing approximate nearest contacts of Mg-N (2.0 Å), Mg-P (2.6 Å), Mg-H (1.8 Å) and Mg···Mg (3.0 Å). The symmetric hexameric

species **6** shows very similar bond lengths compared with **5**, albeit slightly larger Mg···Mg separations and longer apparent Mg-H bonds.

please insert Figure 2 here

Dissolving crystalline [{$L_2Mg_2(nBu)H$}$_2$] **4** in deuterated benzene repeatedly lead to overlapping NMR resonances for two compounds in an approximate 1:1 ratio, see Figure S10-11. We assigned two broad doublets (δ 28.9 and 32.0 ppm, $J_{P-P} \approx$ 119 Hz) in the $^{31}P\{^1H\}$ NMR spectrum with additional unresolved smaller coupling and a significant roof effect, to the isomer (**4A**) resembling the solid state structure with head/head and tail/tail (P,N;N,P;P,N etc) orientation of the phosphinoamide ligands. This isomer is the more dominant species immediately after dissolving crystals of **4**. The other isomer (**4B**) shows two sharp doublets of doublets (δ 27.2 and 38.1, $J_{P-P} \approx$ 20 and 6 Hz) in the $^{31}P\{^1H\}$ NMR spectrum that we believe could result from an isomer with alternating P,N-orientation of the phosphinoamide ligands, and not a different oligomeric form of $L_2Mg_2H(nBu)$. A DOSY NMR experiment on this isomer mixture was not conclusive; however, it did point to two molecules of similar shape or size for **4A** and **4B**. New species are formed when the mixture is allowed to stand in solution at room temperature. Heating the solution of both isomers to 80°C and consecutive cooling leads to a mixture of compounds (see Figure S12-13), including small quantities of **5**, that we could in one instance characterise crystallographically from these mixtures. The non-equivalence of two different phosphinoamide ligands in **4A** becomes apparent, when the crystal structure of **4** is examined. The two phosphinoamide ligands (P1) within the Mg_4 plane that bridge a larger edge of the Mg_4 parallelogram are different to the other two phosphinoamide ligands (P2) which bridge the smaller rhombus edge out of the plane and are affected by *n*-butyl coordination on the opposite side of the plane. An equivalence on the NMR time scale for the two different phosphinoamide environments would mainly require migration of the bridging *n*-butyl group. The MgH units of both isomers resonate as multiplets centred around 6.07 ppm (**4A**) and 5.55 ppm (**4B**) in an ^1H NMR spectrum (Figure S10), or as respective singlets in an $^1H\{^{31}P\}$ NMR spectrum. Solution NMR spectra of [(LMgH)$_4$] **5** show four doublets and two septets for the protons of the isopropyl groups and one singlet (δ 25 ppm) in its $^{31}P\{^1H\}$ NMR spectrum which is in accordance with the essentially symmetrical phosphinoamide environments in the solid state structure. The MgH resonance is found as a very broad doublet-like multiplet ($J \approx$ 54 Hz) that resolves to a sharp singlet at δ 5.14 ppm in its $^1H\{^{31}P\}$ NMR spectrum (see Figure S17-18). Dissolving crystalline samples of **4** and **5** in the donor solvent THF-d$_8$, respectively, show the formation of product mixtures with essentially the same phosphinoamide containing compounds in different ratios (Figure S15-16, S21-22). The ^{31}P NMR spectra for both compounds show

significant quantities of [(L$_2$Mg)$_2$] **1** formed in solution (a singlet at δ 43.9 to 44.0 ppm, compare with Figure S5), especially for the spectrum of **5** (Figure S22). A broad resonance at 2.89 ppm in the ^{1}H NMR spectra of both **4** and **5** likely accounts for a large proportion of the MgH resonances. These observations support Schlenk-type equilibria of heteroleptic complexes such as **5** in inert donor solvents and suggest the formation of [MgH$_2$(THF)$_n$] or other hydride-rich species by implication.

Upon treatment of **5** with four equivalents of the chelating amine ligand PMDETA (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine), only one PMDETA ligand is coordinating to one Mg centre in a dinuclear complex with bridging hydride ligands, see Figure 2, affording [(L$_2$MgH$_2$Mg(PMDETA)] **8** in good yield. Complex **8** is the main isolated product from reactions of varying stoichiometry and as suggested by NMR experiments. In the molecular structure of **8**, Mg2 is six-coordinate binding to the chelating PMDETA ligand (*N,N′,N″*-κ^3-bound), two hydrides and only to one P atom of one phosphinoamide ligand. Mg1 is four-coordinate and is connected to two N-bound phosphinoamides and two hydride ligands. It appears that the chelating PMDETA ligand causes the loss of the sterically demanding DipN-coordination, but retains coordination to the small and hard hydride ligands. In solution, complex **8** shows broadened resonances at room temperature. At 65°C only one septet for the protons of the isopropyl methine groups can be found in its ^{1}H NMR spectrum, and one broad resonance (46.3 ppm) is present in its ^{31}P NMR spectrum between 25 and 65°C, indicating fluxional ligand behaviour. The MgH resonance is found as one broad triplet ($J_{\text{H-P}}$ = 7.7 Hz) in its ^{1}H NMR spectrum, or a singlet in its ^{1}H{^{31}P} NMR spectrum at 4.09 ppm, suggesting solution-averaged interactions with two phosphinoamide ligands of the same environment.

Solution studies on **4** and **5** in THF-d$_8$ as well as complexation of **5** with PMDETA to yield [(L$_2$MgH$_2$Mg(PMDETA)] **8** highlight some of the complexities of heteroleptic coordination compounds of both ionic metal ions and bridging ligands with multiple possible coordination modes. The PMDETA coordination from **5** to **8** may shed light onto ligand redistributions when additional donor groups are available and may be relevant to understand substrate coordination containing donor atoms before a possible hydride transfer can take place. In complex **8**, both "[(PMDETA)MgH$_2$]" and "[L$_2$Mg]" appear to be preformed, held together by the bridging hydride ligands. Equilibria between various species including Schlenk-like equilibria, and species with various phosphinoamide coordination modes have to be considered and many species are expected to have similar energies and can likely convert with small activation energy barriers between them. These observations are important when studying and understanding the stoichiometric and catalytic reactivity of these systems, especially with an excess of molecules that contain donor atoms.

Stoichiometric Reactivity

We studied the reaction of [(LMgH)$_4$] **5** towards several unsaturated organic substrates. No reaction was observed with the alkene 1,1-diphenylethene, diphenylfulvene and diphenylacetylene, respectively in deuterated benzene.

please insert Scheme 2 here

The reaction of [(LMgH)$_4$] **5** with 1-adamantyl azide (AdN$_3$) is surprisingly clean in several stoichiometric ratios as judged by *in-situ* ^{1}H and ^{31}P{^{1}H} NMR spectroscopic studies, and the phosphazide complex [L$_2$L'$_2$Mg$_4$H$_4$] **9** (L' = DipNP(N$_3$Ad)Ph$_2$) was obtained in low to moderate crystallised yield, see scheme 2 and Figure 3. In this complex, the hydride moieties did not react with the organic azide, as was previously found for a β-diketiminate MgH system,[11f] but instead converted two phosphinoamide ligands to anionic iminophosphorano phosphazide ligands (L'$^-$).[19,20] We have previously found that the phosphinoamide ligand L$^-$ can undergo addition reactions to several unsaturated substrates.[14a,20] The overall geometry of the (MgH)$_4^{4+}$ core in **9** is not significantly affected by this reaction compared with **5**, but the supporting ligand environment around each Mg centre has changed. This leads to three types of differently coordinated Mg centres (Figure 3). Mg1 is coordinated by two chelating L'-phosphazide units, Mg2 and Mg4 are each coordinate by an L'-iminophosphorane N atom and phosphinoamide P atom. Consequently, Mg3 is coordinated by two phosphinoamide N atoms. All Mg centres are still further bonding to two bridging hydride ligands. Mg1 is six-coordinate and Mg2-4 are each four-coordinate. In solution, [L$_2$L'$_2$Mg$_4$H$_4$] **9** shows two doublets with a small coupling constant (J = 2.4 Hz) in its ^{31}P{^{1}H} NMR spectrum. The resonance at 32.1 ppm is assigned to the phosphazide centre and the one at 33.7 ppm to the phosphinoamide ligands. The chemical shifts for these resonances are surprisingly similar, considering the different phosphinoamide (P^{III}) and iminophosphorano phosphazide (P^V) environments, which normally resonate further apart. The ^{1}H NMR spectrum shows eight doublets and four septets for the isopropyl groups that are partially overlapping and support the retention of the overall solid state structure in solution. The hydride ligands resonate as two multiplets centred around δ 4.58 and 5.16 ppm which both couple with the ^{31}P centres and each other. This was demonstrated in a ^{1}H,^{1}H COSY NMR spectroscopy experiment (Figure S29) and by the fact that some coupling remains in a ^{1}H{^{31}P} NMR spectrum (Figure S28). In the latter, the resonances appear as broad doublet-like multiplets (J ≈ 8 Hz). Similar couplings between non-equivalant Mg*H* units of 4.5 and 5.2 Hz in magnesium hydride cluster compounds have previously been described.[5e]

please insert Figure 3 here

Reactions of magnesium hydride complexes towards pyridines have previously been reported and include both coordination to form a monomeric species with terminal MgH bond,[5g] as well as several examples of pyridine hydromagnesiation products.[5c,7a,d,8b,12] The reaction of [(LMgH)$_4$] **5** with four equivalents of DMAP (4-dimethylaminopyridine) mainly led to the formation of the bis(phosphinoamido) complex [L$_2$Mg(dmap)$_2$] **10**, scheme 4, and likely MgH reaction products. Complex **10** shows expected spectroscopic features with broadened resonances for the protons of the phosphinoamido ligands and a singlet at 44.9 ppm in its ^{31}P{^{1}H} NMR spectrum. A crystal structure determination of [L$_2$Mg(dmap)$_2$]·2 C$_7$H$_8$, **10**·2 C$_7$H$_8$, shows the expected connectivity and distorted tetrahedral magnesium geometry, but the data quality was too poor to be reported here (see the ESI for an image, Figure S54). The reaction of [(LMgH)$_4$] **5** with 12 equivalents of pyridine (Py) or DMAP (4-dimethylaminopyridine) cleanly led to the 1,2-hydromagnesiation products [LMg(py)$_2$(1,2-dhp)] **11** (1,2-dhp = 1,2-dihydropyridide) and [LMg(dmap)$_2$(1,2-dadhp)] **12** (1,2-dadhp = 4-dimethylamino-1,2-dihydropyridide), respectively, see scheme 4. The latter complex **12** was structurally characterised, see Figure 4. Heating to 60°C for 15 h lead to the clean rearrangement of [LMg(py)$_2$(1,2-dhp)] **11** to the 1,4-dihydropyridide derivative [LMg(py)$_2$(1,4-dhp)] **13**, scheme 4. An analogous rearrangement is not possible for [LMg(dmap)$_2$(1,2-dadhp)] **12** under these conditions; a similar observation has previously been noted for other group 2 metal hydride systems.[12,13a] The molecular structure of [LMg(dmap)$_2$(1,2-dadhp)] **12**, Figure 4, shows a distorted tetrahedrally coordinated Mg^{2+} ion, which binds to a terminal κ^1-N phosphinoamide ligand, a 4-dimethylamino-1,2-dihydropyridide ligand from formal 1,2-addition of a MgH unit onto the DMAP pyridine ring, and two neutral, coordinating DMAP molecules. The shorter Mg-N distance of the dihydropyridide ligand compared with those of the neutral DMAP ligands, the C-C and C-N distances within the hydromagnesiated ring system, and the deviation from planarity of the CH$_2$ unit in question support the formulation as the 1,2-dihydropyridide product. NMR spectroscopic studies also support the clean 1,2 addition reaction to form complexes **11** and **12**, and the thermal conversion of **11** to **13**. Complex **11** shows a doublet ($J_{\text{H-H}}$ = 4.0 Hz) at δ 4.26 ppm for the two hydrogen atoms of the 1,2-dihydropyridide unit in its ^{1}H NMR spectrum that converts to a centred multiplet for the two hydrogen atoms of the 1,4-dihydropyridide ligand at δ 4.03 ppm, see Figure S35 and S41.

please insert Scheme 3 here

please insert Figure 4 here

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We were also interested in the stoichiometric reactivity of non-enolisable ketones with [(LMgH)$_4$] **5**. Previously, group 2 metal hydride complexes have been reported to undergo reductions of ketones,[8a,c,d,f-i,11e,13d-e] including older reports of less well-defined MgH-species. The reaction of four equivalents of 2-adamantanone (2-AdO) with [(LMgH)$_4$] **5** mainly yielded the hydromagnesiated complex [(L$_2$Mg$_2$(2-AdOH)$_2$(2-AdO)] **14**, see Figure 5. The complex was structurally characterised, but because the overall quality was poor, only an image is presented in the ESI (see Figure S55). The isolated product contains one hydrometallated ketone per magnesium centre plus one coordinating ketone per Mg$_2$ unit. Repeating the reaction of **5** with six equivalents of 2-adamantanone showed that essentially one product (**14**) was formed, which was isolated in moderate crystallised yield. Complex **14** contains two Mg^{2+} cations that are bridged by two 2-adamantanolate ligands from hydromagnesiation of 2-adamantanone, and further bridged by a κ^2-P,N phosphinoamide ligand. In addition, one terminal κ^1-N phosphinoamide coordinates to one Mg centre and the other Mg centre is coordinated by one neutral 2-adamantanone molecule. In deuterated benzene solution at room temperature, two very broad resonances (δ 32 and 42 ppm) are found in the ^{31}P NMR spectrum of **14** for the two phosphinoamide ligands. At elevated temperatures, these merge to one broad resonance (δ 37.8 ppm at 65°C) and, accordingly, one septet and one doublet are found for the isopropyl groups of the phosphinoamide ligands in the ^{1}H NMR spectrum of **14** at this temperature (see Figure S45), showing fluxional ligand exchange processes under these conditions.

Catalytic Reactivity

Considering the recent success of employing alkaline earth metal hydride complexes as (pre-) catalysts for the hydroboration or hydrosilylation of unsaturated molecules,[10] we wanted to investigate the applicability of complex [(LMgH)$_4$] **5** in similar catalytic conversions. We reasoned that complexes such as **5**, stabilised by a ligand that favours bridging and terminal coordination modes, can deliver open and reactive "LMgH" fragments and potentially act as a highly active (pre-) catalyst for these reactions.

Hydroboration and hydrosilylation of ketones

Since Mg-catalysed hydroborations of aldehydes and ketones with pinacolborane (HBPin) have previously been reported,[10,11d,21] and considering the rapid hydromagnesiation of 2-adamantanone (2-AdO) with **5** to yield **14**, we chose 2-adamantanone and benzophenone as simple and symmetric substrates, because various side-reactions (enolisation and deprotonation, aldolcondensation) are unlikely or impossible, and to keep the identification of products and intermediates simple for this study. Remarkably, we found that reactions of either ketone with 1.2 equivalents of HBPin in C$_6$D$_6$

at room temperature were complete in under 7 minutes after addition of the magnesium hydride cluster **5** (0.5 mol-% of tetramer, 2.0 mol-% Mg). The catalyst loading for reactions of HBPin with 2-AdO could even be reduced to 0.05 mol-% (0.2 mol-% Mg) without suffering any loss of activity, while the hydroboration yield for Ph_2CO dropped slightly to 88% over 15 minutes when the catalyst loading was decreased to 0.05 mol-% (see Table 1, entries 1-3). These two cases correspond to turnover frequencies (TOFs) of $> 4,243$ h^{-1} and $1,760$ h^{-1} per Mg centre, respectively (or $> 16,970$ h^{-1} and $7,040$ h^{-} per molecule **5**), which is remarkable even for transition metal catalysed hydroborations of ketones.[10d] We also tested derivatives of **5** described above. The PMDETA adduct $[(L_2MgH_2Mg(PMDETA)]$ **8** performed as well as **5** for the hydroboration of 2-adamantanone, entry 4, with rapid and complete conversion at room temperature at low catalyst loading despite only having two Mg and hydride centres (TOF: $> 8,486$ h^{-1} per Mg or $> 16,970$ h^{-1} per molecule). This suggests that the possible lower (pre-) catalyst loading limit of **5** or **8** for this specific reaction could even be further reduced, though it becomes increasingly difficult to accurately perform this with small scale reactions and avoid partial compound decomposition. The performance of the phosphinoamide/phosphazide complex $[L_2L'_2Mg_4H_4]$ **9** on the other hand is significantly poorer. 50% conversion was observed after 60 min, 84% conversion after 130 minutes, entry 5, and this system was not further explored. We also tested the homoleptic phosphinoamide complex $[(L_2Mg)_2]$ **1**, vide infra for the discussion, and found that it performed equally well as our best results, entry 6.

please insert Table 1 here

After successful hydroboration, the ^1H NMR spectra of the reaction mixtures showed new resonances at *ca.* 4.44 ppm (2-AdO) or 6.44 ppm (Ph_2CO), respectively, consistent with the presence of a proton on the former carbonyl carbon atom. Singlets at 1.08 ppm (2-AdO) or 0.98 ppm (Ph_2CO), which integrated to 12 H and were slightly shifted in comparison to the HBPin starting material, were also observed and assigned to the twelve methyl protons of the resulting borate esters, (2-Ad(H)O)BPin or ($Ph_2C(H)O$)BPin. The presence of these products was further confirmed by ^{11}B NMR spectroscopy.[12d,22]

Encouraged by these promising results, we investigated catalytic reductions of these ketones by a silane as the hydride source.[23] To the best of our knowledge, only one example of a magnesium-catalysed hydrosilylation has been reported to date, which is the 1,4-addition of Ph_2SiH_2 to α,β-unsaturated esters in the presence of a sterically demanding magnesium hydridoborate.[24] Thus, we attempted the hydrosilylation of our previous two substrates with $PhSiH_3$ in varying stoichiometries in the presence of catalytic amounts of $[(LMgH)_4]$ **5**. Initial

studies revealed that treatment of benzophenone with phenylsilane in C_6D_6 at 70°C with 1.5 mol-% of compound **5** produces the dialkoxysilane, $Ph(H)Si(OCHPh_2)_2$, as the major product, which was also observed for hydrosilylations of ketones with a calcium hydride catalyst.[13d] The silane/ketone ratio was therefore chosen to be approx. 1:2 for all future reactions (Table 1, entries 7-10). After 24 hours at room temperature, only very small amounts of the dialkoxysilane were present as judged by ^1H NMR spectroscopy. The spectrum mainly showed unreacted $PhSiH_3$ and Ph_2CO. Heating accelerated the hydrosilylation significantly, after 22h at 50°C more than 50% of the ketone had been transformed into the alkoxide. Increasing the temperature to 70°C produced 73% conversion after 24 hours and 93% conversion after 50 hours (Table 1, entry 8). On the other hand, hydrosilylation of 2-adamantanone with $PhSiH_3$ proceeded much more rapidly than the hydrosilylation of benzophenone under similar conditions. After 15 min at 70°C with 1.5 mol-% of **5**, more than 99% of 2-AdO had been transformed into 2-adamantanolate (Table 1, entry 7) and the same could be achieved using complex **8** (entry 9). Here, the product ratios were approximately 70% $R'_2Si(H)Ph$ (R' = 2-adamantanolate) versus 30% R'_3SiPh using complex **5** (entry 7) and a ratio of *ca.* 88:12% for the respective reaction with catalyst **8** (entry 9). This ratio changes quickly towards R'_3SiPh with continued heating. Because no further ketone conversion was possible, this points to a dismutation reaction from $R'_2Si(H)Ph$ to R'_3SiPh. The preferred product in these latter conversions (R'_3SiPh) is the trialkoxysilane, as opposed to the dialkoxysilane when benzophenone is used as the ketone. Catalytic reduction of 2-adamantanone was not observed with **5** and diphenylsilane as the hydride source (entry 11). Once again, investigating complex $[(L_2Mg)_2]$ **1** in this reaction, entry 10, shows that it performs as well as the best magnesium hydride compounds tested by us. Complexes **1** and **8** achieved a turnover frequency of 132 h^{-1} per Mg centre, or 264 h^{-1} per molecule.

We noticed throughout experiments involving magnesium hydride **5**, that all characteristic NMR spectroscopic resonances of the magnesium hydride compound had disappeared during or by the end of the catalysis, especially when the samples were heated. Instead, these provided new sharp ^1H NMR resonances assigned to the compounds LBPin **15** ($^{31}P\{^1H\}$ NMR: 58.8 ppm, $^{11}B\{^1H\}$ NMR: 25.1 ppm), or $PhSiH_2L$ **7** ($^{31}P\{^1H\}$ NMR: 61.7 ppm), respectively, as the L-containing products. Merely in the fastest hydroboration reactions with catalyst loadings ≥ 2.5 mol-% was cluster **5** still identified a few minutes after full conversion of the substrate into the alkoxide, though in much lower concentrations than at the start. Under catalytic conditions, complex **5** is transformed to the phosphinoamide-containing borane, LBPin **15**, or silane, $PhSiH_2L$ **7**, and presumambly, soluble and catalytically active magnesium hydride species. The presence of low concentrations of **5** in isolated cases where high catalyst loadings are used can be explained by the fast conversion and the fact that not all of compound **5** needs to act as the (pre-) catalyst.

Hydroboration and hydrosilylation of pyridine

In light of the successful stoichiometric reactivity of [(LMgH)$_4$] **5** with pyridines (Scheme 3) and previously reported magnesium hydride complexes,[5c,7a,d,8b,12] we studied the respective catalytic hydroboration and hydrosilylation of pyridine using **5**. Equimolar amounts of pyridine and HBPin were treated with 2.5 mol-% of **5** (10 mol-% Mg) in deuterated benzene and complex **5** is, as expected, immediately consumed. The catalytic hydroboration of pyridine is possible at elevated temperatures, though is slow and incomplete. After 48 hours at 70°C, 32% of total dihydropyridide products, PinBdhp (dhp = dihydropyridide) have been formed, with 87.5% being the 1,4-dihydropyridide (1,4-dhp) versus 12.5% of 1,2-dihydropyridide (1,2-dhp). Modification of the reaction temperature to 80°C gives 35% conversion after 24 hours (89% 1,4-dhp : 11% 1,2-dhp) and 58% conversion after 96 hours (93% 1,4-dhp : 7% 1,2-dhp). Increasing the catalyst loading to 5 mol-% of **5** results in slightly higher yields of hydroborated pyridine (53.5% after 37 hours at 70°C). Full conversion of pyridine into PinBdhp is not achieved because pinacolborane slowly decomposes to B$_2$(Pin)$_3$ during the course of this reaction,[11d,12] which could be isolated from one of the catalysis experiments as a crystalline product. In addition, the ^{11}B NMR spectra taken after heating the reaction mixture at 70 or 80°C for at least 15 hours show a broad peak at *ca.* 22 ppm that was attributed to B$_2$Pin$_3$ and a quartet at -11 ppm for py·BH$_3$. Both of these peaks increase in intensity with prolonged heating of the samples, indicating the continued decomposition of HBPin under the employed conditions.

Similarly, catalytic hydrosilylation of pyridine with 2.5 mol-% of **5** is possible, but is slow and does not go to completion. Upon addition of **5** to a mixture of pyridine and PhSiH$_3$ at room temperature, [LMg(py)$_2$(1,2-dhp)] **11**, is formed immediately, which is also the kinetic product in stoichiometric reactions of **5** with excess pyridine (vide supra). More forcing conditions are needed to achieve any catalytic conversion. After 48 hours at 80°C, only *ca.* 52% of pyridine has been transformed into a dihydropyridide species with [(1,4-dhp)$_2$PhSiH] being the main product, though the exact product distribution is unknown, as [(1,4-dhp)$_2$PhSiH], [(1,2-dhp)$_2$PhSiH] and [(1,4-dhp)(1,2-dhp)PhSiH] are all formed alongside each other showing overlapping ^{1}H NMR resonances. The phosphinoamide-containing component at the end of the reaction is yet again PhSiH$_2$L **7**.

Mechanistic considerations

The proposed mechanism for the catalytic hydroboration and hydrosilylation of ketones for several previously reported systems often follows a general insertion/σ-bond metathesis cycle,[10,23] although other possibilities remain. In order to shed light on the mechanism using the

phosphinoamide magnesium complexes reported herein (**1**, **5**, and **8**), and the quest to identify the possible active species, we performed some stoichiometric reactions to assess the feasibility of individual steps for this mechanism. Complex **5** reacts rapidly with 2-adamantanone to give the insertion product [(L$_2$Mg$_2$(2-AdOH)$_2$(2-AdO)] **14** as previously stated. Similarly, **5** reacts readily with benzophenone in a hydromagnesiation reaction, as judged by in situ ^{1}H NMR spectroscopic data. No well-defined products could be isolated from the latter reaction mixtures, and the formed complexes likely depend on the Mg:Ph$_2$CO ratio including coordination of unreacted benzophenone. These findings support that C=O insertion into the MgH moiety could be the first step in the catalytic cycle.

The reaction of [(LMgH)$_4$] **5** with HBpin alone in deuterated benzene is very slow, and the starting materials remain largely unreacted for a few days, though some LBpin **15** is produced eventually, and later other compounds including LH. Although a large excess of HBpin is typically used in catalytic studies, reactions of [(LMgH)$_4$] **5** with unsaturated substrates such as ketones were found to be very rapid in comparison. The treatment of complex [(LMgH)$_4$] **5** with PhSiH$_3$ in deuterated benzene at elevated temperature in the absence of donor molecules or substrates showed no reaction. Complex **5** alone is furthermore stable towards heat in the solid state, in non-coordinating solvents and towards excess phosphinoamine proligand LH; *i.e.* no [(L$_2$Mg)$_2$] **1** is formed, even at elevated temperatures to our surprise. Furthermore, it does not appear to react at room temperature with unsaturated organic molecules lacking good donor atoms. Consequently, the ketone addition must play a role in removing L from magnesium and in the formation of **15** and **7**, respectively. Hydromagnesiation of LMgH units with ketones forms hard alcoholate ligands that bind strongly to hard Mg^{2+} ions, likely labilising the Mg-phosphinoamide bonds and inducing ligand exchange processes. Additionally, the excess of unreacted ketone can act as additional donor molecules and presumably induce equilibria similar to those found when [(LMgH)$_4$] **5** is dissolved in THF, see the previous section and Figure S21-22. This is also illustrated by ligand rearrangements in the molecular structure of [(L$_2$MgH$_2$Mg(PMDETA)] **8** compared with compound **5**. Given the highly symmetrical solution NMR spectra found for [(L$_2$Mg)$_2$] **1** that suggest flexible solution dynamics, vide supra, we also reacted this compound with four equivalents of HBPin and found that it reacted rapidly at room temperature to form LBPin **15** (Figure S49-51). By implication, freshly generated "MgH$_2$" may be the by-product though this could not be spectroscopically verified. A broad resonance at *ca.* 1.5 ppm in the ^{1}H NMR spectrum (Figure S49) could be attributed to a new reactive species. The fast ligand-loss from **1** when treated with HBPin, especially compared to the very slow reaction of **5** with HBPin, and the fact that the phosphinoamide ligands in our catalytic studies of **5** and **8** eventually end up in **7** or **15**, made us test [(L$_2$Mg)$_2$] **1** as a catalyst which yielded the equally best results.

Next, we treated complex [(L$_2$Mg$_2$(2-AdOH)$_2$(2-AdO)] **14** with 2.5 equivalents of HBPin or PhSiH$_3$ to investigate whether our ketone insertion product can easily undergo σ-bond metathesis with each hydride source. Compound **14** and HBPin react instantaneously to give the borate ester 2-Ad(H)OBPin and LBPin **15** and the resonances of the starting materials have completely vanished from multinuclear NMR spectra of the reaction mixtures. The fate of the Mg moiety is unknown and NMR spectroscopic experiments suggest that the magnesium hydride complex **5** is not reformed in detectable quantities after release of the hydroborated product (vide supra). A reaction of complex **14** with PhSiH$_3$ at room temperature was not observed. However, within several minutes at 70°C, complex **14** is consumed, alkoxysilanes form, and the phosphinoamide groups are present as PhSiH$_2$L **7**. The rapid formation of Ad(H)OBPin from **14** at room temperature when treated with pinacolborane, and the comparable reaction of **14** with phenylsilane at elevated temperature gives credibility to a general insertion/σ-bond metathesis mechanism. Importantly, the conditions and reaction rates of the σ-bond metathesis of the alcoholate complex **14** with the hydride source (HBpin or PhSiH$_3$) correlate with the best observed catalysis conditions of the respective reaction and thus may correspond to the rate determining step in the mechanism.

The stoichiometric chemistry reported in the previous sections already shows several possibilities such as donor-induced (THF, PMDETA) rearrangements and redistributions. Catalytic reactions with an excess of unsaturated organic substrates (*e.g.* ketones, pyridines) possessing good donor atoms (O, N), likely induce a series of equilibria to generate compounds of the type "L^{gen}Mg(Do)$_n$H" **A**, see Scheme 4, equation (1), that could be active catalytic species. The ligand, L^{gen-}, can be any general monoanionic ligand that is likely to exist in these reaction mixtures such as L$^-$, R$_2$CHO$^-$ (from direct hydromagnesiations) and/or H$^-$. The donor species (Do) can be neutral donor groups such as R$_3$P (from L$^-$), the large excess of substrates such as ketones (or pyridines) under catalytic regimes, and even the generated reaction products (*e.g.* PhSiH(OR)$_2$). Depending on the donor properties and concentrations, several aggregates can be present in solution. As previously observed for example by dissolving [(LMgH)$_4$] **5** in THF, Schlenk-like equilibria with numerous redistribution possibilities (formulated in a simplified form as equation (2)), could rapidly form donor-stabilised and soluble MgH$_2$ complexes such as **B**. That these equilibria are important may be supported by the fact that both [(L$_2$Mg)$_2$] **1** and [(L$_2$MgH$_2$Mg(PMDETA)] **8** performed equally well as [(LMgH)$_4$] **5** in catalytic hydroborations and hydrosilylations of ketones. Complex **8** is a donor adduct of **5** and appears to have the potentially active complex [(PMDETA)MgH$_2$] preorganised in its molecular structure (see Figure 3): only a long Mg-P coordination bond and two bridging hydride-Mg contacts have to be invested to release an L$_2$Mg fragment and form [(PMDETA)MgH$_2$], which may be aided by additional present donor molecules. The more

sterically shielded and chemically robust complex [$L_2L'_2Mg_4H_4$] **9** was a significantly less effective (pre-) catalyst for comparison.

All these considerations lead to a range of Mg complex possibilities with various donors and monoanionic ligands, L^{gen}. Because the phosphinoamide moiety L^- is bound to boron or silicon as **7** or **15** at the end of the reaction and [(LMgH)$_4$] **5** does not rapidly react with the stoichiometric hydride sources EH (E = BPin, PhSiH$_2$), a more active magnesium complex, simplified as [$L^{gen}Mg(Do)_nL$], likely reacts with EH to form a magnesium hydride complex **C** and the final phosphinoamide species **7** or **15**, respectively (see scheme 4, A, equation (3)). This key step is further supported by the rapid reaction of [(L$_2$Mg)$_2$] **1** with HBpin to generate **15** and likely an active "MgH$_2$" complex (*e.g.* **B**) in a similar fashion to equation (3). Therefore, the catalytic properties of [(L$_2$Mg)$_2$] **1** may be approaching those of freshly generated and solubilised "MgH$_2$". Ligand exchange reactions of species such as **A**-**C** and coordination and aggregation processes would further allow access to a large number of possible active complexes present in actual reaction mixtures of catalytic preparations.

please insert Scheme 4 (A + B) here

These active catalysts likely undergo the hydrometallation/σ-bond metathesis cycle previously proposed for other systems (see scheme 4, B), which has support from our stoichiometric investigations: both the hydrometallation and the σ-bond metathesis steps are possible and show the appropriate rates under the respective conditions. At this stage, we cannot discount other mechanistic possibilities though, and evidence for slightly different mechanistic pathways have been forthcoming for related zinc and calcium systems. In comparison, it has been found that hydrosilylations of carbonyl complexes can already be successfully catalysed at room temperature for a series of heteroleptic, ligand-stabilised zinc hydride complexes.[25,26] For one of these examples, an associative mechanism with a silane/zinc hydride adduct as the active species has been proposed.[26e] For β-diketiminato calcium hydride catalysed ketone hydrosilylations, a concerted mechanism via a hypercoordinated hydridosilicate species was suggested.[10,13d] Also, a simple hydroboration or hydrosilylation mechanism on a Lewis acid activated ketone cannot be completely ruled out.

Conclusions

We have presented the synthesis and interconversion of a series of magnesium(II) complexes bearing the sterically demanding phosphinoamide ligand Ph$_2$PNDip$^-$, L$^-$. Reactions of LH with

Mg(nBu)$_2$ afforded the complexes [(L$_2$Mg)$_2$] **1** and [L$_3$Mg$_2$(nBu)] **2**, and reactions with added PhSiH$_3$ at elevated temperatures yielded the hydride complexes [{L$_2$Mg$_2$(nBu)H}$_2$] **4** and [(LMgH)$_4$] **5**, as well as the hexamer [(LMgH)$_6$] **6**. Complex [(LMgH)$_4$] **5** was studied for its stoichiometric reactivity and afforded the MgH-complex derivatives [(L$_2$MgH$_2$Mg(PMDETA)] **8** and [L$_2$L'$_2$Mg$_4$H$_4$] **9** (L' = DipNP(N$_3$Ad)Ph$_2$), the latter obtained by AdN$_3$ transformation of two phosphinoamides with AdN$_3$ into phosphazide ligands. Several complexes have an overall ring shape such as **4**, **5**, **6**, and **9**, and the solid state structures are dominated by bridging as well as terminal phosphinoamide ligands. Both head/head and head/tail phosphinoamide orientations have been found in aggregated complexes. Solution studies generally revealed symmetric geometries indicating flexible phosphinoamide coordination, with the exception of the n-butyl-bridged complexes [L$_3$Mg$_2$(nBu)] **2** and [{L$_2$Mg$_2$(nBu)H}$_2$] **4** which show retention of the overall solid state geometries and partially suppressed ligand exchange processes.

Further stoichiometric reactivity of [(LMgH)$_4$] **5** with pyridines yielded an example of selective generation of a 1,2 versus a 1,4 hydromagnesiation product with pyridine. The complexes [L$_2$Mg(dmap)$_2$] **10**, [LMg(py)$_2$(1,2-dhp)] **11** (1,2-dhp = 1,2-dihydropyridide), [LMg(dmap)$_2$(1,2-dadhp)] **12** (1,2-dadhp = 4-dimethylamino-1,2-dihydropyridide), and [LMg(py)$_2$(1,4-dhp)] **13** are described. [(LMgH)$_4$] **5** was found to rapidly hydromagnesiate ketones and afforded, for example, the alcoholate complex [(L$_2$Mg$_2$(2-AdOH)$_2$(2-AdO)] **14** (2-AdO = 2-adamantanone).

Extending the study to catalytic transformations revealed that complexes [(L$_2$Mg)$_2$] **1**, [(LMgH)$_4$] **5** and [(L$_2$MgH$_2$Mg(PMDETA)] **8** are highly active precatalysts for the hydroboration of ketones at room temperature with very low catalyst loadings. Respective ketone hydrosilylations can also be achieved rapidly at elevated temperatures. The sterically more shielded complex [L$_2$L'$_2$Mg$_4$H$_4$] **9** shows a much lower stoichiometric reactivity and was a poorer catalyst. For example, the reaction of pinacolborane with 2-adamantanone catalysed by complexes **1** and **8** is rapid at room temperature with a turnover frequency of > 8,485 h^{-1} per Mg centre (> 16,970 h^{-1} per molecule). The hydrosilylation of 2-adamantanone with phenylsilane catalysed by complexes **1** and **8** proceeds in about 15 minutes at 70°C, with a turnover frequency of 132 h^{-1}. Also, catalytic hydroboration and hydrosilylation of pyridine was possible, but required elevated temperatures, long reaction times, and only provided partial conversion. Our studies suggest that complexes **1**, **5** and **8** are precursors to the active catalysts in these systems and likely generate highly active MgH-complexes *in-situ*. The results are supportive of an insertion/σ-bond metathesis-type mechanism for the hydroelementation of ketones with the σ-bond metathesis step likely being rate-determining. Catalytic reactions of [(L$_2$Mg)$_2$] **1** with hydride sources such as HBPin may represent those of freshly generated, highly active and soluble, parent "MgH$_2$", and will likely find further applications in synthesis and catalysis.

Acknowledgements

References

[1]   a) H. Kohlmann, *Metal Hydrides*, Encyclopedia of Physical Sciences and Technology (ed. R. A. Meyers), 3rd edition, Academic Press, **2002**, *9*, 441–458; b) W. Grochala, P. P. Edwards, *Chem. Rev.* **2004**, *104*, 1283-1315; c) S. Aldridge, A. J. Downs, *Chem. Rev.,* **2001**, *101*, 3305–3365; d) H. D. Kaesz, R. B. Saillant, *Chem. Rev.* **1972**, *72*, 231–281; e) W. M. Mueller, J. P. Blackledge, G. G. Libowitz (eds), *Metal hydrides*, Academic Press, New York, 1968.

[2]   S. Harder, *Chem. Commun.* **2012**, *48*, 11165–11177.

[3]   L. Fohlmeister, A. Stasch, *Aust. J. Chem.* **2015**, *68*, 1190–1201.

[4]   M. S. Holzwarth, B. Plietker, *ChemCatChem* **2013**, *5*, 1650–1679.

[5]   a) R. Lalrempuia, C. E. Kefalidis, S. J. Bonyhady, B. Schwarze, L. Maron, A. Stasch and C. Jones, *J. Am. Chem. Soc.* **2015**, *137*, 8944−8947; b) M. Arrowsmith, B. Maitland, G. Kociok-Köhn, A. Stasch, C. Jones, M. S. Hill, *Inorg. Chem.* **2014**, *53*, 10543−10552; c) S. Harder, J. Spielmann, J. Intemann, *Dalton Trans.* **2014**, *43*, 14284–14290; d) J. Intemann, J. Spielmann, P. Sirsch, S. Harder, *Chem. Eur. J.* **2013**, *19*, 8478–8489; e) S. Harder, J. Spielmann, J. Intemann, H. Bandmann, *Angew. Chem. Int. Ed.* **2011**, *50*, 4156–4160; f) S. J. Bonyhady, D. Collis, G. Frenking, N. Holzmann, C. Jones, A. Stasch, *Nat. Chem.* **2010**, *2*, 865–869; g) S. J. Bonyhady, C. Jones, S. Nembenna, A. Stasch, A. J. Edwards, G. J. McIntyre, *Chem. Eur. J.* **2010**, *16*, 938–955; h) S. P. Green, C. Jones, A. Stasch, *Angew. Chem. Int. Ed.* **2008**, *47*, 9079–9083.

[6]   a) D. J. Liptrot, M. S. Hill, M. F. Mahon, *Chem. Eur. J.* **2014**, *20*, 9871–9874; b) D. V. Graham, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, *Acta Cryst. Sect. C* **2006**, *62*, m366–m368; c) P. C. Andrikopoulos, D. R. Armstrong, A. R. Kennedy, R .E. Mulvey, C. T. O'Hara, R. B. Rowlings, *Eur. J. Inorg. Chem.* **2003**, 3354–3362; d) K. W. Henderson, A. R. Kennedy, C. T. O'Hara, R. E. Mulvey, R. B. Rowlings, *Chem. Commun.* **2002**, 376–377.

[7]   a) S. Schnitzler, T. P. Spaniol, L. Maron, J. Okuda, *Chem. Eur. J.* **2015**, *21*, 11330–11334; b) D. Martin, K. Beckerle, S. Schnitzler, T. P. Spaniol, L. Maron, J. Okuda,

Angew. Chem. Int. Ed. **2015**, *54*, 4115–4118; c) R. Lalrempuia, A. Stasch, C. Jones, *Chem. Asian J.* **2015**, *10*, 447–454; d) H. Xie, X. Hua, B. Liu, C. Wu, D. Cui, *J. Organomet. Chem.* **2015**, *798*, 335–340; e) M. Arrowsmith, M. S. Hill, D. J. MacDougall, M. F. Mahon, *Angew. Chem. Int. Ed.* **2009**, *48*, 4013–4016.

[8]   Selected references for the chemistry of less well-defined MgH complexes: a) A. B. Goel, E. C. Ashby, *J. Organomet. Chem.* **1981**, *214*, C1–C6; b) E. C. Ashby, A. B. Goel, *J. Organomet. Chem.* **1981**, *204*, 139–145; c) E. C. Ashby, A. B. Goel, R. N. DePriest, *J. Am. Chem. Soc.* **1980**, *102*, 1119–1180; d) E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1979**, *18*, 1306–1311; e) E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1978**, *17*, 322–326; f) E. C. Ashby, J. J. Lin, A. B. Goel, *J. Org. Chem.* **1978**, *43*, 1564–1566; g) E. C. Ashby, J. J. Lin, A. B. Goel, *J. Org. Chem.* **1978**, *43*, 1560–1563; h) E. C. Ashby, J. J. Lin, A. B. Goel, *J. Org. Chem.* **1978**, *43*, 1557–1560; i) E. C. Ashby, A. B. Goel, J. J. Lin, *Tetrahedron Lett.* **1977**, *18*, 3133–3136; j) E. C. Ashby, A. B. Goel, *J. Org. Chem.* **1977**, *42*, 3480–3485; k) E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1977**, *16*, 2941–2944; l) E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1977**, *16*, 1863; m) E. C. Ashby, A. B. Goel, *Inorg. Chem.* **1977**, *16*, 1441–1445; m) E. C. Ashby, A. B. Goel, *J. Chem. Soc., Chem. Commun.* **1977**, 169; n) E. C. Ashby, R. Arnott, S. Srivatsava, *Inorg. Chem.* **1975**, *14*, 2422–2426; n) R. G. Beach, E. C. Ashby, *Inorg. Chem.* **1971**, *10*, 906–910.

[9]   a) V. Leich, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2016**, *55*, 4794–4797; b) V. Leich, T. P. Spaniol, J. Okuda, *Inorg. Chem.* **2015**, *54*, 4927–4933; c) P. Jochmann, J. P. Davin, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2012**, *51*, 4452–4455; d) S. Harder, J. Brettar, *Angew. Chem. Int. Ed.* **2006**, *45*, 3474–3478.

[10]   For recent reviews see: a) M. Arrowsmith, *Encycl. Inorg. Bioinorg. Chem.,* 2016, DOI: 10.1002/9781119951438.eibc2299; b) M. S. Hill, D. J. Liptrot, C. Weetman, *Chem. Soc. Rev.* **2016**, *45*, 972–988; c) R. Rochat, M. J. Lopez, H. Tsurugi, K. Mashima, *ChemCatChem* **2016**, *8*, 10–20; d) C. C. Chong, R. Kinjo, *ACS Catal.* **2015**, *5*, 3238−3259; e) K. Revunova, G. I. Nikonov, *Dalton Trans.* **2015**, *44*, 840–866; f) M. R. Crimmin, M. S. Hill, *Top. Organomet. Chem.* **2013**, *45*, 191-241; g) M. Arrowsmith, M. S. Hill, in *Comprehensive Inorganic Chemistry II, Alkaline Earth Chemistry: Applications in Catalysis* (eds J.Reedijk, K. Poeppelmeier)*,* Vol. 1, 1189-1216, Elsevier, Waltham, **2013**; (h) S. Harder, *Chem. Rev.* **2010**, *110*, 3852–3876; i) A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. A. Procopiou, *Proc. R. Soc. A* **2010**, *466*, 927–963.

[11]   a) C. Weetman, M. D. Anker, M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, D. J. Liptrot, M. F. Mahon, *Chem. Sci.* **2016**, *7*, 628; b) C. Weetman, M. S. Hill, M. F. Mahon, *Chem. Commun.* **2015**, *51*, 14477–14480; c) M. D. Anker, M. S. Hill, J. P. Lowe, M. F. Mahon,

Angew. Chem. Int. Ed. **2015**, *54*, 10009–10011; d) M. Arrowsmith, M. S. Hill, G. Kociok-Köhn, *Chem. Eur. J.* **2013**, *19*, 2776–2783; e) M. Arrowsmith, T. J. Hadlington, M. S. Hill, G. Kociok-Köhn, *Chem. Commun.* **2012**, *48*, 4567–4569; f) S. J. Bonyhady, S. P. Green, C. Jones, S. Nembenna, A. Stasch, *Angew. Chem. Int. Ed.* **2009**, *48*, 2973–2977.

[12]   a) C. Weetman, M. S. Hill, M. F. Mahon, *Polyhedron* **2016**, *103*, 115–120; b) J. Intemann, M. Lutz, S. Harder, *Organometallics* **2014**, *33*, 5722−5729; c) M. Arrowsmith, M.S. Hill, T. Hadlington, G. Kociok-Köhn, C. Weetman, *Organometallics* **2011**, *30*, 5556–5559; d) M. S. Hill, G. Kociok-Köhn, D. J. MacDougall, M. F. Mahon, C. Weetman, *Dalton Trans.* **2011**, *40*, 12500–12509; e) M. S. Hill, D. J. MacDougall, M. F. Mahon, *Dalton Trans.* **2010**, *39*, 11129–11131.

[13]   a) J. Intemann, H. Bauer, J. Pahl, L. Maron, S. Harder, *Chem. Eur. J.* **2015**, *21*, 11452–11461; b) S. Harder, J. Spielmann, *J. Organomet. Chem.* **2012**, *698*, 7–14; c) J. Spielmann, F. Buch, S. Harder, *Angew. Chem. Int. Ed.* **2008**, *47*, 9434–9438; d) J. Spielmann, S. Harder, *Eur. J. Inorg. Chem.* **2008**, 1480–1486; e) J. Spielmann, S. Harder, *Chem. Eur. J.* **2007**, *13*, 8928–8938.

[14]   a) A. Stasch, *Dalton Trans.* **2014**, *43*, 7078–7086; b) A. Stasch, *Angew. Chem. Int. Ed.* **2012**, *51*, 1930–1933.

[15]   For reviews see: a) Z. Fei, P. Dyson, *Coord. Chem. Rev.* **2005**, 249, 2056–2074; b) M. Alajarin, C. Lopez-Leonardo, P. Llamas-Lorente, *Top. Curr. Chem.* **2005**, *250*, 77–106.

[16]   a) A. Stasch, *Chem. Commun.* **2015**, *51*, 5056–5058; b) A. Stasch, *Angew. Chem. Int. Ed.* **2014**, *53*, 1338–1341.

[17]   A. R. Kennedy, R. E. Mulvey, S. D. Robertson, *Dalton Trans.* **2010**, *39*, 9091–9099.

[18]   For related phosphinoaminosilanes see: a) T. Böttcher, C. Jones, *Dalton Trans.* **2015**, *44*, 14842-14853; b) J. Li, Y. Li, I. Purushothaman, S. De, B. Li, H. Zhu, P. Parameswaran, Q. Ye, W. Liu, *Organometallics* **2015**, *34*, 4209–4217; c) J. Wang, R. Liu, W. Ruan, Y. Li, K. C. Mondal, H. W. Roesky, H. Zhu, *Organometallics* **2014**, *33*, 2696–2703.

[19]   M. W. P. Bebbington, D. Bourissou, *Coord. Chem. Rev.* **2009**, *253*, 1248–1261.

[20]   A. L. Hawley, A. Stasch, *Eur. J. Inorg. Chem.* **2015**, *2015*, 258–270.

[21]   For Mg-catalysed hydroborations of esters see: D. Mukherjee, A. Ellern, A. D. Sadow, *Chem. Sci.* **2015**, *6*, 6901–6907.

[22]   a) H. Braunschweig, F. Guethlein, L. Mailänder, T. B. Marder, *Chem. Eur. J.* **2013**, *19*, 14831–14835; b) T. P. Onak, H. Landesman, R. E. Williams, I. Shapiro, *J. Chem. Phys.* **1959**, *63*, 1533-1535.

[23]   B. Marciniec, *Hydrosilylation: a comprehensive review on recent advances*, Springer, Berlin, 2009.

[24]   N. L. Lampland, A. Pindwal, S. R. Neal, S. Schlauderaff, A. Ellern, A. D. Sadow, *Chem. Sci.* **2015**, *6*, 6901–6907.

[25]   A.-K. Wiegand, A. Rit, J. Okuda, *Coord. Chem. Rev.* **2016**, *314*, 71–82.

[26]   For selected recent examples see: a) W. Sattler, S. Ruccolo, M. R. Chaijan, T. N. Allah, G. Parkin, *Organometallics* **2015**, *34*, 4717–4731; b) Z. Mou, H. Xie, M. Wang, N. Liu, C. Yao, L. Li, J. Liu, S. Li, D. Cui, *Organometallics* **2015**, *34*, 3944–3949; c) A. Rit, A. Zanardi, T. P. Spaniol, L. Maron, J. Okuda, *Angew. Chem. Int. Ed.* **2014**, *53*, 13273–13277; d) P. A. Lummis, M. R. Momeni, M. W. Lui, R. McDonald, M. J. Ferguson, M. Miskolzie, A. Brown, E. Rivard, *Angew. Chem. Int. Ed.* **2014**, *53*, 9347–9351; e) C. Boone, I. Korobkov, G. I. Nikonov, *ACS Catal.* **2013**, *3*, 2336–2340.
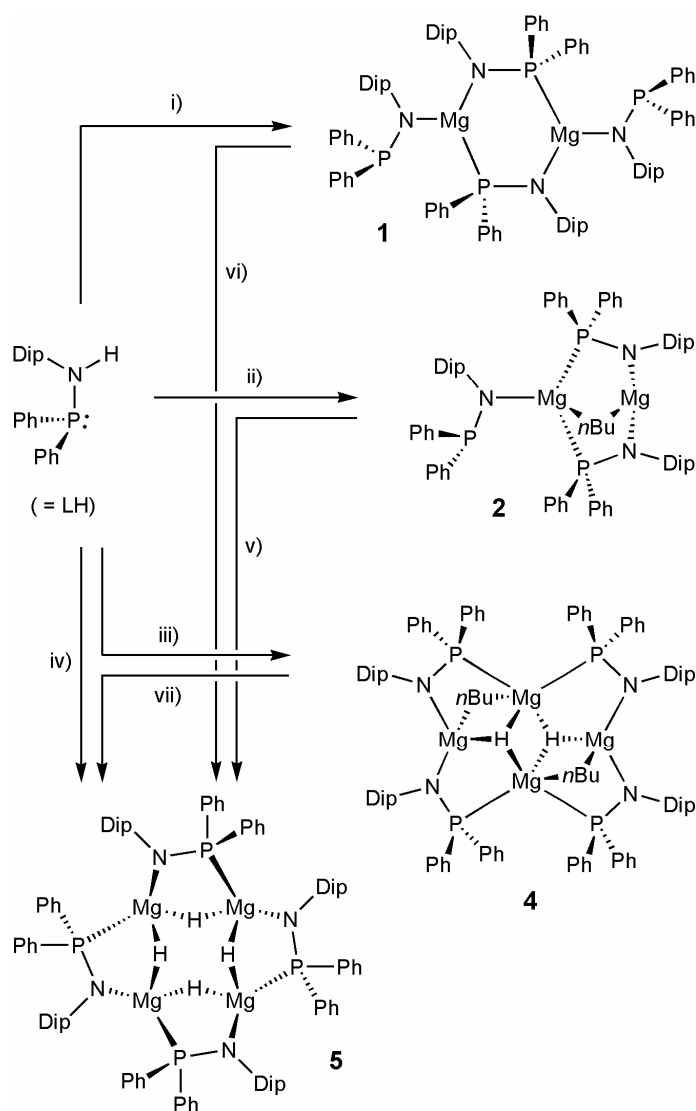
Scheme 1. Synthesis of complexes **1**, **2**, **4** and **5**. i) 0.5 Mg(nBu)$_2$, toluene, r.t.; ii) Mg(nBu)$_2$, toluene, r.t. ; iii) Mg(nBu)$_2$, PhSiH$_3$, n-hexane, 60°C; iv) Mg(nBu)$_2$, PhSiH$_3$, toluene, 70°C; v), vi) and vii) PhSiH$_3$, 60-70°C, benzene or toluene.
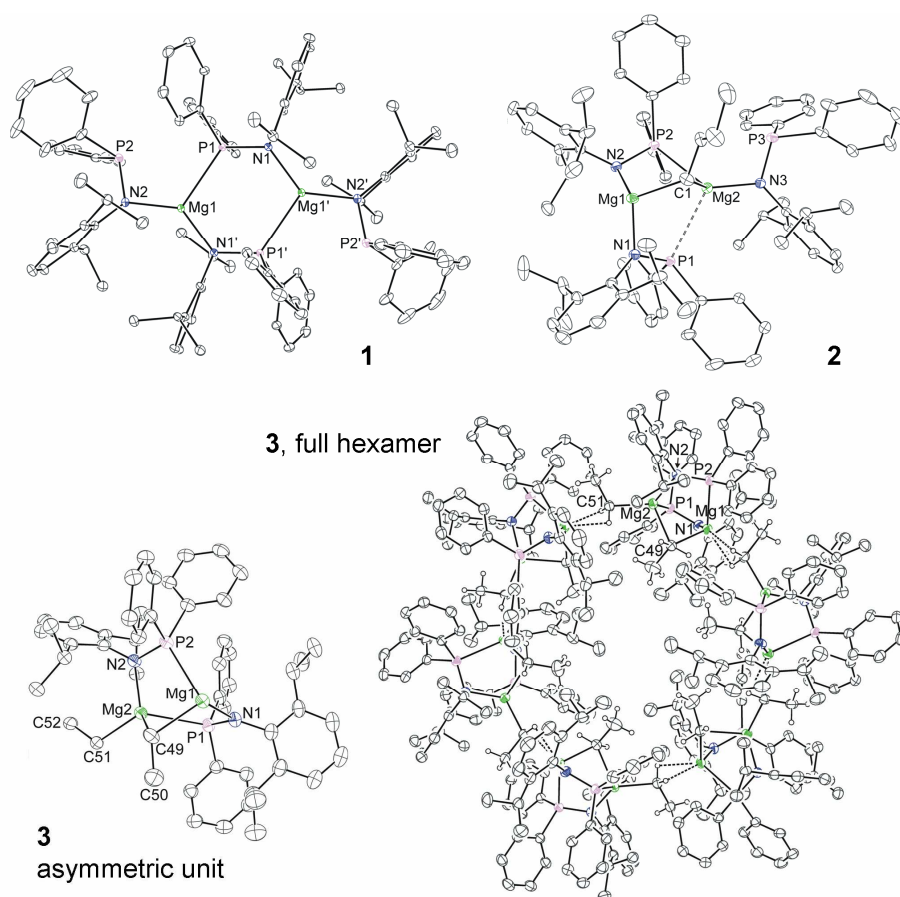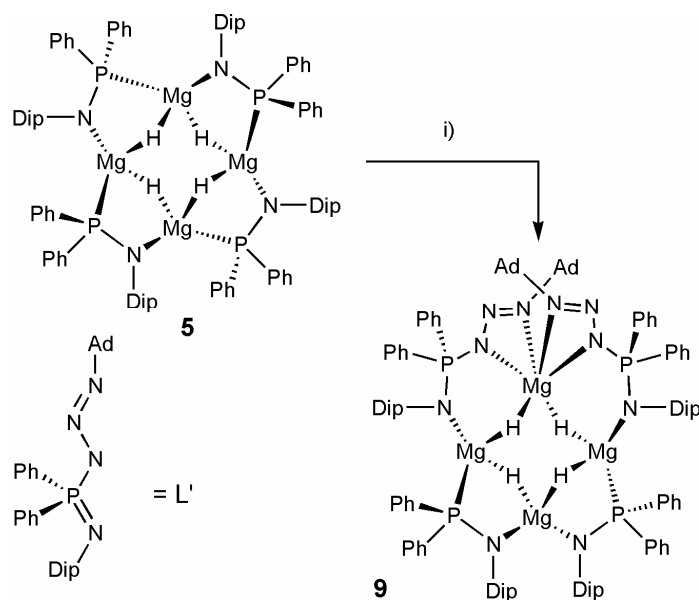
Figure 1. Molecular structures of **1**-**3** (30% thermal ellipsoids). Lattice solvent molecules and hydrogen atoms omitted, except ethyl hydrogens on full molecule **3**. Selected bond lengths [Å] and angles [°]: **1**: P(1)-N(1) 1.6770(12), P(2)-N(2) 1.6904(13), P(1)-Mg(1) 2.6318(7), P(2)-Mg(1) 2.9212(7), N(1)-Mg(1)' 2.0008(12); N(2)-Mg(1)-N(1)' 132.48(5), N(2)-Mg(1)-P(1) 117.77(4), N(1)'-Mg(1)-P(1) 109.68(4). **2**: P(1)-N(1) 1.6618(12), P(2)-N(2) 1.6731(11), P(3)-N(3) 1.6920(12), P(1)-Mg(2) 2.9492(11), P(2)-Mg(2) 2.6910(8), P(3)-Mg(2) 3.0095(10), Mg(2)-N(3) 1.9829(12), Mg(1)-N(1) 1.9938(12), Mg(1)-N(2) 2.0191(12), Mg(1)-C(1) 2.2446(17), Mg(2)-C(1) 2.2583(16); N(3)-Mg(2)-C(1) 122.81(6), N(3)-Mg(2)-P(2) 121.81(4), C(1)-Mg(2)-P(2) 94.77(5), N(3)-Mg(2)-P(1) 120.69(4), C(1)-Mg(2)-P(1) 87.90(5), P(2)-Mg(2)-P(1) 101.30(3), N(1)-Mg(1)-N(2) 125.51(6), N(1)-Mg(1)-C(1) 104.52(6), N(2)-Mg(1)-C(1) 117.26(5). **3**: P(1)-N(1) 1.668(3), P(2)-N(2) 1.648(3), P(1)-Mg(2) 2.7971(15), Mg(1)-P(2) 2.6786(14), Mg(1)-N(1) 2.030(3), Mg(2)-N(2) 2.044(3), Mg(1)-C(49) 2.277(3), Mg(2)-C(49) 2.290(3), Mg(2)-C(51) 2.203(3), C(51)-Mg(1)' 2.400(3); N(1)-Mg(1)-P(2) 113.77(9), N(2)-Mg(2)-C(51) 117.89(12), N(2)-Mg(2)-P(1) 108.61(9), C(51)-Mg(2)-P(1) 121.79(10), Mg(1)-C(49)-Mg(2) 82.07(10).
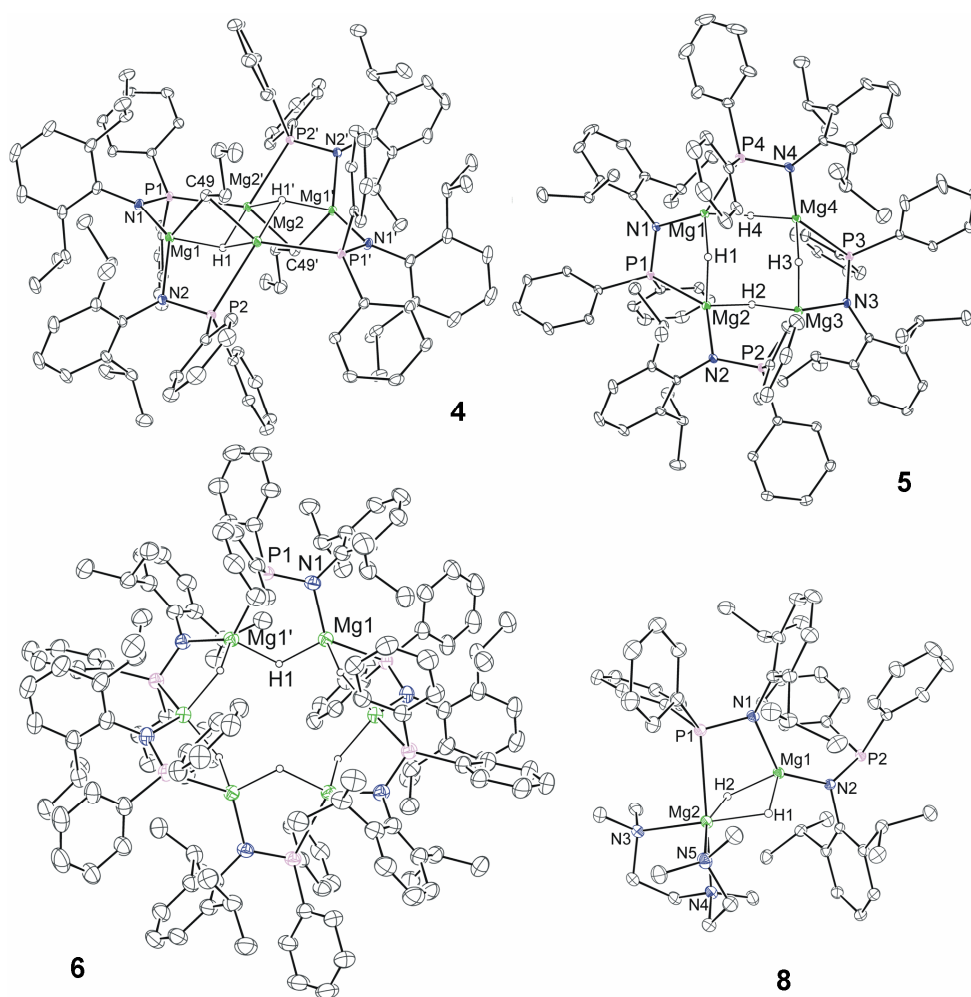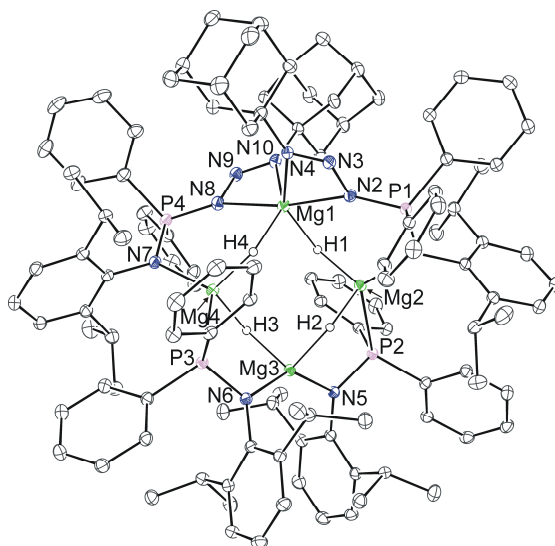
Figure 2. Molecular structures of magnesium hydride species **4-6** and **8** (30% thermal ellipsoids). Lattice solvent molecules and hydrogen atoms omitted, except hydride ligands. Selected bond lengths [Å] and angles [°]: **4**: P(1)-N(1) 1.6621(13), P(2)-N(2) 1.6630(12), P(1)-Mg(2)' 2.6609(7), P(1)-Mg(1) 3.0509(8), Mg(1)-P(2) 2.9555(7), P(2)-Mg(2) 2.6841(9), Mg(2)-P(1)' 2.6609(7), Mg(1)-N(1) 2.0155(13), Mg(1)-N(2) 2.0275(13), Mg(1)-C(49) 2.2668(17), Mg(2)-C(49) 2.2500(16), Mg(2)-C(50) 2.7718(19), Mg(1)-H(1) 1.96(2), Mg(2)-H(1) 1.98(2), Mg(2)'-H(1) 1.92(2); N(1)-Mg(1)-N(2) 132.79(5), N(1)-Mg(1)-C(49) 112.74(6), N(2)-Mg(1)-C(49) 111.70(6), N(1)-Mg(1)-H(1) 99.8(6), N(2)-Mg(1)-H(1) 95.8(6), C(49)-Mg(1)-H(1) 89.4(6), P(1)'-Mg(2)-P(2) 110.18(2), C(49)-Mg(2)-H(1) 89.3(6), P(1)'-Mg(2)-H(1) 133.4(6), P(2)-Mg(2)-H(1) 79.5(6). **5**: P(1)-N(1) 1.6532(11), P(2)-N(2) 1.6507(10), P(3)-N(3) 1.6458(12), P(4)-N(4) 1.6529(11), P(1)-Mg(2) 2.6074(10), Mg(1)-P(4) 2.6094(9), P(2)-Mg(3) 2.6137(8), P(3)-Mg(4) 2.6422(9), Mg(1)-N(1) 2.0029(12), Mg(2)-N(2) 2.0117(13), Mg(3)-N(3) 2.0036(11), Mg(4)-N(4) 2.0197(12), Mg(1)-H(1) 1.770(19), Mg(1)-H(4) 1.84(2), Mg(2)-H(1) 1.825(19), Mg(2)-H(2) 1.762(19), Mg(3)-H(2) 1.842(19), Mg(3)-H(3) 1.822(19), Mg(4)-H(3) 1.811(19), Mg(4)-H(4) 1.83(2), Mg···Mg 3.02 (ave, nearest); N(1)-Mg(1)-P(4) 145.53(4), Mg-H-Mg *ca.* 113 (ave). **6**: P(1)-N(1) 1.6553(17), P(1)-Mg(1)' 2.6351(8), Mg(1)-N(1) 2.0210(16), Mg(1)-H(1) 1.92(2), Mg(1)-H(1) 1.98(2), Mg···Mg 3.24 (nearest); N(1)-Mg(1)-P(1)' 122.16(5), Mg-H-Mg *ca.* 113. **8**: P(1)-N(1) 1.6674(18), P(2)-N(2)

1.6713(17), P(1)-Mg(2) 2.7853(11), Mg(1)-N(2) 2.0428(18), Mg(1)-N(1) 2.0887(18), Mg(1)-H(1) 1.82(3), Mg(1)-H(2) 1.91(3), Mg(2)-H(1) 1.90(3), Mg(2)-H(2) 1.96(3), Mg(2)-N(4) 2.224(2), Mg(2)-N(3) 2.270(2), Mg(2)-N(5) 2.375(2); N(2)-Mg(1)-N(1) 134.61(7), N(4)-Mg(2)-P(1) 171.63(6), N(3)-Mg(2)-H(1) 171.7(8), Mg-H-Mg *ca.* 96 (ave).


**Scheme 2.** i) 2 AdN$_3$, benzene or toluene, r.t.

Figure 3. Molecular structure of **9** (30% thermal ellipsoids). Lattice solvent molecules and hydrogen atoms omitted, except hydride ligands. Only the main disordered parts of the adamantyl groups are shown. Selected bond lengths [Å] and angles [°]: P(1)-N(1) 1.6056(15), P(1)-N(2) 1.6495(15), P(2)-N(5) 1.6656(14), P(3)-N(6) 1.6588(15), P(4)-N(7) 1.6032(15), P(4)-N(8) 1.6501(16), N(2)-N(3) 1.366(2), N(3)-N(4) 1.268(2), N(8)-N(9) 1.365(2), N(9)-N(10) 1.267(2),

Mg(1)-N(4) 2.2072(16), Mg(1)-N(10) 2.2274(17), Mg(1)-N(8) 2.2662(17), Mg(1)-N(2) 2.2700(16), Mg(3)-N(6) 2.0660(15), Mg(3)-N(5) 2.0675(16), Mg(4)-N(7) 2.0546(16), N(1)-Mg(2) 2.0549(15), P(2)-Mg(2) 2.6863(8), P(3)-Mg(4) 2.6775(8), Mg(1)-H(1) 1.88(2), Mg(1)-H(4) 1.88(2), Mg(2)-H(1) 1.81(2), Mg(2)-H(2) 1.79(2), Mg(3)-H(2) 1.85(2), Mg(3)-H(3) 1.87(2), Mg(4)-H(3) 1.84(2), Mg(4)-H(4) 1.78(2) (or: Mg-H: 1.78(2)-1.88(2)); N(8)-Mg(1)-N(2) 170.52(6), N(6)-Mg(3)-N(5) 139.29(6), N(7)-Mg(4)-P(3) 119.67(5), Mg-H-Mg *ca.* 118 (ave).
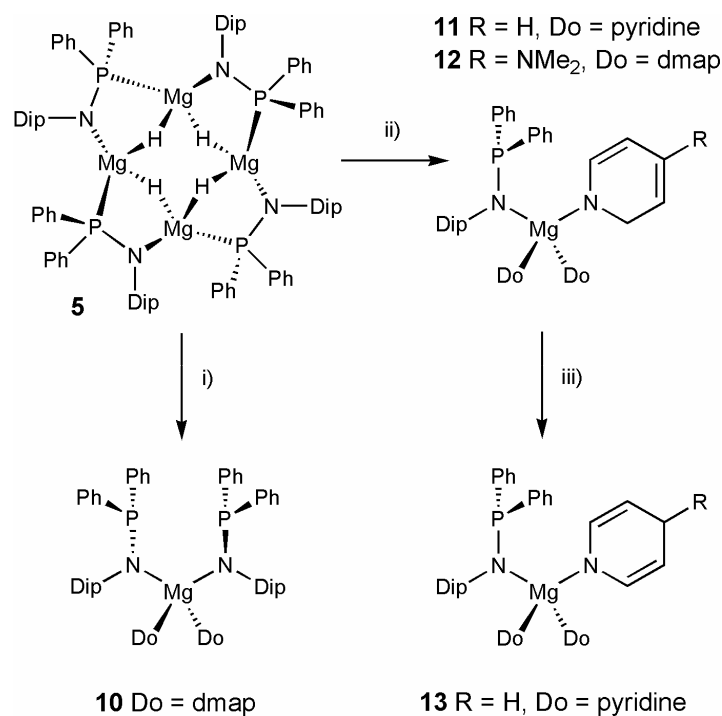
Scheme 3. Stoichiometric reactivity of **5** with pyridines. i) 4 DMAP, toluene, 60°C; ii) 12 pyridine or 12 DMAP, toluene, r.t.; iii) 60°C (for Do = pyridine).
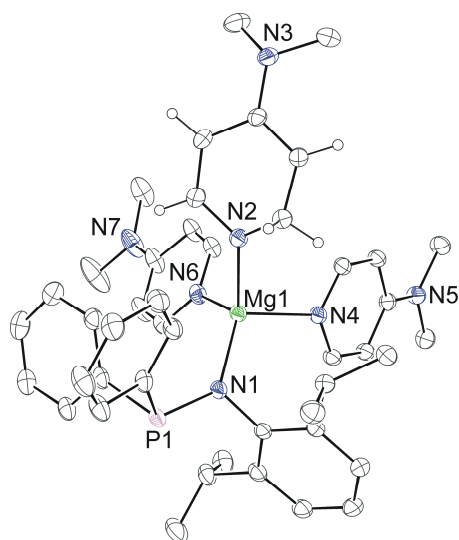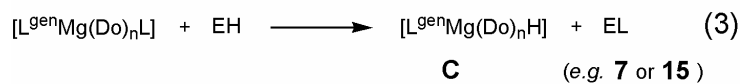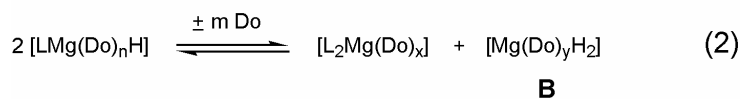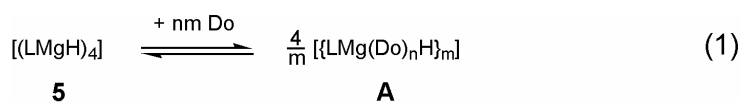
Figure 4. Molecular structure of **12** (30% thermal ellipsoids). A second, severely disordered molecule, lattice solvent and hydrogen atoms omitted, except hydrogens on the 1,2-dihydropyridide ligand. Selected bond lengths [Å] and angles [°]: P(1)-N(1) 1.6845(14), Mg(1)-N(2) 2.0198(16), Mg(1)-N(1) 2.0320(15), Mg(1)-N(4) 2.1279(15), Mg(1)-N(6) 2.1309(17), N(2)-C(25) 1.438(2), C(25)-C(26) 1.449(2), C(26)-C(27) 1.372(2), C(27)-C(28) 1.424(2), C(28)-C(29) 1.375(2), N(2)-C(29) 1.374(2); N(2)-Mg(1)-N(1) 123.63(6), N(4)-Mg(1)-N(6) 93.16(6).
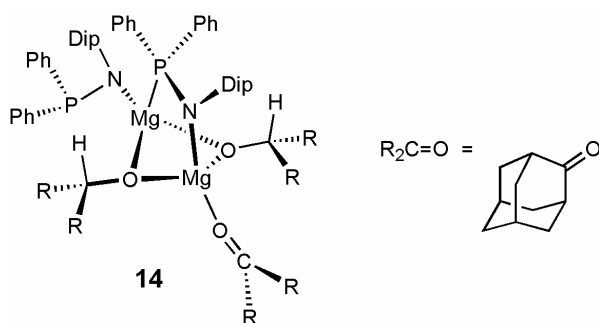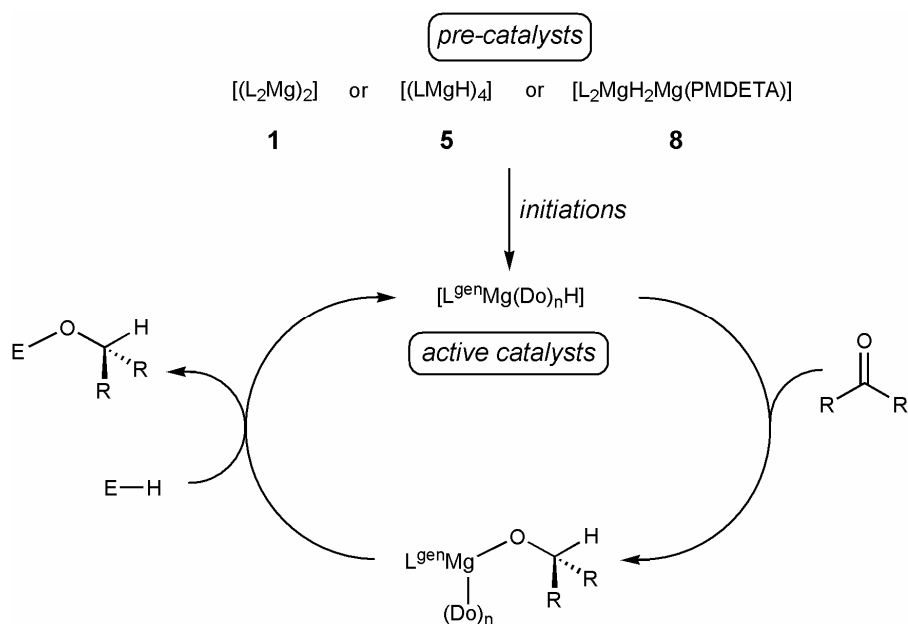

Figure 5 Chemical drawing of [(L$_2$Mg$_2$(2-AdOH)$_2$(2-AdO)] **14**. For an image from a crystal structure determination, see Figure S55.

A:

$$[(LMgH)_4] \; \xrightleftharpoons{+ \, nm \, Do} \; \tfrac{4}{m}[\{LMg(Do)_nH\}_m] \qquad (1)$$

5   **A**

$$2\,[LMg(Do)_nH] \; \xrightleftharpoons{\pm \, m \, Do} \; [L_2Mg(Do)_x] \; + \; [Mg(Do)_yH_2] \qquad (2)$$

                                                      B

$$[L^{gen}Mg(Do)_nL] \; + \; EH \; \longrightarrow \; [L^{gen}Mg(Do)_nH] \; + \; EL \qquad (3)$$

                                                 C   (*e.g.* **7** or **15**)

B:

Scheme 4. A: Possible precatalyst activation reactions (1) - (3), simplified; B: Proposed simplified catalytic cycles for the hydroelementation of ketones with precatalyst **1**, **5** or **8**. n, m, x and y are small natural numbers, L^{gen-} = monoanionic ligand such as L^-, R_2CHO^-, H^- etc, Do = (neutral) donor group, such as R_3P (from L^-), substrates such as ketones, reaction products, R = organic substituent, EH = borane or silane fragment.

Table 1. Hydroelementations of ketones catalysed by compounds **1**, **5**, **8** and **9**.

Entry	Catalyst loading [mol%][a]	Ketone	Hydride source	Temp. [°C]	Time	Conversion [%][b]	TOF [h^{-1}][c]	Main product[d]
1	0.05, **5**	2-adamantanone	HBPin	25	< 7 min	> 99	> 4,243	R'BPin
2	0.05, **5**	benzophenone	HBPin	25	15 min	88	1,760	RBPin
3	0.5, **5**	benzophenone	HBPin	25	< 7 min	> 99	> 424	RBPin
4	0.05, **8**	2-adamantanone	HBPin	25	< 7 min	> 99	> 8,486	R'BPin
5	0.05, **9**	2-adamantanone	HBPin	25	130 min	84	194	R'BPin
6	0.05 **1**	2-adamantanone	HBPin	25	< 7 min	> 99	> 8,486	R'BPin
7	1.5, **5**	2-adamantanone	PhSiH$_3$	70	15 min	> 99[e]	66	R'$_2$Si(H)Ph
8	1.5, **5**	benzophenone	PhSiH$_3$	70	50 hours	93	0.31	R$_2$Si(H)Ph
9	1.5, **8**	2-adamantanone	PhSiH$_3$	70	15 min	> 99[e]	132	R'$_2$Si(H)Ph
10	1.5, **1**	2-adamantanone	PhSiH$_3$	70	15 min	> 99[e]	132	R'$_2$Si(H)Ph
11	1.5, **5**	2-adamantanone	Ph$_2$SiH$_2$	80	15 hours	< 3	-	-

a) based on full molecules **1**, **5**, **8** or **9**; for **1** and **8** two times higher per Mg centre; for **5** and **9** four times higher per Mg centre; b) reaction was monitored via ^{1}H NMR spectroscopy and conversion yields were determined by integration of the proton on the former carbonyl-C atom against an internal standard, c) calculated per Mg centre; TOF are double for molecules **1** and **8**, and four times the value for molecules **5** and **9**; d) > 90% of total products, R = Ph$_2$C(H)O$^-$, R' = 2-adamantanolate; e) hydrosilylations of 2-adamantanone produced a small quantity of a white precipitate at elevated temperatures after longer reaction times than given that appears to reduce the measured conversion in solution likely due to R'$_3$SiPh product precipitation.

Table of contents entry

Ring maker. Phosphinoamide ligands stabilise robust heteroleptic magnesium hydride complexes with unique structures. They are good hydromagnesiation reagents and rapidly catalyse the hydroboration and hydrosilylation of ketones.
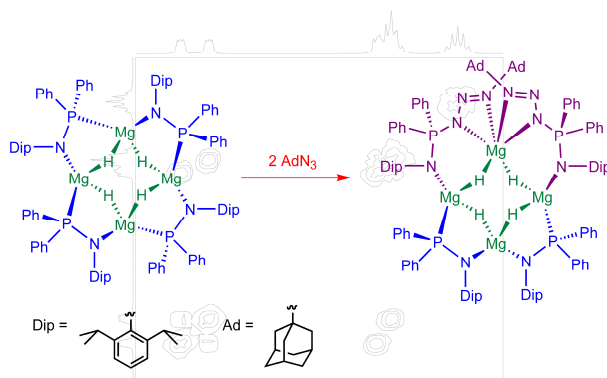
Keywords: hydrides / hydroboration / hydromagnesiation / hydrosilylation / Magnesium