Heterometallic Mg–Ba Hydride Clusters in Hydrogenation Catalysis

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Reaction of a MgN\textsubscript{3}/BaN\textsubscript{3} mixture (N\textsuperscript{--} = (SiMe\textsubscript{3})\textsubscript{2}) with PhSiH\textsubscript{3} gave three unique heterometallic Mg/Ba hydride clusters: Mg\textsubscript{3}Ba\textsubscript{2}H\textsubscript{5}N\textsubscript{7} (benzene)\textsubscript{2} (1), Mg\textsubscript{3}Ba\textsubscript{2}H\textsubscript{12}N\textsubscript{12} (toluene)\textsubscript{2} (2) and Mg\textsubscript{3}Ba\textsubscript{2}H\textsubscript{2}N\textsubscript{12} (3). Product formation is controlled by the Mg/Ba ratio and temperature. Crystal structures are described. While 3 is fully insoluble, clusters 1 and 2 retain their structures in aromatic solvents. DFT calculations and AIM analyses indicate highly ionic bonding with Mg–H and Ba–H bond paths. Also unusual H···H bond paths are observed. Catalytic hydrogenation with MgN\textsubscript{3}/BaN\textsubscript{3} and the mixture MgN\textsubscript{3}/BaN\textsubscript{3}\textsubscript{2} has been studied. Whereas MgN\textsubscript{3} is only active in imine hydrogenation, alkene and alkyne hydrogenation needs the presence of Ba. The catalytic activity of the MgN\textsubscript{3}/BaN\textsubscript{3} mixture lies in general between that of its individual components and strong cooperative effects are not evident.

Introduction

Since the isolation of the first defined Ca hydride complex,[1] the focus in alkaline earth (Ae) metal hydride chemistry has been on the isolation of defined, metal pure complexes. At present, molecular Ae metal hydride complexes throughout group 2 are known.[2–6] Going down the group, increasing dynamics and ligand exchange reactions make it more challenging to isolate stable Ae metal hydride complexes. After a report on the first Mg hydride complex,[7] various Mg hydride complexes have been fully characterized.[4] While there are also ample examples for Ca hydride complexes,[5] well-defined heavier Sr,[7–13] and Ba,[7,14,15] hydride complexes are few and remain a curiosity.

The fascination for Ae metal hydride complexes stems from their very high reactivity and versatility in synthesis of a large range of complexes.[16] They are also regarded intermediates in hydrogenation catalysis, a field that underwent rapid growth and development.[16–27] Their applications also include hydrogenation of challenging arenes,[28–30] Hydrogen-Isotope-Exchange,[30] C–F bond activation,[30–32] ethylene polymerization,[11] and controlled reactions with olefins to isolate first examples of Ca alkyls and a Sr ethyl complex.[31,32]

However, looking back at the beginnings of Ae hydride chemistry, the research field was pioneered by a heterobimetallic system. Mulvey’s heterobimetallic [M\textsubscript{2}Mg\textsubscript{3}H\textsubscript{5}NiPr\textsubscript{3} \textsubscript{2} (toluene)\textsubscript{2}] clusters (M=Na, K) are described as inverse crown ethers forming a ring of metals that encapsulate hydride anions (Scheme 1, A).[33,34] Alternatively they may be seen as two magnesiate anions, (iPr\textsubscript{3}Ni)\textsubscript{2}MgH\textsuperscript{2}, that are bridged by two Mg\textsuperscript{2+} alkali metal cations. Heterobimetallic magnesium hydride systems were further explored by Hill and co-workers, who identified the bisamide stabilized structures of K\textsubscript{3}Mg\textsubscript{3}H\textsubscript{5}N\textsubscript{3} and Na\textsubscript{2}Mg\textsubscript{3}H\textsubscript{2}N\textsubscript{3} (N\textsuperscript{--} = (SiMe\textsubscript{3})\textsubscript{2}) Scheme 1, B–C).[35] These were obtained by simple reaction of MN\textsuperscript{3} (M=Na, K), Mg(nBu)\textsubscript{2}, and HN\textsuperscript{3} in toluene and subsequent treatment with PhSiH\textsubscript{3}. Most recently, Mulvey and co-workers reported crystal structures of M\textsubscript{3}Mg\textsubscript{3}H\textsubscript{5}N\textsubscript{3} \textsubscript{2} (benzene)\textsubscript{2} (M=Na, K, Rb, x=2) (Scheme 1, B and D).[36] These heterometallic complexes have been evaluated for catalytic activity in alkene transfer hydrogenation of olefins, a methodology recently introduced by our group.[36]

The vast majority of heterometallic s-block metal complexes are mixtures of alkali metals with either group 1, group 2, Zn or p-block metals.[38–41] There is also a fast growing trend to disclose structures and reactivities of heterometallic s/d-block combinations.[42–51] With focus on main group chemistry, however, the blend of two group 2 metals seems to be largely unstudied. There is a rare example for Mg/Ca hydride complex (Figure 1, E) which was isolated from a mixture of [([\textsuperscript{19}F\textsubscript{6}BDI][Mg\textsubscript{2}])] \textsubscript{2} \textsubscript{[Al(O\textsubscript{2}C\textsubscript{CF\textsubscript{3}})\textsubscript{3}]} and [([\textsuperscript{19}F\textsubscript{6}BDI][CaH\textsubscript{2}])]. The workup was tedious, involving mechanical separation of single crystals, and the compound was poorly defined in solution. Its contamination with a by-product limited analytical investigations and reactivity studies.

Most recently, Okuda and co-workers presented a mixed Ca/Sr hydride complex (Figure 1, F).[16] The complex appears to be the first fully characterized example of a two alkaline earth metal hydride blend that has been thoroughly studied.

We recently demonstrated that stabilization of well-defined Ae metal hydrides not necessarily needs large bulky ligands. In
in hydrogenation catalysis, with the softer metal binding the substrate and the harder metal delivering the hydride. Similar observations have been made for Li/Al hydride catalysts.\textsuperscript{[58–60]}

We herein present synthesis and structures of well-defined Mg/Ba hydride clusters, which could be seen as potential intermediates during hydrogenation catalysis, and explore the effect of Mg/Ba metal-mixing in hydrogenation catalysis.

**Results and discussion**

**Syntheses**

Monitoring the reaction of MgN"\textsubscript{2} and BaN"\textsubscript{2} in an approximately 1/1 ratio with PhSiH\textsubscript{3} (20 °C, C\textsubscript{6}D\textsubscript{6}) by \textsuperscript{1}H NMR spectroscopy showed immediate conversion of the N" anions to PhSiH\textsubscript{2}N". During the reaction some precipitate was formed but this redissolved within minutes upon stirring. Concentrating the solution led to colorless crystals which were identified as Mg\textsubscript{2}Ba\textsubscript{2}H\textsubscript{11}N"\textsubscript{6}·(benzene)\textsubscript{2} (1, yield: 46%); Scheme 2.

The \textsuperscript{1}H NMR spectrum of a similar reaction of MgN"\textsubscript{2}/BaN"\textsubscript{2} in a 1/2 ratio with PhSiH\textsubscript{3} (20 °C, C\textsubscript{6}D\textsubscript{6}) showed apart from cluster 1 a second species. Removal of 1 by extensive washing with pentane and subsequent crystallization from benzene afforded colorless crystals which were identified as Mg\textsubscript{2}Ba\textsubscript{4}H\textsubscript{13}N"\textsubscript{9}·(benzene)\textsubscript{2} (34% yield). The crystal quality of this product is poor and high quality crystals were obtained by recrystallization from toluene to give Mg\textsubscript{2}Ba\textsubscript{4}H\textsubscript{13}N"\textsubscript{9}·(toluene)\textsubscript{2} (toluene)\textsubscript{2} (2). Although the metal/hydride ratio in both clusters 1 and 2 is more or less similar (1: Aε/H = 0.82, 2: Aε/H = 0.85), the second cluster is clearly richer in Ba (1: Mg/Ba = 1.25, 2: Mg/Ba = 0.57).

In an attempt to optimize reaction conditions in favor for the larger cluster, the reaction was performed at higher temperatures. Reaction of MgN"\textsubscript{2}/BaN"\textsubscript{2} in a circa 1/2 ratio with PhSiH\textsubscript{3} (C\textsubscript{6}D\textsubscript{6}) at room temperature showed \textsuperscript{1}H NMR signals for 1 and 2. Prolonged heating did not affect the cluster 1, which seems thermally quite stable, but led to gradual disappearance of 2. Some formation of BaN"\textsubscript{2} seems to occur along with the appearance of trace compounds (see ESI, Figure S15–S16). However, after 12 hours of heating, crystals of a highly insoluble product could be isolated from the hot reaction mixture.

Crystal structures

Complex Mg\textsubscript{2}Ba\textsubscript{4}H\textsubscript{13}N"\textsubscript{9}·(benzene)\textsubscript{2} (1) crystallizes as a cluster (Figure 1a) in which the Mg\textsubscript{2}Ba\textsubscript{4} core could be best described as a pentagonal bipyramid with five equatorial Mg centers, each
bound to a N” ligand, and two axial Ba centers which are both capped by benzene (Figure 1b). The ten triangular Mg\textsubscript{2}Ba-faces each contain a \(\mu_3\)-bridging hydride and the remaining hydride is located in the center of the pyramid and is best described as an interstitial hydride.\(^{[56,57]}\) The two remaining N”Ba\textsuperscript{+} cations bridge between two N”Mg units, breaking the five-fold symmetry of the cluster. Alternatively, the complex could be thought build up from a central (C\textsubscript{6}H\textsubscript{6})BaH\textsubscript{2} core of \(\text{(MgH}_{2})_{5}(\text{BaH})_{3}\text{)}^{+}\) spindle surrounded by a neutral (MgH\textsubscript{2})\textsubscript{5}-belt in which each Mg\textsuperscript{2+} cation carries a N” ligand from which two out of five are bridged by N”Ba\textsuperscript{+} (Figure 1c). Although the complex does not have crystallographic symmetry, it is approximately mirror symmetric (C\textsubscript{s}). All hydride ligands were localized and freely refined.

The Ba–H bond distances to the ten outer H ligands are in the range of 2.43(6)–2.86(5) Å. Those to the interstitial H ligand range from 2.49(6) to 2.60(6) Å; Table 1. This compares well with...
Ba–H bonds in dimeric complexes: 2.47(5)–2.58(6) Å and is at the lower range for Ba–H distances in (HHaN)₂ (2.55(3)–3.21(3) Å). While the Mg–H bonds between the five equatorial Mg²⁺ ions and the ten outer H⁻ ligands (1.84(4)–2.09(7) Å) are within the range expected for Mg hydride complexes, those to the interstitial H⁻ are much longer (2.25(6)–2.87(6) Å), however, not unprecedented in literature: Mg–H bond distances up to 2.63(3) Å have been reported.

It is more challenging to describe the geometry of the second Mg/Ba hydride cluster: Mg₄Ba₇H₁₃N₉·(toluene)₂ (2); Figure 2. The structure of the cluster, which has no crystallographic symmetry, could be described as a central interstitial hydride ligand surrounded by a distorted tetrahedron of Ba²⁺ cations with Ba–Houter distances in the range 2.75(6)–2.88(6) Å. The Ba₄ tetrahedron is surrounded by 4 Mg²⁺ cations but the Mg–Hₜₚ ligands are too long to be bonding interactions (2.95(6)–3.21(5) Å). The Mg₄Ba₄⁻framework resembles the geometry of a polyeder that is mathematically described as a snub “disphenoid” or “siamese dodecahedron” consisting of four Mg₂Ba and eight MgBa₂ faces, each with a μ₃-H⁻ ligand (the Houter ligands). The periphery of this (Mg₄Ba₇H₁₃)²⁻ unit is stabilized by three barate BaN⁻⁵ anions and two neutral toluene ligands that cap Ba centers in η⁶-fashion. The Mg–Houter (1.88(5)–2.09(6) Å) and Ba–Houter (2.43(6)–2.74(6) Å) bonds are in the expected ranges.

The largest cluster, Mg₇Ba₁₂H₂₆N₁₂ (3), is highly symmetric. It crystallizes in the trigonal spacegroup R3, featuring a threefold inversion axis. The core of the cluster consists of a (MgH₆)₄ octahedron (Figure 3a). This unit with perfect H–Mg–H angles of 90° and 180° is enclosed by a (Ba₁₂H₂₀)⁺icosahedron consisting of 12 Ba²⁺ ions and 20 triangular Ba₂ faces that each contain a μ₃-H⁻ ligand (Figure 3b). The twelve Ba²⁺ ions are adequately shielded by bonding to 6 MgN⁻² units, each bridging between a pair of Ba²⁺ ions (Figure 3c). The formula for this cluster might therefore also be reformulated as [(MgH₆)Ba₁₂H₂₀MgN²]₆. The Ba–H hydride (2.51(2)–2.83(3) Å) and Mg–H bond distances (1.87(3)–2.07(4) Å) are comparable to those of cluster 1 and 2.

The heterometallic Mg/Ba hydride clusters 1–3 are the first of their kind. During our investigation we never found...
precipitation of metal-pure metal hydride species, indicating that the interplay of the hard Lewis acidic Mg\(^{2+}\) ion and soft Ba\(^{2+}\) has a positive influence on the stability of mixed Aė meta1 hydride clusters.

Solution NMR studies

Complex Mg\(_2\)Ba\(_4\)H\(_8\)N\(^{-}\)\(_2\) (benzene\(_2\)) (1) is sparingly soluble in benzene-\(d_6\). At room temperature three hydride singlet signals could be identified at 3.41, 3.36 and 3.29 ppm with an intensity ratio of 4:4:2, respectively. These chemical shifts fit for typical Mg hydride complexes which, with some exceptions, are generally in the 3.0–4.5 ppm range.\(^{40}\) They do not fit for Ba hydride complexes which feature hydride resonances at much lower field (range: 7.9–10.4 ppm). \(^{7,14,15}\) Their ratio of 4:4:2 fits well with the C\(_2\)-symmetry of the cluster (Figure 1c). The fourth hydride signal, observed at 1.35 ppm, is assigned to the interstitial hydride ligand which is the most symmetric and least disturbed hydride ligand. Although this signal does not fit the general range for Mg or Ba hydride signals, its chemical shift is comparable and in a narrow range: Mg \(+1.58/+1.63, Ba +1.70/+1.79\) and \(H –0.80/–0.88\) (Table S3). These values indicate highly ionic bonds. The NPA charges for Mg in 1\(^{-}\)*–3\(^{-}\)* compare well to those in recently reported Mg hydride dimer complexes stabilized by the (Me\(_2\)Si\(_3\))\(^{-}\) anion and neutral Lewis bases: Mg \(+1.63/+1.67,\) \(^{65}\) Charges on the hydrides in the latter Mg hydride dimer (H \(–0.79\)) are at the lower end of those in 1\(^{-}\)*–3\(^{-}\)*. The NPA charges for Ba in 1\(^{-}\)*–3\(^{-}\)* compare well to those in the related (HBarN\(^{3-}\))\(_2\) cluster (F in Scheme 1) which vary from \(+1.68\) to \(+1.77\). Charges on the hydrides in (HBarN\(^{3-}\))\(_2\) range from \(–0.83\) to \(–0.86\) and are at the higher boundary of those in 1\(^{-}\)*–3\(^{-}\)*.

Atoms-in-molecules (AIM) analysis of cluster 1\(^{-}\) shows bond paths between the interstitial hydride and the two axial Ba\(^{2+}\) ions with an electron density in the bond-critical-points (bcps) of 0.162 e \(\cdot\) Å\(^{-3}\). These Ba–H bonds are much stronger than those between Ba and the five outer hydrides in the periphery of the cluster (0.132–0.136 e \(\cdot\) Å\(^{-3}\)). Bonding between the interstitial hydride and the five Mg\(^{2+}\) ions in the equatorial plane is indicated by bcp's but is much weaker (0.103 e \(\cdot\) Å\(^{-3}\)) due to long Mg–H distances (wide supra). Electron densities in bcp's on Mg–H bonds within the (MgH\(_3\))\(_2\) belt are up to twice as high (0.158–0.209 e \(\cdot\) Å\(^{-3}\)). These values are in favor of describing 1\(^{-}\) as a central (C\(_6\)H\(_6\))Ba–H–Ba(C\(_6\)H\(_6\))\(^{3-}\) spindle surrounded by a neutral (MgH\(_3\))\(_2\)-belt. The most pronounced bcp's (0.232 e \(\cdot\) Å\(^{-3}\)) were found between the two barate BaN\(^{3-}\) motifs and the hydride core MgH\(_3\)-belt.

The interstitial hydride in complex 2\(^{-}\) shows only bcp's to the four neighboring Ba\(^{2+}\) ions (0.066–0.111 e \(\cdot\) Å\(^{-3}\)) and not to the more remote Mg\(^{2+}\) ions. This observation is in accordance with the very long distance of the Mg\(^{2+}\) to central hydride in 2 (2.956(5)–3.211(5) Å (Avg. 3.07 Å)) or 2\(^{*}\) (2.91–3.04 Å (Avg. 2.97)). There are, however, bond paths between Mg\(^{2+}\) and neighboring \(H_{outer}\) ligands with electron densities (0.180–0.213 e \(\cdot\) Å\(^{-3}\)) that are considerably higher than the Ba–H\(_{outer}\) bond paths (0.103–0.174 e \(\cdot\) Å\(^{-3}\)). The most pronounced metal hydride interaction was again found between the three barate BaN\(^{3-}\) motifs interacting with one close hydride ligand (0.213 e \(\cdot\) Å\(^{-3}\)).

AIM analysis shows that the Mg–H and Ba–H bonding in 3\(^{-}\) is similar to that in 1\(^{-}\) and 2\(^{-}\). The electron densities in Ba–H

Theoretical considerations

Complexes 1–3 have been analyzed by DFT methods at the B3PW91/def2tzvp level using core potentials at Ba. For simplicity the (Me\(_2\)Si\(_3\))\(^{-}\) anions have been replaced by Me\(_6\)N\(^{-}\) anions (abbreviated as N\(^{-}\)). These model clusters, which are indicated as 1\(^{-}\)*, 2\(^{-}\)* and 3\(^{-}\)*, resemble the experimentally determined crystal structures reasonably well (Table S2). The NPA charges for Mg, Ba and the hydride ligands in 1\(^{-}\)*–3\(^{-}\)* are all comparable and in a narrow range: Mg \(+1.58/+1.63, Ba +1.70/+1.79\) and \(H –0.80/–0.88\) (Table S3). These values indicate highly ionic bonds. The NPA charges for Mg in 1\(^{-}\)*–3\(^{-}\)* compare well to those in recently reported Mg hydride dimer complexes stabilized by the (Me\(_2\)Si\(_3\))\(^{-}\) anion and neutral Lewis bases: Mg \(+1.63/+1.67,\) \(^{65}\) Charges on the hydrides in the latter Mg hydride dimer (H \(–0.79\)) are at the lower end of those in 1\(^{-}\)*–3\(^{-}\)*. The NPA charges for Ba in 1\(^{-}\)*–3\(^{-}\)* compare well to those in the related (HBarN\(^{3-}\))\(_2\) cluster (F in Scheme 1) which vary from \(+1.68\) to \(+1.77\). Charges on the hydrides in (HBarN\(^{3-}\))\(_2\) range from \(–0.83\) to \(–0.86\) and are at the higher boundary of those in 1\(^{-}\)*–3\(^{-}\)*.
bcp’s are in the 0.069–0.147 e Å⁻¹ range while those in Mg–H bcp’s indicate somewhat stronger bonding (0.174–0.209 e Å⁻¹).

Apart from metal-hydride bond paths, we noted in all three clusters unusual bcp’s between two hydride ligands (Figure 4). In complexes 1* and 2* these unexpected H···H interactions are observed between the interstitial hydrides and the Houter ligands (1*: 0.086–0.127 e Å⁻¹, 2*: 0.051–0.082 e Å⁻¹). Bonding between Houter ligands is in both complexes somewhat more pronounced (1*: 0.132 e Å⁻¹, 2*: 0.139–0.140 e Å⁻¹). In cluster 3*, bcp’s were noted between hydrides of the formal core unit [MgH₆]⁴⁺ and twelve Houter ligands located in the Ba₂H₆ shell (0.061–0.073 e Å⁻¹). Although the electron densities in the bcp’s are low they are significant. Electron densities in the bcp’s for H···H interactions in 1*–3* (0.05–0.14 e Å⁻¹), are comparable to those in a recently reported dodecanuclear Ca hydride cluster (0.10–0.13 e Å⁻¹)[56] and considerably larger than those found in a tetranuclear Mg hydride cluster (0.047 e Å⁻¹, H···H = 3.106 Å).[56] It appears that hydride···hydride interaction is a common feature in larger alkaline earth metal hydride aggregates. Shorter H···H distances generally result in high electron densities in the corresponding bcp’s.

Catalytic hydrogenation

Cooperative effects between metal complexes from the first and second main groups are widespread in literature.[38–41] The combination KH/AeN⁺ (Ae=Mg, Ca) was recently put forward as a hydrogenation catalyst for activated (conjugated) alkenes, terminal unactivated alkenes or cyclic internal alkenes.[67] Screening all alkali metals, mixtures of MN⁺ (M=Li, Na, K, Rb, Cs) and MgN⁺, were shown to be catalysts for transferring hydrogen from 1,4-cyclohexadiene to either Ph₂C=C=CH₂ or Ph(H)C=CH₂.[37] It is notable that each component alone was not active in this catalytic transformation. Herein we present first studies on mixed Ae metal hydride catalysts in which we combine a hard metal (Mg) with a soft metal (Ba).

For evaluation of possible cooperative effects between Mg and Ba, catalytic alkene hydrogenation was not only studied with the MgN⁺/BaN⁺ mixture but also with the metal-pure precursors MgN⁺ and BaN⁺, alone. Reaction conditions were adapted from previously established hydrogenation protocols using the AeN⁺ precursors (120 °C, 6 bar H₂).[20,21,23] In order to observe activity for the least active catalyst MgN⁺, high catalyst loadings of 20 mol% were used. In order to compare results, for the MgN⁺/BaN⁺ mixture 10 mol% of each has been used which equals 20 mol% total metal content. Although for consistency the metal-pure BaN⁺ catalyst was also used in 20 mol% quantity in most cases, it must be realized that for this highly active catalyst the loadings can be reduced significantly.[20,21,23] Part of the catalytic runs were repeated with the mixed Mg/Ba cluster 1 in which case catalyst loadings of 1.8 mol% were used. Considering the cluster contains 11 hydrides, this converts to circa 20 mol% based on hydride content.

Table 2 shows that MgN⁺ is generally fully inactive in alkene hydrogenation. A similar observation was made for transfer hydrogenation of alkenes.[51] Also in alkyne hydrogenation no activity was found (entry 6) but, as we reported previously,[50] MgN⁺ is catalytically active in imine hydrogenation (entries 7–12).

In contrast to the poor activity of MgN⁺ in alkene hydrogenation, the mixed-metal system MgN⁺/BaN⁺ can reduce terminal alkenes like 1-hexene (entry 1), however, with low activity. Precatalyst BaN⁺ alone showed under similar conditions full conversion of 1-hexene but considerable isomerization to 2-hexene was found as a side-reaction.[21] As internal alkenes are much harder to reduce than terminal alkenes, no further hydrogenation to n-hexane was observed. The double bonds in vinyltrimethylsilane and 4-vinyl-cyclohexene cannot be isomerized and show higher conversions (entries 2–3). The reluctance

Figure 4. Atoms-in-molecules (AIM) representation of the metal hydride cores in 1*–3* exclusively showing the unusual hydride-hydride bond paths and bond-critical-points (light-blue). For the highly symmetric complex 3* only the asymmetric unit is shown, representing the whole complex.
to hydrogenate internal alkenes is supported by the selective hydrogenation of the vinyl group in 4-vinyl-cyclohexene. Exceptions are the double bonds in norbornadiene which are activated for reduction but also give nortricyclene as a side-product (entry 4). Like for BaN$_2$, conversion of $p$-Cl-styrene is accompanied by nucleophilic aromatic substitution (entry 5) but diphenylacetylene could be fully reduced by the MgN$_2$/BaN$_2$ system (entry 6). Various imines (aldimine or ketimine) could be hydrogenated with the MgN$_2$/BaN$_2$ combination (entries 7–12).

It seems that the presence of Ba is essential for alkene and alkyne hydrogenation whereas for imine hydrogenation MgN$_2$ already showed good activity. This may be explained by activation of the imine substrate by Mg···N(R)$=\text{C}(\text{H})\text{R'}$ coordination, a complex in which a hard Mg cation combines with a hard N Lewis base. The fact that MgN$_2$ alone does not perform in alkene hydrogenation is likely related to the lower ionicity of the Mg–H bond (cf. the Ba–H bond) and its inherently lower reactivity. Additionally, it also could be due to poor coordination of soft alkene ligands to hard Mg$_2^+$ cations. Activation of unsaturated substrates by Ae metal ions has been shown essential in catalysis.\[68,69\] Isolation of unsupported Mg···alkene (or alkyne and arene) complexes so far has only been achieved with highly Lewis acidic cationic Mg complexes which are free of stabilizing Lewis bases.\[70–76\] It has been found that the heavier softer Ae metals Ca, Sr and Ba are superior in activating soft unsaturated substrates.\[11,29,33\] This is also supported by the crystal structures of 1 and 2 in which the arene ligands coordinate exclusively to the larger Ba metal and not to Mg and explains why the presence of Ba is crucial for alkene and alkyne activation.

### Table 2. Catalytic alkene, alkyne and imine hydrogenation (20 mol% catalyst, substrate concentration = 0.11 M, 120 °C, 6 bar H$_2$). Reactions with 1 (1.8 mol% catalyst, substrate concentration = 0.28 M, 120 °C, 6 bar H$_2$). Conversions determined by GC-MS analysis (average of at least three runs).

| Entry | Substrate | t [h] | Product(s) | MgN$_2^+$ [%] | Mg/BaN$_2$ [%] | BaN$_2^+$ [%] | 1 [%] |
|-------|-----------|------|------------|---------------|---------------|---------------|-------|
| 1     |           | 24   | trace      | 27/2          | 42/58$^{[a]}$ | –             |
| 2     |           | 2    | 3          | 88            | 99$^{[a]}$    | 88            |
| 3     |           | 24   | 2          | 64            | 73$^{[a]}$    | –             |
| 4     |           | 24   | 93/5/3/0   | 0/0/67/33     | 0/0/43/57     | 0/0/63/27     |
| 5     |           | 24   | trace      | 1/23          | 4/23          | –             |
| 6     |           | 1    | 1/0        | 100/0         | 100/0         | 79/20         |
| 7     |           | 2    | 75         | 94            | 100           | –             |
| 8     |           | 2    | 79         | 59            | 96            | 47            |
| 9     |           | 2    | 56         | 91            | 99            | 76            |
| 10    |           | 1    | 85         | 100           | 100           | 100           |
| 11    |           | 2    | 43         | 77            | 93            | –             |
| 12    |           | 2    | 0          | 100           | 100           | 100           |

[a] MgN$_2^+$/BaN$_2^+$ ratio 1:1. In this case 10 mol% of each, MgN$_2^+$ and BaN$_2^+$, was used. The total metal amount is 20 mol%. [b] 10 mol% catalyst loading.\[21\] [c] 10 mol% catalyst loading @ 0.5 h reaction time.\[21\]
With few exceptions the activity of the mixed-metal catalyst generally lies between that of its individual components. These results demonstrate that, although there are certainly differences in activity between the three catalysts, mixing Mg and Ba does not have an additional advantage over using Ba alone. In order to understand the nature of the mixed catalyst MgN\textsubscript{2}/BaN\textsubscript{2}, a solution of this combination in C\textsubscript{6}D\textsubscript{6} was pressurized with H\textsubscript{2} (6 bar) and heated to 80°C (6 h). While a similar reaction of CaN\textsubscript{2}, with H\textsubscript{2} led toformation of undefined Ca\textsubscript{2}H\textsubscript{2}N\textsubscript{2} clusters with MW’s up to 7500 g·mol\textsuperscript{-1},\textsuperscript{20b} the MgN\textsubscript{2}/BaN\textsubscript{2} mixture reacted with H\textsubscript{2} to give primarily Mg\textsubscript{2}Ba\textsubscript{2}H\textsubscript{2}N\textsubscript{2} \textsubscript{(benzene)}\textsubscript{2} (1) together with minor quantities of unknown hydride complexes, indicated by \textsuperscript{1}H NMR signals in the 5.0–5.3 ppm region (Figure S42–43). The formation of 1 was further confirmed by its crystallization from this solution. The clusters 1–3 are therefore valid models for intermediates that could form during catalytic hydrogenation with MgN\textsubscript{2}/BaN\textsubscript{2}. Indeed, cluster 1 has been successfully used as a hydrogenation catalyst (Table 2). In all cases the catalytic activity of 1 is comparable to that of the MgN\textsubscript{2}/BaN\textsubscript{2} mixture, supporting the idea that these mixed metal Mg/Ba hydride clusters are the catalytically active species.

Conclusions

Reaction of a mixture of MgN\textsubscript{2} and BaN\textsubscript{2} with PhSiH\textsubscript{3} resulted in the formation of three unique heterometallic Mg/Ba hydride clusters \textit{Mg\textsubscript{2}Ba\textsubscript{2}H\textsubscript{2}N\textsubscript{2} \textsubscript{(benzene)}\textsubscript{2} (1), Mg\textsubscript{2}Ba\textsubscript{2}H\textsubscript{2}N\textsubscript{2} \textsubscript{(solvent)}\textsubscript{2} (2) (solvent = benzene or toluene) and Mg\textsubscript{2}Ba\textsubscript{2}H\textsubscript{2}N\textsubscript{2} \textsubscript{3} (3). The educt composition influences the Mg/Ba ratio in the metal hydride clusters which become richer in Ba with lower MgN\textsubscript{2}/BaN\textsubscript{2} ratios. Cluster composition can also be influenced by temperature. While cluster 1 is thermally stable, cluster 2 is thermolabile and forms at higher temperatures the larger Mg/Ba hydride cluster Mg\textsubscript{2}Ba\textsubscript{2}H\textsubscript{2}N\textsubscript{2} \textsubscript{3} (3) which is completely insoluble in aromatic solvents. These clusters, which can all be prepared phase-pure, are among the first examples of well-characterized A\textsubscript{e} heterobimetallic hydrides. Under no circumstances were homometallic clusters isolated, indicating that the mixing of Mg\textsuperscript{2+} and Ba\textsuperscript{2+} cations has a positive influence on cluster stability.

While the insoluble cluster 3 could not be studied in solution, the solid state structures of 1 and 2 are retained when dissolved in aromatic solvents. The high symmetry of the Mg\textsubscript{2}Ba\textsubscript{2}H\textsubscript{2} core found in the solid state structures of 1 and 2 is broken by coordination of BaN\textsubscript{2} units in the periphery. This makes the hydride ligands in the core inequivalent, leading to several hydride resonances in the \textsuperscript{1}H NMR spectra. It is surprising that the clusters 1 and 2 do not show dynamical ligand exchange processes that are typical for s-block metal compounds, also not at higher temperature (\textdegree{}80°C). The chemical shifts for the hydride ligands in 1 and 2 range from 1.35 to 5.45 ppm, and should be regarded more typical for Mg–H resonances (0.55–6.78 ppm) than for Ba–H resonances (7.9–10.4 ppm).

DFT calculation on model system for 1–3 reproduced their structures reasonably well. AIM analysis showed bcp’s between the metals and hydride ligands. The electron density on the Mg–H bond paths is generally higher than that on Ba–H bond paths which is due to higher covalency in the Mg–H bond. This is confirmed by calculation of the NPA charges which are higher for Ba\textsuperscript{2+} when compared to Mg\textsuperscript{2+}. All clusters also show unusual H\textsuperscript{–}–H bond paths but the electron densities in their bcp’s are generally low (0.05–0.14 e Å\textsuperscript{-2}).

The activity of the mixture MgN\textsubscript{2}/BaN\textsubscript{2}, in hydrogenation catalysis was compared to that of the metal pure catalysts MgN\textsubscript{2} and BaN\textsubscript{2}. A solution of the MgN\textsubscript{2}/BaN\textsubscript{2} mixture in benzene reacts with H\textsubscript{2} to give primarily Mg\textsubscript{2}Ba\textsubscript{2}H\textsubscript{2}N\textsubscript{2} \textsubscript{(benzene)}\textsubscript{2} (1). The MgN\textsubscript{2} \textsubscript{(pre) catalyst is not active in alkene or alkyne hydrogenation but is effective in imine hydrogenation. The MgN\textsubscript{2}/BaN\textsubscript{2} mixture was found to be active in alkene, alkyne and imine hydrogenation, however, the activities are in general lower or equal to that of BaN\textsubscript{2}. This clearly shows that, although imine hydrogenation can also be performed with Mg-based catalysts, for alkene and alkyne hydrogenation the presence of Ba is crucial. This may be explained by the HSAB concept in which hard Lewis acids (Mg\textsuperscript{2+}) bind and activate hard Lewis bases (imines) whereas soft Lewis bases (alkenes and alkenes) need the softer Ba\textsuperscript{2+} for activation. A combination of hard (Mg\textsuperscript{2+}) and soft (Ba\textsuperscript{2+}) does, at least in catalytic hydrogenation, not provide additional benefits. This is mainly due to the very high performance of metal-pure Ba catalysts.

Experimental Section

General Experimental Procedures

All experiments were conducted in dry glassware under an inert nitrogen atmosphere by applying standard Schlenk techniques or gloveboxes (MBraun) using freshly dried and degassed solvents. Benzene, toluene, pentane and hexane were degassed with nitrogen, dried over activated aluminum oxide (Innovative Technology, Pure Solv 400-4-MD, Solvent Purification System) and then stored under inert atmosphere. Deuterated benzene (C\textsubscript{6}D\textsubscript{6} 99.6 ± %D) and toluene-d\textsubscript{8} (99.6 ± %D) were purchased from Deuter GmbH and Euriro-top, degassed and dried over molecular sieves (3 Å). Following reagents were obtained commercially and dried over molecular sieves (3 Å): PhSiH\textsubscript{3} (Alfa Aesar, 97%), cyclohexene (Fluka, 99%), 1-hexene (Acrros Organics, 97%), 4-vinyl-1-cyclohexene (TCI Chemicals, >95%), 4-chlorostyrene (TCI, >98%), norbornadiene (Sigma-Aldrich, 98%), Ph(H)C=NTBu (Sigma-Aldrich, 97%), Diphenylacetylene (Sigma-Aldrich, 98%) was dried under high vacuum for two days at 60°C. Following substrates were synthesized according to literature procedures: m-MeO–Ph(H)=NTBu,[77] Ph(Ph)=C=N(Ph),[76] tBu(H)=C=N(tBu)=C=N(Ph),[79] Mes(H)=C=N(Mes),[83] Mes=H)(C=N(Mes),[92] Mes=H)(C=N(Ph),[92] The following compounds were synthesized according to literature procedures: Mg[NiSiMe\textsubscript{3}]\textsubscript{2}, (MgN\textsubscript{2}) and Ba[NiSiMe\textsubscript{3}]\textsubscript{2}, (BaN\textsubscript{2}) NMR spectra were measured on Bruker Avance III HD 400 MHz and Bruker Avance III HD 600 MHz spectrometers. Chemical shifts (\delta) are denoted in ppm (parts per million), coupling constants in Hz (Hertz). For describing signal multiplicities common abbreviations are used: s (singlet) and m (multiplet). Spectra were referenced to the solvent residual signal. Elemental analysis was performed with an Hekatech Eurovector EA3000 analyzer. All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and an Atlas S2 detector. Crystallo-
Synthesis of Mg$_2$Ba$_4$H$_9$N$_9$(benzene). (1). A mixture of BaN$_2$ (50.0 mg, 0.11 mmol) and MgN$_2$ (47.1 mg, 0.14 mmol) was suspended in 1.5 mL of benzene (the chosen Mg/Ba ratio represents that in 1). The mixture was shortly heated to reflux to dissolve all solids. PhSiH$_3$ (32.5 mg, 0.30 mmol, 37.0 μL) was added dropwise under vigorous shaking of the solution. Colorless crystals formed over the next two days. The crystals were isolated and dried at 60 °C under vacuum to afford 25 mg of pure Mg$_2$Ba$_4$H$_9$N$_9$(benzene) (25 mg, 0.013 mmol, 46% based on BaN$_2$). Yield was calculated on the basis that seven eq. of BaN$_2$ (MW 199.62 g/mol) (isolated without drying step but after washing with pentane. Residual pentane was allowed to evaporate into the glovebox atmosphere): C 35.34, H 7.58, N 4.66.

Synthesis of Mg$_2$Ba$_4$H$_9$N$_9$(benzene). (2). A mixture of BaN$_2$ (232 mg, 0.506 mmol) and MgN$_2$ (100 mg, 0.290 mmol) was suspended in 3 mL of benzene (the chosen Mg/Ba ratio represents that in 2). The mixture was shortly heated to reflux to dissolve all solids. PhSiH$_3$ (102 mg, 0.943 mmol, 116 μL) was diluted in benzene (1.8 mL) and added dropwise to the stirring solution. The brownish solution was stirred for 1.5 h at room temperature. The formation of a white precipitate was observed. The reaction mixture was allowed to settle and the solution was decanted. The remaining white solid was washed with pentane (3 × 1.5 mL) and dried under vacuum at 60 °C to obtain 66 mg (0.022 mmol) of pure Mg$_2$Ba$_4$H$_9$N$_9$(benzene), in 34% yield, based on BaN$_2$. Yield was calculated on the basis that seven eq. of BaN$_2$ are needed to form one eq. of Mg$_2$Ba$_4$H$_9$N$_9$(benzene) complex. H NMR (600.13 MHz, benzene-$d_6$): δ = 3.41 (s, 4H, H), 3.36 (s, 4H, H), 3.29 (s, 2H, H), 1.35 (s, 1H, H), 0.50 (s, 18H, Si(CH$_3$)$_3$), 0.49 (s, 72H, Si(CH$_3$)$_3$), 0.43 (s, 36H, Si(CH$_3$)$_3$) ppm. $^{13}$C(H) NMR (150.92 MHz, benzene-$d_6$): δ = 6.76 (Si(CH$_3$)$_3$), 6.68 (Si(CH$_3$)$_3$), 6.33 (Si(CH$_3$)$_3$), 6.25 (Si(CH$_3$)$_3$) ppm. $^{29}$Si NMR (119.22 MHz, benzene-$d_6$): δ = −4.41 (Si(CH$_3$)$_3$), −5.07 (Si(CH$_3$)$_3$), −8.62 (Si(CH$_3$)$_3$), −16.49 (Si(CH$_3$)$_3$) ppm. FT-IR (ATR, pure): ν ~ 2943 (m), 2891 (w), 1477 (w), 1245 (m), 1107 (m), 1000 (m), 933 (m), 814 (s), 751 (m), 699 (m), 661 (m), 634 (m), 603 (m), 552 (m), 429 (w), 415 (w) cm$^{-1}$. Decomposition point: 210–212 °C. Elemental analysis calculated for Mg$_2$Ba$_4$H$_9$N$_9$(benzene) (MW 2385.95 g/mol) (isolated without drying step but after washing with pentane. Residual pentane was allowed to evaporate into the glovebox atmosphere): C 35.34, H 7.66, N 4.81; Found: C 35.29, H 7.28, N 4.66.

Synthesis of Mg$_2$Ba$_4$H$_9$N$_9$(benzene). (1). A mixture of Mg$_2$Ba$_4$H$_9$N$_9$(benzene) (11.4 mg) was washed with hexane (3 × 1 mL) and dried shortly under vacuum. The compound was poorly soluble in benzene-$d_6$. $^1$H NMR (600.13 MHz, benzene-$d_6$): δ = 5.45 (s, 4H, H), 5.44 (s, 4H, H), 4.65 (s, 2H, H), 4.42 (s, 2H, H), 3.82 (s, 1H, H), 0.52–0.45 (m, 90H, Si(CH$_3$)$_3$), 0.43 (m, 72H, Si(CH$_3$)$_3$) ppm. $^{13}$C(H) NMR (150.92 MHz, benzene-$d_6$): δ = −7.27 (Si(CH$_3$)$_3$), 7.05 (Si(CH$_3$)$_3$), 6.59 (Si(CH$_3$)$_3$), 6.37 (Si(CH$_3$)$_3$), 6.20 (Si(CH$_3$)$_3$) ppm. $^{29}$Si NMR (119.22 MHz, benzene-$d_6$): δ = −4.60 (Si(CH$_3$)$_3$), −5.58 (Si(CH$_3$)$_3$), −12.07 (Si(CH$_3$)$_3$), −16.58 (Si(CH$_3$)$_3$) ppm. FT-IR (ATR, pure): ν ~ 2942 (m), 2890 (w), 1747 (w), 1244 (m), 1142 (w), 1033 (m), 999 (m), 951 (s), 861 (m), 812 (s), 755 (s), 699 (s), 660 (s), 602 (m), 575 (m), 445 (w), 424 (w) cm$^{-1}$. Decomposition point: 240–241 °C. Elemental analysis calculated for Mg$_2$Ba$_4$H$_9$N$_9$(benzene) (MW 2671.32 g/mol): C 29.68, H 7.06, N 4.72; Found: C 29.85, H 7.05, N 4.36.

Synthesis of Mg$_2$Ba$_4$H$_9$N$_9$(benzene) (3). A mixture of BaN$_2$ (60.0 mg, 0.131 mmol) and MgN$_2$ (26.4 mg, 0.076 mmol) was suspended in 1.8 mL of hexane in a 20 mL vial (the chosen Mg/Ba ratio represents that in 3). The mixture was shortly heated to reflux to dissolve all solids. PhSiH$_3$ (30.7 mg, 0.284 mmol, 35 μL) was diluted in hexane (200 μL) and added dropwise to the stirring solution. The solution turned yellowish and was transferred to an NMR tube. The reaction mixture was heated to 70 °C for 12 h to obtain clear, colorless crystals. The crystals (11.4 mg) were washed with hexane (3 × 1 mL) and dried shortly under vacuum. The complex shows no solubility in cyclohexane-$d_8$, hot benzene-$d_6$, benzene-$d_6$/THF-$d_8$ mixture or THF-$d_8$. Its identity was repeatedly confirmed by cell parameter check using X-ray diffractometry. FT-IR (ATR, pure): ν ~ 2948 (m), 2929 (m), 1344 (w), 1245 (m), 1058 (w), 964 (s), 869 (s), 826 (s), 741 (s), 691 (m), 657 (m), 612 (m), 601 (m), 459 (m) cm$^{-1}$. Decomposition point: 278–279 °C. Elemental analysis calculated for Mg$_2$Ba$_4$H$_9$N$_9$(benzene) (MW 3768.91): C 22.95, H 6.47, N 4.46; Found: C 22.27, H 6.14, N 3.43.

Catalytic hydrogenation with MgN$_2$ and BaN$_2$ mixtures. The catalyst, MgN$_2$ (0.022 mmol, 20 μL), BaN$_2$ (0.022 mmol, 20 μL) or the mixture MgN$_2$/BaN$_2$ (0.011 mmol of each), was dissolved in dry toluene (1.0 mL) in a steel autoclave (15 mL) under an atmosphere of nitrogen and the substrate (0.110 mmol) was added to the solution. The tightly sealed autoclave was applied with hydrogen pressure (6 bar), stirred and quickly heated to the desired temperature (120 °C) in a heating block. The conversion after the given time was determined by subsequent GC-MS analysis of the quenched reaction mixture.

Catalytic hydrogenation with Mg$_2$Ba$_4$H$_9$N$_9$(benzene). (1). Complex 1 (10.0 mg, 5.1 μmol, 1.8 mol%) was dissolved in dry toluene (1.0 mL) in a steel autoclave (15 mL) under an atmosphere of pure nitrogen and the substrate (0.28 mmol) was added to the solution. The tightly sealed autoclave was applied with hydrogen pressure (6 bar), stirred and heated to the desired temperature (120 °C) quickly in a heating block. The conversion after the given time was determined by subsequent GC-MS analysis of the quenched reaction mixture. (NOTE: Complex concentration appears to be low at 1.8 mol%, however, normalized to 11 hydrides per complex, the total concentration of hydrides would be ~ 20 mol%)
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Conflict of Interest

The authors declare no conflict of interest.

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