



Alkali Metal (Li, Na, K, Rb, Cs) Mediation in Magnesium Hexamethyldisilazide [Mg(HMDS)₂] Catalysed Transfer Hydrogenation of Alkenes

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Though *s*-block organometallics are indispensable tools in synthetic chemistry, their impact in homogeneous catalysis has been small compared to that for transition metals. Surprisingly, however, Group 1 and 2 compounds have recently been utilised in hydroelementation catalysis. For example, transfer hydrogenation of alkenes to alkanes has been catalysed by Group 2 (Ca, Sr, Ba) bis-hexamethyldisilazides (HMDS), though reactions failed with magnesium. Stimulated by the knowledge that alkali metals can mediate applications of other compounds, this study reports successful catalytic transfer hydrogenation of alkenes with magnesium bis-hexamethyldisilazide when combined with alkali metals in heterobimetallic complexes. By screening all Group 1 metals (Li–Cs), the efficiency of these catalyses gives an indication of the relative power of the synergistic effect exerted on magnesium by the alkali metal. The Cs–Mg partnership shows the best efficiency with styrene, while K–Mg works best with 1,1-diphenylethylene.


Homogeneous hydrogenation is a synthetic procedure of fundamental importance to the chemical industry as well as being one of the most extensively studied reactions in homogeneous catalysis.^[1–3] Classic compounds such as the Wilkinson catalyst or the asymmetric hydrogenation catalysts from Noyori or Knowles exhibit excellent performance under mild conditions alongside high selectivity and good functional group tolerance.^[4–6] Besides the aforementioned benefits these catalysts are centred on late transition metals and the growing awareness of their toxicity and high costs has prompted chemists to seek to develop alternatives. Potential substitutes


for these precious metals are the elements of the *s*-block. They are (mostly) biocompatible, environmentally benign and with their high abundance in the crustal layer and oceans of earth, a low price per mole is guaranteed. Activity in this area has been steadily rising since the turn of the millennium with pioneering contributions by Harder, Hill, Okuda, Cheng and Stock, with several catalytic hydrogenations published.^[7–27]


In most cases the catalytically active species is a highly reactive metal hydride complex. The polar nature of the bond between the electropositive *s*-block metal and the electro-negative hydride ligand equips the latter with strong nucleophilicity, which facilitates the insertion into unsaturated bonds. Although, such high reactivity makes the isolation of these compounds challenging, suitable synthetic procedures are known. The first fully characterised magnesium hydride complex is an inverse crown reported in 2002 by the Mulvey group. Inverse crowns are bimetallic compounds in which cationic rings host anionic guests.^[28] This sodium-magnesium inverse crown was synthesised by heating a 1:1:3 mixture of *n*-butylsodium, *n*-sec-dibutylmagnesium and diisopropylamine in toluene resulting in a β-hydride elimination reaction of one of three isopropyl amide ligands, with the released hydride stored within the sodium and magnesium bimetallic scaffold (Scheme 1a).^[29,30] The analogous potassium magnesiate could be isolated via the same methodology using benzyl potassium as potassium source.^[31] A frequently applied synthetic route to hydride complexes is to exchange a reactive group from the metal precursor with a hydride ligand from the silane PhSiH₃ via σ-bond metathesis. Hill and co-workers used this procedure to good effect to access other heterobimetallic *s*-block hydrides. Their in situ generation of [KMg(^{*n*}Bu)(HMDS)₂] [HMDS=N(SiMe₃)₂] and subsequent treatment with PhSiH₃ resulted in a related inverse crown stabilised by bulky HMDS ligands (Scheme 1b).^[32] In 2018 Harder reported a simple alkene hydrogenation by AEM (HMDS)₂ (AEM=Ca, Sr, Ba) (Scheme 1c).^[13] Although no hydride complex was isolated from this study, the catalytically active species were proposed to be in situ generated hydride clusters reported two years earlier.^[33,34] The same compounds were proposed to catalyse alkene transfer hydrogenation (Scheme 1d). Deprotonation of 1,4-cyclohexadiene (1,4-CHD) by AEM(HMDS)₂ (AEM=Ca, Sr, Ba) gives an unstable Meisenheimer complex, which then undergoes β-hydride elimination to the corresponding hydride and benzene.^[14] A low-cost route to heterobimetallic *s*-block metal hydrides was presented very recently by the Guan group (Scheme 1e). Barely soluble potassium hydride was mixed together with AEM(HMDS)₂ (AEM=Mg, Ca) resulting in formation of an effective hydro-

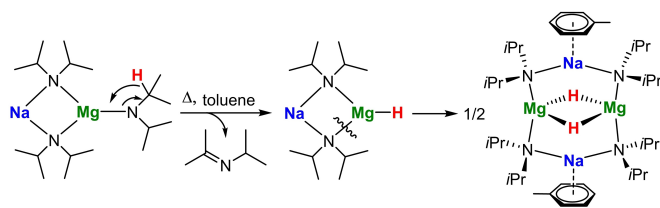
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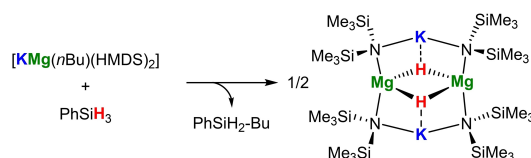
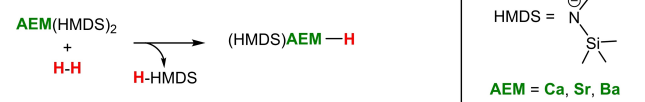
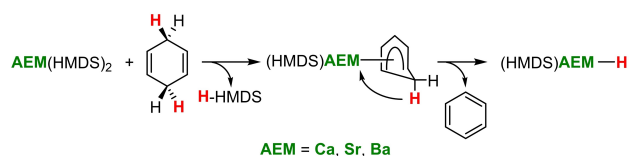
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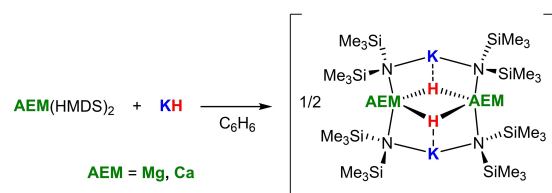
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a) β -hydride elimination

b) ligand exchange reaction

c) protonolyses with H₂d) β -hydride elimination via unstable Meisenheimer complex

e) degradation and activation of saline KH



Scheme 1. Various synthetic routes to s-block metal hydrides.

genation catalyst for olefins.^[35] Although the active species itself could not be isolated, the group found significant evidence that (in the case of magnesium) the compound is presumably the aforementioned $[KMg(H)(HMDS)_2]_2$ reported by Hill *et al.*^[32]

In our continued development of synergistic alkali-metal-mediated bimetallic chemistry of main group metals,^[36] we recently started to investigate their performance in catalysis. Our initial investigations have found that certain bimetallic systems can operate more efficiently compared to their monometallic counterparts. This is evident in aluminium catalysed hydroboration of aldehydes, ketones and imines, where the key reaction intermediate being more polarised in the bimetallic compound than in the neutral complex displays a marked higher reactivity.^[37] In lithium-aluminate catalysed hydrophosphination the lithium boosts the Lewis acidity of the reactive aluminium centre.^[38] A comprehensive summary about alkali metals in bimetallic catalysed reactions and their excep-

tional ability to mediate a plethora of reactions was recently reviewed separately by the Hevia and Mulvey groups.^[39,40]

Studies comprising the complete Group 1 (Li, Na, K, Rb and Cs) are still exceptionally rare in organometallic chemistry and lesser still is the mediation efficiency of the larger siblings rubidium and caesium probed. With their higher electropositivity and preference towards electron rich systems they have the potential in theory to exceed the reactivity limits of the smaller metals lithium, sodium and potassium. Herein, we report the catalytic transfer hydrogenation of alkenes by the whole series of alkali metal magnesiates including a detailed evaluation of the influence of the alkali metal supported by solid state structures. Moreover, we reveal the first example of a rubidium inverse crown of any type, the significance of which is magnified since it incorporates a rubidium hydride moiety.

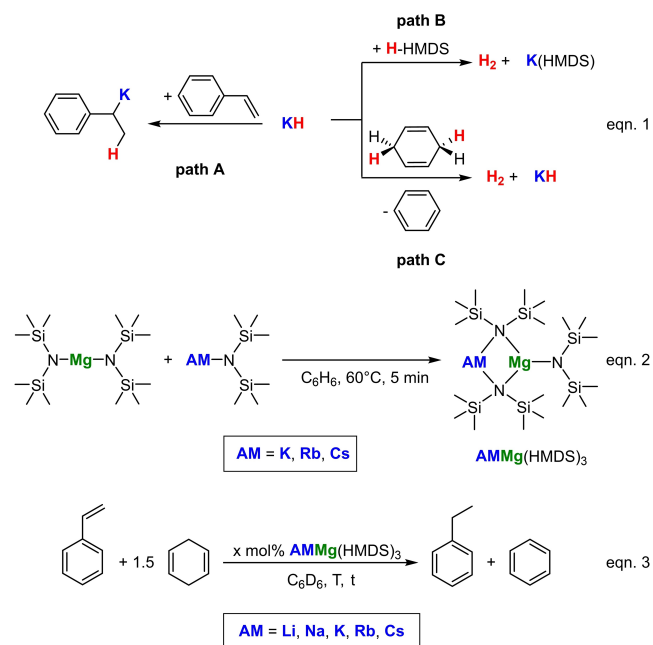
As alluded to in the introduction, in 2019 Harder and co-workers reported the transfer hydrogenation of olefins catalysed by the heavier alkaline earth metal bisamides AEM(HMDS)₂ (AEM=Ca, Sr, Ba). The best performance was obtained with the largest metal, while ascending the group the reactivity decreased from barium to calcium. It sparked our interest that magnesium showed no activity at all.^[14] Our first experiment was therefore to test the reduction of styrene to ethylbenzene with Mg(HMDS)₂ using 1.5 equivalents of 1,4-CHD as the hydrogen source. At 75 °C and 10 mol% catalyst loading no reaction was observed (Table 1, entry 1). Repeating the experiment with additional 10 mol% of K(HMDS) resulted in complete conversion to ethylbenzene within 3.5 h (Table 1, entry 2). To clarify whether a synergistic effect was in operation we tested K(HMDS) as the sole catalyst (Table 1, entry 3). Heating to 75 °C immediately produced strong gas evolution. ¹H NMR spectroscopy revealed that hydrogen was developed and only 36% of styrene was converted after 3 hours, although the majority of CHD was consumed. This modest yield is due to known competing side reactions (Scheme 2, eqn. 1). Thus, in situ generated potassium hydride can either insert into the olefinic double bond of styrene (desired-path A) or undergo two potential side reactions: It can either react with the prior formed protonated amine to generate hydrogen and starting material (side-path B) or dehydrogenate 1,4-CHD (side-path C). These side reactions appear less of a problem for the magnesiates, as the bimetallic compounds display high selectivity as well as high reactivity. The fact that both metal precursors on their own are not (or only partially) able to reduce the alkene catalytically indicates a synergistic effect in the bimetallic case.

To further investigate this phenomenon, we synthesised a series of magnesiates with the whole group of alkali metals (Li, Na, K, Rb, Cs). For the K, Rb and Cs congeners the synthetic procedure is similar to the synthesis of KMg(HMDS)₃ reported in 2002 by our group,^[41] but significantly benzene was used as solvent instead of toluene (Scheme 2, eqn. 2). The advantage of benzene is that the products exhibit solubility at higher temperatures (e.g. 60 °C), but nearly no solubility at room temperature. This facilitates product isolation after filtration giving the target tris-HMDS compounds in good yields as white solids. Working with isolated, rather than in situ generated, mixed-metal compounds should be advantageous since inac-

Table 1. Catalytic alkene transfer hydrogenation.^[a]

Entry	Catalyst	x [mol%]	Substrate	t [h]	conv. [%]	Yield [%]
1	Mg(HMDS) ₂	10	Styrene	16	0	0
2	KMg(HMDS) ₃	10	Styrene	3.5	> 98	> 98
3	K(HMDS)	10	Styrene	3	36	36
4	KMg(HMDS) ₃	5	Styrene	7	> 98	> 98
5	KMg(HMDS) ₃	1	Styrene	14	> 98	> 98
6	KMg(HMDS) ₃	10	Styrene	16	75 ^[b]	75 ^[b]
7	KMg(HMDS) ₃	10	Styrene	16	29 ^[b,c]	15 ^[b,c]
8	NaMg(HMDS) ₃	10	Styrene	16	4	4
9	LiMg(HMDS) ₃	10	Styrene	16	0	0
10	RbMg(HMDS) ₃	10	Styrene	0.75	> 98	93
11	CsMg(HMDS) ₃	10	Styrene	0.5	> 98	89
12	CsMg(HMDS) ₃	5	Styrene	0.5	> 98	92
13	CsMg(HMDS) ₃	1	Styrene	1.5	> 98	90
14	KMg(HMDS) ₃ + 18-crown-6	10	Styrene	0.5	> 98	17
15	KMg(HMDS) ₃	10	1,1-DPE	1.5	> 98	> 98
16	RbMg(HMDS) ₃	10	1,1-DPE	2.25	> 98	> 98
17	CsMg(HMDS) ₃	10	1,1-DPE	2.25	> 98	96
18	KMg(HMDS) ₃ + 18-crown-6	10	1,1-DPE	1	> 98	76
19	RbMg(HMDS) ₃ + 18-crown-6	10	1,1-DPE	1	11	9
20	CsMg(HMDS) ₃ + 18-crown-6	10	1,1-DPE	2.25	37	30

[a] x = catalyst loading; [Substrate] = 0.4 mmol (for x = 10 and 5) and 0.5 mmol (for x = 1) in C₆D₆, T = 75 °C. Reaction time for essentially full conversion (> 98%) have been determined by ¹H NMR spectroscopy via recording a spectrum during the catalysis every 5 minutes. For slower reaction rates the conversion and yield were determined after 16 hours. Yields were obtained by integration against internal standard. [b] at 60 °C [c] at 60 °C in THF-d₈



Scheme 2. Reaction of in situ generated KH with styrene [path A]; H-HMDS [path B] or 1,4-CHD (path C) (eqn. 1); Syntheses of catalysts AMMg(HMDS)₃ [AM=K, Rb, Cs] (eqn. 2); catalytic transfer hydrogenation of styrene with AMMg(HMDS)₃ [AM=Li–Cs] as catalysts (eqn. 3).

curacies in stoichiometry and thus the unwanted side reactions (Scheme 2, eqn. 1, path B + C) may be diminished. We selected the reduction of styrene with 1.5 equivalents of CHD as our benchmark reaction (Scheme 2, eqn. 3) and started to vary the reaction conditions. Lowering the KMg(HMDS)₃ loading to 5 or 1 mol% resulted in prolonged reaction time and gave complete conversion at 75 °C after 7 (Table 1, entry 4) or 14 hours (Table 1, entry 5), respectively. Cooling from 75 °C to 60 °C gave

after 16 hours 75% conversion in benzene (Table 1, entry 6) and 29% conversion in THF (Table 1, entry 7), indicating a negative effect of a polar donor solvent. Additionally, in THF oligomerization of styrene was observed lowering the yield of ethylbenzene to 15%. A significant effect was exerted on the reactivity by changing the alkali metal. Using the smaller, less electropositive metals sodium and lithium gave after 16 hours only 4% (entry 8) and no conversion at all (entry 9), respectively. A plausible factor is that a larger alkali metal interacts more with the π-system of the aromatic ring as was described for a series of monomeric alkali metal benzyl complexes by Robertson and co-workers.^[42,43] This trend has also been observed for the catalytic intramolecular hydroalkoxylation reactions utilizing other alkali-metal magnesiates as catalysts.^[44] As a result, the conjugated double bond is polarised and the insertion of the nucleophilic hydride becomes more favourable. Prompted by the reactivity enhancement seen on descending the first three alkali metals we eagerly investigated the behaviour of the two larger alkali metals rubidium and caesium. We observed that the trend is followed for the whole group. Thus, the rubidium magnesiate converted all styrene within 45 minutes (Table 1, entry 10). The enhanced reactivity comes along with a small but not negligible drawback: besides the high yield of 93% ethylbenzene a small amount of oligomerization was observed. The best performance came when using the largest, most electropositive (non-radioactive) alkali metal. Full conversion with 10 or 5 mol% of CsMg(HMDS)₃ at 75 °C was observed after just half an hour (Table 1, entries 11 and 12). Decreasing catalyst loading to 1 mol% led to an extension of reaction time to only 1 hour and 30 minutes (entry 13). The increased reactivity resulted again in a small decrease of yield (89–92% ethylbenzene) alongside minor oligomerization. Contrary to our observations, Guan reported that the hydrogenation of styrene with KH and Mg(HMDS)₂ under 6 bar of H₂ pressure gave only 5% of

ethylbenzene since most of the substrate immediately undergoes polymerization.^[35] Assuming that the active catalyst is in both cases a hydride complex, a reasonable explanation is that the protonation of the alkyl intermediate is facilitated with the prior formed H–HMDS ($pK_a \approx 26$)^[45] than with H_2 ($pK_a \approx 49$)^[46] and thus liberates the product prior to C–C bond formation. In all catalytic experiments using potassium, rubidium or caesium magnesiates only small amounts of H_2 were observed as side product, indicating that the hydrogenation (Scheme 2, eqn. 1, path A) is strongly favoured over the dehydrogenation (Scheme 2, eqn. 1, path B). A similar observation was made by Harder and co-workers with $Ba(HMDS)_2$ as catalyst.^[14] To further investigate the influence of the alkali metal we added 18-crown-6 to a catalytic reaction with $KMg(HMDS)_3$ (Table 1, entry 14). As crown ethers are well known to sequester alkali metals and form solvent-separated ion pairs we expected a decrease or even shutdown of reactivity,^[47] though it is known that 18-crown-6 does not always completely fill the coordination sphere of potassium.^[44] Surprisingly the substrate was fully consumed within only 30 minutes, however, only 17% of the styrene was converted to ethylbenzene while the rest underwent oligomerization. A possible explanation is that after the addition of Lewis bases like THF or a crown ether smaller aggregates are formed resulting in an increased reactivity.^[15] Again there is no sign of H_2 , underlining the higher selectivity of the ate complexes by suppressing the dehydrogenation. To circumvent the undesired side reaction, we changed the substrate to 1,1-diphenylethylene (DPE) and investigated its reduction with the larger alkali metal (K, Rb, Cs) catalysts. Here, the reactivity follows an opposite trend. For potassium, full conversion of the substrate was obtained after 1.5 hours (Table 1, entry 15); whereas in each case rubidium and caesium catalyst needed 2 hours and 15 minutes (Table 1, entry 16 and 17, respectively). Addition of 18-crown-6 shortened the reaction time for potassium to 1 hour (Table 1, entry 18), but almost shutdown the reactivity for rubidium (11% conversion after 1 hour, Table 1, entry 19) and caesium (37% conversion after 2.25 hours, Table 1, entry 20). Although DPE was fully consumed with $KMg(HMDS)_3/18\text{-crown-6}$, only 76% yield was obtained. A new set of signals in the $^1H\text{-NMR}$ spectrum reveals the presence of a side product (see Supporting Information Figure S20), which might be formed via Brønsted base catalysed C–C addition. The desired product, 1,1-diphenylethane can be deprotonated at the benzylic position and add to the double bond of DPE. An experiment with twice the amount of DPE gave full consumption of the substrate although an under stoichiometric amount of the hydride source (CHD) was present. HMDS based catalysts have been proven to be efficient catalysts in Brønsted base catalysed C–C addition in the past,^[40] for example the Guan group reported benzylic C–H bond addition of diarylmethanes to styrenes catalysed by our $KZn(HMDS)_2(\text{benzyl})$ system,^[48] which is ultimately formed via benzylic cleavage of the methyl group of toluene by $KZn(HMDS)_3$.^[49]

During the catalyses with $AMMg(HMDS)_3$ ($AM=Na, K, Rb, Cs$) further side products were observed: 1,3-cyclohexadiene was found as a result of isomerization of 1,4-cyclohexadiene. For

$RbMg(HMDS)_3$ and $CsMg(HMDS)_3$ also cyclohexene was detected. On the positive side this indicates that the substrate scope might be extended to more challenging-to-hydrogenate alkenes, on the negative side reduction of CHD and substrate would compete with each other. Attempted reduction of 1-hexene, a terminal, non-activated alkene, resulted mainly in the formation of H_2 and reduction of a small quantity of cyclohexadiene to cyclohexene (see Figure S23).

Intriguingly, during the reduction of styrene with $NaMg(HMDS)_3$ we could observe precipitation of crystalline material at the liquid/gas interface. The crystals could be identified via X-ray diffraction experiments as the hydride complex $[(NaMg(HMDS)_2H)_2]_{\infty}$, which is proposed to be an intermediate in the catalytic cycle. Prompted by this observation we tried to rationally synthesise this compound. Thus, we suspended $NaMg(HMDS)_3$ with 10 equivalents of 1,4-CHD in benzene. Heating at $60^\circ C$ (without stirring and placing the flask into the oil bath where a quarter of the suspension is covered by oil) gave the desired compound after 2 days as colourless crystals in 72% yield. With this result we have uniquely managed to isolate an intermediate in the catalytic transfer hydrogenation with CHD and thus give support to the proposed catalytic cycle of Harder *et al.*^[14] Next, we investigated whether this synthetic procedure is suitable for the other alkali metal magnesiates. Carrying out the reaction with $KMg(HMDS)_3$ was also successful (59% yield). However, small amounts of H_2 were observed in the $^1H\text{-NMR}$ spectrum, indicating that the formed hydride complex $[KMg(HMDS)_2H]_2$ can undergo the unwanted side reactions (Scheme 2, eqn. 1, path B + C) to H_2 and starting material. For larger alkali metal magnesiates this procedure seems to be unsuitable, since due to the higher reactivity of the hydride complexes $[AMMg(HMDS)_2H]_2$ ($AM=Rb, Cs$) the side reactions (Scheme 2, eqn. 1, path B + C) becomes more dominant. Moreover, reduction of CHD to cyclohexene was observed in both cases, implying that the desired hydride complexes were consumed during the reaction (see Supporting information Figure S24). We therefore investigated the widely used ligand exchange reaction with a commonly utilised hydride donor source. Treatment with $PhSiH_3$ at $60^\circ C$ in C_6H_6 gave full consumption of $RbMg(HMDS)_3$ and $CsMg(HMDS)_3$ and formation of an insoluble white powder alongside ligand exchange products (e.g. $PhSiH_2(HMDS)$, $PhSiH(HMDS)_2$) as revealed by $^1H\text{-NMR}$ spectroscopy. However, no evidence for a hydride compound of the form $[(AM)Mg(HMDS)_2H]_2$ ($AM=Rb, Cs$) can be found in the $^1H\text{-NMR}$ spectra. The powder, which is even insoluble in THF, reacts immediately with *isopropanol* under strong gas evolution and changes instantly a colourless solution of DPE in C_6H_6 to dark red, which is likely to be an indicator for the presence of a reactive hydride component. Increasing the solubility with polydentate donors such as *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) or *N,N,N',N'*-tetramethylethylenediamine (TMEDA) remained unsuccessful. On one occasion we could isolate a single crystal during the reaction of $RbMg(HMDS)_3$ and $PhSiH_3$ in C_6H_6 at $60^\circ C$, which was formed via convection (placing the flask into the oil bath in which a quarter of the suspension is covered by oil). X-Ray diffraction experiments confirmed the presence of the hydride

compound $[(C_6H_6)RbMg(HMDS)_2H]_2$. However, it is not clear if the composition of the white powder resembles solely this structure since characterization by other methods was not possible and additionally multiple exchange of a HMDS group with a hydride can occur. Hill *et al.* reported this phenomenon in the reaction between $[NaMg(^tBu)(HMDS)_2]$ and $PhSiH_3$.^[32] Instead of a complex consisting of a sodium to hydride ratio of 1:1, a remarkable compound with six sodium and ten hydride moieties was obtained. Considering our sodium hydride complex $[(NaMg(HMDS)_2H)_2]_\infty$ consists of a 1:1, sodium to hydride ratio, we want to emphasise the importance of the hydride source. In comparison to $PhSiH_3$, where several ligand exchanges can occur, the usage of CHD provides a more controlled reaction.

X-ray diffraction experiments revealed the polymeric nature of $[(NaMg(HMDS)_2H)_2]_\infty$. The infinite inverse crown is built up of centrosymmetric dimer units, connected via four anagostic C...Na interactions $[Na...C=3.008(8) \text{ \AA}]$ between a $SiMe_3$ group and a sodium to generate a one-dimensional polymeric chain. These intermolecular contacts are slightly shorter than in the solvent-free inverse crown $[NaMg(DA)_2H]_2$ (DA = diisopropylamide) [mean $Na...C=3.070 \text{ \AA}$].^[30] Each symmetry-equivalent dimer forms an 8-membered ring in a chair conformation with a planar $N1Mg1N2...N1MgN2$ moiety and a tilted chair-back (defined by $N1NaN2$ plane) at an angle of $139.35(10)^\circ$ with respect to the $N1MgN2...N1MgN2$ plane, which is less obtuse than in $[NaMg(DA)_2H]_2$ [$151.33(19)^\circ$ and $143.48(14)^\circ$]^[30] and the arene-solvated analogue $[NaMg(DA)_2H(toluene)]_2$ [$153.5(2)^\circ$].^[29] Hydride ligands are located above and below the chair seat and sit closer coordinated to Mg [mean $Mg-H=1.915 \text{ \AA}$] than to Na [$Na-H=2.49(2) \text{ \AA}$]. The latter distance is shorter than in the DA-stabilised compounds [with toluene: $2.68(3) \text{ \AA}$;^[29] solvent free: mean = 2.58 \AA]^[30] but longer than in the heterododecametallic hydride cluster reported by Hill and co-workers (mean = 2.40 \AA)^[32] and lies close to the value in NaH (2.44 \AA).^[50] The two nitrogen atoms of the HMDS ligands complete the highly distorted tetrahedral coordination around the Mg (mean = 106.6° ; range = $78.0^\circ-133.53^\circ$) with an average $Mg-N$ distance of $2.0731(11) \text{ \AA}$, which is comparable to that in the aforementioned $NaMg$ -inverse crown hydride complexes (mean = 2.062 \AA).^[29,30,32] Due to the polymeric nature of $[(NaMg(HMDS)_2H)_2]_\infty$ and its resulting poor solubility in hydrocarbon and aromatic solvents, NMR spectroscopic investigations were carried out in $THF-d_8$. Similar to the hydride compounds published by Hill, in the 1H NMR spectrum multiplets are observed as well as for the HMDS groups (-0.20 – 0.06 ppm) and the hydrides show (2.93 – 3.07 ppm), suggesting that THF is interfering with the symmetrical structure observed in the solid state. The ^{13}C NMR spectrum shows three resonances for the carbons of the HMDS groups between 5.5 – 5.95 ppm.

The molecular structure of the potassium analogue $[(C_6H_6)KMg(HMDS)_2H]_2$ (note: there is additional C_6H_6 of crystallisation present in the crystal lattice) is very similar to the one published by Hill and co-workers,^[32] but there is one distinct difference: whereas the latter builds up to a polymeric, 2 dimensional framework via four anagostic C...K interactions between $SiMe_3$ groups and a potassium, in our version each dimer is connected

via interactions of each potassium with co-coordinated benzene. $[(C_6H_6)KMg(HMDS)_2H]_2$ shows poor solubility in C_6D_6 but dissolves well in toluene- d_8 . The hydride signal appears at 3.86 ppm in the 1H NMR spectrum and the HMDS groups were detected at 0.30 ppm (1H NMR) and 7.21 ppm (^{13}C NMR).

The structure of the first rubidium inverse crown $[(C_6H_6)RbMg(HMDS)_2H]_2$ (note: there is additional C_6H_6 of crystallisation present in the crystal lattice) is isostructural to $[(C_6H_6)KMg(HMDS)_2H]_2$ (Figure 1). It is a one-dimensional, polymeric chain, which is built up by two crystallographically independent, centrosymmetric inverse crowns connected via $Rb...C$ π -arene interactions with a benzene ring. Thereby, one molecular unit interacts via η^6 -coordination with benzene [range $Rb1...C=3.623(4) \text{ \AA}$ – $3.700(5) \text{ \AA}$; mean = 3.660 \AA], while the other connects the moieties by a single metal-carbon contact [$Rb2...C=3.710(5) \text{ \AA}$]. As already observed for inverse crown hydride complexes with smaller alkali metals, the dimers form 8-membered rings in a chair conformation with a tilted chair-back (NRbN plane) at an angle of $157.17(13)^\circ$ and $145.47(12)^\circ$ with respect to the $NMgN...NMgN$ plane. The major difference between the two dimers is the connection to the hydride ligands. Whereas $Mg-H$ bond lengths deviate by only 0.03 \AA [$Mg1-H1=1.91(3) \text{ \AA}$; $Mg2-H2=1.88(3) \text{ \AA}$], a more significant difference of 0.21 \AA is present in the $Rb-H$ distance ($Rb1-H1=3.136(5) \text{ \AA}$; $Rb2-H2=3.347(5) \text{ \AA}$; saline $RbH: 3.02 \text{ \AA}$)^[50] reflecting the higher coordination of $Rb2$ with the benzene ring (η^6 versus η^1). This also leads to differences in

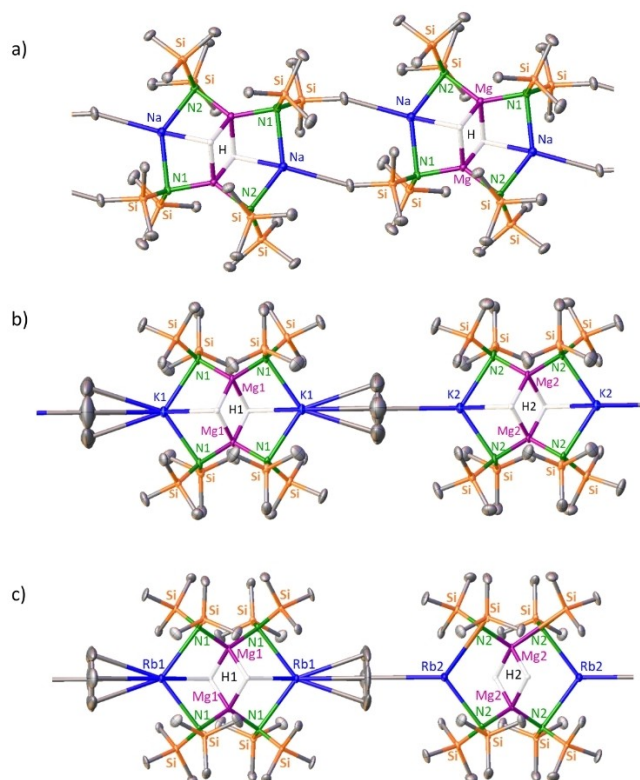


Figure 1. Molecular structure of a) $[(NaMg(HMDS)_2H)_2]_\infty$; b) $[(C_6H_6)KMg(HMDS)_2H]_2$; c) $[(C_6H_6)RbMg(HMDS)_2H]_2$. All hydrogen atoms except hydrides and (selected) co-crystallised C_6H_6 were omitted for clarity.

angles around the tetrahedral distorted magnesium centres (see Table 2). Besides the interaction with the benzene, each rubidium is coordinated by two nitrogen atoms [mean = 3.052 Å] and show two additional anagostic interactions to carbons of one HMDS group with a short and long contact (see Table 2). The Rb–N distances are longer than in dimeric [Rb(HMDS)₂] [Rb–N = 2.878(2) Å]^[51] and compare better to the bond length in [{Rb(HMDS)(ferrocene)}₂]_∞ (2.9724(16) Å),^[52] where an aromatic Cp ring is coordinated to the metal.

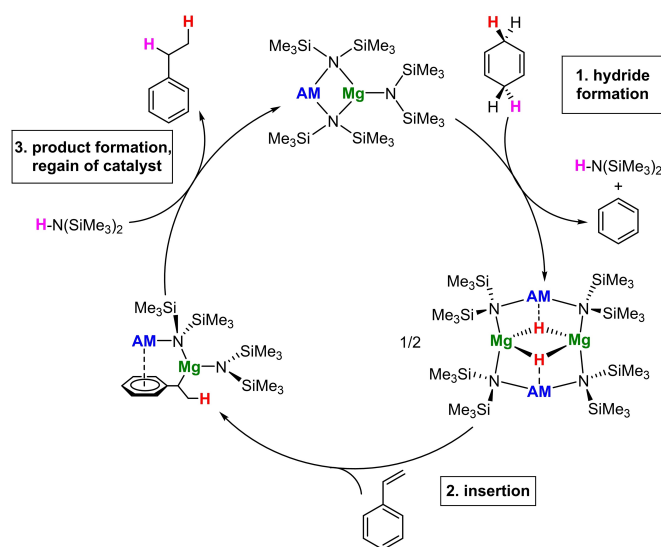
To shed more light on the mechanism we carried out catalytic experiments with the isolated inverse crown hydride complex [(C₆H₆)KMg(HMDS)₂H]₂. Attempted reduction of styrene resulted in immediate precipitation of a white solid, which is the result of polymerization of the substrate. This observation highlights the importance of the HMDS group, since the acidic proton of the liberated H–HMDS enables protonation of the alkyl intermediate and prevents the chain growth. Changing the substrate to 1,1-DPE gave full conversion of the substrate

after 3 hours in a quantitative yield (see Figure S25). We attribute the prolonged reaction time to the low solubility of the hydride complex in benzene. In Scheme 3 a catalytic cycle, adapted from the alkaline earth metal transfer hydrogenation from Harder, is proposed. The tris-HMDS complex deprotonates CHD under the liberation of H–HMDS and formation of an unstable Meisenheimer complex, which immediately undergoes β-hydride elimination to form the catalytically active mixed metal hydride compound and benzene. The formation of the latter is proposed to be the driving force, since creating an aromatic compound is energetically favoured. The hydride complex then undergoes insertion into the double bond of styrene to form an intermediate heterobimetallic alkyl complex, which upon deprotonation of the previously liberated H–HMDS forms the desired product (ethylbenzene) and regenerates the catalyst again to complete the cycle.

In summary, we reported the first example of transfer hydrogenation of alkenes with heterobimetallic s-block com-

Table 2. Selected Bond Distances (Å) and Angles (°) in the Crystal Structures of heterobimetallic hydrides.

Alkali metal	Na	K (this work)	K (Hill et. al.) ^[32]	Rb
mean Mg–H	1.915(20)	1.88(4)	1.86(2)	1.895(20)
mean Mg–N	2.0731(14)	2.070(2)	2.0691(14)	2.0715(20)
mean AM–N	2.49(2)	2.99(6)	2.86(2)	3.245(20)
mean AM–N	2.4971(15)	2.922(2)	2.9104(13)	3.052(2)
mean AM...C(SiMe ₃)	3.008(8)		3.4247(19)	3.388(3)
mean AM...C(C ₆ H ₆)				3.660(4)
Fold angle	139.35(10)	145.81(14)	140.34(5)	3.711(7)
N–Mg–N	133.52(2)	125.07(14)	124.97(5)	145.47(12)
N–Mg–H	112.9(7) 102.0(6)	115.5(18) 106.7(19)	117.5(7) 105.6(7)	122.90(14)
H–Mg–H	78.0(14)	78(3)	74.4(9)	124.11(14)
				105.8(13)
				109.09(13)
				117.5(12)
				113.6(12)
				79(2)
				78(2)



Scheme 3. Proposed catalytic cycle for the transfer hydrogenation of styrene with alkali metal magnesiate.

plexes where the whole series of alkali metal magnesiate (Li–Cs) was investigated. A powerful synergistic effect is present between the alkali metal and magnesium as the monometallic compounds on their own are not or only partially capable of performing this transformation. Clearly the bimetallic partnership brings in advantageous features unavailable to using magnesium on its own: the alkali metal gives anionic activation to the magnesium as it forms a charged ate complex as opposed to a neutral species, and the divergence in the performance of the alkali metals intimates that the propensity for π-coordination favoured by the larger alkali metals can be another advantageous feature. This is consistent with the reduction of styrene being better with increasing size of the alkali metal. Since addition of 18-crown-6 boosted the reactivity for the potassium analogue but impeded the reaction for the rubidium and caesium compounds, other more subtle factors must also be involved. A novel synthetic procedure to heterobimetallic hydride complexes facilitated the isolation and characterization of complexes containing a sodium hydride or a

potassium hydride moiety, which gave support for the catalytic cycle and for the first time the synthesis and molecular structure of a rubidium inverse crown incorporating a hydride group is reported. As the most potent catalysts were capable of reducing the hydride source CHD, we are currently investigating their performance in the hydrogenation of olefins with H₂.

Experimental Section

General Procedures

Hexane, THF, C₆H₆ and toluene were dried by heating to reflux over sodium benzophenone ketyl and then distilled under nitrogen prior to use. C₆D₆, toluene-d₈ and THF-d₈ were degassed by freeze-pump-thaw methods and stored over activated 4 Å molecular sieves. TMEDA, PMDETA, Styrene, 1,1-Diphenylethylene and HMDS(H) were dried over CaH₂, distilled and stored over activated 4 Å molecular sieves prior to use. Li(HMDS), Na(HMDS), K(HMDS), MgⁿBu₂ and 18-crown-6 were purchased from commercial sources and used as received, unless stated otherwise. NMR spectra were recorded on a Bruker AV3 or AV 400 MHz spectrometer operating at 400.13 MHz for ¹H, 100.62 MHz for ¹³C. All ¹³C spectra were proton decoupled. ¹H and ¹³C{¹H} chemical shifts are expressed in parts per million (δ, ppm) and referenced to residual solvent peaks. HSQC measurements were recorded on an AV 400 MHz spectrometer operating at 400.13 MHz, using the pulse program hsqcedetgp. Crystallographic data for compounds [(NaMg(HMDS)₂H)₂]_∞, [(C₆H₆)KMg(HMDS)₂H]₂ and [(C₆H₆)RbMg(HMDS)₂H]₂ were collected on an Oxford Diffraction Gemini S instrument with graphite-monochromated Cu–Kα (λ 1.54184 Å) radiation. All structures were solved and refined to convergence against F₂ for all independent reflections by the full-matrix least-squares method using SHELXL-2018 implemented within WINGX.^[53,54] All non-hydrogen atoms were refined using anisotropic thermal parameters. Selected crystallographic data are shown in Tables S1, S2 and S3 and full details in cif format are available from CCDC (2058374–2058376). Data used within this publication can be accessed at <https://doi.org/10.15129/60411ebee3a1-41f8-a6b3-947815e05b86>.

Experimental Procedure and Product Characterisation

All reactions and manipulations were performed under a protective argon atmosphere using standard glovebox techniques, or under a protective nitrogen atmosphere using standard Schlenk techniques. Mg(HMDS)₂ was prepared by heating a commercially available heptane solution of MgⁿBu₂ with 2 molar equivalents of (HMDS)H for 2 h at 60 °C. Rb(HMDS) and Cs(HMDS) was prepared according to the literature procedure.^[55] The ate complexes AMMg(HMDS)₃ were prepared by a modified literature procedure where toluene was replaced by benzene as a solvent.^[41]

Synthesis of [NaMg(HMDS)₂(H)]_∞

NaMg(HMDS)₃ (0.678 g, 1.23 mmol) was dissolved in C₆H₆ (10 mL) and 5 equivalents of 1,4-cyclohexadiene (0.493 g, 582 μL, 6.15 mmol) were added. After heating the reaction mixture for 2 days at 60 °C colourless crystals were formed, which could be isolated by removal of the mother liquor and subsequent washing with C₆H₆ (3 mL). Yield: 72% (0.327 g, 0.886 mmol).

¹H NMR (400 MHz, THF-d₈, 25 °C): δH = 0.20–0.58 (m, 36 H, Si(CH₃)₃), 2.93–3.07 (m, 1 H, Mg–H). ¹³C NMR (100 MHz, THF-d₈, 25 °C): δC = 5.5–6.0 (m, Si(CH₃)₃).

Synthesis of [(C₆H₆)KMg(HMDS)₂H]₂

KMg(HMDS)₃ (0.531 g, 0.975 mmol) was suspended in C₆H₆ (10 mL) and 5 equivalents of 1,4-cyclohexadiene (0.390 g, 436 μL, 4.86 mmol) were added. After heating the reaction mixture at 40 °C for one day all solvents were removed via cannula filtration (to get rid of the developing HMDS(H)). Subsequently, C₆H₆ (10 mL) and 5 equivalents of 1,4-cyclohexadiene (0.390 g, 436 μL, 4.86 mmol) were added and the reaction mixture was stirred for another day at 40 °C. This procedure was repeated once again and after another day at 40 °C the desired product could be isolated as colourless crystals in 59% yield (0.222 mg, 0.575 mmol).

¹H NMR (400 MHz, Toluene-d₈, 25 °C): δH = 0.20–0.58 (m, 36 H, Si(CH₃)₃), 2.93–3.07 (m, 1 H, Mg–H). ¹³C NMR (100 MHz, Toluene-d₈, 25 °C): δC = 7.2 (m, Si(CH₃)₃).

Catalytic reactions

The catalyst (0.04 mmol for 10 mol%; 0.02 mmol for 5 mol%; 0.005 mmol for 1 mol% catalyst loading) was filled into a NMR J-Youngs tube and 500 μL of the desired solvent (C₆D₆ or THF-d₈) was added. The alkene (0.4 mmol for 10 and 5 mol% catalyst loading; 0.5 mmol for 1 mol% catalyst loading), 1.5 eqv. of 1,4-cyclohexadiene (0.6 mmol for 10 and 5 mol% catalyst loading; 0.75 mmol for 1 mol% catalyst loading) and a suitable standard (Si(SiMe₃)₄ or Adamantane 0.01 mmol) were added and the sealed NMR tube was heated in NMR spectrometer at the desired temperature for 16 h or until completion was observed (a spectrum was measured every 5 minutes).

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Conflict of Interest

The authors declare no conflict of interest.

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