Metathesis

Heterobimetallic s-Block Hydrides by σ-Bond Metathesis

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Abstract: Reactions between PhSiH₃ and alkali-metal diamidoalkylmagnesiates ([M{N(SiMe₃)₂}₂MgBu], M=Li, Na, K) provide either selective alkyl metathesis or the formation of polyhydride aggregates contingent upon the identity of the Group 1 metal. In the case of [M{N-(SiMe₃)₂}₂MgBu], this reactivity results in a structurally unprecedented dodecametallic decahydride cluster species.

Although ionic structures dominate the chemistry of saline s-block hydrides, MH_n (Group 1 n = 1; Group 2 n = 2),^[1] a variety of oligomeric molecular hydrides derived from the elements of Groups 1 and 2 have now been structurally characterized. Related molecular species are postulated intermediates in a variety of H–C^[2] Si–N^[3] Si–O^[4] and B–N^[5] bond-forming reactions and, as a result of the relatively high hydrogen weight percentages of the lighter congeners (LiH 12.7%;^[6] MgH₂ 7.6%), are of interest in potential hydrogen-storage applications.^[7] Recent calculations, for example, have suggested that a reduction in cluster size of $(MgH_2)_n$ (n < 19) can lower the otherwise impractically high hydrogen-release temperature of MgH₂ resulting from its large lattice energy (2791 kJ mol⁻¹) relative to the bulk metal.^[8,9] Consequently, a variety of higher magnesium hydride clusters have now been synthesized through reaction of organomagnesium compounds with phenylsilane. The first hydridemagnesium cluster, [(IPr)₂Mg₄H₆{N(SiMe₃)₂}₂] rich [IPr= (HCN{2,6-*i*Pr₂C₆H₃})₂C:] (I), utilized the kinetic stability provided by bulky amido and N-heterocyclic carbene ligands with a magnesium to hydride ratio of 1:1.5,^[10] whereas the utility of polynucleating β -diketiminate ligands in the formation of even higher nuclearity magnesium hydrides has been demonstrated through the isolation of $[(PARA)_3Mg_8H_{10}]$ (PARA = 1,4-C₆H₄{2,6 $iPr_2C_6H_3NC(Me)C(H)C(Me)N_2)^{[11]}$ and $[{NN-(MgH)_2}_2]$ (NN = {2,6 $iPr_2C_6H_3NC(Me)C(H)C(Me)N_2)$.^{[12}

Structurally characterized molecular hydrides of Group 1 are limited to the photolytically generated "super-aggregate", [(tBuOLi)₁₆(LiH)₁₇],^[13] and Stasch's recent synthesis of spectacu-



lar phosphinoamide-, for example (II), and pyrazolate-supported clusters.^[14,15] These latter species, containing up to 37 lithium centres, are again the outcome of rational reactions between a reactive metal precursor and a silane hydride source. In contrast to these advances, the sole prior examples of molecular hydrides derived from the heavier members of Group 1 are provided by mixed metal "ate" structures,^[16,17] most notably the "inverse crowns" (III–V) reported by Mulvey and coworkers, which are thought to form via serendipitous β -hydride elimination reactions of *iso*-propyl amide residues.^[17] Herein, we demonstrate a rational approach to heterobimetallic s-block hydrides, in which the molecularity of the target species is a consequence of the alkali-metal identity.

Extensive work by Mulvey and co-workers has demonstrated the enhanced reactivity of heterobimetallic s-block amides of the form $[M(NR_2)_2M'NR_2]$ (M = Group 1 metal; M' = Group 2 metal) in a variety of contexts.^[18] Seeking to capitalize on this foundation, our synthetic approach to heterobimetallic hydrides has focused on mixed s-block amidoalkyls of the form [M{N(SiMe₃)₂}₂MgBu], the first related examples of which have only recently appeared in the literature.^[19] The bulky hexamethyldisilazide ligand was utilized for both its relevance in catalysis and its steric characteristics, whereas the reactive alkyl group was predicted to allow selective reactivity with phenylsilane. Addition of one equivalent of $[MN(SiMe_3)_2]$ (M = Li, Na, K) to an equimolar mixture of dibutyImagnesium and hexamethyldisilazane provided the in situ formation of the desired [M{N- $(SiMe_3)_2$ MgBu] species [M = Li (1), Na (2), K (3)] prior to the addition of one equivalent of phenylsilane in [D₈]toluene. The ¹H NMR spectrum resulting from the reaction of compound **3** under these conditions suggested the formation of PhSi(H)₂Bu and three broad, metal-bound hexamethyldisilazide environments between δ = 0.16–0.36 ppm, indicative of Mg–C/Si–H σ bond metathesis, as well as a new signal at 3.66 ppm, which corresponded to a single proton by integration.

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Preparative scale repetition of this reaction in toluene gave crystals of compound 4 suitable for single-crystal X-ray diffraction analysis, the results of which are shown in Figure 1. Although this species is structurally analogous to the previously reported hydride, V, its synthesis is the result of selective Mq-C/Si–H σ -bond metathesis of the more reactive and less sterically encumbered alkyl group of compound 3. The bond length and angle data of 4 are also similar to those observed for the analogous di-iso-propylamide analogue V with some notable elongation of bonds as a consequence of the more sterically encumbered hexamethydisilazide ligands. The previously unattributed peak at $\delta = 3.66$ ppm in the ¹H NMR spectrum of 4 also corresponded to the chemical shift of the hydride peak of V and was, thus, assigned as the bridging hydride resonance. The persistence of the solid-state structure in aromatic solvents was corroborated by the observation of a single-diffusion coefficient in the ¹H diffusion-ordered spectroscopy (DOSY) NMR spectrum for both the hydride and silylmethyl signals, whereas no evidence for fluxional behaviour was observed in variable-temperature experiments.

In contrast to this straightforward behaviour, an analogous reaction of **2** with phenylsilane in [D₈]toluene provided a considerably more complex ¹H NMR spectrum with two notable peaks at $\delta = 4.44$ and 5.12 ppm attributed to the hydride resonances of PhSi(H)₂Bu and PhSi(H)₂N(SiMe₃)₂, respectively. This latter observation is suggestive of not only Mg–C/Si–H, but also M–N/Si–H σ -bond metathesis. Also notable were the complex signals associated with the metal-bound –N(SiMe₃)₂ region, which consisted of overlapping peaks between $\delta = 0.32$ and 0.47 ppm alongside a pair of broad overlapping signals centered on $\delta = 3.87$ and 3.69 ppm, which integrated in a 144:4:6 ratio. To elucidate the origin of these observations,



Figure 1. ORTEP plot of **4** (30% probability ellipsoids). Hydrogen atoms apart from metal-bound hydrides are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mg1–N1 2.0742(13), K1′–N2 2.9283(13), Mg1–H1 1.89(2), K1–H1 2.86(2), N1-Mg1-N2 124.97(5), N1-K1-N2′ 113.50(4), Mg1-H1 Mg1′ 106(1). Symmetry transformations used to generate equivalent atoms: x-1/2, -y+1/2, z+1/2, -x, -y+1, -z+1.



Figure 2. ORTEP plot of **5** (30% probability ellipsoids). Hydrogen atoms (apart from metal-bound hydrides) and carbon atoms in the nitrogen-bound trimethylsilyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Na1–N2 2.6093(17), Na1–H2 2.34(2), Mg1–N2 2.0627(16), Mg2–H2 1.89(2), Mg2–H3 2.01(2), Mg2–H4 2.01(2), Na2–N1 2.5169(17), Na2–H4 2.385(7), Na2–H5 2.46(2), Mg1–N1 2.0534(16), Mg1–N2 2.0627(16), Mg2-H2-Na1 104(1), N2-Na1-N3 175.72(6), Mg2-H7-Mg2' 103(1). Symmetry transformations used to generate equivalent atoms: -x+2, y, -z+3/2.

a preparative scale reaction undertaken in toluene gave compound **5** as crystals suitable for X-ray crystallographic analysis. The results of this analysis are shown in Figure 2.

Compound **5** is a heterododecametallic species ligated by eight hexamethyldisilazide and ten hydride ligands with a formula of $[Mg_6Na_6{N(SiMe_3)_2}_8H_{10}]$. Its formation and the side-product peaks observed in the in situ ¹H NMR experiments are rationalized by the stoichiometry shown in Equation (1). Indeed, a repeat of the in situ NMR scale experiment with this stoichiometry gave a stoichiometric quantity of compound **5**.



The structure of **5** possesses a C_2 symmetry element running through the two central hydrides (H4 and H7), which bridge between two six-coordinate magnesium centres (Mg2, Mg2') ligated only by hydrides in a structural core reminiscent of magnesium dihydride. Perhaps imposed by the imperfect octahedral geometry of its [Mg₂H₁₀] core, the Mg–H bonds of **5** are elongated in comparison to those observed in bulk MgH₂ (1.718 Å).^[1] The remaining four magnesium centres (Mg1, Mg3, Mg1' and Mg3') exist in identical coordination environments, in which the presence of two bulky hexamethyldisilazide li-

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gands lowers their coordination number to four, with the other two sites occupied by hydrides bridging to the [Mg₂H₁₀] core. The terminal sites of the potentially polymeric [Mg₂H₁₀] core are capped by sodium atoms, Na1 and Na1', which exist in a sawhorse conformation ligated axially by two amides. These ligands bridge to the tetracoordinate magnesium ions, whereas two of the equatorial sites share hydrides, H2, H6, H2' and H6', with the $[Mg_2H_{10}]$ core. The residual sodium atoms (Na2, Na3, Na2' and Na3') are located in distorted tetrahedral sites, which bridge, through hydrides H3, H5, H3' and H5', the central magnesium ions and are capped by amides shared with the tetracoordinate magnesium centres. These latter sodium ions form the vertices of cubic $[(NaMgH_2)_2]^{2+}$ clusters reminiscent of those observed by Stasch for the [(LiH)₄] core of the structurally characterized lithium hydride, [{(DipNPPh₂)Li}₄-(LiH)₄].^[14]

DOSY experiments performed on 5 suggested a single-diffusion coefficient for the silylmethyl and hydride regions, corroborating the proposed peak attributions and suggesting that the solid-state structure is retained in aromatic solvents. Although the crystallographically defined structure is suggestive of three hydride environments in a 2:4:4 ratio and two hexamethydisilazide environments in a 1:1 ratio, the ¹H NMR spectrum at room temperature comprised only two broad, complex signals in a 4:6 ratio for the hydrides and a series of overlapping, second-order peaks in the silylmethyl region. The more downfield hydride shift is suggested to be the three-coordinate hydrides H2 and H6, with the six remaining, 4-coordinate hydrides providing the upfield signal at $\delta = 3.87$ ppm. Cooling the sample evidenced a fluxional process as a result of exchange of the tetracoordinate hydrides within the [Mg₂H₁₀] core. At 267 K, the 6H peak at $\delta\!=\!3.69\,\mathrm{ppm}$ was observed to split yielding two broad singlet resonances in a 2:4 ratio at $\delta =$ 3.68 and 3.59 ppm, respectively, and a free energy of activation (ΔG^{\dagger}) for this process of 56 kJ mol⁻¹.^[20] The silymethyl region at 248 K was split into two doublets at δ = 0.32 and 0.48 ppm, which can be attributed to the two observed hexamethyldisilazide environments each further split by the diastereotopic disposition imposed by the rigidity of the cage structure. However, no coalescence temperature for the exchange of each separate hexamethyldisilazide environment could be attained, even to the boiling point of the [D₈]toluene solvent.

Notably, compound **5** did not evidence any discernible hydrogen-evolution behaviour. The NMR spectra of compound **5** were found to be unchanged after either heating in the solid state at 150 °C for 12 h under dynamic vacuum or at 130 °C for the same time period in $[D_8]$ toluene solution. Attempted acquisition of a melting point for compound **5** gave only decomposition with the formation of a brown solid between 162 and 200 °C with no evidence of bubbling that could be attributed to H₂ gas release.

Attempts to extend this reactivity to the lightest congeneric analogue, **1**, gave immediate precipitation of a fine, insoluble, colourless solid, thought to be various metal hydrides. NMR analysis suggested consumption of the PhSiH₃ and formation of PhSi(H)₂Bu and PhSi(H)₂N(SiMe₃)₂, as well as silanes with higher alkyl and amide incorporation indicative of Mg–C/Si–H

and Mg–N/Si–H σ -bond metathesis, respectively. Repetition of this reaction in the more coordinating solvent, THF, gave an identical result, suggesting that extension to complex s-block polyhydrides of the lightest alkali metal is not possible with a hexmethyldisilazide co-ligand set.

In summary, we have demonstrated that heterometallic magnesium hydride clusters may be prepared by a σ -bond metathesis route from the corresponding s-block amidoalkyls bearing only simple ligands of catalytic relevance. Although the formation of compound 4 indicates selective metathesis at the more reactive alkyl substituent, the formation of 5 requires less discriminative metathesis of both alkyl and amide ligands of 2. Nevertheless, this work indicates the under-represented utility of heteroleptic s-block clusters for selective metathesis chemistry and a new approach to higher metal hydride clusters, in which wherein the coordinative flexibility of a mixture of s-block elements allows them to act as both corner-and edge-occupying species. Work to extend this reactivity to the lightest alkali-metal ion is ongoing, alongside studies into the reactivity of these new and structurally interesting s-block species.

Keywords: hydrides · magnesium · metathesis · potassium · sodium

- For a comprehensive review of main-group hydride chemistry, see: S. Aldridge, A. J. Downs, *Chem. Rev.* 2001, 101, 3305.
- [2] For selected recent examples, see: a) F. Buch, H. Brettar, S. Harder, Angew. Chem. 2006, 118, 2807; Angew. Chem. Int. Ed. 2006, 45, 2741;
 b) F. Buch, S. Harder, Organometallics 2007, 26, 5132; c) F. Buch, S. Harder, Z. Naturforsch. B 2008, 63, 169; d) M. Arrowsmith, M. S. Hill, T. Hadlington, G. Kociok-Köhn, C. Weetman, Organometallics 2011, 30, 5556; e) M. Arrowsmith, T. J. Hadlington, M. S. Hill, G. Kociok-Kohn, Chem. Commun. 2012, 48, 4567.
- [3] For selected recent examples, see: a) J. F. Dunne, S. R. Neal, J. Engelkemier, A. Ellern, A. D. Sadow, J. Am. Chem. Soc. 2011, 133, 16782; b) M. S. Hill, D. J. Liptrot, D. J. MacDougall, M. F. Mahon, T. P. Robinson, Chem. Sci. 2013, 4, 4212.
- [4] M. S. Hill, M. F. Mahon, T. P. Robinson, Chem. Commun. 2010, 46, 2498.
- [5] For selected recent examples, see: a) A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, P. A. Procopiou, Organometallics 2007, 26, 4076; b) D. J. Liptrot, M. S. Hill, M. F. Mahon, D. J. MacDougall, Chem. Eur. J. 2010, 16, 8508.
- [6] M. T. Kelly, Struct. Bonding (Berlin) 2011, 141, 169, and references therein.
- [7] a) F. Schüth, B. Bogdanovic, M. Felderhoff, *Chem. Commun.* 2004, 2249;
 b) M. Dornheim, S. Doppiu, G. Barkhordarian, U. Boesenberg, T. Klassen,
 O. Gutfleisch, R. Bormann, *Scr. Mater.* 2007, *56*, 841; c) K.-F. Aguey-Zinsou, J.-R. Ares-Fernandez, *Energy Environ. Sci.* 2010, *3*, 526; d) I. P. Jain, C. Lal, A. Jain, *Int. J. Hydrogen Energy* 2010, *35*, 5133.
- [8] S. Harder, Chem. Commun. 2012, 48, 11165.
- [9] R. W. P. Wagemans, J. H. van Lenthe, P. E. de Jongh, A. J. van Dillen, K. P. de Jong, J. Am. Chem. Soc. 2005, 127, 16675.
- [10] M. Arrowsmith, M. S. Hill, D. J. MacDougall, M. F. Mahon, Angew. Chem. 2009, 121, 4073; Angew. Chem. Int. Ed. 2009, 48, 4013.
- [11] S. Harder, J. Spielmann, J. Intemann, H. Bandmann, Angew. Chem. 2011, 123, 4242; Angew. Chem. Int. Ed. 2011, 50, 4156.
- [12] J. Intemann, J. Spielmann, P. Sirsch, S. Harder, *Chem. Eur. J.* **2013**, *19*, 8478.
- [13] D. Hoffmann, T. Kottke, R. J. Lagow, R. D. Thomas, Angew. Chem. 1998, 110, 1630; Angew. Chem. Int. Ed. 1998, 37, 1537.
- [14] A. Stasch, Angew. Chem. 2012, 124, 1966; Angew. Chem. Int. Ed. 2012, 51, 1930.
- [15] A. Stasch, Angew. Chem. Int. Ed. 2014, 53, 1338.

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- [16] a) D. J. Gallagher, K. W. Henderson, A. R. Kennedy, C. T. O'Hara, R. E. Mulvey, R. B. Rowlings, *Chem. Commun.* 2002, 376; b) D. V. Graham, A. R. Kennedy, R. E. Mulvey, C. T. O'Hara, *Acta Cryst. C: Cryst. Struct. Commun.* 2006, *62*, m366.
- [17] 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.
- [18] a) R. E. Mulvey, Acc. Chem. Res. **2009**, 42, 743; b) R. E. Mulvey, Dalton Trans. **2013**, 42, 6676.
- [19] a) A. J. Martínez-Martínez, D. R. Armstrong, B. Conway, B. J. Fleming, J. Klett, A. R. Kennedy, R. E. Mulvey, S. D. Robertson, C. T. O'Hara, Chem.

Sci. **2014**, *5*, 771; b) F. Ortu, G. J. Moxey, A. J. Blake, W. Lewis, D. L. Kays, Inorg. Chem. **2013**, *52*, 12429.

[20] Calculated utilizing equation from; D. J. Duncalf, P. B. Hitchcock, G. A. Lawless, J. Organomet. Chem. 1996, 506, 347.

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