Cooperative dihydrogen activation at a Na(i)\(_2\)/Mg(i)\(_2\) ensemble†

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The binding and cleavage of the strong (436 kJ mol\(^{-1}\)) H–H σ-bond of dihydrogen at mid and late transition metal centres provided a fulcrum for both a fundamental understanding of d-block complex reactivity and the development of numerous catalytic and stoichiometric processes.\(^{1,2}\) This chemistry is enabled by the narrowly spread manifold of nd valence orbital energies.\(^{1,2}\) The thermodynamic viability of H\(_2\) addition to the Mg–Mg bonds remains to be described.\(^{14}\) In contrast, Harder and co-workers have recently reported that treatment of both the unique Mg(0) species, \([\text{BDI}^*\text{MgMgMg}\text{BDI}^*]\) (4; \(\text{BDI}^* = \text{HC}[\text{C}(\text{r}-\text{Bu})\text{N}(\text{DiPep})]_2;\) DiPep = 2,6-(3-pentyl)-phenyl) and the mixed oxidation state \([\text{Mg}(\text{I})/\text{Mg}(0)]\) compound, \([\text{BDI}^*\text{MgMgMgBDI}^*]\) (5), derived therefrom, with H\(_2\) (1.5 bar) generates the magnesium hydride, \([\text{BDI}^*\text{MgH}]\) (3) in ca. 30% isolated yield (Fig. 2).\(^{15}\) Although no further products were identified from the reaction of 4, the orbitals are introduced as spatially separated basic (HOMO) and acidic (LUMO) components.

There is now significant precedent for orbitally unconstrained \((\text{i.e.} \text{highly polarised})\) H–H σ-bond metathesis at the Ae–X \((\text{Ae = alkaline earth, Mg, Ca, Sr, Ba})\) bonds of group 2 derivatives in their conventional 2+ oxidation state.\(^{11}\) The thermodynamic viability of H\(_2\) addition to the Mg–Mg bonds of Jones and co-workers’ β-diketiminato \((\text{e.g.} \text{1–3, Fig. 2})\) and guanidinato Mg(i) complexes \((\Delta H \approx 24 \text{ kcal mol}^{-1})\) was also assessed soon after their initial report in 2007.\(^{12}\) Despite the synthesis of more than 20 further comparable species, however, and an intense exploration of Mg(i) compounds as potent reducing reagents,\(^{13}\) reductive H\(_2\) activation at an isolable Mg–Mg bonded molecule, either thermal or photoactivated, remains to be described.\(^{14}\) In contrast, Harder and co-workers have recently reported that treatment of both the unique Mg(0) species, \([\text{BDI}^*\text{MgNa}]_2\) (4; \(\text{BDI}^* = \text{HC}[\text{C}(\text{r}-\text{Bu})\text{N}(\text{DiPeP})]_2;\) DiPep = 2,6-(3-pentyl)-phenyl) and the mixed oxidation state \([\text{Mg}(\text{I})/\text{Mg}(0)]\) compound, \([\text{BDI}^*\text{MgMgMgBDI}^*]\) (5), derived therefrom, with H\(_2\) (1.5 bar) generates the magnesium hydride, \([\text{BDI}^*\text{MgH}]\) (3) in ca. 30% isolated yield (Fig. 2).\(^{15}\) Although no further products were identified from the reaction of 4, the

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**Fig. 1** Modes of synergic H\(_2\) activation by (a) a typical late transition metal, (b) heavier group 14 element alkyne analogues, (c) tetrathlenes and (d) an archetypal FLP.
transformation of 5 was noted to result in the extrusion of metallic magnesium. In neither case, however, was the potential mode of H₂ activation assessed.

Inspired in part by the synthesis of 4, we have described the topologically-related, \([\text{SiN}^{\text{Dipp}}_2\text{MgNa}_2]\) 6; \([\text{SiN}^{\text{Dipp}}_2 = \{\text{CH}_3\text{Si-Mg}_x\text{N}^{\text{Dipp}}_y\}]_{12}; \text{Dipp} = 2,6-i-\text{Pr}_2\text{C}_6\text{H}_3\) (Fig. 2). Although 6 bears a resemblance to the previously reported species of Yang and co-workers (e.g. 7), the redox-innocence of the \([\text{SiN}^{\text{Dipp}}_2]\) ligands and the \(N\)-aryl encapsulation of the sodium cations provides significant electronic discrimination. This is reflected in the structure of 6 through an elongation of the Mg–Mg bond \([3.2124(11) \text{ Å}]\) versus \([2.9370(18) \text{ Å}]\). Computational (NBO, QTAIM) analysis also identified a degree of electronic cooperation between the magnesium and sodium centres. This manifests as a pronounced yellow colour arising from an absorption at 409 nm \((3.0 \text{ eV})\) attributed to a transition between the Mg–Mg σ-bond (HOMO), arising from overlap of the magnesium 3s wavefunctions, and a LUMO largely represented by an out-of-plane combination of the sodium 3s atomic orbitals (Fig. 3a).

The behaviour of 6 supports an interpretation of its bonding as a tetrametallic ensemble. Most strikingly, treatment with non-reducible bases such as THF (Fig. 3b) results in the selective extrusion of metallic sodium and oxidation of the Mg(i) centres to the more conventional Mg(II) state. Although treatment of a degassed benzene solution of 6 with H₂ (2 bar) provided no evidence of an observable reaction over 12 hours at room \((ca. \, 25 \, ^\circ \text{C})\) temperature, monitoring by \(^1\text{H}\text{NMR}\) spectroscopy indicated conversion to a predominant new compound (9) was induced after heating at 40 °C for 3 days. This process occurred with the formation of a black metallic precipitate. Compound 9 was isolated as colourless single crystals from hexane at room temperature. The resultant X-ray diffraction analysis (Fig. 4) revealed that compound 9 is a centrosymmetric heterobimetallic hydride species. The hydride ligands of 9 were located and refined with a riding \(U_{iso}\) value to be trigonally encapsulated by a still chelated diamidomagnesium centre and two sodium cations. The sodium atoms are bound in a \(η^4\)-fashion by each of the Dipp substituents of the chelated \([\text{SiN}^{\text{Dipp}}_2]\) ligands, but are differentiated by their interactions with an additional diamide dianion that now adopts a \(\{\text{Na}_2-μ-κ^1-κ^1-κ^1-κ^1-N'\text{-Na}_2\}\) bridging mode reminiscent of those to Mg in the macrocyclic species 8. While Na1/Na1' engage via further polyhapto interactions with C31–C36 (and C31'–C36') comprising the Dipp substituents of the bridging diamiion, the coordination spheres of Na2/Na2' are completed by N3/N3'. The Mg1–N1 [1.9795(13) Å] and Mg1–N2 [1.9711(14) Å] bonds of 9 are significantly shorter than the Mg–N distances observed in 6 (avg. 2.08 Å), consistent with the oxidation of Mg(i) to Mg(II). While several amido-derived Na/Mg hydrides have been reported to result from either \(β-C-H\) elimination or metal amide/Si–H metathesis, compound 9 is the first such species in which the hydride ligands arise from the direct activation of dihydrogen. Although its presence could not be identified by \(^1\text{H}\text{NMR}\) spectroscopy in \(d_6\)-benzene solution, dihydrogen was confirmed as the source of the hydride ligands of 9 by performance of a further reaction of 6 with \(D_2\). This latter process provided similar observations and resulted in the isolation of 9-\(d_2\), which was characterised by a singlet signal at \(δ\) 4.16 ppm as the sole observable resonance in its \(^2\text{H}\text{NMR}\) spectrum in benzene.

Acid digestion and quantitative analysis by ICP-OES revealed that the solid residue deposited during the reaction of 6 with H₂ comprised magnesium as the sole constituent s-block metal...
with levels of sodium below the detection limit of the technique (see ESI†). Furthermore, the quantity of magnesium was consistent with the reaction stoichiometry shown in eqn (1), which we surmise results from the formal disproportionation of the Mg(I) centres of compound 6.

DFT calculations (BP86-D3BJ/BS2(benzene)//BP86/BS1 level of theory, see the ESI† for full details) were performed to assess the kinetics of H₂ addition to 6 (denoted as I in the computational study) and the structure of the resulting H₂ adduct. Initial H₂ addition was identified to take place via TS(II–III) and a barrier of +18.5 kcal mol⁻¹ to form II (+14.1 kcal mol⁻¹). Subsequent H₂ reorientation via a low-lying saddle point, TS(II–III) (+13.6 kcal mol⁻¹), affords a more stable adduct, III (+11.0 kcal mol⁻¹), in which a terminus of the H₂ molecule is directed towards the Mg–Mg bond (Fig. 5a).²⁰ NBO-based donor–acceptor interaction analysis of III reveals two appreciable interactions between H₂ and the tetrametallic Mg₂Na₂ unit: a σMg–Mg → σH₂–H interaction (ΔG(2) = 9.2 kcal mol⁻¹; Fig. 4b) supplemented by a subtle but still significant engagement via σH₂–H → σNa(3s) (ΔG(2) = 1.6 kcal mol⁻¹; Fig. 5c).

While we cannot yet discount alternative polarised metathesis or radical-based pathways,¹¹,¹⁴ these deductions infer that the frontier orbital interactions invoked in the initial coordination of H₂ to 6 bear some analogy to those of the generalised d- and p-block-derived systems depicted in Fig. 1. The semi-heterogeneous nature of the Mg(0) extrusion process and the structural complexity of 9, however, dictate that the onward process does not lend itself to further prudent mechanistic analysis.

These combined experimental and theoretical results imply that the H₂ activation process invoked through its interaction with 6 may be rationalised as a consequence of the frontier orbitals arising from the low oxidation state assembly of the two dissimilar s-block elements (Fig. 3a). This perspective serves to further discriminate the chemistry of the low oxidation state heterobimetallic species, 6, from that so far deduced for the previously described Mg–Mg bonded Mg(i) derivatives (e.g. 1–3 and 7).¹²,¹³ Similarly, the conceptual framework provided by the intermediate III signposts a potential ability to manipulate the frontier orbitals of related systems toward even more challenging small molecule transformations through the
BLM performed the computational analysis and MFP finalised the X-ray diffraction analysis of 9 for publication.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

14. Here, we draw a demarcation between such divalent \{Mg–Mg\}-bonded Mg\(i\) compounds and radicular Mg\(i\) species. Notably, a recent report by Harder and co-workers has highlighted that ball milling of K/KI and [(BDI)Mg\(I\)(OEt\(2\))] under H\(_2\) provides a ca. 1.3 : 1.0 mixture of compound 1 and [(BDI)Mg\(H\)]. While compound 1 remains unreactive, the latter species is interpreted to result from the generation and persistence of highly reactive ‘unquenched’ [(BDI)Mg\(\uparrow\)], radicals under the solvent-free conditions and which are then reactive toward H\(_2\). See: (a) D. Jędrzkiewicz, J. Langer and S. Harder, Z. Anorg. Allg. Chem., 2022, 648, e202200138. The hydrogenation of Mg\(i\) dimers using 1,3-cyclohexadiene has also been described. See: (b) R. Lalrempuia, C. E. Kefalidis, S. J. Bonyhady, B. Schwarze, L. Maron, A. Stasch and C. Jones, J. Am. Chem. Soc., 2015, 137, 8944–8947.

20. Based on the electronic energy, TS(II–III) is 0.1 kcal higher than II with one imaginary frequency of \(-58.5\) cm\(^{-1}\). Corrections have stabilised this TS structure relative to the zero species more than intermediate II.