

# Dimeric magnesium(I) $\beta$ -diketiminates: a new class of quasi-universal reducing agent

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**Abstract** | Since the first report of their isolation in 2007, magnesium(I) dimers have transitioned from being chemical curiosities to versatile reducing agents that are used by an ever-increasing number of synthetic chemists. Magnesium(I) dimers have a unique combination of advantageous properties that sees them used in the syntheses of new, and often applicable, compound types that are impossible or difficult to access using conventional reductants. This Perspective describes the synthesis and properties of these dimers, and provides notable examples of their application in organic and inorganic synthesis. Magnesium(I) dimers, especially complexes of  $\beta$ -diketiminates, may now be viewed as widely applicable, quasi-universal reducing agents with a promising future in synthetic chemistry. It is hoped that the reader will develop a familiarity with these reagents, such that the complexes can be successfully used in many synthetic programmes.

Innumerable chemical transformations make use of reducing agents to transfer one or more electrons to a substrate. As a result, recent decades have seen numerous reducing agents being developed for the synthesis of organic, organometallic and inorganic products<sup>1–3</sup>. When a procedure requires a strong reductant — for example, one that oxidizes at potentials lower than  $-1.5$  V relative to the saturated calomel electrode (SCE)<sup>1</sup> — synthetic chemists often make use of electropositive metals and their complexes because they offer a range of useful properties and reducing strengths (FIG. 1). Some commonly used reductants include elemental alkali and alkaline earth metals, graphite intercalated potassium (KC<sub>8</sub>), alkali metal naphthalenides (M(C<sub>10</sub>H<sub>8</sub>), M = Na or K), SmI<sub>2</sub> and the decamethylmetallocenes [M(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] (M = Co or Sm)<sup>1–6</sup>. Although the synthetic utility of these reagents is not in question, they have drawbacks that limit their applicability, such that selecting a reducing agent becomes a trial-and-error process. For example, reactions that use alkali metals or KC<sub>8</sub> can be difficult to control on account of the strongly cathodic redox potentials of these reductants and

their insolubility in common solvents. This lack of solubility typically results in electron transfer from the reductant to a substrate at a solid/solution interface with little control of selectivity, which often leads to over-reduction of the substrate to give complex product mixtures. Such a problem can be overcome, to some extent, by using soluble reducing agents that can stoichiometrically deliver electrons to the substrate in a more controlled manner; however, these reductants can also be very harsh (for example, Na(C<sub>10</sub>H<sub>8</sub>)), and often lead to by-products (for example, C<sub>10</sub>H<sub>8</sub>) that are difficult to separate from the targeted product(s)<sup>1</sup>. Furthermore, alkali metal-based reducing agents are especially difficult to prepare and store, and their handling may present a considerable fire hazard.

Considering the disadvantages of many reducing agents, and the difficulties faced in selecting such reagents for a given synthetic task, it would be desirable to have a class of universal reducing agent that can be reliably used with a wide range of both organic and inorganic substrates. In 2007, the first stable magnesium(I) dimers [Mg<sub>2</sub>L<sub>2</sub>] (where L<sup>-</sup> is a bulky guanidinato or  $\beta$ -diketiminato

ligand, FIG. 2)<sup>7</sup> were reported. Since that time, various related dimers bearing mono-<sup>8,9</sup>, di-<sup>10</sup> and terdentate<sup>11</sup> anionic ligands have been prepared and their chemistry explored in detail. From these studies, it has become evident that the unique properties of magnesium(I) dimers — especially those featuring  $\beta$ -diketiminato (<sup>Ar</sup>nacnac<sup>-</sup>) ligands — make these systems among the most user-friendly and widely applicable reductants<sup>12–14</sup>. Indeed, many chemists now routinely use [Mg<sub>2</sub>(<sup>Ar</sup>nacnac)<sub>2</sub>] reagents to access synthetic targets that are not easily prepared using other reductants.

The aim of this Perspective is to give the reader a general overview of [Mg<sub>2</sub>(<sup>Ar</sup>nacnac)<sub>2</sub>] complexes — in terms of both their properties and their chemistry — such that these reagents may be successfully applied in the reader's own syntheses. Summaries of the reactivity of magnesium(I) dimers towards both organic and inorganic substrates are provided. Special attention is given to reactions that afford compound types that are not accessible when using other reducing agents. These new products might take the form of novel metal–metal bonded systems and/or compounds that have interesting further reactivity.

## Preparation and properties

For a reducing agent to be of universal appeal, it must be easy to prepare and manipulate. The metal–metal bonded species [Mg<sub>2</sub>(<sup>Ar</sup>nacnac)<sub>2</sub>] meet these criteria: these species can be synthesized at room temperature, in high yields (crude yields are typically >80%) and on multigram scales (up to 10 g) by simple alkali metal reductions of magnesium(II) precursors, which themselves are trivial to prepare<sup>7,15,16</sup> (FIG. 2). In turn, <sup>Ar</sup>nacnac<sup>-</sup> ligands bearing a variety of *N*-aryl substituents can be prepared, such that the reactivity of their respective magnesium(I) compounds can be readily tuned. For kinetic reasons, the reactivity of the magnesium(I) system typically increases with decreasing steric bulk of the *N*-aryl substituent<sup>12,13</sup>. The compounds are stable in isolation, and all known magnesium(I) dimers are crystalline solids that typically do not decompose below 200 °C. The solids are only moderately air and moisture sensitive, present no fire hazard, have no known toxicity and can be

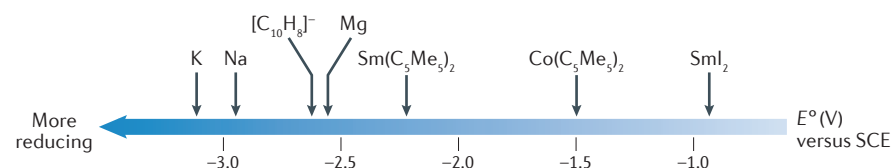


Figure 1 | Oxidation potentials for reductants that are commonly used in organic and organo-metallic synthesis. Values are approximate, and in some cases are converted from potentials that have been reported against other reference electrodes or chemical references<sup>1,4,6</sup>. SCE, saturated calomel electrode.

readily manipulated using standard air-free techniques. Furthermore, their versatility is enhanced by their solubility and stability in most common aprotic organic solvents, including toluene, benzene and diethyl ether.

In addition to being easy to prepare and handle, another attraction of  $[\text{Mg}_2(\text{Ar}^{\text{nacnac}})_2]$  complexes is that they can each act as a soluble, stoichiometric source of electrons that can be delivered with control to a substrate. In many cases, the dimers deliver electrons and convert to poorly soluble by-products that are readily removed by filtration. For example, when using a magnesium(I) dimer to reduce a transition metal halide,  $[\text{Mg}_2(\text{Ar}^{\text{nacnac}})_2]$  is converted to a halido-bridged magnesium(II) complex<sup>12,13</sup> of the form  $[\text{Mg}_2(\text{Ar}^{\text{nacnac}})_2(\mu\text{-X})_2]$ ; this is easily separated from the reduced reaction products and can be reduced to regenerate the magnesium(I) dimer for further use.

Crystallographic studies reveal that  $[\text{Mg}_2(\text{Ar}^{\text{nacnac}})_2]$  complexes have unsupported Mg–Mg bonds ( $r_{\text{Mg-Mg}} = 2.8\text{--}2.9 \text{ \AA}$ ), with each Mg centre being chelated by a  $\kappa^2\text{-Ar}^{\text{nacnac}}$  ligand<sup>12,13,17</sup>. Computational studies show that the highest occupied molecular orbital (HOMO) of the compounds largely comprises the high *s*-character Mg–Mg covalent bond, whereas the lowest unoccupied molecular orbital (LUMO) largely takes the form of a  $\pi$ -type bonding orbital between the Mg atoms<sup>7</sup>. Given the very high polarity of the  $\text{Mg}^{\delta+}\text{-N}^{\delta-}$  bonds, dimers of  $[\text{Mg}_2(\text{Ar}^{\text{nacnac}})_2]$  can be viewed as  $\text{Mg}_2^{2+}$  dications that are stabilized by  $\text{nacnac}^-$  ligands. Indeed, the low-coordinate, electrophilic nature of the metal centres is central to the reducing capabilities of the dimers, the reactions of which proceed by an inner-sphere mechanism whereby substrates bind to the metal sites before delivery of the two electrons from the Mg–Mg bond<sup>18</sup>. Electron transfer is further enhanced by the large and diffuse nature of the metal-centred HOMO, the electrons in which are only weakly associated with the Mg atoms.

Experimental charge density studies have shown that there is a local maximum in the electron density between the Mg centres — a rare case of a so-called non-nuclear attractor<sup>19,20</sup>. Overall, the dimers can be thought of as ‘molecular bottles’ in which two electrons are stored. Unfortunately, all experimental attempts to measure the redox potentials of magnesium(I) dimers have so far been unsuccessful. Although they will certainly be less reducing than the alkali metals from which they are made, given the reported potentials for the  $\text{Mg}^{2+/0}$  and  $\text{Mg}^{2+/+}$  couples ( $-2.61 \text{ V}$  and  $-2.29 \text{ V}$  versus SCE, respectively)<sup>6</sup>, it is likely that magnesium(I) dimers have similar reducing capabilities, such that they can be considered strong reductants<sup>1</sup>.

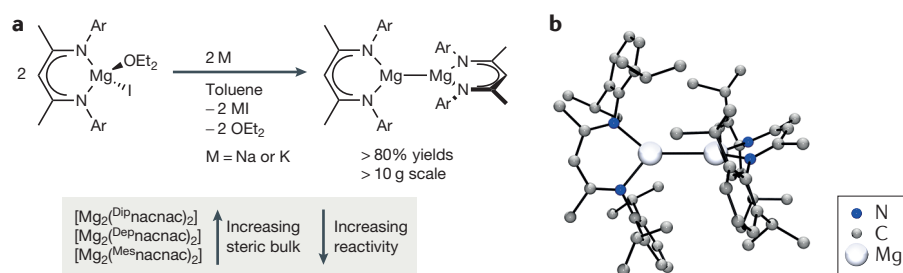
### Use in organic synthesis

Magnesium, both in elemental and organometallic forms, has long been used as a reducing agent in organic synthesis. Its use dates back to the beginning of the 20th century, when it was found that magnesium metal reacts with organic halides to form Grignard reagents, compounds that are thought to act as single electron transfer (SET) reagents in some cases<sup>21</sup>. Other magnesium based reductants that have been applied to organic synthesis include Reike magnesium<sup>22</sup>, as well as mixtures of Mg and  $\text{MgX}_2$  ( $X = \text{Cl}$  or  $\text{Br}$ ), which, at equilibrium, include minute amounts of monovalent magnesium halides ( $\text{MgX}^\bullet$  or  $\text{Mg}_2\text{X}_2$ ) in solution<sup>23</sup>. A further example is magnesium anthracene (for example,  $[\text{Mg}(\text{C}_{10}\text{H}_8)(\text{THF})_3]$ , THF = tetrahydrofuran)<sup>3</sup>, which is a poorly soluble but very reactive source of ‘elemental’ magnesium. It is often difficult to control the selectivity of organic reactions that involve these magnesium compounds, one reason that SET reagents, such as  $\text{SmI}_2$ , have remained so popular<sup>2</sup>. Although  $[\text{Mg}_2(\text{Ar}^{\text{nacnac}})_2]$  compounds have found good use in inorganic chemistry, fewer applications are known in organic chemistry. However, this is about to change, as these highly selective and controllable reducing agents are rapidly being added to the

chemist’s toolkit. The organic reactions in which they have been used are summarized in the following.

**Substrate reductions.** Reactions of magnesium(I) dimers with various unsaturated substrates can lead to the latter being reduced by one, two or three electrons, with the products typically forming in high yields. The only reported one-electron reduction is that of benzophenone, which enabled the first isolation and structural characterization of magnesium ketyl radical **1** (TABLE 1) when carried out in the presence of 4-(dimethylamino)pyridine<sup>24</sup>. Such ketyl radicals were proposed as intermediates in the pinacol coupling of benzophenone as early as 1927 (REF. 25). More common are two-electron reductions, which proceed by insertion of the substrate into the Mg–Mg bond to afford novel diamagnetic, dimagnesian products. Substrates that have been doubly reduced by magnesium(I) dimers include azobenzene, anthracene, cyclooctatetraene (for example, to give **2**), carbodiimides, ketenimines and dioxygen<sup>15,24,26,27</sup>. The three-electron reduction of polyaromatic hexaazatri-naphthylene (HAN) yields **3**, which can be described as  $[\text{HAN}]^{3-}$  coordinated to three  $[\text{Mg}(\text{Dip}^{\text{nacnac}})]^+$  fragments (Dip = 2,6-diisopropylphenyl)<sup>28</sup>. The ground state of the trianionic ligand was found to be a doublet ( $S = 1/2$ ) with some triradicaloid character. The high-yielding formation, ease of preparation and selective formation of all of these reduced systems lends them to, for example, reaction with electrophiles to afford functionalized products.

**Reductive coupling, bond cleavage and C–X bond activation.** The selectivity with which magnesium(I) dimers reduce organic substrates enables their effective use in various high-yielding reductive bond coupling and cleavage processes. For example, several magnesium(I)-induced reductive C–C and N–N bond-forming reactions are now known for nitriles, isonitriles, isocyanates and alkyl azides<sup>15,26,29</sup>. The products of these reactions cannot typically be accessed using other *s*-block-based reductants, but related products can sometimes be prepared using samarium(II) compounds or low-valent first-row transition metals. A prominent family of examples are the remarkably stable hexazenediide complexes, such as **4**, with the only other complexes of this dianionic ligand being those of transition metals<sup>30</sup>. Relative to reductive couplings,



**Figure 2 | Dimagnesium(II) complexes of the form  $[\text{Mg}_2(\text{Ar}^n\text{nacnac})_2]$ .** Although stable in isolation, the complexes are strong and selective reductants, with the least sterically bulky examples being the most reactive. **a** | The metal–metal bonded complexes are readily prepared by reductive coupling of the corresponding  $[\text{Mg}(\text{Ar}^n\text{nacnac})(\text{OEt}_2)]$  species (where  $\text{Ar}^n\text{nacnac}^-$  is a  $\beta$ -diketiminato ligand). The most common examples feature, in order of decreasing steric bulk, 2,6-diisopropylphenyl (Dip), 2,6-diethylphenyl (Dep) or 2,4,6-trimethylphenyl (Mes) substituents at the nitrogen atoms. Complexes with the least bulky substituents are the most reactive as their highest occupied molecular orbitals are more exposed to potential substrates<sup>7,15,16</sup>. **b** | The X-ray crystal structure of  $[\text{Mg}_2(\text{Dip}^n\text{nacnac})_2]$ , with the hydrogen atoms omitted for clarity, shows the perpendicular orientation of the two  $\text{MgN}_2$  planes.

reductive bond cleavages that are effected by magnesium(I) are less prevalent. Despite this, cleavage of the C–N single bonds in alkyl-substituted isocyanides has been found to give  $[\text{Mg}(\text{Dip}^n\text{nacnac})(\text{CN})_3]$  (REF. 29); this is similar to the chemistry that is observed when samarium(II) compounds are used as reductants<sup>31</sup>. More interestingly, magnesium(I) dimers smoothly activate strong C–F bonds in partially fluorinated and perfluorinated arenes — in the absence of catalysts — to give aryl- and fluoro-magnesium(II) products<sup>32</sup>, such as **5** and **6**. Quenching of the arylmagnesium(II) product with an electrophile represents a transition metal-free route to functionalized fluoroarenes. Overall, these C–F activation reactions can be likened to the formation of Grignard reagents. The possible involvement of the magnesium(I) radical  $(\text{Ar}^n\text{nacnac})\text{Mg}^\cdot$  in the activation of C–F bonds has been probed by conducting a reaction between the symmetrical dimers  $[\text{Mg}_2(\text{Dip}^n\text{nacnac})_2]$  and  $[\text{Mg}_2(\text{Mes}^n\text{nacnac})_2]$  (Mes = 2,4,6-trimethylphenyl). Although this does slowly lead to the unsymmetrical redistribution product,  $[\text{Mg}_2(\text{Dip}^n\text{nacnac})(\text{Mes}^n\text{nacnac})_2]$ , it is not apparent whether the reaction proceeds through Mg–Mg bond cleavage (and magnesium(I) radical formation) or ligand exchange.

**Reductive disproportionations and related reactions.** Much like the expensive, paramagnetic and radioactive samarium(II) (and uranium(III)) systems, dimagnesium(I) complexes selectively reduce small molecules such as  $\text{CO}_2$  and  $\text{SO}_2$ . The potentially value-added products that result are not typically accessible using *s*-block reductants. In one example,

reductive disproportionation of  $\text{CO}_2$  affords CO and the carbonato complex  $[\text{Mg}_2(\text{Dip}^n\text{nacnac})_2(\mu\text{-CO}_3)]$  (**7**) as the major (kinetic) products. The thermodynamic product is thought to be the oxalato  $[\text{Mg}_2(\text{Dip}^n\text{nacnac})_2(\mu\text{-C}_2\text{O}_4)]$  (**8**), which also forms in small amounts, in this case by reductive coupling of  $\text{CO}_2$  molecules<sup>27</sup>. The reductive disproportionation reaction was initially believed to proceed via the magnesium oxo intermediate  $[\text{Mg}_2(\text{Dip}^n\text{nacnac})_2(\mu\text{-O})]$ , followed by reaction with a second molecule of  $\text{CO}_2$  to give **7**. However, a later computational study pointed to the formation of **7** occurring through a more concerted mechanism<sup>33</sup>. By analogy to the formation of oxalato **8**,  $\text{SO}_2$  can also be reductively coupled to give  $[\text{Mg}_2(\text{Dip}^n\text{nacnac})_2(\mu\text{-S}_2\text{O}_4)]$  — the first known magnesium dithionite complex — in a clean reaction in which reductive disproportionation is not a competing process<sup>11</sup>.

In a related exploration of the viability of using magnesium(I) dimers to convert feedstock gases into value-added products, two such dimers were treated at room temperature with a molecular source of  $\text{H}_2$  (that is, 1,3-cyclohexadiene) under an atmosphere of CO. Remarkable Fischer–Tropsch-like C–C couplings were observed, which resulted in the formation of alkoxo complexes such as magnesium ethylene diolate  $[\text{Mg}_2(\text{Dip}^n\text{nacnac})_2(\mu\text{-}\kappa^2\text{:}\kappa^1\text{-O}_2\text{C}_2\text{H}_4)]$  (REF. 16). This complex is also accessible directly from  $[\text{Mg}(\text{nacnac})(\mu\text{-H})_2]$  (REF. 34), as is cyclopropanetriolate  $[\text{Mg}_3(\text{Dip}^n\text{nacnac})_3(\mu^3\text{-O}_3\text{C}_3\text{H}_3)]$  (**9**, Dep = 2,6-diethylphenyl). It seems that the bulky  $\text{Dip}^n\text{nacnac}^-$  ligand only permits formation of a dinuclear species, whereas use of the smaller 2,6-diethylphenyl-substituted

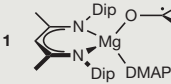
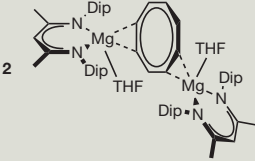
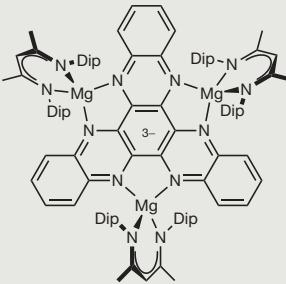
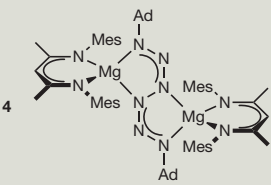
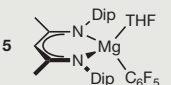
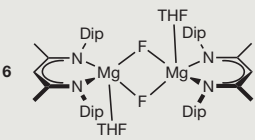
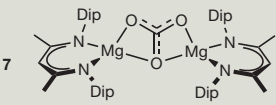
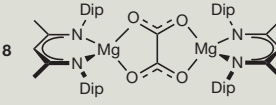
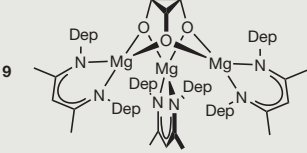
ligand can afford a trinuclear complex, which is the first cyclopropanetriolate complex of any metal. Experiments indicate that the reactions proceed via the magnesium hydrides  $[\text{Mg}(\text{nacnac})(\mu\text{-H})_2]$ , which, according to computational studies, hydromagnesiates CO to give the  $\eta^2$ -formyls  $[\text{Mg}(\text{nacnac})(\eta^2\text{-OCH})]$ ; these then undergo a series of further reactions and rearrangements to eventually give the isolated di- or trinuclear complexes of the C–C coupled ligands. Overall, such work highlights the potential utility of magnesium(I) dimers for the generation of higher alcohols from synthesis gas (a mixture of  $\text{H}_2$  and CO).

### Use in inorganic synthesis

More so than in organic chemistry, magnesium(I) dimers have been widely used as selective reductants in inorganic and/or organometallic syntheses<sup>12,13</sup>. These reagents have proved to be particularly effective in the synthesis of low-valent main group compounds, the chemistry of which has flourished over the past two decades. These highly reactive species are not only fascinating from a fundamental point of view, but have more recently begun to emerge as powerful reagents for the activation of small molecules and catalysis — processes that normally necessitate the use of late transition metals<sup>35–37</sup>. Such chemistry has led to the realization that cheap, benign low-valent main group compounds could eventually replace toxic precious metal complexes in some areas of synthesis and catalysis. Although developing these low-valent compounds is a major focus of main group chemists today, the nascent field has been hindered to some degree by the difficulty that is associated with cleanly accessing low-valent *p*-block species using conventional alkali metal-based reductants. It is in this regard that magnesium(I) dimers have proved to be highly effective, with their readily controllable reducing characteristics affording chemists access to various compound types that cannot otherwise be prepared (or can only be obtained in low yields). A summary of this chemistry and an overview of the use of magnesium(I) compounds to access related low-valent first-row transition metal compounds are provided in the following; this section is organized according to the group of the periodic table from which the reduced element originates.

**Group 2.** There has been only one example of a low-oxidation-state *s*-block compound

Table 1 | Selected reductions of unsaturated substrates with  $[\text{Mg}_2(\text{Ar}^{\text{nacnac}})_2]$

Precursor(s)	Magnesium(I) dimer	Product(s)	Refs
Benzophenone, DMAP	$[\text{Mg}_2(\text{Dip}^{\text{nacnac}})_2]$		24
Cyclooctatetraene, THF	$[\text{Mg}_2(\text{Dip}^{\text{nacnac}})_2]$		26
Hexaazatrinaphthylene	$[\text{Mg}_2(\text{Dip}^{\text{nacnac}})_2]$		28
1-Adamantyl azide	$[\text{Mg}_2(\text{Mes}^{\text{nacnac}})_2]$		15
Hexafluorobenzene, THF	$[\text{Mg}_2(\text{Dip}^{\text{nacnac}})_2]$	 	32
Carbon dioxide	$[\text{Mg}_2(\text{Dip}^{\text{nacnac}})_2]$	 	27
1,3-Cyclohexadiene, carbon monoxide	$[\text{Mg}_2(\text{Dep}^{\text{nacnac}})_2]$		16

Ad, 1-adamantyl; Dep, 2,6-diethylphenyl; Dip, 2,6-diisopropylphenyl; DMAP, 4-(dimethylamino)pyridine; Mes, 2,4,6-trimethylphenyl; THF, tetrahydrofuran.

**Group 13.** The syntheses of several important E–E-bonded group 13 species (where E denotes a group 13 element) rely on the use of magnesium(I) reductants. In the case of boron, reduction of the platinum(II) boryl complex  $[\text{PtBr}(\text{PEt}_3)_2(\text{B}_2\text{Dur}_2\text{Br})]$  (Dur = 2,3,5,6-tetramethylphenyl) afforded the platinum(0) product  $[\text{Pt}(\text{PEt}_3)_2(\text{B}_2\text{Dur}_2)]$  (**11**), the first diborene complex<sup>39</sup>. Analogous to the complexation of electron-rich metals with olefins, experimental and computational evidence has revealed that electron density is donated from Pt to an empty  $\pi$ -bonding orbital on the orthogonal diborene fragment of **11**. This leads to a strengthening of the B=B bond upon coordination; thus, this system is a rare exception of the Dewar–Chatt–Duncanson bonding model.

The reduction of a series of hydridoaluminium(III) complexes has afforded an array of dimeric hydridoaluminium(II) compounds that feature Al–Al covalent bonds. For example, N-heterocyclic carbenes (NHCs), in particular IPr ( $:\text{C}\{\text{N}(\text{Dip})\text{C}(\text{H})_2\}_2$ ), can form alane adducts of the type  $[\text{AlH}_3(\text{IPr})]$ , which upon reduction with  $[\text{Mg}_2(\text{Mes}^{\text{nacnac}})_2]$  give the thermally stable dinuclear species  $[\text{Al}_2\text{H}_4(\text{IPr})_2]$  in good yield<sup>40</sup>.  $[\text{Al}_2\text{H}_4(\text{IPr})_2]$  can be considered an NHC adduct of  $\text{Al}_2\text{H}_4$  (dialane(4)), with the parent compound only being stable at very low temperatures ( $\sim 5\text{ K}$ )<sup>41</sup>. Related amidinato-dihydridoaluminium(III) complexes of the form  $[\text{Al}(\text{amid})\text{H}_2]$  (where amid<sup>−</sup> is a bulky amidinato ligand) also react with  $[\text{Mg}_2(\text{Mes}^{\text{nacnac}})_2]$  (or  $[\text{Mg}_2(\text{Dip}^{\text{nacnac}})_2]$ ), in this case giving the aluminium(II) product  $[\text{Al}_2\text{H}_2(\text{amid})_2]$ . Interestingly, the by-product of this reduction, namely  $[\{\text{Mg}(\text{Dip}^{\text{nacnac}})(\mu\text{-H})\}_2]$ , could be reduced back to the magnesium(I) starting material by treatment with potassium metal<sup>40</sup>. In related chemistry, reduction of a magnesium salt of  $[\text{AlH}_4]^-$  (alanate) yielded  $[\text{Al}_2\text{H}_6]^{2-}$  (dialanate), in what was the first preparation of this dianionic moiety; in this case,  $[\text{Al}_2\text{H}_6]^{2-}$  exists as a contact ion complex with two dimagnesium hydride cations  $[\text{Mg}_4(\text{Dep}^{\text{nacnac}})_4\text{H}_2(\text{Al}_2\text{H}_6)]$  (**12**)<sup>42</sup>. Dialanate is a valence isoelectronic analogue of ethane and was computationally predicted to be an accessible synthetic target the year before it was prepared<sup>43</sup>. The only other example of magnesium(I) dimers being used in group 13 chemistry involved treatment of  $\text{H}_3\text{NBH}_3$  with  $[\text{Mg}_2(\text{Dip}^{\text{nacnac}})_2]$ ; this resulted in the reductive dehydrogenation of ammonia borane, leading to the formation of the magnesium(II) amidoborane complex  $[\text{Mg}_2(\text{Dip}^{\text{nacnac}})_2(\text{H}_2\text{NBH}_2)_2]$  (REF. 44).

being accessed using a magnesium(I) dimer: using  $[\text{Mg}_2(\text{Mes}^{\text{nacnac}})_2]$  as the reducing agent, the (diiminophosphinato)halido-magnesium(II)  $[\text{Mg}\{\text{Ph}_2\text{P}(\text{NDip})_2\}(\text{X})]$

(X = Br or I) precursors can be converted, in moderate yields, into the corresponding magnesium(I) dimer,  $[\text{Mg}_2\{\text{Ph}_2\text{P}(\text{NDip})_2\}_2]$  (**10**, TABLE 2)<sup>38</sup>.

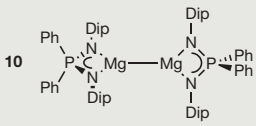
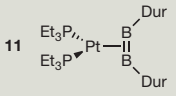
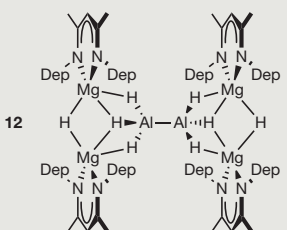
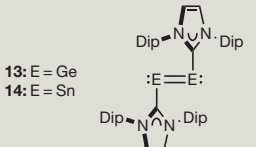
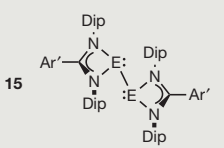
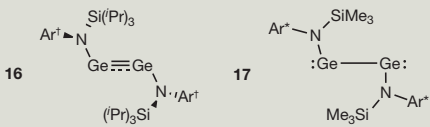


**Group 14.** The application of magnesium(I) reductants has been most successful in the synthesis of group 14 compounds, with many interesting and useful compound types having been made available. This is perhaps unsurprising given that magnesium metal itself is often used to prepare low-valent group 14 systems<sup>45</sup>. One of the first indications of the effectiveness of magnesium(I) reagents came in 2009 with the reduction of the NHC complex  $[\text{Ge}(\text{IPr})\text{Cl}_2]$ , which afforded the  $\text{Ge}^0=\text{Ge}^0$  bonded dimer  $[\text{Ge}_2(\text{IPr})_2]$  (**13**)<sup>46</sup>; the tin(0) analogue (**14**) of this complex is also accessible<sup>47</sup>. Both dimers can be considered as NHC adducts of element fragments ( $\text{E}_2$ ), and like their silicon(0) analogue  $[\text{Si}_2(\text{IPr})_2]$  (REF. 48), are sometimes viewed as ‘allotropes’ that have potential as soluble sources of the elements for synthetic chemistry.

Various ligand-stabilized group 14 element(I) dimers  $[\text{E}_2\text{L}_2]$ , as well as their NHC adducts  $[\text{E}_2\text{L}_2(\text{NHC})_n]$  ( $n = 1$  or  $2$ ), have also been prepared by reduction of di- or tetravalent halido precursors such as  $[\text{ELX}]$  or  $[\text{ELX}_3]$ . Although  $\text{L}^-$  can be a bidentate ligand, such as amidinato (as in **15**)<sup>49</sup> or  $\beta$ -diketiminato<sup>50</sup>, it is more often the case that it takes the form of a very bulky monodentate donor such as a boryl<sup>51</sup>, terphenyl<sup>52</sup> or amido (as in **16** and **17**)<sup>53,54</sup>. When  $\text{L}^-$  is monodentate, the corresponding two-coordinate element(I) dimers  $[\text{E}_2\text{L}_2]$  can have varying bond orders between the central atoms, depending on the metal involved and the steric characteristics of the ligand. For example, digermanium(I) complexes of extremely bulky amido ligands (such as **16**) feature short Ge–Ge multiple bonds ( $\sim 2.36 \text{ \AA}$ ), such that they can be considered diaminodigermynes — the germanium

analogues of diaminoalkynes<sup>55</sup>. In a counter-intuitive result, germanium(I) dimers that bear slightly less bulky amido ligands can have very long Ge–Ge single bonds, as is the case with **17** (REF. 54). Such systems can be viewed as 1,2-diaminodigermynes, which are devoid of Ge–Ge multiple bonding because the smaller amido ligands allow the  $\text{Si}_2\text{C}_2\text{N}_2\text{Ge}_2$  fragments to be planar. This isomer is conducive to  $\text{N} \rightarrow \text{Ge} \pi$  bonding involving the N-centred lone pair and the empty Ge-centred  $4p$ -type orbitals. Both forms of these dimers have been calculated to have very narrow HOMO–LUMO gaps, a factor that contributes to their high reactivity. For example, these germanium dimers can activate strong bonds in small molecules such as  $\text{H}_2$  (REFS 53–55),  $\text{CO}_2$  (REF. 56) and olefins<sup>57</sup> — substrates that are traditionally processed by low-valent transition metal complexes. For example,

Table 2 | Examples of low-oxidation-state group 2, 13 and 14 complexes prepared using  $[\text{Mg}_2(\text{Ar}^{\text{mes}}\text{nacnac})_2]$  as the reducing agent

Precursor	Magnesium(I) dimer	By-product	Product	Refs
$[\text{Mg}(\text{Ph}_2\text{P}(\text{NDip})_2)(\text{X})]$ X = Br or I	$[\text{Mg}_2(\text{Mes}^{\text{mes}}\text{nacnac})_2]$	$[\text{Mg}_2(\text{Mes}^{\text{mes}}\text{nacnac})_2(\text{X})_2]$		38
$[\text{PtBr}(\text{PEt}_3)_2(\text{B}_2\text{Dur}_2\text{Br})]$	$[\text{Mg}_2(\text{Mes}^{\text{mes}}\text{nacnac})_2]$	$[\text{Mg}_2(\text{Mes}^{\text{mes}}\text{nacnac})_2\text{Br}_2]$		39
$[\text{Mg}_2(\text{Dep}^{\text{dep}}\text{nacnac})_2(\text{AlH}_4)_2(\text{NMe}_3)_2]$	$[\text{Mg}_2(\text{Dep}^{\text{dep}}\text{nacnac})_2]$	$2\text{NMe}_3$		42
$[\text{E}(\text{IPr})\text{Cl}_2]$ E = Ge or Sn	$[\text{Mg}_2(\text{Dip}^{\text{dip}}\text{nacnac})_2]$	$[\text{Mg}_2(\text{Dip}^{\text{dip}}\text{nacnac})_2\text{Cl}_2]$		46,47
$[\text{E}(\text{Ar}'\text{C}(\text{NDip})_2)\text{Cl}_n]$ E = Si, Ge or Sn $n = 1$ or $3$	$[\text{Mg}_2(\text{Dip}^{\text{dip}}\text{nacnac})_2]$	$[\text{Mg}_2(\text{Dip}^{\text{dip}}\text{nacnac})_2\text{Cl}_2]$		49
$[\text{Ge}(\text{NAr}(\text{SiR}_3))\text{Cl}]$ Ar = Ar <sup>+</sup> and R = Me; or Ar = Ar <sup>+</sup> and R = <sup>i</sup> Pr	$[\text{Mg}_2(\text{Mes}^{\text{mes}}\text{nacnac})_2]$	$[\text{Mg}_2(\text{Mes}^{\text{mes}}\text{nacnac})_2\text{Cl}_2]$		53,54

Ar' = 4-(<sup>t</sup>Bu)C<sub>6</sub>H<sub>4</sub>; Ar\* = 2,6-[C(H)Ph]<sub>2</sub>-4-MeC<sub>6</sub>H<sub>3</sub>; Ar<sup>+</sup> = 2,6-[C(H)Ph]<sub>2</sub>-4-<sup>i</sup>PrC<sub>6</sub>H<sub>3</sub>; Dep, 2,6-diethylphenyl; Dip, 2,6-diisopropylphenyl; Dur, 2,3,5,6-tetramethylphenyl; Mes, 2,4,6-trimethylphenyl.

**16** and **17** split H<sub>2</sub> at temperatures as low as -10 °C, both in solution and the solid state, to quantitatively afford the diamidodigermene [Ge<sub>2</sub>L<sub>2</sub>H<sub>2</sub>] (where L<sup>-</sup> = [N(2,6-{C(H)Ph<sub>2</sub>}-4-<sup>i</sup>PrC<sub>6</sub>H<sub>2</sub>)(Si<sup>i</sup>Pr<sub>3</sub>)<sup>-</sup>]<sup>53,54</sup>). The formal Ge=Ge bond in this system is weak, such that in solution the dimer can exist in equilibrium with the two-coordinate hydridogermylene monomer GeLH (REF. 53). These unprecedented species, as well as their tin(II) analogues, have been shown to be powerful reagents for the hydrometallation of substrates, such as unactivated alkenes<sup>58</sup>, and are highly efficient catalysts for the hydroboration of aldehydes, ketones<sup>59</sup> and CO<sub>2</sub> (REF. 60).

The reduction of halidogermanium(II) complexes to give species such as **16** and **17** has been postulated to proceed through intermediary germanium(I) radicals

[GeL]<sup>•</sup> that dimerize to give the respective diamagnetic products [Ge<sub>2</sub>L<sub>2</sub>] (REF. 54). Only one example of such a germanium(I) radical, which was generated on reduction of an extremely bulky (β-diketiminato) chlorogermanium(II) complex with [Mg<sub>2</sub>(<sup>Mes</sup>nacnac)<sub>2</sub>], has been stabilized and characterized (**18**, TABLE 3)<sup>61</sup>. The steric bulk of the chelating ligand hinders dimerization of the mononuclear species, which has a half-life of several hours in solution but is indefinitely stable in the solid state. Extensive experimental and computational electron paramagnetic resonance and electron nuclear double resonance studies on **18** revealed that its unpaired spin density is predominantly situated on the germanium atom.

Magnesium(I) dimers can also be used to prepare group 14 systems in higher

oxidation states. In particular, the dimers can reduce dihalidosilicon(IV) precursors R<sub>2</sub>SiX<sub>2</sub> to the stable corresponding silicon(II) products SiR<sub>2</sub>. The two reported examples of such silylenes include an aromatic carbocyclic silylene<sup>62</sup> and a rare example of an acyclic silylene, **19**, which incorporates two bulky arylthiolato ligands<sup>63</sup>. Furthermore, several mixed-valent tin cluster compounds have been prepared by reducing oxidized tin precursors with magnesium(I) systems. The products include [Sn<sub>10</sub>(Trip)<sub>8</sub>] (Trip = 2,4,6-triisopropylphenyl)<sup>64</sup>, [Sn<sub>4</sub>{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>4</sub>(μ-CMe<sub>2</sub>)<sub>2</sub>] (REF. 65) and the remarkable heterometallic complex [Pt<sub>7</sub>Sn<sub>8</sub>Cl<sub>4</sub>(PCy<sub>3</sub>)<sub>6</sub>] (**20**, Cy = cyclohexyl)<sup>66</sup>. The latter features an interstitial Pt atom at the centre of a rhombic dodecahedron with 14 metal vertices, with the average

Table 3 | Examples of low-oxidation-state group 14, 15 and d-block complexes prepared using [Mg<sub>2</sub>(<sup>Ar</sup>nacnac)<sub>2</sub>] as the reducing agent

Precursor	Magnesium(I) dimer	By-product	Product	Refs
[GeCl{HC(C( <sup>t</sup> Bu)NDip) <sub>2</sub> }]	[Mg <sub>2</sub> ( <sup>Mes</sup> nacnac) <sub>2</sub> ]	[Mg <sub>2</sub> ( <sup>Mes</sup> nacnac) <sub>2</sub> Cl <sub>2</sub> ]	<b>18</b>	61
[(Ter) <sub>2</sub> SiBr <sub>2</sub> ]	[Mg <sub>2</sub> ( <sup>Mes</sup> nacnac) <sub>2</sub> ]	[Mg <sub>2</sub> ( <sup>Mes</sup> nacnac) <sub>2</sub> Br <sub>2</sub> ]	<b>19</b>	63
[Pt(PCy <sub>3</sub> ) <sub>2</sub> SnCl <sub>2</sub> ]	[Mg <sub>2</sub> ( <sup>Mes</sup> nacnac) <sub>2</sub> ]	[Mg <sub>2</sub> ( <sup>Mes</sup> nacnac) <sub>2</sub> Cl <sub>2</sub> ]	<b>20</b>	66
[Sb <sub>2</sub> R <sub>4</sub> ] R = Me or Et	[Mg <sub>2</sub> ( <sup>Ar</sup> nacnac) <sub>2</sub> ] Ar = Dip or Mes	[Mg( <sup>Ar</sup> nacnac)R]	<b>21</b>	67
[Fe(R <sub>2</sub> NC(NDip) <sub>2</sub> )Br] R = 2,6-dimethylpiperidinyl	[Mg <sub>2</sub> ( <sup>Dip</sup> nacnac) <sub>2</sub> ]	[Mg <sub>2</sub> ( <sup>Dip</sup> nacnac) <sub>2</sub> Br <sub>2</sub> ]	<b>22</b>	69
[M{NAr(Si( <sup>i</sup> Pr) <sub>3</sub> )}Br] M = Mn and Ar = Ar <sup>†</sup> ; or M = Zn and Ar = Ar <sup>*</sup>	[Mg <sub>2</sub> ( <sup>Mes</sup> nacnac) <sub>2</sub> ]	[Mg <sub>2</sub> ( <sup>Mes</sup> nacnac) <sub>2</sub> Br <sub>2</sub> ]	<b>23</b> : M = Mn; Ar = Ar <sup>†</sup> <b>26</b> : M = Zn; Ar = Ar <sup>*</sup>	71,73
[M{NAr(SiMe <sub>3</sub> )}X] M = Mn, Ar = Ar <sup>*</sup> and X = Br; or M = Zn, Cd or Hg, Ar = Ar <sup>†</sup> and X = Br or I	[Mg <sub>2</sub> ( <sup>Mes</sup> nacnac) <sub>2</sub> ]	[Mg <sub>2</sub> ( <sup>Mes</sup> nacnac) <sub>2</sub> X <sub>2</sub> ]	<b>24</b> : M = Mn; Ar = Ar <sup>*</sup> <b>25</b> : M = Zn, Cd or Hg; Ar = Ar <sup>†</sup>	71,73

Ar<sup>\*</sup> = 2,6-[C(H)Ph<sub>2</sub>]<sub>2</sub>-4-MeC<sub>6</sub>H<sub>3</sub>; Ar<sup>†</sup> = 2,6-[C(H)Ph<sub>2</sub>]<sub>2</sub>-4-<sup>i</sup>PrC<sub>6</sub>H<sub>2</sub>; Cy, cyclohexyl; Dip, 2,6-diisopropylphenyl; Mes, 2,4,6-trimethylphenyl; Ter, 2,6-(Mes)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>.

oxidation state of tin being 0.5. Formed by reduction of the metal-only Lewis pair [Pt(Cy<sub>3</sub>P)<sub>2</sub>SnCl<sub>2</sub>], the large polyhedron represents a small-molecule model for Sn–Pt intermetallics, which are important to several heterogeneous catalytic processes.

**Group 15.** Although the reduction of group 15 complexes using magnesium(I) compounds has not been widely studied, recent work has highlighted the value of these reagents in pnicogen chemistry. Reduction of distibanes [Sb<sub>2</sub>R<sub>4</sub>] (R = Me or Et) with magnesium(I) dimers involves reductive cleavage of Sb–C bonds to afford the magnesium-substituted polystibides [Mg<sub>4</sub>(Ar<sub>2</sub>nacnac)<sub>4</sub>(Sb<sub>8</sub>)] (21, Ar = Mes or Dip)<sup>67</sup>, each of which can be viewed as a [Sb<sub>8</sub>]<sup>4-</sup> core ligated to four [Mg(Ar<sub>2</sub>nacnac)]<sup>+</sup> cations. Thus, the magnesium(I) dimer reacts with the antimony centres and fragments into magnesium(II) monomers that are bound to the reduced metal centres, a reaction scheme that has previously been demonstrated for some reductions of transition metal halides (see below). A subsequent report described the related polystibide [Mg<sub>4</sub>(guan)<sub>4</sub>(Sb<sub>4</sub>)] (guan<sup>-</sup> = [Pr<sub>2</sub>NC(NDip)<sub>2</sub>]<sup>-</sup>), the synthesis of which involved treating the bis(guanidinato) dimagnesium(I) reductant [Mg<sub>2</sub>(guan)<sub>2</sub>] with the tetraantimony(I) butterfly complex [Sb<sub>4</sub>(C<sub>3</sub>Me<sub>5</sub>)<sub>4</sub>] (REF. 68).

**d-Block.** Magnesium(I) dimers have also demonstrated their value in the synthesis of several d-block metal complexes that are not attainable using other reducing agents. A case in point here is the diiron(I) complex 22, which was prepared by reduction of a bromidoguanidinatoiron(II) precursor<sup>69</sup>. The diiron(I) system exhibits the shortest Fe–Fe bond (~2.13 Å) yet reported, an unusual interaction given that it involves significant multiple bond character between two high-spin iron centres. This highly reactive molecule is emerging as a promising reagent in several areas, including in small-molecule activations<sup>30</sup>. A related complex, the Mn–Mn-bonded bis(amidinato) dimanganese(I) complex [Mn<sub>2</sub>(Piso)<sub>2</sub>] (Piso<sup>-</sup> = [(<sup>t</sup>Bu)C(NDip)<sub>2</sub>]<sup>-</sup>), was prepared using a magnesium(I) reductant<sup>69</sup>, as was the related manganese(II) hydride [Mn<sub>2</sub>(Piso)<sub>2</sub>(μ-H)<sub>2</sub>] (REF. 70). Interestingly, the latter complex acts as a ‘masked’ source of manganese(I) in reactions with small molecules such as N<sub>2</sub>O and O<sub>2</sub>.

Treatment of the extremely bulky monodentate amidohalidomanganese(II)

complex [MnLBr] (L<sup>-</sup> = [N(Ar<sup>+</sup>)(Si<sup>+</sup>Pr<sub>3</sub>)]<sup>-</sup>, Ar<sup>+</sup> = 2,6-[C(H)Ph<sub>2</sub>]<sub>2</sub>-4-<sup>i</sup>PrC<sub>6</sub>H<sub>2</sub>) with a magnesium(I) dimer does not, surprisingly, lead to the dimanganese(I) species [Mn<sub>2</sub>L<sub>2</sub>] through a typical one-electron reduction of the manganese(II) centre<sup>71</sup>. Instead, a two-electron reduction of the substrate occurs to afford [Mg<sup>(Mes)</sup>nacnac]MnL (23), which features a high-spin two-coordinate Mn centre bonded to Mg. It is the steric bulk of the amido ligand that is believed to prevent the targeted dimer from forming, and indeed a dimanganese(I) product (24) does form when the manganese(II) precursor bears a slightly smaller amido ligand. The manganese centres in 24 are high-spin and antiferromagnetically coupled. Known reactions of 23 include its use as an inorganic ‘Grignard reagent’ for the transfer of its manganese amide fragment to other metal centres, yielding in one case an unsymmetrically substituted, two-coordinate dimanganese(I) complex [Mn<sub>2</sub>LL’] (L’<sup>-</sup> = [N(Ar<sup>+</sup>)(SiMe<sub>3</sub>)]<sup>-</sup>, Ar<sup>+</sup> = 2,6-[C(H)Ph<sub>2</sub>]<sub>2</sub>-4-MeC<sub>6</sub>H<sub>2</sub>). Moreover, the electron-rich Mn–Mg bond of 23 is reactive towards small-molecule substrates. For example, treatment of 23 with N<sub>2</sub>O afforded [MnL(μ-O)Mg(THF)<sup>(Mes)</sup>nacnac], the first example of a two-coordinate oxomanganese complex<sup>71</sup>.

The chemistry described above also largely translates to the group 12 metals<sup>72,73</sup>. Most importantly, reductions of amidohalidometal(II) precursors with a magnesium(I) dimer give the homologous series of two-coordinate group 12 metal–metal bonded dimers (25) when the bulky monodentate amido ligand bears a trimethylsilyl substituent. However, if the bulkier triisopropylsilyl-substituted amido is used, reduction of the amidobromidozinc(II) precursor instead affords 26, the first example of a complex with an unsupported Zn–Mg bond. The product, like its manganese counterpart 23, acts as an inorganic ‘Grignard reagent’ in reactions with metal halides to give unusual products that include an unprecedented, near linear, two-coordinate mixed-valent trizinc complex [L’’ZnZnZnL’’] and its heavier analogues [L’’ZnMZnL’’] (L’’<sup>-</sup> = [N(Ar<sup>+</sup>)(Si<sup>+</sup>Pr<sub>3</sub>)]<sup>-</sup>, M = Cd or Hg)<sup>73</sup>.

### Conclusions and outlook

With the isolation of the first stable magnesium(I) dimers in 2007 came the realization that such systems have unique properties that make them attractive as soluble, selective, stoichiometric and safe reducing agents in many areas of organic

and inorganic synthesis. This has been amply demonstrated over the past decade, with β-diketiminato-coordinated examples, in particular, being exploited by an increasing number of researchers from around the globe. Such magnesium(I) dimers have allowed access to numerous novel compound types that are not accessible, or can only be prepared in much lower yields, when using more established reducing agents. Furthermore, many of the products of magnesium(I) reductions have gone on to find unique synthetic applications in their own right, a situation which only strengthens the case for magnesium(I) dimers to be viewed as an important new class of quasi-universal reducing agent.

So what does the future hold for the present class of compounds? Although it seems clear that currently available three-coordinate magnesium(I) dimers will continue to find more applications, certain situations will call for species with different steric and electronic properties. The reactivity scope of dimagnesium(I) compounds will be broadened by the emergence of promising new complexes such as the recently reported dimagnesium(I) compound [Mg<sub>2</sub>{N(Ar<sup>+</sup>)(SiMe<sub>3</sub>)<sub>2</sub>}]<sub>2</sub>, which features extremely bulky monodentate amido ligands<sup>8</sup>. Examples in this class of compounds are simple to prepare and thermally very stable. These two-coordinate complexes, given their low coordination number and the higher electrophilicity of their metal centres, are likely to be significantly more reactive than their β-diketiminato-ligated counterparts. A more challenging (although no less appealing) goal is to use magnesium(I) dimers in catalytic transformations that normally require toxic and expensive low-valent, late transition metal complexes. Effecting such transformations would probably necessitate the oxidative addition or reductive elimination of the Mg–Mg bond to substrates under mild conditions, it is not beyond the realm of possibility. Indeed, it is no less likely than the prospect of ‘bottleable’ magnesium(I) dimers seemed to many before 2007. Whatever the case, the future looks promising for the chemistry of magnesium(I) dimers and related low-valent s-block systems.

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doi:10.1038/s41570-017-0059

Published online 19 Jul 2017

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#### Acknowledgements

The author thanks the Australian Research Council and the US Air Force Asian Office of Aerospace Research and Development for funding.

#### Competing interests statement

The author declares no competing interests.

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#### How to cite this article

Jones, C. Dimeric magnesium(II)  $\beta$ -diketimines: a new class of quasi-universal reducing agent. *Nat. Rev. Chem.* **1**, 0059 (2017).