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Alkaline earth metals: heterometallic bonding

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The alkaline earth metals are notorious for their tendency to form ionic compounds of their dications. In recent years, however, chemists have found ways to kinetically skirt around the edges of these thermodynamic sinks, thereby providing access to new pastures of molecular alkaline earth element chemistry. Most prominently, novel low-oxidation state reagents have enabled the synthesis of a wide range of complexes with alkaline earth-metal interactions. There is a growing appreciation of the remarkable properties of these heterometallic complexes, which display unique electronic structures and reactivity patterns. This Frontier article outlines recent advances in the field and proposes pathways to future breakthroughs.

Introduction

Classical models of chemical bonding often fail to effectively describe the true nature of the alkaline earth-metal (Ae-M) bond.^{1–3} Thus, the study of such interactions is of fundamental importance, but also has broader relevance.³ For example, heterometallic Ae complexes are useful precursors to the preparation of activated metals and alloys and have been proposed as key intermediates in the transition metal-catalysed synthesis and cross-coupling of Grignard reagents.^{4–7}

The first structurally characterised complex with an Ae-M bond, CpFe[MgBr(THF)₂](dppe) (**1**, dppe = 1,2-bis(diphenylphosphino)ethane), was reported in 1974.⁸ This molecule was prepared by the reaction of activated magnesium metal with CpFe(dppe)Br; Mg inserts into the Fe-Br bond in a process that resembles the formation of an “inorganic Grignard reagent” (Scheme 1).

Recently, species with Ae-M bonds have received tremendous attention due to the increased synthetic accessibility of such complexes, as well as the greater appreciation for their capacity to exhibit remarkable chemical behaviour.^{9–11} Regarding this reactivity, the Ae elements are amongst the Periodic Table's least electronegative members. As a result, Ae-M bonds are typically highly polarized, with M(δ^-) and Ae(δ^+) sites.^{12,13} This combination of close-proximity Lewis acidic and basic centres is one reason for the unique chemical capa-

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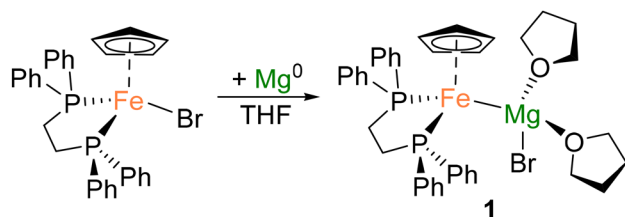
reactivity and electronic structure of low valent Rare Earth complexes.

Liam P. Griffin completed both his MChem and DPhil at the University of Oxford under the supervision of Prof. Simon Aldridge. Liam's research in the area of Main Group chemistry focussed on installing heavy boryl analogues at metal centres in order to better understand these group 13 metallo-ligands. He is now a PDRA in the Goodwin group at the University of Manchester, investigating the



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Scheme 1 Synthesis of “inorganic Grignard” complex **1**.

bilities of these complexes.¹⁴ Additionally, in these heterometallic complexes the highly electron-rich nature of M may lead to this atom displaying exceptional nucleophilicity.²

Bonding considerations

The chemistry of the Ae elements changes considerably as the group is descended.^{15–20} Of all the Periodic Table's metals, the beryllium atom has the smallest radius, at 1.05 Å (Table 1).²⁰ Furthermore, this element has the highest Pauling electronegativity and first ionisation energy of all s-block metals ($\chi = 1.57$; IE_1 ; 215 kcal mol^{−1}).^{19,20} Hence, beryllium is the least reducing Ae, and its bonding comprises a significant degree of covalent character.^{21,22} Calcium, on the other hand, has an atomic radius of 1.80 Å, which is greater even than that of uranium (1.75 Å), for example (Table 1).^{19,20} Additionally, calcium's χ and IE_1 values (1.00 and 141 kcal mol^{−1}, respectively) are very low, meaning that this element's bonding is predominantly ionic in nature and is rather weak (Table 1).^{18,23,24} As might be anticipated, the properties of magnesium are intermediate between those of beryllium and calcium. Chiefly, the variance in chemical properties as group 2 is descended can be ascribed to the filling of 2p- and 3s-orbitals on transitioning from Be to Mg, and 3p- and 4s-orbitals and from Mg to Ca. These orbitals, with small principal (n) and azimuthal (ℓ) quantum numbers, are effectively shielding. Compounding this, the nuclear charges of s-block atoms are always the smallest amongst the successive elements of their respective periods. Therefore, Z_{eff} for the valence electrons increases by relatively small increments upon descending the group from Be to Mg to Ca. As a result, calcium has very diffuse frontier orbitals and is highly reducing.²⁴ The effects of the d-block and f-block contractions (3d- and 4f-orbitals are kinosymmetric – they are the first orbital set with their respective value

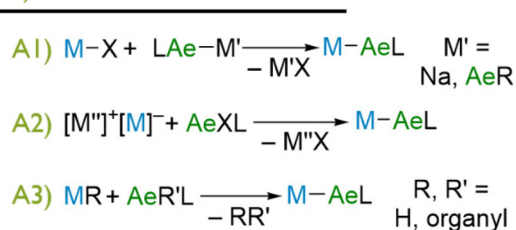
of ℓ and therefore possess zero radial nodes and shield poorly) means that the chemistries of Ca, Sr, and Ba are very similar.¹⁸

In terms of the covalent component to Ae bonding, due to the kinosymmetry of the 2p-orbitals (with zero radial nodes), effective spatial overlap between this orbital set and the 2s-orbital (one radial node) is observed.²⁰ Hence, for beryllium 2s/2p-mixing is important.²⁵ Amongst the Ae metals, the valence orbitals of beryllium are the least diffuse and therefore have the greatest capacity for effective covalent overlap with other atoms. Upon descending the group, the potential for (n)s/(n)p-orbital hybridisation is lessened (even though these orbitals become more similar in energy) because their spatial overlap is poorer.²⁵ Notably, however, the covalent component to the bonding of the heavier Ae elements (Ca, Sr, Ba) may comprise small contributions from the ($n - 1$) d-orbitals, which are rather low lying.^{25–27} For example, in the case of the Ba⁺ ion, the ²D_{3/2} ([Xe]6s⁰5d¹6p⁰) excited states lies <14 kcal mol^{−1} above the ²S_{1/2} ([Xe]6s¹5d⁰6p⁰) ground state.²⁶ The ²P_{1/2} ([Xe]6s⁰5d⁰6p¹) excited state is >40 kcal mol^{−1} higher in energy than the ²D_{3/2} state.

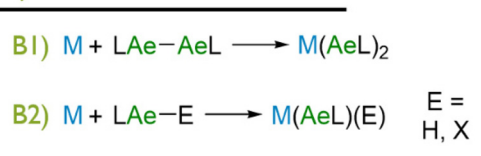
Synthetic approaches

Strategies that have been employed to synthesise complexes with Ae–M bonds are summarised in Fig. 1. Broadly, these could be grouped into three classes: (A) metathesis; (B) Ae–E bond addition; and (C) reduction. Class A includes reaction of a M–X bond with an Ae–M' bond (A1; X = (pseudo)halide), reaction of a nucleophilic source of M with an Ae–X bond (A2), or alkane/arene/H₂ elimination through the reaction of MR

A) Metathesis



B) Ae–E Bond Addition



C) Reduction

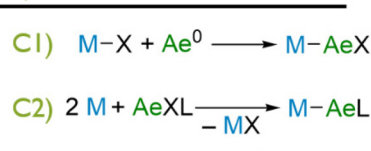


Fig. 1 Synthetic methodologies used to prepared complexes with Ae–M bonds.

Table 1 Ionisation enthalpies (IE), Pauling electronegativities (χ), and atomic/ionic radii of the alkaline earth elements

Element	IE_1 / kcal mol ^{−1}	IE_2 / kcal mol ^{−1}	χ	Atomic radius/Å	Ionic radius Ae ²⁺ /Å
Be	215	421	1.57	1.05	0.59
Mg	177	347	1.31	1.50	0.86
Ca	141	274	1.00	1.80	1.14
Sr	131	254	0.95	2.00	1.32
Ba	120	231	0.89	2.15	1.49
Ra	122	234	0.90	2.15	1.62



and AeR'L (R,R' = hydride, organyl; L = anionic ancillary ligand) (**A3**).^{28–30} Class **B** includes addition of an Ae–Ae bond to M (**B1**), and insertion of M into an Ae–E bond (**B2**; E = hydride, halide).^{31,32} Considering the low electronegativity of Ae elements, class **B** reactions may formally be categorized as “reductive addition” processes in some cases.^{33,34} Class **C** includes the methodology used in the synthesis of “inorganic Grignard” complex **1** (**C1**), as well as the use of alkali metal (AM) reductants to prepare species with Ae–AM bonds (**C2**).^{8,35}

Both routes **A1** and **B1** – which are amongst the most common synthetic methodologies for the preparation of Ae–M bonds – require molecular low-oxidation state Ae reagents.^{11,36} The increasing synthetic availability of such materials has, therefore, been key to the rapid recent developments in the study of heterometallic alkaline earth-metal bonding.

Beryllium

Owing to its toxicity, the chemistry of beryllium remains poorly explored.^{21,37} Nonetheless, this element possesses many unique facets. For example, due to its exceptionally small radius and significant positive charge, the Be²⁺ dication is extraordinarily charge dense and polarising (Table 1).²² Indeed, Be²⁺ is, perhaps, the ‘hardest’ of all Lewis acids. As a result, suitable ligands, solvents, and reaction conditions must be carefully selected for the synthesis of reactive beryllium-containing complexes.³⁸ Indeed, despite beryllium’s capacity to form bonds comprising significant covalent contributions, there remains a dearth of complexes featuring Be–M bonds. In 2009, the first structurally authenticated complexes featuring electron-precise Be–M bonds – dative Pt → Be interactions – were reported (**2**, Fig. 2).³⁹ A decade later, complexes of the form [(NacNac^{Dipp})(X)Al–Be(X)(tmdda)] (**3Br**, X = Br; **3I**, X = I; NacNac^R = [{(R)NC(Me)}₂CH][–]; Dipp = 2,6-diisopropylphenyl) were described (Fig. 2).^{40,41} These complexes each feature a covalent Be–Al bond and were prepared *via* insertion of an aluminylene into a Be–X bond (route **B2**). Notably, due to the similar χ values of aluminium (1.61) and beryllium (1.57), **3Br** and **3I** could be considered pseudo-beryllium(i) species.

Recently, beryllium–aluminyl, –gallyl, and –indyl complexes, CpBe–Tr(NON) (**4**, Tr = Al; **5**, Tr = Ga; **6**, Tr = In; NON =

4,5-bis(2,6-diisopropylanilido)-2,7-ditert-butyl-9,9-dimethylxanthene), were synthesised *via* reaction of BeCp₂ with the respective triaryl nucleophile (route **A2**; Scheme 2).^{12,13} Due to the highly electropositive nature of Al and In, the beryllium centre of both **4** and **6** was shown to display nucleophilic character. By contrast, the marginally higher electronegativity of Ga (*vs.* Al and In) resulted in the Be site in **5** exhibiting electrophilic behaviour. These observations correlate with the charge distribution calculated for **4–6**. The bonding combination of two small electropositive atoms, Be and Al, in **4** leads to other peculiarities for the electronic structure of this complex. Most notably, a non-nuclear attractor (NNA) – a three-dimensional maximum in electron density that is not associated with an atomic nucleus – is calculated for the Al–Be interaction.^{13,42,43} This is likely one reason that **4** reacts as a low-oxidation state beryllium synthon. Whilst NNAs have been previously detected for complexes with Mg–Mg bonds, that in **4** represents the first manifestation of this phenomenon for a heterometallic bond in an experimentally isolated molecule.⁴⁴

Recently, the first stable molecular species with Be–Be bonds have been prepared.^{10,45,46} This advance has provided the means for rapid developments in the study of Be–M bonding. This was initially demonstrated with the synthesis of CpBe–Zn(NacNac^{Dipp}) (**7**) – a complex with a covalent Be–Zn bond.⁴⁵ Complex **7** was prepared by an **A1**-type reaction of diberyllocene (**8**, CpBeBeCp) with IZn(NacNac^{Dipp}) (Scheme 3). Natural Bond Order (NBO) calculations suggest that the Be–Zn bond comprises essentially equal contributions from both metal atoms. Thus, it is possible to formulate this complex as a Zn^I/Be^I species, in contrast with the formal Zn⁰/Be^{II} assignment that would be derived from consideration of χ (Be, 1.57; Zn, 1.65).

Perhaps more interesting is the capacity of the Be–Be bond to add to low-oxidation state metal centres, yielding poly(beryllyl) complexes (route **B1**). This reactivity mirrors that of the B–B bonds of diborane(4) derivatives, for example. Indeed, a recent experimental study compared the addition of Be–Be, B–B, and B–H bonds at a tin(II) centre (Scheme 4).³⁴ Notably, on the basis of χ values the formal natures of Be–Be (reductive), B–B/B–H (oxidative) addition reactions contrast one another. Consequently, quantum chemical calculations indicate that the tin centre of bis(beryllyl) complex **9** is far more electron rich than those of its bis(boryl) and (boryl)hydride analogues.

Translating this chemistry to the d-block, reaction of 0.5 equiv. of Fe₂(CO)₉ with **8** generated diamagnetic 18-electron *cis*-Fe(BeCp)₂(CO)₄ (**10**; Scheme 5).³¹ Compared with isostructural *cis*-Fe(X)₂(CO)₄ species (X = SiMe₃, BCat, *etc.*), ν_{CO} for **10** are of the lowest energy, providing evidence for the exceptional electron richness of the Fe centre in this complex and, indirectly, the σ -donor properties of beryllyl ligands.

In the case of transition metal precursors bearing more labile ligands, the addition of more than one Be–Be bond is possible. Most remarkably, reaction of Ni(COD)₂ (COD = 1,5-cyclooctadiene) with three equivalents of **8** generated Ni(BeCp)₆ (**11**), an unprecedented hexavalent nickel complex (Scheme 5).³¹ This diamagnetic 16-electron complex adopts a

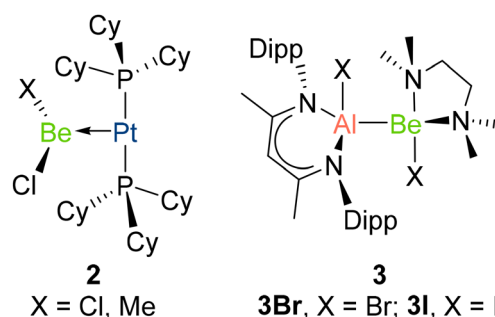
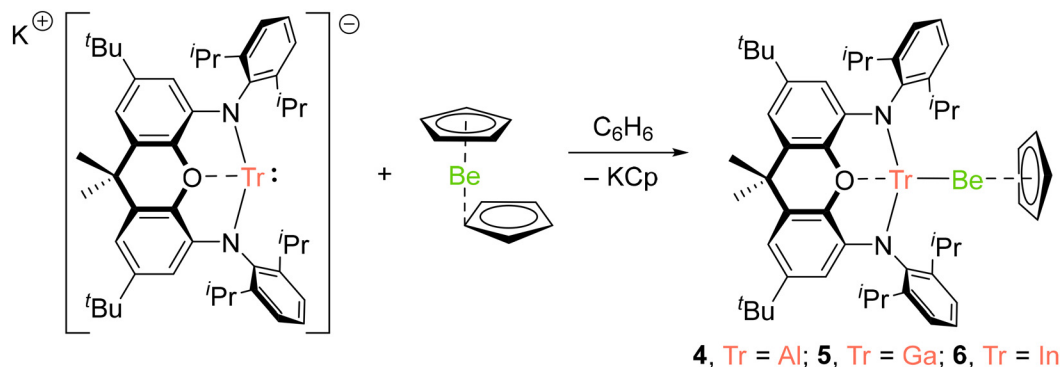
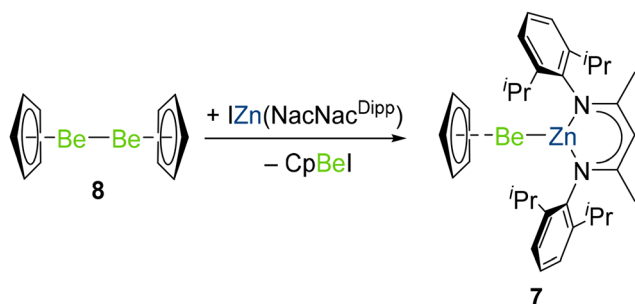


Fig. 2 The first structurally authenticated complexes featuring Be–M bonds.

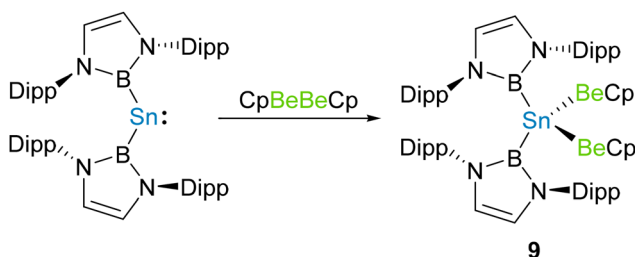




Scheme 2 Synthesis of beryllium-triaryl complexes.



Scheme 3 Synthesis of beryllium-zincyl/zinc-beryllyl complex 7.

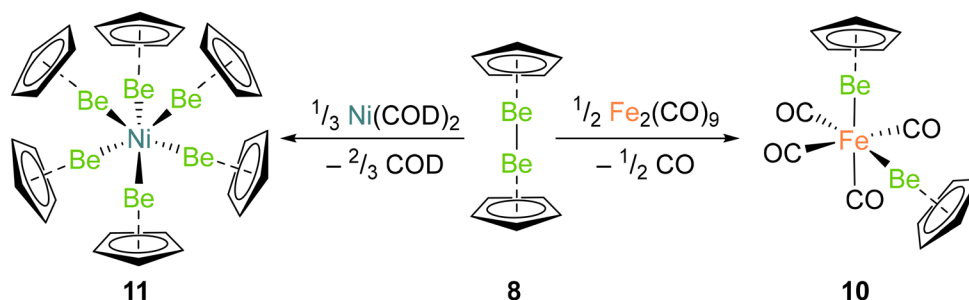


Scheme 4 Synthesis of bis(beryllyl) tin(0) complex 9.

local C_{3v} geometry at Ni – the Ni 4p-orbitals are populated with four electrons and are non-degenerate in this arrangement, resulting in a large energetic separation between the HOMOs

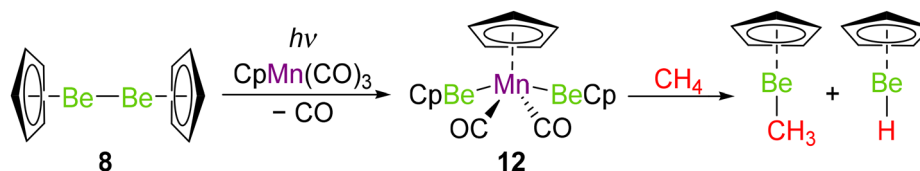
(pseudo-degenerate $4p_x^2$ and $4p_y^2$; -6.7 eV) and LUMO ($4p_z^0$; $+1.5$ eV) for **11**. Furthermore, complex **11** exhibits an inverted ligand field due to the isoenergetic nature of the frontier orbitals of nickel and the beryllyl ligands.⁴⁷ Ligand field inversion is thought to be common amongst high-valent nickel complexes (*e.g.*, tetravalent $K_2[NiF_6]$).⁴⁸ Additionally, quantum chemical methods indicate that **11** may be aromatic in nature, as a result of the seven-centre two-electron HOMO–19, which represents the in-phase combination of the Ni 4s-orbital and six Be 2s-orbitals.³¹ Certainly, the potent σ -donor capabilities of the BeCp ligands are, at least in part, responsible for the stabilisation of this unique nickel valence state.

The ability of beryllyl ligands to engender exceptional chemical reactivity from transition metals is also emerging. Astonishingly, *trans*-CpMn(BeCp)₂(CO)₂ (**12**; synthesised by route **B1**) is capable of catalytically beryllating methane (Scheme 6) under ambient temperature and pressure.⁴⁹ Quantum chemical calculations of the reaction mechanism indicate that this novel C–H elementation process is dependent upon the beryllyl ligands. Indeed, not only are these groups powerfully σ -donating, but each also features a highly Lewis acidic beryllium centre. Synergistic trimetallic (MnBe₂) cooperativity is key to polarizing and cleaving the strong C–H bond of CH₄ (104 kcal mol^{−1}). The bis(boryl) analogue of **12**, *trans*-CpMn(BPin)₂(CO)₂, has not been reported to borylate methane; calculations suggest that the Mn centre is insufficiently electron rich, and the boron atoms are inadequately Lewis acidic to facilitate this chemical transformation.^{49–52}



Scheme 5 Synthesis of iron- and nickel-beryllyl complexes.





Scheme 6 Synthesis of bis(beryllyl)manganese complex **12** and its reactivity towards methane.

The heterometallic bonding combination of beryllium with its heavier analogue has recently been realised. By reacting $[\text{Mg}(\text{NacNac}^{\text{Dipep}})\text{Na}]_2$ (**13**; $\text{NacNac}^{\text{R}} = [(\text{R})\text{NC}(\text{tBu})_2\text{CH}]^-$, $\text{Dipep} = 2,6\text{-diisopentylphenyl}$) – a magnesium(0) nucleophile – with Cp^*BeCl , $\text{Cp}^*\text{Be-Mg}(\text{NacNac}^{\text{Dipep}})$ (**14**) is formed (route **A1**; Scheme 7).^{35,53} This complex is calculated to possess a nucleophilic Be centre, as might be anticipated by consideration of the relative χ values for Be and Mg (Table 1). Whilst decisive experimental evidence of $\text{Be}(\delta^-)\text{-Mg}(\delta^+)$ bond polarity has not been disclosed, **14** can reductively couple AdN_3 to generate a hexazenediide, mirroring the behaviour of complexes with homometallic Mg–Mg bonds.^{53,54}

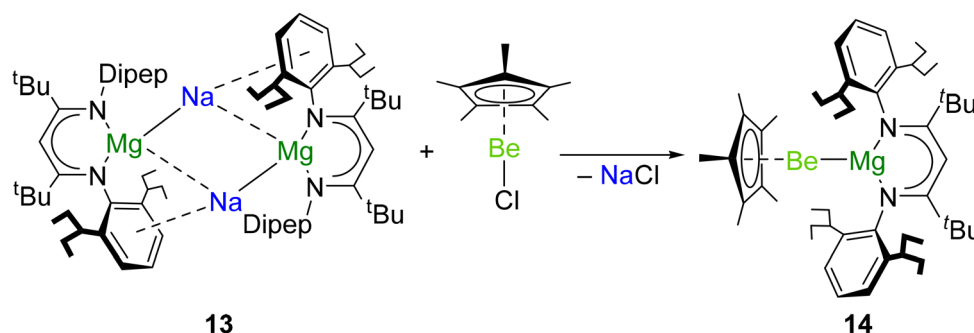
Magnesium

Amongst the alkaline earth elements, the heterometallic bonding chemistry of magnesium is the most comprehensively investigated.² This is likely due to (1) the greater strength and higher covalency of Mg–M bonding compared with heavier Ae–M bonding; (2) the non-toxicity of Mg, which makes the handling of this element less technically challenging than Be; (3) the synthetic availability of low-oxidation state magnesium reagents, the first examples of which were reported nearly two decades ago.^{55,56} Like beryllyl ligands, magnesyl groups have been demonstrated to act as powerful σ -donors, stabilising metals in unusual valence states and engendering novel reactivity modes. Importantly, the smaller IE_1/IE_2 of Mg compared with Be (Table 1) has a bearing on the electronic structure and reactivity of analogous complexes with Mg– and Be–M bonds. For example, the magnesium analogue of complex **4**, $\text{CpMg-Al}(\text{NON})$ (**15**), reacts as an aluminium-centred nucleophile and magnesium-centred electrophile.¹² This contrasts with the

reactivity of complex **4**, in which the Ae atom (Be) acts as a nucleophile and the Al site as an electrophile.¹³

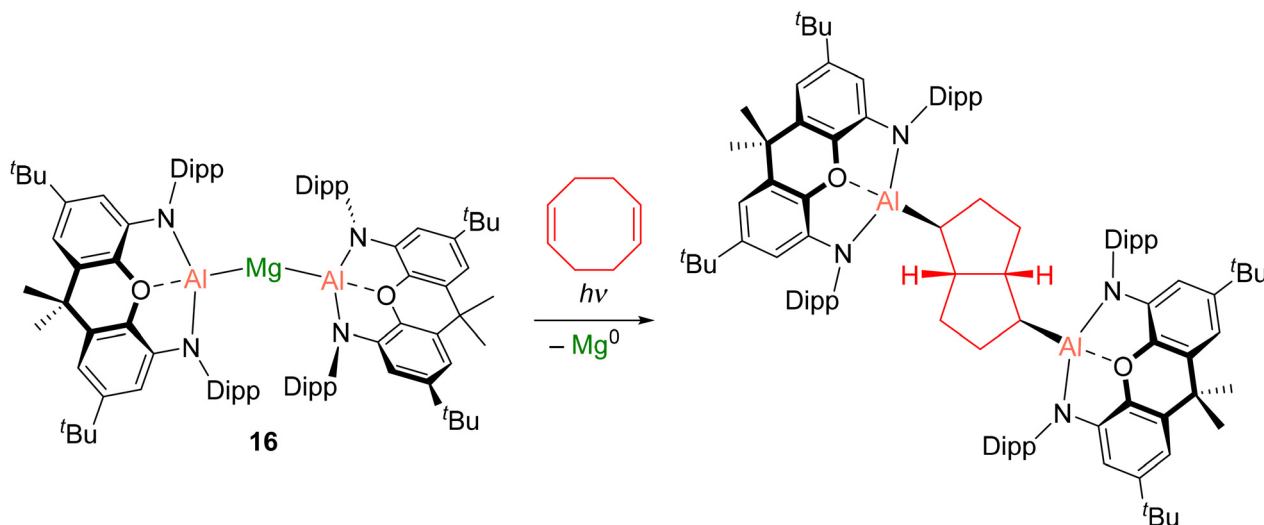
Synthetic routes to complexes with Mg–M bonds are especially diverse, given the well explored chemistry of magnesium and the resulting wide range of available precursor complexes. The reactions of magnesium halides/pseudohalides with aluminyl nucleophiles have been successfully used to prepare several magnesium mono(aluminyl) complexes, such as **15**.^{12,29,57–59} Bis(aluminyl) magnesium complex $\text{Mg}[\text{Al}(\text{NON})]_2$ (**16**) was also recently prepared by reaction of MgI_2 with the dimeric potassium aluminyl reagent $[\text{Al}(\text{NON})\text{K}]_2$ (route **A2**).⁶⁰ Remarkably, coordinated by two potent σ -donor ligands, the Mg centre of complex **16** behaves as if in a low-oxidation state. For example, **16** has been demonstrated to deliver divalent aluminyl radicals to organic substrates (Scheme 8).

Leveraging route **B2**, hexagonal planar complexes of palladium, such as $\text{Pd}[\text{Mg}(\text{NacNac}^{\text{Dipp}})]_3(\text{H})_3$ (**17**), have been prepared *via* the addition of three Mg–H bonds to a single Pd^0 centre (Scheme 9).^{32,61} As with hexavalent Ni complex **11**, the unique geometry and valence state of the transition metal metallo-ligands; the Pd site within **17** is extremely electron rich, and the Mg–Pd interactions are predominantly ionic in nature.^{31,32,61} Reaction of $\text{HZn}(\text{NacNac}^{\text{Dipp}})$ with the same Pd precursor does not lead to Zn–H bond addition, but instead to a Zn–H σ -complex of Pd, $\text{Pd}[\text{HZn}(\text{NacNac}^{\text{Dipp}})]_3$ (**18**).⁶¹ This is due to the less reducing nature of zincyl ligands compared with their magnesyl analogues. Notably, in C_6D_6 complex **17** undergoes H/D exchange, highlighting the capacity of these heterometallic complexes for C–H functionalisation.^{32,61} As somewhat of an aside, the combination of $[\text{Mg}(\text{NacNac}^{\text{Mes}})]_2$ with catalytic quantities of $\text{PdMe}_2(\text{TMEDA})$, $\text{Pt}(\text{PCy}_3)_2$, $\text{Ni}(\text{COD})_2/\text{PCy}_3$, or $\text{Pd}(\text{PCy}_3)_2$ in benzene leads to the magnesia-

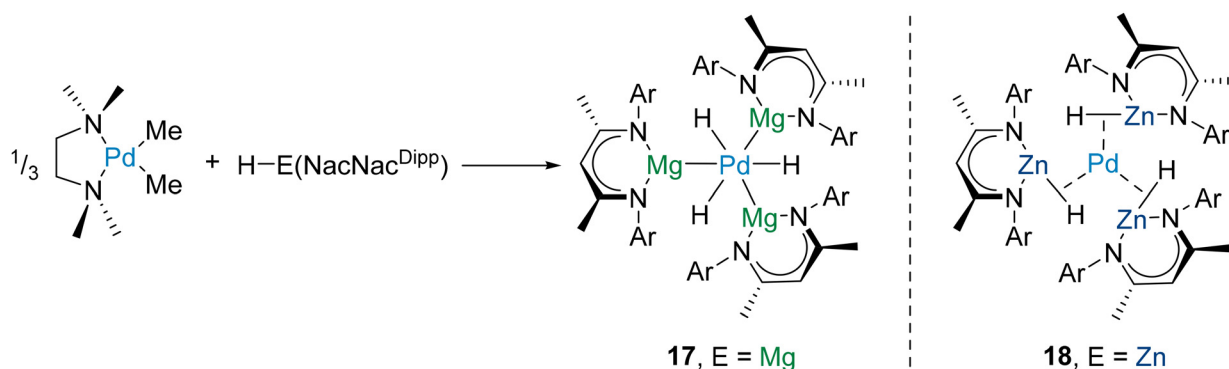


Scheme 7 Synthesis of magnesium–beryllyl complex **14**.





Scheme 8 Photochemical reactivity of complex 16, which acts as an aluminium(III) source.



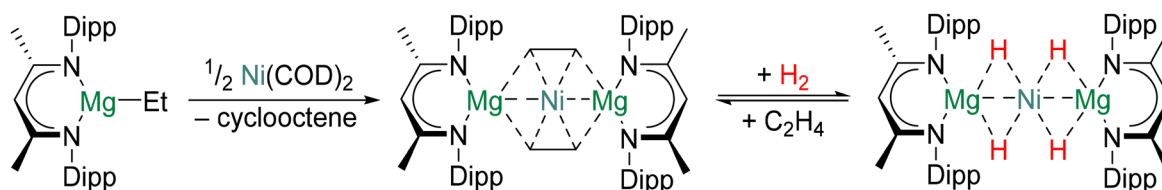
Scheme 9 Syntheses of complexes 17 and 18.

tion of the aromatic solvent.⁶² Whilst the intermediates in these reactions have not been isolated and their mechanisms remain unknown, it could be reasonably postulated that species with Mg–M bonds are responsible for this reactivity.

Recently, the unusual planar hexacoordinate complex $\text{Ni}(\text{C}_2\text{H}_4)_2[\text{Mg}(\text{NacNac}^{\text{Dipp}})]_2$ (**19**) was prepared by reaction of $\text{Ni}(\text{COD})_2$ with $\text{EtMg}(\text{NacNac}^{\text{Dipp}})$ (Scheme 10).⁶³ Cyclooctene was observed as a by-product of this reaction, leading the authors to propose that **19** forms *via* initial β -H elimination from the ethyl ligand, generating ethylene and a heterometallic Mg/Ni hydride complex which subsequently engages in the transfer

hydrogenation of COD. Complex **19** is calculated to feature very weak Ni–Mg bonding (Wiberg bond index = 0.08) and is found, by experimental (X-ray photoelectron spectroscopy) and computational means, to be best described as a low-spin nickel(II) complex. Notably, **19** reversibly activates H_2 , generating $\text{Ni}(\mu\text{-H})_4[\text{Mg}(\text{NacNac}^{\text{Dipp}})]_2$ and ethylene (Scheme 10), and catalytically hydrogenates and hydrosilylates olefins.^{63,64} The cooperative action of nickel and both magnesium sites is proposed to be key to this reactivity.

Stable complexes with direct Mg–Mg bonds present a convenient means for the preparation of complexes with Mg–M



Scheme 10 Synthesis of complex 19 and its reactivity with H_2 .



bonds.^{55,56} Hence, a wide range of complexes of type M–Mg (NacNac^R) have been accessed (*via* route A1) from this starting point, *via* metathesis with metal halides. For example, an open-shell manganese(0) magnesyl complex $L^{\dagger}\text{Mn-Mg}(\text{NacNac}^{\text{Mes}})$ (**20**; $L^{\dagger} = [\text{N}(\text{Ar}^{\dagger})(\text{Si}^i\text{Pr}_3)]^{-}$, $\text{Ar}^{\dagger} = \text{C}_6\text{H}_2[\text{C}(\text{H})\text{Ph}_2]_2$, 2,6,4) was prepared by reaction of $[\text{Mg}(\text{NacNac}^{\text{Mes}})]_2$ with $\{L^{\dagger}\text{Mn}(\text{THF})(\mu\text{-Br})\}_2$ (Fig. 3).²⁸ Complex **20** reacts as a nucleophilic manganese species. Similarly, a complex with a Cu–Mg bond, (6-Dipp)Cu–Mg(NacNac^{Dipp}) (**21**; 6-Dipp, $\text{C}\{\text{N}(\text{Dipp})\text{CH}_2\}_2\text{CH}_2$), was prepared by metathesis of $[\text{Mg}(\text{NacNac}^{\text{Dipp}})]_2$ with (6-Dipp)Cu(OEt) (Fig. 3).⁶⁵ Both quantum chemical calculations and experimental reactivity studies are consistent with the nucleophilic character of the Cu centre in **21**. Additionally, reaction of $[\text{Mg}(\text{NacNac}^{\text{Mes}})]_2$ with $L^*\text{ZnBr}$ ($L^* = [\text{N}(\text{Ar}^*) (\text{Si}^i\text{Pr}_3)]^{-}$, $\text{Ar}^* = \text{C}_6\text{H}_2[\text{C}(\text{H})\text{Ph}_2]_2\text{Me}_{2,6,4}$) was shown to yield $L^*\text{Zn-Mg}(\text{NacNac}^{\text{Mes}})$ (**22**), a stable Zn^0 complex with a Zn–Mg bond.⁶⁶ It was demonstrated that **22** could be used for the preparation of hetero- and homo-trimetallic complexes of the form $L^*\text{Zn-M-ZnL}^*$ ($\text{M} = \text{Zn}, \text{Cd}, \text{Hg}$) (Fig. 3).

The report of sodium magnesyl **13** also dramatically expanded synthetic frontiers in Mg–M bonding.³⁵ Complex **13** was the first structurally authenticated complex to feature a heterometallic interaction between s-block metals. The complex is prepared by the reduction of $\text{IMg}(\text{NacNac}^{\text{Dipep}})$ with Na/NaCl (route C2). The kinetic stabilisation afforded by the very bulky $[\text{NacNac}^{\text{Dipep}}]^{-}$ ligand is crucial to the isolation of this complex. Moreover, Mg–Na bonding is clearly also key to the stability of **13**, lessening build-up of electron density at Mg. Indeed, quantum chemical calculations suggest that the charges at the (formal) sodium mono-cations are far lower than unity (NPA, +0.50; Bader, +0.74).³⁵ Experimental evidence for the partially reduced nature of Na^+ in **13** has also been reported – this complex deposits metallic sodium upon heating to 56 °C in benzene solution. This reactivity is also mirrored by $[\{\text{SiN}^{\text{Dipp}}\}\text{MgNa}]_2$ (**23**; $\text{SiN}^{\text{Dipp}} = [\{\text{CH}_2\text{SiMe}_2\text{N}(\text{Dipp})\}_2]^{2-}$), which features bonding interactions between Na^+ and the electron density associated with the homometallic Mg–Mg bond.⁶⁷ Sodium metal is extruded upon reaction of complex **23** with Lewis bases (*e.g.*, THF, N-heterocyclic carbenes).⁶⁸

Complex **13** has been demonstrated to act as a versatile reagent for the synthesis of new Mg–M bonds. For example, in addition to complex **14**, molecules with heterometallic Mg–Ca, –Sr, and –Ba alkaline earth interactions have recently been described (route A1).⁶⁹ These complexes were all prepared *via*

reaction of $(\text{AeN}''_2)_2$ ($\text{N}'' = [\text{N}(\text{SiMe}_3)_2]^{-}$) with **13**, generating complexes of the form $[\text{N}''_2\text{Ae-Mg}(\text{NacNac}^{\text{Dipep}})\text{Na}]$ (**24Ae**; Ae = Ca, Sr, Ba; Fig. 4). More recently, an ytterbium variant, **24Yb**, was also reported.⁷⁰ Notably, the Mg–Na bond of **13** is also retained in **24M**. Quantum chemical calculations and experimental studies indicate that the Mg–Ae bonds in **24M** are weak, labile, and predominantly electrostatic in nature.⁶⁹ For example, scrambling reactions of **24Ae** with $\text{Ae}'\text{N}''_2$ demonstrate rapid exchange of Ae and Ae'. Only in the case of homometallic $[\text{N}''_2\text{Mg-Mg}(\text{NacNac}^{\text{Dipep}})\text{Na}]$ (**24Mg**) was loss of NaN'' observed, resulting in unsupported covalent Mg–Mg bonding in the absence of a bridging sodium centre. Remarkably, dissolution of **24Ae** in benzene at 20 °C leads to the metalation of the aromatic solvent.

In investigations related to those which yielded **24Ca**, reaction of complex **13** with $\text{ICa}(\text{NacNac}^{\text{Dipep}})$ in benzene was found to form $\text{PhMg}(\text{NacNac}^{\text{Dipep}})$ and $[\text{HCa}(\text{NacNac}^{\text{Dipep}})]_2$.⁷¹ A species with an unsupported Ca–Mg bond has been proposed as an intermediate in this process. However, experimental evidence for the intermediacy of such a complex is, presently, lacking. Indeed, conducting the same reaction in methylcyclohexane solvent does not lead to an observable reaction.⁷¹

It should also be noted that “inorganic Grignard reagents”, particularly clusters with Fe–Mg bonds, have been proposed to be key intermediates in a range of organic transformations.^{6,7} For example, the cross-coupling of 4-chlorobenzoic acid methyl ester with $n\text{-C}_{14}\text{H}_{29}\text{MgBr}$ occurs in the presence of 5 mol% FeCl_2 or FeCl_3 precatalyst.⁶ A slurry of activated iron metal powder does not react with the aforementioned ester under the same conditions. However, the powdered iron ‘dis-

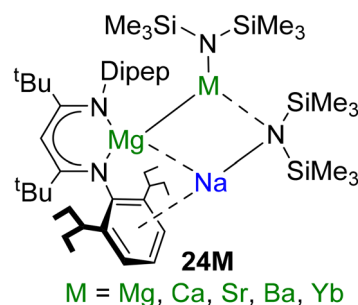


Fig. 4 Complexes with heterometallic Mg–Ae and –Yb bonds (Ae = Ca, Sr, Ba).

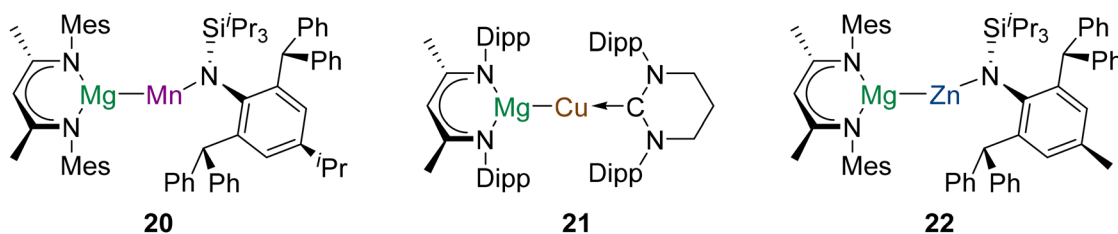


Fig. 3 Manganese-, copper-, and zinc-magnesyl complexes **20–22**.



solves' upon treatment with $n\text{-C}_{14}\text{H}_{29}\text{MgBr}$, yielding a homogeneous solution that catalyses the cross-coupling reaction.⁶ Nonetheless, due to their instability (and possible paramagnetic character), conclusive evidence for the participation of "inorganic Grignard reagents" in such reactions has not yet been divulged.

Calcium and the heavier alkaline earth metals

Due to the large radius and low electronegativity of calcium, this element is predisposed towards the formation of high-coordinate ionic complexes of its dication. Hence, the preparation of Ca–M bonds is challenging and requires sterically demanding ligands that can kinetically stabilise these labile chemical linkages. The difficulties in the preparation of complexes with Ca–M bonds are compounded by the dearth of suitable low-oxidation state Ca precursors. Transient low-oxidation state calcium complexes have been demonstrated to bind and reduce dinitrogen, yielding low-oxidation state calcium synthons.^{72–74} However, such synthons have not yet been employed for the preparation of Ca–M bonds. Similarly, although a dinitrogen complex of strontium was very recently disclosed, low-oxidation state complexes/synthons of strontium and barium are essentially unknown.⁷⁴ Thus, examples of structurally authenticated complexes with M–Ca, –Sr, and –Ba bonds remain rare.

In the absence of suitable molecular alternatives, calcium amalgam has been used as a reductant for the preparation of complexes with Ca–Fe and Ca–Co bonds (route C1).^{75,76} Analogous reactions using strontium- or barium amalgam, however, led only to the isolation of strontium- or barium isocarbonyl complexes, rather than species with Ae–M bonds.⁷⁶

Generally, the synthesis of complexes featuring Ca–M bonds has relied upon the availability of metal centred nucleophiles, which can engage in salt metathesis reactions with calcium(II) precursors (route A2). As with the pursuit of Mg–M bonds, aluminyl anions have been utilized for the generation of $(\text{SiN}^{\text{Dipp}})\text{Al}\text{--}\text{Ca}(\text{NacNac}^{\text{Dipp}})$ (**25**) – a structurally authenticated complex with a Ca–Al bond.⁵⁷ In the solid state, **25** features a Ca–($\eta^6\text{-Dipp}$) interaction, which saturates the coordination sphere of the alkaline earth metal. This contrasts with

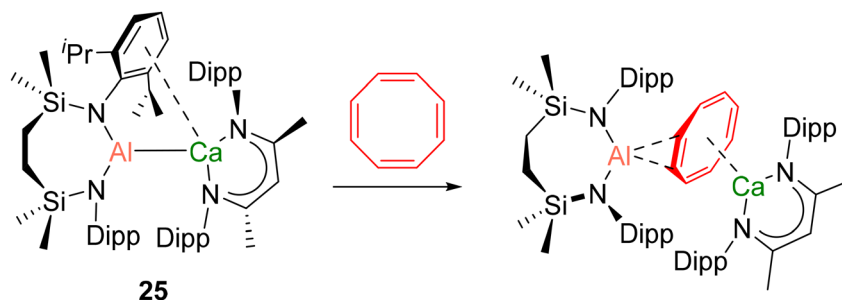
the structure of the analogous $(\text{SiN}^{\text{Dipp}})\text{Al}\text{--}\text{Mg}(\text{NacNac}^{\text{Dipp}})$, which features a three-coordinate Mg centre. Complex **25** also displays more potent reductive capabilities compared with its magnesium analogue on account of the weaker and less covalent bonding between Al and the Ca centre. For example, complex **25** activates THF solvent through C–O bond cleavage, and reduces cyclooctatetraene to the corresponding dianion (Scheme 11).⁵⁷

Aside from the aforementioned complexes, M–Ca, –Sr, and –Ba bonding is very limited. Typically, the stabilisation of such interactions requires electronegative partner metals that form (meta)stable anions. For example, gallyl complexes of calcium, strontium, and barium have been prepared *via* route A2.⁷⁷ Additionally, complexes with covalent Ae–Ge and –Sn bonds have been reported for all three of these heavier Ae elements, again using synthetic protocol A2.^{78–80} In the case of bis(stannylide) complexes, ¹¹⁹Sn NMR data are consistent with highly shielded Sn centres, in line with an ionic bonding picture between a stannyl anion and an alkaline earth cation.⁷⁸ Structurally, a wide range of Sn–Ae–Sn bond angles are observed, resulting from the non-directional ionic type bonding in these complexes.

Summary

The past two decades have seen rapid developments in the field of Ae–M bonding. Whilst the heterometallic bonding chemistry of magnesium remains the most comprehensively explored amongst all the alkaline earths, the study of complexes with Be–M bonds is also now burgeoning. Conspicuously, these advances coincide with the availability of stable low-oxidation state complexes of Mg and Be.^{45,56} The greater accessibility of p-block nucleophiles (*e.g.*, trialkyl anions) has enabled access to a variety of species with Ae–M bonds. However, this synthetic approach is somewhat limited as it necessitates a suitable metallo-nucleophile. Thus, the proliferation of the next generation of versatile low-oxidation Ae complexes (and their synthons) will increase the synthetic options available for the preparation of new Ae–M bonds.

Undoubtedly, the properties of beryllyl and magnesyl ligands are extraordinary. These multitasking species are potent σ -donors and boast extremely *Lewis* acidic Ae element



Scheme 11 Reaction of calcium aluminyl complex **23** with cyclooctatetraene.



sites. Thus, there is great potential for the complexes furnished with these ligands to engage in polymetallic cooperativity, which can enable remarkable and unprecedented chemical transformations. For example, reversible dihydrogen activation, catalytic C–H functionalisation of arenes and alkanes, and catalytic hydrogenation of unsaturated substrates have all been achieved with heterometallic alkaline earth complexes.^{32,49,61–63} Moreover, the ability of beryllyl and magnesyl ligands to stabilise elements in unprecedented valence states and coordination geometries is unsurpassed.^{31,32} The covalent component to M–Be and –Mg bonding, however minor, is likely to be crucial to much of this chemistry.

Complexes that feature M–Ca, –Sr, and –Ba bonds remain rare. This scarcity is associated with the paucity of low-oxidation state complexes of these heavier alkaline earths. Concomitantly, the inherent challenges associated with the stabilisation of weak, ionic heterometallic bonding linkages involving these very large and charge diffuse metal atoms/ions are further obstacles. The design and application of bespoke ligands, or the use of different synthetic routes more suited to these large ions, will likely provide traction for the pursuit of Ae–M bonding involving Ca, Sr, and Ba in coming years.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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