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Mixing and matching *N,N*- and *N,O*-chelates in anionic Mg(I) compounds: synthesis and reactivity with $\text{RN}=\text{C}=\text{NR}$ and CO^\dagger

Andrea O'Reilly,^a Matthew D. Haynes,^b Zoë R. Turner,^b
Claire L. McMullin,^c Sjoerd Harder,^d Dermot O'Hare,^b
J. Robin Fulton^{*a} and Martyn P. Coles^{*a}

Reduction of $[\text{Mg}(\text{NON})]_2$ ($[\text{NON}]^{2-} = [\text{O}(\text{SiMe}_2\text{NDipp})_2]^{2-}$, Dipp = 2, 6-*i*-Pr₂C₆H₃) affords Mg(I) species containing NON- and NNO-ligands ($[\text{NNO}]^{2-} = [\text{N}(\text{Dipp})\text{SiMe}_2\text{N}(\text{Dipp})\text{SiMe}_2\text{O}]^{2-}$). The products of reactions with $\text{iPrN}=\text{C}=\text{NiPr}$ and CO are consistent with the presence of reducing Mg(I) centres. Extraction with THF affords $[\text{K}(\text{THF})_2]_2[\text{NNO}\text{Mg}-\text{Mg}(\text{NNO})]$ with a structurally characterised Mg–Mg bond that was examined using density functional theory.

Since the initial report of (BDI)Mg–Mg(BDI) in 2007 (I, Fig. 1; BDI = $[\text{HC}(\text{C}(\text{Me})\text{NDipp})_2]^-$),¹ Mg(I) reagents have demonstrated their capacity to act as soluble, electron precise reducing agents.² The discovery of these compounds has undoubtedly fuelled the recent development and application of low valent group 2 (alkaline earth, Ae) metal complexes.³ Indeed, over 35 examples of neutral Mg(I) species (L)Mg–Mg(L) (L = monoanionic ligand) have now been structurally characterised. In contrast, examples in which the low valent magnesium centres are present in an anionic $[(\text{L}')\text{Mg}-\text{Mg}(\text{L}')]^{2-}$ unit (L' = dianionic ligand) are a recent addition to this important family of compounds (Fig. 1).

The first anionic Mg(I) compounds II were synthesised in a one-pot reaction of the neutral diimine or diamine with MgCl_2 in the presence of excess potassium.⁴ The products have a coplanar $[(\text{L}')\text{Mg}-\text{Mg}(\text{L}')]^{2-}$ unit with THF-solvated potassium cations above and below the MgN_2C_2 metallacycles. In 2021,

Hill and co-workers isolated the dimeric Na/Mg complex III by reducing the neutral diamido magnesium precursor with 5% Na/NaCl.⁵ The structure showed non-solvated sodium cations with $\text{Na} \cdots \pi(\text{arene})$ interactions to ligand substituents. The $[(\text{L}')\text{Mg}-\text{Mg}(\text{L}')]^{2-}$ unit is twisted, with a long Mg–Mg bond. The most recent addition to this family IV, derives from the steric modulation of a rigid $[\text{xanth-EtNON}^{\text{Ar}}]^{2-}$ backbone ($[\text{xanth-EtNON}^{\text{Ar}}]^{2-} = 4,5\text{-Ar}_2\text{-2,7-Et}_2\text{-9,9-Me}_2\text{-xanthene}$). Previous work had shown that when Ar = 2,4,6-Cy₃C₆H₂, the dinitrogen complex $[\text{K}\{\text{Mg}(\text{xanth-EtNON}^{\text{Ar}})\}]_2(\mu\text{-N}_2)$ was isolated,⁶ presumed to be due to the ligand bulk preventing Mg–Mg bond formation and the resulting Mg(I) radicals reducing

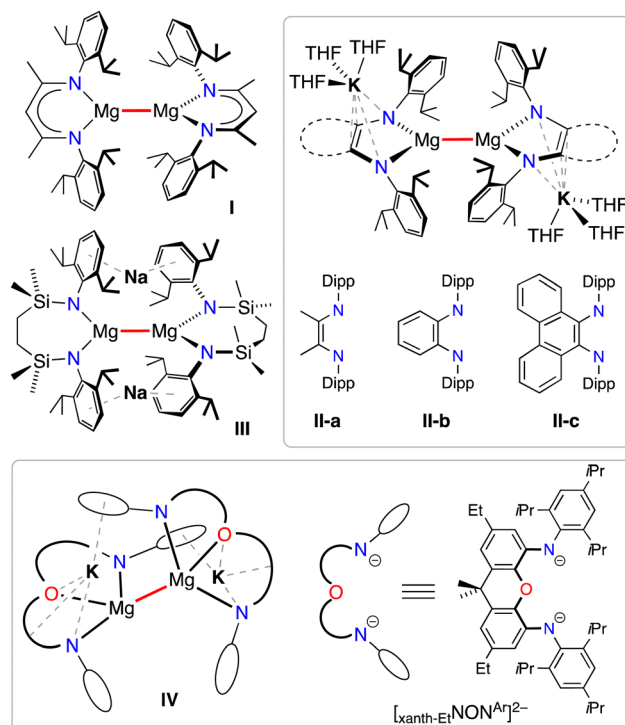


Fig. 1 Examples of neutral (I) and anionic (II, III and IV) Mg(I) compounds.

^a School of Chemical and Physical Sciences, Victoria University of Wellington, PO Box 600, Wellington 6012, New Zealand. E-mail: martyn.coles@vuw.ac.nz, j.rob.fulton@vuw.ac.nz

^b Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Mansfield Road, Oxford OX1 3TA, UK. E-mail: dermot.ohare@chem.ox.ac.uk

^c Department of Chemistry, University of Bath, Bath, BA2 7AY, UK. E-mail: cm2025@bath.ac.uk

^d Inorganic and Organometallic Chemistry, Friedrich-Alexander-Universität, Erlangen-Nürnberg, Egerlandstraße 1, 91058 Erlangen, Germany

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N₂. Reducing the size of the Ar substituents to 2,4,6-*i*Pr₃C₆H₂ allowed Mg–Mg bond formation in **IV**.⁷ The solid-state structure of **IV** adopts a folded structure with the potassium atoms coordinated *via* η⁴-OCN₂ and η⁶-aryl interactions to the ligands.

The reactivity of anionic Mg(i) compounds with a range of small molecules (H₂, CO, N₂O, THF),^{5,7,8} and organic functional groups (alkynes, nitriles, carbodiimides, ketones, polyaromatic compounds)⁹ has been explored, confirming the reductive capability of these species. We report herein the synthesis of a magnesium compound supported by the NON-ligand [(NON)^{2−} = [O(SiMe₂NDipp)₂]^{2−}], its reduction to Mg(i) and the reactivity of the low-valent species with *i*PrN=C=NiPr and CO.

Prior to this work, Mg(NON)(THF)₂ was the only reported group 2 metal NON-compound, isolated as a product of over reduction and ligand transfer during the synthesis of a Bi(II) radical.¹⁰ In this work the non-solvated compound was targeted as a precursor to reduced Mg(i) species, using an alkane elimination route between MgBu₂ and (NON)H₂ (Scheme 1). The reaction proceeded smoothly in hexane or toluene, affording colourless crystals of [Mg(NON)]₂ (**1**).

Compound **1** is sparingly soluble in hydrocarbon solvents, preventing the acquisition of meaningful spectroscopic data at room temperature.¹¹ The crystal structure revealed a dimer located on an inversion centre (Scheme 1). The bidentate ligand adopts a κN¹,O-μ-N²-coordination mode in which the oxygen atom is in a four-membered N–Si–O–Mg metallacycle and the pendant N₂ atom bonds to the symmetry related Mg. We note that the Mg⋯Mg separation of 4.102(1) Å is too great to support a Mg–Mg bond in this dimeric arrangement, necessitating a reorganisation of the ligand to permit formation of the target [(L')Mg–Mg(L')] ^{2−} unit.

The reduction of **1** by KC₈ in Et₂O reproducibly forms a new product **A** (Scheme 2). ¹H NMR analysis indicated two distinct sets of ligand resonances in a 1 : 1 ratio that are consistent with a symmetric and a non-symmetric environment at magnesium. This is most clear from the three SiMe₂ singlets that appear at δ_H 0.38 (12H), 0.04 (6H) and −0.04 (6H). The symmetric environment at magnesium is consistent with a Mg(NON) group with a κN,N'- or κN,O,N'-coordination mode of the

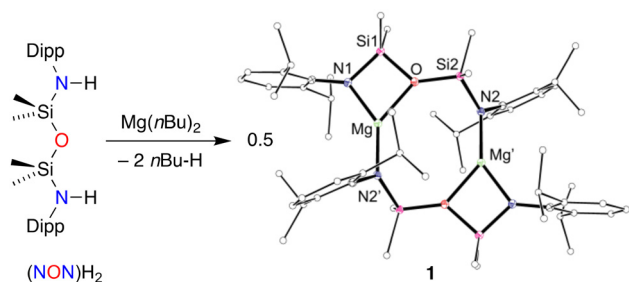
NON-ligand.¹⁰ Based on NMR spectra of a related aluminium system, we attribute the non-symmetric ligand environment to a previously reported intramolecular 1,3-silyl retro-Brook rearrangement of the NON-ligand to form an N,O-chelated Mg(NNO) group [(NNO)^{2−} = [N(Dipp)SiMe₂N(Dipp)SiMe₂O]^{2−}].¹² We are unable to crystallise **A** and cannot therefore assign it a precise chemical structure. Furthermore, analytical data does not allow us to discriminate between a discrete heteroleptic [(NON)Mg–Mg(NNO)] ^{2−} unit or a mixture that also includes homoleptic [(NON)Mg–Mg(NON)] ^{2−} and [(NNO)Mg–Mg(NNO)] ^{2−} species. It is possible that a dynamic equilibrium exists, hindering crystallisation of a single species. However, onward reactivity confirms the presence of both K[Mg(NON)] and K[Mg(NNO)] groups in **A**.

Evidence for **A** reacting as a discrete heteroleptic [(NON)Mg–Mg(NNO)] ^{2−} unit is inferred from its reaction with diisopropylcarbodiimide to form **2** (Scheme 2). Previous studies with **I** and **II-a** showed that addition of RN=C=NR (R = Cy, *t*Bu) afforded the magnesioamidinate species from the reductive insertion of carbodiimide into a Mg–Mg bond.^{1,9c} The proposed mechanism involves initial N-coordination of the carbodiimide to one Mg centre, followed by migration of the second Mg to the sp² carbon of the carbodiimide.^{1,13}

NMR spectra of **2** retain a 1 : 1 ratio of NON- and NNO-ligand resonances, with additional signals for magnetically equivalent NiPr groups, and a high frequency resonance at δ_C 226.1 for the CN₂ carbon atom. The crystal structure reveals both Mg(NON) and Mg(NNO) groups bridged by a [C(NiPr)₂]^{2−} unit (Fig. 2). The C–N distances in the amidinate unit (1.344(3)–1.358(3) Å) indicate delocalisation in the CN₂ fragment, confirming a two-electron reduction of the carbodiimide. The regiochemistry in **2** is consistent with N-coordination of the carbodiimide at the less sterically encumbered Mg(NNO) centre, followed by migration of the Mg(NON) fragment to the carbon atom.^{12a}

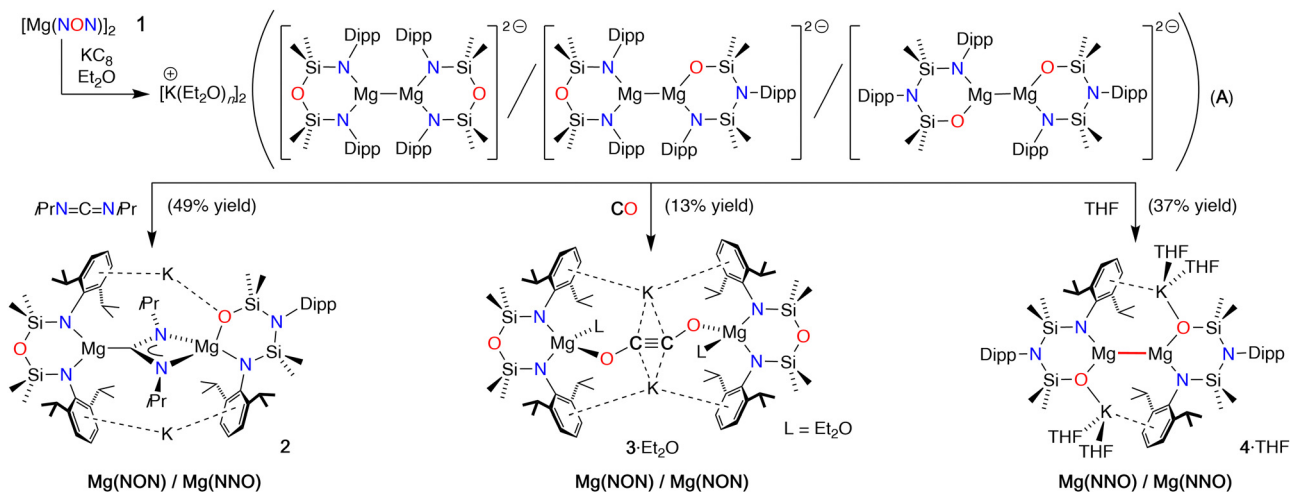
Compounds **III**, **IV** and the aforementioned dimagnesium(μ-N₂) complex reductively dimerise CO to afford ethynediolate complexes.^{5–7} The reaction of **A** with 1 bar CO proceeded with an immediate colour change from yellow to red-orange, affording a low yield of crystals of 3·Et₂O (Scheme 2). The ¹H NMR spectrum showed only symmetric ligand environments, consistent with Mg(NON) fragments. The ¹³C{¹H} NMR spectrum showed a signal at δ_C 76.6, downfield of the [C₂O₂]^{2−} resonances noted in previous ethynediolate products (δ_C 50.2/55.3).

X-ray diffraction analysis of 3·Et₂O confirmed formation of the homoleptic ethynediolate complex, K₂[(Mg(NON)(Et₂O))₂(μ-C₂O₂)] containing Et₂O solvated Mg(NON) groups (Fig. 3). Previous studies showing that the isomerisation of Al(NON) to Al(NNO) is exergonic^{12a} suggest that the formation of Mg(NNO) groups during the synthesis of **A** is non-reversible. The absence of Mg(NNO) groups in 3·Et₂O therefore suggests that its formation involves the preferential reaction of CO with the Mg(NON) components of **A**, and may indicate the presence of symmetrical [(NON)Mg–Mg(NON)] ^{2−} units. The structural parameters of the 'Mg(OC≡CO)Mg' unit closely resemble the previous examples,^{5,6,14} with a short C–C bond of 1.211(8) Å and a slight *trans*-bent geometry (O2–C29–C29' = 164.6(6)°).



Scheme 1 Synthesis and thermal displacement plot (30% probability; H-atoms omitted; peripheral carbons as spheres) of **1** (*r* = −*x*, 1 − *y*, −*z*). Selected bond lengths (Å) and angles (°): Mg–N1 1.9414(10), Mg–O 2.0605(9), Mg–N2' 1.9542(10), Mg⋯Mg' 4.102(1); N1–Mg–O 77.54(4), N1–Mg–N2' 143.74(5), O–Mg–N2' 138.48(4).





Scheme 2 Formation of **A** and reaction with $\text{iPrN}=\text{C}=\text{NPr}$, CO and THF to afford **2**, **3**· Et_2O and **4**· THF (isolated yields reported).

Extraction of **A** with THF afforded a mixture of products including $\text{K}_2[\text{NON}]$, and the new compound **4**· THF that was isolated by fractional crystallisation in 37% yield. The ^1H NMR spectrum of **4**· THF shows splitting according to a compound containing only NNO -ligands. This is confirmed by X-ray diffraction, revealing **4**· THF as the anionic $\text{Mg}(\text{i})$ species, $[(\text{NNO})\text{Mg}-\text{Mg}(\text{NNO})]^{2-}$ charge balanced with two $[\text{K}(\text{THF})_2]^+$ cations (Fig. 4). This result indicates either an analogous redistribution of the $[\text{Mg}(\text{L}')^-]$ fragments from a mixture present in **A**, or isomerisation of the $\text{Mg}(\text{NON})$ group to the more stable $\text{Mg}(\text{NNO})$ isomer during the extraction with THF . There is no residual electron density in the region expected for hydride ligands, confirming formation of the anionic $\text{Mg}(\text{i})$ compound (Fig. S24, ESI[†]). The $\text{Mg}-\text{Mg}$ bond length (2.9393(11) Å) is in the range reported for (solvent free)

$(\text{L})\text{Mg}-\text{Mg}(\text{L})$ compounds (2.7907(9)–3.0513(8) Å),¹⁵ and is shorter than found in the anionic $\text{Mg}(\text{i})$ complexes **II** (3.2077(10) Å/3.2124(11) Å)⁵ and **III** (3.1369(15) Å).¹⁴ We attribute the short bond to the reduction in steric stress imparted by the NNO -isomer, and the reduction in electron density at Mg that results from the high electronegativity of the O -ligand.

DFT analysis of **I** and **IV** revealed a non-nuclear attractor (NNA) at the centre point of the $\text{Mg}-\text{Mg}$ bond.^{7,16} This feature was not prominent in the core of **III**,⁵ which the authors suggest is best described as a $[\text{Mg}_2\text{Na}_2]^{4+}$ unit. Investigation of **4**· THF by DFT (see ESI[†] for details) show that the HOMO corresponds to the $\text{Mg}-\text{Mg}$ σ -bond with equal contribution from both metals and a high s -character of $\sim 93\%$ (Fig. 5a). Natural bond order (NBO) calculations show a $\text{Mg}-\text{Mg}$ Wiberg bond index (WBI) of 0.724, with NPA charges $q_{\text{Mg}} = +1.00$ and $q_{\text{K}} = +0.88$. These values compare well with those reported for **III** (WBI = 0.656, $q_{\text{Mg}} = +1.03$ and $q_{\text{Na}} = +0.84$),⁵ and **IV** (WBI = 0.694, $q_{\text{Mg}} = +0.97$

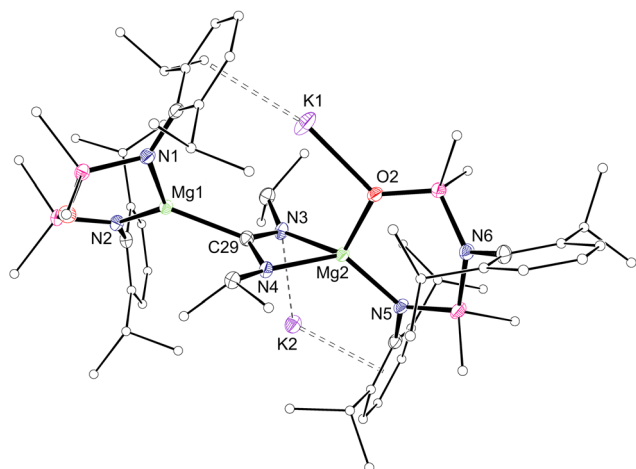


Fig. 2 Thermal displacement plot (30% probability; H-atoms omitted; peripheral carbons as spheres) of one of the independent molecules of **2**. Selected bond lengths (Å) and angles (°): $\text{Mg1}-\text{N1}$ 2.0594(19), $\text{Mg1}-\text{N2}$ 2.0415(19), $\text{Mg2}-\text{N5}$ 2.0513(19), $\text{Mg2}-\text{O2}$ 1.9122(16), $\text{C29}-\text{N3}$ 1.358(3), $\text{C29}-\text{N4}$ 1.344(3), $\text{Mg1}-\text{C29}$ 2.232(2), $\text{Mg2}-\text{N3}$ 2.1737(19), $\text{Mg2}-\text{N4}$ 2.069(2), $\text{N1}-\text{Mg1}-\text{N2}$ 123.18(8), $\text{N5}-\text{Mg2}-\text{O2}$ 106.09(8), $\text{N3}-\text{Mg2}-\text{N4}$ 63.51(7).

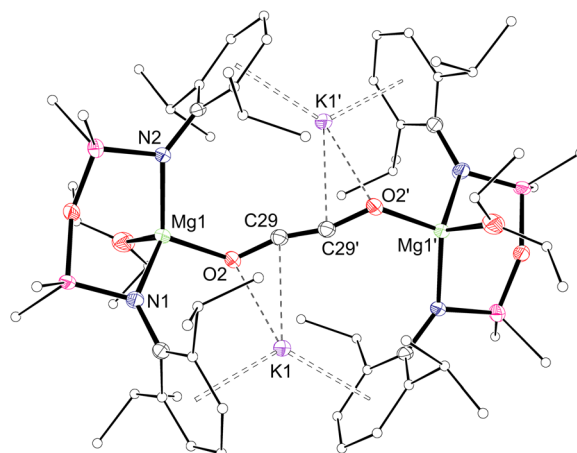


Fig. 3 Thermal displacement plot (30% probability; H-atoms omitted; peripheral carbons as spheres) of one of the independent molecules of **3**· Et_2O . Selected bond lengths (Å) and angles (°): $\text{Mg1}-\text{N1}$ 2.044(4), $\text{Mg1}-\text{N2}$ 2.049(3), $\text{Mg1}-\text{O2}$ 1.936(3), $\text{O2}-\text{C29}$ 1.309(5), $\text{C29}-\text{C29}'$ 1.211(8), $\text{N1}-\text{Mg1}-\text{N2}$ 121.24(17), $\text{O2}-\text{C29}-\text{C29}'$ 164.6(6).



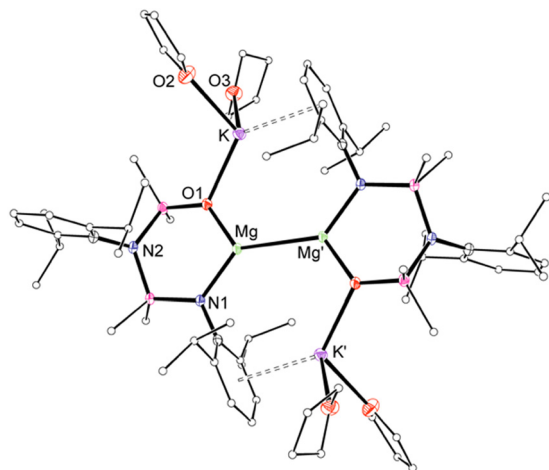


Fig. 4 Thermal displacement plot (30% probability; H-atoms omitted; peripheral carbons as spheres) of **4·THF** ($' = -x, -y, 2 - z$). Selected bond lengths (Å) and angles ($^{\circ}$): Mg–Mg' 2.9393(11), Mg–N1 2.0493(15), Mg–O1 1.9203(13), O1–K 2.5859(13); N1–Mg–O1 106.37(6), N1–Mg–Mg' 131.70(5), O1–Mg–Mg' 121.91(5), Mg–O1–K 109.97(6).

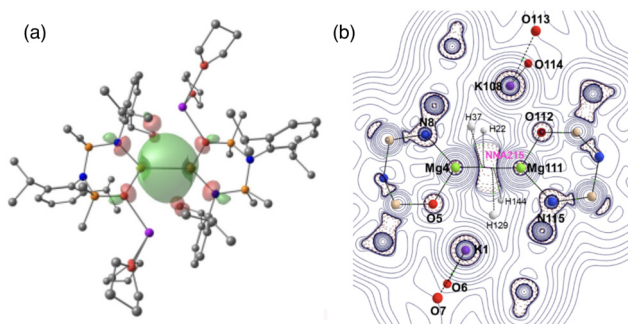


Fig. 5 (a) HOMO of **4·THF**. (b) Laplacian distribution for **4·THF**, showing non-nuclear attractor (NNA215) at the centre of the Mg–Mg bond. Both calculated at the BP86/6-311++G**//BP86/BS1 level of theory.

and $q_K = +0.90$).⁶ An NNA of 0.72 electrons is present in the middle of the Mg–Mg bond in **4·THF** (Fig. 5b), similar to that noted in **I** (0.8 electrons).¹⁶

In conclusion, we have demonstrated that the reduction of the $[Mg(NON)]_2$ dimer **1** affords product **A**, formulated as containing $K[Mg(NON)]$ and $K[Mg(NNO)]$ units. Although the composition of **A** has not been explicitly identified and an equilibrium of different species may be present, analytical data and reactivity studies confirm the presence of reducing $Mg(NON)$ and $Mg(NNO)$ groups. Isolation and structural characterisation of $[K(THF)_2]_2[(NNO)Mg-Mg(NNO)]$ (**4·THF**) prompted analysis by DFT, showing a non-nuclear attractor of 0.72 electrons at the centre of the Mg–Mg bond. Access to both $K[Mg(NON)]$ and $K[Mg(NNO)]$ groups from **A** may expand the scope of reactivity compared with a system in which only one ligand-type was available. This flexibility imparted by the opportunity to 'mix and match' $[Mg(L')]$ fragments according to the reaction may be important in stabilising the reduction products and will form part of our ongoing investigations.

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Data availability

The data supporting this article have been included as part of the ESI†

Conflicts of interest

There are no conflicts to declare.

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