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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

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Reduction of $[\text{Mg}(\text{NON})_2]$ ($[\text{NON}]^{2-} = [\text{O}(\text{SiMe}_2\text{NDipp})_2]^{2-}$, $\text{Dipp} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) 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 $[\text{K}(\text{THF})_2][\text{NNO}\text{Mg}-\text{Mg}(\text{NNO})]$ with a structurally characterised Mg–Mg bond that was examined using density functional theory.

Since the initial report of $(\text{BDI})\text{Mg}-\text{Mg}(\text{BDI})$ in 2007 (I, Fig. 1; $\text{BDI} = [\text{HC}\{\text{C}(\text{Me})\text{NDipp}\}_2]^-$),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 $(\text{L})\text{Mg}-\text{Mg}(\text{L})$ (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 $\text{Ar} = 2,4,6\text{-Cy}_3\text{C}_6\text{H}_2$, 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

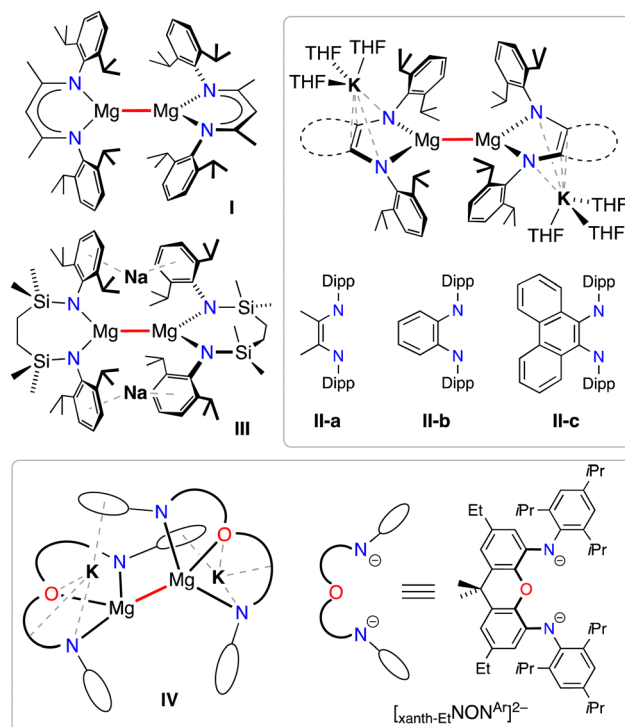


Fig. 1 Examples of neutral (I) and anionic (II, III and IV) Mg(I) compounds.

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† Electronic supplementary information (ESI) available: Experimental details and characterization data; full details of computational experiments. CCDC 2357068 (1), 2357069 (2), 2357070 (3-Et₂O) and 2357071 (4-THF). For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4cc02594f>



N_2 . 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* η^4 -OCN₂ and η^6 -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 $[(NON)]^{2-} = [O(SiMe_2NDipp)_2]^{2-}$, 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 $\kappa N^1, O-\mu-N^2$ -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 $\kappa N, N'$ - or $\kappa N, O, N'$ -coordination mode of the

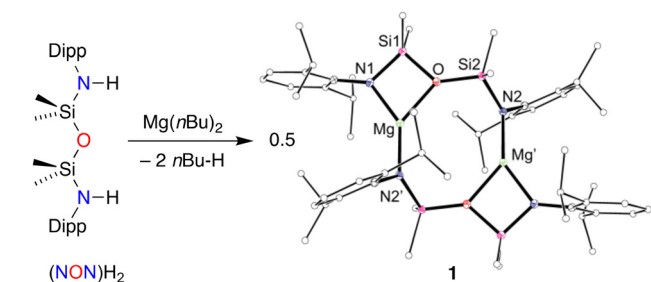
NON-ligand.¹⁰ Based on NMR spectra of a related aluminium system, we attribute the non-symmetric ligand environment to a previously reported intramolecular 1,3-silyl retro-Brook rearrangement of the NON-ligand to form an *N,O*-chelated Mg(NNO) group $[(NNO)]^{2-} = [N(Dipp)SiMe_2N(Dipp)SiMe_2O]^{2-}$.¹² 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}

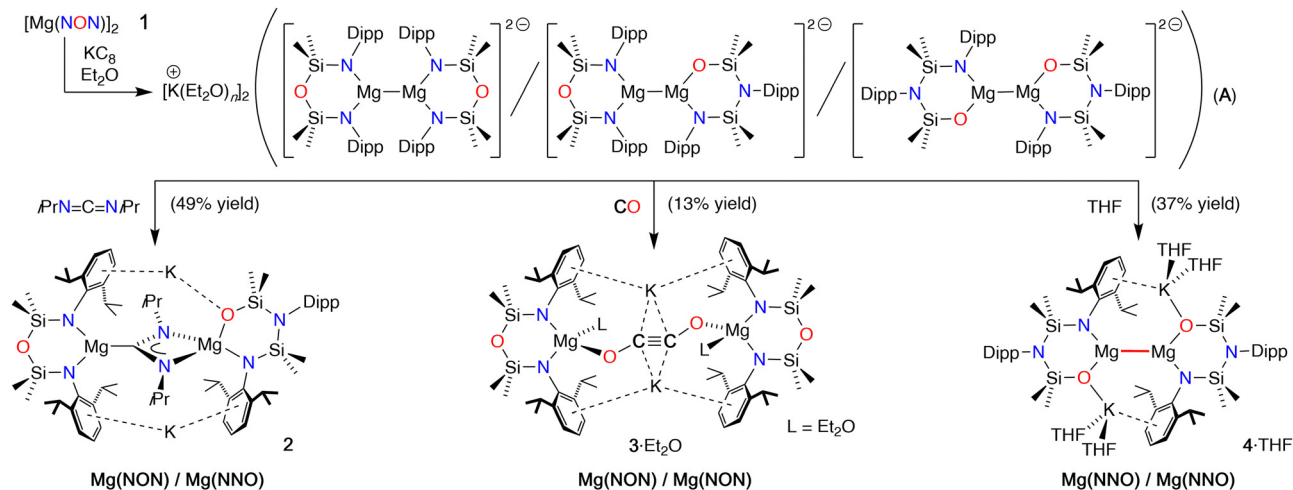
Compounds **III**, **IV** and the aforementioned dimagnesium(μ -N₂) complex reductively dimerise CO to afford ethynediolate complexes.^{5–7} The reaction of **A** with 1 bar CO proceeded with an immediate colour change from yellow to red-orange, affording a low yield of crystals of **3**·Et₂O (Scheme 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 $[C_2O_2]^{2-}$ 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** ($l' = -x, 1 - y, -z$). 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 $i\text{PrN}=\text{C}=\text{NiPr}$, 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 Mg–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 Mg–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 Mg–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 Mg–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, $q_{\text{Mg}} = +0.97$

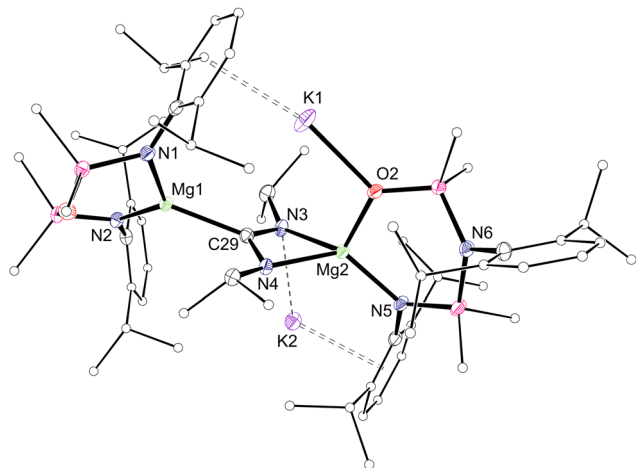


Fig. 2 Thermal displacement plot (30% probability; H-atoms omitted; peripheral carbons as spheres) of one of the independent molecules of **2**. Selected bond lengths (Å) and angles ($^\circ$): Mg1–N1 2.0594(19), Mg1–N2 2.0415(19), Mg2–N5 2.0513(19), Mg2–O2 1.9122(16), C29–N3 1.358(3), C29–N4 1.344(3),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

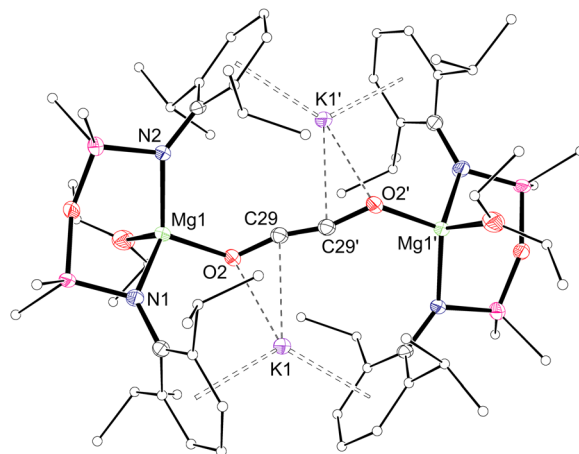


Fig. 3 Thermal displacement plot (30% probability; H-atoms omitted; peripheral carbons as spheres) of one of the independent molecules of **3**· Et_2O . Selected bond lengths (Å) and angles ($^\circ$): Mg1–N1 2.044(4), Mg1–N2 2.049(3), Mg1–O2 1.936(3), O2–C29 1.309(5), C29–C29' 1.211(8), N1–Mg1–N2 121.24(17),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



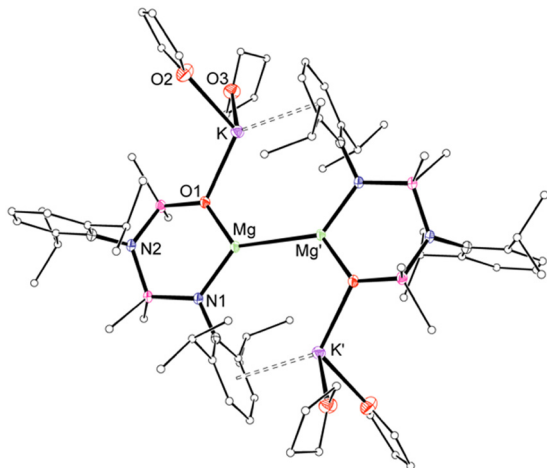


Fig. 4 Thermal displacement plot (30% probability; H-atoms omitted; peripheral carbons as spheres) of **4-THF** ($' = -x, -y, 2 - z$). Selected bond lengths (Å) and angles ($^{\circ}$): Mg–Mg' 2.9393(11), Mg–N1 2.0493(15), Mg–O1 1.9203(13), O1–K 2.5859(13); N1–Mg–O1 106.37(6), N1–Mg–Mg' 131.70(5), O1–Mg–Mg'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

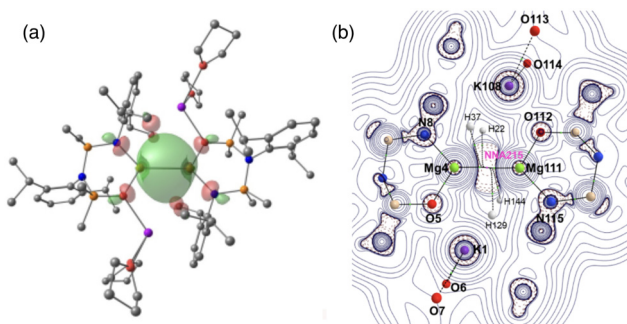


Fig. 5 (a) HOMO of **4-THF**. (b) Laplacian distribution for **4-THF**, showing non-nuclear attractor (NNA215) at the centre of the Mg–Mg bond. Both calculated at the BP86/6-311++G**//BP86/BS1 level of theory.

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 $[\text{Mg}(\text{NON})]_2$ dimer **1** affords product **A**, formulated as containing $\text{K}[\text{Mg}(\text{NON})]$ and $\text{K}[\text{Mg}(\text{NNO})]$ 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 $\text{Mg}(\text{NON})$ and $\text{Mg}(\text{NNO})$ groups. Isolation and structural characterisation of $[\text{K}(\text{THF})_2]_2[(\text{NNO})\text{Mg}-\text{Mg}(\text{NNO})]$ (**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 $\text{K}[\text{Mg}(\text{NON})]$ and $\text{K}[\text{Mg}(\text{NNO})]$ 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' $[\text{Mg}(\text{L}')]^-$ 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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