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Steric Control of Mg–Mg Bond Formation *vs* N_2 Activation in the Reduction of Bulky Magnesium Diamide Complexes

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Reduction of the magnesium(II) diamide $[\mathrm{Mg}(^{\mathrm{Trip}}\mathrm{NON})]$ ($^{\mathrm{Trip}}$NON = 4,5-bis(2,4,6-triisopropylanilido)-2,7-diethyl-9,9-dimethyl-xanthene) with 5% w/w K/KI leads to a good yield of a dianionic dimagnesium(I) species, as its potassium salt, $[\{\mathrm{K}(^{\mathrm{Trip}}\mathrm{NON})\mathrm{Mg}\}_2]$. An X-ray crystallographic analysis shows the molecule to contain a very long Mg–Mg bond (3.137(2) Å). The formation of $[\{\mathrm{K}(^{\mathrm{Trip}}\mathrm{NON})\mathrm{Mg}\}_2]$ contrasts with a previously reported reduction of a magnesium(II) complex incorporating a bulkier diamide ligand, which instead afforded a magnesium-dinitrogen complex. In the current study, $[\{\mathrm{K}(^{\mathrm{Trip}}\mathrm{NON})\mathrm{Mg}\}_2]$ has been shown to be a viable reagent for the reductive activation of CO, H_2 and N_2O.

Since the first report on isolable dimagnesium(I) complexes, LMg–MgL (L = β-diketiminate or guanidinate, e.g. **I** Figure 1) in 2007,[1] more than 40 other examples of this compound class have come forward.[2] The vast majority of such compounds are neutral, and are kinetically stabilised by incorporation of sterically bulky mono-anionic N-donor chelating or mono-dentate ligands. With that said, a handful of dianionic systems in which the Mg–Mg bond is coordinated by a reduced redox active ligand (e.g. 1,4-diazabutadiene) have been described.[3] Furthermore, Hill and co-workers have prepared a dianionic dimagnesium(I) compound **II** by reduction of a bulky diamido magnesium(II) compound, $[\mathrm{Mg}(\mathrm{SiN}^{\mathrm{Dip}})]$ ($\mathrm{SiN}^{\mathrm{Dip}}$ = $[\{\mathrm{CH_2SiMe_2N(Dip)}\}_2]^{2-}$, Dip = 2,6-diisopropylphenyl) with sodium metal.[4] Another breakthrough in this field came from Harder and co-workers who showed that sodium reduction of a magnesium(II) compound bearing a "super bulky" β-diketiminate ligand leads to an anionic magnesium(0) complex **III** that does not possess a Mg–Mg bond.[5] Since their discovery, low oxidation state magnesium complexes such as **I**–**III** have proved invaluable as selective reducing agents in many areas of organic and inorganic synthesis, often allowing access to compound types that cannot be formed using more classical reducing agents, e.g. KC_8.[2]

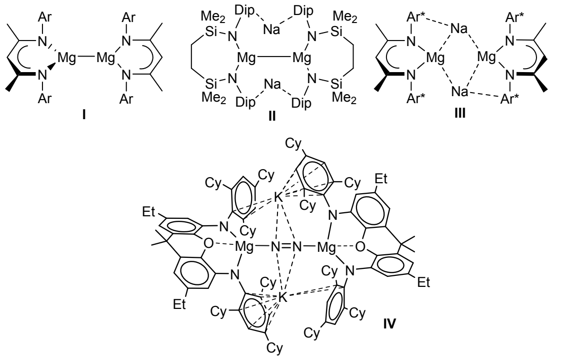

Figure 1. Examples of previously reported magnesium(I), magnesium(0), and magnesium-dinitrogen complexes (Ar = bulky aryl, Dip = 2,6-diisopropylphenyl, Ar* = 2,6-bis(3-pentyl)phenyl, Cy = cyclohexyl).

As an extension of Hill's preparation of **II**, we have investigated the alkali metal reduction of diamido-magnesium(II) compounds that are bulkier than $[\mathrm{Mg}(\mathrm{SiN}^{\mathrm{Dip}})]$, with a view to sterically frustrate the formation of a Mg–Mg bond, and form isolable, well defined dimagnesium(I) diradical species.[6] To this end, we developed the xanthene bridged diamide ligand $^{\mathrm{TCHP}}$NON (4,5-bis(2,4,6-tricyclohexylanilido)-2,7-diethyl-9,9-dimethyl-xanthene) which was used to prepare the magnesium complex, $[\mathrm{Mg}(^{\mathrm{TCHP}}\mathrm{NON})]$.[7] The potassium reduction of this under an N_2 atmosphere did not yield the targeted dimagnesium(I) diradical, $\{\mathrm{K}(^{\mathrm{TCHP}}\mathrm{NON})\mathrm{Mg}\cdot\}_2$, but instead led to the reductive activation of N_2 to give a high yield of the first example of a magnesium dinitrogen complex, **IV**. We had previously prepared a calcium analogue of **IV**, *viz.* $[\{\mathrm{K}(^{\mathrm{TCHP}}\mathrm{NON})\mathrm{Ca}\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$, albeit in low isolated yields.[8] Compound **IV** is extremely reactive, and has negligible solubility in aliphatic solvents. It acts as a "masked" source of the dimagnesium(I) diradical, $\{\mathrm{K}(^{\mathrm{TCHP}}\mathrm{NON})\mathrm{Mg}\cdot\}_2$, in reductive activations of the substrates CO, H_2 and C_2H_4, that are normally inert to reaction with main group complexes. Here, we report that using a xanthene bridged diamide ligand of reduced steric bulk, relative to $^{\mathrm{TCHP}}$NON, allows a long Mg–Mg bond to be

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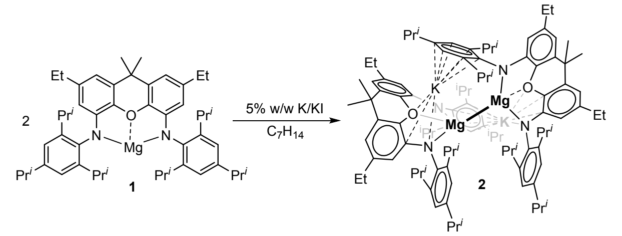
Electronic Supplementary Information (ESI) available: Experimental procedures and characterisation data for all new compounds. Full details of computational studies. Crystal data, details of data collections and refinements. CCDC numbers: 2309545-2309550. For ESI and crystallographic data in CIF format see DOI: 10.xxxxxxx formed in a reduction reaction similar to that which gave **IV**. Moreover, the prepared anionic dimagnesium(I) complex is shown to cleanly reduce H_2, CO and N_2O, thus highlighting its synthetic potential.

At the outset of this study, the new xanthene bridged dianiline pro-ligand, $^{Trip}NONH_2$ (4,5-bis(Trip)-2,7-diethyl-9,9-dimethyl-xanthene; Trip = 2,4,6-triisopropylphenyl), was prepared using a similar route to that originally developed for an *N*-Dip substituted analogue by Emslie and co-workers (see ESI for details).[9] Deprotonation of $^{Trip}NONH_2$ with $Mg\{CH_2(SiMe_3)\}_2$ in methylcyclohexane afforded a high yield (*ca.* 90%) of the magnesium diamide complex **1** (Scheme 1). Although an X-ray crystal structure of **1** could not be obtained, its NMR spectra, collected in C_6D_{12} solutions, indicate that the coordinatively unsaturated compound exists as an equilibrium mixture of the monomer and a Trip bridged dimer (see ESI for further details), similar to the solid-state structure of an *N*-Dip substituted analogue reported by Hicks and co-workers.[10] Subsequent reduction of a methylcyclohexane solution of **1** with excess 5% w/w K/KI[11] gave a good yield (56%) of the anionic dimagnesium(I) complex **2** as an air sensitive, bright orange crystalline solid. It is noteworthy that attempts to similarly reduce **1** with 5% w/w Na/NaCl were not successful.



Scheme 1. Synthesis of compound **2**.

Similar to the computed mechanism of formation of **IV**,[7] it seems reasonable that the formation of **2** proceeds *via* potassium reduction of **1** to give a magnesium(I) radical intermediate, K(^{Trip}NON)Mg•, which then dimerises to give the product. If so, our proposal that the larger ^{TCHP}NON ligand in **IV** frustrates Mg–Mg bond formation from occurring is plausible. We have previously shown that blue or UV light irradiation of neutral dimagnesium(I) complexes can lead to Mg–Mg bond cleavage, and formation of highly reactive transient Mg^I radicals.[12] In this respect, and in an attempt to reductively activate N_2 using **2**, methylcyclohexane solutions of the complex were irradiated with blue or UV light under N_2 atmospheres. However, these irradiations led to no reaction (blue light), or the formation of an intractable mixture of products (UV light).

The NMR spectra of **2** in C_6D_6 are largely consistent with its low symmetry solid-state structure. That is, the molecular structure of **2** (Figure 2) reveals it to be dinuclear with a Mg–Mg bond (3.137(2) Å), the length of which is similar to that of **II** (3.212(1) Å),[4] and at the upper end of the wide range known for such interactions (2.7935(6)–3.212(1) Å).[13] Each Mg centre of **2** has a heavily distorted tetrahedral geometry, which includes κ^3-*N:O:N*-coordination to a ^{Trip}NON ligand, both of which are distorted from planarity by folding about their $OCMe_2$ axes (fold angle = 139.5° mean). This is likely enforced by the unusual coordination of the K centres in **2**, which are η^4-ligated by an OC_2N fragment, and η^6-coordinated to one Trip arene unit on an opposing ^{Trip}NON ligand. We have previously observed a similar bonding situation in the doubly reduced ethylene complex, $[\{K(^{TCHP}NON)Mg\}_2(\mu\text{-}C_2H_4)]$.[7] The central Mg_2K_2 unit is close to planar, and has alternating short (3.393 Å mean) and long (4.068 Å mean) Mg···K distances (Σ van der Waals radii for K and Mg = 4.48 Å[14]).

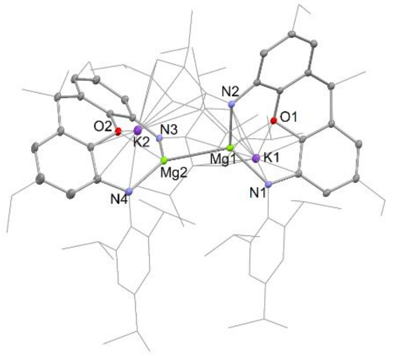


Figure 2. The molecular structure of **2** (20% ellipsoids; Trip, ethyl and methyl substituents shown as wire-frame for clarity; hydrogen atoms omitted). Selected bond lengths (Å): Mg(1)-Mg(2) 3.1369(15), K(1)-Trip centroid 2.853(1), K(1)-OC_2N centroid 2.795(1), K(2)-Trip centroid 2.864(1), K(2)-OC_2N centroid 2.829(1), K(1)···Mg(1) 3.388(1), K(1)···Mg(2) 4.075(1), K(2)···Mg(1) 4.060(1) Å, K(2)···Mg(2) 3.397(1).

So as to shed light on the electronic structure of **2**, DFT calculations (wB97XD) were carried out on the full molecule in the gas phase. The geometry of the molecule optimised to be close to that of the solid-state structure. As with calculations on other Mg–Mg bonded systems,[2] the HOMO of the molecule largely incorporates a diffuse σ-bonded interaction between the two metal centres that is of high 3s character (*ca.* 90%), and has a Wiberg Bond Index (WBI) of 0.694 (Figure 3). The low WBIs for the Mg–N bonds (0.0502), and the associated natural charges (Mg = +0.972 mean, N = -0.912), indicate largely ionic interactions between the Mg and N centres. The LUMO for the molecule is primarily associated with one of the potassium cations (natural charges for K = +0.90 mean) and has a high degree of 4s-character, while the HOMO-LUMO separation at 6.80 eV is considerable. An Atoms in Molecules analysis of **2** revealed a non-nuclear attractor at the centre of the Mg–Mg vector, as we have seen for **I** (Ar = Dip).[1(b)] It is noteworthy that weak bond critical points were located for the two short Mg···K interactions within the Mg_2K_2 unit (see Table S5), whilst there are none for the two longer Mg···K separations.

With compound **2** in hand, a preliminary investigation of its reactivity towards catalytically relevant small molecules was undertaken, with the initial goal of comparing this reactivity with that now well established for neutral dimagnesium(I) systems, e.g. **I**,[2] and the more reactive magnesium-N_2 complex **IV**.[7] Moreover, given the very long Mg–Mg bond in potassium(I)/magnesium(I) compound **2**, it seemed likely that its reducing ability would perhaps be similar to that of the related sodium(I)/magnesium(I) compound **II**.[4] This proved to be the case, in that placing solutions of **2** under 1 atmosphere of CO at room temperature lead to the rapid reduction of the diatomic molecule and formation of good isolated yields (up to

61%) of the magnesium ynediolate compound **3** as a colorless crystalline solid (Scheme 2). Very similar outcomes occurred for reactions of **II** and **IV** with CO, though compounds such as **I** do not react with the gas, unless they are activated by Lewis base coordination.[15]

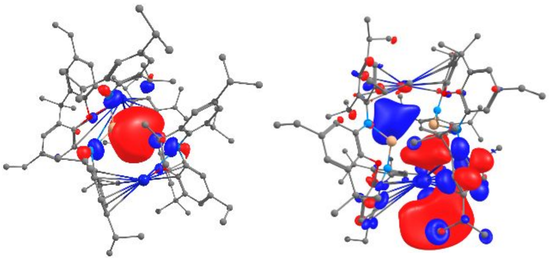
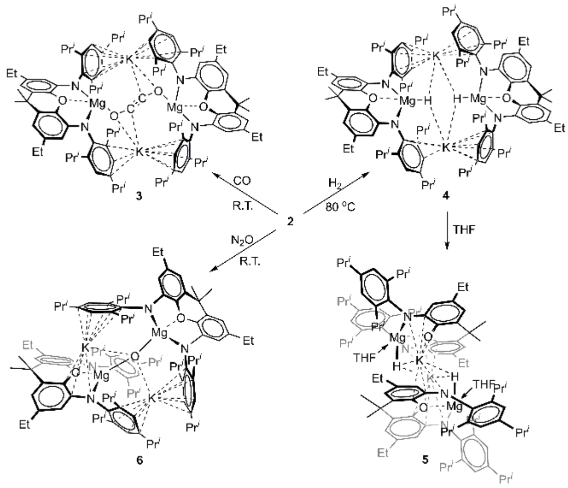


Figure 3. Calculated (wB97XD) HOMO (left), and LUMO (right) of **2**.



Scheme 2. Synthesis of compounds **3**-**6**.

Attention then turned to the reaction of **2** with H_2. No reaction occurred when a solution of the dimagnesium(I) compound was placed under 1 atmosphere of the gas at room temperature, but when this mixture was heated at 80 °C for 36 hours, a good isolated yield (52%) of the magnesium hydride compound **4** was recovered as a pale yellow crystalline solid. Again, this reactivity is broadly similar to that of **II**[16], **III**[5] and **IV**,[7] though neutral magnesium(I) compounds (e.g. **I**) typically do not react with H_2.[2] Interestingly, treatment of **4** with THF led to loss of all Trip arene···K interactions, and formation of the adduct complex **5**, in which the K centres are coordinated solely by the heterocyclic core of the ^{Trip}NON ligands.

Neutral magnesium(I) compounds such as **I** are known to be oxidised by N_2O to give oxo-bridged species, LMgOMgL (L = β-diketiminate).[17] Although similar reactivity has not been reported for **II** or **IV**, the reaction of a methylcyclohexane solution of **2** with N_2O was carried out. Rapid oxidation of the compound occurred, yielding colourless crystals of the unsymmetrical oxo-bridged compound **6**. Finally, the reaction of **2** with THF was investigated. For comparison, compounds such as **I** form simple adducts with the cyclic ether,[18] while a complex mixture of products results when the dinitrogen complex **IV** is treated with THF.[7] Most notably, addition of THF to **II** effects a counter-intuitive reduction of its sodium cations to sodium metal, and concomitant generation of a diamido magnesium(II) species.[19] A similar outcome occurs for **2**, the treatment of which with THF leads to metal precipitation, and formation of $[(^{Trip}NON)Mg(THF)_2]$ as the major soluble product (see ESI for further details). An ICP-OES analysis of an acid digested sample of the deposited metal showed it to be predominantly potassium, though it does contain significant amounts of magnesium (K:Mg ratio = 6.4:1). As was computationally revealed for **II**, the reduction of the alkali metal cations in THF coordinated **2** could occur *via* electron transfer from the Mg–Mg based HOMO to empty orbitals on the potassium centres.[18] However, the presence of magnesium in the metal deposited from the reaction of **2** with THF, and the relatively large HOMO–LUMO separation for **2**, suggests a more complicated situation in this case, with competing processes in operation.

Compounds **3**-**6** are thermally stable at ambient temperature in the solid state, and in non-coordinating solvents for extended periods. The NMR spectra of **3** and **4** are reminiscent of their solid-state structures, and are similar to those of their bulkier analogues, $[\{K(^{TCHP}NON)Mg\}_2(\mu\text{-}C_2O_2)]$ and $[\{K(^{TCHP}NON)Mg(\mu\text{-}H)\}_2]$, respectively.[7] Noteworthy features of those spectra are an alkynic resonance at δ 55.3 ppm (^{13}C NMR) for **3** (*cf.* 55.3 ppm for $[\{K(^{TCHP}NON)Mg\}_2(\mu\text{-}C_2O_2)]^7$), and a hydride resonance at δ 3.64 ppm (^{1}H NMR) for **4** (*cf.* 3.14 ppm for $[\{K(^{TCHP}NON)Mg(\mu\text{-}H)\}_2]^7$). The ^{1}H NMR spectrum of poorly soluble **5** (dissolved in a 10:1 mixture of C_6D_6 and THF-d_8) is also reminiscent of the solid-state structure of that compound, with the hydride resonance occurring at δ 3.51 ppm. Compound **6** has poor solubility in non-coordinating solvents once crystallised, but its ^{1}H NMR spectrum was obtained, and this suggests it has a time-averaged solution state structure in solution that is more symmetric than the unsymmetrical solid-state structure of the compound (see below). The poor solubility of the compound prevented an analysis of fluxional processes by variable temperature NMR spectroscopic studies.

In the solid-state, compounds **3** and **4** are essentially isostructural to their ^{TCHP}NON coordinated analogues,[7] so their structures will not be discussed here (see ESI for molecular structures). On the other-hand, the structures of **5** and **6** are novel, and are depicted in Figures 4 and 5, respectively. That for **5** shows it to be a centrosymmetric potassium bridged dimer. The magnesium centres of the compound have distorted square based pyramidal geometries (τ_5 = 0.35[20]), with the hydride ligands in apical positions. This arrangement is unusual and contrasts with the hydride ligands in the basal coordination plane of the closely related square based pyramidal (τ_5 = 0.43) compound, $[\{K(^{Dip}NON)(THF)Mg(\mu\text{-}H)\}_2]$ (^{Dip}NON = 4,5-bis(Dip)-2,7-di-*tert*-butyl-9,9-dimethyl-xanthene).[21] In **5**, the potassium centres are unusually solely η^4-coordinated by the OC_2N fragments of the ^{Trip}NON ligands. Again, this contrasts to $[\{K(^{Dip}NON)(THF)Mg(\mu\text{-}H)\}_2]$, in which the K cations are both η^6-coordinated to Dip arene units.

The solid-state structure of compound **6** reveals it to be an oxo-bridged dinuclear compound with both Mg-O interactions being similar, and in the normal range for oxo-bridged dimagnesium compounds.[13] Moreover, the short O-K distances (2.678 Å mean) seemingly arise from the oxo-centre coordinating both K cations. Those K centres are additionally ligated by both ^{Trip}NON ligands, but in an unsymmetrical fashion. That is, the Trip substituents of one ligand are η^6-coordinated to both potassiums, while the other ligand η^6-coordinates to one K centre through one of its Trip groups, and η^4-OC_2N ligates the other potassium cation.

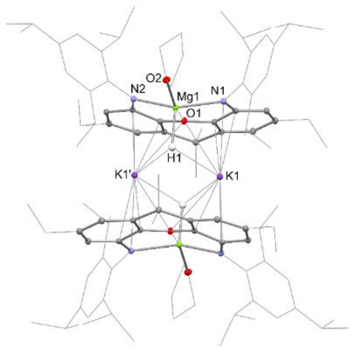


Figure 4. The molecular structure of **5** (20% ellipsoids; Trip, ethyl and methyl substituents shown as wire-frame for clarity; hydrogen atoms, except H(1) omitted). Selected bond lengths (Å) and angles (°): Mg(1)-H 1.83(4), K(1)-H 2.59(4), K(1)'-H 2.57(4), O(1)-Mg(1)-H 94.4(14), O(2)-Mg(1)-H 105.0(14), N(2)-Mg(1)-H 105.3(14), N(1)-Mg(1)-H 103.9(14).

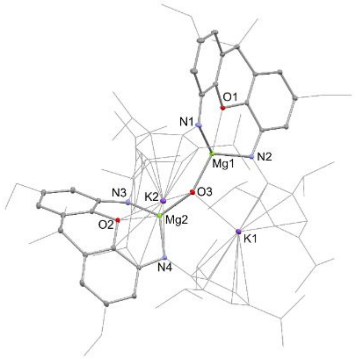


Figure 5. The molecular structure of **6** (20% ellipsoids; Trip, ethyl and methyl substituents shown as wire-frame for clarity; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): K(1)-O(3) 2.678(2), K(2)-O(3) 2.6765(19), Mg(1)-O(3) 1.910(2), Mg(2)-O(3) 1.899(2), Mg(2)-O(3)-Mg(1) 144.26(11), K(2)-O(3)-K(1) 109.99(7).

In summary, a new xanthene bridged diamide ligand has been developed and used to prepare a magnesium(II) diamide complex. Reduction of this with 5% w/w K/KI has given a potassium salt of a dianionic dimagnesium(I) species, **2**, as a contact ion pair. The preparation of this compound gives good evidence that Mg–Mg bond formation is frustrated from occurring in the synthesis of our previously reported magnesium-dinitrogen complex **IV**. Compound **2** has been shown to be a viable reagent for the reductive activation of the catalytically relevant molecules, CO, H_2 and N_2O. We are currently developing diamide ligands, the steric bulk of which is intermediate between those of ^{Trip}NON and ^{TCHP}NON. We aim to use these to prepare highly reactive dimagnesium(I) compounds which will test the limits of Mg–Mg bond lengths.

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Conflicts of interest

There are no conflicts to declare

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