

Metal–Metal Bonds

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Two-Coordinate Magnesium(I) Dimers Stabilized by Super Bulky Amido Ligands

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Abstract: A variety of very bulky amido magnesium iodide complexes, $\text{LMgI}(\text{solvent})_{0/1}$ and $[\text{LMg}(\mu\text{-I})(\text{solvent})_{0/1}]_2$ ($\text{L} = \text{N}(\text{Ar})(\text{SiR}_3)$; $\text{Ar} = \text{C}_6\text{H}_2[\text{C}(\text{H})\text{Ph}_2]_2\text{R}'\text{-2,6,4}$; $\text{R} = \text{Me}$, Pr^i , Ph , or OBu^t ; $\text{R}' = \text{Pr}^i$ or Me) have been prepared by three synthetic routes. Structurally characterized examples of these materials include the first unsolvated amido magnesium halide complexes, such as $[\text{LMg}(\mu\text{-I})]_2$ ($\text{R} = \text{Me}$, $\text{R}' = \text{Pr}^i$). Reductions of several such complexes with KC_8 in the absence of coordinating solvents have afforded the first two-coordinate magnesium(I) dimers, LMg-MgI ($\text{R} = \text{Me}$, Pr^i or Ph ; $\text{R}' = \text{Pr}^i$, or Me), in low to good yields. Reductions of two of the precursor complexes in the presence of THF have given the related THF adduct complexes, $\text{L}(\text{THF})\text{Mg-Mg}(\text{THF})\text{L}$ ($\text{R} = \text{Me}$; $\text{R}' = \text{Pr}^i$) and $\text{LMg-Mg}(\text{THF})\text{L}$ ($\text{R} = \text{Pr}^i$; $\text{R}' = \text{Me}$) in trace yields. The X-ray crystal structures of all magnesium(I) complexes were obtained. DFT calculations on the unsolvated examples reveal their Mg–Mg bonds to be covalent and of high s-character, while $\text{Ph}\cdots\text{Mg}$ bonding interactions in the compounds were found to be weak at best.

Interest in the chemistry of molecular compounds bearing homonuclear p- or d-block metal–metal bonds has rapidly escalated over the past 50 years.^[1] Despite this, isolable compounds containing s-block metal–metal bonds have only been known since 2007,^[2] and all but one of these examples are three- or four-coordinate magnesium(I) dimers. In every case, these compounds are kinetically stabilized by sterically bulky $\text{N,N}'$ -chelating, or N,N',O -tripodal, anionic ligands, so far confined to a range of β -diketiminates, a guanidinate, a diiminophosphinate, an ene-diamide, and several diimine-enolates (Figure 1).^[3–7] Additional examples include a remarkable mixed valence magnesium cluster anion, $[\text{Mg}_{16}\text{Cp}^*\text{Br}_4\text{K}]^-$ ($\text{Cp}^* = \text{C}_5\text{Me}_5^-$), which was recently reported and shown by computational studies to contain no less than 27 Mg–Mg bonds.^[8]

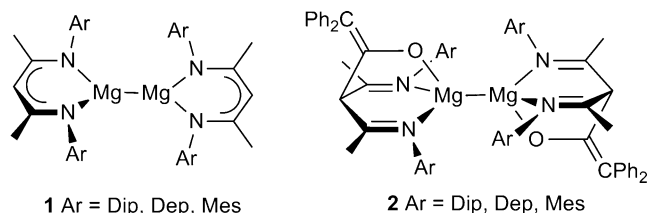


Figure 1. Examples of three- and four-coordinate magnesium(I) dimers (Dip = 2,6-diisopropylphenyl, Dep = 2,6-diethylphenyl, Mes = mesityl).

More than being just chemical curiosities, dimeric magnesium(I) complexes, especially those incorporating β -diketiminates, have been widely applied as soluble, selective, and safe reducing agents in a diverse range of inorganic and organic synthetic transformations.^[3] The growing popularity of these reagents lies in the fact that their use can lead to synthetic outcomes that are not achievable with traditional reducing agents, such as alkali metals, KC_8 , and sodium naphthalide. To allow the synthetic applicability of magnesium(I) dimers to flourish further, new examples of this compound class will need to be developed. In this respect, perhaps the most attractive targets are two-coordinate dimers, which should be markedly more electrophilic, and thus more reactive, than their three- and four-coordinate counterparts.

Problematically, all prior attempts to prepare magnesium(I) dimers devoid of chelating ligands (for example, $\text{Cp}^*\text{MgMgCp}^*$) have met with failure.^[9,10] Indeed, based on the results of experimental and computational studies, Schnöckel and co-workers have suggested that the synthesis of stable non-chelated magnesium(I) dimers will be “difficult, and perhaps impossible”.^[10] It should be noted that the same group have developed specialized synthetic routes to metastable (decomposition $> \text{ca. } -40^\circ\text{C}$) solutions of XMgMgX ($\text{X} = \text{Cl}$ or Br), though the metal centers of these dimers are possibly coordinated by additional donors (for example, NEt_3) present in those solutions.^[9,10]

Our group has developed an extremely bulky class of monodentate amide ligands (L); for example, $\text{L} = \text{N}(\text{Ar})(\text{SiR}_3)$; $\text{R} = \text{Me}$, Pr^i , Ph , OBu^t ; $\text{Ar} = \text{C}_6\text{H}_2[\text{C}(\text{H})\text{Ph}_2]_2\text{R}'\text{-2,6,4}$, $\text{R}' = \text{Me}$ or Pr^i).^[11] These ligands have been utilized to stabilize a series of novel unsupported metal–metal bonded systems, containing at least one two-coordinate, low oxidation state p- or d-block metal center. These systems include, LM-ML ($\text{M} = \text{Ge}$ or Sn), $\text{LM-Mg}(\text{Nacnac})$ ($\text{M} = \text{Mn}$ or Zn , $\text{Nacnac} = \beta$ -diketiminates), and LZn-Zn-ZnL .^[3,12] Given our success in this arena, we proposed that such amide ligands could possess sufficient

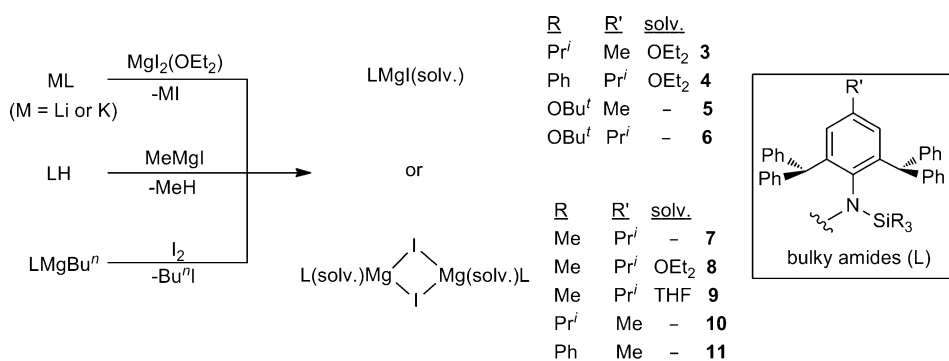
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steric bulk to kinetically stabilize two-coordinate magnesium(I) dimers, which should be considerably more reactive than compounds such as **1** and **2**. Herein, we report our efforts to confirm this proposal.

Based on our prior work with higher coordinate magnesium(I) dimers, it seemed to us that the most useful route to their two-coordinate counterparts, LMgMgL, would be by the reduction of the Hauser base magnesium(II) iodide precursor complexes of the type LMgI(donor)_n (*n* = 0 or 1). However, structurally characterized examples of such systems bearing monodentate amide ligands are relatively rare because of their propensity to participate in Schlenk equilibria and other degradation pathways.^[13] In the current study, it was believed that such pathways would be largely circumvented by the considerable steric bulk of the amide ligands available to us. This proved to be the case, and a series of amido magnesium(II) iodide complexes, **3–11**, were accessed by three preparative routes (Scheme 1). These involved either, 1) salt elimination reactions between an alkali metal amide and MgI₂(OEt)₂; 2) methane elimination



Scheme 1. Synthesis of the amido magnesium iodide complexes **3–11** (reaction solvents: diethyl ether, THF, or toluene).

reactions between a secondary amine (LH) and MeMgI; or 3) iodination of amido magnesium(II) butyl complexes, which were prepared in turn by reaction of LH with one equivalent of MgBu₂. All of these complexes were prepared in good to excellent yields, and all are thermally very stable in solution and the solid state. It is of note that manipulations involving route (3) of Scheme 1 can be carried out in the absence of coordinating solvents, which allows for the formation of unsolvated complexes, such as **5–7** and **11**. The advantage of this is that coordination of ethers to the magnesium centers of subsequent magnesium(I) reduction products is avoided. With that said, for some of the solvated amido magnesium(II) iodide complexes (**3** for example), the coordinated ether can be largely removed by dissolving the complex in warm toluene, and subsequently removing all volatiles in vacuo.

A selection of the amido magnesium(II) iodide compounds were crystallographically characterized, which revealed them to be either monomers or iodide bridged dimers in the solid state (see the Supporting Information). The structure of one of these complexes (**7**) is depicted in Figure 2; it is the first example of a crystallographically

characterized unsolvated monodentate amido magnesium halide complex. Not surprisingly, it is an iodide bridged dimer, which exhibits several Mg...C_{Ph} interactions of <2.7 Å (Σ C/Mg covalent radii = 2.14 Å) because of its unsolvated nature.^[14] These observations probably indicate a weak bonding interaction between the π -cloud of a phenyl group and each metal atom, though the simplicity of the NMR spectra of the complex suggests that coordination and dissociation of the phenyl group with respect to the magnesium center is rapid in solution on the NMR timescale at 20 °C.

Reductions of toluene solutions of the amido magnesium(II) iodide precursors, **3–11**, were attempted using an excess of either Na, K, or KC₈. The reactions involving the alkali metals all led to mixtures of products, the predominant component of which was the alkali metal salt of the amide ligand involved (see the Supporting Information for crystallographic details). Similar outcomes typically resulted from reduction of the precursor complexes with KC₈. Although, in the case of the reductions involving the

unsolvated precursors, **7** and **10**, good yields of the novel, pale yellow and crystalline magnesium(I) dimers, **12** and **13**, were obtained (Scheme 2). It is noteworthy that several crystals (yield <5%) of the dimer **14** were isolated from one reduction of **11**, though this synthesis was not reproducible in our hands. Similarly, reduction of **9** and **10** in the presence of THF gave very low yields of the bis- and mono-THF complexes **15** and **16**,

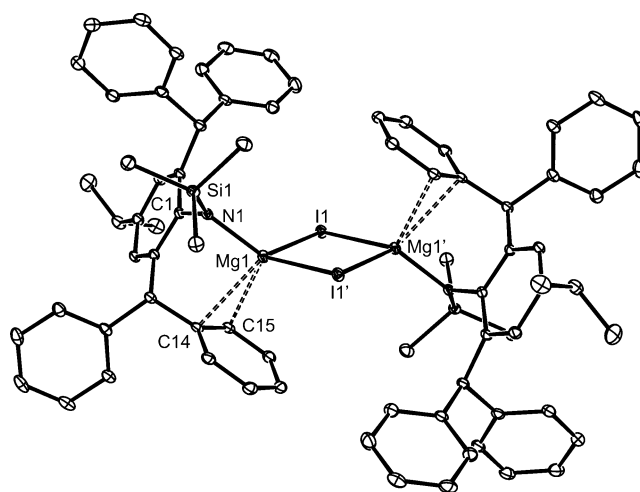
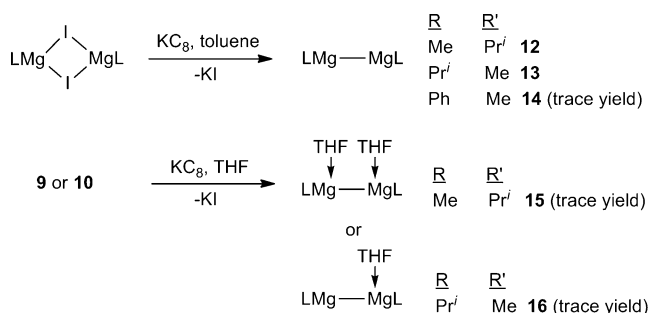


Figure 2. Molecular structure of **7** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): I(1)–Mg(1) 2.7450(12), I(1)–Mg(1') 2.7753(11), Mg(1)–N(1) 1.9675(19), Mg(1)–C(15) 2.573(2), Mg(1)–C(14) 2.678(2), Mg(1)–I(1)–Mg(1') 82.72(3), I(1)–Mg(1)–I(1') 97.28(3). Symmetry operation: '–x + 2, –y + 2, –z + 1.



Scheme 2. Synthesis of the amido magnesium(I) dimers **12**–**16** (see Scheme 1 for a definition of the ligands involved).

respectively; no spectroscopic data could be acquired for these materials. Interestingly, attempts to prepare these adducts in higher yields by treating solutions of **12** and **13** with THF, led to decomposition into intractable product mixtures.

Compounds **12** and **13** are remarkably thermally stable in the solid state (melting points (°C): 240 (**12**); 174 (**13**)), and are stable for weeks in solution at ambient temperature. However, they are air sensitive in solution and in the solid state. The molecular structures of the compounds are depicted in Figure 3. They are dimers, bearing unsupported Mg–Mg bonds, the lengths of which lie within the previously reported range for such connections.^[15] Moreover, there is no crystallographic or spectroscopic evidence for the presence of hydride ligands bridging the metal centers of the dimers. Not surprisingly the Mg–N separations in the two-coordinate compounds are significantly shorter than those bonds in all three-coordinate *N,N'*-chelated magnesium(I) dimers (mean bond length, 2.06 Å).^[15] The N–Mg–Mg angles in **12** and **13** are similar and presumably distorted from linear so as to minimize intramolecular interactions between their two extremely bulky amino aryl substituents. In **12**, these interactions are further relieved by the bulky aryl substituents taking up *transoid* positions relative to one another. In contrast, the significantly more bulky silyl substituents of **13** seem to require a *cisoid* arrangement of aryl groups to curtail steric density in the compound. Despite these geometric differences, the imposing steric profile of the amide ligands in both **12** and **13** leads to their Mg–Mg bonds being enshrouded by flanking benzhydryl phenyl groups. However, there are no *C_{ph}...Mg* separations in **12** that are < 3.0 Å long, which implies that any interactions between the phenyl groups and the magnesium centers in that compound are weak. This situation can be compared to that for the presumably more electrophilic Mg(II) centers of the precursor complex, **7**, which do exhibit significant Ph...Mg interactions. Furthermore, one Mg(I) center of the bulkier dimer, **13**, appears to be weakly η²-coordinated by one phenyl group, whereas the other is not.

Although the THF adducts of **12** and **13** (namely, **15** and **16**) were only formed in trace yields, it is informative to compare their structures (Figure 4) with those of their unsolvated counterparts. Two THF molecules coordinate the Mg centers of **15**, whereas only one metal center of **16** is coordinated, presumably because of the greater steric bulk of the amide ligands in the latter. The Mg–Mg and Mg–N bonds

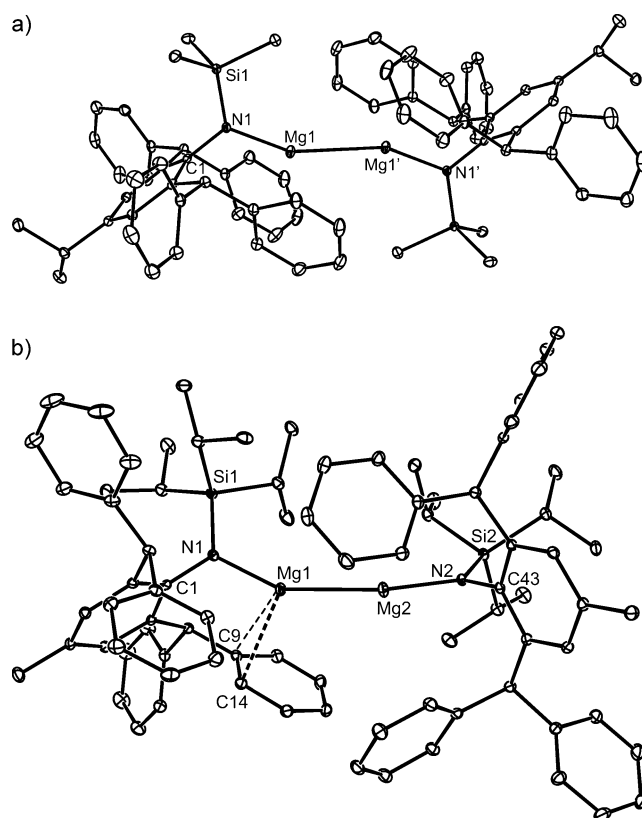


Figure 3. Molecular structures of a) **12** and b) **13** (25 % thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°) for **12**: Mg(1)–Mg(1') 2.8223(11), Mg(1)–N(1) 1.9855(12), N(1)–Mg(1)–Mg(1') 157.06(4). Symmetry operation: $-x+1, -y+1, -z+1$. Selected bond lengths (Å) and angles (°) for **13**: Mg(1)–Mg(2) 2.8504(13), Mg(1)–N(1) 1.985(2), Mg(2)–N(2) 1.982(2), Mg(1)–C(14) 2.771(3), Mg(1)–C(9) 2.962(3), N(1)–Mg(1)–Mg(2) 151.66(8), N(2)–Mg(2)–Mg(1) 149.05(8).

of the THF adducts are significantly longer than those of **12** and **13**, as has previously been found for THF adducts of β-diketiminato Mg(I) dimers (**1** for example).^[3] The ligands of both adducts adopt a *cisoid* arrangement, as opposed to the *transoid* geometry of **12**, and the *NMg_(THF)Mg* angles are more than 17° (for **15**) and 10° (for **16**) narrower than in the THF-free molecules, **12** and **13**. Moreover, it is apparent that the greater steric crowding of the metal centers in the adducts leads to a lengthening of their *C_{ph}...Mg* separations, relative to those in **12** and **13**, as all are greater than 3.0 Å in length.

To investigate the nature of the metal–metal bonding in the magnesium(I) compounds **12**–**14**, dispersion corrected DFT calculations (B3PW91-D3BJ; Supporting Information) were carried out in the gas phase on the full molecules, **12'**–**14'**. The geometries of the compounds were optimized to be similar to those determined from the crystal structures, but with underestimated Mg–Mg distances (**12'**, 2.725 Å; **13'**, 2.776 Å; **14'**, 2.708 Å). Natural Bond Orbital (NBO) and Natural Population (NPA) analyses of the compounds revealed that their metal–metal bonds have high covalent character, while the N–M interactions in all are largely ionic (for example, NPA charges for **14'**: Mg 0.70, N –1.50). The highest occupied molecular orbitals (HOMOs) of the

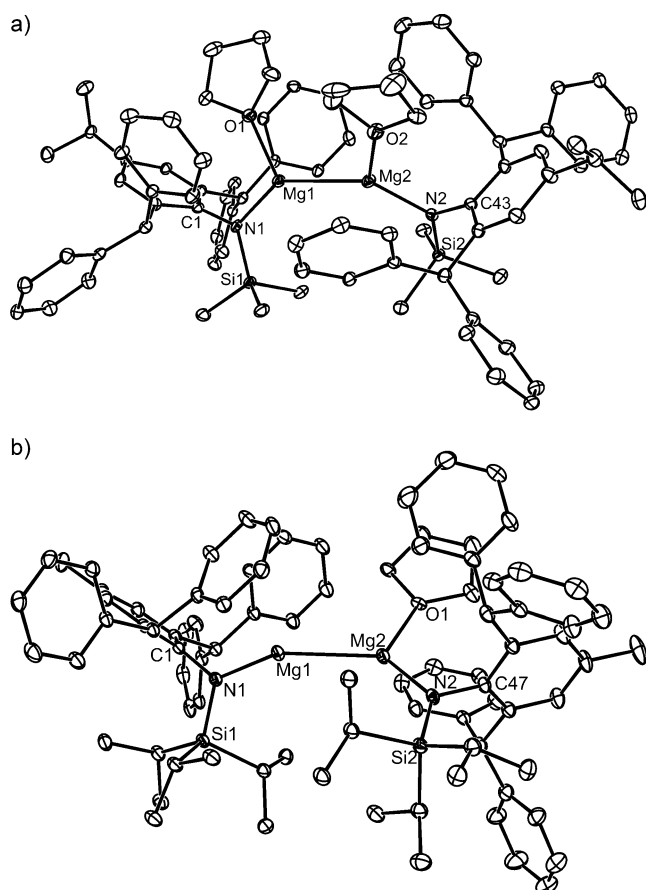


Figure 4. Molecular structures of a) **15** and b) **16** (25 % thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°) for **15**: Mg(1)–Mg(2) 2.930(2), N(1)–Mg(1) 2.027(4), O(1)–Mg(1) 2.082(4), N(2)–Mg(2) 2.024(4), O(2)–Mg(2) 2.081(4), N(1)–Mg(1)–Mg(2) 139.18(13), O(1)–Mg(1)–Mg(2) 113.09(11), N(2)–Mg(2)–Mg(1) 136.79(12), O(2)–Mg(2)–Mg(1) 115.69(12). Selected bond lengths (Å) and angles (°) for **16**: Mg(1)–Mg(2) 2.9049(17), Mg(1)–N(1) 2.002(3), Mg(2)–N(2) 2.013(3), O(1)–Mg(2) 2.084(11), N(1)–Mg(1)–Mg(2) 155.43(10), N(2)–Mg(2)–Mg(1) 138.77(9), O(1)–Mg(2)–Mg(1) 110.1(3).

computed molecules exhibit significant metal–metal σ -bonding character, which is largely derived from overlap of valence s-orbitals on the metals (> 90 % s-character in each case, see Figure 5). Furthermore, the level of covalency of these bonds is reflected in their Wiberg Bond Orders (WBOs: **12'** 0.90, **13'** 0.88, **14'** 0.89). The lowest unoccupied molecular orbitals (LUMOs) for the dimers are ligand-based, while the LUMO + 2 of each displays significant Mg–Mg π -bonding character. This view of the Mg–Mg bonding in these compounds reflects that which was previously reported for related *N,N'*-chelated dimers.^[3] With that said, no occupied orbitals could be found for **12'–14'**, which display significant Ph...Mg bonding interactions, thereby validating our assertion that these systems possess essentially two-coordinate metal centers.

In conclusion, the first examples of stable two-coordinate magnesium(I) dimers have been synthesized and analyzed by spectroscopic, crystallographic, and computational techniques. The kinetic stability of the compounds is almost

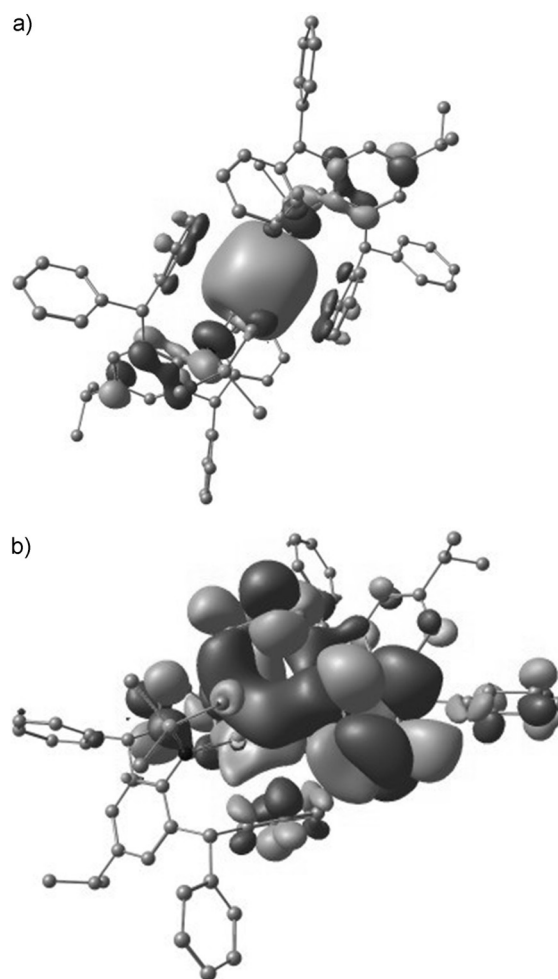


Figure 5. a) HOMO and b) LUMO + 2 of **12'**.

certainly a result of the considerable steric protection afforded to the metal–metal bonds by the extremely bulky amide ligands of the dimers. There is considerable potential to develop these coordinatively unsaturated magnesium(I) compounds as a second generation of highly reactive, bespoke reducing agents in inorganic and organic synthesis. We will report on our efforts in this direction in due course.

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Keywords: bulky amides · DFT calculations · magnesium(I) · metal–metal bonding

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