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

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Summary for contents page:

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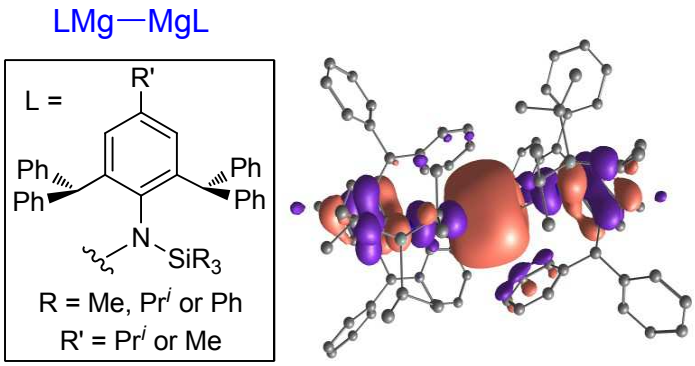
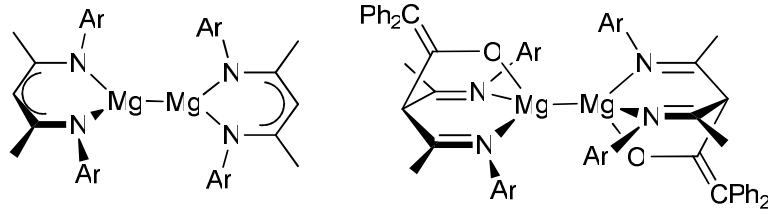


Two's company. Reduction of extremely bulky amido magnesium iodide complexes with KC_8 yields the first examples of two-coordinate magnesium(I) dimers. LMg-MgL (L= -N(Ar)(SiR_3); Ar = $C_6H_2\{C(H)Ph_2\}_2R'$-2,6,4; R = Me, Pr^i or Ph; R' = Pr^i or Me), which crystallographic and DFT computational studies show to possess unsupported Mg-Mg covalent bonds of high s-character. THF adducts of two of these complexes are also reported.

Keywords: magnesium(I), metal-metal bonding, bulky amide, DFT calculations.

Abstract: *A variety of extremely bulky amido magnesium iodide complexes, LMgI(solvent)$_{0or1}$ and [LMg(μ-I)(solvent)$_{0or1}$]$_2$ (L= -N(Ar)(SiR$_3$); Ar = C$_6$H$_2${C(H)Ph$_2$}$_2$R'-2,6,4; R = Me, Pr^i, Ph or OBu^t; R' = Pr^i or Me) have been prepared via three synthetic routes. Structurally characterized examples of these include the first unsolvated amido magnesium halide complexes, e.g. [LMg(μ-I)]$_2$ (R = Me, R' = 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-MgL (R = Me, Pr^i or Ph; R' = 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, L(THF)Mg-Mg(THF)L (R = Me; R' = Pr^i) and LMg-Mg(THF)L (R = Pr^i; R' = Me) in trace yields. The X-ray crystal structures of all magnesium(I) complexes have been obtained. DFT calculations on the unsolvated examples reveal their Mg-Mg bonds to be covalent and of high s-character, while Ph···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 are three- or four-coordinate magnesium(I) dimers. In every case, these compounds are kinetically stabilized by sterically bulky *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, e.g. in **1** and **2**.[3-7] In addition to these, a remarkable mixed valence magnesium cluster anion, [Mg$_{16}$Cp*$_8$Br$_4$K]$^-$ (Cp* = C$_5$Me$_5^-$), was recently reported, and shown by computational studies to contain no less than 27 Mg-Mg bonds.[8]



1 Ar = Dp Dep Mes **2** Ar = Dp Dep Mes

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-diketiminate ligands, 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 with 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. In order for the synthetic applicability of magnesium(I) dimers to further flourish, 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.

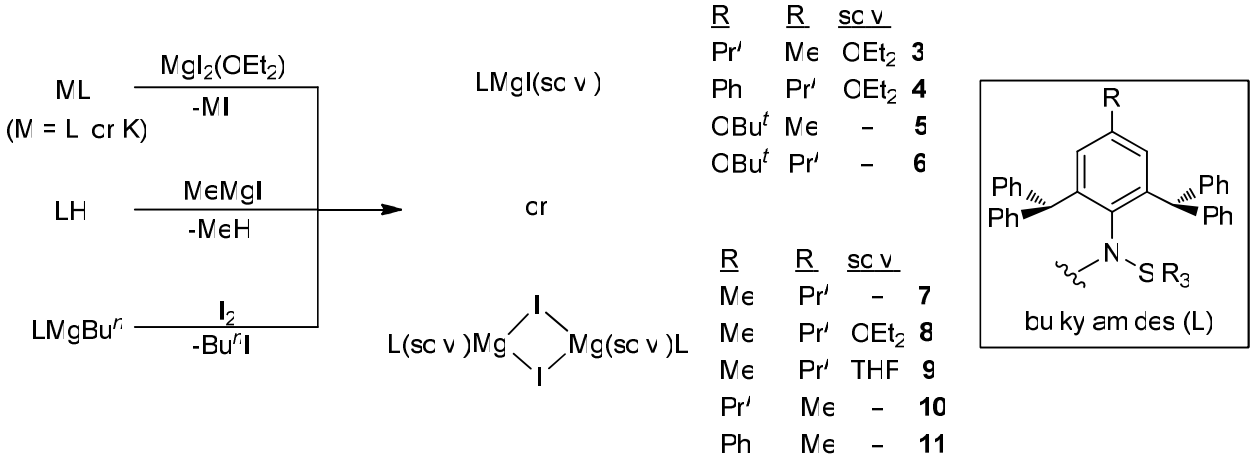
The problem here is that all prior attempts to prepare magnesium(I) dimers devoid of chelating ligands, e.g. Cp*MgMgCp*, have met with failure.[9,10] Indeed, based on the results of experimental and computational studies, Schnöckel and co-workers have suggested that the synthesis of stable non-chelated magnesium(I) dimers will be "difficult, and perhaps impossible".[10] It should be noted here that the same group have developed specialized synthetic routes to metastable (decomp. > *ca.* -40°C) solutions of XMgMgX (X = Cl or Br), though the metal centers of these dimers are quite possibly additionally coordinated by donors (e.g. NEt_3) present in those solutions.[9,10]

Our group has developed an extremely bulky monodentate amide class of ligands (L), e.g. -N(Ar)(SiR_3) (R = Me, Pr^i, Ph, OBu^t; Ar = $C_6H_2\{C(H)Ph_2\}_2R'$-2,6,4, R' = Me or Pr^i).[11] These

have been utilized for the stabilization of a series of novel unsupported metal-metal bonded systems, containing at least one two-coordinate, low oxidation state p- or d-block metal center, e.g. LM-ML (M = Ge or Sn), LM-Mg(Nacnac) (M = Mn or Zn; Nacnac = β-diketiminate), LZn-Zn-ZnL.[3,12] Given our success in this arena, we proposed that such amide ligands could possess sufficient steric bulk to kinetically stabilize two-coordinate magnesium(I) dimers, which should be considerably more reactive than compounds such as **1** and **2**. Here, we report on 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 *via* the reduction of 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, due to 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) iodode complexes, **3**-**11**, were accessed *via* three preparative routes (Scheme 1). These involved either (i) salt elimination reactions between an alkali metal amide and $MgI_2(OEt_2)_2$; (ii) methane elimination reactions between a secondary amine (LH) and MeMgI; or (iii) iodination of amido magnesium(II) butyl complexes, which were, themselves, prepared *via* reaction of LH with one equivalent of $MgBu^n_2$. All of these complexes were prepared in good to excellent isolated yields, and all are thermally very stable in both solution and the solid state. It is of note that manipulations involving route (iii) can be carried out in the absence of coordinating solvents, which allows for the formation of unsolvated complexes, e.g. **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 (e.g. **3**), the coordinated ether can

be largely removed by dissolving the complex in warm toluene, then removing all volatiles *in vacuo*.



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

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 Supporting Information (SI) for full details). The structure of one of these complexes (**7**) is depicted in Figure 2, as this represents the first example of a crystallographically characterized unsolvated monodentate amido magnesium halide complex. Not surprisingly, it is an iodide bridged dimer, that because of its unsolvated nature, exhibits several Mg···C_{Ph} interactions of < 2.7 Å (Σ C/Mg covalent radii = 2.14 Å[14]). These probably indicate a weak bonding interaction between the π-cloud of a phenyl and each metal, though the simplicity of the NMR spectra of the complex suggests that coordination and de-coordination of the phenyl group to the magnesium centre is rapid in solution on the NMR timescale at 20 °C.

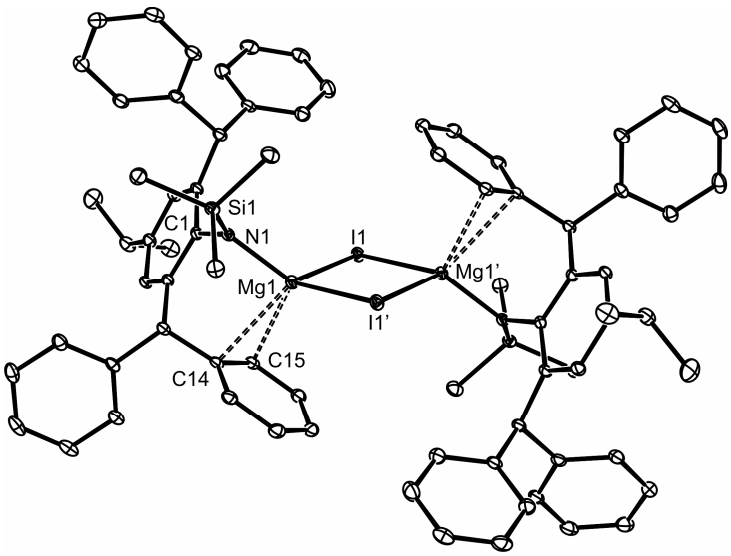
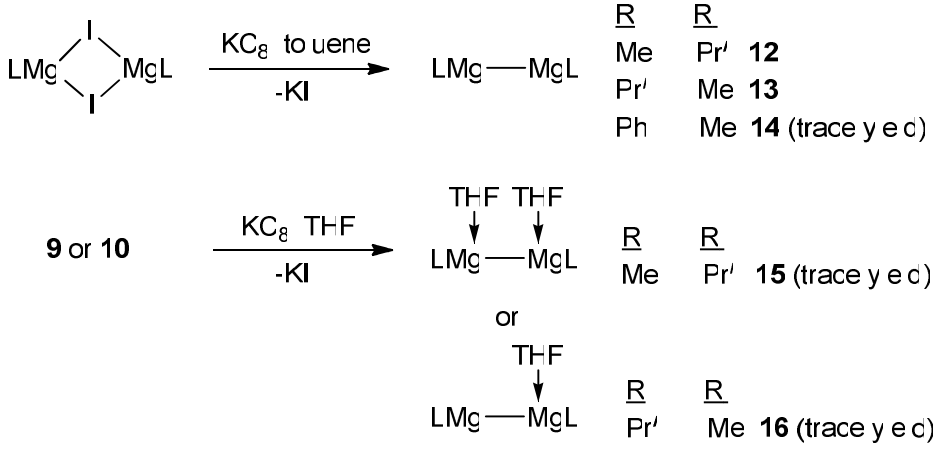


Figure 2. Molecular structure of **7** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°): I(1)-Mg(1) 2.7450(12), I(1)-Mg(1)' 2.7753(11), Mg(1)-N(1) 1.9675(19), Mg(1)-C(15) 2.573(2), Mg(1)-C(14) 2.678(2), Mg(1)-I(1)-Mg(1)' 82.72(3), I(1)-Mg(1)-I(1)' 97.28(3). Symmetry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

Reductions of toluene solutions of the amido magnesium(II) iodide precursors, **3-11**, were attempted using excesses of either Na, K or KC_8. 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 SI for crystallographic details). Similar outcomes typically resulted from reduction of the precursor complexes with KC_8, though in the case of the reductions involving the unsolvated precursors, **7** and **10**, good yields of the new pale yellow, 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** respectively, no spectroscopic data for which could be acquired. Interestingly, attempts to prepare these adduct complexes in higher yields by treating solutions of **12** and **13** with THF, led to decomposition to intractable product mixtures.



Scheme 2. Synthesis of the amido magnesium(I) dimers **12**-**16** (see Scheme 1 for ligand definition).

Compounds **12** and **13** are remarkably thermally stable in the solid state (m.p. **12** 240 °C; **13** 163 °C), and are indefinitely stable in solution at ambient temperature. They are, however, both air sensitive in solution and the solid state. The molecular structures of the compounds are depicted in Figure 3. The compounds 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 (2.06 Å mean[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 its bulky aryl substituents taking up transoid positions relative to one another. In contrast, the significantly more bulky silyl substituents of **13** seemingly require a cisoid arrangement of its aryl groups, in order to curtail steric buttressing 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. There are, however, no $C_{Ph}\cdots Mg$ separations

in **12** that are < 3.0 Å, which implies that any interactions between the phenyl groups and the magnesium centers in that compound are weak at best. 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, oneMg^{I} center of the bulkier dimer, **13**, appears to be weakly η^2-coordinated by one phenyl group, whereas the other is not.

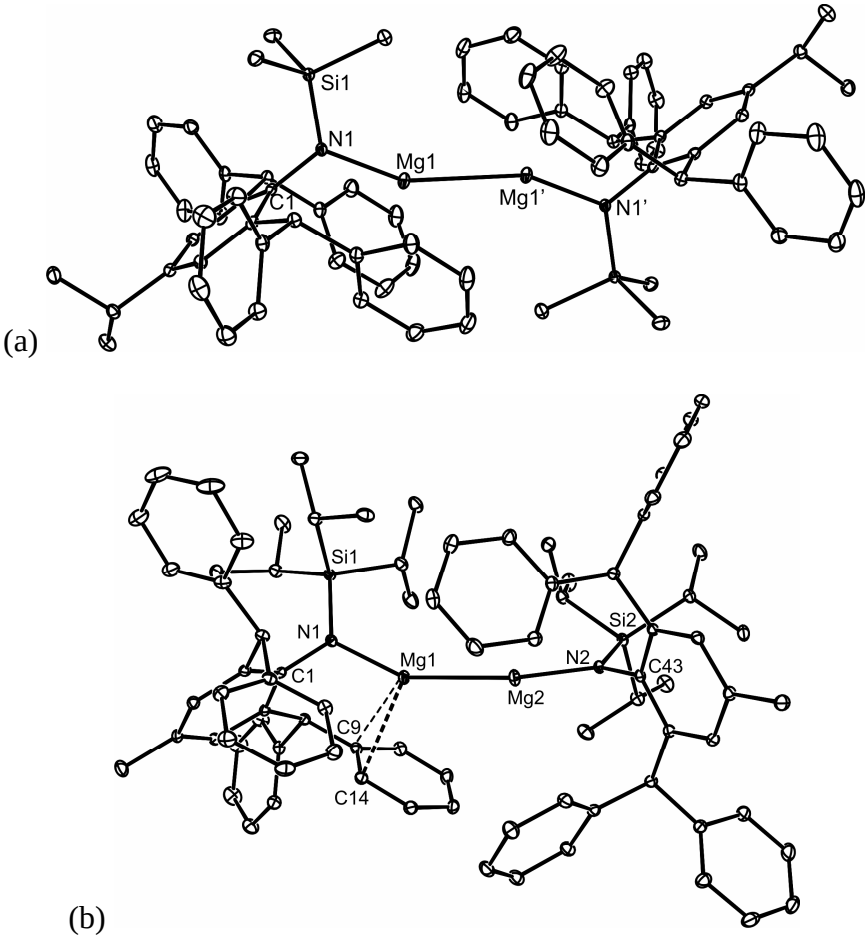
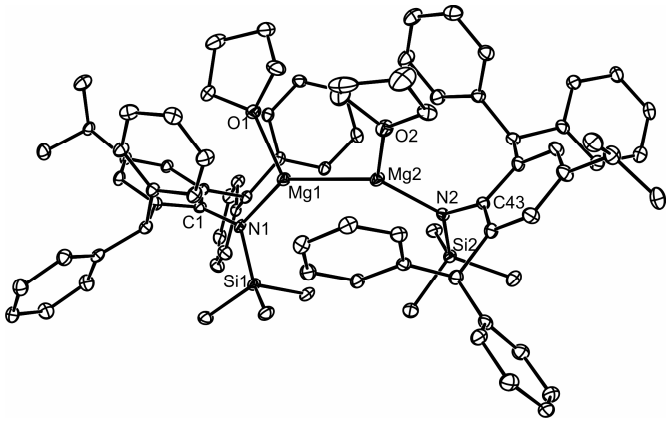
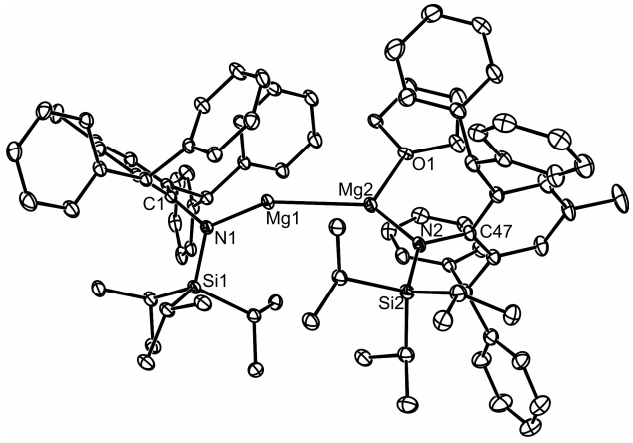


Figure 3. Molecular structures of (a) **12** and (b) **13** (25% thermal ellipsoids; hydrogen atoms omitted). Selected bond lengths (Å) and angles (°) for **12**: Mg(1)-Mg(1)' 2.8223(11), Mg(1)-N(1) 1.9855(12), N(1)-Mg(1)-Mg(1)' 157.06(4). Symmetry operation: ' -x+1, -y+1, -z+1. Selected bond lengths (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).

Although the THF adducts of **12** and **13** (*viz.* **15** and **16**) were only formed in trace yields, it is instructive 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 due to the greater steric bulk of the amide ligands in the latter. The Mg-Mg and Mg-N bonds 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, e.g. **1**.[3] The ligands of both adducts adopt cisoid dispositions, 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 $C_{Ph}\cdots Mg$ separations, relative to those in**12** and **13**, as all are greater than 3.0 Å.



(a)



(b)

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).

In order to investigate the nature of the metal-metal bonding in the magnesium(I) compounds **12**-**14**, dispersion corrected DFT calculations (B3PW91/B3PW91-D3, see SI for full details) were carried out in the gas phase on the full molecules, **12'**-**14'**. The geometries of the compounds optimized to be similar to those determined from the crystal structures, but with underestimated Mg-Mg distances (**12'**: xxx Å, **13'**: 2.776 Å, **14'**: 2.708 Å). NBO and 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 (e.g. NBO? charges for **14'**: Mg 0.70, N -1.50). The HOMOs of the 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'** xxx, **13'** 0.88, **14'** 0.89). The 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 the compounds reflects that which has previously been reported for related *N,N'*-chelated dimers.[3] With that said, no occupied orbital could be found for **12'**-**14'** which displays a significant Ph···Mg bonding interaction, thereby validating our ascertion that these systems possess essentially two-coordinate metal centers.

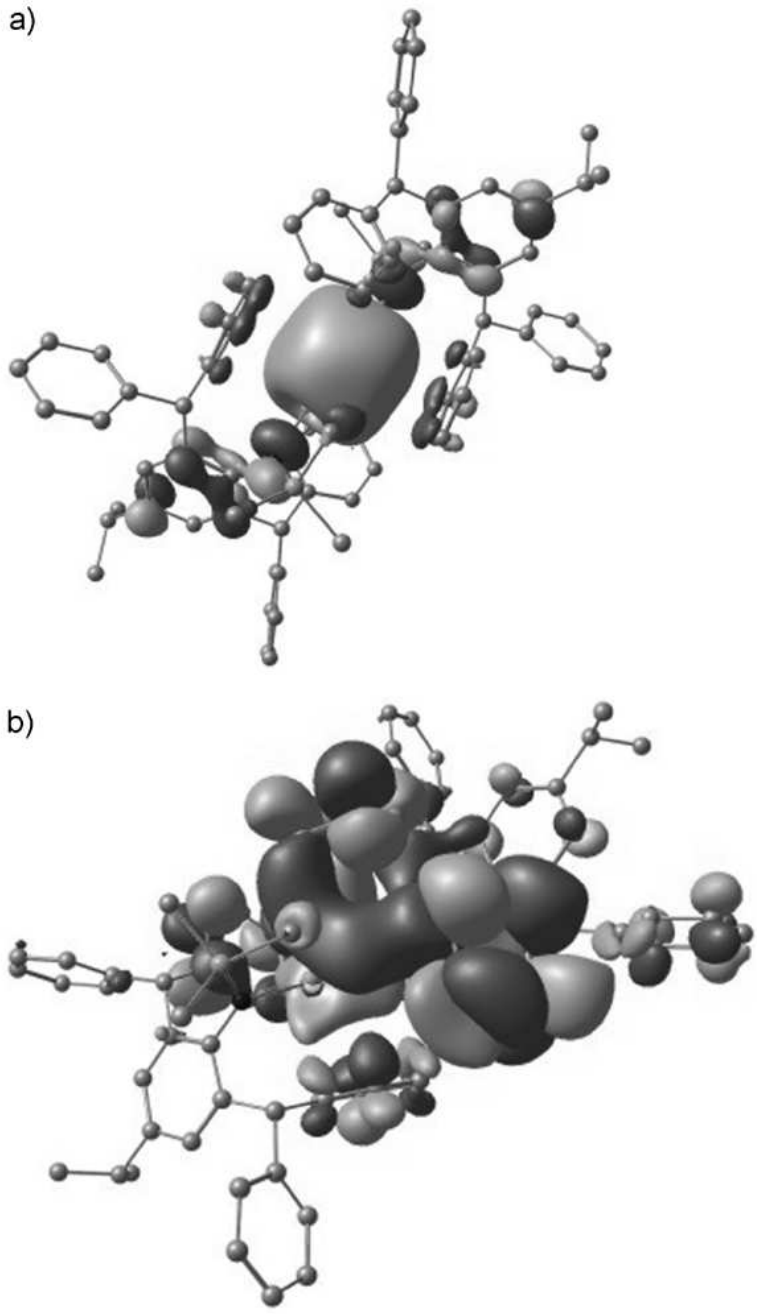


Figure 5. (a) HOMO and (b) LUMO+2 of **12'**.

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

Experimental Section

Full synthetic, spectroscopic and crystallographic details for new compounds; and full details and references for the DFT calculations can be found in the Supporting Information.

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