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Mg–Mg Bonds

Stable Adducts of a Dimeric Magnesium(I) Compound**

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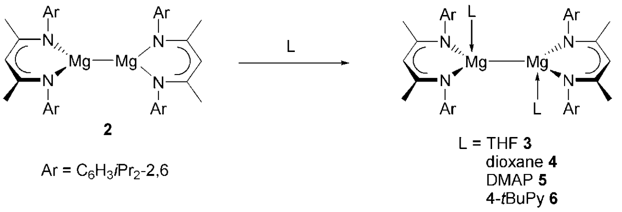
The chemistry of compounds containing metal–metal bonds is an extensive and fundamentally important field that has greatly added to our understanding of chemical bonding.[1] Traditionally, activity in the area has focused on the d-block metals, yielding landmark results which include Cotton's quadruply bonded dianion, $[Re_2Cl_8]^{2-}$,[2] and more recently, Power's quintuply bonded chromium(I) dimer, [Ar′CrCrAr′] (Ar′ = $C_6H_3(C_6H_3i\mathrm{Pr}_2\text{-}2,6)_2\text{-}2,6$).[3] In the past three decades rapid progress has also been made by many groups working with the p-block metals and metalloids. Now, a vast array of dimeric compounds with heavier p-block element–element bonds possessing orders of up to 3 are known.[4] At the interface of the p and d blocks, undoubtedly the most important breakthrough in the new millenium has been Carmona's synthesis of the dimeric zinc(I) compound [Cp*ZnZnCp*] (Cp* = $C_5Me_5^-$).[5] This has led to a flurry of activity in the area and the preparation of a handfull of other Zn–Zn bonded complexes.[6]

Conspicuously absent from the arena of metal–metal bonded complexes have been those involving the s-block metals.[7] However, given the unexpected stability of zinc(I) dimers, and the chemical similarities between zinc and the Group 2 metals, a number of theoretical studies have predicted that thermally stable compounds of the type RMMR (M = Be, Mg, or Ca) should be accessible.[8] For magnesium, we have shown that this is the case with the preparation of the bulky guanidinate or β-diketiminate coordinated magnesium(I) dimers, [LMgMgL] (L = $[(\mathrm{ArN})_2\mathrm{CN}i\mathrm{Pr}_2]^-$, priso$^-$ (**1**) or $[(\mathrm{ArNCMe})_2\mathrm{CH}]^-$, nacnac$^-$ (**2**) (Ar = $C_6H_3i\mathrm{Pr}_2\text{-}2,6$).[9,10] These are remarkably thermally stable compounds (**1** decomp. 170–173 °C; **2** decomp. 301–303 °C) with Mg–Mg distances of 2.8508(12) Å (**1**) and 2.8457(8) Å (**2**). Theoretical studies on a model of **1**, $[\{\mathrm{Mg}\{[(C_6H_3Me_2\text{-}2,6)\mathrm{N}]_2\mathrm{CNMe}_2\}\}_2]$, showed it to contain a high-s-character, covalently bonded Mg_2^{2+} core, having largely ionic interactions with its guanidinate ligands. Preliminary reactivity studies on the magnesium(I) compounds have revealed them to act as facile two-center/two-electron reductants towards a range of unsaturated substrates. In our initial report this was demonstrated with the facile insertion of a carbodiimide, CyNCNCy (Cy = cyclohexyl), into the Mg–Mg bond of **2** to give the unusual magnesium magnesioamidinate complex [(nacnac)Mg{μ-C(NCy)$_2$}Mg(nacnac)], which we proposed was formed via an intermediate carbodiimide–Mg complex.[9] Herein we show that less reducible Lewis bases readily complex **2** to give adducts that are surprisingly stable towards disproportionation reactions and that have exceptionally long Mg–Mg bonds. For comparison, closely related magnesium(II) hydride complexes have been prepared and studied.

Although we originally noted that the addition of tetrahydrofuran (THF) to yellow C_6D_6 solutions of **2** did not lead to any changes in its NMR spectra, it did lead to the solutions taking on an orange color. One explanation for this observation is that a transient coordination of the magnesium centers of **2** by THF was occurring. To assess the possibility that **2** could form stable adducts with cyclic ethers, it was dissolved in either neat THF or dioxane to yield red-orange and orange solutions, respectively. When volatiles were removed from these solutions in vacuo, uncoordinated **2** was quantitatively recovered. However, concentration and cooling of the solutions afforded good yields of the crystalline adducts, red-orange **3** and orange **4** (Scheme 1).[11] Placing crystalline samples of **3** or **4** under vacuum leads to the loss of their coordinated ethers and the regeneration of **2**. This process is considerably more rapid for **4** than for **3**. The same outcome occurs if they are heated to greater than ca. 70 °C (**3**) or 60 °C (**4**) under dinitrogen atmospheres. These properties indicate that the ether ligands of **3** and **4** are only weakly coordinated. Moreover, the lower decomposition temperature of **4**, and the fact that it can co-crystallize with **2** from neat dioxane solutions, signifies that dioxane is a weaker donor towards **2** than THF.[12] It is noteworthy, however, that treatment of THF solutions of **4** with the carbodiimide CyNCNCy led to no reaction. This shows that a large excess of THF successfully competes with the carbodiimide for



Scheme 1. The preparation of the magnesium(I) adducts **3**–**6**.

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coordination to **2** and adds weight to our original proposal that the formation of [(nacnac)Mg{μ-C(NCy)$_2$}Mg(nacnac)] proceeds via an intermediate complex such as [**2**(η^1-*N*-CyNCNCy)].

In attempts to prepare more robust adducts of **2**, toluene solutions of the compound were treated with an excess of either quinuclidine or tmeda (tetramethylethylenediamine), or the compound was dissolved in neat diethylether or 1,2-dimethoxyethane. In each instance, no reaction or color change occurred, and **2** was recovered intact. Attention then turned to the highly Lewis basic substituted pyridines 4-dimethylaminopyridine (DMAP) and 4-*tert*-butylpyridine (4-*t*BuPy), which when reacted with **2** in non-coordinating solvents gave good yields of the deep red-brown compounds **5** and **6**, respectively (Scheme 1). These compounds are very thermally stable and display no evidence for the loss of their pyridine ligands up to their decomposition temperatures (159–160 °C and 248–250 °C, respectively), or when they are placed under vacuum. Indeed, a molecular ion peak envelope was observed in the accurate-mass EI mass spectrum of **6**.

These results suggest that the pyridine ligands are significantly stronger donors towards **2** than either THF or dioxane. This is also borne out by the results of NMR spectroscopic studies on **3**–**6** which imply that in C_6D_6 (or [D$_8$]toluene), **3** and **4** exist in equilibria that heavily favor **2** and the free ether, whereas resonances for the free pyridine ligands were not seen in the spectra of **5** and **6**. Despite this, their NMR spectra, and those of **3** and **4** (recorded in [D$_8$]THF and [D$_8$]dioxane, respectively) are more symmetrical than would be expected if their solid-state structures are retained in solution. A reasonable explanation for these observations is that fluxional ligand dissociation/coordination processes are occurring for the complexes, which are rapid compared to the NMR timescale. Attempts to investigate these processes by variable-temperature NMR studies were thwarted by the low solubility of the complexes at temperatures below 0 °C or, in the case of **4**, the melting point of [D$_8$]dioxane (11 °C).

The X-ray crystal structures of compounds **3**–**6** were determined and show the compounds to have broadly similar structural features. As a result, only the molecular structure of **3** is depicted in Figure 1 (see the Supporting Information for the molecular structures of **4**–**6**), though relevant metrical parameters for all compounds can be found in the figure caption. Although the Mg(nacnac) heterocycles are significantly distorted from planar, the delocalized backbones of both nacnac ligands in each compound are close to planar and effectively parallel to each other. This contrasts to the situation in **2** in which these planes are close to orthogonal. The magnesium centers of the compounds all exhibit heavily distorted tetrahedral coordination geometries with considerably larger Mg–N(nacnac) distances than those in **2** (2.060 Å mean), which has three-coordinate Mg centers. In addition, the ether or pyridine O/N–Mg distances in all complexes are significantly larger than any previously reported examples involving these ligands coordinated to four-coordinate Mg centers.[13] Furthermore, there is no structural (or spectroscopic) evidence for the reduction of the pyridine ligands in **5** and **6**, or, indeed, the nacnac ligands in all complexes.

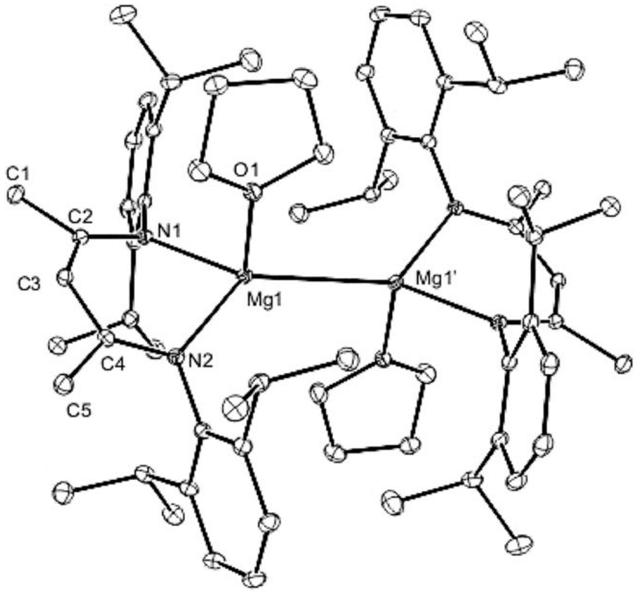


Figure 1. Molecular structure of [{Mg(nacnac)(THF)}$_2$] (**3**) (symmetry operation: ′ $-x+1$, $-y$, $-z$). Relevant bond lengths [Å] and angles [°] for **3**: Mg–Mg 3.0560(12), Mg–O 2.1733(13), Mg–N 2.159 (mean), N-Mg-N 87.08(5); **4**: Mg–Mg 3.1499(18), Mg–O 2.2438(18), Mg–N 2.152 (mean), N-Mg-N 87.79(8); **5**: Mg–Mg 3.1962(14), Mg–N-(DMAP) 2.2353(18), Mg–N(nacnac) 2.178 (mean), N-Mg-N 86.11(6); **6**: Mg–Mg 3.1260(15), Mg–N(4-*t*BuPy) 2.2257(18), Mg–N(nacnac) 2.162 (mean), N-Mg-N 86.30(7).

The most remarkable features of the structures of compounds **3**–**6** are their Mg–Mg distances. Although each compound co-crystallizes with small amounts of the corresponding hydroxide complex, [{Mg(nacnac)(L)(μ-OH)}$_2$] (L = THF, dioxane, DMAP, or 4-*t*BuPy), the apparent Mg–Mg distances vary over more than 0.14 Å and are from ca. 0.21 to 0.35 Å larger than that in **2** (2.8457(8) Å).[9,14,15] To put this into context, the revised sum of two divalent Mg covalent radii is 2.82 Å,[16] and the Mg–Mg distances in elemental and diatomic magnesium are 3.20 Å and 3.890 Å, respectively.[17] Moreover, there seems to be little correlation between the ligand donor strength and Mg–Mg separation in the compounds. This is best illustrated by the fact that, although compound **4** readily loses its weakly donating dioxane ligands, it has the second largest Mg–Mg distance of the four compounds. This suggests that the origin of the large Mg–Mg distances in **3**–**6** has less to do with electronics than other factors, for example, sterics. For sake of comparison, we are unaware of any p-block compound incorporating a metal–metal single bond which increases in length by more than 0.2 Å upon coordination by one or more neutral Lewis base ligands.[13] That said, it is noteworthy that the Ge–Ge distance of a singlet diradicaloid digermyne, [Ar′GeGeAr′], increases by ca. 0.38 Å upon coordination by two isonitrile molecules (to give [Ar′Ge(CNMes)Ge(CNMes)Ar′], Mes = mesityl). This is, however, accompanied by a reduction in the Ge–Ge bond order from approximately 2 to 1.[18]

In order to provide insight into the exceptional lengthening of the Mg–Mg bond of **2** upon coordination, DFT calculations were carried out on a simplified model of it, [{Mg[(HNCH)$_2$CH]}$_2$] **7**, and its THF adduct, [{Mg[(HNCH)$_2$CH](THF)}$_2$] **8**, using the B3LYP method, and appropriate basis sets (see the Supporting Information for full details). The optimized geometries of the two compounds are similar to those of **2** and **3**, albeit with Mg heterocycles that are closer to being planar, a consequence of the minimal steric bulk of the model β-diketiminate ligands.[19] In both **7** and **8**, the HOMO largely corresponds to a high-s-character (NBO analysis for **7**: 92.0 % s, 7.5 % p character; **8**: 92.2 % s, 7.3 % p character), single covalent Mg–Mg interaction with a bond order close to unity (Wiberg bond indices for **7**: 0.97; **8**: 0.99). In addition, their β-diketiminate–Mg interactions are predominantly ionic (natural charges for **7**: Mg +0.87 mean, N −1.01 mean; **8**: Mg +0.91 mean, N −0.99 mean) which is indicative of them possessing anion-stabilized Mg_2^{2+} cores. A similar view has previously been established for models of **1** and other Mg–Mg bonded species.[8–10] In contrast to the model of **1**, [{Mg{[(C$_6$H$_3$Me$_2$-2,6)N]$_2$CNMe$_2$}}$_2$], the LUMO and LUMO+1 of which correspond to Mg–Mg π-bonding orbitals, the low-lying unoccupied orbitals of **7** and **8** are ligand-based. It is of note that the HOMO–LUMO gaps of the model compounds (**7**: 3.87 eV, 89.5 kcal mol^{-1}; **8**: 3.02 eV, 69.7 kcal mol^{-1}) are less than that of [{Mg{[(C$_6$H$_3$Me$_2$-2,6)N]$_2$CNMe$_2$}}$_2$] (4.02 eV, 93.0 kcal mol^{-1}), which might explain why **2** and **3** are colored, while **1** is colorless.

The most obvious difference between the experimentally observed complexes and their calculated models is the much smaller change in Mg–Mg bond length upon THF coordination for the model pair, **7** and **8** (difference between 2.865 and 2.945 Å, respectively = 0.08 Å), as compared with the experimental pair, **2** and **3** (difference = 0.21 Å). This could be due to increased steric interactions between the monomeric units of **3**, as compared with those of **8**. If this is the case, the elongation of the Mg–Mg bond of **2** upon THF coordination would still have to be a relatively low-energy process. Saying this, the calculated metal–metal bond dissociation energy for the model, **7**, is not insignificant at 45.4 kcal mol^{-1}, though this is considerably lower than the value of 65.2 kcal mol^{-1} calculated for its zinc(I) analogue, [{Zn[(HNCH)$_2$CH]}$_2$].[20] In order to quantify the energy required to elongate the metal–metal bond of **7**, a partial potential energy curve for the compound (as a function of Mg–Mg separation) was calculated. Figure 2 shows this to be shallow about the equilibrium bond distance, so that a 0.20 Å increase in the metal–metal bond increases the energy of the system by only 1.2 kcal mol^{-1} (an 0.35 Å elongation requires 3.5 kcal mol^{-1}).

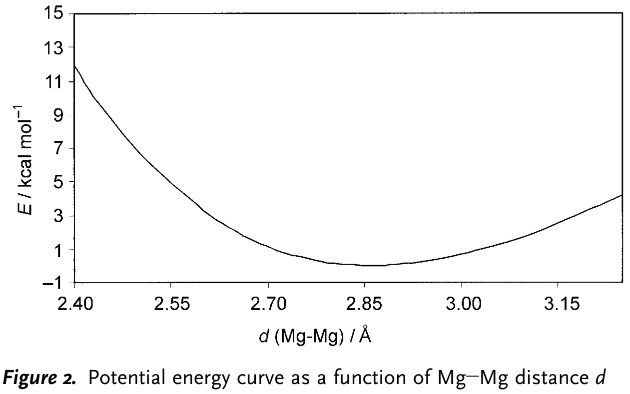
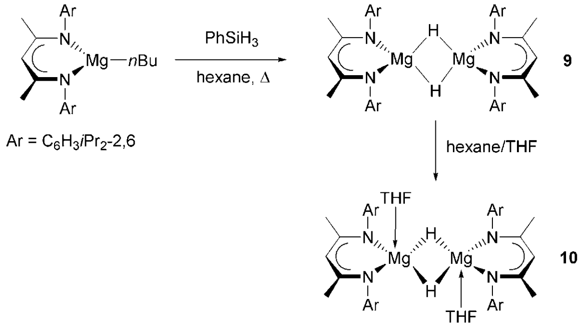


Figure 2. Potential energy curve as a function of Mg–Mg distance *d* for **7**.

In order to confirm the absence of bridging hydride ligands in **3**, and for purposes of comparison, efforts were made to prepare the magnesium(II) hydride analogue of this compound. This was eventually achieved using a synthetic methodology similar to that developed by Harder et al. for the preparation of [{Ca(nacnac)(THF)(μ-H)}$_2$].[21] That is, the uncoordinated, colorless magnesium hydride complex **9** was prepared in moderate yield by reaction of a magnesium alkyl precursor[22] with PhSiH$_3$, according to Scheme 2. Treatment of this with an excess of THF then led to colorless **10** in good yield. Attempts to form crystalline dioxane, DMAP, and 4-*tert*-butylpyridine complexes of **9** were not so far successful. Although the THF ligand appears to be more strongly bound in **10** than in **3**, dissolution of **10** in toluene and subsequent removal of volatiles in vacuo did lead to the regeneration of **9**. The NMR spectroscopic patterns for **9** and **10** are similar to those of **2** and **3**, with the exception of hydride resonances being present in the ^{1}H NMR spectra of the former pair (**9**: $\delta = 4.03$ ppm (sharp); **10**: $\delta = 4.21$ ppm (broad)).



Scheme 2. The preparation of the magnesium(II) hydride complexes **9** and **10**.

The molecular structures of **9** and **10** are depicted in Figures 3 and 4 and represent the first examples for neutral compounds of the type [{L$_n$Mg(μ-H)}$_2$] ($n = 1$ or 2).[23,24] The symmetrically bridging hydride ligands of both structures were located from difference maps and their positional parameters freely refined. As we have previously predicted,[9] the magnesium heterocycles of **9** are close to co-planar with each other, which contrasts to the nearly orthogonal heterocycles in **2** (and **1**). The Mg···Mg separation in **9** is slightly larger (2.890(2) Å) than that in **2** (2.8457(8) Å), but significantly greater than that calculated (2.795 Å, B3LYP; Wiberg bond index: 0.34) for the sterically unencumbered model system, [{Mg[(HNCH)$_2$CH](μ-H)}$_2$], in which the magnesium heterocycles are also close to co-planar. Comparisons of the structures of **3** and **10** show that they have similar molecular geometries, though the Mg–Mg separation is slightly smaller in the latter. Similarly, the Mg–O/N distances in the magnesium(II) hydride complex are significantly less than those of **3**, which might be expected considering the lower metal oxidation state of that compound.

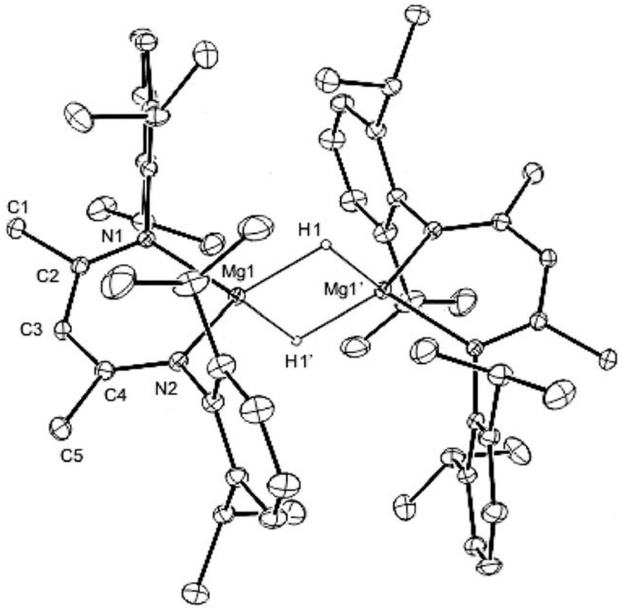


Figure 3. Molecular structure of $[\{\mathrm{Mg(nacnac)}(\mu\text{-H})\}_2]$ (**9**) (25% ellipsoids; non-hydride H atoms omitted for clarity). Relevant distances [Å] and angles [°]. Mg1···Mg1′ 2.890(2), Mg1–N1 2.064(2), Mg1–N2 2.065(2), Mg1–H1 1.95(3), Mg1′–H1 1.97(3); N1-Mg1-N2 93.14(9), Mg1-H1-Mg1′ 95(1). Symmetry operation: ′ 1−*x*, −*y*, −*z*

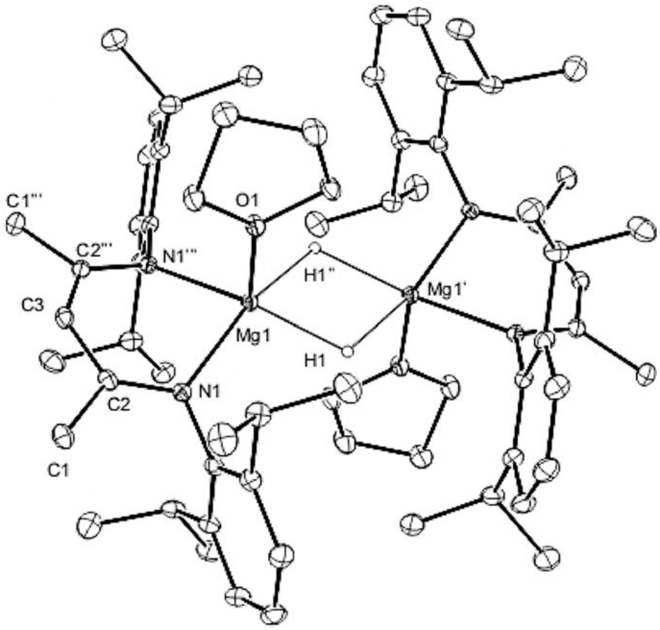


Figure 4. Molecular structure of $[\{\mathrm{Mg(nacnac)(THF)}(\mu\text{-H})\}_2]$ (**10**) (25% ellipsoids; non-hydride H atoms omitted for clarity). Relevant distances [Å] and angles [°]. Mg1···Mg1′ 3.0332(18), Mg1–N1 2.1432(14), Mg1–O1 2.0996(16), Mg1–H1 1.947(19), N1-Mg1-N1′′′ 93.14(9), Mg1-H1-Mg1′ 102(1). Symmetry operations: ′ −*x*, −*y*, −*z*; ″ −*x*+1, −*y*, −*z*; ′′′ x, −*y*, *z*.

In conclusion, a series of remarkably stable Lewis base adducts of a dimeric magnesium(I) complex have been prepared and shown to possess markedly larger Mg–Mg separations than the uncoordinated precursor molecule. Theoretical studies have been carried out which indicate that these elongations may arise from a combination of steric buttressing between the monomeric fragments of the adducts and from shallow potential energy curves for their Mg–Mg bonds. The absence of hydride ligands in one complex has been confirmed by the preparation of its magnesium(II) hydride analogue. We are currently investigating the ability of $[\{\mathrm{Mg(nacnac)}\}_2]$ (**2**) to coordinate functionalized unsaturated substrates, prior to their reduction. We will report on this in a future publication.

Experimental Section

Full synthetic, spectroscopic and crystallographic details for **3**–**6**, **9** and **10**, crystallographic details for a polymorph of **2**, and full details and references for the DFT calculations on **7**, **8** and $[\{\mathrm{Mg}[(\mathrm{HNCH})_2\mathrm{CH}](\mu\text{-H})\}_2]$ can be found in the Supporting Information.

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Keywords: low oxidation states · magnesium · metal hydrides · metal–metal bonding · structure elucidation

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Information). Its Mg–Mg distance was measured at 2.8624(15) Å.

[15] Despite considerable efforts to exclude moisture from the reactions that gave complexes **3**–**6**, each co-crystallized from the reaction mixture with small amounts (ca. 5–9%) of the corresponding hydrolysis product, [{Mg(nacnac)(L)(μ-OH)}$_2$] (L = THF, dioxane, DMAP, or 4-*t*BuPy). It is believed that the presence of these co-crystallized contaminants has a significant, though not substantial, effect on the Mg–Mg bond lengths observed for **3**–**6**. See the Supporting Information for a full discussion on this point.

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