

# Preference for bridging versus terminal ligands in magnesium dimers

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**Abstract** Magnesium dimers play important roles in inorganic and organometallic chemistry. This study evaluates the inherent bridging ability of a range of different ligands in magnesium dimers. In the first part, the Cambridge Structural Database is interrogated to establish the frequency of different types of ligands found in bridging versus terminal positions in two key structural motifs: one in which there are two bridging ligands (the  $D_{2h}$  “ $Mg_2(\mu-X_2)$ ” structure); the other in which there are three bridging ligands (the  $C_{3v}$  “ $Mg_2(\mu-X_3)$ ” structure). The most striking finding from the database search is the overwhelming preference for magnesium dimers possessing two bridging ligands. The most common bridging ligands are C-, N-, and O-based. In the second part, DFT calculations (at the B3LYP/6-311+G(d) level of theory) are carried out to examine a wider range of structural types for dimers consisting of the stoichiometries  $Mg_2Cl_3R$  and  $Mg_2Cl_2R_2$ , where  $R = CH_3, SiH_3, NH_2, PH_2, OH, SH, CH_2CH_3, CH=CH_2, C\equiv CH, Ph, OAc, F$  and  $Br$ . Consistent with the database search, the most stable magnesium dimers are those that contain two bridging ligands. Furthermore, it was demonstrated that the electronic effect of the bridging ligands is important in influencing the stability of the

magnesium dimers. The preference for a bridging ligand, which reflects its ability to stabilize a magnesium dimer, follows the order:  $OH > NH_2 > C\equiv CH > SH > Ph > Br > PH_2 = CH=CH_2 > CH_2CH_3 > CH_3 > SiH_3$ . Finally, the role that the ether solvent  $Me_2O$  has on the stability of isomeric  $Mg_2Cl_2Me_2$  dimers was studied. It was found that the first solvent molecule stabilizes the dimers, while the second solvent molecule can either have a stabilizing or destabilizing effect, depending on the isomer structure.

**Keywords** Bridging ability of ligands · Dimers · Inorganic and organometallic chemistry · Magnesium · X-ray crystallography · DFT calculations

## Introduction

Ionic magnesium (II) aggregates (clusters) play important roles in inorganic and organometallic chemistry and the degree of aggregation can depend on the concentration, the nature of the ligand(s) and the solvent. Since there are numerous examples of magnesium dimers in both the condensed and gas phases, they provide an important foundation to attempt to establish key structural motifs in clusters [1–10]. Specifically, data from X-ray crystal structures and theoretical calculations provide a basis to address fundamental questions such as: (i) What is the preferred number of ligands to bridge between the two magnesium centers? (ii) What role do ligands play (bridging versus terminal) for dimers that have more than one type of ligand present?

With regard to the first question, a large number of magnesium dimers have been found to contain only two bridging ligands. For example, gas phase electron diffraction data is consistent with the chloride and bromide of

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$\text{Mg}_2\text{X}_4$  having the  $D_{2h}$  “ $\text{Mg}_2(\mu\text{-X}_2)$ ” structure, (structure 1 of Scheme 1), rather than the  $C_{3v}$  structure “ $\text{Mg}_2(\mu\text{-X}_3)$ ” 2 [11, 12]. Previous theoretical studies, which considered a much wider range of potential structures for magnesium halide dimers, also found that the  $D_{2h}$  structure 1 is more stable than the  $C_{3v}$  structure 2 [13, 14]. There are, however, several examples of the “ $\text{Mg}_2(\mu\text{-X}_3)$ ” bridging structure, including: the X-ray structure of  $(\text{Me}_3\text{Si})_3\text{CMg}(\mu\text{-Br})_3\text{Mg}(\text{THF})_3$ , 3 [15]; the proposed “ $\text{Mg}_2(\mu\text{-Cl}_3)$ ” core structure 4 for methylmagnesium chloride in THF solution [16]; and the “ $\text{Mg}_2(\mu\text{-X}_3)$ ” cations which have been characterized in a number of X-ray structures, 5 [4, 17]. In addition, theoretical studies on the mechanisms of Grignard reactions suggest that  $\text{Mg}_2(\mu\text{-X}_3)$  bridging structures may play roles as transient intermediates [18].

With regard to the second question, the well-known Schlenk equilibrium of Grignard reagents provides a potent example of structural isomers associated with dimers possessing two different types of ligands [19]. For example, a number of different isomers have been proposed for alkyl magnesium chlorides, including structures 6–9 (Scheme 2) [20–23]. In one of the first theoretical studies on dimers associated with the Schlenk equilibrium, Axten et al. found three stable doubly-bridged dimers with the following stability order:  $6 > 7 > 8$  at both the HF/6-31G\* and MP2/6-31G\* levels of theory [20]. Subsequent density functional theory (DFT) calculations at the B3LYP/6-31G\* level by Yamazaki and Yamabe found that stability order was maintained even when the dimers were solvated by 2 or 4 dimethyl ether solvent molecules [21]. More recently, Mori and Kato have shown that solvation of dimers leads to a similar stability order:  $6 > 7 > 9$  [22], but structure 9 is now stabilized by dimethylether solvent.

A consideration of the ability of ligands to bridge between two magnesium centers in magnesium dimers can clearly be extended beyond alkyl magnesium chlorides. Indeed, in an early review of the X-ray crystallography literature, Markies et al. noted that “the ability of X to act as a bridging group is of importance (alkoxide, amide > halogen > alkyl, aryl group)” [1]. This empirical observation has proven to be remarkably robust and has only been challenged by a few special X-ray crystal structures. For

example, Yang et al. found halides as bridging ligands in halo-magnesium amides, which are stabilized by bulky amides [24]. As far as we are aware, apart from the studies described above, as well as other theoretical studies on isolated systems [25], there has been no systematic study that has addressed the fundamental issue of how different types of ligands influence the bridging arrangements and selectivity (i.e. terminal versus bridging) between two magnesium centers in dimers. In this study we: (i) perform a new evaluation of all known X-ray crystallography structures of inorganic and organometallic magnesium dimers; (ii) use DFT calculations to examine the relative stabilities of “bare” structural isomers of the neutral dimers  $\text{Mg}_2\text{Cl}_3\text{X}$  (10–15) and  $\text{Mg}_2\text{Cl}_2\text{X}_2$  (16–23) shown in Scheme 3; (iii) use DFT calculations to examine solvation of  $\text{Mg}_2\text{Cl}_2\text{Me}_2$  isomers (16–23) by one and two dimethyl ether molecules.

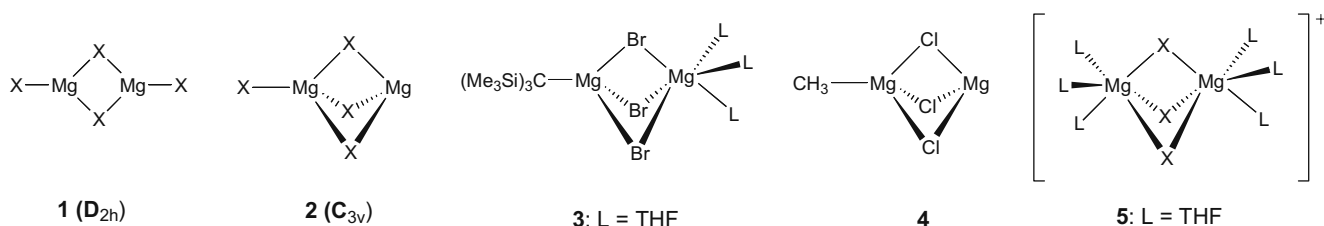
## Theoretical approach

### Evaluation of the X-ray crystallography literature

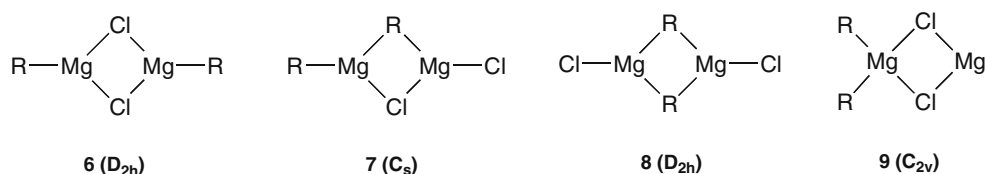
The Cambridge Structural Database (CSD) [26] and the Inorganic Crystal Structure Database (ICSD) [27] have been examined to evaluate the types of bridging and terminal groups involved in all known magnesium dimer structures. In both databases we search for known discrete molecular Mg dimer structures of the type  $\text{Mg}_2\text{X}_x\text{R}_y$  where  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$ , and R is any ligand with  $x + y = 4$ . In the search we ensured that the structures are not part of a network and we allowed for cyclic ligands. Overall there are 74 known Mg dimer structures, all of which are found from the CSD. These structures are categorized into two main types, based on whether there are two or three bridging ligands, and they are further divided into ligand types.

### DFT calculations

The Gaussian 03 suite of programs [28] was used to examine the structures and energies of a series of  $\text{Mg}_2\text{Cl}_3\text{R}$



**Scheme 1** Examples of magnesium dimer structures

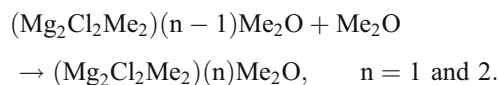
**Scheme 2** Examples of isomeric Grignard structures

and  $Mg_2Cl_2R_2$  dimers, where  $R=CH_3$ ,  $SiH_3$ ,  $NH_2$ ,  $PH_2$ ,  $OH$ ,  $SH$ ,  $CH_2CH_3$ ,  $CH=CH_2$ ,  $C\equiv CH$ ,  $Ph$ ,  $OAc$ ,  $F$  and  $Br$ . Full geometry optimizations and frequency calculations were carried out for each structure at the B3LYP level of theory using the 6-311+G(d) basis set with ultrafine grid. In addition, to provide a better estimate of relative energies, single point energies were calculated at the MP2(FC)/6-311+G(2d,p) level of theory. Comparisons of the relative energies of isomers calculated using these two levels of theory are given in Supplementary Tables S4 and S5. All of the resultant structures from the DFT calculations are collated in the Supplementary material section.

#### Calculation of $\Delta G$ of solvation of $Mg_2Cl_2Me_2$ dimers

We have used the approach of Yamazaki and Yamabe to examine the solvation energies of isomeric  $Mg_2Cl_2Me_2$  dimers solvated by one and two  $Me_2O$  solvent molecules [21]. Briefly, by using  $G = \epsilon_0 + G_{corr}$  from the output of Gaussian calculations, which are the sum of electronic energy and thermal free energies contributions, the  $\Delta G$  of

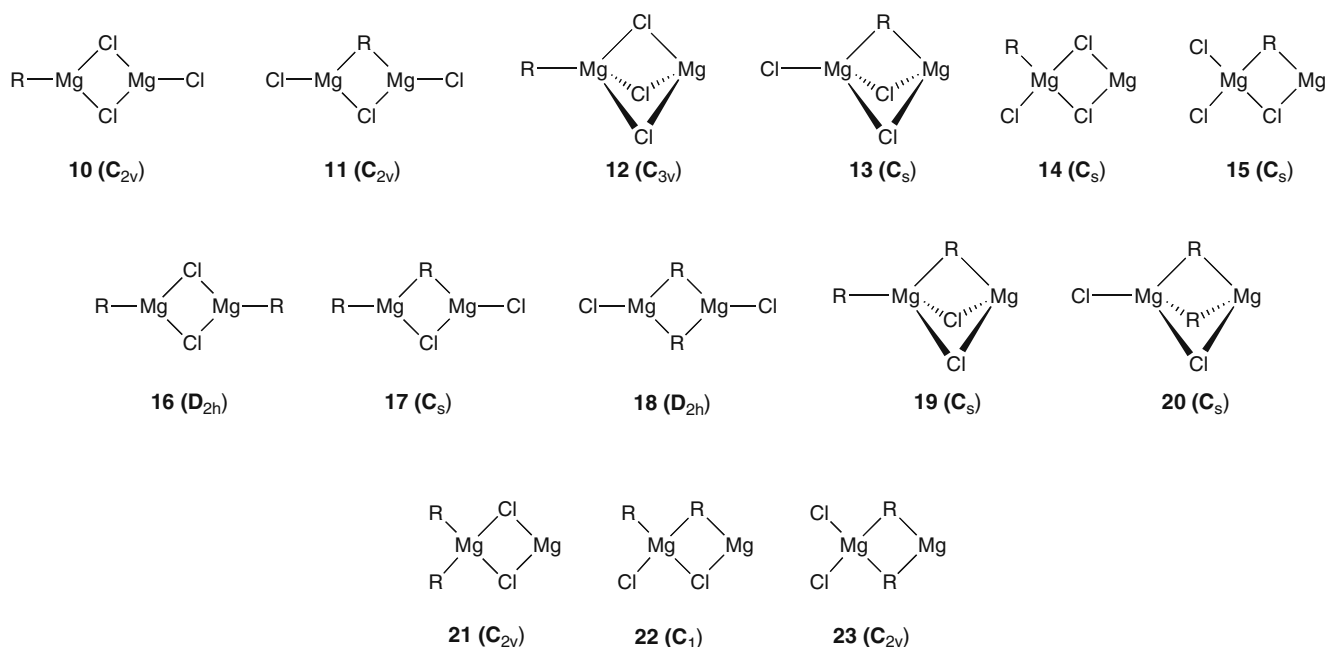
solvation was calculated at the B3LYP/6-311+G(d) level of theory via the equation:

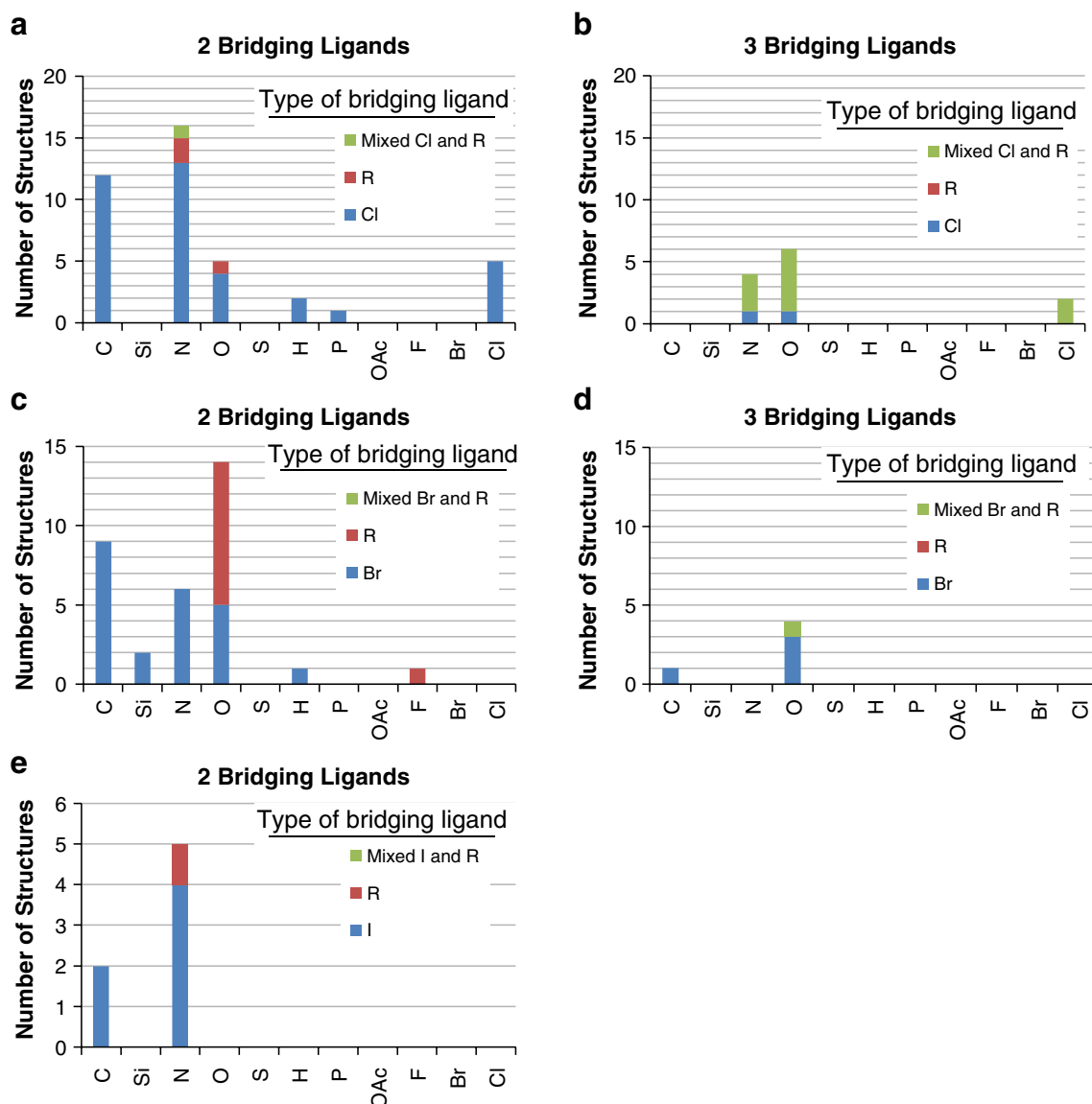


## Results

Analysis of bridging ligands in magnesium dimers from known X-ray crystallography structures

Figure 1 summarizes the structures found in the database search that contain either 2 or 3 bridging ligands for  $Mg_2Cl_xR_y$ ,  $Mg_2Br_xR_y$  and  $Mg_2I_xR_y$ . The structures are further categorized into whether the bridging ligand is halide, ligand R, or mixed halide and R. There is only one structure when  $X = F$  (possessing two F as the bridging ligands and terminal ligand that is bound by nitrogen) and therefore it is not shown in Fig. 1.

**Scheme 3** Isomeric  $Mg_2Cl_3R$  and  $Mg_2Cl_2R_2$  structures considered in this work



**Fig. 1** Column representation for magnesium dimer structures  $Mg_2X_xR_y$ . The different structures are categorized into 2 bridging ligands (**a**, **c** and **e**) or 3 bridging ligands (**b**, **d**), and further divided into the type of atom that is bound to the ligand and also the type of bridging ligand. (**a**) and (**b**) are for  $X = Cl$ ; (**c**) and (**d**) are for  $X = Br$ ;

(**e**) is for  $X = I$ . No structures were found with 3 bridging ligands when  $X = I$ . The most notable observation is that there are more structures containing 2 bridging ligands and that those structures found have Cl, N, or O as the bound atom

An examination of Fig. 1 reveals that there are more dimer structures containing the “ $Mg_2(\mu-X_2)$ ” motif than those possessing the “ $Mg_2(\mu-X_3)$ ” motif. In contrast to the other series of Mg dimer structures, very few structures are found with the type  $Mg_2I_xR_y$ . In fact when  $X = I$ , no structures containing 3 bridging ligands were found. The number of Mg dimers containing 2 bridging ligands found for  $X = Cl$  and Br is roughly the same. More interestingly, most structures found are those that have ligands with Cl, N or O as the atom that bridges the Mg centres, even though most O-based ligands are solvent molecules.

DFT calculations on “bare”  $Mg_2Cl_3R$  and  $Mg_2Cl_2R_2$  dimers

We next used DFT calculations to examine the structures and stabilities of the  $Mg_2Cl_3R$  and  $Mg_2Cl_2R_2$  dimers shown in Scheme 3 for the cases where  $R = CH_3, SiH_3, NH_2, PH_2, OH, SH, CH_2CH_3, CH=CH_2, C\equiv CH, Ph, OAc, F$  and Br. All calculations involved full structural optimizations at the B3LYP/6-311+G(d) level of theory. The results of these calculations are summarized in Tables 1 ( $Mg_2Cl_3R$ ) and 2 ( $Mg_2Cl_2R_2$ ), as a function of the symmetry of the parent structures,  $Mg_2Cl_3R$  and  $Mg_2Cl_2R_2$ , respectively, while

**Table 1** Summary of the calculated  $\text{Mg}_2\text{Cl}_3\text{R}$  structures for different R ligands. All energy is relative to the structure 10 ( $\text{C}_{2v}$ ). DE, eV ( $\text{kcal mol}^{-1}$ )

R	2 bridging ligands		3 bridging ligands	
	11 ( $\text{C}_{2v}$ )	12 ( $\text{C}_{3v}$ )	13 ( $\text{C}_s$ )	
$\text{CH}_3$	0.33 (7.5)	0.65 (15.1)		<b>(10)</b>
$\text{SiH}_3$	0.64 (14.8) <sup>a</sup>	0.63 (14.4)		<b>(10)</b>
$\text{NH}_2$	<b>-0.59 (-13.7)</b>	0.69 (16.0)		<b>-0.06 (-1.5)</b>
$\text{PH}_2$	0.11 (2.6)	0.63 (14.6)	0.45 (10.3)	
OH	<b>-0.79 (-18.3)<sup>b</sup></b>	0.65 (15.0)		<b>(11)</b>
SH	<b>-0.03 (-0.6)</b>	0.62 (14.4)	0.38 (8.7)	
$\text{CH}_2\text{CH}_3$	0.31 (7.2)	0.65 (15.0)		<b>(10)</b>
$\text{CH}=\text{CH}_2$	0.11 (2.6)	0.65 (15.1) <sup>c</sup>	0.50 (11.5)	
$\text{C}\equiv\text{CH}$	<b>-0.10 (-2.4)<sup>d</sup></b>	0.62 (14.2)	0.47 (10.8)	
Ph	0.05 (1.2)	0.64 (14.8)	0.45 (10.3)	
OAc	0.12 (2.7) <sup>e</sup>	0.77 (17.7)	0.10 (2.3) <sup>f</sup>	
F	N/A	0.60 (13.7)	0.27 (6.2)	
Br	0.09 (2.0)	0.59 (13.6)	0.61 (14.2)	
Cl	-	0.67 (15.5) <sup>g</sup>		

<sup>a</sup> Unusual agostic interaction<sup>b</sup> Distorted structure observed<sup>c</sup> Distorted structure observed<sup>d</sup> Distorted structure observed<sup>e</sup> 2 isomers were found.; the *symmetric* structure is lower in energy (0.12 eV) compared to the *asymmetric* structure (0.14 eV)<sup>f</sup> Asymmetrical interaction of OAc ligand with Mg<sup>g</sup> From reference 3(b)

individual structures are given in the supplementary material section. In Tables 1 and 2 the energy values displayed are relative to the most stable respective structures 10 and 16. In all cases, the dimers 14 and 15 for  $\text{Mg}_2\text{Cl}_3\text{R}$  and structures 21 - 23 for  $\text{Mg}_2\text{Cl}_2\text{R}_2$ , in which all structures contain a two-bonded Mg center, are unstable and rearrange to other structures. This result is consistent with previous calculations on  $\text{Mg}_2\text{Cl}_4$  dimer [14]. The following sections highlight a number of interesting trends in the data.

#### (i) Mg dimers prefer to have two bridging ligands.

For all ligand studied, the preferred  $\text{Mg}_2\text{Cl}_3\text{R}$  and  $\text{Mg}_2\text{Cl}_2\text{R}_2$  dimers are those that contain only two bridges, i.e., structures 10 and 11 for  $\text{Mg}_2\text{Cl}_3\text{R}$  and structures 16 - 18 for  $\text{Mg}_2\text{Cl}_2\text{R}_2$ . While all of the  $\text{Mg}_2\text{Cl}_3\text{R}$  dimers with structure 12 (with three bridging chlorides) are stable, several of the dimers of structure 13 underwent rearrangement to the most stable isomer (structure 10 when  $\text{R} = \text{CH}_3$ ,  $\text{SiH}_3$  and  $\text{CH}_3\text{CH}_2$  or structure 11 when  $\text{R} = \text{OH}$ ). In contrast, fewer  $\text{Mg}_2\text{Cl}_2\text{R}_2$  dimers with three bridging ligands are stable compare to  $\text{Mg}_2\text{Cl}_3\text{R}$ . This result is

consistent with the X-ray crystallography database survey described above.

#### (ii) The terminal ligand has little influence on the stability of the $\text{C}_{3v}$ Mg dimer.

The energy of structure 12, the  $\text{C}_{3v}$  structure with R as the terminal ligand is almost invariant (ranging from +0.59 eV (+13.6  $\text{kcal mol}^{-1}$ ) to +0.77 eV (+17.7  $\text{kcal mol}^{-1}$ ), Table 1) relative to the most stable structure 10 for all R. This suggests that the terminal ligand has little influence on the stability of the  $\text{C}_{3v}$  dimer structure.

#### (iii) Stability of Mg dimers is greatly influenced by the electronic effect of the bridging ligands.

For both  $\text{Mg}_2\text{Cl}_3\text{R}$  and  $\text{Mg}_2\text{Cl}_2\text{R}_2$  dimers with 2 bridging ligands, generally the most favorable structures are structures 10 and 16 respectively, in which chlorides are the two bridging ligands. The exceptions to this are for electron rich ligands ( $\text{R} = \text{OH}$ ,  $\text{SH}$ ,  $\text{NH}$ ,  $\text{C}\equiv\text{CH}$ ), which are the preferred bridging ligand. Thus, structures 11 and 17 (and 18) are more stable structures in these cases.

A further examination of the data shown in Tables 1 and 2 suggests that the bridging ligand stabilizes the dimer on going across the periodic table. Thus, the dimers follow the stability order  $\text{CH}_3 < \text{NH}_2 < \text{OH}$ . All dimers with bridging fluoride ligands failed to optimize, possibly due to the small size of F. The bridging ligand destabilizes the dimer on going down the periodic table (i.e.,  $\text{CH}_3 \rightarrow \text{SiH}_3$ ,  $\text{NH}_2 \rightarrow \text{PH}_2$ , and  $\text{OH} \rightarrow \text{SH}$ ). For carbon based ligands, hybridization plays an important role in bridging ability. Thus changing the hybridization of the bridging ligand to increase its s character (i.e.  $\text{sp}^3 \rightarrow \text{sp}^2 \rightarrow \text{sp}$  for  $\text{CH}_2\text{CH}_3 \rightarrow \text{CH}=\text{CH}_2 \rightarrow \text{C}\equiv\text{CH}$ ) helps decrease the energies of 11 relative to 10 (Table 1) and 17 and 18 relative to 16 (Table 2). This is further demonstrated when  $\text{R} = \text{C}\equiv\text{CH}$  that 11 and 18 become the thermodynamically preferred structures. An examination of the structures of with carbon bridging ligands reveals that the  $\text{CH}_2\text{CH}_3$  and  $\text{CH}=\text{CH}_2$  ligands bridge in a symmetrical fashion but that the acetylide ligand bridges in a non-symmetrical fashion (Supporting Information Fig. S1). This is entirely consistent with known X-ray crystal structures of magnesium dimers with bridging acetylide ligands [24], where the bonding of the acetylide ligand can be described as  $\sigma$  to one Mg center and  $\pi$  to the other Mg center.

For dimers with 3 bridging ligands the effect of the ligand on structures 13, 19 and 20 could not be studied due to instability and rearrangement of these dimers.

#### (iv) Ligand effect on the stability of the dimer is additive

Comparison of the energies of structures 17 and 18 of Table 2 ( $\text{Mg}_2\text{Cl}_2\text{R}_2$ ) reveals that any stabilization or destabilization effect of the ligand is multiplied if a second

**Table 2** Summary of the calculated  $Mg_2Cl_2R_2$  structures for different R ligands. All energy is relative to the structure 16 ( $D_{2h}$ ). DE, eV ( $kcal\ mol^{-1}$ )

R	2 bridging ligands		3 bridging ligands	
	17 ( $C_s$ )	18 ( $D_{2h}$ )	19 ( $C_s$ )	20 ( $C_s$ )
CH <sub>3</sub>	0.37 (8.5)	0.60 (13.9)	<b>(16)</b>	<b>(17)</b>
SiH <sub>3</sub>	0.61 (14.0)	0.90 (20.7) <sup>a</sup>	<b>(16)</b>	<b>(17)</b>
NH <sub>2</sub>	<b>-0.53 (-12.3)</b>	<b>-1.01 (-23.2)</b>	<b>(17)</b>	<b>(18)</b>
PH <sub>2</sub>	0.13 (2.9) <sup>b</sup>	0.22 (5.1)	0.49 (11.3)	0.38 (8.8)
OH	<b>-0.77 (-17.8)</b>	<b>-1.50 (-34.6)</b>	<b>(17)</b>	<b>(18)</b>
SH	<b>-0.03 (-0.6)<sup>c</sup></b>	<b>0.06 (-1.4)<sup>d</sup></b>	0.42 (9.6)	0.20 (4.7)
CH <sub>2</sub> CH <sub>3</sub>	0.36 (8.3)	0.60 (13.9)	<b>(16)</b>	<b>(17)</b>
CH=CH <sub>2</sub>	0.17 (3.9)	0.29 (6.8) <sup>e</sup>	0.59 (13.6)	0.56 (12.9)
C≡CH	<b>-0.07 (-1.6)</b>	<b>-0.16 (-3.6)</b>	0.52 (12.1)	0.39 (9.1)
Ph	0.08 (1.9)	0.24 (5.5)	0.50 (11.5)	0.52 (12.0)
OAc	0.13 (3.0) <sup>f</sup>	0.39 (8.9)	0.30 (7.0)	<b>-0.19 (-4.5)</b>
F	N/A <sup>g</sup>	N/A <sup>g</sup>	0.28 (6.4)	N/A <sup>h</sup>
Br	0.08 (1.8)	0.17 (3.9)	0.61 (14.0)	0.65 (14.9)

<sup>a</sup> Unusual agostic interaction

<sup>b</sup> Distorted structure observed

<sup>c</sup> Asymmetrical structure observed

<sup>d</sup> 2 isomers were found depending on the position of the H of SH. The *cis*- isomer has a lower relative energy (-0.06 eV) compared to the *trans*- isomer (-0.01 eV)

<sup>e</sup> Asymmetrical structure observed

<sup>f</sup> Asymmetrical structure observed

<sup>g</sup> Structures failed to optimize possibly due to the small size of the fluoride ligand

<sup>h</sup> Structure failed to optimize, but converging to structure **18** ( $D_{2h}$ )

similar ligand is added. Some exceptions are for R = Ph and OAc, whereby the bonding orientation of the bridging ligand in structures 17 and 18 is different.

#### DFT calculations on “solvated” $Mg_2Cl_2Me_2$ dimers

Although it would be of significant interest to examine the role of solvation of all the possible dimer structures shown in Scheme 2 for all R groups, such a task is beyond the scope of the current work. Rather, given the continued interest in the structures of Grignard reagents, we have focused on the solvation of all  $Mg_2Cl_2Me_2$  dimers 16 – 23 by one and two dimethyl ether solvent molecules. We considered solvation at each magnesium site for the dimers 16 – 23, with the dimethyl ether acting as either a terminal solvent molecule or a bridging solvent molecule. This gave rise to a total of 53 input geometries for the DFT calculations. The optimized structures of these studies are summarized in the supplementary material section (Supplementary Fig. S1), and also shown in Scheme 4. The relative energy of Mg dimers are shown in eV ( $kcal\ mol^{-1}$ ) at the MP2(FC)/6-311+G(2d,p) level of theory while the  $\Delta G$  for solvation are shown in parenthesis (at the B3LYP/6-311+G(d) level of theory).

An examination of the data on the bare and solvated  $Mg_2Cl_2Me_2$  dimers reveals the following:

(i) Stability orders for stable dimer structures 16, 17 and 18:

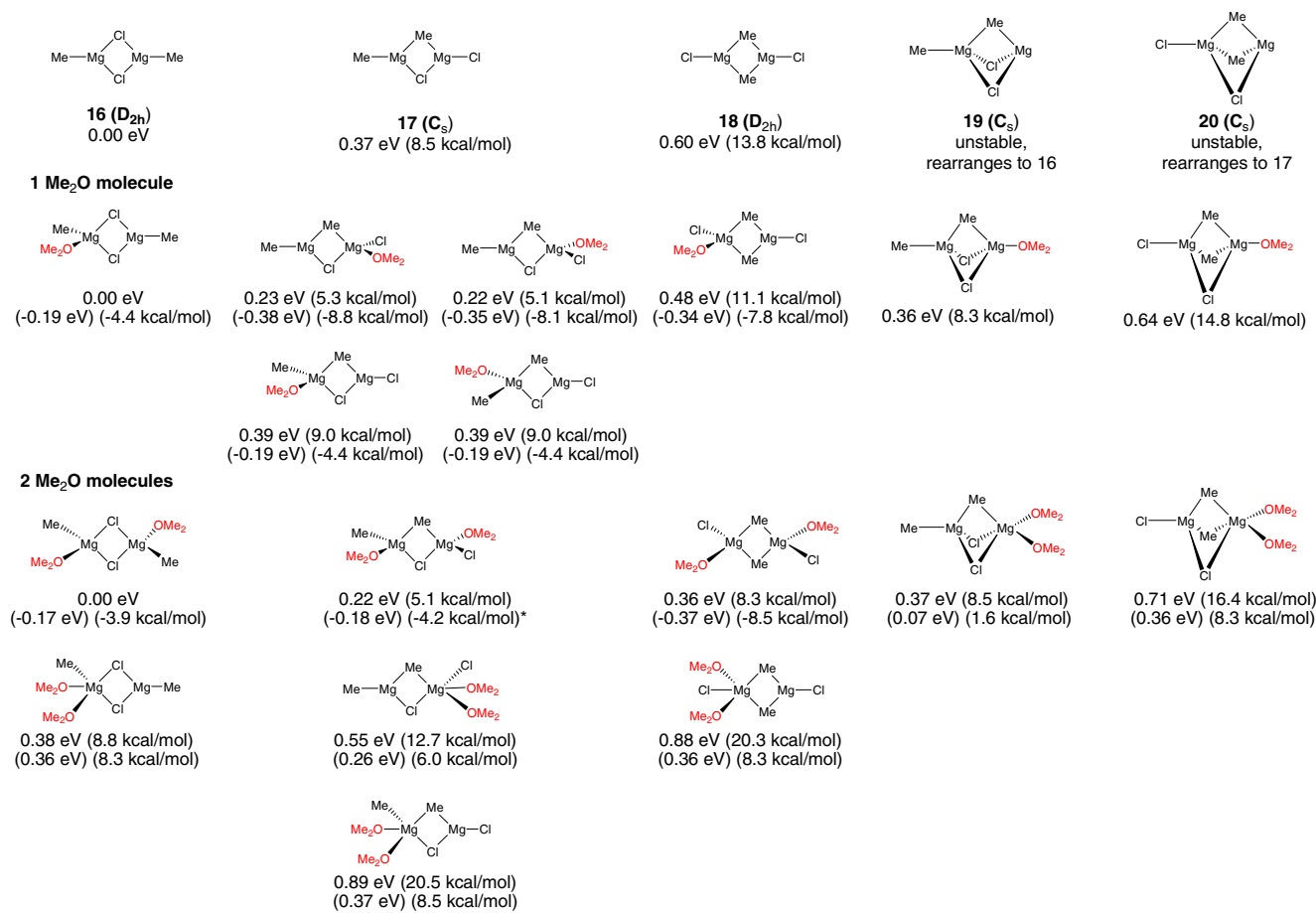
Both bare and solvated dimers follow the same stability order: 16>17>18. This is consistent with data from a previous study [21]. Solvation does, however, have a minor effect on the energy differences between these dimers. It decreases the energy gap between the pairs of isomers “16 and 17” and “17 and 18”.

(ii) Solvation of dimers 19 – 23

As noted in section (2) above, isomers 19 – 23 are all unstable for bare  $Mg_2Cl_2Me_2$  dimers. We have found that solvation can have a profound effect on stabilizing some of these isomers. While solvation by one or two dimethylether molecules fails to stabilize isomers 21, 22 and 23, structures 19 and 20 are stabilized by the addition of one solvent molecule. (Scheme 4).

(iii) Favored site(s) of solvation for terminal solvent molecules- the first solvent molecule

The only dimer with two bridging ligands that exhibits a difference in solvation for the two magnesium sites is



**Scheme 4** Results of DFT calculations examining the solvation of isomeric  $Mg_2Cl_3Me$  and  $Mg_2Cl_2Me_2$  Grignard structures by one and two  $Me_2O$  solvent molecules. Solvation energies are given in parentheses

17. In this case the favored solvation site is the Mg center with the terminal Cl group. For dimers with three bridging ligands (19 and 20), the favored solvation site is the three coordinate Mg center, which results in both Mg centers adopting a tetrahedral arrangement.

(iv) Favored site(s) of solvation for terminal solvent molecules- the second solvent molecule

The dimers 16 – 28 with two bridging ligands prefer the second dimethylether molecule to solvate the second magnesium site, resulting in both Mg sites being occupied by one solvent molecule and thus adopting a tetrahedral geometry. The three dimensional arrangement of the solvent molecules is important for these dimers, with the preferred arrangement between the two solvent molecules being *trans*. For dimers with three bridging ligands (19 and 20), both dimethylether molecules solvate the same Mg site, giving a four coordinate Mg site with a terminal Cl or  $CH_3$  ligand and a five coordinate site with two terminal solvent molecules.

(v) Solvation can destabilize!

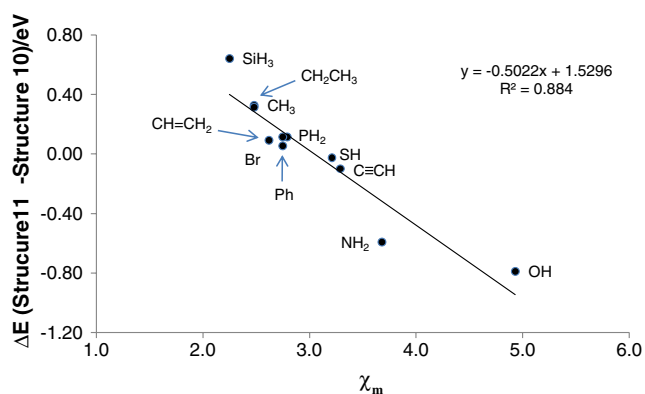
All Mg dimers are stabilized when solvated by the first  $Me_2O$  solvent molecule, with some dimers being stabilized by as much as 0.38 eV (8.8 kcal mol<sup>-1</sup>) (Scheme 4). In addition, Mg dimers with 3 bridging ligands are found to be stable only when there is at least one  $Me_2O$  molecule (structure 19 and 20). Solvation by a second  $Me_2O$  molecule, on the other hand, shows mixed results. The preferred coordination site for the second  $Me_2O$  molecule is one that results in the formation of two tetrahedral Mg centers. However, a destabilizing effect can be observed if one of the resultant Mg centers is coordinated to five ligands.

## Discussion

The results of the X-ray crystal structure database and DFT calculations presented in sections (1) - (3) above provide a consistent view of the propensities for groups to act as bridging ligands in magnesium dimers. Our computational studies found that solvent molecules generally stabilize Mg dimers with  $R = CH_3$  (structures 16 - 18 of Scheme 4), even

for those dimers that are not stable in the absence of solvent (structures 19 - 20 of Scheme 4). Dimers containing two-coordinated Mg centers are unstable and do not optimize under DFT calculations.

Consistent with the database search, the computational studies also show that Mg dimers prefer to contain only two bridging ligands. While the type of terminal ligand does not affect the stability of Mg dimer, the type of bridging ligand greatly influences its structural stability. The most effective bridging ligand was found to be for  $R = OH$  and this stability decreases when the ligand is substituted by one that is to the left of the periodic table (dimer stability follows the order  $OH > NH_2 > CH_3$ ) and down the periodic table ( $OH > SH, NH_2 > PH_2, CH_3 > SiH_3$ ). Furthermore, a change in hybridization of the bridging ligand from  $sp^3 \rightarrow sp^2 \rightarrow sp$  (as in the case of  $CH_2CH_3 \rightarrow CH=CH_2 \rightarrow C\equiv CH$ ) stabilizes the Mg dimer. Therefore, it appears that the most stable bridging ligand is the one that is the most electronegative ligand, and thus the stability of the dimer follows the electronegativity of the ligand. When  $\Delta E$  between structures 11 and 10, which is a measure of stability of the dimer solely by the bridging ligands, is plotted against the Mulliken–Jaffé electronegativity scale ( $\chi_m$ ) [29] of the bound atom, an excellent linear correlation is displayed (Fig. 2). Several electronegativity scales are available in the literature that account for different specific effects [30–32]. However, since the Mulliken–Jaffé electronegativity scale describes electronegativity as the average of the electron affinity,  $EA_v$ , and the ionization potential,  $IE_v$ , of the *valence orbital*, thus allowing for slight changes for different functional groups, we find that it is the most consistent electronegative scale for the comprehensive list of ligand studied here (for example, the Allen scale [32] does not take into account the different types of hybridization for alkyl, alkenyl and alkynyl ligands).



**Fig. 2** Plot of calculated  $\Delta E$  (structure 11 – structure 10) against  $\chi_m$ , which denotes the Mulliken – Jaffé electronegativity scale suggesting that the effect of bridging ligand on the stability of the Mg dimer is primarily due to the ionic character of the ligand

Figure 2 also shows that as the bound atom of the ligand becomes more electronegative, the ligand has more ionic character. Therefore, we propose that the stronger ionic character of the bridging ligand, the more effective it can stabilize the dimer. The overall preferred bridging ligands in this study follow the order:  $OH > NH_2 > C\equiv CH > SH > Ph > Br > PH_2 = CH=CH_2 > CH_2CH_3 > CH_3 > SiH_3$ . We note that this order is consistent with, but substantially expands upon that suggested by Markies et al. [1]. The knowledge that bridging ligand ability in Mg dimer follows the Mulliken–Jaffé electronegativity scale is a powerful one, which when combined with other effects (e.g., number of bridging ligands, steric crowding of the structure), should allow for a simple prediction of the molecular properties and stability of Mg dimers.

On a final note, it appears from recent theoretical studies that anionic magnesium dimers may exhibit slightly different structural trends [33–35]. Thus, calculations on the halides  $[Mg_2X_5]^-$  reveal that structure 24 with three bridging halides is more stable than 25 with two bridging ligands [33, 34]. This holds true for the organomagnesate dimer  $[HCCMg_2Cl_4]^-$ , which also prefers three bridging ligands [35]. The limited trends in anionic dimers maybe a result of the preference of each magnesium center to maximize its coordination.

## Conclusions

In the absence of metal-metal bonds, bridging ligands are the “glue” that hold together metal centers in metal clusters. Here we have re-evaluated the ability of ligands to bridge between two magnesium centers by: (i) performing database interrogation within the CSD and the ICSD to examine the number of X-ray crystal structure of dimers with two Mg centers; (ii) carrying out DFT calculations to probe the various effects that influence Mg dimer stability. Both approaches highlight that dimers with two bridging ligands are preferred over those with three bridging ligands. While terminal ligands have little influence on the stability of the magnesium dimers, the electronic effect of the bridging ligand has a significant effect on the stability of the



dimer. The best bridging ligands are those that are the most electronegative, leading to the following bridging ability order:  $\text{OH} > \text{NH}_2 > \text{C}\equiv\text{CH} > \text{SH} > \text{Ph} > \text{Br} > \text{PH}_2 = \text{CH}=\text{CH}_2 > \text{CH}_2\text{CH}_3 > \text{CH}_3 > \text{SiH}_3$ . The effect of solvation of  $\text{Mg}_2\text{Cl}_2\text{Me}_2$  by  $\text{Me}_2\text{O}$  molecules was also studied. The first solvent molecule stabilizes each of the magnesium dimers, while the second solvent molecule can either have a stabilizing influence (when both magnesium centers achieve a coordination number of 4) or a destabilizing effect (when a magnesium center adopts a coordination number  $>4$ ). Further studies are warranted to establish the fundamental bridging orders for other metal centers. It will be interesting to establish whether bridging ligand ability in other metals dimers also follows the Mulliken–Jaffé electronegativity scale.

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