

# Complications in metathesis reactions involving Grignard reagents: Effect of solvent on products obtained from the interaction of PhMgBr with GaCl<sub>3</sub> or InBr<sub>3</sub>

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## Abstract

The important role of supporting solvent in transmetalation reactions involving Grignard reagents is highlighted in the formation and crystallisation of the Group 13 ‘ate’ species, [Mg<sub>3</sub>Br<sub>3</sub>Cl<sub>2</sub>(Et<sub>2</sub>O)<sub>6</sub>][GaPh<sub>2</sub>Br<sub>2</sub>] (1), [Mg<sub>3</sub>Br<sub>5</sub>(Et<sub>2</sub>O)<sub>6</sub>][InPh<sub>2</sub>Br<sub>2</sub>] (2), [MgBr(THF)<sub>5</sub>][GaPh<sub>3</sub>Br] (3), [MgBr(THF)<sub>5</sub>][InPh<sub>3</sub>Br] (4), [Mg(THF)<sub>6</sub>][GaPh<sub>2</sub>Br<sub>2</sub>]<sub>2</sub> (5) obtained by reaction of PhMgBr with gallium and indium halides. The compounds have been characterised by <sup>1</sup>H NMR, elemental analyses, and single-crystal X-ray diffraction.  
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**Keywords:** Grignard reagent; Crystal structure; Indium; Gallium; Group 13 ‘ate’ species

## 1. Introduction

The nucleophilic character of Grignard reagents has allowed their use in a wide variety of reactions, including transmetalation and metathesis reactions. Traditionally, metathesis has been one of the most important synthetic approaches towards organometallic, organoamido and alkoxometallic species, the synthesis of main group organometallic species being no exception. We have recently found BiPh<sub>3</sub> (obtained in greater than 90% yield from the treatment of BiCl<sub>3</sub> with three equivalents of PhMg(Et<sub>2</sub>O)<sub>n</sub>Br in Et<sub>2</sub>O) to be a very convenient reagent in the preparation of a wide range of other organobismuth complexes and it was our intention to extend this chemistry to the use of GaPh<sub>3</sub> and InPh<sub>3</sub> as precursors for gallium and indium compounds. The typical and obvious route to these compounds is via treatment of the commercially available

PhMg(S)<sub>n</sub>Br (S = Et<sub>2</sub>O or THF; Et<sub>2</sub>O = diethylether, THF = tetrahydrofuran) with anhydrous GaCl<sub>3</sub> or InBr<sub>3</sub>. However, we found that these reactions were not as straightforward as expected, and are significantly affected by the polarity of the supporting solvent and Lewis acidity of the metal centre.

The nature of Grignard reagents in different solvents, their role in synthesis, as well as the characterisation of products formed between RMgX and various substrates (of interest here, metal halides), has been well documented [1–8]. It is well understood that the polarity and Lewis basicity of the solvent can significantly affect the aggregation of the Grignard reagent species in solution. Thus, halogen-bridged dimers tend to dominate in diethylether (Et<sub>2</sub>O), while mononuclear species predominate in the more strongly coordinating tetrahydrofuran (THF) [9], although we recently showed that, for very bulky ligands, dinuclear species are also common when crystallised from THF [10]. Presumably in this case, the metal centres are close to being coordinatively saturated and have insufficient space in their

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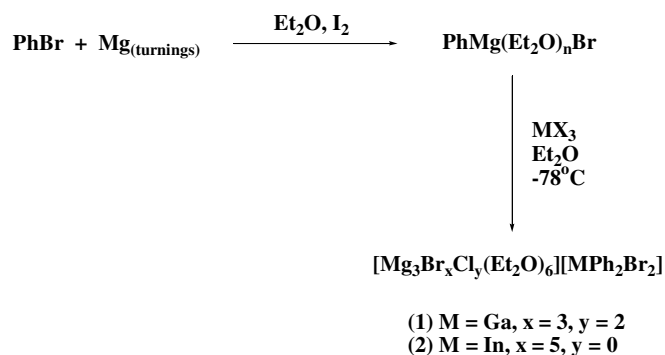
coordination sphere for the attachment of further relatively bulky THF ligands and preferentially aggregate to form dimers through bridging halides. The Schlenk equilibrium plays an important role in the nature of species existing in solution. The concentration of the solution, the nature of the solvent and temperature can all affect this equilibrium. In many cases aggregated species are isolated in the solid state from Grignard reagent solutions while mononuclear, species such as  $\text{RMg}(\text{solvent})_n\text{X}$  are rare (but here, the nature of R and X also play important roles).

In this contribution, we present the synthesis and characterisation of the solvent separated gallium and indium complexes  $[\text{Mg}_3\text{Br}_3\text{Cl}_2(\text{Et}_2\text{O})_6][\text{GaPh}_2\text{Br}_2]$  (**1**),  $[\text{Mg}_3\text{Br}_5(\text{Et}_2\text{O})_6][\text{InPh}_2\text{Br}_2]$  (**2**),  $[\text{MgBr}(\text{THF})_5][\text{GaPh}_3\text{Br}]$  (**3**),  $[\text{MgBr}(\text{THF})_5][\text{InPh}_3\text{Br}]$  (**4**), and  $[\text{Mg}(\text{THF})_6][\text{GaPh}_2\text{Br}_2]_2$  (**5**). Compounds **1**, **2**, **4** and **5** have also been characterised by X-ray crystallography. There have been some previous reports describing X-ray crystal structures similar to those described herein [11–14]. For example, the formation of the cationic motif  $[\text{Mg}_3\text{X}_5(\text{Et}_2\text{O})_6]^+$ , where X = Cl, Br, is proposed to play an important role in the magnesium behaviour in the ethereal solutions of Grignard reagents. It is pertinent to note, however, that this structural motif for the cation has *only* been obtained from diethylether, suggesting  $\text{Et}_2\text{O}$  does favour the formation of aggregates. Group 13 metallate chemistry has been extensively reviewed [15] and these anions have been obtained in related attempts to generate  $\text{MPh}_3$  species. We find that the solvent plays an important role in determining the final product and we propose this arises from the tendency of the Grignard reagent to aggregate in solution while the Lewis acidity of the relevant metal (Ga, In) favours the formation of ‘ate’ species. Our present contribution confirms previous reports on the synthesis and isolation of  $\text{MPh}_3$  (M = Ga, In) in which it has been shown that a judicious choice of solvents is crucial in obtaining the final organometallic species [16,17].  $\text{InPh}_3$  has been formed in reasonable yield (ca. 50%) by treatment of  $\text{InCl}_3$  with  $\text{PhMgBr}$  in  $\text{Et}_2\text{O}$ , but *only* after the addition of dioxane [16]. It is well established that dioxane shifts the Schlenk equilibrium to favour the formation of  $\text{MgR}_2$  and  $\text{MgX}_2$  suggesting that the clean formation of  $\text{InPh}_3$  most likely requires  $\text{MgPh}_2$  to be the dominant organomagnesium species in the Schlenk equilibrium. It has also been recently reported that  $\text{GaPh}_3$  can be prepared in high yield by the treatment of  $\text{GaCl}_3$  with  $\text{PhMgBr}$  in  $\text{Et}_2\text{O}$ , but it seems critical that the addition of a significant amount of hexane is required to ensure complete conversion to the organometallic [17]. Here again, dilution of the ether content by hexane forces  $\text{MgBr}_2$  polymerisation as the amount of ether decreases and forces completion of the metathesis reaction through an overall increase in the concentration of  $\text{MgPh}_2$ .

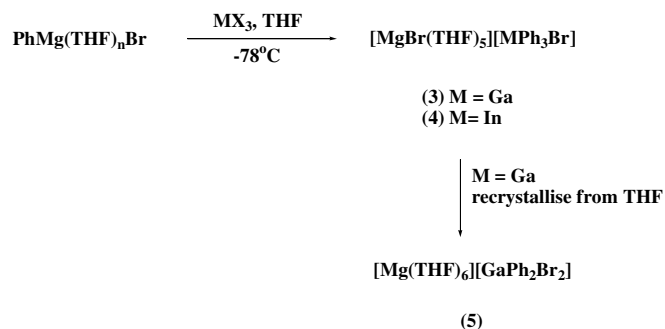
## 2. Results and discussion

In typical metathesis reactions, main group organometallic species are synthesised by treatment of either a Group

1 organometallic species or a Grignard reagent as the ligand transfer reagent. In our attempts to prepare  $\text{MPh}_3$  (M = Ga, In), we therefore treated  $\text{GaCl}_3$  and  $\text{InBr}_3$  with  $\text{PhMgBr}$  in either  $\text{Et}_2\text{O}$  or THF. Rather than forming the homoleptic organometallic species, we continually isolated Group 13 metallate species and observed that the composition of these compounds was dictated primarily by the Lewis basicity of the solvent. Treatment of  $\text{GaCl}_3$  with three equivalents of  $\text{PhMg}(\text{Et}_2\text{O})_n\text{Br}$  (prepared in situ) in  $\text{Et}_2\text{O}$  resulted in the formation of  $[\text{Mg}_3\text{Br}_3\text{Cl}_2(\text{O}(\text{Et})_2)_6][\text{GaPh}_2\text{Br}_2]$  (**1**), while a similar reaction involving  $\text{InBr}_3$  in place of  $\text{GaCl}_3$  yielded a product with analytical data consistent with the composition  $[\text{Mg}_3\text{Br}_5(\text{O}(\text{Et})_2)_6][\text{InPh}_2\text{Br}_2]$  (**2**) (although X-ray crystallography revealed the formation of  $[\text{Mg}_3\text{Br}_4\text{Br}_{0.87}(\text{OEt})_{0.13}(\text{O}(\text{Et})_2)_6][\text{InPh}_2\text{Br}_2]$  see below) (Scheme 1). On the other hand, when analogous reactions were performed in THF,  $[\text{MgBr}(\text{THF})_5][\text{GaPh}_3\text{Br}]$  (**3**), and  $[\text{MgBr}(\text{THF})_5][\text{InPh}_3\text{Br}]$  (**4**), were the major products (Scheme 2). While we were unable to obtain X-ray quality crystals of compound **3**, a further recrystallisation from THF gave  $[\text{Mg}(\text{THF})_6][\text{GaPh}_2\text{Br}_2]_2$  (**5**) with a homoleptic solvated cation (see below). The  $^1\text{H}$  NMR spectrum for compound **1** integrated for an aromatic to solvent ratio of 1:3 and is consistent with the formulation obtained by X-ray crystallography (see below). However, complications arose for  $^1\text{H}$  NMR spectra on all other compounds. Compounds **2** and **5** suffered from loss of solvent from the crystals upon isolation and therefore integration for solvent



Scheme 1.



Scheme 2.

versus phenyl groups were lower than that obtained by X-ray crystallography. For compounds **3** and **4**, the only suitable solvent for  $^1\text{H}$  NMR spectra was  $d_8$ -THF due to solubility problems and this masked the resonances for the THF solvate molecules. Microanalyses for compounds **1**, **3** and **5** were consistent with data obtained by X-ray crystallography, while compound **4** analysed for only 2.5 THF molecules of solvent, consistent with a loss of solvent. The microanalysis of compound **2** was inconsistent with that shown in X-ray studies (below) and indicated that the bulk material was  $[\text{Mg}_3\text{Br}_5(\text{O}(\text{Et})_2)_6][\text{InPh}_2\text{Br}_2]$ . All compounds have low thermal stability and begin decomposing at temperatures just above the boiling point of the solvent bound to the magnesium centres. At these temperatures, all compounds appeared to melt, but then dried as solvent evaporated and the residue gradually darkened on continued heating. In all reactions, we saw no evidence to suggest that formation of  $\text{MPh}_3$  ( $\text{M} = \text{Ga}$ ,  $\text{In}$ ) was successful, and while the effect of the solvent plays

an important role in determining the aggregation of the final product (see below), the Lewis acidity of  $\text{Ga}$  and  $\text{In}$  influences the formation of metallate species. In stark contrast, the formation of  $\text{BiPh}_3$  from  $\text{PhMgBr}$  and  $\text{BiCl}_3$  is straightforward with no evidence of 'ate' formation and presumably is due to the much lower Lewis acidity of aryl bismuth compounds. In previous accounts on the synthesis of  $\text{MPh}_3$  ( $\text{M} = \text{Ga}$ ,  $\text{In}$ ) [16,17], either hexane or dioxane was added to the reaction mixture and reasonable yields of the organometallic species were obtained. Our findings further emphasise the importance of the addition of these solvents during the reaction sequence, and we surmise that their overall effect is to increase the concentration of  $\text{MgPh}_2$  in solution.

### 2.1. X-ray crystallography

Compounds **1** and **2** are structurally similar and are comprised of a  $[\text{Mg}_3\text{X}_5(\text{Et}_2\text{O})_6]^+$  cation and  $[\text{MPh}_2\text{Br}_2]^-$

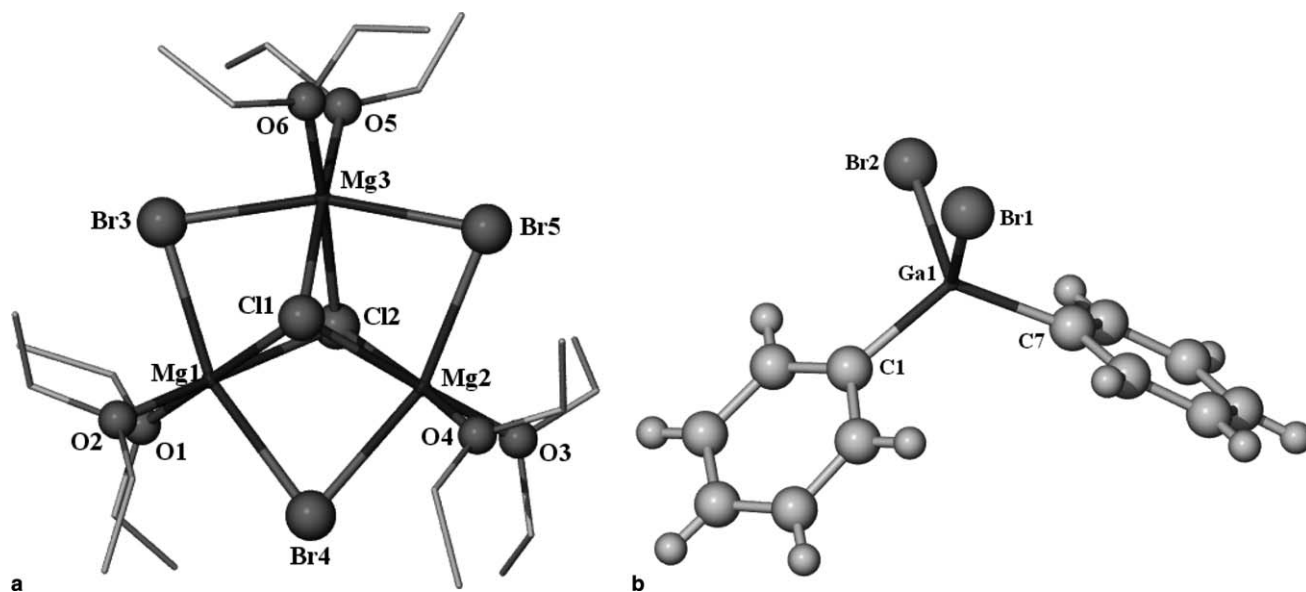


Fig. 1. (a) X-ray structure of the cation in  $[\text{Mg}_3\text{Br}_3\text{Cl}_2(\text{O}(\text{C}_2\text{H}_5)_2)_6][\text{GaPh}_2\text{Br}_2]$  (**1**). Hydrogen atoms have been omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{Mg}(1)\text{--Cl}(1)$  2.575(4),  $\text{Mg}(1)\text{--Cl}(2)$  2.587(4),  $\text{Mg}(1)\text{--Br}(3)$  2.561(3),  $\text{Mg}(1)\text{--Br}(4)$  2.626(3),  $\text{Mg}(1)\text{--O}(1)$  2.065(7),  $\text{Mg}(1)\text{--O}(2)$  2.053(7),  $\text{Mg}(2)\text{--Cl}(1)\text{--Mg}(2)$  2.574(4),  $\text{Mg}(2)\text{--Cl}(2)$  2.579(4),  $\text{Mg}(2)\text{--Br}(4)$  2.637(3),  $\text{Mg}(2)\text{--Br}(5)$  2.644(3),  $\text{Mg}(2)\text{--O}(3)$  2.055(7),  $\text{Mg}(2)\text{--O}(4)$  2.047(7),  $\text{Mg}(3)\text{--Cl}(1)$  2.554(4),  $\text{Mg}(3)\text{--Cl}(2)$  2.600(4),  $\text{Mg}(3)\text{--Br}(3)$  2.554(4),  $\text{Mg}(3)\text{--Br}(5)$  2.621(3),  $\text{Mg}(3)\text{--O}(5)$  2.059(8),  $\text{Mg}(3)\text{--O}(6)$  2.068(8),  $\text{Mg}(1)\text{--Mg}(2)$  3.320(4),  $\text{Mg}(1)\text{--Mg}(3)$  3.302(4),  $\text{Mg}(2)\text{--Mg}(3)$  3.320(4);  $\text{O}(1)\text{--Mg}(1)\text{--O}(2)$  92.6(3),  $\text{O}(1)\text{--Mg}(1)\text{--Cl}(1)$  177.0(2),  $\text{O}(1)\text{--Mg}(1)\text{--Cl}(2)$  93.0(2),  $\text{O}(1)\text{--Mg}(1)\text{--Br}(3)$  95.2(2),  $\text{O}(1)\text{--Mg}(1)\text{--Br}(4)$  96.5(2),  $\text{O}(2)\text{--Mg}(1)\text{--Cl}(1)$  90.4(2),  $\text{O}(2)\text{--Mg}(1)\text{--Cl}(2)$  174.3(2),  $\text{O}(2)\text{--Mg}(1)\text{--Br}(3)$  98.9(2),  $\text{O}(2)\text{--Mg}(1)\text{--Br}(4)$  95.8(2),  $\text{Br}(3)\text{--Mg}(1)\text{--Cl}(1)$  83.67(11),  $\text{Br}(3)\text{--Mg}(1)\text{--Cl}(2)$  81.55(11),  $\text{Br}(3)\text{--Mg}(1)\text{--Br}(4)$  160.72(14),  $\text{Br}(4)\text{--Mg}(1)\text{--Cl}(1)$  83.85(10),  $\text{Br}(4)\text{--Mg}(1)\text{--Cl}(2)$  82.60(10),  $\text{Cl}(1)\text{--Mg}(1)\text{--Cl}(2)$  84.06(11),  $\text{O}(3)\text{--Mg}(2)\text{--O}(4)$  92.2(3),  $\text{O}(3)\text{--Mg}(2)\text{--Cl}(1)$  178.0(3),  $\text{O}(3)\text{--Mg}(2)\text{--Cl}(2)$  94.1(3),  $\text{O}(3)\text{--Mg}(2)\text{--Br}(4)$  97.3(2),  $\text{O}(3)\text{--Mg}(2)\text{--Br}(5)$  96.9(2),  $\text{O}(4)\text{--Mg}(2)\text{--Cl}(1)$  89.5(2),  $\text{O}(4)\text{--Mg}(2)\text{--Cl}(2)$  173.3(2),  $\text{O}(4)\text{--Mg}(2)\text{--Br}(4)$  94.5(2),  $\text{O}(4)\text{--Mg}(2)\text{--Br}(5)$  97.6(2),  $\text{Cl}(1)\text{--Mg}(2)\text{--Cl}(2)$  84.25(11),  $\text{Cl}(1)\text{--Mg}(2)\text{--Br}(4)$  83.65(10),  $\text{Cl}(2)\text{--Mg}(2)\text{--Br}(4)$  82.54(10),  $\text{Cl}(1)\text{--Mg}(2)\text{--Br}(5)$  81.78(10),  $\text{Cl}(2)\text{--Mg}(2)\text{--Br}(5)$  83.90(10),  $\text{Br}(4)\text{--Mg}(2)\text{--Br}(5)$  160.98(13),  $\text{O}(5)\text{--Mg}(3)\text{--O}(6)$  90.0(3),  $\text{O}(5)\text{--Mg}(3)\text{--Cl}(1)$  177.2(3),  $\text{O}(5)\text{--Mg}(3)\text{--Cl}(2)$  93.1(3),  $\text{O}(5)\text{--Mg}(3)\text{--Br}(3)$  96.3(3),  $\text{O}(5)\text{--Mg}(3)\text{--Br}(5)$  96.2(3),  $\text{O}(6)\text{--Mg}(3)\text{--Cl}(1)$  92.7(3),  $\text{O}(6)\text{--Mg}(3)\text{--Cl}(2)$  176.5(3),  $\text{O}(6)\text{--Mg}(3)\text{--Br}(3)$  96.7(2),  $\text{O}(6)\text{--Mg}(3)\text{--Br}(5)$  97.3(2),  $\text{Cl}(1)\text{--Mg}(3)\text{--Cl}(2)$  84.22(11),  $\text{Cl}(1)\text{--Mg}(3)\text{--Br}(3)$  84.21(12),  $\text{Cl}(1)\text{--Mg}(3)\text{--Br}(5)$  82.60(11),  $\text{Cl}(2)\text{--Mg}(3)\text{--Br}(3)$  81.43(11),  $\text{Cl}(2)\text{--Mg}(3)\text{--Br}(5)$  83.96(11),  $\text{Br}(3)\text{--Mg}(3)\text{--Br}(5)$  161.20(14). (b) X-ray structure of the anion in  $[\text{Mg}_3\text{Br}_3\text{Cl}_2(\text{O}(\text{C}_2\text{H}_5)_2)_6][\text{GaPh}_2\text{Br}_2]$  (**1**). The  $[\text{InPh}_2\text{Br}_2]^-$  and  $[\text{GaPh}_2\text{Br}_2]^-$  anions in compounds **2** and **5**, respectively, are similar. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ): Compound **1**:  $\text{Ga}(1)\text{--Br}(1)$  2.4045(17),  $\text{Ga}(1)\text{--Br}(2)$  2.3867(16),  $\text{Ga}(1)\text{--C}(7)$  1.958(11),  $\text{Ga}(1)\text{--Cl}(1)$  1.962(10);  $\text{C}(1)\text{--Ga}(1)\text{--C}(7)$  119.4(4),  $\text{C}(1)\text{--Ga}(1)\text{--Br}(1)$  106.1(3),  $\text{C}(1)\text{--Ga}(1)\text{--Br}(2)$  108.9(3),  $\text{C}(7)\text{--Ga}(1)\text{--Br}(1)$  107.0(4),  $\text{C}(7)\text{--Ga}(1)\text{--Br}(2)$  107.9(4),  $\text{Br}(1)\text{--Ga}(1)\text{--Br}(2)$  106.94(6). Compound **2**:  $\text{In}(1)\text{--C}(1)$  2.155(4),  $\text{In}(1)\text{--C}(7)$  2.154(4),  $\text{In}(1)\text{--Br}(1)$  2.5803(5),  $\text{In}(1)\text{--Br}(2)$  2.6047(5);  $\text{C}(1)\text{--In}(1)\text{--C}(7)$  128.18(16),  $\text{C}(1)\text{--In}(1)\text{--Br}(1)$  101.49(12),  $\text{C}(1)\text{--In}(1)\text{--Br}(2)$  110.19(11),  $\text{C}(7)\text{--In}(1)\text{--Br}(1)$  106.19(12),  $\text{C}(7)\text{--In}(1)\text{--Br}(2)$  103.20(11),  $\text{Br}(1)\text{--In}(1)\text{--Br}(2)$  105.81(2). Compound **5**:  $\text{Ga}(1)\text{--C}(1)$  1.991(8),  $\text{Ga}(1)\text{--C}(7)$  2.009(7),  $\text{Ga}(1)\text{--Br}(1)$  2.3724(13),  $\text{Ga}(1)\text{--Br}(2)$  2.3552(14);  $\text{C}(1)\text{--Ga}(1)\text{--C}(7)$  122.2(3),  $\text{C}(1)\text{--Ga}(1)\text{--Br}(1)$  107.9(2),  $\text{C}(1)\text{--Ga}(1)\text{--Br}(2)$  106.0(2),  $\text{C}(7)\text{--Ga}(1)\text{--Br}(1)$  104.3(2),  $\text{C}(7)\text{--Ga}(1)\text{--Br}(2)$  106.6(2),  $\text{Br}(1)\text{--Ga}(1)\text{--Br}(2)$  109.54(5).

(M = Ga, X = 5 (**1**); M = In, X = 0.86OEt/0.13Br (**2**)) anion. The cations have a trinuclear magnesium core bridged around the perimeter by bromide ions (Mg–Br ave. = 2.61 Å in **1** and 2.67 Å in **2**) and capped above and below the Mg<sub>3</sub> triangle by either two chloride ions in **1** (mean Mg–Cl bond lengths 2.57 Å) or one bromide (mean bond length 2.76 Å for Mg–Br(4)) and bromide/ethoxide ions (**2**) (Mg–Br(3) ave. = 2.60 Å and Mg–O(7) 2.11 Å) (Figs. 1a and 2a and b). The latter components arise from disorder in the cation of (**2**) where Br(3) is disordered with an ethoxide ion in a ratio of 14:86. The Mg–Cl and Mg–Br bond lengths are similar to those reported for capping halide ions in related compounds, viz. [Mg<sub>3</sub>BrCl<sub>3</sub>(OEt)(Et<sub>2</sub>O)<sub>6</sub>][Ada<sub>3</sub>AlBr], [Mg<sub>3</sub>Br<sub>2</sub>Cl<sub>3</sub>(Et<sub>2</sub>O)<sub>6</sub>]-[Ada<sub>2</sub>GaBr<sub>2</sub>] and [Mg<sub>3</sub>Br<sub>4</sub>(OEt)(Et<sub>2</sub>O)<sub>6</sub>][Ada<sub>3</sub>MMe<sub>2</sub>] [13] (Ada = adamantyl, M = Al, Ga). Each of the magnesium ions of the cation are also bound to two ether molecules completing the six-coordination about these metal centres. The mean Mg–O<sub>(ether)</sub> distance is 2.06 Å and compares well with those in the three adamantyl analogues mentioned above [13]. The effect of capping chloride ions in compound **1** compared with Br/EtO in compound **2** has a small influence on the Mg···Mg distances (3.31 and 3.26 Å in compounds **1** and **2**, respectively).

Compounds **4** and **5** also exist as ion pairs, however, in these compounds, the aggregation in the cation is limited to a mononuclear species (Figs. 3a and 4). Presumably the stronger basicity of the coordinating solvent results in deaggregation, resulting in a mononuclear cation. Compound **4** crystallizes with the whole cation/anion species comprising the asymmetric unit and the cation retaining a halide ligand, viz. [MgBr(THF)<sub>5</sub>]<sup>+</sup>, while in compound **5**, the asymmetric unit is comprised of half the [Mg(THF)<sub>6</sub>]<sup>2+</sup> cation and one anion. The cation in **4** represents a rare example of the [MgBr(THF)<sub>5</sub>]<sup>+</sup> species, and interestingly, the three other structurally authenticated instances of this ion were all also derived from Grignard reagents [18–20]. The bond lengths and angles are given in the captions for Figs. 3a and 4. The cation in compound **5** has been observed on a number of occasions [21] with the most relevant example being in [Mg(THF)<sub>6</sub>][GaBz<sub>2</sub>Br<sub>2</sub>]<sub>2</sub> (Bz = benzyl) [22] where the mean Mg–O bond length of 2.10 Å are the same in both compounds.

The anions in compounds **1**, **2** and **5** are all similar (Fig. 1b). The ligands about the metal centre are arranged in a distorted tetrahedral array (Fig. 1b caption). The angles about the metal centres deviate significantly from ideal tetrahedral geometry with the range being 106.1(3)–

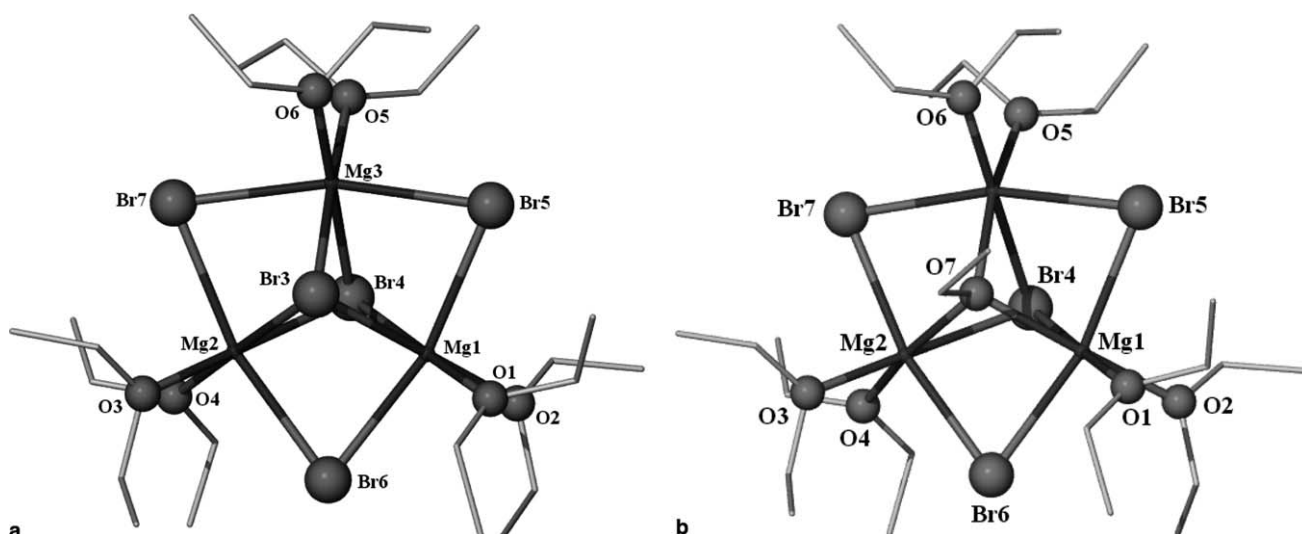


Fig. 2. (a) X-ray structure of the [Mg<sub>3</sub>Br<sub>5</sub>(O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>6</sub>]<sup>+</sup> component in compound **2** which comprises 87% of the disorder. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Mg(1)–Br(3) 2.577(6), Mg(1)–Br(4) 2.7762(13), Mg(1)–Br(5) 2.6727(13), Mg(1)–Br(6) 2.6535(13), Mg(1)–O(1) 2.087(3), Mg(1)–O(2) 2.091(3), Mg(2)–Br(3) 2.636(5), Mg(2)–Br(4) 2.7518(14), Mg(2)–Br(6) 2.6555(13), Mg(2)–Br(7) 2.6589(13), Mg(2)–O(3) 2.078(3), Mg(2)–O(4) 2.084(3), Mg(3)–Br(3) 2.603(5), Mg(3)–Br(4) 2.7612(14), Mg(3)–Br(5) 2.6923(13), Mg(3)–O(5) 2.093(3), Mg(3)–O(6) 2.078(3), Mg(1)–Mg(2) 3.2292(18), Mg(1)–Mg(3) 3.2488(18), Mg(2)–Mg(3) 3.2201(18); O(1)–Mg(1)–O(2) 87.50(12), O(1)–Mg(1)–Br(3) 91.68(14), O(1)–Mg(1)–Br(4) 176.23(10), O(1)–Mg(1)–Br(5) 95.67(9), O(1)–Mg(1)–Br(6) 94.59(9), O(2)–Mg(1)–Br(3) 179.12(14), O(2)–Mg(1)–Br(4) 88.75(9), O(2)–Mg(1)–Br(5) 95.55(9), O(2)–Mg(1)–Br(6) 95.61(9), Br(3)–Mg(1)–Br(4) 92.07(11), Br(3)–Mg(1)–Br(5) 84.87(10), Br(3)–Mg(1)–Br(6) 84.11(9), Br(4)–Mg(1)–Br(5) 84.27(4), Br(4)–Mg(1)–Br(6) 86.20(4), Br(5)–Mg(1)–Br(6) 165.14(6), O(3)–Mg(2)–O(4) 89.77(12), O(3)–Mg(2)–Br(3) 91.84(15), O(3)–Mg(2)–Br(4) 176.79(10), O(3)–Mg(2)–Br(6) 94.13(9), O(3)–Mg(2)–Br(7) 92.99(9), O(4)–Mg(2)–Br(3) 178.25(16), O(4)–Mg(2)–Br(4) 87.04(9), O(4)–Mg(2)–Br(6) 96.27(10), O(4)–Mg(2)–Br(7) 96.71(10), Br(3)–Mg(2)–Br(4) 91.35(13), Br(3)–Mg(2)–Br(6) 82.93(9), Br(3)–Mg(2)–Br(7) 83.89(9), Br(4)–Mg(2)–Br(6) 86.66(4), Br(4)–Mg(2)–Br(7) 86.95(4), Br(6)–Mg(2)–Br(7) 165.20(6), O(5)–Mg(3)–O(6) 90.19(12), O(5)–Mg(3)–Br(3) 177.44(15), O(5)–Mg(3)–Br(4) 86.19(9), O(5)–Mg(3)–Br(5) 94.18(9), O(5)–Mg(3)–Br(7) 97.10(9), O(6)–Mg(3)–Br(3) 91.82(15), O(6)–Mg(3)–Br(4) 176.09(10), O(6)–Mg(3)–Br(5) 97.54(9), O(6)–Mg(3)–Br(7) 92.36(9), Br(3)–Mg(3)–Br(4) 91.85(12), Br(3)–Mg(3)–Br(5) 83.97(9), Br(3)–Mg(3)–Br(7) 84.42(9), Br(4)–Mg(3)–Br(5) 84.20(4), Br(4)–Mg(3)–Br(7) 86.64(4), Br(5)–Mg(3)–Br(7) 164.95(6). (b) X-ray structure of the [Mg<sub>3</sub>Br<sub>4</sub>(OEt)(O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>)<sub>6</sub>]<sup>+</sup> component in compound **2** which comprises 13% of the disorder. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Mg(1)–O(7) 2.107(4), Mg(2)–O(7) 2.123(4), Mg(3)–O(7) 2.092(4), O(7)–C(37) 1.459(11).

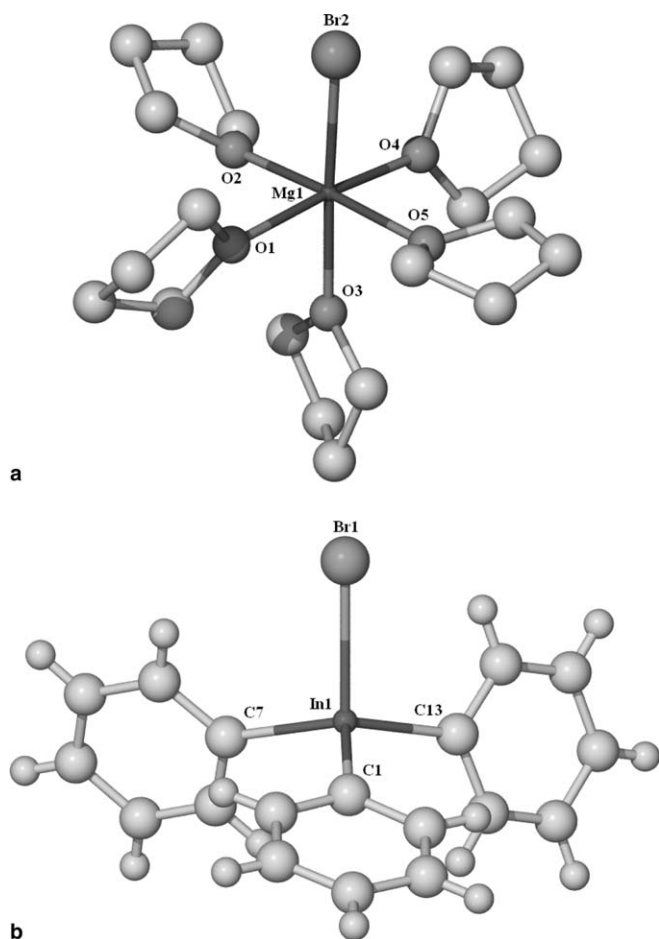


Fig. 3. (a) X-ray structure of the cation in  $[\text{Mg}_3\text{Br}(\text{THF})_5][\text{InPh}_3\text{Br}]$  (**4**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Mg(1)–Br(2) 2.5771(9), Mg(1)–O(1) 2.135(2), Mg(1)–O(2) 2.094(2), Mg(1)–O(3) 2.144(2), Mg(1)–O(4) 2.102(2), Mg(1)–O(5) 2.116(2); O(1)–Mg(1)–O(2) 87.96(9), O(1)–Mg(1)–O(3) 85.18(8), O(1)–Mg(1)–O(4) 172.08(8), O(1)–Mg(1)–O(5) 92.93(9), O(2)–Mg(1)–O(3) 90.12(8), O(2)–Mg(1)–O(4) 89.52(9), O(2)–Mg(1)–O(5) 175.21(9), O(3)–Mg(1)–O(4) 87.32(8), O(5)–Mg(1)–O(3) 85.27(8), O(4)–Mg(1)–O(5) 88.98(8), O(1)–Mg(1)–Br(2) 92.92(6), O(2)–Mg(1)–Br(2) 95.08(6), O(3)–Mg(1)–Br(2) 174.40(7), O(4)–Mg(1)–Br(2) 94.78(6), O(5)–Mg(1)–Br(2) 89.57(6). (b) X-ray structure of the anion in  $[\text{MgBr}(\text{THF})_5][\text{InPh}_3\text{Br}]$  (**4**). Selected bond lengths (Å) and angles ( $^\circ$ ): In(1)–C(1) 2.184(3), In(1)–C(7) 2.188(3), In(1)–C(13) 2.182(3), In(1)–Br(1) 2.6239(4); C(1)–In(1)–C(7) 112.24(11), C(1)–In(1)–C(13) 113.93(11), C(1)–In(1)–Br(1) 108.51(8); C(7)–In(1)–C(13) 114.52(11), C(7)–In(1)–Br(1) 103.30(8), C(13)–In(1)–Br(1) 103.15(8).

$119.4(4)^\circ$  for compound **1**,  $103.20(11)$ – $128.18(16)^\circ$  for compound **2** and  $104.3(2)$ – $122.2(3)^\circ$  for compound **5** and in each the largest angle is for that between the two sterically demanding phenyl groups. The anion in compound **5** is also very similar to that in compound **1** as expected (see Fig. 1b caption).

The anion in compound **4** also consists of a distorted tetrahedral indium atom bound to three phenyl groups with mean In–C bond length of 2.18 Å and one bromine atom (In(1)–Br(1) 2.6239(4) Å). The range of bond angles from  $103.30(8)^\circ$  for C(7)–In(1)–Br(1) to  $114.52(11)^\circ$  for C(13)–In(1)–C(7) shows the distortion from ideal tetrahedral geometry is less pronounced than in compounds **1**, **2** and **4**.

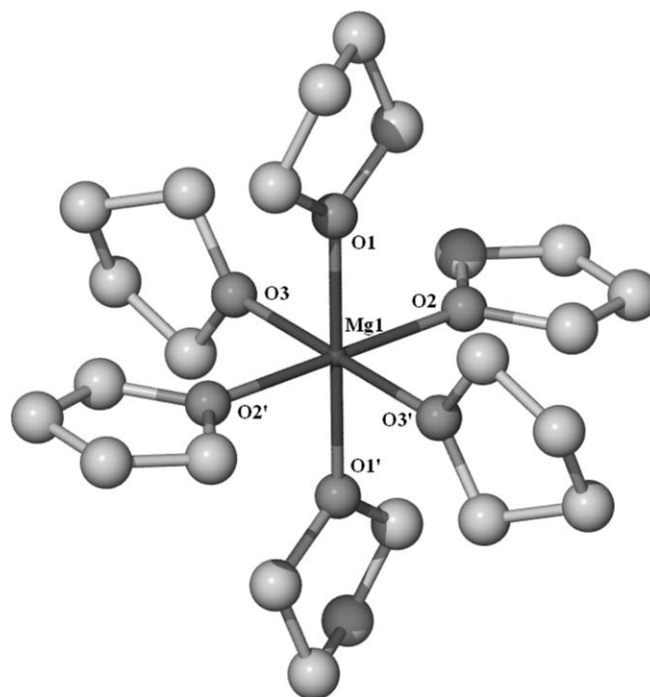


Fig. 4. X-ray structure of the cation in  $[\text{Mg}(\text{THF})_6][\text{GaPh}_2\text{Br}_2]$  (**5**). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Mg(1)–O(1) 2.073(5), Mg(1)–O(2) 2.128(5), Mg(1)–O(3) 2.112(5); O(1)–Mg(1)–O(2) 88.9(2), O(1)–Mg(1)–O(3) 90.7(2), O(1)–Mg(1)–O(1)<sup>#1</sup> 180.000(1), O(2)–Mg(1)–O(3) 90.5(2).

### 3. Conclusions

The complicated nature of Grignard solutions where equilibria between many aggregated species dominate, tend to make some of this chemistry very complex. We have shown that the nature of the solvent is of utmost importance in determining the final products in metathesis. Using  $\text{Et}_2\text{O}$  as a solvent in metathesis reactions leads to the formation of multinuclear magnesium cations with Group 13 metallate anions, whereas in THF, the cations tend to be mononuclear. The Lewis acidity of the metal also plays an important role and for the strongly Lewis acidic Group 13 metals, ‘ate’ species tend to dominate.

### 4. Experimental

#### 4.1. General procedures, materials, and solvents

Reactions were carried out under dry nitrogen using standard Schlenk and/or glovebox techniques. Bromobenzene, phenylmagnesiumbromide, magnesium turnings, 0.5 M  $\text{GaCl}_3$  in pentane,  $\text{InCl}_3$  were purchased from Aldrich and used as received.  $\text{InCl}_3$  and 0.5 M  $\text{GaCl}_3$  in pentane were stored under inert atmosphere. Diethyl ether and tetrahydrofuran were distilled from sodium wire and then stored under an inert atmosphere over molecular sieves (4 Å). Quoted yields are those of isolated crystalline

product and were not optimised. The high solubility of the products in Et<sub>2</sub>O or THF meant that these yields were generally low.

Proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded at 300 MHz on a Bruker DRX-300 spectrometer or 200 MHz on a Bruker AC-200 spectrometer. Chemical shifts were referenced relative to residual protons in the deuterated solvents, *d*<sub>6</sub>-benzene or *d*<sub>8</sub>-THF. Compounds **2** and **5** suffered from loss of solvent from the crystals prior to performing the <sup>1</sup>H NMR spectra and therefore integration for solvent versus phenyl groups were not correct. For compounds **3** and **4**, the only suitable solvent for <sup>1</sup>H NMR spectra was *d*<sub>8</sub>-THF due to solubility problems. For these compounds, the NMR solvent masked solvent in the complex, thus making integration non-meaningful. Elemental analyses were performed by Chemical & MicroAnalytical Services Pty Ltd., Australia.

#### 4.2. Synthesis of [Mg<sub>3</sub>Br<sub>3</sub>Cl<sub>2</sub>(O(Et)<sub>2</sub>)<sub>6</sub>][GaPh<sub>2</sub>Br<sub>2</sub>] (**1**)

Phenylmagnesium bromide was prepared by refluxing bromobenzene (3.25 ml, 30 mmol) and Mg turnings (0.73 g, 30 mmol) activated with iodine in Et<sub>2</sub>O (10 ml). This was then added dropwise to a stirred solution of GaCl<sub>3</sub> (20 ml, 0.5 M in pentane; pentane was replaced by Et<sub>2</sub>O) in Et<sub>2</sub>O at –78 °C. The reaction mixture was stirred overnight while warming up to room temperature. Two liquid phases resulted; Et<sub>2</sub>O was the upper layer, while an oily residue of [Mg<sub>3</sub>Br<sub>3</sub>Cl<sub>2</sub>(O(Et)<sub>2</sub>)<sub>6</sub>][GaPh<sub>2</sub>Br<sub>2</sub>], which crystallised at room temperature, was the lower layer. Yield: 69%. M.p. decomposition began at 35–40 °C and at ca. 190 °C the material became dark brown. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.97 (t, 36H, CH<sub>2</sub>CH<sub>3</sub>), 3.29 (q, 24H, CH<sub>2</sub>CH<sub>3</sub>), 7.21 (m, 6H, aromatics), 7.89 (m, 4H, aromatics). Anal. Calc. for C<sub>36</sub>H<sub>70</sub>Br<sub>5</sub>Cl<sub>2</sub>GaMg<sub>3</sub>O<sub>6</sub>: C, 35.68; H, 5.82. Found: C, 35.54; H, 5.90%.

#### 4.3. Synthesis of [Mg<sub>3</sub>Br<sub>5</sub>(O(Et)<sub>2</sub>)<sub>6</sub>][InPh<sub>2</sub>Br<sub>2</sub>] (**2**)

Phenylmagnesium bromide was prepared by refluxing bromobenzene (3.25 ml, 30 mmol) and Mg turnings (0.73 g, 30 mmol) activated with iodine in Et<sub>2</sub>O (10 ml). This solution was then added dropwise to a stirred solution of InBr<sub>3</sub> (3.54 g, 10 mmol) in Et<sub>2</sub>O at –78 °C. The reaction mixture was stirred overnight and allowed to warm to room temperature. Two liquid phases resulted – the upper layer was Et<sub>2</sub>O while the lower layer was an oily residue or [Mg<sub>3</sub>Br<sub>5</sub>(O(Et)<sub>2</sub>)<sub>6</sub>][InPh<sub>2</sub>Br<sub>2</sub>], which was crystallised at room temperature. Yield: ≈10%. M.p. decomposition began at ca. 35–40 °C and ≈200 °C the material became dark brown. <sup>1</sup>H NMR (300 MHz, THF) δ 1.11 (br m, 15H, CH<sub>2</sub>CH<sub>3</sub>), 3.38 (br m, 10H, CH<sub>2</sub>CH<sub>3</sub>), 7.24 (br m, 6H), 7.68 (br m, 4H). Anal. Calc. for C<sub>36</sub>H<sub>70</sub>Br<sub>7</sub>InMg<sub>3</sub>O<sub>6</sub>: C, 32.12; H, 5.24. Found: C, 32.05; H, 5.35%. Elemental analysis implies that the bulk sample contained the fully brominated cation [Mg<sub>3</sub>Br<sub>5</sub>(O(Et)<sub>2</sub>)<sub>6</sub>][InPh<sub>2</sub>Br<sub>2</sub>] rather than the

disordered cation (see below) as seen in the X-ray crystal structure, viz. [Mg<sub>3</sub>Br<sub>4</sub>Br<sub>0.14</sub>(OEt)<sub>0.86</sub>(O(Et)<sub>2</sub>)<sub>6</sub>][InPh<sub>2</sub>Br<sub>2</sub>].

#### 4.4. Synthesis of [MgBr(THF)<sub>5</sub>][GaPh<sub>3</sub>Br] (**3**)

GaCl<sub>3</sub> (0.5 M in pentane, pentane was replaced THF, 5 mmol) was dissolved in THF and phenylmagnesiumbromide (1 M in Et<sub>2</sub>O; 15 ml, 15 mmol) was dropwise added to the solution at –78 °C. The reaction mixture was left to warm to room temperature over night. A white solid precipitated from solution but this easily dissolved after heating of the mixture yielding a yellowish oil in THF from which crystals of [MgBr(THF)<sub>5</sub>][GaPh<sub>3</sub>Br] grew over 5 days.

M.p. decomposition began at 70 °C and at 200 °C the material became dark brown. <sup>1</sup>H NMR (300 MHz, THF) δ 1.77 (m, OCH<sub>2</sub>), 3.61 (m, CH<sub>2</sub>CH<sub>2</sub>), 7.25 (m, 9H, aromatics), 7.72 (m, 6H, aromatics). Anal. Calc. for C<sub>38</sub>H<sub>55</sub>Br<sub>2</sub>GaMgO<sub>5</sub>: C, 53.97; H, 6.56. Found: C, 53.61; H, 6.47%.

#### 4.5. Synthesis of [MgBr(THF)<sub>5</sub>][InPh<sub>3</sub>Br] (**4**)

InBr<sub>3</sub> (1.77 g, 5 mmol) was dissolved with THF (20 ml) and phenylmagnesiumbromide (1 M in Et<sub>2</sub>O; 15 ml, 15 mmol) was dropwise added to the solution at –78 °C. The reaction mixture was allowed to warm up to room temperature over night and a white solid precipitated from solution. This residue was dissolved with gentle resulting in an oily residue in THF from which crystals of [MgBr(THF)<sub>5</sub>][InPh<sub>3</sub>Br] grew over 6 days. M.p. melting began at 90 °C and at 198 °C the white solid decomposed to a brown liquid. <sup>1</sup>H NMR (300 MHz, THF) δ 1.75 (m, OCH<sub>2</sub>), 3.60 (m, CH<sub>2</sub>CH<sub>2</sub>), 7.15–7.24 (m, 4H, aromatics), 7.75–7.78 (m, 6H, aromatics). Anal. Calc. for C<sub>38</sub>H<sub>55</sub>Br<sub>2</sub>InMgO<sub>5</sub>: C, 51.24; H, 6.22. Found: C, 47.32; H, 5.40%. (Anal. Calc. for Ph<sub>3</sub>THF<sub>2.5</sub>Br<sub>2</sub>InMgO<sub>5</sub>: C, 47.33; H, 4.97%.)

#### 4.6. Synthesis of [Mg(THF)<sub>6</sub>][GaPh<sub>2</sub>Br]<sub>2</sub> (**5**)

[MgBr(THF)<sub>5</sub>][GaPh<sub>3</sub>Br]<sub>2</sub> (**3**) was recrystallised from THF yielding the *title compound*. M.p. 68 °C, at 72 °C the liquid turned cloudy and at 83 °C a white solid remained with condensation observed on the walls of the melting tube. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.29 (br s, OCH<sub>2</sub>), 3.52 (br s, CH<sub>2</sub>CH<sub>2</sub>), 7.15 (br, H). Anal. Calc. for C<sub>60</sub>H<sub>78</sub>Br<sub>2</sub>Ga<sub>2</sub>MgO<sub>6</sub>: C, 59.13; H, 6.45. Found: C, 59.07; H, 6.32%.

#### 4.7. X-ray crystallography

Crystalline samples of compounds **1**, **2**, **4** and **5** were mounted upon glass fibres in highly viscous hydrocarbon oil at –150 °C (123 K). Crystal data for all compounds were obtained using an Enraf-Nonius Kappa CCD. X-ray

data were processed using the DENZO program [23]. Structural solution and refinement was carried out using SHELXL-97 [24] and SHELXS-97 [25] utilising the graphical interface X-Seed [26]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions (riding model) and were not refined. Crystal data and refinement parameters for all complexes are compiled below. For compound **1** data were poor and one diethylether molecule was disordered over two sites and this was successfully modelled. Hydrogen atoms were not placed on this molecule and the carbon atoms were refined with ISOR restraints. For compound **2** there was disorder between the ethoxy group and a bromide ion (Br(3)) in the apical position of the cation. This disorder was successfully refined with occupancies of 86% for the OEt group and 14% for the bromide ion.

*Crystal data for compound 1:* C<sub>36</sub>H<sub>70</sub>Br<sub>5</sub>Cl<sub>2</sub>GaMg<sub>3</sub>O<sub>6</sub>, *M* = 1212.02, 1.05 × 0.50 × 0.30 mm, orthorhombic, space group *Pbca* (No. 61), *a* = 21.800(4) Å, *b* = 18.087(4) Å, *c* = 26.410(5) Å, *V* = 10414(4) Å<sup>3</sup>, *Z* = 8, *D*<sub>calc</sub> = 1.546 g/cm<sup>3</sup>, *F*(000) = 4880, Mo Kα radiation, λ = 0.71073 Å, 2θ<sub>max</sub> = 55.7°, 113 712 reflections collected, 12 318 unique (*R*<sub>int</sub> = 0.1003). Final goodness-of-fit = 0.987, *R*<sub>1</sub> = 0.1089, *wR*<sub>2</sub> = 0.2892, *R* indices based on 7272 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 508 parameters, 36 restraints. Lp and absorption corrections applied, μ = 4.541 mm<sup>-1</sup>.

*Crystal data for compound 2:* C<sub>37.76</sub>H<sub>74.39</sub>Br<sub>6.13</sub>InMg<sub>3</sub>O<sub>6.88</sub>, *M* = 1315.62, 0.45 × 0.30 × 0.30 mm, triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 11.68640(10) Å, *b* = 14.1648(2) Å, *c* = 16.7793(2) Å, α = 100.5350(10)°, β = 91.2230(10)°, γ = 93.1180(10)°, *V* = 2725.32(6) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc</sub> = 1.603 g/cm<sup>3</sup>, *F*(000) = 1311, Mo Kα radiation, λ = 0.71073 Å, 2θ<sub>max</sub> = 56.4°, 48 024 reflections collected, 13 124 unique (*R*<sub>int</sub> = 0.0567). Final goodness-of-fit = 1.032, *R*<sub>1</sub> = 0.0459, *wR*<sub>2</sub> = 0.1133, *R* indices based on 10596 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 519 parameters, 0 restraints. Lp and absorption corrections applied, μ = 4.996 mm<sup>-1</sup>.

*Crystal data for compound 4:* C<sub>38</sub>H<sub>55</sub>Br<sub>2</sub>InMgO<sub>5</sub>, *M* = 890.77, 0.21 × 0.20 × 0.10 mm, triclinic, space group *P* $\bar{1}$  (No. 2), *a* = 10.9124(3) Å, *b* = 11.7196(3) Å, *c* = 16.4413(5) Å, α = 75.0570(10)°, β = 77.157(2)°, γ = 82.8200(10)°, *V* = 1975.61(10) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc</sub> = 1.497 g/cm<sup>3</sup>, *F*(000) = 908, Mo Kα radiation, λ = 0.71073 Å, 2θ<sub>max</sub> = 56.4°, 26 878 reflections collected, 9528 unique (*R*<sub>int</sub> = 0.0632). Final goodness-of-fit = 1.012, *R*<sub>1</sub> = 0.0399, *wR*<sub>2</sub> = 0.0731, *R* indices based on 6654 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 424 parameters, 0 restraints. Lp and absorption corrections applied, μ = 2.676 mm<sup>-1</sup>.

*Crystal data for compound 5:* C<sub>48</sub>H<sub>68</sub>Br<sub>4</sub>Ga<sub>2</sub>MgO<sub>6</sub>, *M* = 1224.41, 0.20 × 0.15 × 0.10 mm, monoclinic, space group *P*2<sub>1</sub>/*n* (No. 14), *a* = 12.1664(3) Å, *b* = 15.6764(5) Å, *c* = 13.1772(4) Å, β = 92.165(3)°, *V* = 2511.43(13) Å<sup>3</sup>, *Z* = 2, *D*<sub>calc</sub> = 1.619 g/cm<sup>3</sup>, *F*(000) = 1236, Mo Kα radiation, λ = 0.71073 Å, 2θ<sub>max</sub> = 56.6°, 35 769 reflections collected, 6142 unique (*R*<sub>int</sub> = 0.1185). Final goodness-of-fit = 1.036, *R*<sub>1</sub> = 0.0844, *wR*<sub>2</sub> = 0.2346, *R* indices based

on 3606 reflections with *I* > 2σ(*I*) (refinement on *F*<sup>2</sup>), 277 parameters, 0 restraints. Lp and absorption corrections applied, μ = 4.313 mm<sup>-1</sup>.

## 5. Supplementary data

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-297752 for compound **1**, CCDC-297753 for compound **2**, CCDC-297754 for compound **4** and CCDC-297755 for compound **5**. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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