

# The cationic cluster Grignard $[\{\text{MgCl}(\text{thf})_2\}_3(\mu_3\text{-C}_3\text{H}_5)_2]^+\ddagger$

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The synthesis and structure of  $[\{\text{MgCl}(\text{thf})_2\}_3(\mu_3\text{-C}_3\text{H}_5)_2][\text{Mg}(\text{C}_3\text{H}_5)_4]$ , which contains both a cationic cluster Grignard and a tetraorganomagnesiato dianion, are reported.

Discovered over one hundred years ago, Grignard reagents are still amongst the most valuable reagents available to the chemist and their widespread synthetic applications have been extensively documented.<sup>1</sup> In comparison, however, fundamental studies of Grignard reagents in their own right have been sporadic and are relatively few in number. Only during the last 20 years or so have detailed, systematic investigations into the solution and solid-state structures of organomagnesium halides,  $\text{RMgX}$ , become prominent.

In solution, the lability of the ligands in compounds of formula  $\text{RMgX}$  is described by the well known and ostensibly simple Schlenk equilibrium. This equilibrium has in fact shown itself to be more complicated than first thought and although  $\text{MgX}_2$  and  $\text{R}_2\text{Mg}$  are known to play important roles, several other species may also be present.<sup>2</sup> Indeed, the precise composition of the equilibrium depends intimately upon factors such as solvent, concentration, halide and the nature of the carbanion, and a dominant species cannot always be identified unambiguously. In the solid-state the majority of quantitative structural information has been provided by single crystal X-ray diffraction. The 'expected' structure of a Grignard reagent corresponds to the general formula  $[\text{RMgX}(\text{solvent})_n]$  ( $n = 2\text{--}4$ ) and many species of this type have been structurally authenticated.<sup>3–7</sup> In addition to these monomeric structures, several examples of Grignard oligomers such as  $[\text{Mg}_2(\mu\text{-Cl})_3(\text{thf})_6]^+[\text{RMgCl}_2(\text{thf})]^-$ ,  $2[\text{Mg}_2(\mu\text{-Cl})_3(\text{thf})_6]^+[\text{R}_2\text{Mg}(\mu\text{-Cl})_2]^{2-}$  and  $[\text{R}_2\text{Mg}_4\text{Cl}_6(\text{thf})_6]$  have also been reported. It is noteworthy that in each of these polynuclear derivatives the organyl groups always occupy terminal coordination sites and that the halide usually acts as a  $\mu$ -ligand between magnesium cations.<sup>5–7</sup> Recently, metal vapour synthesis of organotetramagnesium halides,  $[\text{RMg}_4\text{X}]$ , so-called 'cluster Grignard reagents', has afforded what are thought to be the first Grignard derivatives based on a polyhedral arrangement of magnesium atoms. The composition of these clusters was determined by MALDI-TOF mass spectrometric measurements and hydrolysis studies, while the presence of  $\text{Mg}_4$  tetrahedra, containing direct Mg–Mg bonding, was suggested by supporting theoretical investigations.<sup>8</sup>

In this communication, as a part of our continuing work on metal allyl and organomagnesium chemistry,<sup>9</sup> we present the

synthesis and crystal structure of  $[\{\text{MgCl}(\text{thf})_2\}_3(\mu_3\text{-C}_3\text{H}_5)_2][\text{Mg}(\text{C}_3\text{H}_5)_4]$ ,  $[\mathbf{1}]_2[\mathbf{2}]$ , formed unexpectedly in the reaction of allylmagnesium chloride with methylaluminium dichloride in thf solvent according to Scheme 1.<sup>‡</sup>



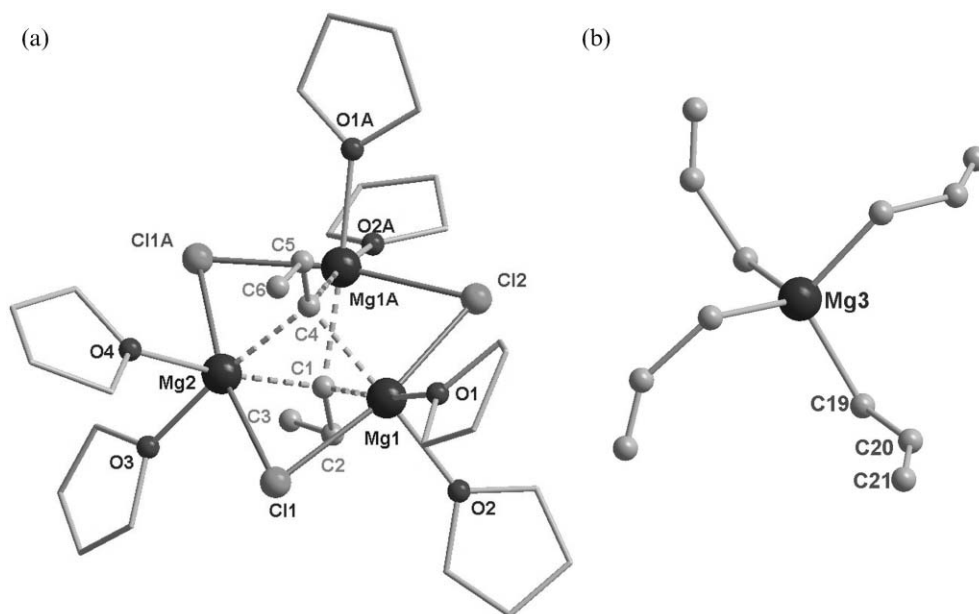
Scheme 1

Evaporating the thf solvent and extracting the residue into ether allowed, upon filtration, removal of a colourless, insoluble material.<sup>§</sup> Storing the concentrated filtrate at room-temperature for several days afforded colourless, very air-sensitive crystals of  $[\mathbf{1}]_2[\mathbf{2}]$ . In addition to basic characterization by microanalysis and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (see below), a single-crystal was selected for X-ray diffraction analysis and the molecular structures of the cation  $[\mathbf{1}]^+$  and its counter ion  $[\mathbf{2}]^{2-}$ , which crystallise in the orthorhombic space group *Ibam*, are shown in Figs. 1a and 1b, respectively.<sup>¶</sup>

The unusual structure of  $[\mathbf{1}]^+$  (Fig. 1a) consists of a trigonal bipyramidal  $[\text{Mg}_3\text{C}_2]$  core in which two  $\mu_3$ -allyl ligands reside in positions perpendicular to the  $\text{Mg}_3$  equatorial plane and three  $\mu_2$ -chloride ligands bridge across the magnesium cations in the plane. The coordination environment of each cation is completed by two thf ligands. The terminal allyl carbon atoms C(3) and C(6) are each partially disordered over two sites in the crystal at 230(2) K (not illustrated) due to the mirror symmetry that bisects  $[\mathbf{1}]^+$  in the plane generated by Mg(2), C(2) and C(4). The coordination geometry in which Mg(1) resides is best described as highly distorted octahedral since the average Mg(1)–O, Mg(1)–Cl and Mg(1)–C bond distances are 2.078(4), 2.504(2) and 2.086(4) Å, respectively, and the O(1)–Mg(1)–C(1), O(2)–Mg(1)–C(4) and Cl(1)–Mg(1)–Cl(2) *trans*-bond angles are 170.1(1), 172.5(1) and 168.5(1)°, respectively. Similarly, the average Mg(2)–O, Mg(2)–Cl and Mg(2)–C bond distances are 2.087(5), 2.513(1) and 2.084(5) Å and the O(4)–Mg(2)–C(1), O(3)–Mg(2)–C(4) and Cl(1)–Mg(2)–Cl(1A) *trans*-bond angles are 171.4(2), 170.7(1) and 168.0(1)°, respectively. The distorted octahedral  $\text{Mg}^{2+}$  coordination environment probably stems from a combination of the steric requirements of the different ligands and the electronic demands placed upon the  $\mu_2$ -chloride and  $\mu_3$ -allyl ligands, which additionally bond either to one or two  $\text{Mg}^{2+}$  cations, respectively. In contrast to the irregularity of the octahedral coordination to magnesium, the precise three-fold symmetry of the trigonal bipyramidal  $[\text{Mg}_3\text{C}_2]$  core of  $[\mathbf{1}]^+$  is revealed through the Mg(1)–Mg(1A)–Mg(2) and Mg(1)–Mg(2)–Mg(1A) angles of 60.14(3) and 59.72(6)°, the Mg(1)–Mg(1A) and Mg(1)–Mg(2) separations of 2.926(3) and 2.939(2) Å, and the distances between the  $\text{Mg}_3$  mean plane and C(1) and C(4) of 1.208 and 1.210 Å. Although Mg–Mg bonding in

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‡ Electronic supplementary information (ESI) available: details of the crystal data and structure refinement of  $[\mathbf{1}]_2[\mathbf{2}]$  and  $\mathbf{3}$  in .cif format. See DOI: 10.1039/b602059c



**Fig. 1** (a) Structure of the cation  $[1]^+$ , hydrogen atoms omitted for clarity. Symmetry operator used to generate equivalent 'A' atoms =  $x, y, 1-z$ . Selected bond lengths (Å) and angles ( $^\circ$ ): Mg(1)–C(1) 2.082(4), Mg(1)–C(4) 2.089(3), Mg(2)–C(1) 2.085(4), Mg(2)–C(4) 2.083(5), C(1)–C(2) 1.423(10), C(2)–C(3) 1.374(19), C(4)–C(5) 1.342(12), C(5)–C(6) 1.320(13), Mg(1)–Cl(1) 2.5122(18), Mg(1)–Cl(2) 2.4965(18), Mg(2)–Cl(1) 2.5131(11), Mg(1)–O(1) 2.081(4), Mg(1)–O(2) 2.074(4), Mg(2)–O(3) 2.094(5), Mg(2)–O(4) 2.080(5), C(1)–Mg(1)–O(1) 170.0(1), C(4)–Mg(1)–O(2) 172.5(1), Cl(1)–Mg(1)–Cl(2) 168.5(1), C(1)–Mg(2)–O(4) 171.4(2), C(4)–Mg(2)–O(3) 170.7(1), Cl(1)–Mg(2)–Cl(1A) 168.0(1). (b) Structure of the anion  $[2]^{2-}$ . Hydrogen atoms omitted. Selected bond lengths (Å) and angles ( $^\circ$ ): Mg(3)–C(19) 1.996(8), C(19)–C(20) 1.538(17), C(20)–C(21) 1.113(12), Mg(3)–C(19)–C(20) 114.7(5), C(19)–C(20)–C(21) 143.9(17).

$[1]^+$  is highly unlikely the polyhedral arrangement of atoms in  $[1]^+$  means that this species is the first structurally authenticated cluster Grignard in which Mg–C bonding has been observed. The structures of the cationic clusters  $[Mg_3Br_4(OEt)(OEt_2)_6]^+$  are reminiscent of  $[1]^+$ , being based on an  $Mg_3$  triangle capped in this case by  $\mu_3$ -halide and -ethoxide ligands.<sup>10</sup> If considered as two face-sharing  $[Mg_3C]$  tetrahedra, the cluster is formally based on 4 centre–2 electron bonds in a manner that is reminiscent of the closely related, classic structures of the organolithiums  $(^nBuLi)_6$  and  $(^tBuLi)_4$ .<sup>11</sup> Further similarities between the structures of  $[1]^+$  and these important organolithiums are apparent since the  $\mu_3$ -allyl carbon atoms within the cation are also 6-coordinate. However, this is the first time that a  $\mu_3$ -bonding mode has been observed in a Main Group metal allyl complex.

The structure of the counter anion  $[2]^{2-}$  (Fig. 1b) is relatively simple in comparison to that of  $[1]^+$ ; the magnesium cation resides on a site with inversion symmetry at the centre of a tetrahedral coordination environment with respect to the symmetry-equivalent allyl groups. In the anion, the C–Mg–C bond angles are in the range 108.4(6)–110.5(6) and the Mg–C bond distance is 1.996(8) Å. The broader significance of the structure of  $[2]^{2-}$  stems from the fact that it is only the second crystallographically characterized example of an ion-separated tetraorganomagnesium 'ate' complex, with  $[Mg^tBu_4]^{2-}$  having been reported recently.<sup>12</sup> Although the bonding mode of the allyl ligand in  $[1]^+$  is highly unusual, the Mg–C bond distances do in fact fall within the range of 1.892–2.639 Å normally observed in organomagnesium compounds. This is also true of the Mg–C distances in  $[2]^{2-}$ , however these are somewhat shorter than the expected average distance of 2.173 Å.<sup>13</sup> In the structure of the related allyl Grignard  $[(C_3H_5)Mg$

$(tmeda)(\mu_2-Cl)_2$ , which contains an  $[MgCl]_2$  core, the allyl ligand adopts a terminal coordination position with the Mg–C distance of 2.179 Å being somewhat longer than the analogous distances in  $[1]^+$  and  $[2]^{2-}$ .<sup>3</sup> In the only other crystallographically characterised allylmagnesium, the unusual macrocyclic species  $[(N,N'$ -bis(2,6-diisopropylphenyl)- $\beta$ -diketiminate) $Mg(C_3H_5)]_6$ , the magnesium cations are bridged by  $\mu:\eta^1:\eta^1$ -allyl ligands and the Mg–C distances lie in the range 2.252–2.328 Å.<sup>14</sup>

Placing crystals of  $[1]_2[2]$  under high-vacuum (10 mbar) for 1–2 hours afforded a colourless powder. Due to the insolubility of the compound in non-coordinating solvents the  $^1H$  and  $^{13}C$  NMR spectra were recorded in pyridine- $d_5$  and found to contain a set of resonances characteristic of the allyl group. The relative simplicity of the spectra belies the elaborate solid-state structure of  $[1]^+$ , yet this is not unexpected since previous  $^1H$ ,  $^{13}C$  and  $^{25}Mg$  NMR investigations of organomagnesiums and Grignards have revealed that the ligands in these systems undergo rapid exchange in coordinating solvents and that several species may be present in solution simultaneously.<sup>2</sup> Furthermore, the ligand scrambling commonly observed in organoaluminiums coupled with the lability of Grignard reagents means that a mechanism (or mechanisms) accounting for the formation of  $[1]_2[2]$  would be particularly difficult to discern without very detailed extensions of this work. However, possible mechanistic insight may be obtained upon considering the composition of the core of  $[1]_2[2]$ , i.e.  $[R_8Mg_7Cl_6]$  ( $R = allyl$ ). The presence of 8 allyl groups suggests that  $[1]_2[2]$  may be regarded as a Grignard reagent deficient in  $MgCl_2$  and that  $MeAlCl_2$  probably acts as some sort of Lewis acid trap for chloride anion, resulting in the formation of a magnesium aluminate. As a further testament to the complicated solution-phase behaviour of

[1]<sub>2</sub>[2] we have observed that storage of saturated pyridine-*d*<sub>5</sub> solutions of [1]<sub>2</sub>[2] at room-temperature overnight affords diffraction quality crystals of *trans*-[MgCl<sub>2</sub>(py-*d*<sub>5</sub>)<sub>4</sub>] (**3**). Complex **3** crystallises in the triclinic space group *P*-1 with two independent molecules in the unit cell and with the Mg atoms residing on inversion centres.\*\* The structure of **3** is unremarkable since many examples of complexes of the type [MgX<sub>2</sub>(py)<sub>4</sub>] are known (see Supporting Information for salient structural parameters and diagram).<sup>15</sup> However, its formation is intriguing and is most likely due to it being the least labile and least soluble component of a mixture of several species, underlining the complicated solution-phase behaviour of organomagnesium compounds.

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## Notes and references

† All syntheses were conducted using standard Schlenk techniques under an inert atmosphere of dinitrogen.

**Synthesis of [1]<sub>2</sub>[2]:** A solution of MeAlCl<sub>2</sub> in hexane (1 M, 1.0 ml, 1.0 mmol) in thf (20 ml) was cooled to -78 °C and a solution of allylmagnesium chloride in thf (2 M, 1.5 ml, 3.0 mmol) was added dropwise over *ca.* 1 minute. The resulting mixture was warmed to room temperature and stirred for 12 hours, after which time the thf was removed *in vacuo* and replaced with an equal volume of ether. The clear solution was separated from the insoluble material by filtration (Celite, porosity 3). The solvent volume was reduced until the first signs of precipitation were observed and then thf was added dropwise until a homogeneous mixture was obtained. Storage of the solution at +5 °C overnight afforded colourless needles of [1]<sub>2</sub>[2] (1.10 g, 65%). Found: C, 53.29; H, 8.76; Calc. for C<sub>72</sub>H<sub>128</sub>Cl<sub>6</sub>Mg<sub>7</sub>O<sub>12</sub>: C, 55.13; H, 8.22%; we attribute the discrepancies to the air-sensitivity of this compound. δ<sub>H</sub> NMR (400.13 MHz, 298 K, pyridine-*d*<sub>5</sub>, *J*/Hz) 6.12 (1H, dd, <sup>3</sup>*J* = 17.2 and 10.4 Hz, *trans*-CH<sub>2</sub>:CH-CH<sub>2</sub>), 5.46 (1H, dm, <sup>3</sup>*J* = 17.2, *trans*-CH<sub>2</sub>:CH-CH<sub>2</sub>; <sup>2</sup>*J* = 2.0, *gem*-CH<sub>2</sub>:CH-CH<sub>2</sub>), 5.08 (1H, dm, <sup>3</sup>*J* = 10.4, *cis*-CH<sub>2</sub>:CH-CH<sub>2</sub>; <sup>2</sup>*J* = 2.0, *gem*-CH<sub>2</sub>:CH-CH<sub>2</sub>), 4.31 (2H, br m, CH<sub>2</sub>:CH-CH<sub>2</sub>), 3.57 (12H, m, thf), 1.55 (12H, m, thf). δ<sub>C</sub> (500.05 MHz, 298 K, pyridine-*d*<sub>5</sub>) 139.0 (CH), 112.6 (CH<sub>2</sub>:CH), 67.0 (thf), 62.2 (CH<sub>2</sub>:CH-CH<sub>2</sub>), 24.9 (thf).

§ In attempting to rationalize the surprising outcome of the reaction depicted in Scheme 1 we undertook an analysis of the ether-insoluble, colourless material. Microanalytical results were inconclusive but the <sup>1</sup>H NMR spectrum recorded in pyridine-*d*<sub>5</sub> displayed characteristic allyl resonances. The <sup>27</sup>Al NMR spectrum did not reveal the presence of any aluminium: our analysis of this system is ongoing.

¶ **Crystal data for [1]<sub>2</sub>[2]:** C<sub>72</sub>H<sub>136</sub>Cl<sub>6</sub>Mg<sub>7</sub>O<sub>12</sub>, F.W. = 1576.68, *T* = 230(2) K, orthorhombic, space group *Ibam*, *a* = 22.2467(4), *b* = 24.4885(5), *c* = 19.6433(4) Å, *V* = 10701.4(4) Å<sup>3</sup>, *Z* = 4, ρ(calc.) = 0.979 Mg m<sup>-3</sup>,

μ = 0.244 mm<sup>-1</sup>, *F*(000) = 3400, crystal size = 0.10 × 0.10 × 0.05 mm, θ range for data collection = 3.60–24.00°, a total of 27938 reflections were collected of which 4290 were unique (*R*<sub>int</sub> = 0.0543), 98.9% completeness to θ = 24.00°. The structure was solved by direct methods and refined by full-matrix least-squares on *F*<sup>2</sup> to final *R* indices [*I* > 2σ(*I*)] *R*1 = 0.1067, *wR*2 = 0.3094, *R* indices (all data) *R*1 = 0.1257, *wR*2 = 0.3278, largest diff. peak and hole 1.141 and -0.758 e Å<sup>-3</sup>. Further data collections were made for [1]<sub>2</sub>[2] at lower *T*, resulting in significantly greater overall structural disorder due to multiple site occupancies of coordinated thf molecules. CCDC 298100. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602059c

|| **Synthesis of 3:** Crystals of **3** were prepared in an NMR tube by heating a saturated solution of [1]<sub>2</sub>[2] in pyridine-*d*<sub>5</sub> and allowing it to cool slowly to room-temperature. Satisfactory elemental analysis was obtained.

\*\* **Crystal data for 3:** C<sub>20</sub>H<sub>20</sub>Cl<sub>2</sub>MgN<sub>4</sub>, FW = 411.61, *T* = 180(2) K, triclinic, space group *P*-1, *a* = 9.1636(2), *b* = 9.2462(2), *c* = 13.4528(3) Å, α = 74.8540(10), β = 78.9020(10), γ = 77.6580(10)°, *V* = 1063.47(4) Å<sup>3</sup>, *Z* = 2, density (calc.) = 1.285 Mg m<sup>-3</sup>, μ = 0.346 mm<sup>-1</sup>, *F*(000) = 428, crystal size = 0.42 × 0.28 × 0.23 mm, θ range for data collection = 3.66–27.53°, 12285 reflections collected with 4817 unique (*R*<sub>int</sub> = 0.0268), 98.4% completeness to θ = 27.53°. The structure was solved by direct methods and refined by full-matrix least-squares on *F*<sup>2</sup> to final *R* indices [*I* > 2σ(*I*)] *R*1 = 0.0505, *wR*2 = 0.1262, *R* indices (all data) *R*1 = 0.0576, *wR*2 = 0.1313, largest diff. peak and hole 0.408 and -0.357 e Å<sup>-3</sup>. CCDC 298101. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b602059c

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