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Unusual trimetallic magnesium cations and adamantyl anions of aluminum and gallium

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Dedicated to Professor Jerry L. Atwood on the occasion of his 60th birthday in appreciation of his outstanding contributions to organometallic chemistry

Abstract

Reaction of adamantylmagnesium bromide, AdaMgBr (Ada = $-C_{10}H_{15}$) with aluminum(III) chloride, gallium(III) chloride, dimethylgallium chloride, or dimethylaluminum chloride gives $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ (**I**), $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ (**II**), $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ (**III**), and $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2AlMe_2]$ (**IV**), respectively. These ionic compounds, characterized by ^{1}H- and ^{13}C-NMR, elemental analyses, and single crystal X-ray diffraction, contain trimetallic magnesium cations with each alkaline earth metal residing in a distorted octahedral environment. The aluminum and gallium atoms in the adamantyl-based anions reside in distorted tetrahedral environments. These substances are the first examples of adamantyl-based Group 13 organometallic compounds.

Keywords: Adamantane; Adamantylmagnesium bromide; Aluminum; Gallium

1. Introduction

To a certain extent the organometallic chemistry of aluminum and gallium has been shaped by a relatively small group of ligand systems. To be sure, the organometallic chemistry of the simple aluminum and gallium alkyls (R = Me, Et) has been extensively developed [1]. The corresponding organometallic chemistry of aluminum and gallium aryls has not developed in parallel with that of the alkyls. Indeed, the molecular structures of triphenylaluminum (di-μ-phenyl-bis(diphenylaluminum)) [2,3] and triphenylgallium [4] were only reported in the 1970s. Utilizing the sterically demanding mesityl ligand, reports of the syntheses and molecular structures of trimesitylaluminum [5] and trimesitylgallium [6], followed in the 1980s. Sterically demanding ligands played a critical role in the synthesis of the first compounds containing Al–Al [7] and Ga–Ga bonds [8]. In addition, sterically demanding ligands proved significant in the isolation of the first metalloaromatic compounds [9–12] and in the stabilization of the first compound reported to contain a Ga–Ga triple bond [13–15]. Ligands such as adamantyl present interesting possibilities in organometallic chemistry. Even though the adamantyl ligand has been examined in various aspects of organo-transition metal chemistry [16–18], it has not been significantly investigated relative to the Group 13 metals.

Chemists have long found both inspiration and fascination in the adamantane molecule. The symmetrical fusion of the cyclohexyl units of adamantane not only results in a virtually strain-free molecule [19], but this configuration also affords a uniquely beautiful and conceptually pleasing structural motif. Indeed, the first convenient synthesis of adamantane by Schleyer [20] in 1957 remains a significant accomplishment. Although the adamantyl ligand (Ada) has found some utility in organometallic compounds of phosphorus [21–23],

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silicon, germanium, and tin [24], it is surprising that it has not been more widely embraced as a viable ligand in the organometallic chemistry of the main group elements. In particular, the literature does not reveal any adamantyl derivatives of the Group 13 (III) metals. Herein, we report the syntheses and molecular structures of $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ (**I**), $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ (**II**), $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ (**III**) and $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2AlMe_2]$ (**IV**). These compounds, isolated from reaction of adamantylmagnesium bromide, AdaMgBr, with aluminum(III) chloride, gallium(III) chloride, dimethylgallium chloride, or dimethylaluminum chloride (Scheme 1) and characterized by ^{1}H- and ^{13}C-NMR, elemental analyses, and single crystal X-ray diffraction, are the first examples of adamantyl-Group 13 organometallic complexes.

2. Experimental

2.1. General comments

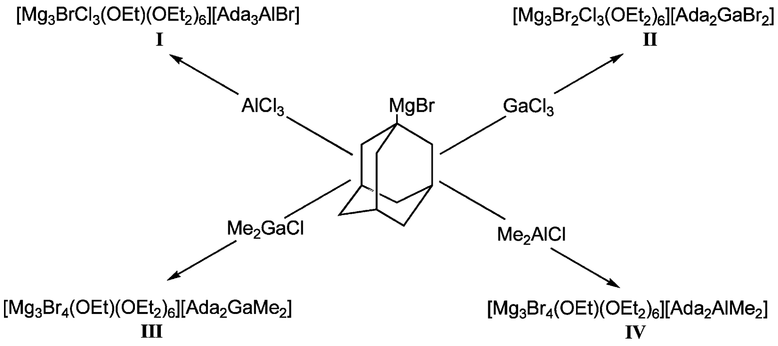
Standard Schlenk techniques were employed in conjunction with an inert atmosphere drybox (MBraun Labmaster 130). Solvents were distilled over sodium–potassium benzophenone under an atmosphere of nitrogen prior to use. Nitrogen was passed through copper-based purification and molecular sieve columns prior to use. Gallium(III) chloride was obtained from Strem Chemical Co. (Newburyport, MA) while bromoadamantane, aluminum(III) chloride, and dimethylaluminum chloride were purchased from Aldrich Chemical Co. (Milwaukee, WI). All reagents were used without further purification. Adamantylmagnesium bromide was prepared by reaction of bromoadamantane with magnesium metal in Et_2O [25]. The concentration of the Grignard reagent solution was determined using published methods [26]. Dimethylgallium chloride [27] was prepared as previously noted. E&R Microanalytical Laboratories (Parsipanny, NJ) performed the elemental analyses. Chemical shifts are reported in parts per million. Single crystal X-ray diffraction data were collected on a Bruker SMART^{TM} CCD instrument.

2.2. Synthesis of $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ (*I*)

Adamantylmagnesium bromide (100.00 ml, 0.10 M) in Et_2O was slowly added to a stirred solution of $AlCl_3$ (0.264 g, 2.00 mmol) in Et_2O at −78 °C. The solution was stirred for 15 h and allowed to warm to room temperature (r.t.). The solution was then refluxed for 3.5 h. After filtration, the solution was cooled to −30 °C and this afforded X-ray quality crystals. Yield: 34% (0.86 g; 0.68 mmol). M.p. 257 °C (dec.). Anal. Calc. (Found) for $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ ($C_{56}H_{110}AlBr_2Cl_3Mg_3O_7$): C, 53.30 (53.19); H, 8.80% (8.68). ^{1}H-NMR (400 MHz, 298 K, THF-d_8): δ 1.09 (t, 39H), $-OCH_2C\mathit{H}_3$; 1.60 (m, 18H), Ada; 1.69 (m, 18H), Ada; 1.83 (m, 9H), Ada; 3.36 (q, 26H), $-OC\mathit{H}_2CH_3$. ^{13}C-NMR (400 MHz, 298 K, THF-d_8): δ 15.8, $-OCH_2\mathit{C}H_3$; 30.4, $-Al-\mathit{C}_{Ada}$; 38.6, $-Al-C_{Ada}-\mathit{C}H_2-$; 40.4, $-Al-C_{Ada}-CH_2-\mathit{C}H-$; 43.4, $-Al-C_{Ada}-CH_2-CH-\mathit{C}H_2-$; 66.4, $-O\mathit{C}H_2CH_3$. The X-ray crystal structure of **I** is given in Fig. 1.

2.3. Synthesis of $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ (*II*)

Adamantylmagnesium bromide (100.00 ml, 0.127 M) in Et_2O was slowly added to a stirred solution of $GaCl_3$ (0.45 g, 2.55 mmol) in Et_2O at −78 °C. The solution was stirred for 15 h and allowed to warm to r.t. The solution was then refluxed for 3.5 h. After filtration, the solution was cooled to −30 °C and this afforded X-ray quality crystals. Yield: 36% (1.18 g; 0.92 mmol). M.p. 257 °C (dec.). Anal. Calc. (Found) for $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ ($C_{44}H_{90}Br_4Cl_3GaMg_3O_6$): Mg, 5.70 (5.62); Cl, 8.30 (8.57); Br, 24.90% (24.77). ^{1}H-NMR (400 MHz, 298 K, THF-d_8): δ 1.08 (t, 36H), $-OCH_2C\mathit{H}_3$; 1.63 (m, 12H), Ada; 1.69 (m, 12H), Ada; 1.79 (m, 6H), Ada; 3.35



Scheme 1.

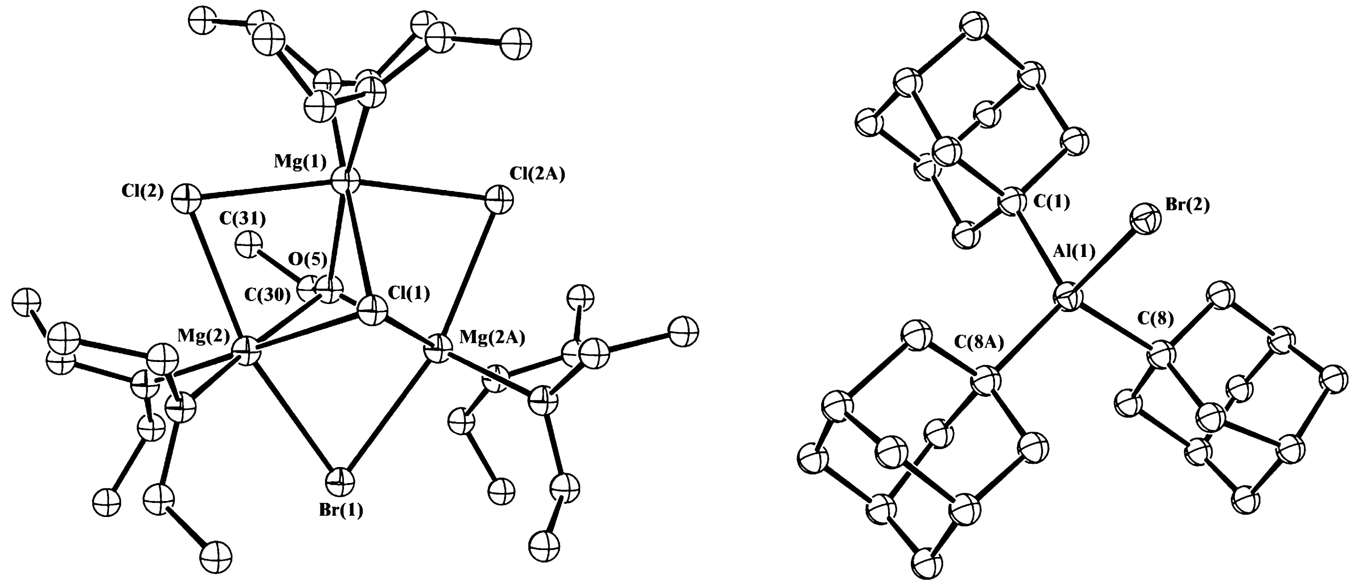


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Fig. 1. Molecular structure of $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ (**I**). Selected bond distances (Å) and angles (°): Mg(1)–Cl(1), 2.681(4); Mg(2)–Cl(1), 2.595(3); Mg(2A)–Cl(1), 2.595(3); Mg(1)–O(5), 2.122(7); Mg(2)–O(5), 2.100(5); Mg(2A)–O(5), 2.100(5); Al(1)–C(1), 2.041(10); Al(1)–C(8), 2.042(8); Al(1)–C(8A), 2.042(8); Al(1)–Br(2) 2.439(3); Cl(2)–Mg(1)–Cl(2A), 166.51(14); Cl(2)–Mg(2)–Br(1), 165.80(10); Cl(1)–Mg(2)–O(5), 77.64(19); Cl(1)–Mg(2)–Cl(2), 86.57(9); C(1)–Al(1)–C(8), 115.4(3); C(1)–Al(1)–C(8A), 115.4(3); C(8)–Al(1)–C(8A), 113.7(4); C(1)–Al(1)–Br(2), 102.3(3); C(8)–Al(1)–Br(2), 103.9(2); C(8A)–Al(1)–Br(2), 103.9(2).

(q, 24H), $-OCH_2CH_3$. ^{13}C-NMR (400 MHz, 298 K, THF-d_8): δ 15.7, $-OCH_2CH_3$; 30.4, $-Ga-C_{Ada}$; 39.6, $-Ga-C_{Ada}-CH_2-$; 42.4, $-Ga-C_{Ada}-CH_2-CH-$; 44.5, $-Ga-C_{Ada}-CH_2-CH-CH_2-$; 66.3, $-OCH_2CH_3$. The X-ray crystal structure of **II** is given in Fig. 2.

2.4. Synthesis of $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ (III)

Adamantylmagnesium bromide (100.00 ml, 0.15 M) in Et_2O was slowly added to a stirred solution of

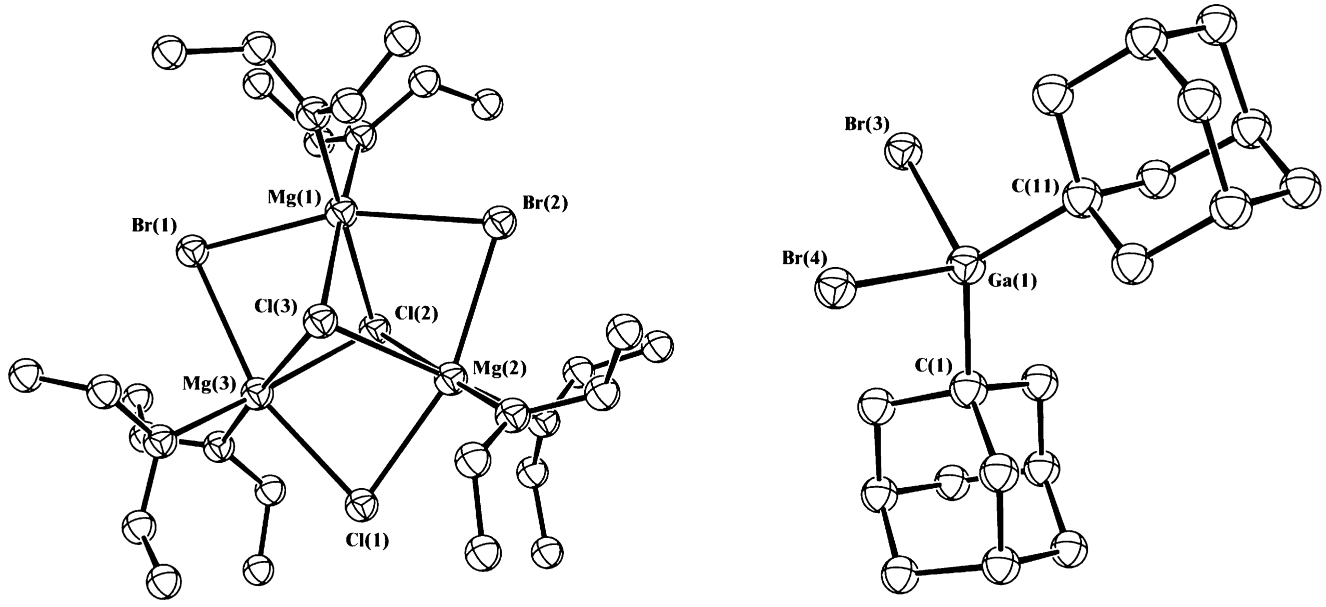

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Fig. 2. Molecular structure of $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ (**II**). Selected bond distances (Å) and angles (°): Mg(1)–Cl(2), 2.556(4); Mg(1)–Cl(3), 2.542(3); Mg(2)–Cl(2), 2.581(4); Mg(2)–Cl(3), 2.593(4); Mg(3)–Cl(2), 2.594(4); Mg(3)–Cl(3), 2.580(3); Ga(1)–C(1), 2.024(9); Ga(1)–C(11), 2.005(9); Ga(1)–Br(3), 2.4347(18); Ga(1)–Br(4), 2.4463(16); Br(1)–Mg(1)–Br(2) 162.19(12); Cl(1)–Mg(2)–Br(2) 161.90(12); Cl(1)–Mg(3)–Br(1) 161.27(12); Cl(2)–Mg(1)–Br(2), 83.27(10); Cl(3)–Mg(3)–Cl(2), 83.54(11); C(1)–Ga(1)–C(11) 126.2(4); C(1)–Ga(1)–Br(3) 106.7(3); C(11)–Ga(1)–Br(3) 104.6(3); C(1)–Ga(1)–Br(4) 104.6(3); C(11)–Ga(1)–Br(4) 107.3(3); Br(3)–Ga(1)–Br(4) 105.83(7).

Me_2GaCl (0.405 g, 3.00 mmol) in Et_2O at −78 °C. The solution was stirred for 15 h and allowed to warm to r.t. The solution was then refluxed for 3.5 h. After filtration the solution was cooled to −30 °C and this afforded X-ray quality crystals. Yield: 37% (1.39 g; 1.11 mmol). M.p. 260 °C (dec.). Anal. Calc. (Found) for $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ ($C_{48}H_{101}Br_4GaMg_3O_7$): C, 46.00 (45.96); H, 8.10 (8.21)%. ^{1}H-NMR (400 MHz, 298 K, THF-d_8): δ 0.10 (s, 6H), $-Ga-CH_3$; 1.11 (t, 39H), $-OCH_2CH_3$; 1.61 (m, 12H), Ada; 1.70 (m, 12H), Ada; 1.78 (m, 6H), Ada; 3.38 (q, 26H), $-OCH_2CH_3$. ^{13}C-NMR (400 MHz, 298 K, THF-d_8): δ 15.8, $-OCH_2CH_3$; 30.5, $-Ga-C_{Ada}$; 36.1, $-Ga-CH_3$; 38.5, $-Ga-C_{Ada}-CH_2-$; 40.0, $-Ga-C_{Ada}-CH_2-CH-$; 43.8, $-Ga-C_{Ada}-CH_2-CH-CH_2-$; 66.4, $-OCH_2CH_3$. The X-ray crystal structure of **III** is given in Fig. 3.

2.5. Synthesis of $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2AlMe_2]$ (IV)

Adamantylmagnesium bromide (100.00 ml, 0.15 M) in Et_2O was slowly added to a stirred solution of $AlMe_2Cl$ (0.277 g, 3.00 mmol) in Et_2O at −78 °C. The solution was stirred for 15 h and allowed to warm to r.t. The solution was then refluxed for 3.5 h. After filtration, the solution was cooled to −30 °C and this afforded X-ray quality crystals. Yield: 33% (1.20 g; 0.99 mmol). M.p. 260 °C (dec.). ^{1}H-NMR (400 MHz, 298 K, THF-d_8): δ 0.10 (s, 6H), $-Al-CH_3$; 1.11 (t, 39H), $-OCH_2CH_3$; 1.60 (m, 12H), Ada; 1.70 (m, 12H), Ada; 1.83 (m, 6H), Ada; 3.38 (q, 26H), $-OCH_2CH_3$. ^{13}C-NMR (400 MHz, 298 K, THF-d_8): δ 15.8, $-OCH_2CH_3$; 30.0, $-Al-C_{Ada}$; 36.2, $-M-CH_3$; 38.5, $-Al-C_{Ada}-CH_2-$; 39.8, $-Al-C_{Ada}-CH_2-CH-$; 42.7, $-Al-C_{Ada}-CH_2-CH-CH_2-$; 66.5, $-OCH_2CH_3$. The X-ray crystal structure of **IV** is given in Fig. 3.

2.6. X-Ray structural characterization

Crystals of compounds **I**, **II**, **III**, and **IV** were mounted in glass capillaries under an atmosphere of nitrogen in the drybox and flame-sealed upon exiting. X-ray intensity for all compounds were collected on a Bruker SMART^{TM} CCD diffractometer, with graphite-monochromatic Mo–K_α radiation ($\lambda = 0.710\ 73$ Å) at 21 °C. The structures of the compounds were solved using the SHELXTL package of computer programs [28]. All non-hydrogen atoms were placed at ideal positions riding on the attached carbon atoms without further refinement. The Et_2O and halides groups in **I** and **II** were observed to be disordered and appropriately

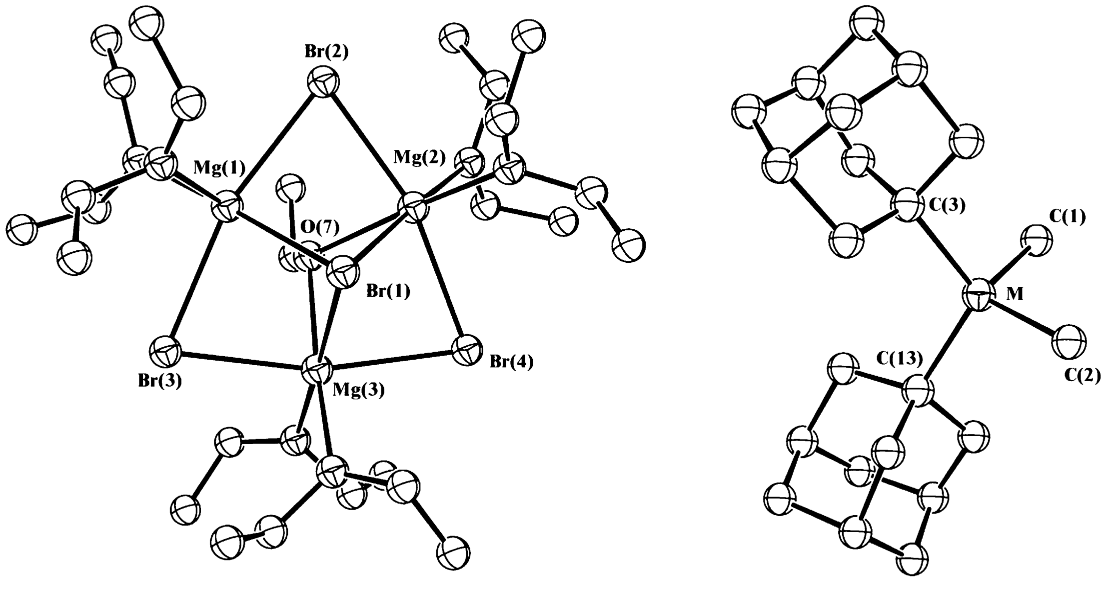

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Fig. 3. Molecular structure of $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2MMe_2]$, M = Ga, **III**. Selected bond distances (Å) and angles (°): Mg(1)–Br(1) 2.763(2); Mg(2)–Br(1) 2.7676(18); Mg(3)–Br(1) 2.768(2); Mg(1)–O(7) 2.107(4); Mg(2)–O(7) 2.124(4); Mg(3)–O(7) 2.123(4); Ga(1)–C(1), 2.031(7); Ga(1)–C(2), 2.038(6); Ga(1)–C(3), 2.058(6); Ga(1)–C(13), 2.039(5); Br(2)–Mg(2)–Br(4), 165.14(7); Br(2)–Mg(1)–Br(3), 164.98(7); Br(3)–Mg(3)–Br(4), 165.87(8); Br(1)–Mg(3)–O(7), 76.26(11); O(7)–Mg(1)–Br(1), 76.61(11); C(2)–Ga(1)–C(1), 107.9(4); C(13)–Ga(1)–C(1), 107.6(3); C(2)–Ga(1)–C(3), 109.6(3); C(13)–Ga(1)–C(3), 116.6(2); C(1)–Ga(1)–C(3), 107.7(3); C(2)–Ga(1)–C(13) 107.2(3). M = Al, **IV**. Selected bond distances (Å) and angles (°): Mg(3)–Br(1), 2.713(2); Mg(2)–Br(1), 2.703(2); Mg(1)–Br(1), 2.710(2); Mg(3)–O(7), 2.141(4); Mg(2)–O(7), 2.124(4); Mg(1)–O(7), 2.125(4); Al(1)–C(2), 2.012(8); Al(1)–C(3), 2.039(7); Al(1)–C(13), 2.029(7); Al(1)–C(1), 2.023(9); Br(3)–Mg(3)–Br(4), 165.58(9); Br(3)–Mg(2)–Br(2), 165.31(9); Br(1)–Mg(3)–Br(3), 165.06(9); Br(1)–Mg(3)–O(7), 76.93(13); O(7)–Mg(1)–Br(1), 77.26(13); C(2)–Al(1)–C(3), 109.2(3); C(2)–Al(1)–C(13), 107.9(3); C(3)–Al(1)–C(13), 115.5(3); C(2)–Al(1)–C(1), 108.5(5); C(3)–Al(1)–C(1), 107.8(4); C(13)–Al(1)–C(1), 107.8(4).

Table 1
Crystallographic data

	$[Mg_3BrCl_3(OEt)(OEt_2)_6]$-$[Ada_3AlBr]$ (**I**)	$[Mg_3Br_2Cl_3(OEt_2)_6]$-$[Ada_2GaBr_2]$ (**II**)	$[Mg_3Br_4(OEt)(OEt_2)_6]$-$[Ada_2GaMe_2]$ (**III**)	$[Mg_3Br_4(OEt)(OEt_2)_6]$-$[Ada_2AlMe_2]$ (**IV**)
Empirical formula	$C_{56}H_{110}AlBr_2Cl_3Mg_3O_7$	$C_{44}H_{90}Br_4Cl_3GaMg_3O_6$	$C_{48}H_{101}Br_4GaMg_3O_7$	$C_{48}H_{101}AlBr_4Mg_3O_7$
Formula weight	1261.52	1283.8	1252.58	1209.84
Color, habit	Colorless, plate	Colorless, cubic	Colorless, cubic	Colorless, cubic
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/m$ (No. 11)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Unit cell parameters				
a (Å)	11.528(2)	11.593(2)	13.220(3)	13.216(2)
b (Å)	19.322(4)	20.546(4)	14.270(3)	14.328(2)
c (Å)	15.494(3)	26.162(5)	17.580(4)	17.472(2)
α (°)			80.37(3)	80.242(3)
β (°)	101.257(4)	90.69(3)	79.67(3)	79.961(2)
γ (°)			79.20(3)	79.805(2)
V (Å^3)	3384.7(11)	6231(2)	3174.1(11)	3173.6(8)
Formula units/cell	2	4	2	2
D_{calc} (g cm^{-3})	1.238	1.368	1.311	1.266
Absorption coefficient (mm^{-1})	1.4	3.202	3.021	2.62
Maximum 2θ angle (°)	46.52	46.52	52.8	42.08
Reflections collected	14 807	31 827	21 289	13 320
Unique reflections	5023 ($R_{int} = 0.0658$)	8932 ($R_{int} = 0.0497$)	12898 ($R_{int} = 0.0326$)	6836 ($R_{int} = 0.0294$)
Refinement method	Least-squares on F^2	Least-squares on F^2	Least-squares on F^2	Least-squares on F^2
Parameters refined	370	645	589	589
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0709$	$R_1 = 0.0747$	$R_1 = 0.0612$	$R_1 = 0.0649$
	$wR_2 = 0.1771$	$Wr_2 = 0.2339$	$wR_2 = 0.1667$	$wR_2 = 0.1847$
Goodness-of-fit	$S = 1.019$	$S = 0.990$	$S = 1.018$	$S = 1.012$
Largest difference peak, hole (e Å^{-3})	0.919, −0.609	2.243, −1.206	1.019, −0.293	0.815, −0.274

modeled. Relevant crystallographic data for compounds **I**, **II**, **III**, and **IV** are given in Table 1.

3. Results and discussion

Adamantylmagnesium bromide reacts smoothly with the appropriate aluminum or gallium organometallic starting compound to give the ionic complexes $[Mg_3BrCl_3(OEt)(OEt_2)_6][Ada_3AlBr]$ (**I**), $[Mg_3Br_2Cl_3(OEt_2)_6][Ada_2GaBr_2]$ (**II**), $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2GaMe_2]$ (**III**), and $[Mg_3Br_4(OEt)(OEt_2)_6][Ada_2AlMe_2]$ (**IV**). The unusual trimetallic-magnesium cations common in all four cations warrant discussion. While the cations in all four compounds are quite similar containing a trimetallic $Mg_3(OEt_2)_6$ cluster, subtle differences exist. For example, cation **II** is the only one that does not have an ethoxy group at the center (apical position) of the cluster as it only contains halides (two bromine and three chlorine atoms) about the three magnesium atoms. In the remaining three cations an OEt group is opposite a halide (Br or Cl) atom. Cations **III** and **IV** are identical being composed only of four bromine atoms and one OEt group about the $Mg_3(OEt_2)_6$ framework. Indeed, identical cations would be expected as compounds **III** and **IV** were prepared from reaction of AdaMgBr with Me_2GaCl and Me_2AlCl, respectively. Cation **I** is distinctive as it is the only cation which contains a singular bromine atom in the cluster. The central oxygen atom in cations **I**, **III**, and **IV** are four-coordinate bonding to the three magnesium atoms and the Et group. It is significant that the three magnesium atoms in all four cations are six-coordinate residing in (distorted) octahedral environments. A similar tri-magnesium halide cation, $[Mg_3Cl_5(OEt_2)_6]^+$, isolated from Ga_2Cl_4–$MgCp^*_2$ [29] and i-Pr_3In–'MgBrCl' [30] systems, has been reported. Other Group 13 metallates have been reviewed [31].

The anion of compound **I**, $[Ada_3AlBr]^-$, is distinctive as the aluminum atom accommodates three adamantyl units at an Al–C_{ada} mean bond distance of 2.042(8) Å. This value compares well to the mean Al–C bond distance of 2.091 (4) Å observed for the *tert*-amylchloroaluminate $[(EtMe_2C)_3AlCl]^-$ anion [32]. Although there appears to be ample space to accommodate four adamantyl units about the aluminum center, we only isolated the triadamantyl derivative (from numerous experiments). The Al–Br bond distance is also rather long at 2.439(3) Å. The anion approximates C_3 symmetry. The C_{ada}–Al–C_{ada} bond angles are quite consistent at values of 115.4(3), 115.4(3), and 113.7(4)°. These values compare to 102.3(3), 103.9(2), and 103.9(2)° for the C_{ada}–Al–Br bond angles. Perhaps expectedly, the steric interactions between the adamantyl moieties are manifest in the angles about the bromine atom and the Al–Br bond.

The gallium atom in anion **II**, $[Ada_2GaBr_2]^-$, accommodates two adamantyl units at Ga–C bond distances of 2.024(9) and 2.005(9) Å and two bromine atoms at distances of 2.4347(18) and 2.4463(16) Å. Both the Ga–C (1.95(1) and 1.99(1) Å) and Ga–Br (2.402(2) and 2.402(2) Å) bond distances of the dibenzyldibromogallate anion, $[(PhCH_2)_2GaBr_2]^-$ [33], are comparable to those observed in **II**. For a measure of perspective, the Ga–Br bond (2.3284(1) Å) and the Ga–C bonds (1.988(6) and 1.984(6) Å) in the neutral tri-coordinate T-shaped $(Mes_2C_6H_3)_2GaBr$ [34] molecule are considerably shorter than those in **II**. It should also be noted that the C_{Ada}–Ga–C_{Ada} bond angle is considerably widened from the expected four-coordinate tetrahedral value to 126.2(4)°, even as the remaining bond angles about the gallium center are slightly contracted (106.7(3), 104.6(3), and 107.3(3)°). It should be noted that for both **I** and **II** anions, the reactions were initiated with aluminum chloride and gallium chloride. Yet, the halides observed in the anions are bromines with the chlorines being situated in the magnesium cluster cations. While the mechanism of formation of these ionic species remains unclear, this point is noteworthy.

The anions of **III**, $[Ada_2GaMe_2]^-$, and **IV**, $[Ada_2AlMe_2]^-$, differ only in the Group 13 metal center. The tetrahedral coordination spheres of the gallium and aluminum atoms are saturated with carbon atoms, two adamantyl groups and two methyl groups each. The mean Ga–C bond distance in $[Ada_2GaMe_2]^-$ of 2.035 Å compares well to 2.018 Å for the corresponding Al–C bond distance in $[Ada_2AlMe_2]^-$. As evidenced by a mean M–C ($M = Ga$ or Al) bond angle of 109.4° for both **III** and **IV**, the coordination about the metal atoms in these anions is virtually idealized tetrahedral. The M–C bond distances in **III** and **IV** are conveniently compared to other tetra-alkyl (or aryl)metallates of aluminum or gallium. For example, the Al–C bond distances in $[Et_4Al]^-$ (2.023 Å) [35] are quite comparable to those observed in **IV** while the corresponding Ga–C distances in $[(PhCH_2)_4Ga]^-$ (1.961(6) Å) [36] are shorter than observed for **III**. The mean M–C bond distance in the neutral Me_3M–carbene [37] ($M = Al$ and Ga) complexes (2.053 and 2.063 Å, for gallium and aluminum, respectively) compares well with the anions of **III** and **IV**.

That adamantyl has been shown to be a viable ligand in the organometallic chemistry of aluminum and gallium is significant. This study will serve as a benchmark as we continue to explore the organometallic chemistry of this ligand.

4. Supplementary material

Tables of atomic co-ordinates and anisotropic temperature factors are available as supplementary data. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 187037–187040 for compounds **I**, **II**, **III**, and **IV**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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