Chemical Reactivities of $[Me_2Al(\mu\text{-}NPr^i_2)_2MgMe]_4$ and $[Me_2Al(\mu\text{-}NEt_2)_2MgMe]_2$: Crystal Structures of $[Me_2Al(\mu\text{-}NPr^i_2)_2Mg(\mu\text{-}I)]_2$, $[Me_2Al(\mu\text{-}OBu^t)_2Mg(\mu\text{-}OBu^t)]_2$, $Me_2Al(\mu\text{-}NPr^i_2)(\mu\text{-}OEt)Mg(\mu\text{-}NPr^i_2)(\mu\text{-}OEt)AlMe_2$ and $Me_2Al(\mu\text{-}OBu^t)_2Mg(\mu\text{-}OBu^t_2)_2AlMe_2$†

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The nucleophilic attack of alcohols, amines and iodine on the magnesium atoms of $[Me_2Al(\mu\text{-}NPr^i_2)_2MgMe]_4$ **A** and $[Me_2Al(\mu\text{-}NEt_2)_2MgMe]_2$ **B** has been investigated. Compound **A** undergoes metathesis with amines (Et_2NH and Pr^i_2NH) and iodine to give $[Me_2Al(\mu\text{-}NPr^i_2)_2Mg(\mu\text{-}NR_2)]$(R = Et **7** or Pr^i **4**) and $[Me_2Al(\mu\text{-}NPr^i_2)_2Mg(\mu\text{-}I)]_2$ **5**, respectively. Partial degradation of **A** with MeOH or ethanol gives $Me_2Al(\mu\text{-}NPr^i_2)(\mu\text{-}OMe)Mg(\mu\text{-}NPr^i_2)(\mu\text{-}OMe)AlMe_2$ **1a** and $[Me_2Al(\mu\text{-}NPr^i_2)(\mu\text{-}OEt)Mg(\mu\text{-}NPr^i_2)(\mu\text{-}OEt)AlMe_2$ **1b**, respectively, whereas partial degradation with Bu^tOH gives $Me_2Al(\mu\text{-}OBu^t)_2Mg(\mu\text{-}OBu^t)_2AlMe_2$ **2** and $[Me_2Al(\mu\text{-}OBu^t)_2Mg(\mu\text{-}OBu^t)]_2$ **3**. Compound **B** undergoes metathesis with Bu^tOH also to give **2** and **3**. The intermediate, $Me_2Al(\mu\text{-}NR_2)_2Mg(\mu\text{-}Me)(\mu\text{-}OBu^t)Mg(\mu\text{-}NR_2)_2AlMe_2$ **I** in the reactions of **A** and **B** with Bu^tOH is also examined. The molecular structures of compounds **1b**, **2**, **3** and **5** were determined by X-ray diffraction.

The dialuminium organomagnesium complexes $Mg[Al(OMe)_2Me_2]_2$ and $Mg(AlMe_4)_2$[1,2] are among the best known examples of mixed-metal organoaluminium complexes[1-4] and are applied as catalysts in the polymerization of ethylene.[5] Even so, the first crystal structure of a monoaluminium magnesium dimer, $[(Me_2Si)(Me_2Al)(\mu\text{-}NBu^t)_2MgI]_2$, was not reported until 1987.[6] Recently, we synthesised and determined the crystal structures of an organoaluminium–magnesium tetramer $[Me_2Al(\mu\text{-}NPr^i_2)_2MgMe]_4$ **A** and a dimer $[Me_2Al(\mu\text{-}NEt_2)_2MgMe]_2$ **B** which contain three- and four-co-ordinate magnesium atoms, respectively.[7] During the course of our work, Han and Parkin[8] reported that the compounds $MgMe[HB(C_3N_2H_2Bu^t\text{-}3)_3]$ and $MgMe[HB(C_3N_2HMe_2\text{-}3,5)_3]$,[8] when treated with nucleophiles, undergo metathesis and insertion reactions. They also found that the latter compound undergoes redistribution upon heating, yielding a six-co-ordinate organomagnesium complex.[9] The present work concerns the reactions of ROH (R = Me, Et or Bu^t) and HNR_2 (R = Et or Pr^i) with aluminium–magnesium complexes. The metathesis and insertion reactions are similar to those of compounds previously reported by Han and Parkin. However, this study yielded interesting results due to the rich co-ordination chemistry[10] and the partially positive magnesium centres.[11]

Results and Discussion

The polymeric derivatives $[Me_2Al(\mu\text{-}NR_2)_2MgMe]_n$ (R = Et, $n = 2$ **B**; R = Pr^i, $n = 4$ **A**) were synthesised according to equation (1). The stoichiometric reaction of compounds **A** and **B** with protic acids were then studied, as described in the following sections.

$$Mg(NR_2)_2 + AlMe_3 \longrightarrow [Me_2Al(\mu\text{-}NR_2)_2MgMe]_n \quad (1)$$

Preparations.—Reaction of equimolar quantities of compound **A** and MeOH in diethyl ether gave a pale yellow solution from which $Me_2Al(\mu\text{-}NPr^i_2)(\mu\text{-}OMe)Mg(\mu\text{-}NPr^i_2)(\mu\text{-}OMe)AlMe_2$ **1a** can be isolated by sublimation of the reaction mixture at 100 °C. The compound is colourless, soluble in benzene and very air-sensitive. However, the quality of the crystal was not suitable for X-ray diffraction. In order to elucidate the structure, the reaction of compound **A** with EtOH was carried out in the same manner and a viscous fluid was obtained. Transparent colourless crystals of $Me_2Al(\mu\text{-}NPr^i_2)(\mu\text{-}OEt)Mg(\mu\text{-}NPr^i_2)(\mu\text{-}OEt)AlMe_2$ **1b** suitable for X-ray diffraction were obtained by sublimation at 78 °C. The residues were insoluble, and are expected to comprise polymeric $Mg(OR)_2$ coproducts.

The reaction of an excess of Bu^tOH with compound **A** yielded $Me_2Al(\mu\text{-}OBu^t)_2Mg(\mu\text{-}OBu^t)_2AlMe_2$ **2** and $[Me_2Al(\mu\text{-}OBu^t)_2Mg(\mu\text{-}OBu^t)]_2$ **3** in nearly equal amounts, whereas that with **B** only yielded **3** according to ^1H NMR spectroscopy. Sublimation of the reaction mixture from the reaction of **B** with Bu^tOH at 120 °C *in vacuo* gave **3** and a smaller amount of **2**. However, sublimation of the mixture from the reaction of **A** with Bu^tOH at 100 °C *in vacuo* gave only **2**. An experiment on the pyrolysis of **3** gave no evidence of compound **2**.

Reaction of compound **A** with diisopropylamine in diethyl ether gave a light yellow solution. The reaction mixture was refluxed for 36 h. The crude product crystallized from ether was $[Me_2Al(\mu\text{-}NPr^i_2)_2Mg(\mu\text{-}NPr^i_2)]_2$ **4** in addition to methane. The ^1H NMR spectrum in C_6D_6 showed one singlet at δ −0.40, one quartet at δ 1.21, one doublet at δ 1.25 and one multiplet at δ 3.28. The ^{13}C NMR spectrum in C_6D_6 gave peaks at δ −2.94, 25.95, 26.16, 28.00, 47.74 and 48.57. This indicated compound **4** had two sets of isopropyl groups. Reaction of compound **A** with diethylamine in the same manner gave a light yellow solution. The product $[Me_2Al(\mu\text{-}NPr^i_2)_2Mg(\mu\text{-}NEt_2)]_2$ **7** was detected

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† *Supplementary data available:* see instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

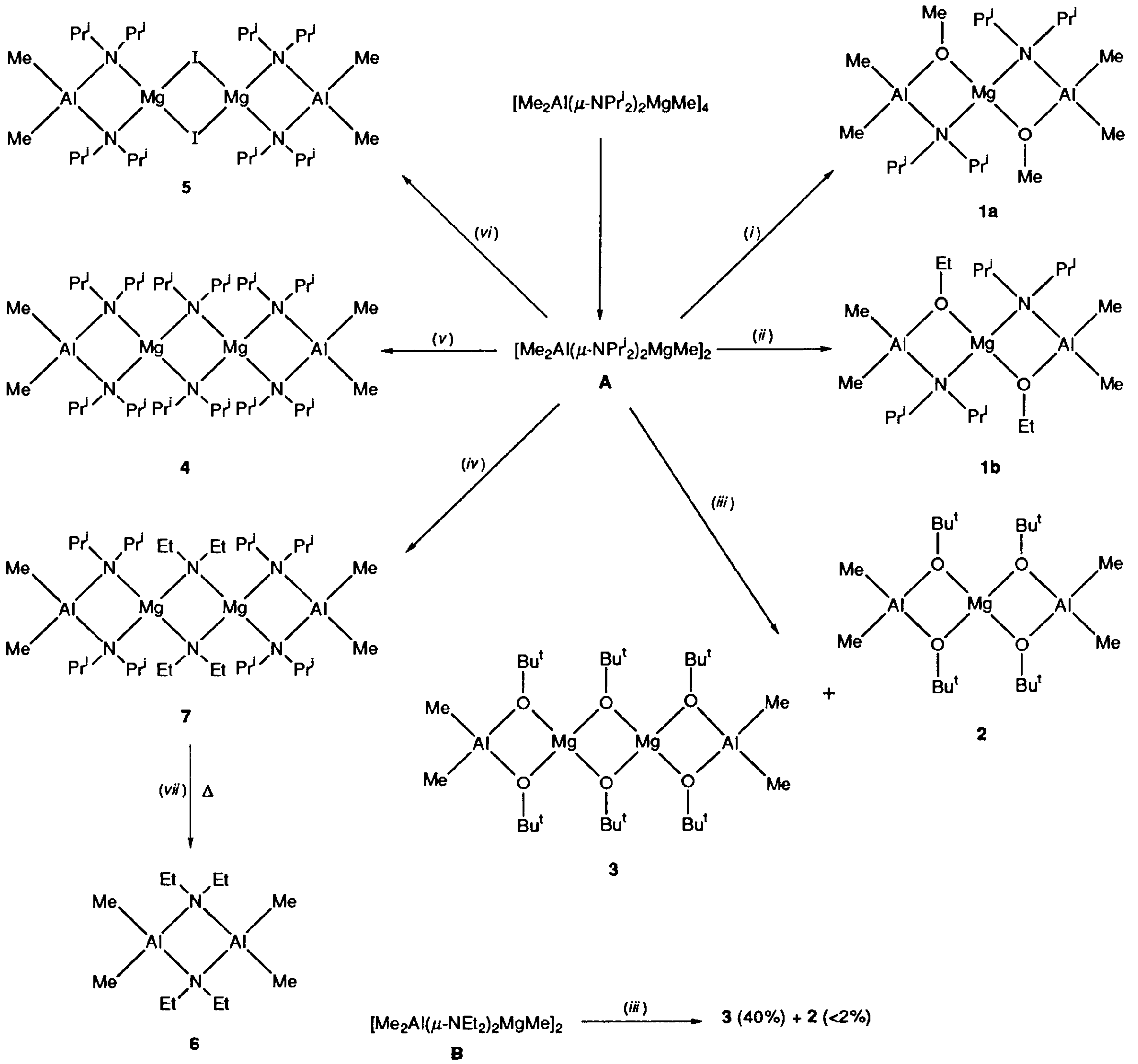
by ^{1}H and ^{13}C NMR spectroscopy at low temperature, however the only [Me$_2$Al(μ-NEt$_2$)]$_2$ **6** was obtained after sublimation.

The reaction of compound **A** with I$_2$ in diethyl ether gave a light yellow solution. The crude product contained [Me$_2$Al(μ-NPr$^i_2$)$_2$Mg(μ-I)] **5** and MeI in low yield owing to precipitation of MgI$_2$. Sublimation of the crude product at 120 °C yielded transparent colourless crystals of **5** suitable for X-ray analysis. In order to achieve a good yield of compound **5** the reaction was repeated in benzene and gave a nearly quantitative yield. The ^{1}H NMR spectrum in C$_6$D$_6$ showed one singlet at δ −0.26, two doublets at δ 1.23 and 1.31 and one septet at δ 3.53. The ^{13}C NMR spectrum in C$_6$D$_6$ gave peaks at δ −3.73, 26.67, 27.30 and 48.05. This indicated that two methyls of the isopropyl group had different environments.

Metathesis Reactions.—Compounds **A** and **B** are useful precursors to a wide variety of other mixed aluminium–magnesium derivatives as a result of metathesis. Reaction of these complexes with protic reagents is accompanied by elimination of methane and amine, as shown in Scheme 1.

Reaction of compound **A** with diethylamine or diisopropylamine gave respectively **7** and **4** in addition to methane. The product **7** was detected by ^{1}H and ^{13}C NMR spectroscopy at low temperature, however only **6** was obtained after sublimation. Compound **4** decomposed during X-ray data collection. Its structure is expected to retain the Al$_2$Mg$_2$ framework in compound **5**. Reaction of compound **B** with Bu^{t}OH yielded compound **3** in addition to methane and amine. Interestingly, the metathesis reaction occurred not only at the magnesium–alkyl bond, but also at the amido-bridge as evidenced by X-ray crystallography (see Fig. 1). Selected bond lengths and angles for the two independent molecules A and B of **3** are given in Table 1. Each molecule possesses an inversion centre. The whole molecule contains three orthogonal metal–(μ-O)–metal planes. The Al–Mg–Mg–Al backbone is almost linear as evidenced by the 178.44° angle of Al(1A)–Mg(1A)–Mg(1A′). The Al and Mg atoms exist in a distorted-tetrahedral environment with the distance Mg(1A)–O(1A) 1.953(7) Å being shorter than Mg(1A)–O(2A) 2.043(8) Å and Mg(1A)–O(3A) 2.033(8) Å. The Al(1A)$\cdots$Mg(1A) 2.888(5) Å and Mg(1A)$\cdots$Mg(1A) 2.886(7) Å distances are much shorter than the sum of van der Waals radii. Overlap between the metal and bridging ligand orbitals, *i.e.* d$_\pi$–p$_\pi$ interactions between Al and O atoms and p$_\pi$–p$_\pi$ interactions between Mg and O atoms, is expected.[13]

Metathesis reactions are observed with non-protic reagents such as iodine and oxygen in other systems.[9] The reaction of compound **A** with I$_2$ gave **5** and MeI in nearly quantitative yield. Compound **5** exists as a dimer with an inversion centre in the middle of the molecule as shown in Fig. 2. Selected bond



Scheme 1 Compound **A** was identified in solution, **7** by NMR spectroscopy. (*i*) MeOH; (*ii*) EtOH; (*iii*) Bu^{t}OH; (*iv*) Et$_2$NH; (*v*) Pr$^i_2$NH; (*vi*) I$_2$; (*vii*) heat

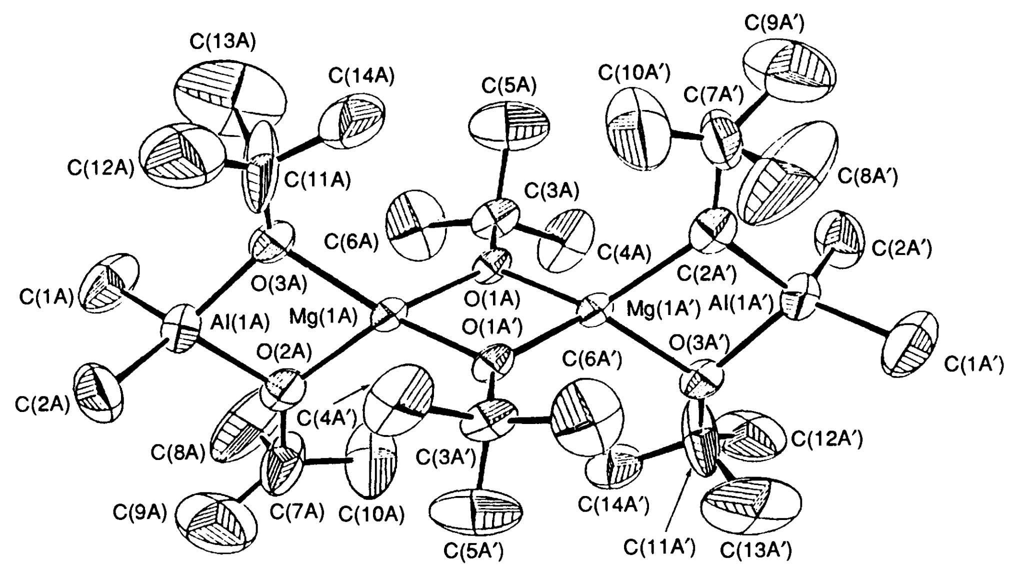


Fig. 1 An ORTEP[12] drawing of [Me$_2$Al(μ-OBu^t)$_2$Mg(μ-OBu^t)]$_2$ **3**

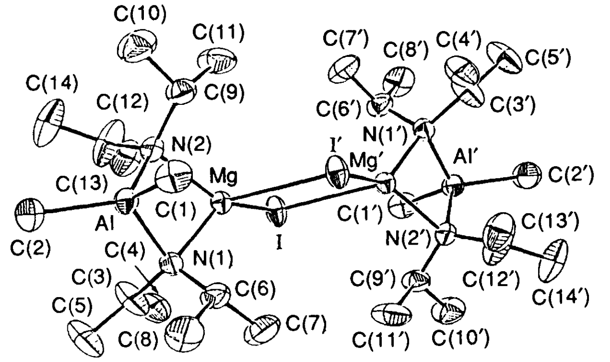


Fig. 2 An ORTEP drawing of [Me$_2$Al(μ-NPr$^i_2$)$_2$Mg(μ-I)]$_2$ **5**

distances and angles are given in Table 1. Note that the Al and Mg atoms exist in a distorted-tetrahedral environment, and that the Mg, I, Mg', I' atoms form an asymmetric coplanar four-membered ring in a spiro structure. Also that the Al, N(1), Mg and N(2) atoms form a non-coplanar four-membered ring. The N(1)–Al–N(2), N(1)–Mg–N(2) and I–Mg–I' angles are 94.78, 86.18 and 88.66°, respectively, all less than 109.5°.

Partial Degradation.—Although the amido ligands in compound **A** are highly nucleophilic and metathesis is expected, reaction with alcohol proceeded with partial degradation to dialuminium–magnesium complexes. The rate of the reaction is much faster than that of the metathesis reaction.

Reaction of compound **A** with methanol or ethanol gave **1a** and **1b** in addition to methane and amine. In each case the methyl groups on the magnesium atoms disappear and one of the bridging amido ligands is replaced by the alcohol. The structure of compound **1b** is shown in Fig. 3. Selected bond angles and bond distances are given in Table 1. Note that the Al(1), N(1), O(1), Mg and Al(2), N(2), P(2), Mg atoms form two coplanar four-membered rings in the spiro structure. Owing to the different bridging ligands, the Al(1)–Mg–Al(2) angle of 150° denotes strong bending when compared with the structures of compounds **3**–**5**, in which Al–Mg–Mg and Al–Mg–Al are very nearly 180°. The Mg atom of compound **1b** exists in a strongly distorted-tetrahedral environment, as evidenced by O(1)–Mg–N(1) and O(2)–Mg–N(2) angles of 80.2(3) and 79.9(3)°, respectively; the geometry is dictated by the strong repulsion of the isopropyl group. The Al(1)···Mg and Al(2)···Mg distances of 2.875(5) and 2.877(5) Å are short as is usual in compounds in which metals are bridged by donor atoms.

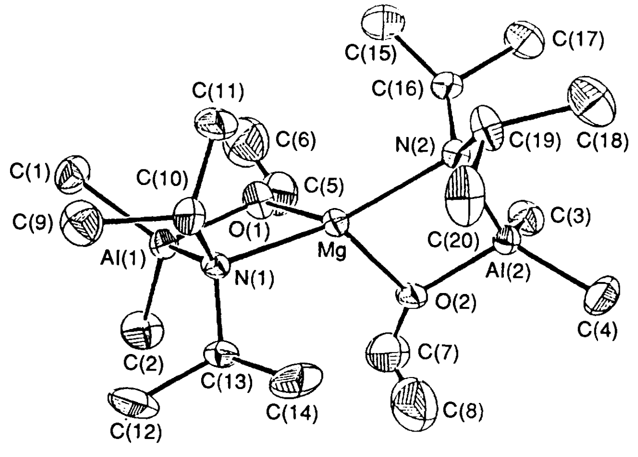


Fig. 3 An ORTEP drawing of Me$_2$Al(μ-NPr$^i_2$)(μ-OEt)Mg(μ-NPr$^i_2$)(μ-OEt)AlMe$_2$ **1b**

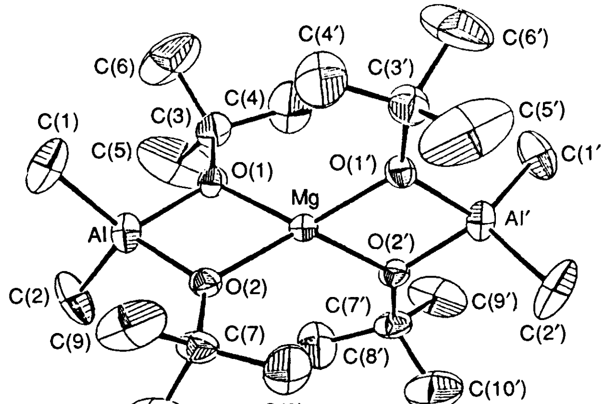


Fig. 4 An ORTEP drawing of Me$_2$Al(μ-OBu^t)$_2$Mg(μ-OBu^t)$_2$AlMe$_2$ **2**

The highly nucleophilic and bulky Bu^{t}OH reacts with compound **A** to give **2** in addition to methane and amine. In contrast to the products obtained in the reactions with methanol and ethanol, the amido ligand is completely replaced. The structure of compound **2**, with crystallographic C_2 symmetry, is shown in Fig. 4. Selected bond angles and bond distances are listed in Table 1. Note that the spiro structure consists of two planes, formed by the AlO(1)–O(2)Mg atoms, and that the Al and Mg atoms also exist in a distorted-tetrahedral environment.

Table 1 Selected bond distances (Å) and angles (°)

$Me_2Al(\mu\text{-}NPr^i{}_2)(\mu\text{-}OEt)Mg(\mu\text{-}NPr^i{}_2)(\mu\text{-}OEt)AlMe_2$ **1b**

Mg···Al(1)	2.875(5)	Al(1)–N(1)	1.944(1)	O(1)–C(5)	1.520(2)	C(5)–C(6)	1.22(3)*
Mg–N(1)	2.162(8)	Al(1)–O(1)	1.805(8)	N(1)–C(10)	1.46(1)	C(9)–C(10)	1.53(2)
Mg–O(1)	1.931(9)	Al(1)–C(1)	1.94(1)				
Al(1)–Mg–Al(2)	150.1(2)	C(1)–Al(1)–C(2)	110.3(6)	O(1)–Al(1)–N(1)	89.6(4)	Mg–N(1)–C(13)	107.7(6)
O(1)–Mg–O(2)	109.7(4)	Mg–O(1)–Al(1)	100.6(4)	O(1)–Al(1)–C(1)	110.8(5)	Al(1)–N(1)–C(10)	119.0(6)
O(1)–Mg–N(1)	80.2(3)	Mg–O(1)–C(5)	126.5(7)	O(1)–Al(1)–C(2)	109.3(6)	Al(1)–N(1)–C(13)	111.3(7)
O(1)–Mg–N(2)	122.0(3)	Al(1)–O(1)–C(5)	124.6(8)	N(1)–Al(1)–C(1)	120.5(5)	C(10)–N(1)–C(13)	114.8(8)
O(2)–Mg–N(1)	119.8(3)	Mg–N(1)–Al(1)	88.7(4)	N(1)–Al(1)–C(2)	114.2(5)	O(1)–C(5)–C(6)	106(2)
O(2)–Mg–N(2)	79.9(3)	Mg–N(1)–C(10)	111.9(6)	C(9)–C(10)–C(11)	108(1)	N(1)–C(10)–C(9)	115.5(9)
N(1)–Mg–N(2)	145.5(4)						

$Me_2Al(\mu\text{-}OBu^t)_2Mg(\mu\text{-}OBu^t)_2AlMe_2$ **2**

Mg···Al	2.836(2)	Al–O(2)	1.815(5)	Mg–O(2)	1.941(4)	O(1)–C(3)	1.422(8)
Mg–O(1)	1.942(4)	Al–C(1)	1.943(8)	Al–O(1)	1.807(5)	C(3)–C(4)	1.422(1)
Al–Mg–Al′	179.3(2)	Mg–O(1)–Al	98.2(2)	O(1)–Al–O(2)	85.3(2)	Al–O(1)–C(3)	130.5(4)
O(1)–Mg–O(1′)	126.0(3)	Mg–O(2)–Al	98.0(2)	O(1)–Al–C(1)	113.8(4)	O(1)–C(3)–C(4)	111.8(6)
O(1)–Mg–O(2)	78.4(2)	Mg–O(1)–C(3)	131.3(4)	O(1)–Al–C(2)	111.5(3)		

$[Me_2Al(\mu\text{-}OBu^t)_2Mg(\mu\text{-}OBu^t)]_2$ **3**

Al(1A)···Mg(1A)	2.888(5)	Mg(1A)–O(2A)	2.043(8)	Al(1B)···Mg(1B)	2.895(6)	Mg(1B)–O(2B)	2.035(8)
Al(1A)–O(2A)	1.855(8)	O(1A)–C(3A)	1.41(1)	Al(1B)–O(2B)	1.870(9)	O(1B)–C(3B)	1.41(1)
Al(1A)–C(1A)	1.96(2)	O(2A)–C(7A)	1.31(2)	Al(1B)–C(1B)	1.95(2)	O(2B)–C(7B)	1.27(2)
Mg(1A)···Mg(1A′)	2.886(7)	C(3A)–C(4A)	1.46(2)	Mg(1B)...Mg(1B)	2.901(8)	C(3B)–C(4B)	1.43(2)
Mg(1A)–O(1A)	1.953(7)	C(7A)–C(8A)	1.40(3)	Mg(1B)–O(1B′)	1.979(8)	C(7B)–C(8B)	1.36(3)
Mg(1A)–O(1A)	1.955(7)			Mg(1B)–O(1B)	1.952(8)		
O(2A)–Al(1A)–O(3A)	89.2(3)	Al(1A)–O(2A)–C(7A)	130.7(8)	O(2B)–Al(1B)–O(3B)	88.1(4)	Al(1B)–O(2B)–C(7B)	130.0(8)
O(2A)–Al(1A)–C(1A)	111.7(5)	Mg(1A)–O(2A)–C(7A)	132.7(8)	O(2B)–Al(1B)–C(1B)	113.0(6)	Mg(1B)–O(2B)–C(7B)	132.6(8)
C(1A)–Al(1A)–C(2A)	116.0(7)	Al(1A)–O(3A)–Mg(1A)	96.3(4)	C(1B)–Al(1B)–C(2B)	114.9(8)	Al(1B)–O(3B)–Mg(1B)	96.8(4)
O(1A)–Mg(1A)–O(1A′)	84.8(3)	Al(1A)–O(3A)–C(11A)	133.2(8)	O(1B)–Mg(1B)–O(1B′)	84.8(3)	Al(1B)–O(3B)–C(11B)	128(1)
O(1A)–Mg(1A)–O(2A)	124.1(3)	Mg(1A)–O(3A)–C(11A)	129.7(8)	O(1B)–Mg(1B)–O(2B)	126.4(4)	Mg(1B)–O(3B)–C(11B)	130(1)
O(1A)–Mg(1A)–O(3A)	126.0(3)	O(1A)–C(3A)–C(4A)	110(1)	O(1B)–Mg(1B)–O(3B)	122.5(4)	O(1B)–C(3B)–C(4B)	112(1)
O(2A)–Mg(1A)–O(3A)	79.0(3)	C(4A)–C(3A)–C(5A)	110(1)	O(2B)–Mg(1B)–O(3B)	79.1(3)	C(4B)–C(3B)–C(5B)	105(2)
Mg(1A)–O(1A)–Mg(1A′)	95.2(3)	O(2A)–C(7A)–C(8A)	121(2)	Mg(1B)–O(1B)–Mg(1B′)	95.2(3)	O(2B)–C(7B)–C(8B)	125(2)
Mg(1A)–O(1A)–C(3A)	131.7(6)	C(8A)–C(7A)–C(9A)	109(2)	Mg(1B)–O(1B)–C(3B)	130.3(7)	C(8B)–C(7B)–C(9B)	107(2)
Al(1A)–O(2A)–Mg(1A)	95.5(4)			Al(1B)–O(2B)–Mg(1B)	95.6(3)		

$[Me_2Al(\mu\text{-}NPr^i{}_2)_2Mg(\mu\text{-}I)]_2$ **5**

I′–Mg	2.831(2)	Al–C(1)	1.961(6)	Al···Mg	2.800(2)	N(1)–C(3)	1.486(7)
I–Mg	2.783(2)	Mg–N(1)	2.114(4)	Al–N(1)	1.962(4)	C(3)–C(4)	1.440(9)
Mg–I–Mg′	91.34(5)	Al–N(1)–Mg	86.7(2)	C(1)–Al–C(2)	111.5(3)	C(3)–N(1)–C(6)	115.5(4)
N(1)–Al–N(2)	94.78(2)	Al–N(1)–C(3)	114.7(4)	I–Mg–I′	88.66(5)	N(1)–C(3)–C(4)	119.3(5)
N(1)–Al–C(1)	108.2(2)	Mg–N(1)–C(3)	112.6(3)	N(1)–Mg–N(2)	86.2(2)	C(4)–C(3)–C(5)	115.7(5)
N(1)–Al–C(2)	116.0(2)						

* This very low value is attributed to structural disorder.

Possible Intermediate.—The ^1H NMR spectrum of the reaction mixture resulting from compound **A** and Bu^tOH in a 1 : 1 molar ratio is shown in Fig. 5. The peaks P_{e1} and P_{e2} are due to the 'released' diisopropylamine, while P_{A1} and P_{A2}, P_{B1} and P_{B2}(d) arise from compounds **2** and **3**, respectively. The P_d peak is assumed to be due to the 'released' methane, since it disappeared after the reaction mixture had been pumped under vacuum. The peaks I_1 (δ −0.80), I_2(δ −0.34), I_3(δ −0.18), I_4(d) (δ 1.37), I_5(δ 2.79) (the low-intensity septet in the area denoted 'X'), I_6(δ 3.64) and I_7(δ 1.41) are from the intermediate (**I**) and originate, respectively, from the methyl attached to the magnesium atoms, the different environments of the two methyls attached to the respective aluminium atoms, the methyl and methine group in the amino group, and the *tert*-butoxide group. Also note that the two low-intensity peaks, P_{c1}(δ −0.27) and P_{c2}(δ 1.35) (in the area denoted as 'y') are expected to be due to the dimethylaluminium *tert*-butoxide. A determination of the reaction kinetics was unsuccessful due to the rapidity and complicated system.

Finally from the chemical reactivities of compound **A** and **B** with amines and alcohols in a nitrogen-atmosphere flow system it can be concluded that the less volatile alcohols/secondary amines will displace more volatile alcohols/amines completely. Thus all $Pr^i{}_2NH$ is displaced by Bu^tOH, but by MeOH, EtOH or Et_2NH is only partially displaced.

Experimental

Apparatus and Materials.—All manipulations were carried out in a N_2-flushed glove-bag, dry-box, or vacuum system. Solvents were distilled and degassed prior to use. All ^1H, ^{13}C and ^{27}Al NMR spectra were measured on a Varian VXR-300 spectrometer. Chemical shifts are referenced relative to either $SiMe_4$(^1H) or C_6D_6(^1H, δ 7.15; $^{13}C\text{-}\{^1H\}$, δ 128.00), while ^{27}Al NMR spectra were referenced to $[Al(H_2O)_6]^{3+}$. Mass spectral data were obtained on a VG-7025 GC/MS/MS spectrometer, IR spectra as Nujol mulls between KBr disks on a FT-IR spectrometer. Elemental analyses (C, H, N) were performed at the Analytische Laboratorien, Germany. Deviations in the results from calculated values are attributed to the extremely air-sensitive and hygroscopic nature of these compounds.

The starting materials $[Me_2Al(\mu\text{-}NPr^i{}_2)_2MgMe]_4$ **A** and $[Me_2Al(\mu\text{-}NEt_2)_2MgMe]_2$ **B**, were prepared according to the literature method.[7]

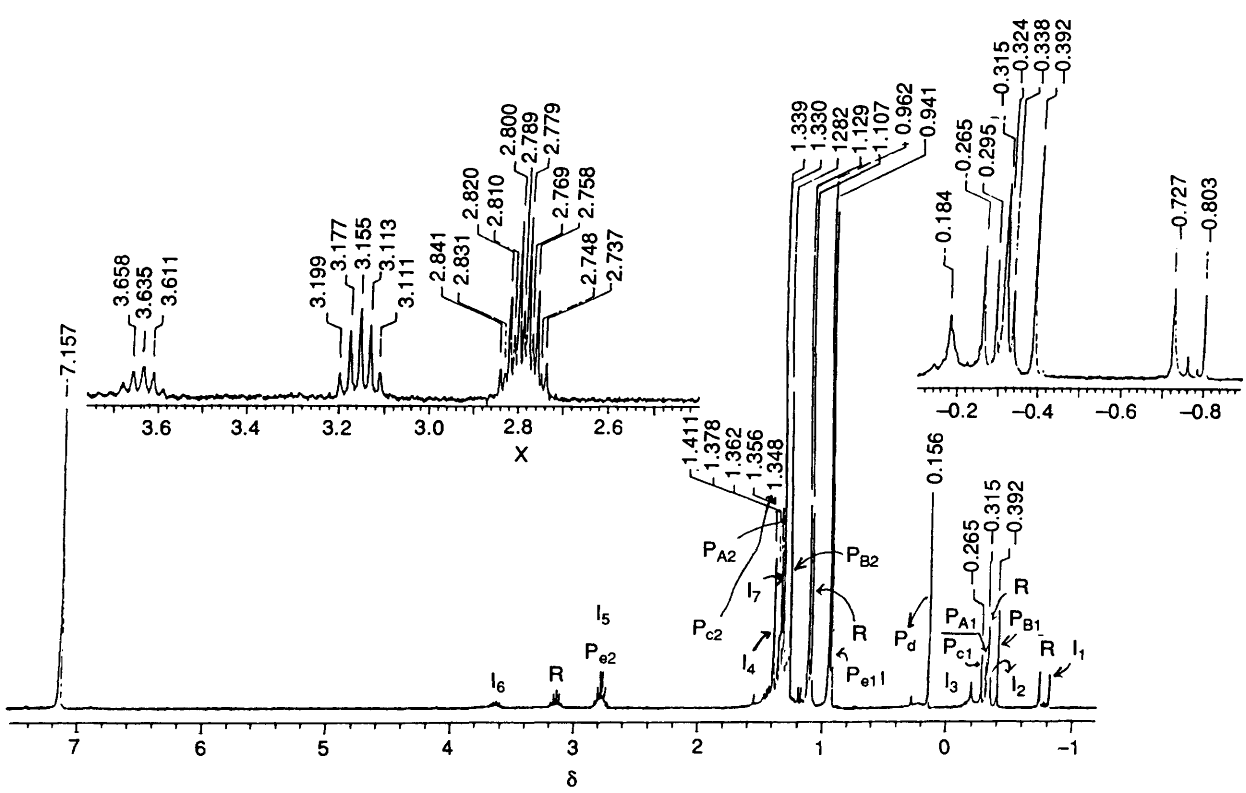
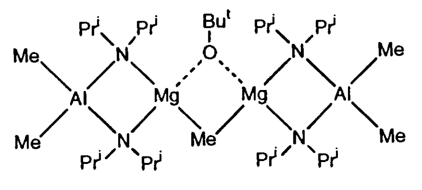


Fig. 5 The ^{1}H NMR spectrum of the reaction of compound **A** with Bu^{t}OH



I

Syntheses of $\mathrm{Me_2Al(\mu\text{-}NPr^i{}_2)(\mu\text{-}OR)Mg(\mu\text{-}NPr^i{}_2)(\mu\text{-}OR)\text{-}AlMe_2}$ (R = Me **1a** or Et **1b**).—A solution of methanol (0.162 cm^3, 4.0 mmol) or ethanol (0.235 cm^3, 4.0 mmol) in diethyl ether (10 cm^3) was added dropwise *via* a funnel to a round-bottomed flask containing an ether solution (4.0 cm^3) of compound **A** (1.184 g, 10 mmol) under nitrogen. Gas was immediately released and following addition, the solution was clear and colourless. After removal of solvent a viscous fluid was obtained. Transparent colourless crystals were obtained by sublimation at 100 or 78 °C for **1a** or **1b**.

Compound **1a**: m.p. 124–127 °C; yield 30%. NMR(C_6D_6): ^{1}H, δ −0.37 [s, Al(CH$_3$)$_2$, 12 H], 1.11 [t(d of d), NCH(C*H*$_3$)$_2$, 24 H], 3.09 [spt, NC*H*(CH$_3$)$_2$, 4 H] and 3.28(s, OCH$_3$, 6 H); ^{13}C, δ −7.16 [br, Al(CH$_3$)$_2$], 24.32 and 25.20 [NCH(*C*H$_3$)$_2$], 47.67 [N*C*H(CH$_3$)$_2$] and 49.19(OCH$_3$); ^{27}Al, δ 150 (br). Mass spectrum (30 eV, the ten most intense peaks): *m*/*z* 228, 124; 385, [*M* − CH$_3$]$^+$; 86, 229, 212, 242, 284, 142, 300. IR: 2952s, 2922s, 2855s, 1462m, 1370w, 1173w, 1131w, 1041w, 1001w, 952w, 931w, 885w, 830w, 770w, 639w, 574w and 500w cm^{-1} (Found: C, 53.5; H, 11.4; N, 6.8. Calc.: C, 53.95; H, 11.55; N, 7.05%).

Compound **1b**: 77–79 °C; yield 30%. NMR(C_6D_6): ^{1}H, δ −0.33, [s, Al(CH$_3$)$_2$, 12 H], 1.14 [m, OCH$_2$C*H*$_3$ and NCH(C*H*$_3$)$_2$, 30 H], 3.14 [spt, NC*H*(CH$_3$)$_2$, 4 H] and 3.71 (t, OC*H*$_2$CH$_3$); ^{13}C, δ −5.55 [br, Al(CH$_3$)$_2$], 19.21 (OCH$_2$*C*H$_3$), 24.49 and 25.55 [NCH(*C*H$_3$)$_2$], 47.61 [N*C*H(CH$_3$)$_2$] and 58.26 (O*C*H$_2$CH$_3$); ^{27}Al, δ 150 (br). Mass spectrum (70 eV, the eight most intense peaks): *m*/*z* 44 (100), 142 (46), 124 (45), 256 (24), 226 (12); 413, [*M* − CH$_3$]$^+$ (7); 270 (6) and 312 (5%). IR: 2967m, 2873m, 2833m, 1460s, 1387s, 1367s, 1351s, 1320w, 1263m, 1200m, 1160s, 1140m, 1120m, 1107m, 1023w, 980m, 947m, 924m, 849m, 800s, 697s, 676s, 663s, 613m, 500w, 436m and 400w cm^{-1} (Found: C, 53.2; H, 11.2; N, 6.0. Calc.: C, 55.05; H, 11.65; N, 6.55%).

Reaction of Compound **A** *with* Bu^{t}OH.—A solution of Bu^{t}OH (0.162 cm^3, 4.0 mmol) in ether (10 cm^3) was added dropwise *via* an addition funnel to a round-bottomed flask containing an ether solution (40 cm^3) of compound **A** (1.184 g, 1.0 mmol) under nitrogen. Gas was immediately released and following addition the solution was clear and colourless. The mixture was stirred for 1 h at room temperature. After removal of solvent a viscous fluid remained. Sublimation at 120 °C yielded two kinds of transparent colourless crystals. The more volatile product was $\mathrm{Me_2Al(\mu\text{-}OBu^t)_2Mg(\mu\text{-}OBu^t)_2AlMe_2}$ **2** m.p. > 176 °C (decomp.), yield 30%. NMR (C_6D_6): ^{1}H, δ −0.40 [s, Al(CH$_3$)$_2$, 12 H] and 1.28 [s, OC(CH$_3$)$_3$, 36 H]; ^{13}C, δ −4.76 [br, Al(CH$_3$)$_2$], 33.04 [OC(*C*H$_3$)$_3$] and 71.19 [O*C*(CH$_3$)$_3$]; ^{27}Al, δ 140 (br). Mass spectrum (70 eV, the eight most intense peaks): *m*/*z* 57 (100), 416 (42), 343 (25), 286 (14), 99 (12), 431 (10), 229 (10) and 213 (10%). IR: 2819–2293br, 1471m, 1383m, 1352w, 1290w, 1230m. 1196m, 1147m, 1113m, 1073w, 1044m, 974m, 946w, 916m, 843m and 806m cm^{-1} (Found: C, 56.0; H, 11.2; N, < 0.05. Calc.: C, 55.6; H, 11.05; N, 0.0%). The less volatile compound was $\mathrm{[Me_2Al(\mu\text{-}OBu^t)_2Mg(\mu\text{-}OBu^t)]_2}$ **3**, m.p. 238–239 °C, yield 20%. NMR(C_6D_6): ^{1}H, δ −0.30 [s, Al(CH$_3$)$_2$, 12 H], 1.33 [s, OC(CH$_3$)$_3$, 36 H] and 1.36 [s, OC(CH$_3$)$_3$, 18 H]; ^{13}C, δ −3.96 [br, Al(CH$_3$)$_2$], 33.41 [OC(*C*H$_3$)$_3$], 34.76 [OC(*C*H$_3$)$_3$], 68.77 [O*C*(CH$_3$)$_3$] and 70.83 [O*C*(CH$_3$)$_3$]; ^{27}Al, δ 140 (br). Mass spectrum (30 eV, the eight most intense peaks): *m*/*z* 70, 69, 174, 138, 160, 71, 218, 286. IR: 2955s, 2921s, 2852s, 1458m, 1376m, 1357m, 1262m, 1216w, 1138m, 1085m, 1047m, 1009m, 859m, 792m, 742m, 694w, 652w, 622w and 537m cm^{-1}. (Found: C, 55.7; H, 10.9. Calc.: C, 55.90; H, 11.05%).

Table 2 Crystallographic data and refinement results

	1b	**2**	**3**	**5**
Formula	$C_{20}H_{50}N_2O_2Al_2Mg$	$C_{20}H_{48}Al_2MgO_4$	$C_{28}H_{66}Al_2Mg_2O_6$	$C_{28}H_{68}Al_2Mg_2N_4$
M	428.89	430.86	601.39	817.25
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/n$
a/Å	11.433(2)	18.614(2)	15.477(5)	7.767(2)
b/Å	16.557(4)	9.057(2)	14.578(4)	16.072(3)
c/Å	14.824(3)	29.781(5)	18.822(6)	16.482(5)
β/°	90.47(2)	122.87(2)	110.04(3)	97.68(2)
U/Å^3	2806(1)	2942(1)	3990(2)	2039(1)
Z	4	4	4	2
F(000)	951.77	951.81	1327.72	839.83
D_c/g cm^{-3}	1.015	0.973	1.001	1.331
μ/mm^{-1}	0.14	0.13	0.13	1.62
Crystal diemnsions mm	0.20 × 0.35 × 0.45	0.25 × 0.50 × 0.50	0.50 × 0.55 × 0.75	0.35 × 0.50 × 0.60
No. of measured reflections	3647	1931	5208	2685
No. of unique reflections	3647	1931	5208	2685
No. of observations [$I > 2.0\sigma(I)$]	1306	815	1786	2062
No. of atoms	77	38	104	53
No. of parameters	244	123	343	173
R	0.063	0.065	0.080	0.030
R'	0.061	0.065	0.077	0.030
Goodness of fit	1.51	2.88	1.62	1.80
Highest peak in different map/e Å^{-3}	0.220	0.200	0.330	0.560

Reaction of Compound **B** *with* Bu^{t}OH.—A solution of *tert*-butyl alcohol (0.38 cm^3, 4.0 mmol) in ether (10 cm^3) was added slowly to compound **B** (0.960 g, 2.0 mmol) in ether (10 cm^3) under nitrogen. The reaction took place immediately, with the solution turning light yellow. After removal of solvent a light yellow fluid remained. Sublimation at 120 °C yielded transparent colourless crystals of compounds **3** and **2** in different temperature sectional areas from a gradient-temperature sublimator. Yields: 40, **3**; < 2% **2**.

Synthesis of $[Me_2Al(\mu\text{-}NPr^i{}_2)_2Mg(\mu\text{-}NPr^i{}_2)]_2$ **4**.—An excess of diisopropylamine in ether (10 cm^3) was added dropwise to compound **A** (2.95 g, 2.5 mmol) in ether (40 cm^3) under nitrogen. The reaction mixture was refluxed for 36 h. After removal of solvent, the crude product was crystallized from ether, yielding semi-transparent crystals, m.p. > 56 °C (decomp.), yield 90%. NMR (C_6D_6): ^{1}H δ −0.40 [s, $Al(CH_3)_2$, 12 H], 1.21 and 1.25 [m, $AlNCH(CH_3)_2Mg$ and $MgNCH(CH_3)_2Mg$, 72 H] and 3.28 [m, $AlNCH(CH_3)_2Mg$ and $MgNCH(CH_3)_2Mg$, 12 H]; ^{13}C, δ −0.29 [br, $Al(CH_3)_2$], 25.95 and 26.16 [$MgNCH(CH_3)_2Mg$], 28.00 [$AlNCH(CH_3)_2Mg$], 47.74 [$MgNCH(CH_3)_2Mg$] and 48.57 [$AlNCH(CH_3)_2Mg$]; ^{27}Al, δ 154(br). Mass spectrum (the nine most intense peaks): 44 (100), 124 (98), 86 (98), 142 (68), 281 (49), 223 (24), 209 (22), 366 (15%); and 381, $[M/2]^+$ (5%). IR: 2979s, 2950w, 2886m, 2833s, 1467s, 1450s, 1372s, 1335w, 1301w, 1193m, 1163s, 1124m, 1065s, 971w, 893m, 839w, 671m and 614w cm^{-1} (Found: C, 61.8; H, 11.5; N, 10.5. Calc.: C, 62.95, H; 12.60, N; 11.00%).

Synthesis of $[Me_2Al(\mu\text{-}NPr^i{}_2)_2Mg(\mu\text{-}I)]_2$ **5**.—A solution of iodine (0.43 g, 1.7 mmol) in benzene (10 cm^3) was added dropwise to compound **A** (1.0 g, 0.85 mmol) in benzene (40 cm^3) under nitrogen. The reaction took place immediately, with the solution turning light yellow. The solvent was evaporated to dryness, leaving a viscous fluid in nearly quantitative yield. Sublimation at 120 °C yielded a transparent solid, m.p. 135–136 °C. NMR(C_6D_6): ^{1}H, δ −0.26 [s, $Al(CH_3)_2$, 12 H], 1.27 [d of d, $NCH(CH_3)_2$, 48 H], and 3.53 [spt, $NCH(CH_3)_2$, 8 H]; ^{13}C, −3.73 [br, $Al(CH_3)_2$], 26.67 and 27.30 [$NCH(CH_3)_2$], 48.05 [$NCH(CH_3)_2$]; ^{27}Al, 140 (br). Mass spectrum (70 eV, the eight most intense peaks): *m*/*z* 250 (100), 393 (88), 43 (86), 308 (48), 142 (39), 124 (16), 335 (15), 281 (12) and 408, $[M/2]^+$ (< 0.1%). IR: 2963m, 2929m, 2860m, 1460s, 1383s, 1319w, 1258w, 1200m, 1169m, 1148m, 1131m, 1075w, 989m, 946w 800w, 775w, 694m and 675m cm^{-1} (Found: C, 41.0; H, 8.3; N, 6.7. Calc.: C, 41.10; H, 8.30; N, 6.85%).

Reaction of Compound **A** *with Diethylamine*.—A solution of diethylamine (0.53 cm^3, 5 mmol) in ether (10 cm^3) was added slowly to compound **A** (1.5 g, 5 mmol) in ether (40 cm^3). Gas was immediately released. The solvent was then evaporated and a semi-solid was obtained. Sublimation at 60 °C gave a white solid, $[Me_2Al(\mu\text{-}NEt_2)]_2$ **6** characterized by comparison of its spectral data with those published.[14]

Structure Determinations.—Crystals for X-ray measurements were sealed in glass capillaries. Preliminary examination and intensity data collection were carried out with an Enraf-Nonius CAD-4 automatic diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Intensity data were collected using the θ–2θ scan mode for $2\theta \leqslant 45°$ and then corrected for absorption and decay. All structures were solved by MULTAN[15] and refined with full-matrix least squares on F with $w = 1.0/[\sigma^2(F_o) + 0.0001F_o{}^2]$. In the final cycles all non-hydrogen atoms were refined anisotropically and all hydrogen atoms were fixed at idealized positions (d_{C-H} = 1.00 Å) calculated during the anisotropic convergence stage. Scattering factors for neutral atoms and anomalous scattering coefficients for non-hydrogen atoms were taken from ref. 16. All calculations were carried out with a Micro VAX 3600 computer using the NRC VAX program package.[17] A summary of the data collection and structure solution is given in Table 2; final atomic coordinates in Table 3. The C(5)–C(6) bond length (1.22 Å) of complex **1b** is unreasonable. This is attributed to the disorder of structure which is due to inappropriate thermal parameters.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

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Table 3 Atomic parameters

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Compound **1b**							
Mg	0.777 5(3)	0.904 49(24)	0.235 20(24)	C(8)	0.671 4(17)	0.959 2(17)	0.469 0(14)
Al(1)	0.987 6(3)	0.999 6(3)	0.228 55(25)	C(9)	1.145 3(11)	0.824 7(9)	0.202 7(9)
Al(2)	0.535 7(3)	0.887 6(3)	0.283 85(24)	C(10)	1.012 3(9)	0.823 4(7)	0.210 3(7)
O(1)	0.837 2(6)	1.006 1(5)	0.191 2(5)	C(11)	0.961 8(11)	0.820 4(9)	0.118 2(8)
O(2)	0.669 7(6)	0.923 9(5)	0.332 8(5)	C(12)	1.099 1(12)	0.881 9(11)	0.402 7(8)
N(1)	0.961 6(6)	0.888 2(5)	0.264 3(5)	C(13)	0.975 2(9)	0.877 8(8)	0.364 0(7)
N(2)	0.620 4(7)	0.849 5(5)	0.179 5(5)	C(14)	0.913 6(13)	0.806 1(9)	0.401 9(8)
C(1)	1.093 3(11)	1.025 2(9)	0.131 0(9)	C(15)	0.674 5(11)	0.890 4(9)	0.021 3(8)
C(2)	1.012 2(13)	1.073 4(8)	0.328 9(9)	C(16)	0.588 7(9)	0.895 0(8)	0.096 8(7)
C(3)	0.433 5(11)	0.978 4(9)	0.259 9(9)	C(17)	0.467 6(11)	0.882 4(10)	0.057 8(8)
C(4)	0.460 6(11)	0.811 2(9)	0.363 5(9)	C(18)	0.512 4(13)	0.717 5(9)	0.155 3(10)
C(5)	0.769 0(15)	1.084 3(12)	0.180 9(12)	C(19)	0.629 4(10)	0.762 6(8)	0.163 9(9)
C(6)	0.796 5(15)	1.112 1(14)	0.107 7(13)	C(20)	0.701 3(11)	0.721 6(8)	0.233 6(11)
C(7)	0.678 6(14)	0.995 4(15)	0.402 9(11)				
Compound **2**							
Mg	1/2	0.190 1(4)	1/4	C(4)	0.647 7(6)	0.439 1(13)	0.313 9(5)
Al	0.506 43(14)	0.192 1(4)	0.116 74(11)	C(5)	0.699 4(7)	0.339 5(16)	0.242 5(10)
O(1)	0.558 43(24)	0.287 4(5)	0.207 68(21)	C(6)	0.598 2(8)	0.528 0(14)	0.190 4(7)
O(2)	0.447 58(24)	0.095 5(5)	0.150 53(21)	C(7)	0.382 9(4)	−0.016 8(9)	0.115 0(4)
C(1)	0.435 3(5)	0.319 1(12)	0.029 1(4)	C(8)	0.351 4(7)	−0.058 4(13)	0.162 4(5)
C(2)	0.585 2(5)	0.064 2(13)	0.109 7(5)	C(9)	0.312 4(6)	0.033 8(13)	0.037 9(5)
C(3)	0.623 6(4)	0.396 9(10)	0.238 8(4)	C(10)	0.421 2(7)	−0.149 6(12)	0.103 6(6)
Compound **3**							
Al(1A)	0.397 3(3)	0.601 1(3)	0.172 34(21)	Al(1B)	0.859 0(3)	0.985 3(3)	0.163 4(3)
Mg(1A)	0.465 47(24)	0.532 01(23)	0.057 74(20)	Mg(1B)	0.952 19(24)	0.990 4(3)	0.053 76(21)
O(1A)	0.541 8(4)	0.431 6(4)	0.044 1(3)	O(1B)	1.004 1(5)	0.090 2(4)	0.009 5(4)
O(2A)	0.357 1(5)	0.515 4(5)	0.095 2(4)	O(2B)	0.822 6(5)	0.984 8(6)	0.057 8(4)
O(3A)	0.499 8(5)	0.621 4(5)	0.146 0(4)	O(3B)	0.979 3(6)	0.978 0(7)	0.166 4(5)
C(1A)	0.316 5(10)	0.708 7(10)	0.152 7(9)	C(1B)	0.832 6(12)	1.101 0(13)	0.203 7(10)
C(2A)	0.430 5(10)	0.547 9(10)	0.273 7(8)	C(2B)	0.819 6(12)	0.876 9(15)	0.202 9(11)
C(3A)	0.588 6(8)	0.360 4(7)	0.092 9(6)	C(3B)	1.007 7(9)	1.185 5(8)	0.022 9(8)
C(4A)	0.604 3(13)	0.385 5(14)	0.171 5(8)	C(4B)	1.023 2(18)	1.236 0(11)	−0.036 8(12)
C(5A)	0.536 7(13)	0.274 7(10)	0.074 7(12)	C(5B)	1.088 0(15)	1.205 8(12)	0.091 4(13)
C(6A)	0.678 6(10)	0.345 0(12)	0.087 2(10)	C(6B)	0.926 7(13)	1.217 4(10)	0.036 8(13)
C(7A)	0.278 3(11)	0.473 1(17)	0.066 9(11)	C(7B)	0.743 8(11)	0.998 5(20)	0.008 3(9)
C(8A)	0.195 6(12)	0.516 7(15)	0.062 0(13)	C(8B)	0.679 1(14)	1.053 5(20)	0.019 8(13)
C(9A)	0.303 6(20)	0.399 2(18)	0.133 3(13)	C(9B)	0.706 7(22)	0.887 8(14)	0.008 7(16)
C(10A)	0.279 0(15)	0.402 7(23)	0.013 8(16)	C(10B)	0.740 9(10)	1.020 2(15)	−0.067 1(10)
C(11A)	0.566 3(16)	0.682 9(12)	0.166 9(13)	C(11B)	1.054 7(12)	0.998(3)	0.222 8(9)
C(12A)	0.612 3(15)	0.646 0(22)	0.250 1(14)	C(12B)	1.044 6(15)	0.888 7(24)	0.247 8(22)
C(13A)	0.541 9(14)	0.781 6(11)	0.168 2(12)	C(13B)	1.065 4(16)	1.036 5(21)	0.290 2(13)
C(14A)	0.646 1(13)	0.656 9(15)	0.142 4(14)	C(14B)	1.133 5(12)	0.937(3)	0.200 0(11)
Compound **5**							
I	0.248 32(4)	0.024 67(3)	0.027 434(25)	C(6)	0.112 3(7)	0.036 2(3)	0.246 4(3)
Al	0.039 66(21)	0.207 88(10)	0.198 37(10)	C(7)	0.076 8(9)	−0.055 4(4)	0.234 0(4)
Mg	−0.059 89(20)	0.085 13(11)	0.080 90(10)	C(8)	0.188 4(9)	0.053 0(4)	0.334 8(4)
N(1)	−0.031 7(5)	0.091 87(24)	0.210 12(22)	C(9)	0.060 1(7)	0.249 9(3)	0.029 0(3)
N(2)	−0.062 9(5)	0.217 03(25)	0.082 87(24)	C(10)	0.111 8(9)	0.341 4(4)	0.042 6(4)
C(1)	0.293 3(7)	0.210 6(4)	0.203 6(3)	C(11)	0.008 1(9)	0.232 8(4)	−0.061 1(4)
C(2)	−0.041 7(9)	0.287 4(4)	0.274 7(4)	C(12)	−0.239 3(8)	0.253 7(4)	0.065 1(5)
C(3)	−0.199 3(8)	0.081 2(5)	0.243 1(4)	C(13)	−0.377 5(8)	0.205 9(4)	0.024 5(5)
C(4)	−0.329 3(8)	0.026 7(4)	0.201 4(4)	C(14)	−0.274 6(10)	0.337 3(4)	0.089 9(5)
C(5)	−0.212 6(9)	0.096 9(5)	0.328 0(4)				

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