Halogen-containing tetrametallic aluminium alkoxides†‡

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New halogen-containing tetrametallic aluminium alkoxides of formula [Al{(μ-OEt)$_2$AlMeCl}$_3$] (**2**-*cis*; **2**-*trans*), and [Al{(μ-OEt)$_2$AlBr$_2$}$_3$] (**4**), have been synthesized by combining Al(OEt)$_3$ and Me$_2$AlCl (for **2**) or EtAlBr$_2$ (for **4**). They were fully characterized by (^{1}H, ^{27}Al) NMR, IR, mp, elemental analysis, and single-crystal X-ray diffractometry. The chloride analogue of **4**, [Al{(μ-OEt)$_2$AlCl$_2$}$_3$] (**3**), prepared previously using a different route, was also prepared here by combining Al(OEt)$_3$ and EtAlCl$_2$.

Introduction

Due to the continuous impact of aluminium oxide on the contemporary economy, many researchers have focused on the development of new synthetic methods for its production.[1] This is particularly true for nanoparticulate Al$_2$O$_3$, which is expected to have new and unusual properties.[2] Typical methodologies for making n-Al$_2$O$_3$ involve either gas phase reactions, sol–gel processes and mineral transformations.

Recently, the tetrametallic aluminium alkoxides [Al{(μ-OEt)$_2$AlR$_2$}$_3$] (R = Me, Et, ^{i}Bu)[3] (see Fig. 1) were used as molecular precursors for the preparation of nanoparticulate alumina (n-Al$_2$O$_3$).[4] The nano-particles (17.7 ± 7.4 nm) were prepared by decomposing the precursor molecules in toluene open to air at room temperature. n-Al$_2$O$_3$ particles formed in this way were used to immobilize the enzyme pepsin, with activity exceeding that found for pepsin–Al$_2$O$_3$ composites formed with microsized particles.[5]

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‡ CCDC reference numbers 192160 and 665929. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716812h
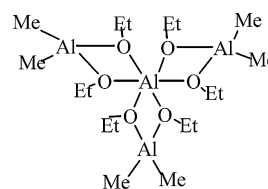

Fig. 1 The structure of [Al{(μ-OEt)$_2$AlMe$_2$}$_3$] (**1**).

In the hydrolytic decomposition the Mitsubishi™ [6] Al$_4$O$_6$ core appears to act as a template for the formation of pure Al$_2$O$_3$ rather than boehmite, with the alkoxide groups being sequentially hydrolyzed. The hydrolysis mechanism was partially confirmed in the open-air hydrolysis of [Al{μ-OEt)$_2$Al(OSiPh$_3$)$_2$}$_3$] to [Al{μ-OH)$_2$Al(OSiPh$_3$)$_2$}$_3$] (see Fig. 2). The presence of the OSiPh$_3$ groups "protected" the terminal Al atoms from hydrolysis allowing the OEt groups in the core to be selectively hydrolyzed.

A wide range of tetrametallic aluminium compounds are now known,[7,8] and derivatives containing gallium and indium have recently been added to the group.[9] Considering the advantage of ternary aluminium heterometallic oxides over the binary systems in physical properties[10] and especially, the extensive applications as catalysts[11] and pigments[12] it would be ideal to have new 'Mitsubishi' type monomolecular precursors which contain both aluminium and transition metal elements such as iron, cobalt,
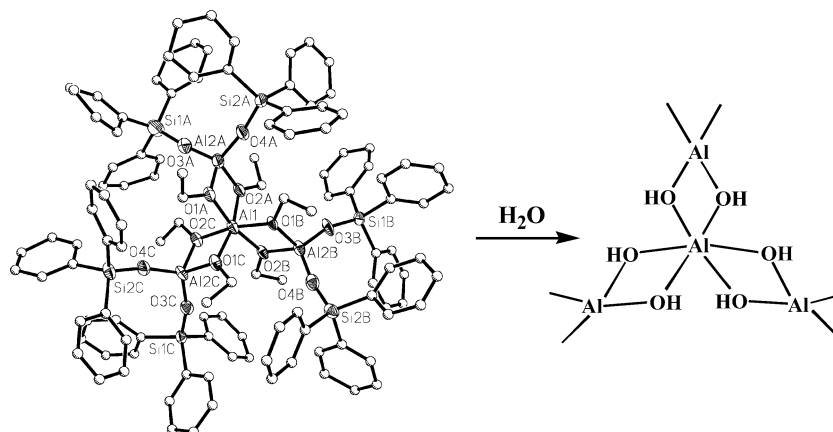

Fig. 2 Mitsubishi™ siloxide derivative and hydrolysis of central ethoxide groups.

and nickel. Despite the fact that some of the earliest compounds in the class contained a central lanthanide element,[13] derivatives containing transition metals have not been achieved. From these precursors it should be possible to prepare novel nano-scale aluminium-containing mixed metal oxide particles. The challenge, however, is to modify the peripheral aluminium atoms using transition metal species. All of the terminal functional groups of the typical Mitsubishi™ molecules, $[Al\{(\mu\text{-}OEt)_2AlR_2\}_3]$ (R = Me, Et, ^{i}Bu), are alkyl groups and this limits the potential modification reactions to those with acidic protons. In order to extend the routes available to prepare transition metal modified Mitsubishi™ clusters, herein are reported new chlorine and bromine containing compounds of formula $[Al\{(\mu\text{-}OEt)_2AlMeCl\}_3]$ (**2**-*cis*; **2**-*trans*), and $[Al\{(\mu\text{-}OEt)_2AlBr_2\}_3]$ (**4**). The chloride analogue of **4**, $[Al\{(\mu\text{-}OEt)_2AlCl_2\}_3]$ (**3**), has been reported previously from the reaction of $MeAlCl_2$ and EtOH.[14,15] Compound **3** was also prepared in the present work using the same method as for **4**. Compounds **2–4** should be suitable for derivatization at the halide position through salt elimination reactions. Especially for **2**, the terminal groups consist of three chlorines and three methyl groups, which afford the possibility of selective modification of the peripheral aluminium atoms. The bromine containing compound $[Al\{(\mu\text{-}OEt)_2AlBr_2\}_3]$ (**3**) could be more suitable for derivatization compared to the chlorine analogue because of the higher lability of the Al–Br bond compared to the Al–Cl bond.

Results and discussion

Synthesis and characterization

The synthesis of the Mitsubishi™ molecules of formula $[Al\{(\mu\text{-}OEt)_2AlR_2\}_3]$, where R = Me, Et, ^{i}Bu, and $[Al\{(\mu\text{-}OEt)_2GaR_2\}_3]$, where R = Me and Et, was described previously.[3] The structure of $[Al\{(\mu\text{-}OEt)_2AlMe_2\}_3]$ (**1**), is shown in Fig. 1. These compounds were formed through functional group (*e.g.*, alkyl and alkoxyl group) rearrangements.

Based on the same idea, compounds **2–4** were prepared in an inert atmosphere by combining three moles of dimethyl aluminium

chloride, ethyl aluminium dichloride or ethyl aluminium dibromide with two moles of aluminium triethoxide in toluene, followed by heating at reflux for 12 h (Scheme 1).

All three reactions led to the isolation of oils as observed for the previously noted tetrametallics. For reaction (a), the chlorine substituents in Me_2AlCl led to not only lower reactivity of Al–C bonds owing to the high electronegativity of chlorine, but also the presence of *cis* and *trans* isomeric products. The resulting NMR spectra for both reactions were consequently very complex. Thus, the presence of chloride leads to more complex reactions than the reaction to synthesize compound **1**, in which the oil is pure and in quantitative yield. Fortunately, however, compounds **2–4** crystallized from the oils of reactions (a) and (b). The yields were 40–45%. The purity of these materials may be increased by recrystallization in toluene or by washing with a small amount of hexane. By studying the effect of stoichiometry on reactions (a) and (b), the optimal stoichiometry was found to be 2 $Al(OEt)_3$ and 3 Me_2AlCl, $EtAlCl_2$ or $EtAlBr_2$ with the consequent elimination of AlR_3 (R = Me for (a) and Et for (b)) from the reaction.

The ^{1}H NMR of the crystals from reaction (a) reveals that they consist of isomeric products (**2**-*cis* and **2**-*trans*). This is strongly supported by the fact that there are two singlets ($\delta = -0.48$ and -0.50 ppm) in the ^{1}H NMR, whose integration ratio is 5 to 4. If the crystals only consist of **2**-*cis*, the three terminal methyl groups on the aluminium atoms should be displayed as one singlet in the high field of the ^{1}H NMR. If the crystals only consist of **2**-*trans*, the three terminal methyl groups should be shown as two singlets in a ratio of 2 to 1. Hence the ratio 5 to 4 of the two singlets indicates not only the existence of isomeric products but also the overlap between the singlet of **2**-*cis* and one of the two singlets of **2**-*trans*. Furthermore, based on calculation, the only reasonable overlap happens between Me(A) and Me(B) (as shown in Fig. 3) at -0.48 ppm. The conclusion that the *cis*/*trans* ratio of **2** is 1 to 2 can be made. The presence of *cis* and *trans* isomers is also observed for the oligomeric compound $[MeClAlOMe]_3$.[16] In that case, however, the *cis*/*trans* ratio was found to be 1 : 4. It should be noted that in both cases the *trans* product is in a higher percentage compared to the corresponding *cis* product. These observations may reflect that
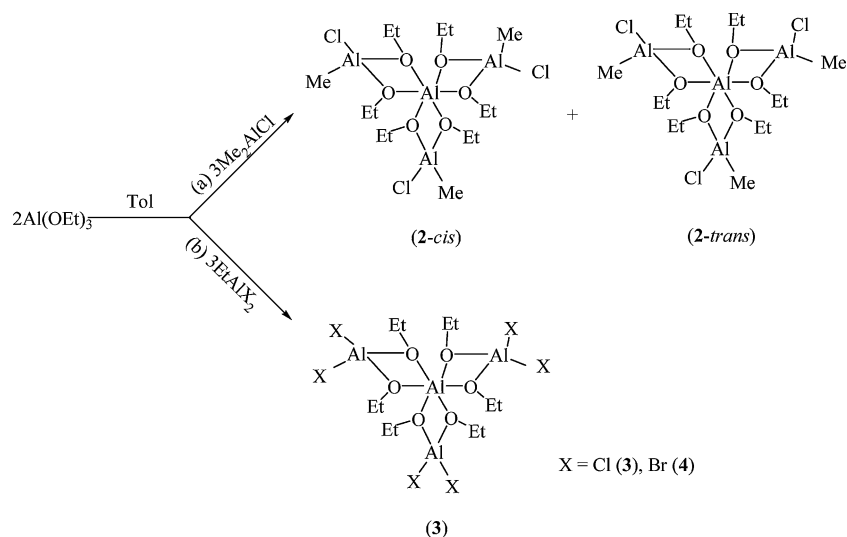
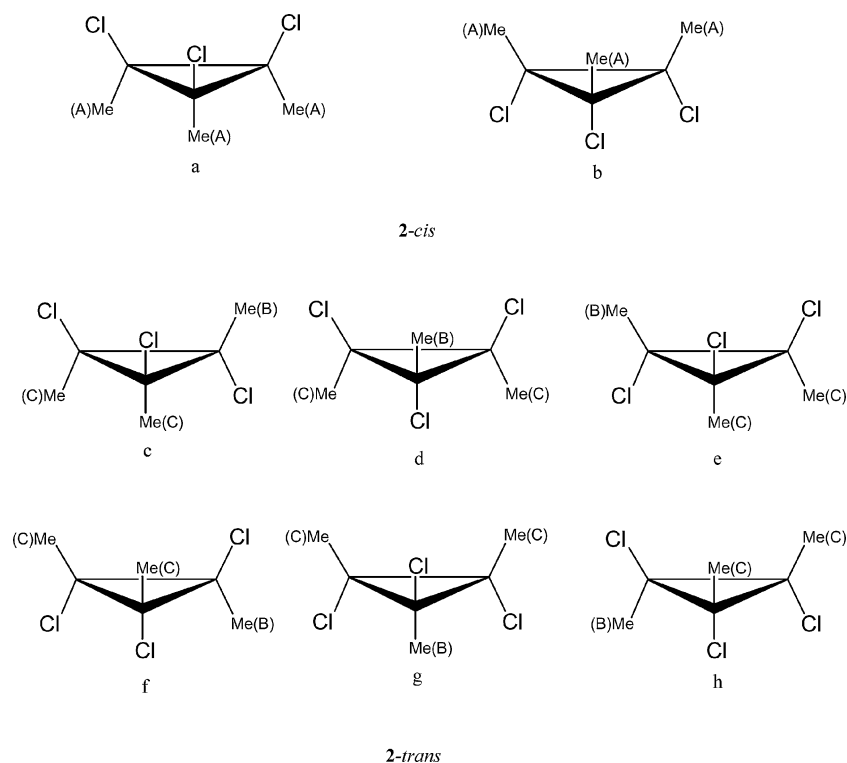**Scheme 1** Syntheses of compounds **2–4**.

Fig. 3 The possible *cis* isomeric products (a and b) and the *trans* isomeric products (c–h) for **2**. For simplicity, the plane that is defined by three peripheral four-coordinate aluminium atoms in **2**-*cis* and **2**-*trans* is denoted by a triangle.

the *cis/trans* ratio of those oligomers, to some extent, is decided by all of the possibilities of combinations between monomers (in this case, between the Al(OEt)$_3$ core and three (OEt)Al(Me)Cl species, as shown in Fig. 3).

In the ^{1}H NMR of **2–4** the chemical shifts of the bridging ethoxy groups for **2** are $\delta_{CH2} = 3.88, 4.21$ ppm, $\delta_{CH3} = 1.40$ ppm; for **3**, $\delta_{CH2} = 3.95, 4.24$ ppm; $\delta_{CH3} = 1.53$ ppm; for **4**, $\delta_{CH2} = 3.53, 4.14$ ppm, $\delta_{CH3} = 1.29$ ppm. Thus, the ethoxy groups for **2** and **3** and the terminal methyl groups for **2** ($\delta = -0.48$ and -0.50 ppm) shift downfield compared to those of **1** (for ethoxyl groups, $\delta_{CH2} = 3.77, 3.88$ ppm, $\delta_{CH3} = 1.30$ ppm; for terminal methyl groups $\delta = -0.78$ ppm). This can be ascribed to the electronegativity of the terminal chlorine groups in **2** and **3**, which deshield the bridging ethoxy and terminal methyl groups. Like those of **1**, the OCH_2 groups in **2–4** are also manifested as two multiplets. This can be explained by the presence of diastereotopic methylene groups. For compounds **2–4**, the ^{27}Al NMR consists of two peaks that can be assigned to six-coordinate (6, 4 and 5 ppm, respectively) and four-coordinate (116, 112, and 90 ppm, respectively) aluminium atoms. Furthermore, by comparing the IR spectra of **2–4**, it is found that the replacement of methyl groups by chlorine groups causes the Al–C symmetric stretching band at 1205 cm^{-1} for **2** to disappear in the IR of **3** and **4**. The Al–C absorption band of **2** ($\nu = 1205$ cm^{-1}) shifts to a relatively high wavenumber compared to that of **1** ($\nu = 1197$ cm^{-1}), due to the presence of the electron-withdrawing chlorine group.

Molecular structures of 2 and 4

The single crystal X-ray structure of the crystalline product of **2** (Fig. 4) reveals that the product is a *trans*-trichloro-
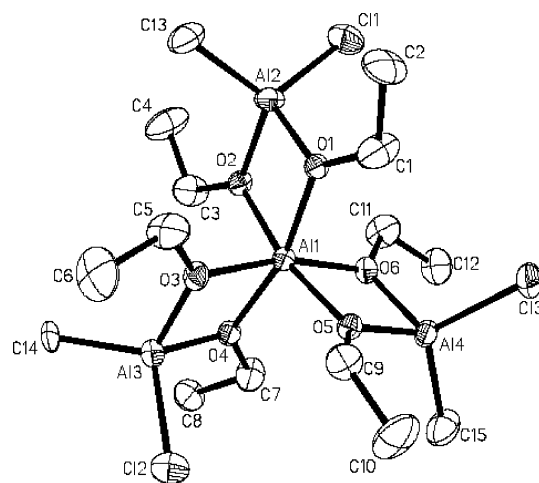
Fig. 4 Molecular structure of [Al{μ-OEt)$_2$AlCl(Me)}$_3$] (**2**).

substituted 'Mitsubishi molecule' derivative of formula [Al{(μ-OEt)$_2$AlMeCl}$_3$] (**2**-*trans*). The two chlorine atoms are above the plane defined by the three peripheral aluminium atoms while the other chlorine is below it. The disorder of chlorine and methyl group at the Al(2) and Al(4) atoms, however, further verifies the presence of the *cis* isomer in the crystalline material. The crystals isolated from the oil product of reaction (a) contain two isomeric products **2**-*cis* and **2**-*trans*. The crystal data of the hexachloride compound [Al{(μ-OEt)$_2$AlCl$_2$}$_3$] (**3**) matched with the data reported before.[14,15]

These structures may be regarded as an assembly of three MeClAlOEt units (for **2**), Cl$_2$AlOEt units (for **3**) and Br$_2$AlOEt

(for **4**) to an Al(OEt)$_3$ core. The central aluminium atom is six-coordinate, having a distorted octahedral geometry, while the three peripheral aluminium atoms are four-coordinate, with a distorted tetrahedral geometry. This is consistent with the ^{27}Al NMR data in which only four (~100 ppm) and six-coordinate (~5 ppm) Al environments are indicated. The Al$_2$O$_2$ rings are planar and adopt a propeller-type D_3 arrangement around the central aluminium atom. The Al$_4$O$_6$ frameworks of **1–4** have similar Al–O bond lengths and angles. The Al–O distances are slightly longer around the central six-coordinate aluminium (av. 1.9 Å) than for the terminal four-coordinate aluminium (av. 1.8 Å) (Tables 1 and 2). This can be ascribed to the increase of atomic radii with increasing coordination number. The bond angles CH$_3$–Al–CH$_3$ (av. 114.0°) (**1**) > CH$_3$–Al–Cl (av. 113.7°) (**2**) > Cl–Al–Cl (av. 112.4°) (**3**) decrease with the increasing p character of the Al–X(R) bonds.[17]

In the hexabromide compound [Al{(μ-OEt)$_2$AlBr$_2$}$_3$] (**4**) (Fig. 5) the average Al–Br bond length (2.26 Å) is slightly longer than the average Al–Cl bond length of **2** and **3** (~2.0 Å). This is consistent with the higher atomic radius of bromine compared to chlorine.

The average Br–Al–Br bond angle (~112°) is remarkably close to the Cl–Al–Cl angle (~113°) indicating that electronic factors have more influence over the angles than steric factors.
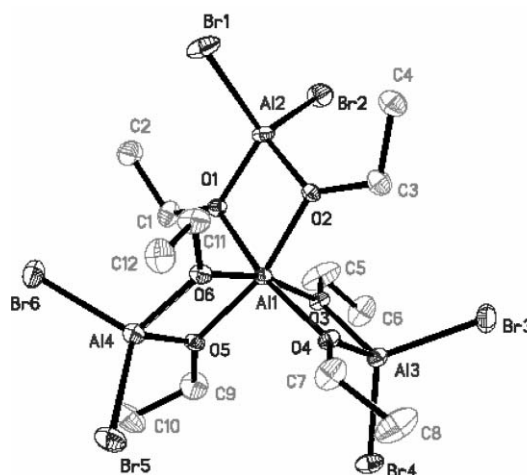

Fig. 5 Molecular structure of [Al{μ-OEt)$_2$AlBr$_2$}$_3$] (**4**).

Conclusion

Two new halogen-containing Mitsubishi™ derivatives (compounds **2** and **4**) have been synthesized and fully characterized. Compound **3** was prepared and structurally characterized

Table 1 Selected bond lengths and angles for **2**

[Al{μ-OEt)$_2$AlMeCl}$_3$] (**2**-*cis* and **2**-*trans*)

Al(1)–O(6)	1.894(2)	Al(1)–O(1)	1.899(2)	Al(3)–O(4)	1.796(2)	Al(3)–O(3)	1.798(2)
Al(1)–O(5)	1.902(2)	Al(1)–O(4)	1.903(2)	Al(3)–C(14)	1.954(3)	Al(3)–Cl(2)	2.1396(13)
Al(1)–O(3)	1.907(2)	Al(1)–O(2)	1.913(2)	Al(4)–O(5)	1.796(2)	Al(4)–O(6)	1.807(2)
Al(2)–O(1)	1.797(2)	Al(2)–O(2)	1.798(2)	Al(4)–C(15)	1.971(14)	Al(4)–Cl(3)	2.108(3)
Al(2)–C(13)	1.946(13)	Al(2)–Cl(1)	2.100(3)	Al(4)–C(15′)	1.960(14)	Al(4)–Cl(3′)	2.096(4)
Al(2)–C(13′)	1.964(14)	Al(2)–Cl(1′)	2.044(5)				
O(1)–Al(1)–O(2)	76.05(8)	O(3)–Al(1)–O(4)	76.43(9)	C(14)–Al(3)–Cl(2)	113.63(11)	O(4)–Al(3)–Cl(2)	108.20(8)
O(5)–Al(1)–O(6)	76.36(9)	O(1)–Al(2)–O(2)	81.55(9)	O(5)–Al(4)–C(15)	118.3(8)	O(5)–Al(4)–O(6)	81.30(9)
O(1)–Al(2)–C(13)	115.6(9)	O(1)–Al(2)–Cl(1)	111.07(12)	O(6)–Al(4)–C(15)	116.5(8)	O(5)–Al(4)–Cl(3)	112.71(18)
O(2)–Al(2)–C(13)	114.0(8)	O(2)–Al(2)–Cl(1)	115.46(11)	O(5)–Al(4)–C(15′)	115.1(10)	O(6)–Al(4)–Cl(3)	112.03(18)
O(1)–Al(2)–C(13′)	117.1(8)	O(1)–Al(2)–Cl(1′)	115.5(3)	O(6)–Al(4)–C(15′)	115.1(10)	O(5)–Al(4)–Cl(3′)	112.9(2)
O(2)–Al(2)–C(13′)	109.2(7)	O(2)–Al(2)–Cl(1′)	116.6(3)	C(15)–Al(4)–Cl(3)	112.5(7)	O(6)–Al(4)–Cl(3′)	114.4(2)
C(13)–Al(2)–Cl(1)	114.9(8)	C(13′)–Al(2)–Cl(1′)	113.2(9)	C(15′)–Al(4)–Cl(3′)	114.0(10)	Al(1)–O(1)–Al(2)	101.47(9)
O(3)–Al(3)–C(14)	116.65(13)	O(3)–Al(3)–O(4)	81.96(9)	Al(1)–O(2)–Al(2)	100.90(9)	Al(1)–O(3)–Al(3)	100.55(10)
O(4)–Al(3)–C(14)	119.68(13)	O(3)–Al(3)–Cl(2)	112.89(8)	Al(1)–O(4)–Al(3)	100.77(9)	Al(1)–O(5)–Al(4)	101.20(10)
Al(1)–O(6)–Al(4)	101.13(10)						

Table 2 Selected bond lengths and angles for **4**

[Al{μ-OEt)$_2$AlBr$_2$}$_3$] (**4**)

Al(1)–O(1)	1.905(2)	Al(1)–O(2)	1.908(2)	Al(3)–O(3)	1.776(2)	Al(3)–O(4)	1.778(2)
Al(1)–O(3)	1.900(2)	Al(1)–O(4)	1.914(2)	Al(3)–Br(3)	2.2708(11)	Al(3)–Br(4)	2.2634(10)
Al(1)–O(5)	1.904(2)	Al(1)–O(6)	1.913(2)	Al(4)–O(5)	1.773(3)	Al(4)–O(6)	1.783(2)
Al(2)–O(1)	1.774(2)	Al(2)–O(1)	1.786(2)	Al(4)–Br(5)	2.2546(11)	Al(4)–Br(6)	2.2746(12)
Al(2)–Br (1)	2.2694(11)	Al(2)–Br(2)	2.2600(11)				
O(1)–Al(1)–O(2)	76.31(10)	O(1)–Al(1)–O(3)	95.87(10)	Br(1)–Al(2)–Br(2)	112.14(4)	O(3)–Al(3)–O(4)	83.02(11)
O(1)–Al(1)–O(4)	167.93(11)	O(1)–Al(1)–O(5)	92.85(10)	O(3)–Al(3)–Br(3)	113.23(9)	O(3)–Al(3)–Br(4)	115.06(8)
O(1)–Al(1)–O(6)	96.11(11)	O(2)–Al(1)–O(3)	97.19(10)	O(4)–Al(3)–Br(3)	115.22(9)	O(4)–Al(3)–Br(4)	114.90(9)
O(2)–Al(1)–O(4)	95.35(10)	O(2)–Al(1)–O(5)	164.43(11)	Br(3)–Al(3)–Br(4)	112.44(5)	O(5)–Al(4)–O(6)	83.04(11)
O(2)–Al(1)–O(6)	93.55(10)	O(3)–Al(1)–O(4)	76.30(10)	O(5)–Al(4)–Br (5)	114.81(9)	O(5)–Al(4)–Br(6)	115.84(9)
O(3)–Al(1)–O(5)	94.99(11)	O(3)–Al(1)–O(6)	165.50(11)	O(6)–Al(4)–Br(5)	116.59(9)	O(6)–Al(4)–Br(6)	110.77(9)
O(4)–Al(1)–O(5)	96.93(10)	O(4)–Al(1)–O(6)	93.07(10)	Br(5)–Al(4)–Br(6)	112.70(5)	Al(1)–O(1)–Al(2)	100.68(11)
O(5)–Al(1)–O(6)	76.29(10)	O(1)–Al(2)–O(2)	76.31(10)	Al(1)–O(2)–Al(2)	100.15(11)	Al(1)–O(3)–Al(3)	100.65(11)
O(1)–Al(2)–Br(1)	116.02(9)	O(1)–Al(2)–Br(2)	113.46(9)	Al(1)–O(4)–Al(3)	100.03(11)	Al(1)–O(5)–Al(4)	100.44(11)
O(2)–Al(2)–Br(1)	115.03(9)	O(2)–Al(2)–Br(2)	114.45(9)	Al(1)–O(6)–Al(4)	99.75(11)		

previously,[14,15] but the preparation described here is slightly different. This serves to reinforce the fact that the tetrametallic structural arrangement is inherent to the compounds prepared and not directed by the type of reagents used. The presence of chloride or bromide in the terminal positions of the halide compounds opens up the possibility of preparing cationic derivatives or new mixed-metal derivatives by salt elimination reactions. The presence of alkyl groups on the terminal aluminiums could be used to derivatize the trimetallic compounds by alkane elimination, for example, by using a phenol. These possible derivatives and the use of similar reaction strategies in preparing transition metal-containing 'Mitsubishi' clusters is currently in progress.

Experimental

General considerations

All air-sensitive manipulations were conducted using standard bench-top Schlenk line techniques in conjunction with an inert atmosphere glove box. All solvents were rigorously dried prior to use. All glassware was cleaned with a base and an acid wash and dried in an oven at 130 °C overnight. Al(OEt)$_3$, Me$_2$AlCl, AlBr$_3$, EtAlCl$_2$ and Et$_3$Al were purchased from either Strem or Aldrich and used as received. **CAUTION**: Et$_3$Al, Me$_2$AlCl and EtAlCl$_2$ are highly pyrophoric and must be handled under an inert atmosphere. IR spectra were recorded as KBr pellets on a MAGNA-IR 560 spectrometer. ^{1}H and ^{27}Al NMR spectra were obtained on Varian 200 and 400 spectrometers. Chemical shifts were reported relative to SiMe$_4$ for ^{1}H, and AlCl$_3$ in D$_2$O for ^{27}Al, and are reported in ppm. Elemental analyses were obtained on a Elementar Americas Vario EL III analyzer. X-Ray data were collected on a Nonius Kappa CCD diffractometer ($\lambda_{MoK\alpha} = 0.71073$ Å, monochromator: graphite, $T = 90$ K). Scaling and merging were performed with Scalepack,[18] which also provided correction of anisotropic absorption effects. Direct methods (SHELXS-97)[19] were used for structure solution. The structures were refined using SHELXL-97.

Hydrogen atoms were refined using a riding model with isotropic U tied to their respective heavy atom. Further details of the structure analyses are given in Table 3. Selected bond lengths and angles are given in Tables 1 and 2.

[Al{(μ-OEt)$_2$AlMeCl}$_3$] (2-*cis* and 2-*trans*)

To a stirred suspension of aluminium triethoxide (30.83 mmol, 5.000 g) in toluene (40 mL) at 25 °C was added a solution of dimethylaluminium chloride (46.25 mmol, 4.279 g) in toluene (20 mL). The mixture was brought to reflux and the solid was observed to dissolve over 30 min. The solution was refluxed overnight, cooled to ambient temperature and filtered to remove a small amount of insoluble material. The volatiles were removed under reduced pressure, yielding a nearly colorless viscous oil, which crystallized in one to three weeks. Single crystals suitable for X-ray analysis were obtained from a sample which was allowed to sit undisturbed for one week at 25 °C. Recrystallizing in toluene or using 3 mL of hexane to wash the crystals can further purify the crystalline product. X-Ray analysis confirmed that the crystals were **2**-*cis* and **2**-*trans* (3.22 g, 40.6%). Mp: 222–223 °C. ^{1}H NMR (CDCl$_3$, 400 MHz): δ −0.50 (s, 12H, Me(C) of two **2**-*trans*), −0.48 (s, 15H, Me(B) of two **2**-*trans* and Me(A) of one **2**-*cis*), 1.40 (m, 54H, OCH$_2$CH_3 of two **2**-*trans* and one **2**-*cis*), 3.88 and 4.21 (m, 36H, OCH_2CH$_3$ of two **2**-*trans* and one **2**-*cis*). ^{27}Al NMR (CDCl$_3$, 52.1 MHz): δ 6 (W$_{1/2}$ 18 Hz), 116 (W$_{1/2}$ 2605 Hz). IR (KBr; v, cm^{-1}): 2980(s), 2938(m), 2906(m), 1453(w), 1393(m), 1205(m), 1167(w), 1102(m), 1051(vs), 901(s), 867(w), 680(vs), 604(s), 533(m), 416(w). Anal. calcd: C, 34.01; H, 7.42. Found: C, 34.23; H, 7.49%.

[Al{(μ-OEt)$_2$AlCl$_2$}$_3$] (3)

The procedure was similar to **2** using aluminium triethoxide (30.83 mmol, 5.000 g), toluene (60 mL), ethylaluminium dichloride (46.25 mmol, 5.87 g), yielding a nearly colorless viscous oil, which crystallized in a period of time from two weeks to one month.

Table 3 Crystal structure refinement data for **2** and **4**

	2	**4**
Formula	C$_{15}$H$_{39}$Al$_4$Cl$_3$O$_6$	C$_{12}$H$_{30}$Al$_4$Br$_6$O$_6$
M	529.73	857.74
Color	colorless	colorless
Crystal size/mm	$0.25 \times 0.20 \times 0.18$	$0.25 \times 0.22 \times 0.20$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{1/n}$	$P2_{1/n}$
a/Å	14.2120(5)	14.3134(2)
b/Å	11.5650(4)	11.7178(2)
c/Å	16.7880(5)	17.0046(3)
β/°	90.646(2)	90.2588(6)
V/Å^3	2759.13(16)	2852.01(8)
Z	4	4
$F(000)$	1120	1648
D(calcd)/g cm^{-3}	1.275	1.998
μ/mm^{-1}	0.484	8.593
Unique data measd	4856	6533
Obsd data, n [$F \geq 4\sigma(F)$]		4643
No. of variables, p	273	259
$R1$ [$I > 2\sigma$]	$R1 = 0.0561$, $wR2 = 0.1147$	$R1 = 0.0340$, $wR2 = 0.0650$
$R1$ (all data)	$R1 = 0.0746$, $wR2 = 0.1211$	$R1 = 0.0660$, $wR2 = 0.0729$
S (goodness of fit on F^2)	1.09	1.016
Largest diff. peak and hole/e Å^{-3}	0.448 and −0.441	0.762 and −0.647

Single crystals suitable for X-ray analysis were obtained from a sample which was allowed to sit undisturbed for one week at 25 °C. Recrystallizing in toluene or using 3 mL of hexane to wash the crystals can further purify the crystalline product. X-Ray analysis confirmed that the crystals were of the structure of compound (**3**) (4.06 g, 44.6%). Mp: 210–212 °C. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 1.53 (t, 18H, OCH$_2$CH_3), 3.95 (m, 6H, OCH_aH$_b$), 4.23 (m, 6H, OCH$_a$$H_b$). ^{27}Al NMR (CDCl$_3$, 52.1 MHz): δ 4 (W$_{1/2}$ 48 Hz), 112 (W$_{1/2}$ 2709 Hz). IR (KBr; v, cm^{-1}): 2985(s), 2938(m), 2913(m), 2875(w), 1481(w), 1453(w), 1395(m), 1166(w), 1104(m), 1043(vs), 899(s), 842(w), 657(vs), 596(s), 542(s), 459(w). Anal. calcd: C, 24.39; H, 5.12. Found: C, 24.24; H, 5.34%.

[Al{(μ-OEt)$_2$AlBr$_2$}$_3$] (4)

The procedure was similar to **2** using aluminium triethoxide (2.5 mmol, 0.408 g), toluene (20 mL), ethylaluminium dibromide, prepared *in situ* by the redistribution of triethylaluminium (0.63 mmol, 8.6 mL) and aluminium(III) bromide (1 M solution in dibromomethane (1.26 mmol, 1.26 mL)). The solutions were combined at −78 °C and then allowed to warm to 25 °C with stirring for 4 h. Solvent removal yielded a nearly colorless viscous oil. Single crystals suitable for X-ray analysis were obtained from a sample which was allowed to sit undisturbed for one week at 25 °C. Yield: 0.8 g, 40%. Mp: 205 °C (decomp.). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 1.29 (t, 18H, OCH$_2$CH_3), 3.53 (m, 6H, OCH_aH$_b$), 4.14 (m, 6H, OCH$_a$$H_b$). ^{27}Al NMR (CDCl$_3$, 52.1 MHz): δ 5 (W$_{1/2}$ 17 Hz), 90 (W$_{1/2}$ 78 Hz). IR (KBr; v, cm^{-1}): 2984 (m), 2932 (m), 2905 (m), 2866 (w), 1479 (w), 1469 (w), 1392 (m), 1165 (m), 1100 (m), 1038 (vs), 895 (s), 807 (w), 672 (m), 645 (s), 565 (m), 522 (w), 464 (w). Anal. calcd: C, 16.42; H, 3.53. Found: C, 16.18; H, 3.69%. MS (EI, positive): 602 (M$^+$ − 2Br, 3%), 281 (M$^+$ − 6Br, 100%).

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