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Tetrametallic D_3-Symmetric Alkoxide Molecules Containing Aluminum

David A. Atwood,* Jolin A. Jegier, Shengming Liu, Drew Rutherford,
Pingrong Wei, and Robert C. Tucker†

*Department of Chemistry, The University of Kentucky, Lexington, Kentucky 40506-0055, and
Praxair Surface Technologies, Inc., 1500 Polco Street, Indianapolis, Indiana 46224*

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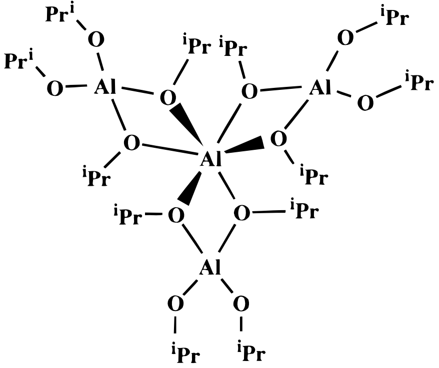
A new series of aluminum alkoxide molecules of formula $[Al\{(\mu\text{-}OEt)_2AlR_2\}_3]$, where R = Me (**1**), Et (**2**), ^iBu (**3**), and $[Al\{(\mu\text{-}OEt)_2GaR_2\}_3]$, where R = Me (**4**) and Et (**5**), have been synthesized and fully characterized. In pure form **1**, **2**, and **4** are crystalline solids. However, in the presence of a small amount of solvent or impurity all of the compounds exist as oils. They were characterized by ^1H NMR, IR, elemental analysis, mp, and single-crystal X-ray diffractometry for compounds **1**, **2**, and **4**.

Introduction

The search for a unimolecular precursor to Al_2O_3 is somewhat problematic since any relevant molecules must be crafted to incorporate an Al/O ratio of 2:3. This is a rare ratio for the group 13/16 elements, which generally form compounds having stoichiometries of 1:1 ($[R_2AlOR']_n$ or $[RAlO]_n$[1]), 1:2 ($[RAl(OR')_2]_n$), and 1:3 ($[Al(OR')_3]_n$) (where *n* is commonly 2, 3, and 4).[2] Previously employed precursors to Al_2O_3 have almost always contained an excess of oxygen (or have been used with a second oxygen source such as H_2O). This is true in some recently reported precursors of the type $Al(acac)_3$,[3] $Al(OOCR)_3$,[4] and $Al(OR)_3$[5] (R = alkyl). These types of precursors, which were all used in the gas phase, have met with a measure of success in the fabrication of aluminum oxide thin films for use as passivating layers and insulating films in electronic devices.[6]

This article details attempts to synthesize molecules that contain a group 13:oxygen stoichiometry of 2:3. The resulting complexes are tetrameric with a core of group 13 element and O atoms in the shape of the emblem of the Mitsubishi company.[7] They are of formula $[Al\{(\mu\text{-}OEt)_2AlR_2\}_3]$, where R = Me (**1**), Et (**2**), ^iBu (**3**), and $[Al\{(\mu\text{-}OEt)_2GaR_2\}_3]$, where R = Me (**4**) and Et (**5**). Only two such molecules, $[Al[\{2\text{-}(OCH_2)SC_4H_3)_2\}_2AlMe_2]_3]$[8] and $[Al\{(\mu\text{-}OR)_2AlMe_2\}_3]$ (where R = 10-undecene),[9] have been previously reported. However, as a class these molecules have as a foundation the extensive studies[7,10,11] into the structure[12] of $[Al(O^iPr)_3]_4$, which is tetrametallic (below). A wide range of heterobimetallic complexes $[M\{(\mu\text{-}OR)_2Al(OR)_2\}_3]$ (where M = gallium, indium, transition metal,[13] or lanthanide[14] and R = alkyl) also adopt a Mitsubishi structure. These previously reported complexes may be viewed as homoleptic metal alkoxides, whereas those reported herein are alkyl group 13 alkoxides.



Results and Discussion

Synthesis and Characterization. Compounds **1**−**5** (below) are prepared by combining the appropriate alkyl group 13 reagent with aluminum triethoxide. The initial

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(1) Mason, M. R.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, *115*, 4971, and references therein.

(2) Oliver, J. P. In *Coordination Chemistry of Aluminum*; Robinson, G. H., Ed.; VCH Publishers: New York, 1993; Chapter 4. Taylor, M. J.; Brothers, P. J. In *Chemistry of Aluminum, Gallium, Indium and Thallium*; Downs, A. J., Ed.; Chapman and Hall: London, 1993; pp 148−152 (and references therein).

(3) Temple, D.; Reisman, A. *J. Electron. Mater.* **1990**, *19*, 995. Kim, J. S.; Marzouk, H. A.; Reucroft, P. J.; Robertson, J. D.; Hamrin, C. E., Jr. *Appl. Phys. Lett.* **1993**, *62*, 681.

(4) Maruyama, T.; Nakai, T. *Appl. Phys. Lett.* **1991**, 58.

(5) van Corbach, H. D.; Haanappel, V. A. C.; Fransen, T.; Gellings, P. J. *Thin Solid Films* **1994**, *239*, 31. Saraie, J.; Ono, K.; Takeuchi, S. *J. Electrochem. Soc.* **1989**, *136*, 3139.

(6) Kobayashi, T.; Okamura, M.; Yamaguchi, E.; Shinoda, Y.; Hirota, Y. *J. Appl. Phys.* **1981**, *52*, 6434.

(7) They were first called by that name in: Folting, K.; Streib, W. E.; Caulton, K. G.; Poncelet, O.; Hubert-Pfalzgraf, I. G. *Polyhedron* **1991**, *10*, 1639.

(8) Oliver, J. P.; Kumar, R. *Polyhedron* **1990**, *9*, 409. Kumar, R.; del Mel, V. S. J.; Sierra, M. L.; Hendershot, D. G.; Oliver, J. P. *Organometallics* **1994**, *13*, 2079.

(9) Turunen, J.; Pakkanen, T. T.; Lofgren, B., *J. Mol. Catal. A* **1997**, *123*, 35.

(10) Joung, W. G.; Hartung, W. H.; Krossley, F. S. *J. Am. Chem. Soc.* **1936**, *58*, 100.

(11) It was first proposed to be tetrametallic by: Bradley, D. C. *Nature* **1958**, *182*, 1211. Bradley, D. C. *Adv. Chem. Ser.* **1959**, *23*, 10.

(12) Turova, N. Y.; Kozunov, V. A.; Yanovskii, A. I.; Bokii, N. G.; Struchkov, Y. T.; Tarnopol'ski, B. L. *J. Inorg. Nucl. Chem.* **1979**, *41*, 5.

(13) Singh, J. V.; Jain, N. C.; Mehrotra, R. C. *Synth. React. Inorg. Met.-Org. Chem.* **1979**, *9*, 79.

(14) Mehrotra, R. C.; Mehrotra, A. *Inorg. Chim. Acta* **1971**, *5*, 127. Mehrotra, R. C.; Mehrotra, A. *Ind. J. Chem.* **1972**, *10*, 532. Mehrotra, R. C.; Agrawal, M. M.; Mehrotra, A. *Synth. Inorg. Met-Org. Chem.* **1973**, *3*, 181. Mehrotra, R. C.; Agrawal, M. M.; Mehrotra, A. *Synth. Inorg. Met-Org. Chem.* **1973**, *3*, 407. Mehrotra, R. C.; Kapoor, P. N.; Batwara, J. M. *Coord. Chem. Rev.* **1980**, *31*, 67. Wijk, M.; Norrestam, R.; Nygren, M.; Westin, G. *Inorg. Chem.* **1996**, *35*, 1077.

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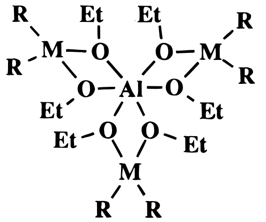
mixture is prepared in an inert atmosphere glovebox using toluene as the solvent. It is then taken out of the drybox, connected to a vacuum line, and refluxed for a minimum of 4 h. The heating may be conducted for a longer period of time with no detrimental effect. As the reflux begins, the originally insoluble $Al(OEt)_3$ becomes soluble and a clear solution results. After terminating the reflux, filtration, and solvent removal, viscous oils result. For **1**−**3** the synthesis involves the 1:1 addition of the reagents with no additional byproducts. For **4** and **5** the optimal stoichiometry was 3 GaR_3 with 2 $Al(OEt)_3$ with the consequent elimination of AlR_3 from the reaction. By the existence of $[Al\{(\mu\text{-}O^iPr)_2Al(O^iPr)_2\}_3]$ it would appear that the synthesis of the complexes $[Al\{(\mu\text{-}O^iPr)_2AlR_2\}_3]$, where R = Me, Et, ^{i}Bu, would also be possible. However, under the same conditions employed in the synthesis of **1**−**3**, these complexes were not accessible. Rather, the reactions led to isolation of the tetrameric starting material, $\{^iPrO_2Al(\mu\text{-}O^iPr)_2\}_3Al$. This may imply that such tetramers do not easily redistribute to give the desired products in the same manner as dimeric $[Al(OEt)_3]_2$. Additionally, attempts to form derivatives stemming from the use of AlH_3−NMe_3 were not successful, perhaps due to the sensitivity of the Al−H group for thermal decomposition.[15]



M= Al; R = Me (1); Et (2); ^{i}Bu (3)

M = Ga; R = Me (4); Et (5)

These oils give very clean ^{1}H NMR spectra. A primary feature in the spectra for **1**−**3** is the presence of one set of resonances for the Al−R group and one for the OCH_2CH_3 protons. These data are consistent with a symmetrical structure like that shown above. However, the OCH_2 groups are manifested as two closely spaced multiplets. This type of behavior is consistent with the presence of diastereotopic methylene groups which would be a consequence of the D_3 symmetry of the molecule. The fact that two resonances are not observed for the CH_3 groups may be attributed to an averaging process or coincidence of the two resonances. Thus, it is likely that the compounds are not interconverting to other species in solution.

Furthermore, the ^{27}Al NMR of **1** and **2** consists of two peaks in the expected range for six-coordinate (~11 ppm) and four-coordinate aluminum atoms (~150 ppm). This is in contrast to the behavior of $[Al(O^iPr)_3]_4$ and others of general formula $[Me_2Al(OR)]_{2,3}$,[16] which do undergo interconversion in solution. For $[Al(O^iPr)_3]_4$ there is interconversion between the tetramer and a trimer (Scheme 1).[13] This may also be occurring in solution for **3**, which has a more complex ^{1}H NMR spectrum than was observed for **1** and **2**. It contains three peaks in the ^{27}Al NMR, which can be assigned to four-, five-, and six-coordinate species. This could be interpreted as resulting from a tetramer−trimer equilibrium, the trimer giving rise to the five-coordinate ^{27}Al resonance (Scheme 2).

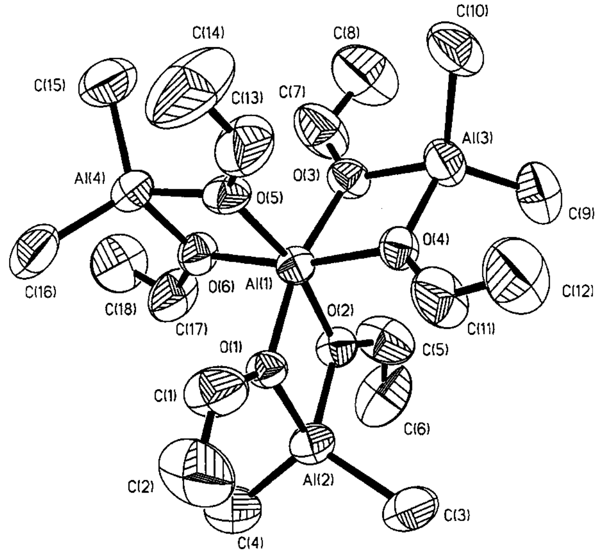


Figure 1. ORTEP view (30% probability) of $[Al\{(\mu\text{-}OEt)_2AlMe_2\}_3]$ (**1**).

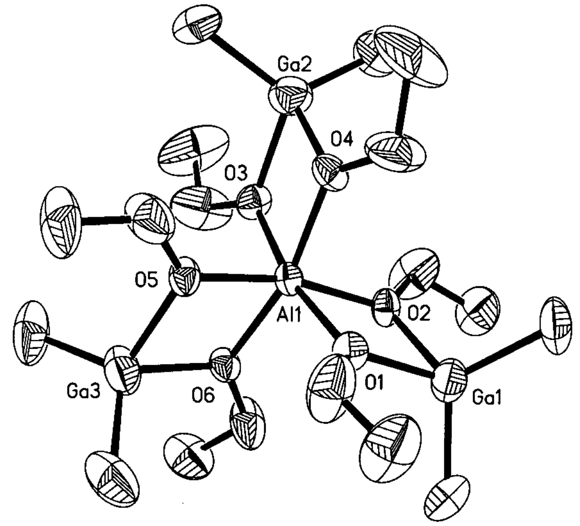


Figure 2. ORTEP view (30% probability) of $[Al\{(\mu\text{-}OEt)_2GaMe_2\}_3]$ (**4**).

A different situation is observed in the NMR spectra of the mixed-metal derivatives, **4** and **5**. For these compounds, the ^{27}Al spectra contained resonances for more than one six-coordinate aluminum atom in solution (in the range δ 11−16 ppm). There were no peaks in the regions associated with four- and five-coordinate aluminum species. This was an indication that the central atom was aluminum and that the peripheral atoms were gallium (confirmed in a crystal structure of **4**; see below). Based upon the elemental analyses it was clear that **4** and **5** were pure. Moreover the ^{1}H NMR data did not indicate other products in solution. Obtaining ^{27}Al NMR data at low temperatures had little effect on the positions of the multiple six-coordinate resonances until −90 °C. At this temperature only one

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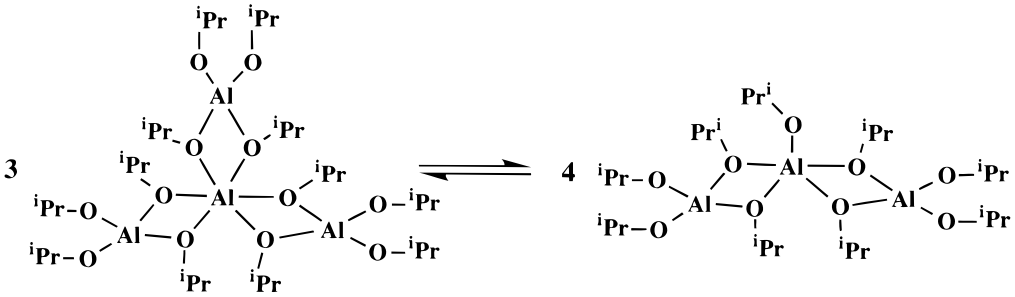
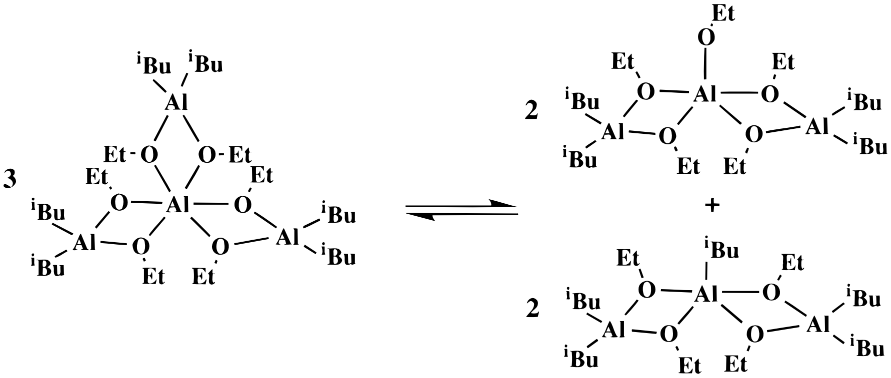
(15) Kovar, R. A.; Callaway, J. O. *Inorg. Synth.* **1990**, *17*, 36.

(16) Rogers, J. H.; Apblett, A. W.; Cleaver, W. M.; Tyler, A. N.; Barron, A. R. *J. Chem. Soc., Dalton Trans.* **1992**, 3179.

Scheme 1. Tetramer−Trimer Equilibrium for [Al(O^{i}Pr)$_3$]$_4$



Scheme 2. Proposed Equilibrium for [Al{(μ-OEt)$_2$Al^{i}Bu$_2$}$_3$] (3)



resonance was observed for **4** and **5** at a value of δ 15 ppm for both and $W_{1/2}$ of 140.2 and 112.3 Hz, respectively. An explanation for the multiple resonances at warmer temperatures could be that the GaR_2 groups are rapidly dissociating and reattaching in solution. That this does not occur for the all-aluminum analogues could be attributed to the greater Al−O bond strength when compared to a Ga−O bond.[17]

Initial work found that the oils originally isolated for **1**−**4** slowly became crystalline over the course of days to months. Compound **5** remains indefinitely as an oily solid. The ^{1}H NMR spectra of the resulting crystalline material were close to being identical to that shown for the oils. Upon closer inspection and after obtaining numerous examples, two observations could be made. The oils that did not solidify within one or 2 days had at least one of two features in common. The first was an impurity ^{1}H NMR resonance falling close to that seen for the $OCH_2C\mathit{H}_3$ groups. The second was the presence of a toluene peak at δ 2.1 ppm. In cases where neither of these peaks were observed in the ^{1}H NMR, the oils crystallized within 24 h. Moreover, the occurrence of oils with greater longevity took place more frequently as the bottle of $Al(OEt)_3$ aged. Thus, the maintenance of an oil for an extended period of time for **1**−**3** could be attributed to the presence of solvent or the use of aged $Al(OEt)_3$. The as-prepared oils (after being evacuated to 10^{-3} Torr for 3 h) contained one molecule of toluene for every 10 tetramers for **1** and **2**, and one toluene for every 20 tetramers for **3** and **4**. Compound **5**, which does not solidify, contains substantially more toluene, with one molecule of toluene for four tetramers. An alternate means of preventing solidification of the pure oils is to mix two of them immediately after synthesis. In the case of combinations of **1** and **2**, and **2** and **3**, no solidification occurred over the course of 3 months.

Molecular Structures of 1, 2, and 4. In several instances the solids that crystallized from the original oils were of sufficient crystallinity to warrant an X-ray crystallographic investigation. This was successfully performed for **1**, **2**, and **4**. Compounds **1** and **2** were isomorphous, so only the strucutre of **2** will be described (Figure 1). The central six-coordinate Al atom is chelated in a bidentate fashion through the oxygens of the three $R_2Al(OEt)_2$ groups. The Al−O distances (Table 1) are longer around the central six-coordinate aluminum (av 1.9 Å) than for the terminal four-coordinate aluminums (av 1.8 Å). This is in keeping with the increase in atomic radii with increasing coordination number. All of the Al_2O_2 four-membered rings are planar. They adopt a propeller-type arrangement around the central aluminum atom. The Al_2O_2 rings form dihedral angles of 59.2°(av) for **1** and 60.5°(av) for **2** with the coplanar aluminum atoms. The structure of **4** (Figure 2) is unusual in that the heavier element occupies the peripheral positions in the tetramer. All of the other heterobimetallics have the heavier element in the central position.[11,12] This is apparently a consequence of these elements being able to better accommodate a six-coordinate rather than four-coordinate geometry. In **4** this might be an indication that Ga(III) (six-coordinate) is, indeed, smaller than aluminum(III) (due to the contraction of the d orbitals on the fourth period). However, textbook values indicate that this is not the case with Al = 0.68 Å and Ga = 0.73 Å.[17] The Al−O distances (av 1.9 Å) are similar to what was observed in **1** and **2**. The O−Ga distances (av 1.92 Å) are somewhat longer than those observed to the terminal Al atoms in **1** and **2**.

The tetrametallic Mitsubishi structural motif is not limited to metals supported by alkoxide groups. Other

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(17) *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th ed.; Huheey, J. E., Keiter, E. A.; Keiter, R L., Eds.; Harper Collins: New York, 1993; p 114.

Table 1. Bond Lengths (Å) for 1, 2 (Isomorphous to 1), and 4

1		2		3	
Al(1)−O(1)	1.896(8)	Al(1)−O(1)	1.875(20)	Al(1)−O(1)	1.898(4)
Al(1)−O(2)	1.904(8)	Al(1)−O(2)	1.852(25)	Al(1)−O(2)	1.905(4)
Al(1)−O(3)	1.891(8)	Al(1)−O(3)	1.837(25)	Al(1)−O(3)	1.888(4)
Al(1)−O(4)	1.900(7)	Al(1)−O(4)	1.908(19)	Al(1)−O(4)	1.903(4)
Al(1)−O(5)	1.888(9)	Al(1)−O(5)	1.863(20)	Al(1)−O(5)	1.903(4)
Al(1)−O(6)	1.904(7)	Al(1)−O(6)	1.862(25)	Al(1)−O(6)	1.909(4)
Al(2)−O(1)	1.815(8)	Al(2)−O(1)	1.811(22)	Ga(1)−O(1)	1.915(4)
Al(2)−O(2)	1.813(9)	Al(2)−O(2)	1.781(26)	Ga(1)−O(2)	1.922(4)
Al(2)−C(3)	1.952(12)	Al(2)−C(3)	1.856(35)	Ga(1)−C(1)	1.938(8)
Al(2)−C(4)	1.960(13)	Al(2)−C(5)	1.874(41)	Ga(1)−C(2)	1.939(9)
Al(3)−O(3)	1.816(8)	Al(3)−O(3)	1.752(24)	Ga(2)−O(3)	1.927(4)
Al(3)−O(4)	1.815(8)	Al(3)−O(4)	1.802(22)	Ga(2)−O(4)	1.913(4)
Al(3)−C(9)	1.920(15)	Al(3)−C(11)	1.968(43)	Ga(2)−C(3)	1.946(8)
Al(3)−C(10)	1.944(13)	Al(3)−C(13)	1.919(56)	Ga(2)−C(4)	1.934(8)
Al(4)−O(5)	1.807(8)	Al(4)−O(5)	1.826(22)	Ga(3)−O(5)	1.922(4)
Al(4)−O(6)	1.813(9)	Al(4)−O(6)	1.757(28)	Ga(3)−O(6)	1.915(4)
Al(4)−C(15)	1.941(15)	Al(4)−C(19)	1.952(49)	Ga(3)−C(15)	1.920(10)
Al(4)−C(16)	1.923(15)	Al(4)−C(21)	1.889(37)	Ga(3)−C(16)	1.950(11)

Table 2. Bond Angles (deg) for 1, 2 (Isomorphous to 1), and 4

1		2		3	
O(1)−Al(1)−O(2)	75.8(3)	O(1)−Al(1)−O(2)	74.2(9)	O(1)−Al(1)−O(2)	77.1(2)
O(1)−Al(1)−O(3)	165.7(4)	O(1)−Al(1)−O(3)	95.4(9)	O(1)−Al(1)−O(3)	167.9(2)
O(2)−Al(1)−O(3)	95.0(4)	O(2)−Al(1)−O(3)	98.1(11)	O(2)−Al(1)−O(3)	94.5(2)
O(1)−Al(1)−O(4)	94.3(3)	O(1)−Al(1)−O(4)	164.0(10)	O(1)−Al(1)−O(4)	94.8(2)
O(2)−Al(1)−O(4)	96.2(3)	O(2)−Al(1)−O(4)	97.0(9)	O(2)−Al(1)−O(4)	97.0(2)
O(3)−Al(1)−O(4)	75.4(3)	O(3)−Al(1)−O(4)	72.3(9)	O(3)−Al(1)−O(4)	77.3(2)
O(1)−Al(1)−O(5)	94.6(4)	O(1)−Al(1)−O(5)	93.4(8)	O(1)−Al(1)−O(5)	93.9(2)
O(2)−Al(1)−O(5)	165.7(4)	O(2)−Al(1)−O(5)	162.5(10)	O(2)−Al(1)−O(5)	166.7(2)
O(3)−Al(1)−O(5)	96.2(4)	O(3)−Al(1)−O(5)	95.2(10)	O(3)−Al(1)−O(5)	95.8(2)
O(4)−Al(1)−O(5)	95.2(3)	O(4)−Al(1)−O(5)	97.8(9)	O(4)−Al(1)−O(5)	93.5(2)
O(1)−Al(1)−O(6)	96.7(3)	O(1)−Al(1)−O(6)	98.4(10)	O(1)−Al(1)−O(6)	96.3(2)
O(2)−Al(1)−O(6)	94.3(3)	O(2)−Al(1)−O(6)	95.7(11)	O(2)−Al(1)−O(6)	93.7(2)
O(3)−Al(1)−O(6)	94.9(4)	O(3)−Al(1)−O(6)	162.7(11)	O(3)−Al(1)−O(6)	93.0(2)
O(4)−Al(1)−O(6)	166.3(4)	O(4)−Al(1)−O(6)	95.7(10)	O(4)−Al(1)−O(6)	166.0(2)
O(5)−Al(1)−O(6)	75.9(3)	O(5)−Al(1)−O(6)	73.6(10)	O(5)−Al(1)−O(6)	77.3(2)
O(1)−Al(2)−O(2)	80.1(4)	O(3)−Al(3)−O(4)	76.9(10)	O(1)−Ga(1)−O(2)	76.3(2)
O(1)−Al(2)−C(3)	115.2(5)	O(3)−Al(3)−C(11)	112.4(15)	O(1)−Ga(1)−C(1)	112.3(3)
O(2)−Al(2)−C(3)	113.8(5)	O(4)−Al(3)−C(11)	113.6(14)	O(2)−Ga(1)−C(1)	111.7(3)
O(1)−Al(2)−C(4)	114.3(5)	O(3)−Al(3)−C(13)	113.7(19)	O(1)−Ga(1)−C(2)	112.3(3)
O(2)−Al(2)−C(4)	115.4(5)	O(4)−Al(3)−C(13)	116.4(19)	O(2)−Ga(1)−C(2)	114.1(3)
C(3)−Al(2)−C(4)	113.9(6)	C(11)−Al(3)−C(13)	117.3(22)	C(1)−Ga(1)−C(2)	121.5(4)
O(3)−Al(3)−O(4)	79.4(4)	O(1)−Al(2)−O(2)	77.5(10)	O(3)−Ga(2)−O(4)	76.2(2)
O(3)−Al(3)−C(9)	115.0(5)	O(1)−Al(2)−C(3)	119.7(17)	O(3)−Ga(2)−C(4)	111.3(3)
O(4)−Al(3)−C(9)	115.3(6)	O(2)−Al(2)−C(3)	112.9(15)	O(4)−Ga(2)−C(4)	112.7(3)
O(3)−Al(3)−C(10)	114.2(5)	O(1)−Al(2)−C(5)	117.1(15)	O(3)−Ga(2)−C(3)	112.9(4)
O(4)−Al(3)−C(10)	114.5(5)	O(2)−Al(2)−C(5)	113.8(15)	O(4)−Ga(2)−C(3)	113.2(3)
C(9)−Al(3)−C(10)	114.0(7)	C(3)−Al(2)−C(5)	111.5(19)	C(3)−Ga(2)−C(4)	121.8(4)
O(5)−Al(4)−O(6)	80.2(4)	O(5)−Al(4)−O(6)	77.1(10)	O(5)−Ga(3)−O(6)	76.7(2)
O(5)−Al(4)−C(15)	114.9(5)	O(5)−Al(4)−C(19)	112.0(16)	O(6)−Ga(3)−C(5)	112.8(4)
O(6)−Al(4)−C(15)	114.6(5)	O(6)−Al(4)−C(19)	115.2(14)	O(5)−Ga(3)−C(5)	113.2(4)
O(5)−Al(4)−C(16)	115.2(5)	O(5)−Al(4)−C(21)	116.2(13)	O(6)−Ga(3)−C(6)	112.0(3)
O(6)−Al(4)−C(16)	113.6(5)	O(6)−Al(4)−C(21)	116.5(15)	O(5)−Ga(3)−C(6)	113.5(3)
C(15)−Al(4)−C(16)	114.2(7)	C(19)−Al(4)−C(21)	114.6(17)	C(5)−Ga(3)−C(6)	120.6(5)
Al(1)−O(1)−Al(2)	102.1(4)	Al(1)−O(1)−Al(2)	103.1(9)	Al(1)−O(1)−Ga(1)	102.1(4)
Al(1)−O(2)−Al(2)	101.9(4)	Al(1)−O(2)−Al(2)	105.2(11)	Al(1)−O(2)−Ga(1)	101.9(4)
Al(1)−O(3)−Al(3)	102.7(4)	Al(1)−O(3)−Al(3)	107.9(12)	Al(1)−O(3)−Ga(2)	102.7(4)
Al(1)−O(4)−Al(3)	102.4(4)	Al(1)−O(4)−Al(3)	102.9(10)	Al(1)−O(4)−Ga(2)	102.4(4)
Al(1)−O(5)−Al(4)	102.3(4)	Al(1)−O(5)−Al(4)	103.2(10)	Al(1)−O(5)−Ga(3)	102.3(4)
Al(1)−O(6)−Al(4)	101.5(4)	Al(1)−O(6)−Al(4)	106.0(11)	Al(1)−O(6)−Ga(3)	101.5(4)

group 13 element complexes have demonstrated an Al_4E_6 central core (E = O or N). For instance, these species can occur when the stoichiometry of the heteroatom containing starting material is in a 3:2 ratio with the aluminum reagent.[18] Structurally characterized examples include $[\{(CH_3)_3Si\}_2Al(NH_2)_2]_3Al$,[19] as well as those with open chain amines,[20] and alumatranes.[21]

The fact that group 13 alkoxides can take this geometry is somewhat surprising in view of the predominance of the bridged dimeric type of structures. For instance, $Al(OEt_3)_3$ and $Al(OSiMe_3)_3$[7] (where the $SiMe_3$ group may be envisioned to have the steric effect of a ^{t}Bu) have been shown to be dimeric. The O^{i}Pr group is

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(18) Eisch, J. J. In *Comprehensive Organometallic Chemistry*, Vol 1; Wilkinson, G. A., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: New York 1983; p 555.

(19) Janik, J. F.; Duesler, E. N.; Paine, R. T. *Inorg. Chem.* **1988**, *27*, 4335.

(20) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1987**, *109*, 6852. Robinson, G. H.; Self, M. F.; Pennington, W. T.; Sangokoya, S. A. *Organometallics* **1988**, *7*, 2424. Robinson, G. H.; Moise, F.; Pennington, W. T.; Sangokoya, S. A. *Polyhedron* **1989**, *8*, 1279. Lee, B.; Pennington, W. T.; Robinson, G. H.; Rogers, R. D. *J. Organomet. Chem.* **1990**, *396*, 269. Robinson, G. H.; Pennington, W. T.; Lee, B.; Self, M. F.; Hrncir, D. C. *Inorg. Chem.* **1991**, *30*, 809.

Table 3. Summary of X-ray Data for 1, 2, and 4

	1	2	4
formula	$C_{18}H_{48}Al_4O_6$	$C_{24}H_{60}Al_4O_6$	$C_{18}H_{48}AlGa_3O_6$
fw	468.5	552.6	596.70
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	11.646(1)	12.205(2)	8.3373(6)
b (Å)	11.444(2)	12.248(1)	10.6313(8)
c (Å)	22.759(2)	24.440(2)	17.339(1)
α (deg)	90	90	89.835(1)
β (deg)	98.51(1)	98.75(1)	89.993(1)
g (deg)	90	90	76.309(1)
V (Å^3)	2999.9(6)	3611.3(7)	1493.1(2)
Z	4	4	2
D_{calc} (g/cm^3)	1.037	1.016	1.327
cryst size (mm)	0.7 × 0.4 × 0.4	$(0.5)^3$	$(0.4)^3$
temp (K)	298	298	298
2θ range (deg)	3.5−45	3.5−45	2.34−38
scan type	$2\theta-\theta$	$2\theta-\theta$	$2\theta-\theta$
scan speed (deg/min)	10−60	8−60	
scan range (deg)	0.31	0.40	
no. of reflns collected	5182	5182	4168
no. of indp reflns	3937	4754	2377
no. of obsd reflns ($F > 4.0\sigma(F)$)	1588	1021	2364
no. of parameters	253	307	253
R	0.0776	0.0896	0.0561
R_w	0.0765	0.0876	0.1684
GOF	2.51	3.79	1.422
lar diff peak (e/Å^3)	0.23	0.21	0.470

clearly intermediary in steric encumbrance between the groups used in these two examples but gives the tetrameric structure.

Conclusion

A series of tetrametallic alkyl group 13 alkoxide molecules have been synthesized and fully characterized. They possess D_3 symmetric structures and have the appropriate metal:oxygen stoichiometry for use as unimolecular precursors to metal oxide materials. Preliminary results indicate that **1**−**3** can be decomposed to form relatively pure Al_2O_3 at ambient temperatures.

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glovebox. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-400 and -270 instruments at 270.17 (^{1}H), 62.5 (^{13}C), and 104.5 (^{27}Al) MHz. Chemical shifts are reported relative to $SiMe_4$ and are in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer and were found to be within acceptable limits for crystalline **1**−**5**. The oils analyzed were found to include a certain amount of toluene as described in the text. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}. X-ray powder diffraction data were collected on a Philips diffractometer. Thermogravimetric and elemental analyses (C and H) were conducted on Perkin-Elmer analyzers. R_3Al, Me_3Ga, Et_3Ga, and $Al(OEt)_3$ were purchased from either Aldrich or Strem and used as received. Caution: R_3Al and R_3Ga reagents are highly pyrophoric and must be handled under an inert atmosphere. This is not the case for compounds **1**−**5**, which decompose slowly over the course of hours to days when exposed to the atmosphere.

[Al{(μ-OEt)$_2$AlMe$_2$}$_3$] (1). To a stirred suspension of aluminum triethoxide (30.83 mmol, 5.000 g) in toluene (30 mL) at 25 °C was added a solution of trimethylaluminum (30.83 mmol, 2.223 g) in toluene (30 mL). The mixture was then brought to reflux and the solid dissolved after 20 min. The solution was refluxed for a total of 4 h, cooled to 25 °C, and filtered to remove a small amount of insoluble material. The volatiles were removed under reduced pressure, yielding a nearly colorless, viscous oil (6.742 g, 93%), which crystallized in a period of time from 1 day to 3 months. Single crystals suitable for X-ray analysis were obtained from a sample which was allowed to sit undisturbed for 3 months at 25 °C. Mp: 162−65 °C. ^{1}H NMR (C_6D_6): δ −0.43 (s, 18H, AlCH_3), 1.12 (t, 18H, OCH$_2$CH_3), 3.59 (m, 6H, OCH_aH$_b$), 3.83 (m, 6H, OCH$_a$$H_b$). ^{27}Al NMR ($C_6D_6$): 12 ($W_{1/2}$ 19.6 Hz) 151 ($W_{1/2}$ 5.62 kHz), IR (KBr): ν 2984 s, 2943 m, 2906 m, 2818 m, 1471 m, 1390 m, 1197 s, 1103 s, 1060 s, 900 s, 680 s(br), 582 s, 523 m. Analysis based on $C_{18}H_{48}O_6Al_4$: calcd, C 46.15, H 10.33; found, C 46.23, H 10.29.

[Al{(μ-OEt)$_2$AlEt$_2$}$_3$] (2). The procedure was as for **1** using aluminum triethoxide (30.83 mmol, 5.000 g), toluene (60 mL), and triethylaluminum (30.83 mmol, 21.336 g of a 1 M solution in hexanes), yielding a nearly colorless, viscous oil (8.308 g, 98%). This oil also crystallized in a period of time from 3 days to several months. Single crystals suitable for X-ray analysis were obtained from a sample which was allowed to sit undisturbed for 5 days at 25 °C. Mp: 124−27 °C. ^{1}H NMR (C_6D_6): δ 0.17 (m, 12H, AlCH_2CH$_3$), 1.12 (t, 18H, AlCH$_2$CH3), 1.38 (t, 18H, OCH$_2$CH_3), 3.56 (m, 6H, OCH_aH$_b$), 3.78 (m, 6H, OCH$_a$$H_b$). ^{27}Al NMR ($C_6D_6$): 12 ($W_{1/2}$ 24.9 Hz) 148 ($W_{1/2}$ 5.31 kHz). IR (KBR): ν 2978 s, 2939 s, 2911 s, 2817 m, 1452 m, 1408 s, 1321 m, 1195 m, 1165 m, 1101 s, 1060 s, 896 s, 640 s(br). Analysis based on $C_{24}H_{60}O_6Al_4$: calcd, C 52.16, H 10.94; found, C 52.09, H 10.85.

[Al{(μ-OEt)$_2$Al^{i}Bu$_2$}$_3$] (3). The procedure was as for **1** using aluminum triethoxide (30.83 mmol, 5.000 g), toluene (60 mL), and triisobutylaluminum (30.83 mmol, 6.115 g), yielding a nearly colorless, viscous oil (10.528 g, 95%). Crystalline material was never obtained from this reaction. ^{1}H NMR (C_6D_6): δ 0.15 (d, 12H, AlCH_2CH(CH$_3$)$_2$), 1.08 (d, 18H, AlCH$_2$CH(CH_3)$_2$), 1.19 (t, 18H, OCH$_2$CH_3), 2.01 (m, 6H, AlCH$_2$CH(CH$_3$)$_2$), 3.73 (m, 6H, OCH_aH$_b$), 3.92 (m, 6H, OCH$_a$$H_b$), ^{27}Al NMR ($C_6D_6$): 12 ($W_{1/2}$ 25.5 Hz) 41 ($W_{1/2}$ 1.18 kHz) 164 ($W_{1/2}$ 6.02 kHz), IR (neat): ν 2949 s, 2866 s, 2773 m, 1462 s, 1390 s, 1359 s, 1340 m, 1160 s, 1059 s, 896 s, 871 s(br). Analysis based on $C_{36.68}H_{84.78}O_6Al_4$ (tetramer with 1/10 toluene): calcd, C 60.36, H 11.72; found, C 60.31, H 11.69.

[Al{(μ-OEt)$_2$GaMe$_2$}$_3$](4). The procedure was as for **1** using aluminum triethoxide (18.5 mmol, 3.00 g), toluene (40 mL), and trimethylgallium (27.7 mmol, 3.19 g), yielding a nearly colorless, viscous oily solid (5.12 g, 93%). Crystals of **4** were grown from a separate reaction (in a 1:1 stoichiometry) which was left standing at 25 °C for 10 days. Mp: 130−133 °C. ^{1}H NMR (C_6D_6): δ −0.29 (s, 18H, GaCH$_3$), 1.02 (t, 18H, OCH$_2$CH_3), 3.74 (m, 6H, OCH_aH$_b$), 4.02 (m, 6H, OCH$_a$$H_b$). ^{27}Al NMR ($C_6D_6$): 12.55 ($W_{1/2}$ 38.2 Hz) 12.78 ($W_{1/2}$ 25.5 Hz) 13.95 ($W_{1/2}$ 47.3 Hz) 15.12 ($W_{1/2}$ 21.8 Hz) at −94 °C = 15.36 ($W_{1/2}$ 140.2 Hz). IR (neat): ν 2949 s, 2866 s, 2773 m, 1462 s, 1390 s, 1359 s, 1340 m, 1160 s, 1059 s, 896 s, 871 s(br). Analysis based on $C_{18}H_{48}O_6Ga_3Al$: calcd, C 36.23, H 8.11; found, C 36.41, H 8.28.

[Al{(μ-OEt)$_2$GaEt$_2$}$_3$] (5). The procedure was as for **1** using aluminum triethoxide (19.2 mmol, 3.12 g), toluene (40 mL), and triethylgallium (28.9 mmol, 4.53 g), yielding a nearly colorless, viscous oily solid (6.42 g, 98%). ^{1}H NMR (C_6D_6): δ 0.29−0.71 (m, 18H, GaEt), 1.35 (t, 18H, OCH$_2$CH_3), 3.74 (m, 6H, OCH_2). ^{27}Al NMR (C_6D_6): 13 (d, $W_{1/2}$ 23.7 and 19.1 Hz) 14

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(21) Pinkas, J.; Verkade, J. G. *Polyhedron* **1996**, *15*, 1567. Shklover, V. E.; Struchkov, Y. T.; Voronkov, M. G.; Ovchinnikova, Z. A.; Baryshok, V. P. *Dokl. Acad. Nauk SSSR (Engl. Trans.)* **1984**, *277*, 723. Pinkas, J.; Verkade, J. G. *Inorg. Chem.* **1993**, *32*, 2711. Paz-Sandoval, M. A.; Fernandez-Vincent, C.; Vribe, G.; Contreras, R.; Klaebe, A. *Polyhedron* **1988**, *71*, 679.

($W_{1/2}$ 69.9 Hz) 15 ($W_{1/2}$ 23.7 Hz) at −94 °C = 15 ($W_{1/2}$ 112.3 Hz). IR (neat): ν 2968 s, 2940 s, 2914 m, 2870 s, 1451 s, 1385 s, 1163 m, 1101 s, 1065 s, 999 s, 895 m, 637 m, 561 m, 515 m. Analysis based on $C_{25.75}H_{62}O_6Ga_3Al$ (one tetramer with 1/4 toluene): calcd, C 43.94, H 8.88; found, C 44.02, H 8.91.

X-ray Experimental Data. In each of the data collections the check reflections indicated a less than 5% decrease in intensity over the course of data collection, and hence, no correction was applied. All calculations were performed on a personal computer using the Siemens software package SHELXTL-Plus. The structures were solved by direct methods and successive interpretation of difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters. With the exception of having a weakly diffracting crystal for **2**, which exacerbated the problem of ethyl group motion, there were no other problems in the structure solutions.

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Supporting Information Available: Tables of bond lengths and angles, positional parameters, anisotropic thermal parameters, and unit cell views for **1**, **2**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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