

**A New Synthetic Route to Organoalumoxanes (RAIO)<sub>n</sub>: Synthesis of (Mes\*AlO)<sub>4</sub> (Mes\* = –C<sub>6</sub>H<sub>2</sub>-2,4,6-*t*-Bu<sub>3</sub>) and Its Reactions with AlR<sub>3</sub> (R = Me or Et)**

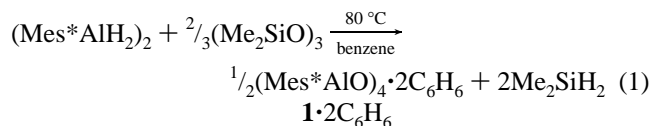
Rudolf J. Wehmschulte and Philip P. Power\*

Department of Chemistry, University of California  
Davis, California 95616

Received May 1, 1997

Monosubstituted organoalumoxanes of formula (RAIO)<sub>n</sub> are normally synthesized by hydrolysis of organoaluminum compounds with water or water contained in hydrated metal salts.<sup>1</sup> The simplest derivative, methylalumoxane, i.e., (MeAlO)<sub>n</sub> or MAO, is of great industrial importance, particularly in olefin polymerization.<sup>2,3</sup> Full details of the structure of MAO are currently unknown, but analytical and phase separation data have been interpreted in terms of three-dimensional, cage structures.<sup>4,5</sup> In an important development, it has been shown that the hydrolysis of Al(*t*-Bu)<sub>3</sub> using either water or the hydrated salt Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·14H<sub>2</sub>O leads to the characterizable compounds (*t*-BuAlO)<sub>n</sub> (*n* = 6,<sup>5</sup> 7,<sup>6</sup> 8,<sup>6</sup> or 9<sup>5</sup>). X-ray data for the aggregates *n* = 6, 8, or 9 show that they have cage structures composed of alternating μ<sub>3</sub>-O and μ<sub>3</sub>-Al(*t*-Bu) units with three-coordinate O and four-coordinate Al centers. Recent work<sup>7</sup> on related highly hindered Al imides has suggested that lower aggregate monoorganoalumoxanes (e.g., (RAIO)<sub>n</sub>, *n* = 1–4) should also be obtainable. Attempts to synthesize them via hydrolysis of sterically encumbered organoaluminum precursors involving the Mes\* substituent led to cleavage of the Al–C(Mes\*) bond and the deposition of insoluble materials containing Al and O.<sup>8</sup> Noting the effectiveness of the (Mes\*AlH<sub>2</sub>)<sub>2</sub> precursor<sup>9</sup> in the synthesis of low-aggregate imido derivatives,<sup>7d</sup> it was thought that it might also be used to synthesize the related alumoxanes by reaction with suitable oxygen substrates. In this paper the synthesis of the alumoxane (Mes\*AlO)<sub>4</sub> (**1**) via the reaction of (Mes\*AlH<sub>2</sub>)<sub>2</sub> with (Me<sub>2</sub>SiO)<sub>3</sub> and its treatment with AlMe<sub>3</sub> or AlEt<sub>3</sub> to produce the adducts [Mes\*(R)AlOAlR<sub>2</sub>(Mes\*AlO)]<sub>2</sub> (R = Me, **2**; Et, **3**) are now described.

The reaction of (Mes\*AlH<sub>2</sub>)<sub>2</sub> with (Me<sub>2</sub>SiO)<sub>3</sub> proceeded smoothly, under mild conditions, to afford **1**<sup>10a</sup> (isolated as a benzene or mesitylene solvate) in good yield (eq 1). This reaction type, involving a metal hydride reduction of a siloxane to give a metal oxide and a silane, apparently has not been described in the literature and represents a new synthetic approach to alumoxanes.<sup>11</sup> Related reactions<sup>12</sup> between silox-



anes and trialkylaluminums or metal hydrides to afford aluminum siloxides<sup>12c</sup> or metal siloxides<sup>12d</sup> are also known.

The X-ray crystal structure<sup>13a</sup> of **1** consists of an almost planar Al<sub>4</sub>O<sub>4</sub> ring involving a crystallographically required inversion center with each aluminum substituted by a Mes\* group oriented almost perpendicularly to the plane of the Al<sub>4</sub>O<sub>4</sub> ring. The tetrameric formula (Figure 1), attributable to the large size of the Mes\* substituents, is the lowest aggregation number known for alumoxanes in the solid state. The average Al–O bond length of 1.688(2) Å in **1** is close to the 1.6877(4) Å observed in O[Al{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]<sub>2</sub><sup>14</sup> but shorter than the 1.753(3) Å in O[Al{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]<sub>2</sub>·ONMe<sub>3</sub>.<sup>14</sup> The ring angles at O and Al are near 151° and 119°. The two O–Al–C angles at the Al centers are different (*ca.* 125° vs 116°) and there are also two short Al···H (*o*-*t*-Bu) distances of *ca.* 2.2 Å. The aromatic ring C(ipso)–C(para) vectors deviate (by *ca.* 7°) from the extended

(10) All manipulations were under a N<sub>2</sub> atmosphere using Schlenk techniques. C and H analyses of **1**–**3** were satisfactory. (a) [Mes\*AlO]<sub>4</sub>·2C<sub>6</sub>H<sub>6</sub> (**1**·2C<sub>6</sub>H<sub>6</sub>): A slurry of (Mes\*AlH<sub>2</sub>)<sub>2</sub> (1.00 g, 1.82 mmol) and (Me<sub>2</sub>-SiO)<sub>3</sub> (0.27 g, 1.21 mmol, freshly sublimed) in C<sub>6</sub>H<sub>6</sub> (15 mL) were placed in a preheated 85 °C oil bath to give a colorless solution after 1 h. The stopcock to the Schlenk line was closed, and the solution was kept at 85 °C for 19 h. The resulting clear solution was slowly (12 h) allowed to cool to room temperature. After *ca.* 3 h colorless crystals began to form. Storage at +6 °C for five days afforded colorless crystals (1–2 mm average size) of **1**·2C<sub>6</sub>H<sub>6</sub>. Yield: 0.89 g, 74.7%. <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>): δ 7.49 (s, *m*-H, 8H), 7.12 (s, C<sub>6</sub>H<sub>6</sub>, 12H), 1.72 (s, *o*-CH<sub>3</sub>, 72H), 1.42 (s, *p*-CH<sub>3</sub>, 36H). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>): δ 157.8 (*o*-C), 150.0 (*p*-C), 128.5 (C<sub>6</sub>H<sub>6</sub>), 120.7 (*m*-H), 37.7 (*o*-C(CH<sub>3</sub>)<sub>3</sub>), 34.9 (*p*-C(CH<sub>3</sub>)<sub>3</sub>), 32.8 (*o*-CH<sub>3</sub>), 31.7 (*p*-CH<sub>3</sub>). Mp: 253–258 °C. IR: 1052 (m), 1012 (v st; ν<sub>Al–O–Al</sub>) cm<sup>–1</sup>. Crystals of **1**·2MesH (MesH = 1,3,5-Me<sub>3</sub>C<sub>6</sub>H<sub>3</sub>) were obtained by recrystallization of **1**·2C<sub>6</sub>H<sub>6</sub> (0.1 g) from hot (90 °C) MesH (*ca.* 5 mL). Filtration and storage of the solution for 1 day at room temperature afforded X-ray quality crystals. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 7.53 (s, *m*-H, 8H), 6.72 (s, CH(Mes), 6H), 2.16 (s, CH<sub>3</sub>-(Mes), 18H), 1.73 (s, *o*-CH<sub>3</sub>, 72H), 1.44 (s, *p*-CH<sub>3</sub>, 36H). (b) [Mes\*Et-AlOAlEt<sub>2</sub>(Mes\*AlO)]<sub>2</sub> (**3**): A slurry of [Mes\*AlO]<sub>4</sub>·2C<sub>6</sub>H<sub>6</sub> (0.21 g, 0.16 mmol) in C<sub>6</sub>H<sub>6</sub> (*ca.* 20 mL) was treated with 0.34 mL of a 1.9 M AlEt<sub>3</sub> solution (0.64 mmol) in PhMe at room temperature. The resulting clear solution was stirred for 2 days, and the volatile materials were removed under reduced pressure to give a pale yellow glass. Recrystallization from *n*-pentane (2–3 mL) at –20 °C for one week afforded colorless crystals of **3**-pentane of sufficient quality for X-ray diffraction studies. The cocrystallized pentane is readily lost upon isolation. Yield: 0.10 g, 22.6% (based on **1**). Mp: 139–145° (with gas evolution). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): (Al(1)) δ 7.29 (s, *m*-H, 4H), 1.30 (s, *o*-CH<sub>3</sub>, 36H), 1.15 (s, *p*-CH<sub>3</sub>, 18H), 1.07 (t, CH<sub>3</sub>, 6H), <sup>3</sup>J<sub>HH</sub> = 8.4 Hz, 0.86 (q, CH<sub>2</sub>, 4H); (Al(2)) δ 7.44 (s, *m*-H, 2H), 7.22 (s, *m*-H, 2H), 1.80, 1.26, 1.18 (s, *o*- and *p*-CH<sub>3</sub>, 18H each); (Al(3)) δ 1.72 (t, CH<sub>3</sub>, 6H), <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 0.59 (q, CH<sub>2</sub>, 4H); 1.61 (t, CH<sub>3</sub>, 6H), <sup>3</sup>J<sub>HH</sub> = 8.1 Hz, 0.59, 0.36 (*m*, CH<sub>2</sub>, 2H each). IR: 710 (vs), 640 (cm<sup>–1</sup>). The synthesis of **2** was carried out in a similar manner; however, crystals suitable for X-ray crystallography were not obtained owing to its poor solubility in hydrocarbon solvents.

(11) Alumoxanes can be synthesized by the reaction of triorganoaluminum compounds with species containing reactive oxygen such as CO<sub>2</sub>, RC(O)NR<sub>2</sub>, and MeCO<sub>2</sub>H. The products are diorganoalumoxanes (R<sub>2</sub>AlOAlR<sub>2</sub>)<sub>n</sub> rather than monoorganoalumoxanes. See ref 2 and the following: (a) Ziegler, K.; Krupp, F.; Weyer, K.; Larbig, W. *Liebigs Ann. Chem.* **1960**, 628, 251. (b) Zakharkin, L. J.; Khorlina, I. M. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1959**, 2146. (c) Harney, D. W.; Meisters, A.; Mole, T. *Aust. J. Chem.* **1974**, 27, 1639.

(12) (a) Jenkner, H. Z. *Naturforsch.* **1959**, 146, 133. (b) Apblett, A. W.; Barron, A. R. *Organometallics* **1990**, 9, 2137. (c) Bissinger, P.; Paul, M.; Riede, J.; Schmidbauer, H. *Chem. Ber.* **1993**, 126, 2579. (d) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *Organometallics* **1991**, 10, 134.

(13) (a) Crystal data for **1**·2MesH at 126 K with Cu Kα (λ = 1.541 78 Å) radiation: C<sub>90</sub>H<sub>140</sub>Al<sub>4</sub>O<sub>4</sub>, M<sub>r</sub> = 1393.94, triclinic, space group P1, a = 13.773(3) Å, b = 14.124(4) Å, c = 14.293(3) Å, α = 63.91(2)°, β = 73.32(2)°, γ = 62.58(2)°, V = 2204.0(8) Å<sup>3</sup>, D<sub>calc</sub> = 1.050 g cm<sup>–3</sup>, Z = 1, R = 0.0646 for 5126 reflections with I > 2σ(I). (b) Crystal data for **3**-pentane at 130 K with Cu Kα (λ = 1.541 78 Å) radiation: C<sub>89</sub>H<sub>138</sub>Al<sub>6</sub>O<sub>4</sub>, M<sub>r</sub> = 1454.04, monoclinic, space group P2<sub>1</sub>/c, a = 11.568(6) Å, b = 20.268(9) Å, c = 21.311(7) Å, β = 98.76(3)°, V = 4938(4) Å<sup>3</sup>, D<sub>calc</sub> = 0.978 g cm<sup>–3</sup>, Z = 2, R = 0.1125 for 4250 reflections with I > 2σ(I).

(14) (a) Uhl, W.; Koch, M.; Hiller, W.; Heckel, M. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 989. (b) Uhl, W.; Koch, M.; Pohl, S.; Saak, W.; Hiller, W.; Heckel, M. Z. *Naturforsch.* **1995**, 50b, 635.

(1) (a) Ishida, S. I. *J. Polym. Sci.* **1962**, 62, 1. (b) Razuvaeva, G. A.; Sangalov, Yu.; Nel'kenbaum, Yu. Ya.; Minsker, K. S. *Izv. Akad. Nauk SSSR Ser. Khim.* **1975**, 2547.

(2) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, 18, 99.

(3) (a) Pasynkiewicz, S. *Polyhedron* **1990**, 9, 429. (b) Barron, A. R. *Comments Inorg. Chem.* **1993**, 14, 123. (c) Eisch, J. J. *Comprehensive Organometallic Chemistry II*; Pergamon: New York, 1995; Vol. 1, Chapter 10, p. 450. (d) Sinn, H.; Kaminsky, W., Eds. *Macromol. Symp. 97-Alumoxanes* **1995**, 97, 1–246. (e) Atwood, J. L. In *Coordination Chemistry of Aluminum*; G. H., Robinson, Ed.; VCH: New York, 1993; Chapter 6, p. 219.

(4) Sinn, H. Reference 3d, p. 27.

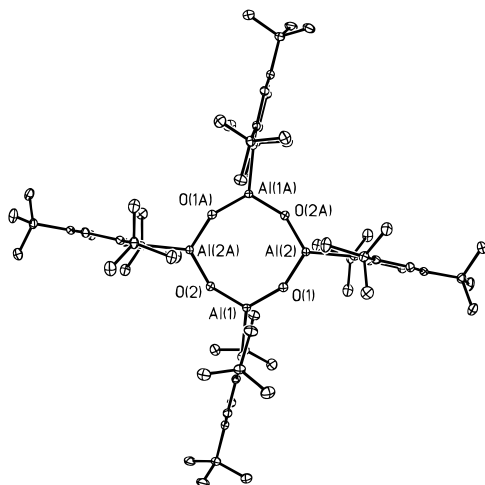
(5) Mason, M. K.; Smith, J. M.; Bott, S. G.; Barron, A. R. *J. Am. Chem. Soc.* **1993**, 115, 4971.

(6) Harlan, C. J.; Mason, M. R.; Barron, A. R. *Organometallics* **1994**, 13, 2957.

(7) Several dimeric and trimeric organoaluminum imides have been synthesized. See the following: (a) Waggoner, K. M.; Hope, H.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 1699. (b) Schulz, S.; Häming, L.; Herbst-Irmer, R.; Roesky, H. W.; Sheldrick, G. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 969. (c) Fisher, J. D.; Shapiro, P. J.; Yap, G. P. A.; Rheingold, A. L. *Inorg. Chem.* **1996**, 35, 271. (d) Wehmschulte, R. J.; Power, P. P. *J. Am. Chem. Soc.* **1996**, 118, 791.

(8) Wehmschulte, R. J.; Power, P. P. Unpublished observations.

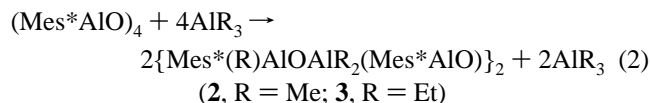
(9) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1994**, 33, 5611.



**Figure 1.** Thermal ellipsoidal (30%) plot of **1**. H atoms are not shown. Selected bond lengths (Å) and angles (deg) are: Al(1)–O(1) = 1.687(2), Al(1)–O(2) = 1.688(2), Al(2)–O(1) = 1.688(2), Al(2)–O(2A) = 1.691(2), Al(1)–C(1) = 1.966(3), Al(2)–C(19) = 1.967(3), O(1)–Al(1)–O(2) = 119.85(10), O(1)–Al(1)–C(1) = 125.13(11), O(2)–Al(1)–C(1) = 114.98(11), Al(1)–O(1)–Al(2) = 151.32(13), O(1)–Al(2)–O(2A) = 117.92(10), O(1)–Al(2)–C(19) = 116.66(11), C(19)–Al(2)–O(2A) = 125.42(11), and Al(1)–O(2)–Al(2A) = 150.51(13).

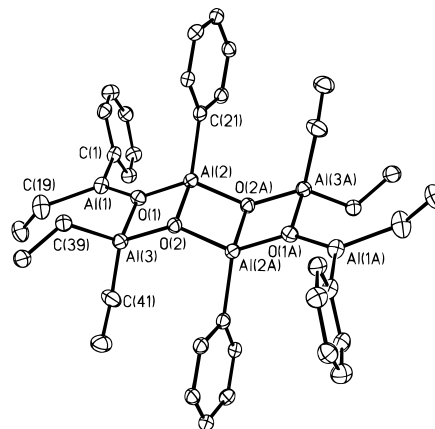
lines of the Al(1)–C(1) and Al(2)–C(19) bonds. The essentially perpendicular orientations of the aromatic rings and the deviation from idealized geometries at the Al and C(ipsos) carbons are consistent with the steric congestion provided by the four ring Mes\* substituents. The “open” planar structure of **1** may be contrasted with the related tetrameric organoaluminum imides which display cubane Al<sub>4</sub>N<sub>4</sub> structures.<sup>15</sup>

Although the structure of **1** indicates that the Al centers are quite hindered, the two-coordinate O atoms have a more open environment. Accordingly, it was decided to treat **1** with 4 equiv of either AlMe<sub>3</sub> or AlEt<sub>3</sub> according to eq 2.<sup>10b</sup> Even



though 4 equiv of AlR<sub>3</sub> were added, only 2 equiv were consumed. A crystal structure<sup>13b</sup> of the product was obtained for the ethyl derivative **3**. This showed (Figure 2) that **3** consisted of a centrosymmetric Al–O ladder framework composed of three edge-fused (Al–O)<sub>2</sub> rings. It may be described as an adduct of two Mes\*(Et)AlOAlEt<sub>2</sub> molecules to a central dimeric (Mes\*AlO)<sub>2</sub> unit. The O and Al atoms within the ladder are three- and four-coordinate, respectively, with Al–O distances in the range 1.811(5)–1.901(5) Å. The terminal Mes\*(Et)Al substituents feature a three-coordinate Al with a shorter Al(1)–O(1) distance of 1.762(5) Å which is comparable to the exocyclic Al–O distance (1.750(3) Å) in the dimer {(*t*-Bu)<sub>2</sub>AlOAl(*t*-Bu)<sub>2</sub>}<sub>2</sub>.<sup>5</sup> In addition, there is a low torsion angle (16.8°) between the perpendiculars to the Al(1) and O(1) planes.

The novelty in the structure of **3** is that it seems to be the first structurally characterized product formed by the addition of a trialkylaluminum to an alumoxane. A ladder structure of this type has not been observed previously although the structure



**Figure 2.** Thermal ellipsoidal (30%) plot of **3**. H atoms and aryl *t*-Bu substituents are not shown. Selected bond lengths (Å) and angles (deg) are: Al(1)–O(1) = 1.762(5), Al(1)–C(1) = 1.959(7), Al(1)–C(19) = 1.946(8), Al(2)–O(1) = 1.850(5), Al(2)–O(2) = 1.853(4), Al(2)–O(2A) = 1.819(4), Al(2)–C(21) = 1.995(7), Al(3)–O(1) = 1.901(5), Al(3)–O(2) = 1.811(5), Al(3)–C(39) = 1.983(7), Al(3)–C(41) = 1.965(9), O(1)–Al(1)–C(1) = 127.4(3), O(1)–Al(1)–C(19) = 116.0(3), C(1)–Al(1)–C(19) = 116.6(3), Al(1)–O(1)–Al(2) = 146.0(3), Al(1)–O(1)–Al(3) = 118.2(2), Al(2)–O(1)–Al(3) = 94.9(2), O(1)–Al(2)–O(2) = 83.7(2), Al(2)–O(2)–Al(3) = 97.9(2), Al(2)–O(2)–Al(2A) = 97.1(2), and O(2)–Al(2)–O(2A) = 82.9(2).

of the compound {Al<sub>4</sub>(*t*-Bu)<sub>7</sub>(μ<sub>3</sub>-O)<sub>2</sub>(μ-OH)}<sup>6</sup> bears some resemblance since it features two edge-sharing Al<sub>2</sub>O<sub>2</sub> four-membered rings. The formula of **3**—Al<sub>6</sub>(Mes\*)<sub>4</sub>(Et)<sub>6</sub>(μ<sub>3</sub>-O)<sub>4</sub>—features an Al:O:R ratio of 6:4:10, and the addition of a further 2 equiv of AlR<sub>3</sub> (as attempted in eq 2) would change this to 8:4:16 (i.e., 2:1:4) which is the same as that found for diorganoalumoxanes (i.e., R<sub>2</sub>AlOAlR<sub>2</sub>)<sub>n</sub>. Thus, **3** represents a midpoint in the “titration” of alumoxanes with organoaluminum compounds. Since commercial MAO features a significant AlMe<sub>3</sub> component,<sup>2,3,16</sup> such structures may be of relevance to the actual structure of the active component in the MAO/AlMe<sub>3</sub> cocatalyst. For example, a recently proposed model<sup>4</sup> involves a cage compound of formula Al<sub>16</sub>O<sub>12</sub>(CH<sub>3</sub>)<sub>24</sub> interacting with one Al(CH<sub>3</sub>)<sub>3</sub> molecule and a metallocene. The inclusion of a further equivalent of Al(CH<sub>3</sub>)<sub>3</sub> in this model system would give an overall Al:oxide:alkyl ratio of Al<sub>18</sub>O<sub>12</sub>(CH<sub>3</sub>)<sub>30</sub> or 3:2:5 which is the same as the 6:4:10 ratio observed for **3**.

Initial testing of cocatalytic properties of **1** for ethylene polymerization have indicated no activity. Thus, a *ca.* 5 mM solution of a 1:1 mixture of **1** and (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrMe<sub>2</sub> in PhMe effects no polymerization of ethylene under 1 atm of pressure at either 25 or 85 °C. The addition of 2 equiv of AlMe<sub>3</sub> (i.e., 10 mM concentration) also results in no polymerization of ethylene even at 100 °C. It seems probable that the large size of the Mes\* substituent inhibits catalytic activity, and the lack of reaction between **1** and (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>ZrMe<sub>2</sub> is consistent with this view.

**Acknowledgment.** We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support.

**Supporting Information Available:** Tables of data collection parameters, atom coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates (28 pages). See any current masthead page for ordering and Internet access instructions.

JA9713901

(15) Cesari, M.; Cucinella, S. In *The Chemistry of Inorganic Homo- and Heterocycles*; Haiduc, I.; Sowerby, D. B., Eds.; Academic: New York, 1987; Vol. 1, Chapter 6, p 167.

(16) (a) Barron, A. R. *Organometallics* 1995, 14, 3581. (b) Thorn-Csányi, E.; Dehmel, J.; Dahlke, B. Reference 2d, p 91.