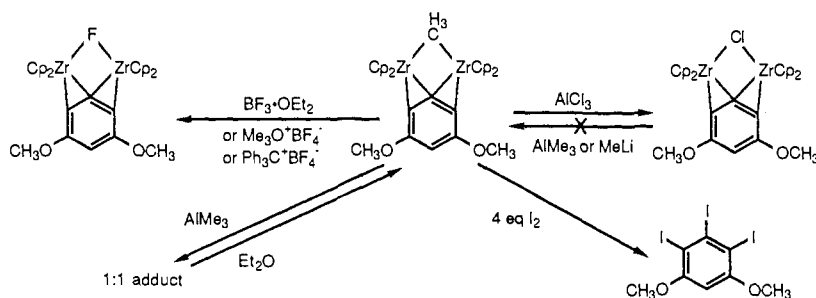
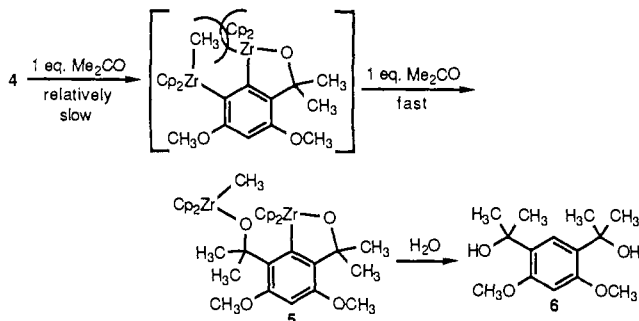


Scheme IV



Scheme V



Proof of the structure of **4** is provided by a single-crystal X-ray analysis.<sup>6</sup> An ORTEP plot of **4** is shown in Figure 1, along with important bond lengths and angles. There are several interesting features to the structure. The arene ring is completely planar, and the bond lengths in the ring are the same as those in benzene<sup>7</sup> to within experimental error. The ring is slightly distorted from a perfect hexagon, however, with the bridging carbon atom being moved toward the center of the ring, causing an opening of the C16-C11-C12 angle to 126.1° and a concomitant decrease in both of the neighboring ring angles (C15-C16-C11 and C11-C12-C13) to 115.5°. The bonds from each zirconium to its two arene ring carbons are different (2.203 and 2.177 Å for the outer bonds, versus 2.307 and 2.315 Å for the inner bonds), making each a highly distorted zirconocene benzyne moiety.<sup>8a</sup> The zirconium-methyl distances, 2.617 and 2.591 Å, are considerably longer than normal terminal zirconium alkyl bond lengths (ca. 2.30 Å<sup>9</sup>), although they are only somewhat longer than the ones in Grubbs's  $\mu$ -CH<sub>3</sub> complex (2.559 and 2.456 Å). Finally, the zirconium atoms and the bridging methyl carbon are all slightly displaced from the plane of the arene ring, by 0.130 Å for Zr1, 0.204 Å for Zr2, and 0.275 Å for the methyl carbon.

We have just begun to study the reactivity of **4**, and some of the reactions are shown in Scheme IV. The bridging methyl in **4** can be replaced with Cl or F, although the fluoride can be isolated in only about 90% purity. Compound **4** also forms a weak 1:1 adduct of unknown structure with AlMe<sub>3</sub> and reacts cleanly with 4 equiv of I<sub>2</sub> to give triiodide, **7**. Interestingly, preliminary studies show that **4** fails to react cleanly with alkynes, nitriles, and isonitriles, which are substrates for other zirconocene benzyne complexes.<sup>8a,b</sup> However, **4** reacts cleanly with 2 equiv of acetone to give a product with spectral and combustion analysis data consistent with structure **5** (Scheme V). Hydrolysis of **5** gives the previously unknown diol, **6**, which we have made independently to support the structure shown. Treatment of **4** with less than 2 equiv of acetone gives only a mixture of **5** and **4**, with no observable intermediate. Presumably this reaction proceeds as shown in Scheme V. Once the first equivalent of acetone adds

to one benzyne moiety, there are significant steric interactions between the cyclopentadienyl groups of the oxametallacycle and the other zirconocene unit. Insertion of acetone into the acyclic zirconium aryl bond, to our knowledge an unknown reaction in normal zirconocene aryl complexes,<sup>9</sup> relieves this strain and produces the observed product.

In summary, we have prepared and structurally characterized only the second example of a molecule having an arene ring bridging two metals both in the plane of the ring, in this case also bridging a methyl group. Because of the unusual reactivity and structure of this compound, we are continuing to investigate its reactions and are searching for further examples of organometallic compounds with unusual structures, including other bridging aryl compounds and trimetallic complexes of benztriyne.

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**Supplementary Material Available:** Experimental section containing the preparation and characterization of compounds along with crystallographic procedures, a table of final positional and thermal parameters for **4**, and tables of intramolecular bond distances and angles for **4** (26 pages); table containing observed and calculated structure factor for **4** (29 pages). Ordering information is given on any current masthead page.

(9) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and -Hafnium Compounds*; Wiley: New York, 1986.

### Synthesis and Molecular Structure of $\{[N(CH_2CH_2O)_3]Al_2(CH_3)_3\}_2$ : The First Six-Coordinate Aluminum Alkyl

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The tendency of aluminum alkoxide and aryloxy compounds to maximize their coordination number by associating to give aggregates containing tetrahedral and octahedral centers is well-documented.<sup>1</sup> Recent work in our laboratory<sup>2</sup> and by Ittel and co-workers<sup>3</sup> has focused on the isolation of monomeric aryloxy compounds of aluminum by use of the sterically hindered aryloxy derived from 2,6-di-*tert*-butyl-4-methylphenol. In an effort to control the oligomerization of aluminum compounds we have investigated the use of multidentate alkoxides as ligands. We report here the synthesis and structural characterization of  $\{[N-$

(6) Details of the structure determination are included in Supplementary Material.

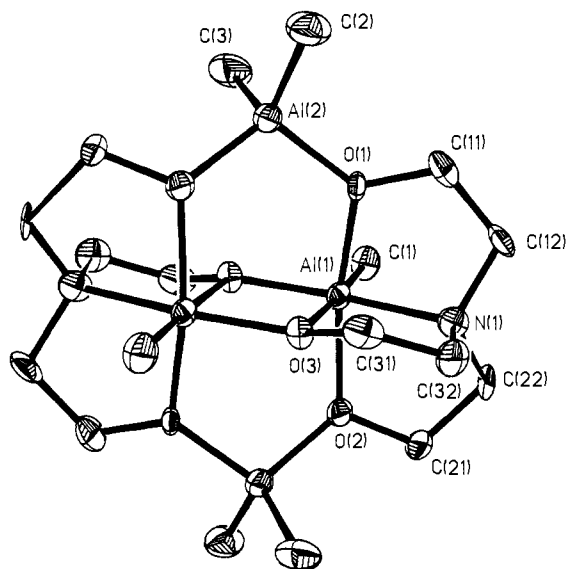
(7) Bastiansen, O.; Fernholt, L.; Seip, H. M. *J. Mol. Struct.* **1973**, *18*, 163. Tamagawa, K.; Iijima, T.; Kimura, M. *J. Mol. Struct.* **1976**, *30*, 243.

(8) (a) Buchwald, S. L.; Watson, B. T.; Lum, R. T.; Nugent, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 7137. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

(1) Bradley, D. C. *Adv. Chem. Ser.* **1959**, *23*, 10.

(2) Healy, M. D.; Wierda, D. A.; Barron, A. R. *Organometallics* **1988**, *7*, 2543.

(3) Shreve, A. P.; Mulhaupt, R.; Fultz, W.; Calabrese, J.; Robbins, W.; Ittel, S. D. *Organometallics* **1988**, *7*, 409.

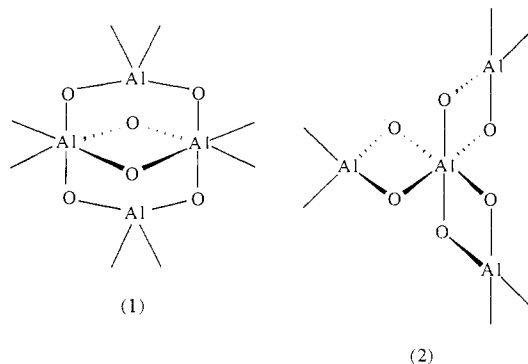


**Figure 1.** A view of the  $\{[N(CH_2CH_2O)_3]Al_2(CH_3)_3\}_2$  molecule showing the atom-labeling scheme. Thermal ellipsoids show 50% probability levels. Hydrogen atoms have been omitted for clarity.

$(CH_2CH_2O)_3Al_2(CH_3)_3\}_2$ , which contains a novel  $Al_4O_6$  core and the first structurally characterized octahedral aluminum alkyl.

The reaction of  $AlMe_3$  with  $N(CH_2CH_2OH)_3$  results in the formation of  $\{[N(CH_2CH_2O)_3]Al_2(CH_3)_3\}_2$ ,<sup>4</sup> the structure of which has been confirmed by X-ray crystallography,<sup>5</sup> and is consistent with all spectroscopic data.<sup>6</sup> The molecular structure of  $\{[N(CH_2CH_2O)_3]Al_2(CH_3)_3\}_2$  is shown in Figure 1. The molecule is a centrosymmetric tetranuclear structure with an aluminum-oxygen framework consisting of two fused six-membered  $Al_3O_3$  rings (1). The bridge head atoms Al(1) and Al(1a) (see Figure 1) have a distorted octahedral configuration [ $N(1)-Al(1)-O(3a) = 158.0(4)^\circ$ ,  $C(1)-Al(1)-O(3) = 176.9(4)^\circ$ , and  $O(1)-Al(1)-O(2) = 162.4(3)^\circ$ ]. The  $Al_4O_6$  core (1) consisting of two six-coordinate and two four-coordinate aluminum is unlike those previously reported which contain one central octahedral aluminum surrounded by three tetrahedral aluminum sites (2), e.g.,  $[Al(O-i-Pr)_3]_4$ <sup>7</sup> and  $[N(CH_2CH_2O)_3Al]_4$ .<sup>8</sup>

The triethoxyamine ligands are tetradentate about the six-coordinate aluminums, with each oxygen atom also bridging to one other aluminum center. Each oxygen atom has one long (average



= 1.97 Å) and one short (average = 1.84 Å) Al-O bond length. When the oxygen bridges Al(1) and Al(2), the greater distance is to the six-coordinate aluminum, Al(1). The  $Al(\mu-O)_2Al$  bridges are, however, also asymmetric [ $Al(1)-O(3) = 1.982(9)$  Å,  $O(3)-Al(1A) = 1.837(8)$  Å] with the longer bond being to the encapsulated aluminum. The reason for the longer Al-O bond length around the encapsulated aluminum is presumably due to the greater steric strain involved in coordination to an octahedral center. Indeed the Al-O bond lengths observed for the pseudo-tetrahedral aluminums in  $[N(CH_2CH_2O)_3Al]_4$ ,<sup>8</sup> 1.755(4), 1.763(5), 1.820(4) Å, are comparable to the shorter Al-O bond lengths found in  $\{[N(CH_2CH_2O)_3]Al_2(CH_3)_3\}_2$ . None of the distances, however, are outside the normal range found for Al-O bonds (1.7-2.0 Å).<sup>9</sup>

The Al(1)-N(1) distance [2.058(9) Å] is similar to that observed for amine adducts of  $AlMe_3$  (1.88-2.09 Å)<sup>10</sup> and indicates a significant Al←N interaction. The Al(1)-C(1) distance is 1.99(1) Å and is within the range reported for Al-C bonds in three-,<sup>11</sup> four-,<sup>11</sup> five-,<sup>12</sup> and seven-<sup>13</sup>coordinate aluminum (1.90-2.01 Å). This suggests that the Al-C bond is insensitive toward changes in the Al coordination number.

The coordination geometries about Al(2) and Al(2a) are distorted tetrahedral. The  $O(1)-Al(2)-O(2a)$  angle [ $108.0(4)^\circ$ ] is significantly larger than those found in other  $Al_xO_y$  ring systems (89.4-103.2°).<sup>14</sup> The Al(2)-O and Al(2)-C bond distances, however, are in the range observed previously for four-coordinate aluminum.<sup>9,11</sup>

Although octahedral coordination is common in the chemistry of aluminum,  $\{[N(CH_2CH_2O)_3]Al_2(CH_3)_3\}_2$  is the first example of a six-coordinate organometallic aluminum compound.

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**Supplementary Material Available:** Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, and bond distances and angles (3 pages); listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

(4) The dropwise addition of  $N(CH_2CH_2OH)_3$  (1.3 mL, 9.8 mmol) to a toluene (30 mL) solution of  $AlMe_3$  (5.0 mL, 2 M hexane) at 0 °C led to the immediate precipitation of a white solid. The reaction mixture was refluxed for 12 h, which resulted in a homogeneous solution. The solvent was removed under vacuum, and the residue was extracted with  $CH_2Cl_2$  (30 mL). Reduction of the volume and cooling (-20 °C) gave colorless crystals. Yield 0.45 g, 37% (based on Al). mp = 233 °C dec.

(5) Crystal data for  $\{[N(CH_2CH_2O)_3]Al_2(CH_3)_3\}_2$ : monoclinic,  $P2_1/n$ ,  $a = 9.372(6)$  Å,  $b = 14.026(8)$  Å,  $c = 9.610(4)$  Å,  $\beta = 92.35(4)^\circ$ ,  $V = 1262(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D(\text{calcd}) = 1.29$  g cm<sup>-3</sup>, (Mo K $\alpha$ )  $\lambda = 0.71073$  Å (graphite monochromator),  $T = -80$  °C. A Nicolet R3m/V diffractometer, equipped with a LT-1 low-temperature device, was used to collect 3347 reflections ( $4^\circ < 2\theta < 55^\circ$ ) on a colorless crystal  $0.13 \times 0.21 \times 0.45$  mm. Of these 1592 were independent,  $R_{\text{int}} = 7.44$ , and 950 observed [ $F_o > 5\sigma F_o$ ]. A semi-empirical absorption correction based on  $\psi$  scans and Lorentz and polarization corrections were applied to the data. The Al atoms were located by direct methods. Standard difference map techniques were used to find the remaining non-hydrogen atoms. All Al, N, O, and C atoms were refined anisotropically. The hydrogen atoms were included as idealized contributions.  $R = 8.71$ ,  $R_w = 9.46$ ,  $GOF = 0.78$ , final residual =  $0.67$  e Å<sup>-3</sup>. All computations used SHELXTL-PLUS: Sheldrick, G., Nicolet XRD, Madison, WI, 1987.

(6) <sup>1</sup>H NMR ( $C_6D_6$ ,  $\delta$ ) 3.52 (m, 6 H, N-CH<sub>2</sub>), 2.60 (m, 2 H, O-CH<sub>2</sub>), 2.01 (m, 2 H, O-CH<sub>2</sub>), 1.78 (m, 2 H, O-CH<sub>2</sub>), -0.42 (s, 6 H, Al-CH<sub>3</sub>), -0.69 (s, 3 H, Al-CH<sub>3</sub>); <sup>13</sup>C NMR ( $C_6D_6$ ,  $\delta$ ) 99.9 (N-CH<sub>2</sub>), 98.4 (O-CH<sub>2</sub>), -1.1 (Al-CH<sub>3</sub>), -13.5 (Al-CH<sub>3</sub>); IR (Nujol, NaCl, cm<sup>-1</sup>) 3470 (w), 1330 (w), 1280 (w), 1255 (w), 1175 (m), 1105 (m), 1070 (sh), 1050 (s), 1035 (sh), 1015 (w), 940 (m), 910 (sh), 900 (s), 875 (w), 765 (m).

(7) Oliver, J. G.; Philips, P. K.; Wowall, I. J. *Inorg. Nucl. Chem.* **1969**, *31*, 1609.

(8) Shklover, V. E.; Struchkov, Y. T.; Voronkov, M. G.; Ovchinnikova, Z. A.; Baryshok, V. P. *Dokl. Akad. Nauk. USSR* **1984**, *277*, 1185.

(9) (a) Zaworotko, M. J.; Rogers, R. D.; Atwood, J. L. *Organometallics* **1982**, *1*, 1179. (b) Atwood, J. L.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1983**, 302.

(10) Robinson, G. H.; Zhang, H.; Atwood, J. L. *J. Organomet. Chem.* **1987**, *331*, 153 and references therein.

(11) See: Eisch, J. J. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 6.

(12) (a) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1987**, *109*, 6852. (b) Robinson, G. H.; Sangokoya, S. A. *J. Am. Chem. Soc.* **1988**, *110*, 1494. (c) Robinson, G. H.; Sangokoya, S. A.; Moise, F.; Pennington, W. T. *Organometallics* **1988**, *7*, 1887.

(13) Bott, S. G.; Alvanipour, A.; Marley, S. D.; Atwood, D. A.; Means, C. M.; Coleman, A. W.; Atwood, J. L. *Angew. Chem., Int. Ed. Engl.* **1988**, *26*, 485.

(14) (a) Hausen, H. D.; Schmoger, G.; Schwarz, W. *J. Organomet. Chem.* **1978**, *153*, 271. (b) Drew, D. A.; Haaland, A.; Wiedlein, J. Z. *Anorg. Allg. Chem.* **1973**, *398*, 241.