ORGANOMETALLICS

Volume 21, Number 17, August 19, 2002

Communications

Trapping of $AlMe_3$ with the Oxygen Atom of the $Zr_3(\mu_3\text{-}O)$ Unit

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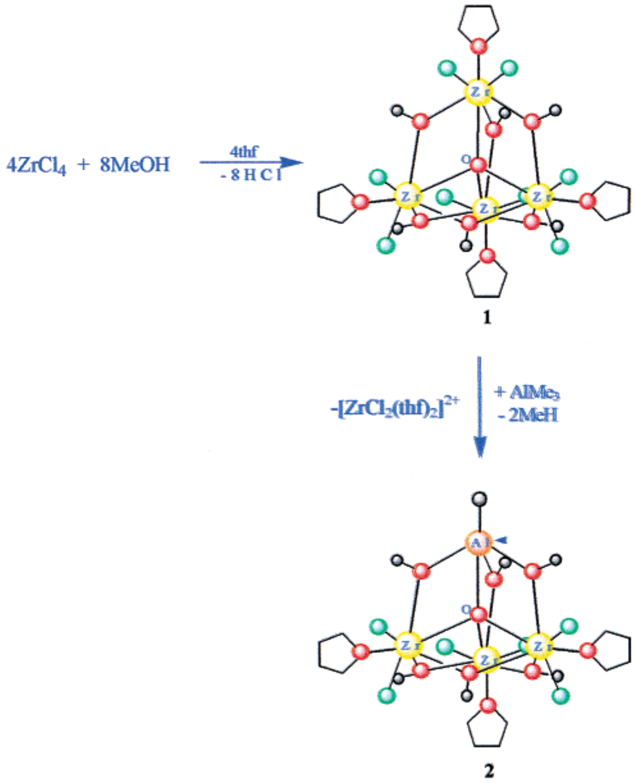
Received April 1, 2002

*Summary: We report for the first time the direct complexation of $AlMe_3$ by a $Zr_3(\mu_3\text{-}O)$ core. The precursor $[Zr_4(\mu_4\text{-}O)(\mu\text{-}OMe)_6Cl_8(thf)_4]$ (**1**) was obtained in the direct reaction of $ZrCl_4$ with methanol. When **1** was allowed to react with $AlMe_3$, $[Zr_3Al(\mu_4\text{-}O)(\mu\text{-}OMe)_6Cl_6(Me)(thf)_3]$ (**2**) was isolated. An analogous trend was observed in the compound $[Zr_4Al_2(\mu_4\text{-}O)_2(OEt)_{12}Cl_6]$ (**3**), which was obtained in the direct reaction of $ZrCl_4$ with $Zr(OEt)_4$ and Al in thf/EtOH.*

The high activity of single-site or metallocene-catalyzed polymerization imported by methylalumoxane (MAO) has caused it for many years to be one of the most industrially important activators.[1] Although the role of MAO seems to be understood,[2] the structure of the catalytically active species remains unknown. Very recently we have found that in the reaction of $AlMe_3$ with magnesium alkoxide $[Mg_4(thffo)_8]$ (thffo = 2-tetrahydrofurfuroxide) the elementary methylalumoxane unit $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ is formed. This can be capped with the magnesium $[Mg(thffo)_3]^-$ moiety as the molecular solid $[Al_3Mg(\mu_3\text{-}O)(thffo)_3(Me)_6]$.[3] This raises the question whether $AlMe_3$ can also be trapped by a Ziegler–Natta catalyst component such as titanium and zirconium alkoxides. For example, Orpen described the

Scheme 1. Preparation of 2



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10.1021/om020258t CCC: \$22.00 © 2002 American Chemical Society
Publication on Web 07/16/2002

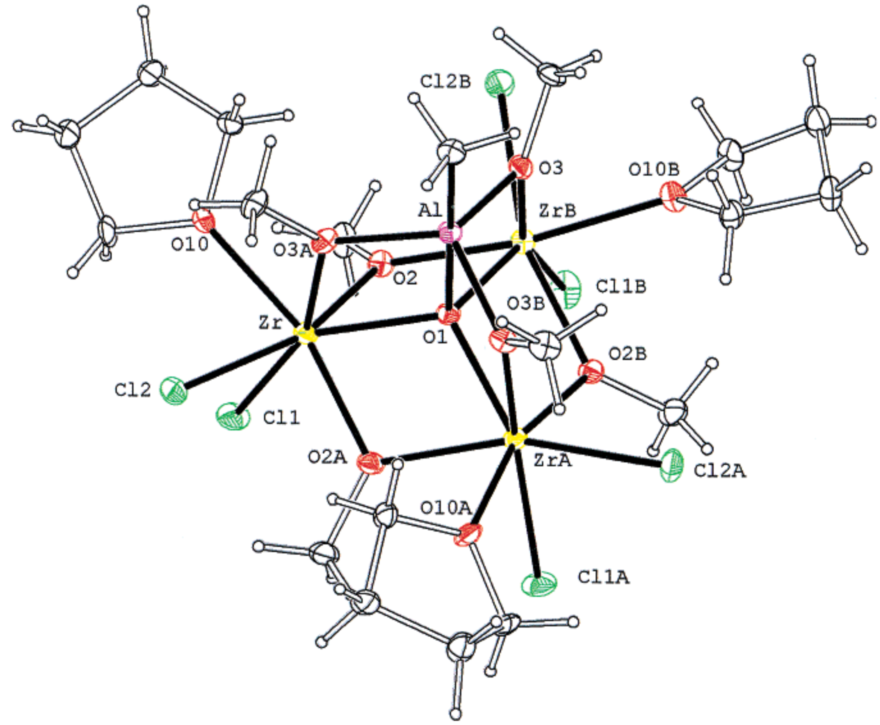

Figure 1. Ortep drawing for **2**. Thermal ellipsoids are at the 50% probability level. Selected bond lengths (Å): Zr−O1 = 2.124(2), Zr−O2A = 2.150(5), Zr−O3A = 2.164(5), Zr−O2 = 2.184(5), Zr−O10 = 2.256(5), Zr−Cl1 = 2.4739(18), Zr−Cl2 = 2.4809(19), Zr−Al = 3.286(3), Zr−ZrA = 3.5386(13), Al−O3 = 1.851(5), Al−C1 = 1.967(12), Al−O1 = 1.992(9). Symmetry transformations used to generate equivalent atoms: (A) $1 - y$, $x - y$, z; (B) $1 - x + y$, $1 - x$, z.

syntheses and catalytic activity of the series of biphenoxides and binaphthoxides of Ti and Zr.[4] These compounds were activated with MAO-polymerized ethylene with an activity up to 4740 kg of polyethylene/((mol of catalyst) h), which is comparable to the activity for various (indenyl)$ZrCl_2$/MAO catalysts.[5]

Herein we report the direct complexation of $AlMe_3$ by the $Zr_3(\mu_3\text{-}O)$ core. The precursor $[Zr_4(\mu_4\text{-}O)(\mu\text{-}OMe)_6Cl_8(thf)_4]$ (**1**) was obtained in the direct reaction of $ZrCl_4$ with methanol at −78 °C in 83% yield.[6] When **1** was allowed to react with $AlMe_3$ in a 1:4 molar ratio in thf, $[Zr_3Al(\mu_4\text{-}O)(\mu\text{-}OMe)_6Cl_6(Me)(thf)_3]$ (**2**) was isolated in 87% yield.[7] For a deeper understanding of the reaction pathway of the formation of cluster **2**, we additionally studied the reactions of ZrX_4 (X = Cl, OR) species with Al alkoxides.[8] The compound $[Zr_4Al_2(\mu_4\text{-}O)_2(\mu\text{-}OEt)_{12}Cl_6]$ (**3**) was obtained in the direct reaction of $ZrCl_4$ with $Zr(OEt)_4$ and Al in thf/EtOH in 23% yield.[9] **1**−**3** are reasonably stable and can be stored as solids at room temperature under dinitrogen for weeks. They are insoluble in aliphatic and aromatic hydrocarbons but are soluble in CH_3CN and CH_2Cl_2.

Complexes **1**−**3** were characterized by ^1H and ^{27}Al NMR spectroscopy and X-ray crystallography. As shown in Scheme 1, **1** is a tetranuclear species. Unfortunately, the poor-quality X-ray data do not make it possible to discuss the bond lengths and angles, but no unprecedented values should be expected here.[10] Nonetheless, the central inorganic core of **1** is clearly visible (Scheme 1) and can be discussed. Complex **2** (Figure 1) possesses a similar core that is held together by an μ_4-O oxygen atom that originates from **1**.[11] The significant difference between **1** and **2** is that one of the $[ZrCl_2(thf)]^{2+}$ moieties coordinated to μ_4-O oxygen atom in **1** is substituted by the $[Al{-}Me]^{2+}$ unit in **2**. As can be seen in Figure 2,

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(6) $ZrCl_4$ (5.00 g, 4.39 mmol) was dissolved in cold (−78 °C) methanol (20 mL). HCl immediately started to evolve and was removed under vacuum. The mixture was stirred at room temperature with applied vacuum until oil was formed. Then MeOH (30 mL) and toluene (5 mL) were added and removal of the solvents and HCl under vacuum was continued until an oil was obtained. This procedure was repeated twice. The volume was then reduced to 10 mL, and hexane (50 mL) was added. The white precipitate was filtered off, washed with hexane (3 × 5 mL), and dried under vacuum to give a white powder of **1** (5.05 g, 83%). Recrystallization from thf gave after 30 days colorless crystals of **1**. ^1H NMR (300 MHz, $CDCl_3$, ppm): δ 0.15 (s, 18H; μ-OCH_3), 1.87 (br s, 8H; $O(CH_2)_2(CH_2)_2$), 3.81 (br s, 8H; $O(CH_2)_2(CH_2)_2$). Anal. Calcd for $C_{22}H_{50}Cl_8O_{11}Zr_4$ (1139.14): C, 23.20; H, 4.42; Cl, 24.90; Zr, 32.03. Found: C, 22.97; H, 4.70; Cl, 24.10; Zr, 32.19.

(7) $AlMe_3$ (2 M in toluene) (3.12 mL, 6.10 mmol) was added at room temperature to a stirred solution of **1** (1.81 g, 1.59 mmol) in thf (60 mL). After 10 min the volume was reduced to 20 mL. Colorless crystals of **2** suitable for X-ray analysis were obtained after about 12 h (1.30 g, 87%). ^1H NMR (300 MHz, CD_3CN, ppm): δ 0.05 (s, 3 H; CH_3), 0.19 (s, 18 H; μ-OCH_3), 1.85 (br s, 8H; $O(CH_2)_2(CH_2)_2$), 3.77 (br s, 8H; $O(CH_2)_2(CH_2)_2$). ^{27}Al NMR (400 MHz, CD_3CN, ppm): δ 45.0, 54.0. Anal. Calcd for $C_{19}H_{45}AlCl_6O_{10}Zr_3$ (946.92): C, 24.10; H, 4.79; Cl, 22.46; Zr, 28.90. Found: C, 23.90; H, 4.69; Cl, 22.06; Zr, 28.59.

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(9) $ZrCl_4$ (1.76 g; 6.48 mmol), $Zr(OEt)_4$ (1.51 g; 6.48 mmol), and Al (foil) (0.27 g; 10.01 mmol) in thf (50 mL) was stirred for about 1 h. Then 30 mL of EtOH was added and the mixture refluxed until the aluminum was consumed. The white precipitate was filtered off, and the filtrate was evaporated. The oily product was dissolved in 25 mL of toluene. A 40 mL portion of *n*-hexane was added, and the solution was left to crystallize at −20 °C. Crystals suitable for structure determination were obtained after 1 week (0.90 g, 0.75 mmol, 23%). ^1H NMR (300 MHz, CD_3CN, ppm): δ 1.11 (t, 24H; μ-OCH_2CH_3), 1.28 (br s, 12H; OCH_2CH_3), 3.54 (q, 16H; μ-OCH_2CH_3), 4.21 (br s, 8H; OCH_2CH_3). ^{27}Al NMR (400 MHz, CD_3CN, ppm) δ 42.6. Anal. Calcd for $C_{24}H_{60}Al_2Cl_6O_{14}Zr_4$ (1204.29): C, 23.94; H, 5.02; Cl, 17.66; Zr, 30.30. Found: C, 23.90; H, 5.00; Cl, 17.70; Zr, 30.26.

(10) X-ray data parameters for **1**·4thf: $a = 11.964(1)$ Å, $b = 13.838(1)$ Å, $c = 19.340(1)$ Å, $\alpha = 101.07(1)°$, $\beta = 90.27(1)°$, $\gamma = 102.91(1)°$.

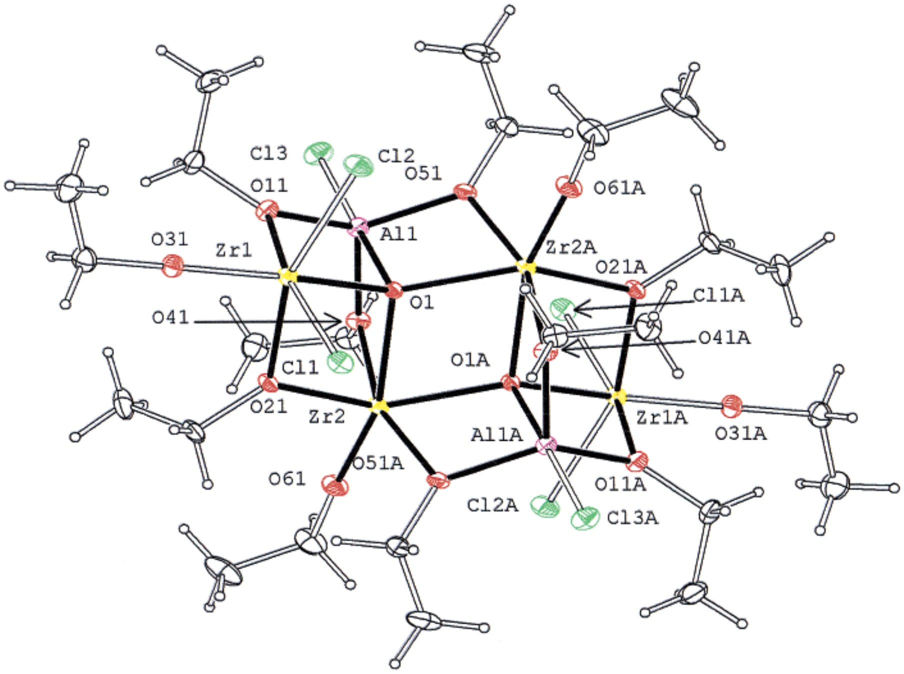

Figure 2. Ortep drawing for **3**. Thermal ellipsoids are at the 50% probability level. Selected bond lengths (Å): Zr1−O31 = 1.894(2), Zr1−O1 = 2.1591(18), Zr1−O11 = 2.1867(19), Zr1−O21 = 2.2014(18), Zr1−Cl2 = 2.4527(8), Zr1−Cl1 = 2.4568(8), Zr1−Al1 = 3.2486(9), Zr1−Zr2 = 3.4927(6), Zr2−O61 = 1.8969(19), Zr2−O21 = 2.0857(19), Zr2−O1A = 2.1354(18), Zr2−O41 = 2.1355(19), Zr2−O51 = 2.1411(19), Zr2−O1 = 2.2234(18), Zr2−Al1A = 3.1789(9), Zr2−Al1 = 3.2034(9), Zr2−Zr2A = 3.5008(5), Cl3−Al1 = 2.1997(11), Al1−O51A = 1.813(2), Al1−O11 = 1.816(2), Al1−O41 = 1.825(2), Al1−O1 = 1.995(2). Symmetry transformations used to generate equivalent atoms: (A) $-x$, $-y$, $1 - z$.

the centrosymmetric $Zr_4Al_2(\mu_4\text{-}O)_2$ macro unit of **3** is clearly derived from **2** and can be formally constructed by dimerization through the center of symmetry to form a common $Zr2Zr2A(\mu_4\text{-}O)_2$ rhombus. The entropy effect might be a driving force for such a reaction. This suggests that compound **2** could undergo further agglomeration, for instance, to $[Zr_4Al_2(\mu_4\text{-}O)_2(\mu\text{-}OMe)_{12}Cl_4(Me)_2]$ (**3a**), which is relevant to **3** but up to now has not been isolated in pure form. During the preparation of alkoxometal complexes it is not uncommon for products to contain “lone” oxo ligands to be formed, which are encapsulated in ensembles among three or more metal atoms.[12,13] Preliminary tests of catalytic properties of **2** for ethylene polymerization have indicated no activity. This result agrees with our presumptions due to the lack of a $Zr-CH_3$ bond in **2**. Further investigation on **2** and **3** showed that even with a strong alkylating agent the terminal chlorine atoms remained untouched, proving the high stability of the $AlZr_3(\mu_4\text{-}O)$ core.

Acknowledgment. We thank the State Committee for Scientific Research (Poland) for support of this research (Grant No. 15/T09/99/01f).

Supporting Information Available: Tables giving atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[11] Crystal data for **2**, $C_{19}H_{45}AlCl_6O_{10}Zr_3$: $M_r = 946.89$, trigonal crystal system, space group $R3c$ (No. 161), $a = b = 12.985(2)$ Å, $c = 39.907(4)$ Å, $V = 5827.2(14)$ Å^3, $Z = 6$, $D_{calcd} = 1.619$ g/cm^3, $T = 100.0(5)$ K, scan type ω, μ(Mo Kα) = 1.264 mm^{-1} , 12 589 measured reflections, 3099 independent reflections ($R_{int} = 0.0588$), refinement on F^2, $R_1(F^2 > 4\sigma(F^2)) = 0.0482$, $wR_2 = 0.1285$. Crystal data for **3**, $C_{24}H_{60}Al_2Cl_6O_{14}Zr_4$: $M_r = 1204.26$, monoclinic crystal system, space group $P2_1/c$ (No. 14), $a = 11.859(1)$ Å, $b = 18.997(1)$ Å, $c = 10.993(1)$ Å, $\beta = 108.39(1)°$, $V = 2350.1(3)$ Å^3, $Z = 2$, $D_{calcd} = 1.702$ g/cm^3, $T = 100.0(5)$ K, scan type ω, μ(Mo Kα) = 1.291 mm^{-1} , 15 036 measured reflections, 5511 independent reflections ($R_{int} = 0.0278$), refinement on F^2, $R_1(F^2 > 4\sigma(F^2)) = 0.0346$, $wR_2 = 0.0761$.

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