

# Syntheses and Molecular Structure of $[\text{Mg}_2(\text{OR})_4(\text{AlMe}_3)_2]$ and $[\text{ZrCl}_3(\text{OR})_2(\text{AlMe}_2)]$ (OR = 1-methoxy-2-propoxide)

Józef Utko, Agnieszka Lizurek, Lucjan B. Jerzykiewicz, and Piotr Sobota\*

Faculty of Chemistry, University of Wrocław, 14, F. Joliot-Curie, 50-383 Wrocław, Poland

Received October 28, 2003

**Summary:** The magnesium dicubane-like species  $[\text{Mg}_4(\text{OR})_8]$  (**1**, 99%) react with  $\text{AlMe}_3$  to form  $[\text{Mg}_2(\text{OR})_4(\text{AlMe}_3)_2]$  (**2**, 58%), which react with  $\text{ZrCl}_4$  to give  $[\text{ZrCl}_3(\text{OR})_2(\text{AlMe}_2)]$  (**3**, 43%).

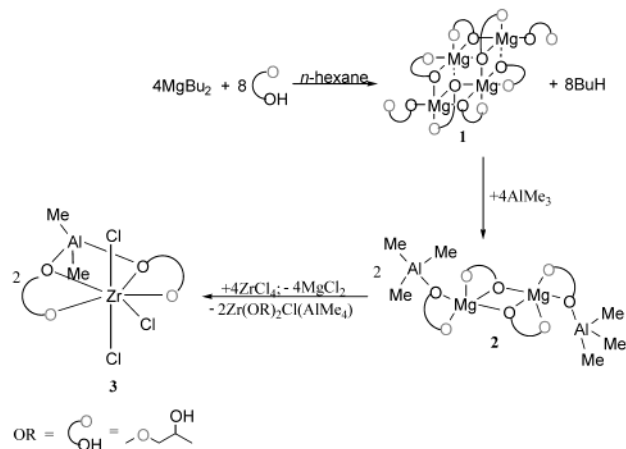
## Introduction

Our knowledge concerning the interaction among components of the inherently very complex  $\text{MX}_{(3/4)}/\text{MgX}_2/\text{AlEt}_3$  (M = Ti, Zr; X = OR or Cl) Ziegler–Natta polymerization catalyst system is still very limited and presents a challenge.<sup>1,2</sup> Our research has focused on determining the role of each of the components of the catalyst, which is still extensively used in the polyolefin industry.<sup>3</sup> Very recently we reported the coordination of  $\text{AlMe}_3$  to the oxygen atom of the  $\text{Zr}_3(\mu_3\text{-O})$  core present in the product of the reaction of  $\text{ZrCl}_4$  with  $\text{MeOH}$ ,  $[\text{Zr}_3\text{-Al}(\mu_4\text{-O})(\mu\text{-OMe})_6\text{Cl}_6(\text{Me})(\text{thf})_3]$ .<sup>4a</sup> To provide further information on compounds and reaction steps that lead to the formation of the active catalyst species, we report here the complexation of  $\text{AlMe}_3$  by the alkoxide oxygen atoms of  $\text{Mg}_2(\text{OR})_4$  and  $\text{Zr}(\text{OR})_2$  units.

## Results and Discussion

The precursor  $[\text{Mg}_4(\text{OR})_8]$  (**1**) was obtained by the reaction of magnesium turnings with 1-methoxy-2-propanol in toluene at room temperature in 99% yield.<sup>5</sup> As shown in Scheme 1, **1** is a tetranuclear species possessing an open dicubane-like structure.  $\text{AlMe}_3$  reacted with **1** (4 equiv, toluene, 0 °C) to give a thermally stable, neutral heterobimetallic complex  $[\text{Mg}_2(\text{OR})_4(\text{AlMe}_3)_2]$  (**2**, 58%). Compound **2** was shown by X-ray diffraction to have a centrosymmetric tetranuclear chain structure. An overall view of the molecule is presented in Figure 1. Complex **2** contains two five-coordinate magnesium atoms and two four-coordinate aluminum centers. The alkoxide oxygen atoms of the

## Scheme 1. Preparation of **2** and **3**



chelating 1-methoxy-2-propoxide ligands bridge all of the metal atoms. Two of the alkoxide oxygen atoms bridge two magnesium atoms, and each of the two remaining ones bridge to one  $\text{AlMe}_3$  unit. The central  $\text{Mg}_2\text{O}_2$  four-membered ring in **2** is planar, with the ligands adopting a *trans* orientation. The Mg–O and Al–C bond distances are in accordance with those found in  $[\text{Mg}_4(\text{OR})_8]$ <sup>5</sup> and  $[\text{Al}_3\text{Mg}(\mu_3\text{-O})(\text{thffo})_3(\text{Me})_6]$ <sup>4b</sup> (thffo = 2-tetrahydrofurfuroxide). The formation of a magnesium complex **2** containing  $\text{AlMe}_3$  units coordinated to the  $\mu$ -alkoxide oxygen atom is unusual. The presence of magnesium atoms in **2** is an additional advantage of this compound. The driving force of the reaction between  $\text{MCl}_4$  (M = Ti, Zr, Hf) and **2** should be the formation of  $\text{MgCl}_2$ , providing in return alkyl functions.

The compound  $[\text{ZrCl}_3(\text{OR})_2(\text{AlMe}_2)]$  (**3**) was obtained in the reaction of **2** with  $\text{ZrCl}_4$  (0 °C, toluene, Scheme 1) in 1:2 molar ratio in 43% yield. **2** and **3** are reasonably stable and can be stored as solids at room temperature under dinitrogen for weeks and gave correct microanalyses. They are soluble in aliphatic and aromatic hydrocarbons as well as in tetrahydrofuran and  $\text{CH}_2\text{Cl}_2$ . The X-ray crystal structure of **3** was determined as shown in Figure 2. The results clearly demonstrate that in the  $2/\text{ZrCl}_4$  system a reorganization of the zirconium metal centers had taken place and that the 1-methoxy-2-propoxide ligands have been transferred from magnesium to zirconium, yielding the  $\text{ZrCl}_3(\text{OR})_2^-$  macroanion. In the  $\text{ZrCl}_3(\text{OR})_2^-$  moiety the seven-coordinate zirconium atom is surrounded by three chlorine atoms and four oxygen atoms of two bidentate 1-methoxy-2-propoxide ligands. Formation of complex **3** can be considered to proceed by an ionic mechanism. According to this, **3** is formed by entrapment of an  $\text{AlMe}_2^+$  interme-

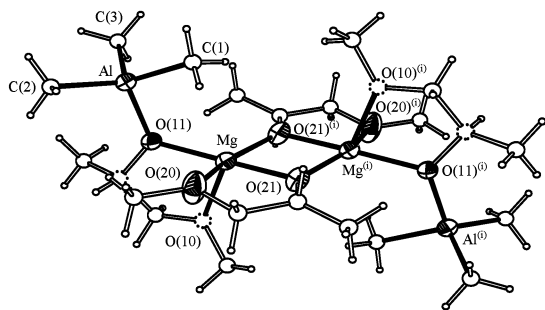
(1) Schumacher, J. In *Chemical Economics Handbook*; SRI International: Menlo Park, CA, 1994; p 50.

(2) (a) Gavens, P. D.; Bottrill, M.; Kelland, J. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.-in-Chief; Pergamon: New York, 1982; Vol. 3. (b) Albizzati, E.; Giannini, U.; Collina, G.; Noristi, L.; Resconi, L. In *Polypropylene Handbook*; Moore, E. P., Jr.; Hasner: New York, 1996. (c) Soga, K.; Shiono, T. *Prog. Polym. Sci.* **1997**, *22*, 1503. (d) Bochmann, M. *J. Chem. Soc., Dalton Trans.* **1996**, 255. (e) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413. (f) Böhm, L. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 5010.

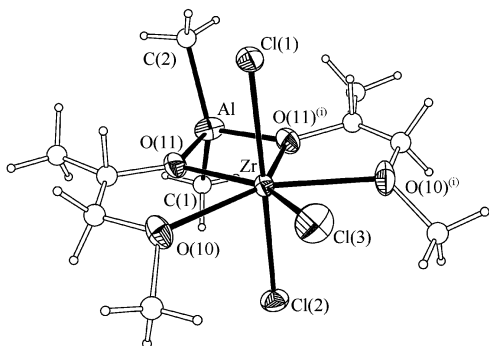
(3) Sobota, P.; Szafert, S. *J. Chem. Soc., Dalton Trans.* **2001**, 1379. Sobota, P.; *Chem. Eur. J.* **2003**, *9*, 4854.

(4) (a) Sobota, P.; Przybylak, S.; Utko, J.; Jerzykiewicz, L. B. *Organometallics* **2002**, *21*, 3497. (b) Sobota, P.; Utko, J.; Ejfler, J.; Jerzykiewicz, L. B. *Organometallics* **2000**, *19*, 4929.

(5) Albaric, L.; Hovbanian, N.; Julbe, A.; Guizard, C.; Alvarez-Larena, A.; Piniella, J. F. *Polyhedron* **1997**, *4*, 587.



**Figure 1.** Molecular structure of  $[\text{Mg}_2(\text{OR})_4(\text{AlMe}_3)_2]$  (**2**) in the crystal. The displacement ellipsoids are drawn at the 50% probability level. The C atoms are represented by circles of an arbitrary radius. The second positions of disordered carbon and oxygen atoms are omitted for clarity. Selected bond lengths [Å]: Al–C(1) 1.992(3), Al–C(2) 1.991(3), Al–C(3) 1.984(3), Al–O(11) 1.836(2), Al–Mg 3.245(2), Mg–O(11) 2.012(2), Mg–O(21) 1.989(2), Mg–O(10) 2.122(6), Mg–O(20) 2.149(3), Mg–Mg<sup>(i)</sup> 3.041(2). Symmetry transformations used to generate equivalent atoms: <sup>(i)</sup> $-x, -y+1, -z+1$ .



**Figure 2.** Molecular structure of  $[\text{ZrCl}_3(\text{OR})_2(\text{AlMe}_2)]$  (**3**) in the crystal. Selected bond lengths [Å]: Zr–Cl(1) 2.449(2), Zr–Cl(2) 2.441(2), Zr–Cl(3) 2.465(3), Zr–O(11) 2.133(2), Zr–O(10) 2.296(2), Al–O(11) 1.826(2), Al–C(1) 1.946(6), Al–C(2) 1.948(5). Symmetry transformations used to generate equivalent atoms: <sup>(i)</sup> $x, -y+1/2, z$ .

diated by the alkoxo oxygen atoms of the  $\text{Zr}(\text{OR})_2\text{Cl}_3^-$  anion to give the molecular solid  $[\text{ZrCl}_3(\text{OR})_2(\text{AlMe}_2)]$  (**3**, 43%). The  $^1\text{H}$  and  $^{27}\text{Al}$  NMR spectra supported the structural assignment of **2** and **3**. Preliminary tests of the catalytic properties of **3** for ethylene polymerization have shown no activity. This result agrees with the absence of a Zr–CH<sub>3</sub> bond in **3**. The tendency of the alkylaluminum species to exchange one of its methyl groups with a zirconium chloride is strongly reduced when one Me group of  $\text{AlMe}_3$  is replaced by OR in **3**.<sup>6</sup>

In summary, we have demonstrated that the magnesium dicubane-like species  $[\text{Mg}_4(\text{OR})_8]$  (**1**) can graft  $\text{AlMe}_3$  to form  $[\text{Mg}_2(\text{OR})_4(\text{AlMe}_3)_2]$  (**2**). This is reminiscent of the hydrolysis of  $\text{AlMe}_3$ , which produces the methylalumoxane (MAO) polymerization cocatalyst, which is believed to contain both  $\text{AlMe}_3$  and  $\text{AlMe}_x(\text{O})$  units.<sup>7</sup> Moreover, compounds **2** react further with  $\text{ZrCl}_4$  and  $[\text{ZrCl}_3(\text{OR})_2(\text{AlMe}_2)]$  (**3**) is formed.

## Experimental Section

All experiments were performed under dry dinitrogen atmosphere using Schlenk-type glassware. Solvents were dried over sodium wire and then distilled from the appropriate drying reagent (sodium benzophenone ketyl for THF, calcium

hydride for  $\text{CH}_2\text{Cl}_2$ , sodium for *n*-hexane and toluene) under dinitrogen prior to use. Deuterated solvents were degassed before use. Starting materials were obtained from commercial suppliers and used as received, except as specifically noted. NMR spectra were recorded at room temperature on a Bruker ESP 300E spectrometer operating at 300 MHz. Chemical shifts are reported in parts per million and referenced to the residual protons in deuterated solvents. IR spectra were measured on a Perkin-Elmer 180 instrument in Nujol mulls. Microanalyses were conducted by an ASA-1 (GDR, Karl-Zeiss-Jena) instrument (in-house).

**[Mg<sub>2</sub>(OR)<sub>4</sub>(AlMe<sub>3</sub>)<sub>2</sub>] (2).** A solution of  $[\text{Mg}_4(\text{OR})_8]$ <sup>5</sup> (2.3 g, 11.5 mmol) in toluene (60 mL) was treated at 273 K under dinitrogen with  $\text{AlMe}_3$  (24 mL, 48.0 mmol). Stirring was continued at room temperature for 12 h followed by filtration to remove a small amount of insoluble material. The solution was concentrated to 15 mL, and *n*-hexane (20 mL) was added. After 3 days colorless diffraction-quality crystals of **2** appeared in the filtrate. Yield: 1.8 g (58%). IR (Nujol):  $\nu$  1158 (vs), 1136 (m), 1102 (s), 1076 (vs), 982 (vs), 682 (vs, br), 638 (s), 600 (s), 530 (s), 466 (m), 454 (w), 368 (m), 306 (m), 284 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  –0.98 (s, 18H, Al-CH<sub>3</sub>), 1.09 (d, 6H, CH<sub>3</sub>), 1.23 (d, 6H, CH<sub>3</sub>), 3.18 (m, 4H, CH<sub>2</sub>), 3.35 (m, 4H, CH<sub>2</sub>), 3.58 (s, 6H, OCH<sub>3</sub>), 3.66 (s, 6H, OCH<sub>3</sub>), 4.98 (m, 2H, CH), 4.25 (m, 2H, CH).  $^{27}\text{Al}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  151.15. Anal. Calcd for  $\text{C}_{21}\text{H}_{45}\text{O}_7\text{Al}_3\text{Mg}$ : C, 48.11; H, 9.91; Al, 9.83; Mg, 8.85. Found: C, 48.20; H, 9.61; Al, 9.71; Mg, 8.59.

**[ZrCl<sub>3</sub>(OR)<sub>2</sub>(AlMe<sub>2</sub>)] (3).** To a suspension of 1.03 g (4.42 mmol) of  $\text{ZrCl}_4$  in toluene (40 mL) was added **2** (0.76 g, 1.40 mmol) under dinitrogen. The reaction mixture turned dark brown and was stirred at room temperature overnight, followed by filtration to remove an insoluble light brown material. The solution was reduced in volume under vacuum to 20 mL and left to crystallize at room temperature. After 1 day colorless diffraction-quality crystals of **3** appeared in the filtrate. Yield: 0.26 g (43%). Good-quality crystals, suitable for X-ray examination, were taken directly from the postreaction mixture. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu$  1194 (s), 1176 (w), 1152 (s), 1124 (m), 1090 (s), 1022 (s), 964 (vs), 906 (s), 870 (m), 724 (vs), 692 (vs), 654 (vs), 586 (m), 538 (m), 514 (m), 454 (m), 368 (s), 330 (vs, br), 274 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  –0.69 (s, 6H, Al-CH<sub>3</sub>), 1.37 (d, 6H, CH<sub>3</sub>), 4.01 (m, 4H, CH<sub>2</sub>), 4.27 (s, 6H, O-CH<sub>3</sub>), 4.73 (m, 2H, CH).  $^{27}\text{Al}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  53.81. Anal. Calcd for  $\text{C}_{66}\text{H}_{84}\text{Si}_2\text{O}_{14}\text{Mg}_4$ : C, 63.18; H, 6.75; Mg, 7.75. Found: C, 62.91; H, 6.63; Mg, 7.71.

**Crystal Structure Analysis.** Preliminary examination and intensity data collections were carried out on a KUMA KM4  $\kappa$ -axis diffractometer with graphite-monochromated Mo K $\alpha$  and with a CCD camera<sup>8</sup> (**2**) or a scintillation counter<sup>9</sup> (**3**). All data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined by the full-matrix least-squares method on all  $F^2$  data using the SHELXTL (version 5.10) program.<sup>10</sup> Carbon-bonded hydrogen atoms were included in calculated positions and refined in the riding mode. In the structure of **2** one carbon atom C(11) and one oxygen atom O(10) of OR ligand are disordered between two sites. In the structure **3** high-temperature factors of some carbon atoms suggest their disorder, which, unfortunately, could not be resolved. Crystal data: **2**,  $\text{C}_{22}\text{H}_{54}\text{Al}_2\text{Mg}_2\text{O}_8$ ;  $M = 549.24$ , monoclinic crystal system, space group  $P2_1/c$  (No. 14),  $a = 8.155(1)$  Å,  $b = 22.599(3)$  Å,  $c = 9.644(2)$  Å,  $\beta = 114.49(1)^\circ$ ,

(6) Wrobel, O.; Schaper, F.; Wieser, U.; Gregorius, H.; Brintzinger, H. H. *Organometallics* **2003**, *22*, 1320.

(7) Barron, A. R. *Organometallics* **1995**, *14*, 3581.

(8) *Kuma Diffraction. KM-4 User's Guide*, Version 10.1; Kuma Diffraction: Wrocław, Poland, 1996.

(9) *Kuma Diffraction. Kuma KM4 CCD System Software. User's Guide*, Version 1.166; Kuma Diffraction: Wrocław, Poland, 1995–2000.

(10) *SHELXTL*, v. 5.10; Bruker Analytical X-Ray: Madison, WI, 1997.

$V = 1617.4(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $D_{\text{calcd}} = 1.128 \text{ g/cm}^3$ ,  $T = 100.0(5) \text{ K}$ , scan type  $\omega$ ,  $\mu_{(\text{MoK}\alpha)} = 0.165 \text{ mm}^{-1}$ , 10 951 measured reflections, 3807 independent reflections [ $R_{(\text{int})} = 0.0370$ ], refinement on  $F^2$ ,  $R[F^2 > \sigma(F^2)] = 0.0643$ ,  $wR = 0.1658$ . **3**,  $\text{C}_{10}\text{H}_{24}\text{AlCl}_3\text{O}_4\text{Zr}$ :  $M = 432.84$ , orthorhombic crystal system, space group  $Pnma$  (No. 62),  $a = 18.340(4) \text{ \AA}$ ,  $b = 10.932(2) \text{ \AA}$ ,  $c = 9.062(2) \text{ \AA}$ ,  $V = 1816.9(7) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{calcd}} = 1.582 \text{ g/cm}^3$ ,  $T = 100.0(5) \text{ K}$ , scan type  $\omega - 2\theta$ ,  $\mu_{(\text{MoK}\alpha)} = 1.099 \text{ mm}^{-1}$ , 3330 measured reflections, 1696 independent reflections [ $R_{(\text{int})} = 0.0306$ ], refinement on  $F^2$ ,  $R[F^2 > \sigma(F^2)] = 0.0298$ ,  $wR_2 = 0.0809$ .

**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 and figures giving additional views for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM034263O