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## Communications

# Syntheses and Molecular Structures of $[Mg_4(THFFO)_6(OSiPh_3)_2]$ and $[Al_3Mg(\mu_3\text{-}O)(THFFO)_3(Me)_6]$ Relevant to Ziegler−Natta Catalyst Intermediates (THFFO = 2-Tetrahydrofurfuroxide)

Piotr Sobota,* Józef Utko, Jolanta Ejfler, and Lucjan B. Jerzykiewicz

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

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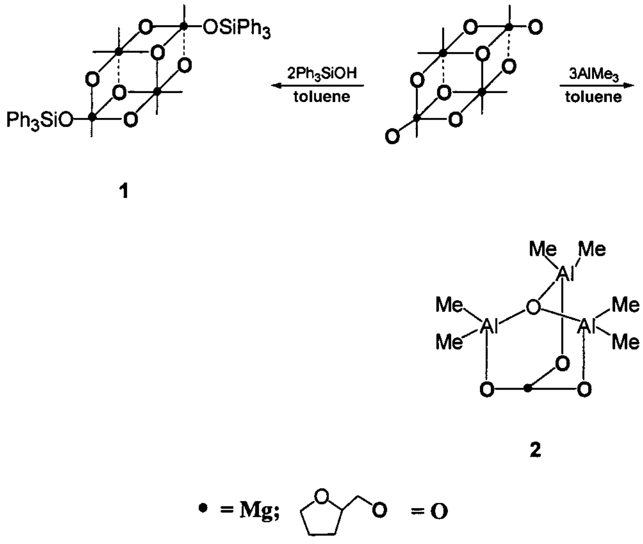
*Summary: $[Mg_8(THFFO)_8]$ used as a olefin polymerization catalyst component can be trapped by $Ph_3SiOH$ groups to form $[Mg_4(THFFO)_6(OSiPh_3)_2]$ (**1**; 77%). We have also shown that in the reaction of magnesium alkoxide with $AlMe_3$ the methylalumoxane $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ unit is formed, which was isolated and characterized as the molecular compound $[Al_3Mg(\mu_3\text{-}O)(THFFO)_3(Me)_6]\cdot C_6H_5CH_3$ (**2**; 40%) (THFFO = 2-tetrahydrofurfuroxide).*

High-activity, stereoregular olefin polymerization catalysts can be produced from an organoaluminum cocatalyst and titanium−magnesium procatalyst precursor containing alkoxide groups. The catalysts are useful in the polymerization or copolymerization of lower α-olefins.[1,2] Hence, studies on the interaction between each of the catalyst components and ≡SiOH surface groups are very important. Very recently we have found that in the reaction of $[Mg_4(THFFO)_8]$ with $Ti(DIPP)_4$ the compound $[Mg_4(THFFO)_6\{OTi(DIPP)_3\}_2]$ (DIPP = diisopropylphenolate) is formed.[3] Here we describe the reactions of $[Mg_4(THFFO)_8]$ with $Ph_3SiOH$ and the cocatalyst $AlMe_3$.

**Scheme 1. Synthesis of Compounds 1 and 2**



The direct reaction of the dicubane-like tetramer $[Mg_4(THFFO)_8]$ with $Ph_3SiOH$ in a 1:2 molar ratio in toluene gives the air-sensitive colorless compound $[Mg_4(THFFO)_6\text{-}$

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(1) (a) Toyota, A.; Kashiwa, N. Japan Pat. Kokai 75-30,983, 1975. (b) Gavens, P. D.; Botrrill, M.; Kelland, J. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. W., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1982; Vol. 3. (c) Giannini, U.; Albizzati, E.; Parodi, S.; Pirinoli, F. U.S. Patents 4,124,532, 1978, and 4,174,429, 1979. (d) Yamaguchi, K.; Kanoh, N.; Tanaka, T.; Enokido, N.; Murakami, A.; Yoshida, S. U.S. Patent 3,989,881, 1976. (e) Arzoumanidis, G. G.; Karayannis, N. M. *CHEMTECH* **1993**, *23*, 43. (f) Sobota, P. *Macromol. Symp.* **1995**, *89*, 63. (g) Soga, K.; Shiono, T. *Prog. Polym. Sci.* **1997**, *22*, 1503.

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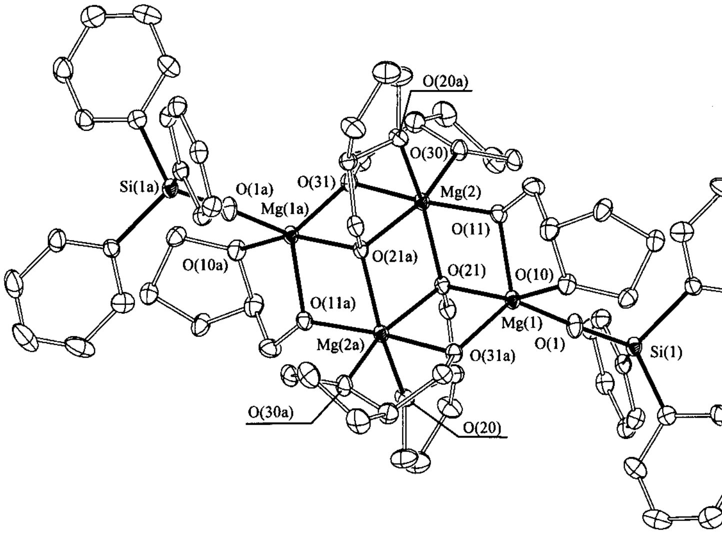

**Figure 1.** Molecular structure of $[Mg_4(THFFO)_6(OSiPh_3)_2]$ (**1**) in the crystal. Hydrogen atoms, the second position of disordered carbon atoms, are omitted for clarity. Selected bond lengths (Å) and angles (deg): Si−O(1), 1.570(2); Mg(1)−O(1), 1.891(2); Mg(1)−O(10), 2.162(2); Mg(1)−O(11), 1.979(2); Mg(1)−O(21), 2.113(2); Mg(1)−O(31a), 1.964(2); Mg(2)−O(11), 1.979(2); Mg(2)−O(31), 2.024(2); Mg(2)−O(20a), 2.206(2); Mg(2)−O(21), 2.086(2); Mg(2)−O(21a), 2.078(2); Mg(2)−O(30), 2.101(2); Si−O(1)−Mg(1), 169.38(15); O(1)−Mg(1)−O(31a), 123.90(11); O(1)−Mg(1)−O(11), 120.60(11); O(31a)−Mg(1)−O(11), 115.33(10); O(1)−Mg(1)−O(21), 102.13(9); O(31a)−Mg(1)−O(21), 82.63(9); O(11)−Mg(1)−O(21), 80.32(9); O(11)−Mg(2)−O(31), 173.24(10); O(11)−Mg(2)−O(21a), 104.68(9); O(31)−Mg(2)−O(21a), 82.07(9); O(11)−Mg(2)−O(21), 80.98(9); O(31)−Mg(2)−O(21), 100.55(9); O(21a)−Mg(2)−O(21), 82.09(9).

$(OSiPh_3)_2]$ (**1**; Scheme 1).[4a] A view of the structure of **1** is shown in Figure 1. The $Mg_4(THFFO)_6$ core in **1** is similar to that of $[Mg_4(THFFO)_6\{OTi(DIPP)_3\}_2]$.[3] The difference is that the two $OTi(DIPP)_3$ groups bound to the five-coordinated magnesium atoms in $[Mg_4(THFFO)_6\{OTi(DIPP)_3\}_2]$ are replaced by two $OSiPh_3$ groups in **1**.

The $^1H$ NMR spectrum supported the structural assignment of **1**.[5] In our opinion the structure of **1** is very important, because for the first time it is shown that the magnesium alkoxide may be trapped by ≡SiOH silica surface groups during the heterogeneous catalyst preparation. Up to now it has been believed that the silica surface is only impregnated by the $MgX_2/TiX_4/AlR_3$ catalyst components.[6]

The reaction of $[Mg_4(THFFO)_8]$ with $AlMe_3$ proceeds by a reaction course different from that for **1**. In this case the dicubane-like magnesium species $[Mg_4(THFFO)_8]$ splits and reacts with $AlMe_3$ to form colorless crystals of $[Al_3Mg(\mu_3\text{-}O)(THFFO)_3(Me)_6]\cdot C_6H_5CH_3$ (**2**), which are extremely sensitive toward moisture.[7] The X-ray crystal structure of **2** was determined[4b] as shown in Figure 2. The four-coordinated aluminum atom in **2** is surrounded by two methyl groups and one $\mu_3$-$O_{oxo}$ and one $\mu$-$O_{alkoxo}$ oxygen atom of the $[Mg(THFFO)_3]^-$ moiety. Three $AlMe_2$ moieties are held together by $\mu_3$-$O_{oxo}$ oxygen atoms to form a trinuclear $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ macro unit. The coordination sphere of the magnesium atom in **2** is formed by six oxygen atoms: three ether and three bridging $\mu$-$O_{alkoxo}$ atoms of the THFFO ligands. The $\mu_3$-O oxygen atom lies on a pseudo-3-fold axis and exhibits bond angles as expected for $sp^2$

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(4) Complete X-ray experimental details are given in the Supporting Information. (a) X-ray crystal data for **1**: $M_r$ = 1260.72, monoclinic, space group $P2_1/n$, $a$ = 11.058(2) Å, $b$ = 20.704(4) Å, $c$ = 14.213(3) Å, $\beta$ = 95.25(3)°, $V$ = 3240.2(11) Å$^3$, $Z$ = 2, $F(000)$ = 1348, $\rho_{calcd}$ = 1.292 Mg m$^{-3}$, $\mu$ = 0.157 mm$^{-1}$, crystal dimensions 0.5 × 0.4 × 0.2 mm, $T$ = 100.0(5) K, radiation Mo K$\alpha$ ($\lambda$ = 0.710 73 Å), scan type $\omega$, $\theta_{max}$ = 28.8°, 21 050 measured reflections, 7686 independent reflections, 7686 reflections in refinement, 388 parameters, $R$ = 0.0672, $R_w$ = 0.1701, maximum/minimum residual electron density 0.847/−0.662 e Å$^{-3}$. (b) X-ray crystal data for **2**: $M_r$ = 1113.7, monoclinic, space group $P2_1/n$, $a$ = 9.713(2) Å, $b$ = 17.856(4) Å, $c$ = 17.983(4) Å, $\beta$ = 96.04(3)°, $V$ = 3101.6(12) Å$^3$, $Z$ = 2, $F(000)$ = 1196, $\rho_{calcd}$ = 1.193 Mg m$^{-3}$, $\mu$ = 0.179 mm$^{-1}$, crystal dimensions 0.5 × 0.4 × 0.2 mm, $T$ = 100.0(5) K, radiation Mo K$\alpha$ ($\lambda$ = 0.710 73 Å), scan type $\omega$, $\theta_{max}$ = 28.6°, 18 618 measured reflections, 7024 independent reflections, 7024 reflections in refinement, 356 parameters, $R$ = 0.0567, $R_w$ = 0.1545, maximum/minimum residual electron density 0.472/−0.364 e Å$^{-3}$.

(5) To a suspension of 0.64 g (2.8 mmol) of $[Mg_4(THFFO)_8]$ in toluene (25 mL) was added $Ph_3SiOH$ (0.39 g, 1.4 mmol) under dinitrogen. The mixture was stirred overnight to complete dissolution of the solid. The solution was reduced in volume under vacuum to 10 mL and left to crystallize at room temperature. Yield: 0.68 g (77%). Good-quality crystals, suitable for X-ray examination, were taken directly from the post-reaction mixture. IR (Nujol): $\nu$ 1960 (w), 1928 (w), 1884 (w), 1586 (w), 1108 (vs), 1096 (vs), 1060 (vs), 1008 (s), 956 (m), 852 (m), 810 (m), 748 (vs), 568 (s), 518 (vs), 458 (s), 420 (s), 350 (m), 328 (m) cm$^{-1}$. $^1H$ NMR ($CDCl_3$, $T$ = 297 K): $\delta$ 1.6 (m, 5H, THFFO), 3.8 (m, 4H, THFFO), 7.6 (m, 5H, Ph). Anal. Calcd for $C_{66}H_{84}Si_2O_{14}Mg_4$: C, 63.18; H, 6.75. Mg, 7.75. Found: C, 62.91; H, 6.63. Mg, 7.71.

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(7) A solution of $[Mg_4(THFFO)_8]$ (2.2 g, 10 mmol) in toluene (60 mL) was treated at 273 K under argon with $AlMe_3$ (1 mL, 10 mmol). Stirring was continued at room temperature for 12 h, followed by filtration, to remove a small amount of insoluble material, and the solution was concentrated to 30 mL.[3] After 1 week colorless diffraction-quality crystals appeared in the filtrate. Yield: 0.6 g (40%). IR (Nujol): $\nu$ 1128 (vs), 1064 (vs), 1020 (s), 994 (w), 826 (s), 606 (m), 548 (m), 468 (s), 430 (s), 370 (s) cm$^{-1}$. Anal. Calcd for $C_{21}H_{45}O_7Al_3Mg$: C, 49.0; H, 8.82. Al, 15.76. Mg, 4.66. Found: C, 49.20; H, 8.61. Al, 15.71. Mg, 4.59.

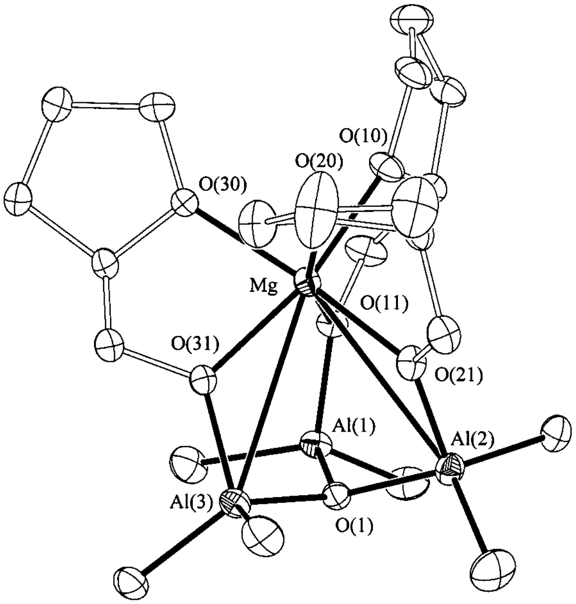

**Figure 2.** Molecular structure of $[Al_3Mg(\mu_3\text{-}O)(THFFO)_3(Me)_6]\cdot C_6H_5CH_3$ (**2**) in the crystal. Hydrogen atoms and the second position of disordered carbon atoms and the toluene molecule are omitted for clarity. Selected bond lengths (Å) and angles (deg): Al(1)−O(1), 1.8151(18); Al(1)−O(11), 1.8073(17); Al(2)−O(1), 1.8162(19); Al(2)−O(21), 1.8133(19); Al(3)−O(31), 1.8088(18); Al(3)−O(1), 1.8219(19); Mg−O(11), 2.0425(19); Mg−O(21), 2.0386(19); Mg−O(31), 2.0496(19); Mg−O(30), 2.0935(19); Mg−O(20), 2.110(2); Mg−O(10), 2.1125(19); O(11)−Al(1)−O(1), 96.27(8); O(21)−Al(2)−O(1), 96.13(8); O(31)−Al(3)−O(1), 97.25(8); Al(1)−O(1)−Al(2), 116.25(9); Al(1)−O(1)−Al(3), 116.93(9); Al(2)−O(1)−Al(3), 116.07(9).

hybridization (average 116.42(9)°). Thus, the $Al_3(\mu_3\text{-}O)$ system is almost planar, with the triply bridging oxide O(1) being 0.35(1) Å out of the $Al_3$ plane. The Al−$\mu_3$-O distances (average 1.8177(19) Å) in **2** are similar to the corresponding bond lengths (1.808(3) Å)[8a] in $[Al_7O_6Me_{16}]^-$ and slightly longer (1.78(2) and 1.80(2) Å)[8b] than in $[\{Me_2Al(\mu_3\text{-}O)AlMe_3\}_2]^{2-}$. Attempts to obtain $^{27}Al$ NMR spectra were frustrated by the very poor solubility of **1**.

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.[9] It is apparent that decomposition to an oxo species is facilitated by THFFO ligand deoxygention.[10] Some alkylalumoxanes have been characterized crystallographically by Barron and co-workers,[11] who obtained them by partial hydrolysis of aluminum alkyls. Thus, hydrolysis of $Al(^tBu)_3$ gave tetranuclear $[Al_4(\mu_3\text{-}O)_2(^tBu)_8]$ together with the $[Al_8(\mu_3\text{-}O)_8(^tBu)_8]$.

In summary, we have for the first time demonstrated that magnesium alkoxo species can be grafted by ≡SiOH groups to form complex **1**. Moreover, in the reaction of $AlMe_3$ with the magnesium species the methylalumoxane $[Al_3(\mu_3\text{-}O)(Me)_6]^+$ macro unit is formed. This can be trapped by magnesium species as the molecular solid **2**.

It is noteworthy that magnesium compounds with a $Mg_4(THFFO)_6$ core are good additives, boosting the activity of the catalytic mixture. For example, the preliminary results of an ethylene polymerization test on $[Mg_4(THFFO)_6Cl_2]/TiCl_4/AlEt_3$ catalyst gave ca. 170 kg of polyethylene (g of Ti)$^{-1}$ h$^{-1}$, while only 11.6 kg of polyethylene (g of Ti)$^{-1}$ h$^{-1}$ were obtained under the same conditions when $MgCl_2/TiCl_4/AlEt_3$ catalyst was used.[12]

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**Supporting Information Available:** Tables giving atomic coordinates, bond lengths and angles, and anisotropic thermal parameters and figures giving additional views for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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