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Polynuclear Magnesium and Magnesium−Titanium Species. Syntheses and Crystal Structures of [$Mg_4(\mu_3,\eta^2$-ddbfo$)_2(\mu,\eta^2$-ddbfo$)_2(\mu,\eta^1$-ddbfo$)_2(\eta^1$-ddbfo$)_2$], [$Mg_4(\mu_3$-OMe$)_2(\mu,\eta^2$-ddbfo$)_2(\mu,\eta^1$-ddbfo$)_2(\eta^1$-ddbfo$)_2(CH_3OH)_5$], and [$Mg_4(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_2(\mu,\eta^1$-thffo$)_2\{\mu$-OTi(DIPP$)_3\}_2$] Aggregates

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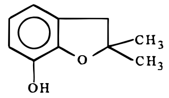
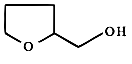
Tetranuclear magnesium complexes with chelating alkoxo ligands have been synthesized with the aim of investigating coordinatively unsaturated magnesium sites able to bind TiX_4 (X = Cl, OR), of the type necessary for the formation of the active centers in polymerization catalysts. The magnesium compound [$Mg_4(\mu_3,\eta^2$-ddbfo$)_2(\mu,\eta^2$-ddbfo$)_2(\mu,\eta^1$-ddbfo$)_2(\eta^1$-ddbfo$)_2$]·$2CH_2Cl_2$ (**1**) (ddbfo = 2,3-dihydro-2,2-dimethyl-7-benzofuranoxide) was prepared by the reaction of $MgBu_2$ with ddbfoH in dichloromethane. Complex **1** exists as a centrosymmetric tetranuclear species with two different types of magnesium centers corresponding to octahedral MgO_6 and trigonal bipyramidal MgO_5 geometry. Compound **1** is monoclinic, space group $P2_1/c$, with a = 12.053(2) Å, b = 13.323(3) Å, c = 17.069(3) Å, β = 98.50(3)°, and Z = 4. The reaction of **1** with methanol in tetrahydrofuran (THF) gave compound [$Mg_4(\mu_3$-OMe$)_2(\mu,\eta^2$-ddbfo$)_2(\mu,\eta^1$-ddbfo$)_2(\eta^1$-ddbfo$)_2(CH_3OH)_5$]·CH_3OH·THF (**2**). During this reaction one of the two five-coordinate MgO_5 centers in **1** is completed by a methanol molecule and becomes octahedral in **2**. Species **2** belongs to the $P2_1/n$ monoclinic space group, with a = 13.323(3) Å, b = 20.768(4) Å, c = 27.584(6) Å, β = 104.26(3)°, and Z = 4. Compound [$Mg_4(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_2(\mu,\eta^1$-thffo$)_2\{\mu$-OTi(DIPP$)_3\}_2$]·$2CH_2Cl_2$ (**3**) is formed as a result of substitution of two thffo (thffo = 2-tetrahydrofurfuroxide) ligands bonded to the five-coordinate magnesium atom in [Mg_4(thffo$)_8$] by bulky OTi(DIPP$)_3$ (DIPP = diisopropylphenolate) groups. Crystals of **3** are monoclinic, space group $P2_1/n$, with a = 17.069(3) Å, b = 18.421(4) Å, 17.815(4) Å, β = 90.77(3)°, and Z = 4. The X-ray crystal structures of complexes **1**−**3** are discussed in terms of explaining the role of the coordinatively unsaturated magnesium site in chiral catalyst active center formation.

Introduction

The frequently dramatic and sometimes beneficial influence of electropositive metal species such as $MgCl_2$ on the polymerization activity of early-transition-metal compounds is widely recognized[1,2] but poorly understood.[3−5] $MgCl_2(THF)_{1.5}$, as a catalyst component, is especially attractive for studying the factors which favor polynuclear aggregation of magnesium dichloride with $TiCl_4$.[1] Up to now, only the structures of $MCl_2(THF)_{1.5}$ for Fe, Co, and Mg derivatives have been well documented.[6−8] The metal species exist as centrosymmetric tetranuclear [$M_4(\mu_3$-Cl$)_2(\mu$-Cl$)_4X_2(THF)_6$] (X = Cl for M = Fe,[6] Co;[7] X = C_2H_5 for M = Mg[8]) compounds with two different types of M(II) centers corresponding to six-coordinate octahedral MCl_4O_2 and five-coordinate trigonal bipyramidal MCl_4O chromophores. A similar structure is seen in [$Mg_4(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_4Cl_2$].[9]



ddbfoH



thffoH

To extend this chemistry we have been attempting to synthesize a new magnesium species with the ddbfo (ddbfo = 2,3-dihydro-2,2-dimethyl-7-benzofuranoxide) and thffo (2-tet-

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rahydrofurfuroxide) ligands. These ligands seemed to have attractive features. Containing two oxygen donor atoms, ether and aryloxide, they can act not only as chelate ligands and occupy two coordination sites on the metal but also as a tether between the metal atoms to create multinuclear species.

Herein, we report the syntheses and crystal structures of tetranuclear $[\mathrm{Mg_4}(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_2(\mu,\eta^1\text{-ddbfo})_2(\eta^1\text{-ddbfo})_2]$, $[\mathrm{Mg_4}(\mu_3\text{-OMe})_2(\mu,\eta^2\text{-ddbfo})_2(\mu,\eta^1\text{ddbfo})_2(\eta^1\text{-ddbfo})_2(\mathrm{CH_3OH})_5]$, and $[\mathrm{Mg_4}(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_2(\mu,\eta^1\text{-thffo})_2\{\mu\text{-OTi(DIPP)}_3\}_2]$ species.

Experimental Section

General Methods. All the syntheses were performed under a dry dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried and then distilled under N_2 by following conventional methods. $\mathrm{MgBu_2}$ (1 M in *n*-hexane), 2,3-dihydro-2,2-dimethyl-7-benzofuranol, furfuryl alcohol, magnesium turnings, and $\mathrm{TiCl_4}$ were purchased from Aldrich. $[\mathrm{Mg_4(thffo)_8}]$ was prepared by following the published procedure.[10] IR spectra were measured on a Perkin-Elmer 180 instrument in Nujol mulls.

Preparation of $[\mathrm{Mg_4}(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_2(\mu,\eta^1\text{-ddbfo})_2(\eta^1\text{-ddbfo})_2]\cdot 2\mathrm{CH_2Cl_2}$ (1). A solution of 2,3-dihydro-2,2-dimethyl-7-benzofuranol (6.72 g; 40 mmol) in hexane (100 $\mathrm{cm^3}$) was added to a rapidly stirred solution of $\mathrm{MgBu_2}$ (2.77 g; 20 mmol) in hexane (20 $\mathrm{cm^3}$) at room temperature. After the mixture was stirred overnight, the white solid was filtered off, washed with hexane (3 × 5 $\mathrm{cm^3}$), and dried under vacuum. Yield: 6.7 g (95.8%). Anal. Calcd for $\mathrm{C_{80}H_{88}Mg_4O_8}$: C, 63.98; H, 5.91; Mg, 6.40. Found: C, 63.72; H, 6.18; Mg, 6.24. IR (Nujol, $\mathrm{cm^{-1}}$): 268 (m), 302 (m), 323 (s), 348 (vs), 406 (vs), 432 (w), 471 (m), 482 (s), 493 (m), 519(m), 530 (m), 570 (vs), 594 (vs), 620(sh), 712 (sh), 720 (s), 759 (s), 859 (s), 768 (m), 905 (w), 932 (w), 968 (w), 1029 (vs), 1042 (sh), 1101 (m), 1123 (m), 1164 (m), 1225 (m), 1585 (m), 1600 (m), 1621 (s). Crystals suitable for structure determination were obtained by heating of the white solid (0.5 g) in a mixture of toluene (60 $\mathrm{cm^3}$) and dichloromethane (20 $\mathrm{cm^3}$) under reflux up to dissolution of the solid and filtered off. The filtrate was reduced in volume under vacuum to 50 $\mathrm{cm^3}$ and left to crystallize at room temperature. After 2 weeks, colorless crystals of **1** were taken directly from the solution.

Preparation of $[\mathrm{Mg_4}(\mu_3\text{-OMe})_2(\mu_2,\eta^2\text{-ddbfo})_2(\mu_2,\eta^1\text{-ddbfo})_2(\eta^1\text{-ddbfo})_2(\mathrm{CH_3OH})_5]\cdot\mathrm{CH_3OH}\cdot\mathrm{THF}$ (2). To a suspension of **1** (1.58 g; 4.5 mmol) in $\mathrm{CH_3OH}$ (20 $\mathrm{cm^3}$) were added THF (15 $\mathrm{cm^3}$) and $\mathrm{CH_2Cl_2}$ (20 $\mathrm{cm^3}$). The mixture was stirred to complete dissolution of the solid. After 1 week the colorless crystals settled down and were filtered off and washed with hexane (3 × 5 $\mathrm{cm^3}$). Yield: 0.7 g (47.5%). Anal. Calcd for $\mathrm{C_{72}H_{104}Mg_4O_{21}}$: C, 61.65; H, 7.47; Mg, 6.93. Found: C, 61.48; H, 7.52; Mg, 6. 81. IR (Nujol, $\mathrm{cm^{-1}}$): 383 (s), 450 (s, br), 484 (s), 603 (m), 715 (s), 752 (s), 778 (w), 831 (w), 860 (m), 1027 (s), 1050 (vs), 1069 (sh), 1094 (w), 1126 (m), 1203 (w), 1594 (m), 1618 (m), 3300 (vs). Good-quality crystals, suitable for X-ray examination, were taken directly from postreaction mixture.

Preparation of $[\mathrm{Mg_4}(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_2(\mu,\eta^1\text{-thffo})_2\{\mu\text{-OTi(DIPP)}_3\}_2]\cdot 2\mathrm{CH_2Cl_2}$ (3). $\mathrm{Ti(DIPP)_4}$ (6.5 g, 8.7 mmol) and $[\mathrm{Mg_4(thffo)_8}]$ (3.9 g, 17.4 mmol) were dissolved in $\mathrm{CH_2Cl_2}$ (100 $\mathrm{cm^3}$). The reaction mixture was stirred for 2 h during which the initial orange color faded to pale yellow. The resulting solution was treated with a THF (20 $\mathrm{cm^3}$) solution of water (0.15 g, 8.7 mmol) and stirred for 5 h. Reduction in volume to 30 $\mathrm{cm^3}$ and cooling in a freezer at 258 K afforded compound **3** as light lemon crystals. Yield: 2.45 g (30%). Anal. Calcd for $\mathrm{C_{102}H_{156}Mg_4O_{20}Ti_2}$: C, 64.60; H, 8.23; Mg, 5.13; Ti, 5.06. Found: C, 64.71; H, 8.18; Mg, 5.24; Ti, 5.12. IR (Nujol, $\mathrm{cm^{-1}}$): 350 (sh), 388 (m), 432(m), 480 (m), 542 (m), 565 (m), 703 (vs), 748 (vs), 808 (m, br), 874 (s), 896 (vs, br), 988 (w), 1016 (m), 1038 (s), 1060 (vs), 1096 (vs), 1112 (s), 1121(s), 1206 (vs), 1258 (vs), 1583 (m).

Table 1. Crystallographic Data for **1**−**3**

param	compound no. 1	2	3
chem formula	$\mathrm{C_{41}H_{46}Cl_2Mg_2O_8}$	$\mathrm{C_{72}H_{104}Mg_4O_{21}}$	$\mathrm{C_{52}H_{80}Cl_2Mg_2O_{10}Ti}$
fw	786.30	1402.79	1032.58
T, K	100.0(4)	100.0(5)	100.0(4)
λ, Å	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
unit cell dimens			
a, Å	12.053(2)	13.323(3)	17.069(3)
b, Å	12.090(2)	20.768(4)	18.421(4)
c, Å	26.864(5)	27.584(6)	17.815(4)
β, deg	98.50(3)	104.26(3)	90.77(3)
V, Å^3	3871.6(12)	7397(3)	5601(2)
Z	4	4	4
ρ_{calcd}, g/cm^3	1.349	1.260	1.225
μ, cm^{-1}	2.53	1.21	3.23
R_1	0.0482	0.0629	0.0565
wR_2	0.111	0.1571	0.1312

[a] $R_1 = \sum(F_o - F_c)/\sum F_o$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Crystallographic Studies. Crystals of title compounds were mounted on a glass fiber and then flash-frozen to 100 K (Oxford Cryosystem-Cryostream Cooler). Data were collected on a KUMA KM4 four-circle diffractometer[11] equipped with a CCD area detector and a graphite monochromator utilizing Mo Kα. The final parameters and specific data collection parameters are summarized in Table 1. The recorded data were corrected for Lorentz and polarization factors. All the three structures were solved by direct methods (SHELXS97)[12] and refined by full-matrix least squares (SHELXL97).[13] The carbon-bonded H atoms were placed in calculated positions. The hydrogen atoms of hydroxyl groups were located from a difference Fourier map and refined without any restraints. In structure **3** the chiral carbon atoms of the thffo rings are split over two sites; occupancy factors for these two positions were refined.

Results and Discussion

Synthesis and Characterization of $[\mathrm{Mg_4}(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_2(\mu,\eta^1\text{-ddbfo})_2(\eta^1\text{-ddbfo})_2]\cdot 2\mathrm{CH_2Cl_2}$ (1). Protonolysis of the readily available precursor $\mathrm{MgBu_2}$ with 2,3-dihydro-2,2-dimethyl-7-benzofuranol in *n*-hexane yields **1.** Compound **1** is insoluble in tetrahydrofuran and hydrocarbons and slightly soluble in $\mathrm{CH_2Cl_2}$ and toluene. The IR spectrum of **1** shows bands at 268 (m), 302 (m), 323 (s), 348 (vs), and 406 (vs) $\mathrm{cm^{-1}}$ suggesting Mg−μ-O and Mg−μ_3-O alkoxide bridges as well as stretching bands at 1029 (vs) and 1042 (sh) $\mathrm{cm^{-1}}$ due to ν(C−O−C) vibrations of a coordinated ether oxygen atom of ddbfo. Liberation of butane during reaction 1 and the absence of ν(OH) vibration in the IR spectrum suggested a multinuclear character of **1** in the solid state.

$$4\mathrm{MgBu_2} + 8\mathrm{ddbfoH} + 2\mathrm{CH_2Cl_2} \rightarrow [\mathrm{Mg_4}(\mu_3,\eta^2\text{-ddbfo})_2(\mu,\eta^2\text{-ddbfo})_2(\mu,\eta^1\text{-ddbfo})_2(\eta^1\text{-ddbfo})_2]\cdot 2\mathrm{CH_2Cl_2}\ (\mathbf{1}) + 8\mathrm{BuH} \quad (1)$$

Compound **1** can be isolated as a crystalline material from dichloromethane/toluene solution. The structure of the complex consists of centrosymmetric tetranuclear molecules, and an overall view and numbering scheme are shown in Figure 1. The selected bond lengths and angles are given in Table 2. In **1** a

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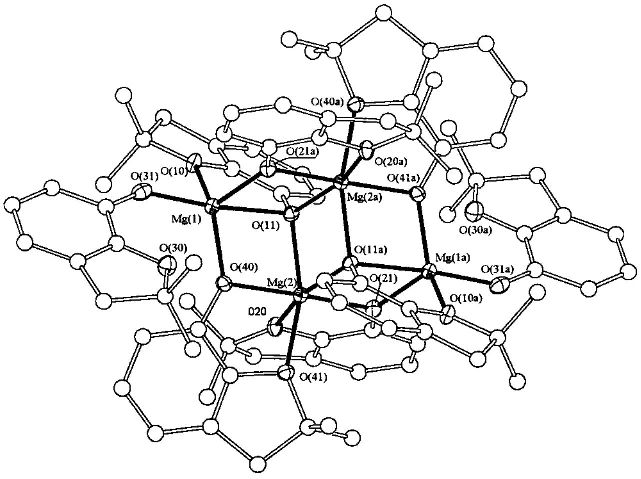

Figure 1. Molecular structure of **1** with atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. The C-bonded H atoms are excluded for clarity. The C atoms are represented by circles of an arbitrary radii.

Table 2. Selected Bond Lengths (Å)[a]

	Compound **1**		
Mg(1)−O(31)	1.9384(17)	Mg(2)−O(40)	2.0445(16)
Mg(1)−O(40)	1.9702(16)	Mg(2)−O(11a)	2.0592(15)
Mg(1)−O(21a)	1.9713(16)	Mg(2)−O(11)	2.0763(15)
Mg(1)−O(10)	2.1129(16)	Mg(2)−O(41)	2.1728(16)
Mg(1)−O(11)	2.3481(16)	Mg(2)−O(20)	2.2439(15)
Mg(2)−O(21)	2.0379(16)		
	Compound **2**		
Mg(1)−O(31)	1.923(3)	Mg(3)−O(4)	2.044(2)
Mg(1)−O(21)	1.977(2)	Mg(3)−O(61)	2.059(2)
Mg(1)−O(11)	2.018(2)	Mg(3)−O(3)	2.073(2)
Mg(1)−O(3)	2.020(2)	Mg(3)−O(21)	2.075(2)
Mg(1)−O(10)	2.155(2)	Mg(3)−O(7)	2.112(3)
Mg(2)−O(51)	2.035(3)	Mg(3)−O(8)	2.137(3)
Mg(2)−O(4)	2.036(2)	Mg(4)−O(41)	2.023(2)
Mg(2)−O(2)	2.078(3)	Mg(4)−O(11)	2.043(2)
Mg(2)−O(61)	2.080(2)	Mg(4)−O(5)	2.077(3)
Mg(2)−O(41)	2.082(3)	Mg(4)−O(3)	2.080(2)
Mg(2)−O(40)	2.173(3)	Mg(4)−O(6)	2.083(3)
Mg(2)−C(47)	2.855(4)	Mg(4)−O(4)	2.101(2)
	Compound **3**		
Ti−O(1)	1.687(2)	Mg(1)−O(11)	2.245(2)
Ti−O(51)	1.828(2)	Mg(2)−O(31)	2.017(2)
Ti−O(41)	1.8494(19)	Mg(2)−O(21)	2.018(2)
Ti−O(61)	1.854(2)	Mg(2)−O(11a)	2.065(2)
Mg(1)−O(21a)	1.926(2)	Mg(2)−O(11)	2.067(2)
Mg(1)−O(31)	1.935(2)	Mg(2)−O(30)	2.126(2)
Mg(1)−O(1)	2.006(2)	Mg(2)−O(20)	2.162(2)
Mg(1)−O(10)	2.033(2)		

[a] Symmetry transformations used to generate equivalent atoms: compound **2**, a, $-x + 1$, $-y$, $-z$; compound **3**, a, $-x$, $-y + 2$, $-z + 2$.

nearly regular Mg$_4$ rhombus is bridged by two μ_3-oxygen O(11) and O(11a) atoms of aryloxide groups, one above and below the Mg$_4$ plane, and in addition four μ-O$_{\text{aryloxide}}$ atoms bridge Mg−Mg edges. The species **1** contains two types of magnesium centers: the five-coordinate Mg(1) and Mg(1a) atoms and the six-coordinate Mg(2) and Mg(2a). The Mg(1) atom has bipyramidal geometry with O(31)−Mg(1)−O(11) [167.87(6)°], representing the nearly linear group. The equatorial plane of the bipyramid is formed by two μ-O$_{\text{aryloxide}}$ oxygen atoms and one ether oxygen from the ddbfo ligand. The coordination sphere around Mg(2) is a slightly distorted octahedron formed by two μ_3-O$_{\text{aryloxide}}$, two μ-O$_{\text{aryloxide}}$, and two ether oxygens from the ddbfo ligand (in cis position). The average Mg−O$_{\text{ether}}$, M−μ-O$_{\text{aryloxide}}$, and Mg−μ_3-OMe bond distances are of the order of the corresponding magnesium−oxygen distances observed in other magnesium compounds.[9,14,15]

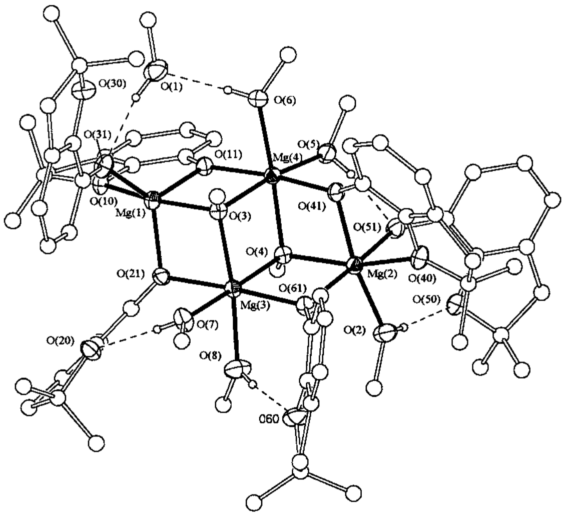

Figure 2. Molecular structure of **2** with atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. The C and H atoms are represented by circles of an arbitrary radii. Hydrogen bonds are shown by dashed lines.

Synthesis and Characterization of [Mg$_4$(μ_3-OMe)$_2$(μ,η^2-ddbfo)$_2$(μ,η^1-ddbfo)$_2$(η^1ddbfo)$_2$ (CH$_3$OH)$_5$]·CH$_3$OH·THF (2). A deeper understanding of the preference of the coordinatively unsaturated five-coordinate magnesium centers in **1,** which offer a free coordination place for an incoming molecule, is of great importance. The reaction of **1** with CH$_3$OH gave new colorless, cubic-shaped crystals which were identified by elemental analysis and the IR spectrum as Mg$_4$(ddbfo)$_6$(OCH$_3$)$_2$(CH$_3$OH)$_6$(THF) (**2**). The IR spectrum shows stretching ν(Mg−μ-O) and ν(Mg−μ_3-O) modes at 383 (s), 450 (s, br), and 484 (s) and bands at 1027 (s), 1050 (vs), and 1069 (sh) cm^{-1} due to ν(C−O−C) vibratitions characteristic of coordinated and noncoordinated ether oxygen atoms as well as stretching the ν(OH) mode at 3300 (s, br) cm^{-1}. The crystalline compound is well soluble in methanol and tetrahydrofuran.

$$\mathbf{1} + 6\mathrm{CH_3OH} + \mathrm{THF} \rightarrow [\mathrm{Mg_4}(\mu_3\text{-OMe})_2(\mu,\eta^2\text{-ddbfo})_2(\mu,\eta^1\text{-ddbfo})_2(\eta^1\text{-ddbfo})_2(\mathrm{CH_3OH})_5]\cdot\mathrm{CH_3OH}\cdot\mathrm{THF}\ (\mathbf{2}) + 2\mathrm{ddbfoH} \quad (2)$$

The solid-state structure of the complex **2** consists of the tetranuclear [Mg$_4$(μ_3-OMe)$_2$(μ_2,η^2-ddbfo)$_2$(μ_2,η^1-ddbfo)$_2$(η^1-ddbfo)$_2$(CH$_3$OH)$_5$] species and two solvents CH$_3$OH and THF of crystallization (Figure 2). The selected bond lengths and angles are given in Table 2. Four magnesium atoms bridged by two μ_3-OMe groups and four μ-O$_{\text{aryloxide}}$ oxygen atoms from the ddbfo ligand constitute a rhombus with an average Mg···Mg distance of 3.093(2) Å. The molecule contains one five-coordinate Mg(1) atom and three six-coordinate Mg(2), Mg(3), and Mg(4) atoms. The inequivalence between Mg(1) and Mg(2) atoms arises from the six-coordinate sphere of Mg(2) which is completed additionally by the O(2) methanol oxygen atom. The environments of the Mg(3) and Mg(4) atoms are

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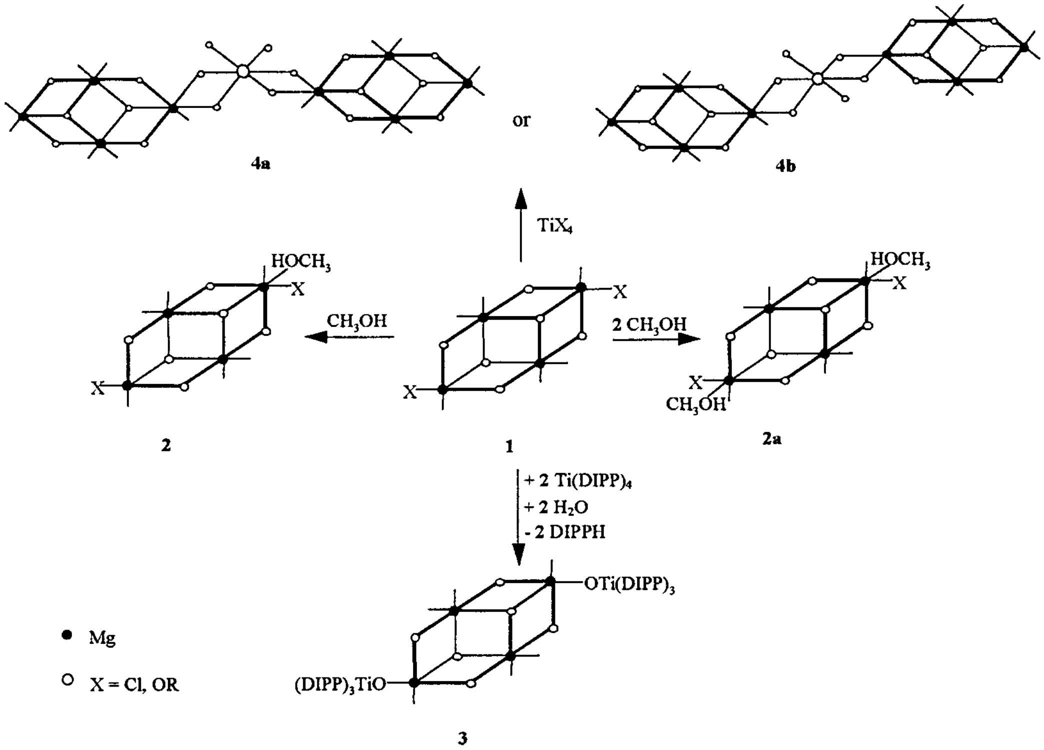
Scheme 1



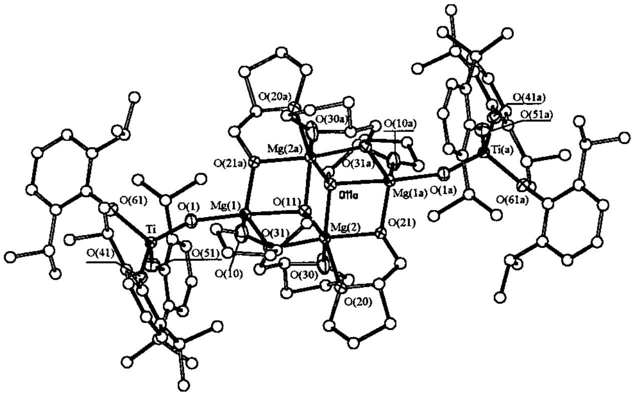


Figure 3. View of the packing in compound **3**. The displacement ellipsoids are drawn at the 30% probability level. The C-bonded H atoms are excluded for clarity. The C atoms are represented by circles of an arbitrary radii.

equivalent and formed by two μ_3-OMe, two μ-O$_{\text{aryloxide}}$ groups, and two methanol oxygen atoms (in cis position).

Synthesis and Characterization of [$Mg_4(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_2(\mu,\eta^1$-thffo$)_2\{\mu$-OTi (DIPP$)_3\}_2]\cdot 2CH_2Cl_2$ (3). As an aid to explain the formation of the catalytically active centers, we are studying the binding of titanium species to the unsaturated magnesium centers in the $Mg_4(OR)_6$ moiety. The complex **3** was prepared by treatment of the [Mg_4(thffo$)_8$][10] with Ti(DIPP)$_4$[16] (see Experimental Section). Presumably it was formed during the course of the reaction by adventitious ingress of moisture. The direct reaction of **1** with Ti(DIPP)$_4$ and two equivalent of H_2O molecules was difficult to control, and up to now we were not able to isolate a product with satisfactory elemental analysis. However, the hydrolysis of the reaction product formed between [Mg_4(thffo$)_8$] and Ti(DIPP)$_4$ in hexane, although difficult to control, gives compound **3** as mentioned above.

$$[Mg_4(\text{thffo})_8] + 2Ti(\text{DIPP})_4 + 2H_2O + 2CH_2Cl_2 \rightarrow [Mg_4(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_2(\mu,\eta^1\text{-thffo})_2\text{-}\{\mu\text{-OTi(DIPP)}_3\}_2]\cdot 2CH_2Cl_2\ (\mathbf{3}) + 2\text{thffoH} + 2\text{DIPPH} \quad (3)$$

The bulky aryloxide $OC_6H_3Pr^i{}_2$-2,6 (DIPP) ligand was used to favor the formation of soluble species and prevent aggregation. A view of the structure **3**, as determined in an X-ray study, is shown in Figure 3, and bond distances and angles are in Table 2. It is instructive to compare the structure of **3** with the earlier published structure of [$Mg_4(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_4Cl_2$].[9] The Mg_4X_6 (X = O or Cl) cores in both compounds are similar. The significant difference is that the two terminal chlorine atoms bonded to the five-coordinated magnesium atoms in [$Mg_4(\mu_3,\eta^2$-thffo$)_2(\mu,\eta^2$-thffo$)_4Cl_2$] are replaced by bulky OTi(DIPP)$_3$ groups in **3** (Scheme 1).

Conclusion

As stated above, we were interested in determining the role of the reactive coordination site at the five-coordinate metal center in the M_4X_6 (X = Cl, OR) core. This study has shown that a series of tetranuclear compounds with $Mg_4(OR)_6$ units exists and can be readily formed under the appropriate conditions. The solid-state structures offer little assistance in the understanding of the reaction pathways involved in the formation of **1**−**3**. A plausible mechanism for **2** formation is shown in Scheme 1. We suppose that substitution of two ddbfo ligands, in **1**, by two methoxide groups leads first to the formation of the centrosymmetric [$Mg_4(\mu_3$-OMe$)_2(\mu_2,\eta^2$-ddbfo$)_2(\mu_2,\eta^1$-ddbfo$)_2$-(η^1-ddbfo$)_2(CH_3OH)_4$] complex which has a Mg_4O_6 core similar to that of **1** and is probably an intermediate in the formation of species **2**. Thus two unsaturated five-coordinate metal sites in **1** offer free coordination centers for incoming methanol molecules. However, only one CH_3OH is coordinated by the

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[16] Minhas, R.; Duchateau, R.; Gambarotta, S.; Bensimon, C. *Inorg. Chem.* **1992**, *31*, 4933.

Mg(2) atom and complex **2** is created. It follows that compound **2** is the least soluble species and precipitates preferentially so driving the equilibrium to its final position. We expect that compound **2a** (**2**·CH_3OH; Scheme 1**)** also exists in the solution as a result of saturation of the Mg(1) coordination sphere by a CH_3OH molecule. In actual fact, the second methanol molecule is present in the lattice of compound **2** and is linked through intermolecular hydrogen bonds to O(31) [O(1)−H(1)···O(31), 2.774(5) Å, 163(8)°] and O(6) [O(6)−H(6)···O(1), 2.673(4) Å, 176(4)°] atoms (see Figure 2).

Up to now there was no crystallographic evidence for magnesium−titanium species of type **4a**,**b**. However for $MnCl_2$, which has properties similar to those of $MgCl_2$, the formation of **4b** species is well documented, e.g., $MnCl_2$ in the solid forms polymer species in which tetranuclear $[Mn_4(\mu_3\text{-Cl})_2(\mu\text{-Cl})_4Cl_2(THF)_6]$ units are linked by μ-chlorine bridges of $MnCl_2(THF)_2$ moieties.[17] The two THF molecules are in a trans position. We believe that the TiX_4 species block the reactive coordination site at the five-coordinate magnesium center in the Mg_4X_6 core and compounds **4a**,**b** are formed (Scheme 1). Unfortunately, these aggregates are insoluble and up to now it was impossible to obtain them in a crystalline form. In our model compounds **4a**,**b**, the titanium atom is bridge-bonded to the two magnesium atoms through two pairs of X (X = Cl, OR). Due to the presence of these bidentate chelating agents and terminal two X ligands in the cis position, the geometry of coordination at the Ti atoms, in **4a**, is chiral, and can be denoted as Δ or Λ according to IUPAC rules for chiral octahedral compounds.[18] As is apparent from Scheme 1, aggregate **4a** is very similar to Ti_2Cl_6 reliefs proposed earlier by Corradini,[19] as precursors of stereospecific active centers experimentally observed for the two $TiCl_3/AlR_3$ and $TiCl_4/MgCl_2/AlR_3$ classes of catalysts.[20,21] The **4b** species has a symmetry center, because the two terminal X atoms are in the trans position and the titanium atom could be regarded as a nonstereospecific center.

It is noteworthy that magnesium compounds with a Mg_4X_6 core are good additives boosting the activity of the catalytic mixture. For example the preliminary results of an ethylene polymerization test on $[Mg_4(\mu_3,\eta^2\text{-thffo})_2(\mu,\eta^2\text{-thffo})_4Cl_2]/TiCl_4/AlEt_3$ catalyst gives ca. 170 kg of polyethylene/g of Ti h^{-1} while only 11.6 kg of polyethylene/g of Ti h^{-1} was obtained under the same conditions when the $MgCl_2/TiCl_4/AlEt_3$ catalyst was used.[9]

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Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determinations of complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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