A Family of Group 4 Metal Alkoxo Complexes with an $M_3(\mu_3\text{-O})$ Core Relevant to Ziegler–Natta Catalyst Intermediates

Józef Utko, Szymon Przybylak, Lucjan B. Jerzykiewicz, Sławomir Szafert, and Piotr Sobota*[a]

Abstract: Reactions of $[Mg(thffo)_2]$ (**1**) or $[Ca(thffo)_2]$ (**2**) with $ZrCl_4$ or $HfCl_4$ in a $CH_2Cl_2/THF/CH_3CN$ mixture give thermally stable neutral heterobimetallic tetranuclear complexes $[M_3M'(\mu_x\text{-O})(\mu,\eta^2\text{-thffo})_6(Cl)_6]$ (thffo = tetrahydrofurfuroxide; M/M'/x: **3**, Zr/Mg/3; **4**, Hf/Mg/3; **5**, Zr/Ca/4; **6**, Hf/Ca/4) as colorless crystals in 75–82% yield. X-ray diffraction studies show complexes **3**–**5** to contain oxo-bridged M_3 triangles that are capped by an alkaline earth metal-containing moiety to form species of C_3 symmetry. Reactions of $ZrCl_4$ and $HfCl_4$ with pure tetrahydrofurfuryl alcohol in EtOH and MeOH provide ionic complexes $[M_3(\mu_3\text{-O})(\mu,\eta^2\text{-thffo})_3(L)_3(Cl)_6]Cl$ (M/L: **8**, Zr/EtOH; **9**, Hf/EtOH; **10**, Zr/MeOH) in 66–79% yield. Complexes **8**–**10** consist of M_3 triangles that are analogous to those in **3**–**6** and possess similar overall symmetry, as shown by X-ray crystallography. Changes in the reaction conditions afforded the asymmetric neutral dimer $[Zr_2(\mu\text{-thffo})_2(thffoH)(Cl)_6]$ (**7**) and the homometallic $[Zr_3(\mu_3\text{-O})(\mu,\eta^2\text{-thp})_3(thf)_2(Cl)_7]$ (**11**).

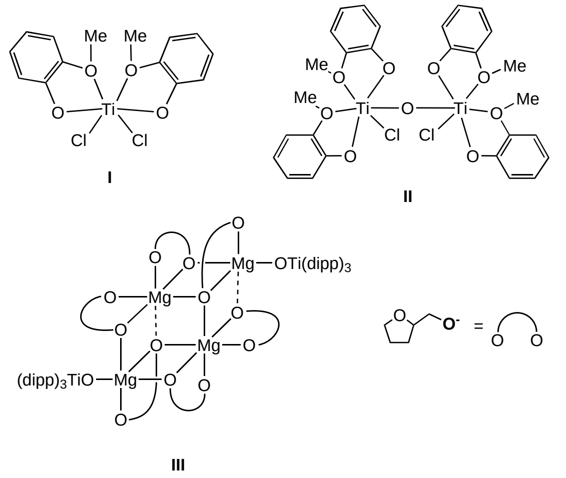
Keywords: alkoxides · crystal structures · hafnium · Ziegler–Natta catalysis · zirconium

Introduction

Research on olefin polymerization catalysts has been dominated in recent decades by metallocene complexes of the early transition metals which were first introduced to olefin polymerization more than 40 years ago.[1] Such complexes activated by methylalumoxane (MAO) form highly active homogeneous catalysts which produce polymers with narrow molecular weight distributions. The continual search for novel catalysts resulted in the development of constrained-geometry catalysts[2] and a variety of non-metallocene complexes of metals across the periodic table.[3] Much interest has been directed toward Group 4 metal complexes with chelating di(amido) ligands,[4] imido ligands,[5] N_2O_2 chelates such as tetradentate Schiff bases,[6] and others.[7]

Alkoxo complexes have also attracted much attention. Due to their acid–base properties they are important in many organic reactions such as oxidation of alcohols,[8] allylation of aldehydes,[9] Diels–Alder reactions,[10] and many others.[11] They are especially important in enantioselective catalysis, one of the most important area of synthetic organic chemistry.[12] From the olefin polymerization perspective, chelating phenoxo ligands are the most recognized.[13] For example, Schaverien described the synthesis and catalytic activity of the biphenoxide and binaphthoxide series of titanium and zirconium.[13a] These compounds, activated with MAO, polymerized ethylene with an activity of up to 4740 kg of polyethylene mol^{-1} catalyst h^{-1}, which is comparable with that of various (indenyl)$ZrCl_2$/MAO catalysts.[14]

Intrigued by Schaverien's and other reports, we have synthesized several titanium alkoxo species that are active precatalysts in Z–N polymerization.[15] Complex **I** (Scheme 1) possesses C_2 symmetry due to utilization of 2 equiv of bidentate ether-alcohol that coordinates to the



Scheme 1. Titanium alkoxo complexes: active Z–N precatalysts.

---

[a] Prof. P. Sobota, Dr. J. Utko, Dr. S. Przybylak,
Dr. L. B. Jerzykiewicz, Dr. S. Szafert
Department of Chemistry, University of Wrocław
F. Joliot-Curie 14, 50-383 Wrocław (Poland)
Fax: (+48) 71-328-2348
E-mail: plas@wchuwr.chem.uni.wroc.pl

metal center in *cis* fashion. Compound **II** with a bridging oxo atom was obtained when crude ligand was used for the synthesis. Such catalysts supported on MgCl$_2$ and activated with AlEt$_3$ produce polyethylene with an activity up to 27840 kg mol^{-1} titanium h^{-1}.

We have also investigated the interaction of titanium alkoxides with alkoxo magnesium compounds that are used as Z–N catalyst supports.[16] Compound **III** (Scheme 1) resulted from the substitution of two tetrahydrofurfuroxo (thffo) ligands at the two five-coordinate magnesium atoms in [Mg(thffo)$_2$] by bulky [OTi(dipp)$_3$]$^-$ groups (dipp = diisopropyl phenolate).

Our attempts to extend this chemistry to other Group 4 metals have interesting mechanistic value since catalysts based on Zr and Hf complexes with oxo donors exhibit much lower activities than titanium analogs.[17] Such research also helps to reveal the role of the components in the supported high-activity MCl$_4$/MgX$_2$/AlR$_3$/SiO$_2$ (M = Ti, Zr, Hf; X = OR, Cl) olefin polymerization catalysts, and the mechanism of procatalyst formation. In the course of our efforts we have discovered interesting reactions of zirconium and hafnium chlorides with alkaline earth metal alkoxides. In this paper we report the syntheses and characterization of several hetero- and homometallic polynuclear alkoxo Zr and Hf species.

Results and Discussion

Synthesis of [Ca(OR)$_2$]: Preparation of alkoxides [Ca(thffo)$_2$] (**2**) and [Ca(ddbfo)$_2$] (**2a**) (Scheme 2) paralleled the route developed for the synthesis of [Mg(thffo)$_2$] (**1**) and [Mg(ddbfo)$_2$].[16, 18] Direct reaction of Ca with tetrahydrofurfuryl alcohol (thffoH) or 2,3-dihydro-2,2-dimethyl-7-benzofuran alcohol (ddbfoH) in toluene at 100 °C afforded, after 10–12 h, **2** or **2a** in 80–88 % isolated yields as analytically pure white powders. Crystallization of **2a** from MeOH gave molecular adduct **2b**.

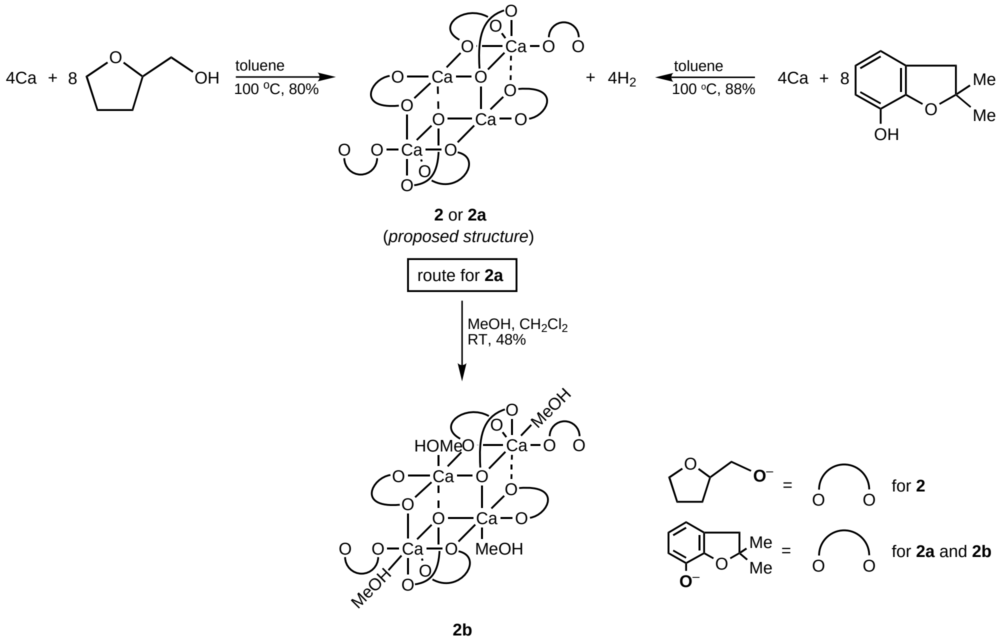
In the solid state **2**, **2a**, and **2b** can be stored at room temperature for extended periods under dinitrogen without appreciable decomposition. They are well soluble in CH$_3$CN and only slightly soluble in CH$_2$Cl$_2$ and toluene. Interestingly, **2** is light-sensitive.

Crystal structure of 2b: On the basis of the crystal structure analysis of **2b**, in the solid state **2** and **2a** are presumably tetrameric species and form open dicubane structures similarly to their magnesium analogs.[16] Four Ca atoms form an almost regular rhombus (Figure 1). There are four μ,η^2, two μ_3,η^2, and two terminal alkoxo ligands in the complex.

The discrete centrosymmetric molecule of **2b** contains two hexa- and two heptacoordinated calcium atoms. Ca1 and symmetrically equivalent Ca1a have distorted octahedral geometry with bent O1-Ca1-O20 (or alternatively O1a-Ca1a-O20a) angles of 162.39(5)°. The coordination spheres around Ca2 and Ca2a are distorted pentagonal bipyramids.

It seems clear from the positions of the MeOH molecules in **2b** that in **2** and **2a** these sites may remain unoccupied, in which case we may suspect that two penta- and two hexacoordinated molecules are present in **2** and **2a** similarly to those in magnesium analogs **1** and [Mg(ddbfo)$_2$]. Interestingly, the pentacoordinated centers in **2** and **2a** are probably located at "inside" calcium centers. The average Ca–O distances in **2b** are of the same order as in the corresponding compounds.[19]

Synthesis of [M$_3$M′(μ_x-O)(μ,η^2-thffo)$_6$(Cl)$_6$] (M = Zr, Hf; M′ = Mg, Ca; x = 3, 4): For several purposes we sought an easy and high-yield method for preparation of mixed metal polynuclear alkoxides of Zr and Hf. Structural information from such compounds is interesting, as it can reveal steps in



Scheme 2. Syntheses of **2**, **2a**, and **2b**.

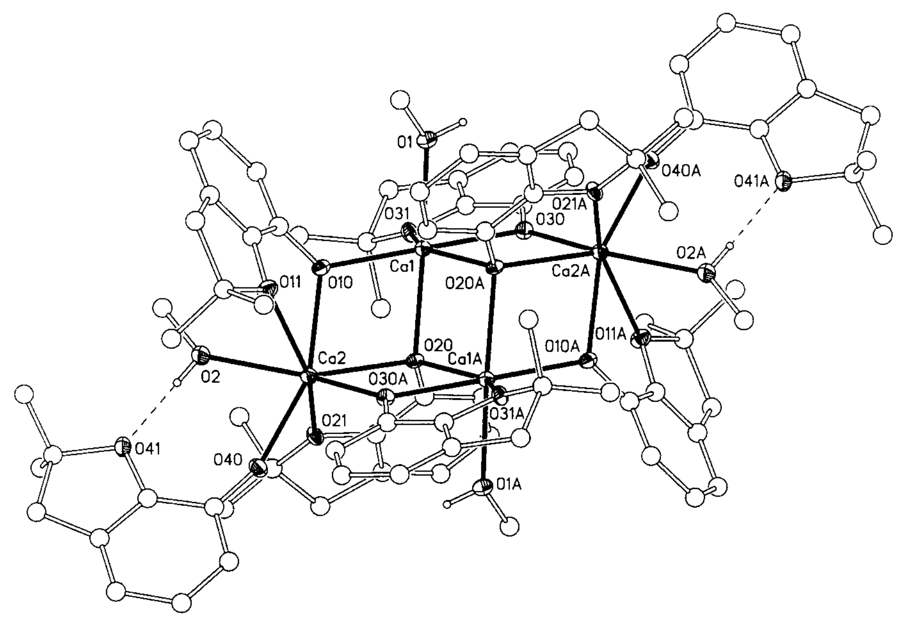
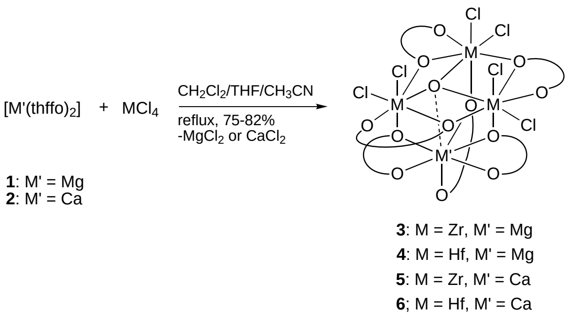


Figure 1. Molecular structure of **2b**, with atom numbering scheme. The displacement ellipsoids are drawn at the 50 % probability level. The C-bonded H atoms are excluded for clarity. The C atoms are represented by circles of arbitrary radius. Selected bond lengths [Å]: Ca1–O1 2.3430(15), Ca2–O2 2.4042(15), Ca1–O10 2.2811(14), Ca1–O20 2.3567(13), Ca1–O20a 2.3697(14), Ca1–O31 2.4078(14), Ca1–O30 2.3386(14), Ca2–O11 2.7975(15), Ca2–O10 2.3568(14), Ca2–O21 2.5379(14), Ca2–O20 2.5022(14), Ca2–O30a 2.2974(14), Ca2–O40 2.2918(14). Symmetry transformations used to generate equivalent atoms: $-x+1$, $-y+1$, $-z$.

Z–N catalyst formation, as indicated in the Introduction. Thus, MCl_4 (M = Zr or Hf) were treated with **1** or **2** at a slightly elevated temperature in a mixture of CH_2Cl_2, THF, and CH_3CN (Scheme 3). Presence of CH_2Cl_2 in the solvent mixture is highly desirable since the insolubility of $MgCl_2$, which forms as a side-product of the reaction, in CH_2Cl_2 allows its precipitation and easy separation from the final product. Workups gave neutral heterobimetallic tetranuclear complexes $[M_3M'(\mu_x\text{-}O)(\mu,\eta^2\text{-thffo})_6(Cl)_6]$ (M/M′/x: **3**, Zr/Mg/3; **4**, Hf/Mg/3; **5**, Zr/Ca/4; **6**, Hf/Ca/4) as white powders in 75–82% yield. These were stable for months as solids under dinitrogen and were characterized by IR and ^1H NMR spectroscopy, and X-ray diffraction studies as summarized in the Experimental Section. They are insoluble in aliphatic and aromatic hydrocarbons and are well soluble in CH_3CN and THF. Complexes **3**–**6** also gave correct microanalyses.



Scheme 3. Syntheses of **3**–**6**.

As can be concluded from the reaction pathway a small excess of **1** or **2** is necessary to reach the optimum yield of the final products, because of decomposition of some thffo⁻ ligands (even under strictly anaerobic conditions) to produce the residual bridging oxo atom. Such a phenomenon has abundant literature precedence.[20] Indeed, top yields were reached when 3 equiv of MCl_4 were treated with 4 equiv of $[M'(thffo)_2]$. Nevertheless, reactions were tried at different molar ratios (from 1:1 to 1:2) to give analogous compounds, based on ^1H NMR and X-ray measurements of the unit cells. Reaction in a 1:1 molar ratio with an additional amount of free alcohol gave an oily product, purification of which was demanding and eventually produced a "problematic" result.

The ^1H NMR spectra of **3**–**6** in CD_3CN are rather complicated, because of the high order of the pure tetrahydrofurfuryl alcohol spectrum.[21] Spectra are also obscured by multiple phenomena such as intramolecular bridge/terminal permutation, which are typical for heterometallic alkoxides.[22] Moreover, the thffoH utilized in this research was a racemic mixture of isomers, so the spectra may additionally be complicated by splittings of the diastereotopic hydrogen atom signals. Finally there are two different types of thffo⁻ ligands, as evidenced by the X-ray crystal structures of **3**–**6** (see below). One type bridges magnesium and transition metal atoms and the other links two transition metal atoms. The complexity of the spectra prevented their detailed analysis but observation of some multiplets was helpful in revealing whether a reaction proceeds. These multiplets provided an informative (although not very convenient) NMR handle. For example, the multiplets (CD_3CN) at $\delta = 4.25–4.50$ (**3**), 4.19–4.48 (**4**), 3.92–4.20 (**5**), and 4.27–4.45 (**6**) were assigned to the proton that is bonded to the asymmetric carbon of the ligand ring. These multiplets are shifted downfield relative to free tetrahydrofurfuryl alcohol. All the other multiplets are also shifted downfield relative to the signals of the free alcohol. Bands found in the far-IR are typical of M–Cl and M–O stretches, proving coordination of alkoxo groups to Zr or Hf atoms.

Crystal structures of 3–5: The crystal structures of **3**–**5** (Table 1) were determined as described in the Experimental Section. Refinement afforded the structures depicted in Figures 2 and 3.

Complexes **3** and **4** are isostructural (Figure 2). When the structures of **3** and **4** were superposed, they overlapped well.

Table 1. Crystallographic data.

Complex	**2b**$\cdot 2(CH_3OH)\cdot 2(CH_2Cl_2)$	$2($**3**$)\cdot 5(CH_3CN)$	$2($**4**$)\cdot 5(CH_3CN)$	**5**$\cdot 2(CH_2Cl_2)$	**7**$\cdot 2(CH_2Cl_2)$	**8**	$2($**10**$)\cdot 2C_6H_5CH_3$
empirical formula	$C_{88}H_{112}Ca_4Cl_4O_{22}$	$C_{70}H_{123}Cl_{12}Mg_2N_5O_{26}Zr_6$	$C_{70}H_{123}Cl_{12}Hf_6Mg_2N_5O_{26}$	$C_{32}H_{58}CaCl_{10}O_{13}Zr_3$	$C_{17}H_{32}Cl_{10}O_6Zr_2$	$C_{21}H_{45}Cl_7O_{10}Zr_3$	$C_{50}H_{94}Cl_{14}O_{20}Zr_6$
formula weight	1823.90	2472.08	2995.69	1319.02	869.37	979.38	2058.87
T [K]	100.0(5)	100.0(5)	100.0(5)	100.0(5)	100.0(5)	100.0(5)	100.0(5)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Cc	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
a [Å]	12.204(1)	10.904(1)	10.894(1)	21.544(2)	10.967(2)	11.717(1)	12.991(1)
b [Å]	12.440(1)	12.574(1)	12.568(1)	18.667(2)	12.419(2)	13.911(1)	13.071(1)
c [Å]	17.935(2)	20.183(2)	20.153(2)	13.067(2)	12.839(3)	22.449(2)	23.053(1)
α [°]	89.22(1)	100.11(1)	99.86(1)	90	111.08(3)	90	89.19(1)
β [°]	79.98(1)	100.33(1)	100.22(1)	105.34(1)	101.65(3)	90	82.79(1)
γ [°]	61.77(1)	108.88(1)	108.66(1)	90	101.65(3)	90	88.42(1)
V [Å^3]	2355.0(4)	2493.5(4)	2494.6(4)	5067.8(11)	1549.9(5)	3659.1(5)	3881.8(4)
Z	1	1	1	4	2	4	2
λ_{calcd} [g cm^{-3}]	1.286	1.646	1.994	1.729	1.863	1.778	1.761
μ [mm^{-1}]	0.411	1.007	6.618	1.287	1.565	1.394	1.319
$F(000)$	2064	1254	1446	2656	864	1960	2064
crystal size [mm^3]	$0.4 \times 0.3 \times 0.3$	$0.3 \times 0.2 \times 0.2$	$0.4 \times 0.4 \times 0.05$	$0.3 \times 0.2 \times 0.2$	$0.5 \times 0.4 \times 0.2$	$0.4 \times 0.2 \times 0.2$	$0.4 \times 0.2 \times 0.05$
range for data collection [°]	3.3 to 28.6	3.3 to 28.4	3.4 to 28.5	3.3 to 28.7	2.2 to 25.1	3.4 to 28.4	3.2 to 28.6
index ranges (h, k, l)	− 15 to 15, − 12 to 16, − 23 to 23	− 14 to 14, − 16 to 15, − 26 to 24	− 9 to 14, − 16 to 15, − 26 to 26	− 27 to 24, − 25 to 23, − 17 to 17	0 to 12, − 13 to 13, − 14 to 14	− 15 to 14, − 18 to 18, − 21 to 29	− 17 to 16, − 16 to 17 − 31 to 22
reflections collected	16794	14008	15741	16973	5634	21936	24747
independent reflections	10607	9051	10129	9264	5338	7813	16416
reflections [$I > 2\sigma(I)$]	7760	8064	9528	7760	4418	7008	9379
data/parameters	10607/582	9051/582	10129/562	9264/542	5338/350	7813/404	16416/837
goodness-of-fit on F^2	1.037	1.036	1.077	1.046	1.054	1.048	0.959
final R indices [$I > 2\sigma(I)$]	$R1 = 0.0433$ $wR2 = 0.1042$	$R1 = 0.0384$ $wR2 = 0.0688$	$R1 = 0.0351$ $wR2 = 0.0791$	$R1 = 0.0534$ $wR2 = 0.1348$	$R1 = 0.0323$ $wR2 = 0.0922$	$R1 = 0.0387$ $wR2 = 0.0887$	$R1 = 0.0591$ $wR2 = 0.1111$
R indices (all data)	$R1 = 0.0654$ $wR2 = 0.1121$	$R1 = 0.0494$ $wR2 = 0.0703$	$R1 = 0.0391$ $wR2 = 0.0811$	$R1 = 0.0630$ $wR2 = 0.1438$	$R1 = 0.0450$ $wR2 = 0.0983$	$R1 = 0.0457$ $wR2 = 0.0917$	$R1 = 0.1224$ $wR2 = 0.1358$
$\Delta\varrho$ (max and min) [e Å^{-3}]	0.670 and − 0.822	1.197 and − 0.471	3.109 and − 1.728	1.588 and − 1.295	1.103 and − 0.689	0.665 and − 0.611	0.882 and − 1.083

Both include three seven-coordinated zirconium or hafnium atoms, each surrounded by two mutually *cis* terminal chlorine atoms, three bridging oxo atoms from thffo$^-$ ligands, and one oxygen atom from a substituted tetrahydrofuran ring. The coordination sphere of each transition metal is completed by a triply bridging oxo atom which holds the M_3 triangle together. It lies 0.280(3) and 0.254(4) Å above the M_3 plane in **3** and **4**, respectively. The Zr−Zr (3.5001(6), 3.4893(7), 3.5009(6) Å; av. 3.4968 Å) and Hf−Hf (3.4866(4), 3.4914(5), and 3.4880(6) Å; av. 3.4887 Å) distances far exceed the sums of their van der Walls radii. The Zr−Cl (av. 2.5101 Å), Hf−Cl (av. 2.4983 Å), Zr−O, and Hf−O distances as well as the transition metal-centered bond angles are typical.[23, 24] The magnesium atom in **3** and **4** shows octahedral coordination. In both species three magnesium sites are occupied by oxygen atoms of substituted tetrahydrofuran rings. The remaining three are occupied by alkoxo atoms of three thffo$^-$ ligands that also constitute three bridges between magnesium and transition metal atoms. All values of the selected bond lengths and angles in Table 2 fall within the normal range for magnesium alkoxo species.[25]

The crystal structure of **5** (Figure 3) contains zirconium atoms with coordination geometry analogous to that in **3** and **4** with Zr−Cl (av. 2.5118 Å), Zr−O, and all bond angles similar to those of **3**. The significant difference between **3**/**4** and **5** is the coordination of the alkaline earth metal. The calcium atom in **5** takes advantage of its bigger ionic radius to coordinate additionally with the only remaining electron lone pair of the oxo atom, which now becomes quadruply bridged. Coordination of Ca to the oxo atom draws the former 0.508(6) Å out of the Zr_3 plane. Surprisingly this does not affect the Zr−Zr bond lengths (3.5212(10), 3.5083(11), 3.5220(11) Å; av. 3.5172 Å).

Syntheses of $[Zr_2(\mu,\eta^2\text{-thffo})_2(\eta^2\text{-thffoH})(Cl)_6]$ and $[M_3(\mu_3\text{-O})(\mu,\eta^2\text{-thffo})_3(L)_3(Cl)_6]Cl$ (M = Zr, Hf; L = EtOH, MeOH): We attempted to reveal the formation mechanism of **3**–**6** by accessing homometallic complexes that were possible precursors of **3**–**6**. A family of compounds was synthesized by combining $ZrCl_4$ or $HfCl_4$ with thffoH in noncoordinating (toluene) and coordinating (EtOH or MeOH) solvents at low temperature (Scheme 4). Workups followed by recrystallization gave analytically pure neutral dimeric **7** in 81 % yield and ionic homopolymetallic **8**–**10** in 66–79 % yield. Complexes **7**–**10** could be stored under dinitrogen for extended periods but tolerated only very brief exposure to moisture. They are all well soluble in toluene and alcohols. Compounds **8** and **9** are not soluble in THF.

The complexes were characterized by IR and ^1H NMR spectroscopy, and X-ray crystallography. The ^1H NMR spectra

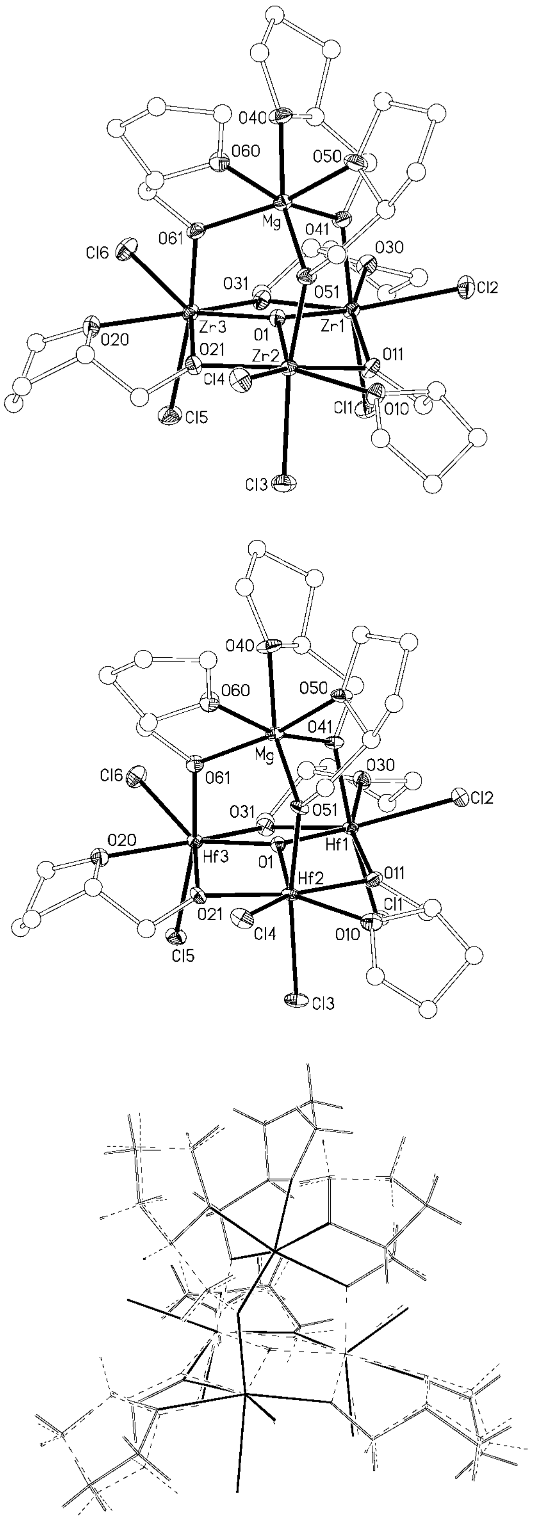


Figure 2. Molecular structure of **3** (top) and **4** (middle), and superposition (bottom). Hydrogen atoms and second positions of disordered carbon atoms are omitted for clarity. The displacement ellipsoids are drawn at the 50% probability level. The C atoms are represented by circles of arbitrary radius.

of **8**–**10** showed CH_2 spacer multiplets (CD_3CN) at $\delta = 3.98$, 3.89, and 4.17 (peak centers). These signals are shifted slightly downfield relative to **3**–**6**. The signals of asymmetric carbon protons in **8**–**10** unfortunately overlap with CH_2 protons of the ring.

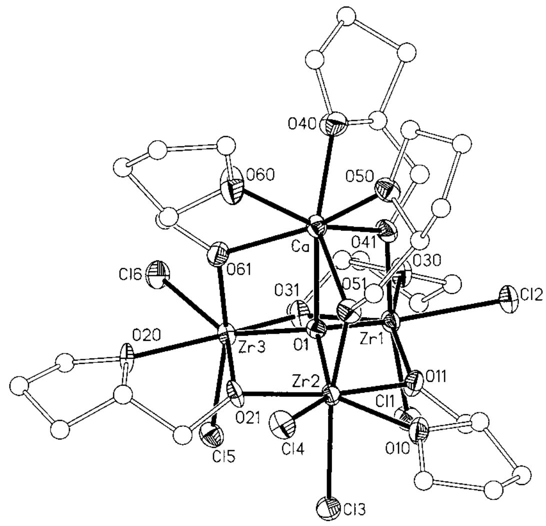


Figure 3. Molecular structure of **5**. Hydrogen atoms and second positions of disordered carbon atoms are omitted for clarity. The displacement ellipsoids are drawn at the 50% probability level. The C atoms are represented by circles of arbitrary radius.

The IR spectra of **8**–**10** showed typical absorptions for M–Cl and M–O stretches with similar patterns to **3**–**6**.

Crystal structure of 7: The molecular structure of **7** (Figure 4) shows a neutral dimeric species with zirconium atoms that have slightly different coordination spheres. Although both metals have analogous Cl_3O_4 pentagonal-bipyramid arrangements, one coordinates two bridging oxo ligands and two substituted tetrahydrofuran rings while the other coordinates one molecule of tetrahydrofurfuryl alcohol, apart from two bridging alkoxo atoms.

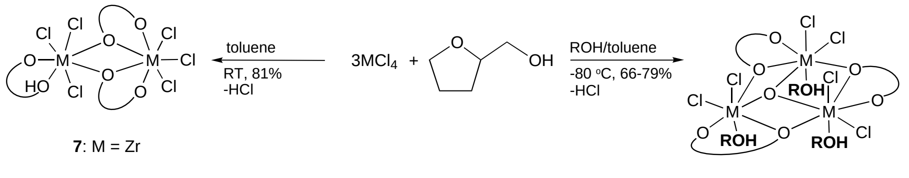
The key bond lengths and angles are listed in the Figure 4 caption. The M–Cl bond angles fall within the typical range. The tetrahydrofurfuroxo bridges are a little asymmetric: Zr1–O11 2.161(3), Zr1–O21 2.173(2), Zr2–O11 2.115(2), and Zr2–O21 2.124(3) Å. The neutral OH group is 2.262(3) Å from the Zr2 atom. No short hydrogen bonds were observed in this structure.

Crystal structures of 8 and 10: The result of solvent exchange from toluene to ROH is quite surprising. It shows clearly the magnitude of the role of solvent coordination ability in the final product composition. An X-ray diffraction study of **8** and **10** showed the complexes to be ionic species with a bulky monocation comprising three Zr atoms and Cl^- as a counterion. Three metal atoms in **8** (Figure 5) and **10** (Figure 6) are coordinated similarly to those in **3**–**5**. They also form M_3 triangles that are held together by an oxo atom which originates from alcohol decomposition. Compound **10** crystallizes with two molecules in the asymmetric unit.

The transition metals are in a typical pentagonal-bipyramid arrangement. Each has analogous surroundings consisting of one μ_3 bridging oxo atom, two terminal Cl atoms, one oxygen atom from a substituted tetrahydrofuran ring, two bridging alkoxo oxygens, and one oxygen atom from coordinated EtOH (for **8**) or MeOH (for **10**). In both structures oxo atoms are above the Zr_3 plane, 0.578(4) Å in **8** and 0.586(5) and

Table 2. Selected bond lengths [Å] and angles [°] for **3**–**5**, **8**, and **10**.

	3; M/M′ = Zr/Mg	**4**; M/M′ = Hf/Mg	**5**; M/M′ = Zr/Ca	**8**; M = Zr	**10**; M = Zr
M1–Cl1	2.4967(9)	2.4768(14)	2.491(2)	2.4373(14)	2.441(2)
M1–Cl2	2.5139(10)	2.5265(14)	2.526(2)	2.4517(15)	2.479(2)
M2–Cl3	2.4962(9)	2.4666(14)	2.512(2)	2.4413(13)	2.426(2)
M2–Cl4	2.5317(9)	2.5260(14)	2.529(2)	2.4812(12)	2.477(2)
M3–Cl5	2.4846(9)	2.4811(13)	2.486(2)	2.4381(13)	2.432(2)
M3–Cl6	2.5376(9)	2.5129(15)	2.527(2)	2.4747(15)	2.495(2)
M1–O1	2.035(2)	2.038(4)	2.091(5)	2.090(3)	2.086(4)
M2–O1	2.048(2)	2.019(4)	2.096(5)	2.082(3)	2.093(4)
M3–O1	2.031(2)	2.034(4)	2.093(5)	2.090(3)	2.084(4)
M1–O11	2.155(2)	2.145(4)	2.152(5)	2.123(4)	2.125(4)
M1–O30	2.289(2)	2.293(4)	2.338(6)	2.270(3)	2.280(4)
M1–O31	2.201(2)	2.173(4)	2.155(5)	2.140(4)	2.144(4)
M1–O41	2.083(2)	2.074(4)	2.040(6)	–	–
M2–O10	2.306(2)	2.290(4)	2.303(5)	2.260(4)	2.283(4)
M2–O11	2.178(2)	2.194(4)	2.171(5)	2.148(3)	2.172(4)
M2–O21	2.146(2)	2.160(4)	2.130(5)	2.135(3)	2.144(4)
M2–O51	2.086(2)	2.069(4)	2.036(5)	–	–
M3–O20	2.305(2)	2.270(4)	2.284(5)	2.276(3)	2.290(4)
M3–O21	2.204(2)	2.187(4)	2.170(5)	2.158(3)	2.149(4)
M3–O31	2.156(2)	2.146(4)	2.154(5)	2.133(3)	2.127(4)
M3–O61	2.082(2)	2.072(4)	2.037(6)	–	–
M1–O1E	–	–	–	2.225(4)	2.239(4)
M2–O2E	–	–	–	2.226(4)	2.213(5)
M3–O3E	–	–	–	2.211(4)	2.216(5)
M′–O1	2.698(2)	2.717(4)	2.457(6)	–	–
M′–O40	2.118(3)	2.164(5)	2.359(6)	–	–
M′–O41	2.078(2)	2.092(4)	2.346(5)	–	–
M′–O50	2.158(3)	2.136(4)	2.384(5)	–	–
M′–O51	2.095(2)	2.100(4)	2.330(5)	–	–
M′–O60	2.129(2)	2.124(4)	2.381(6)	–	–
M′–O61	2.095(3)	2.082(4)	2.351(5)	–	–
M1–M2	3.5001(6)	3.4866(5)	3.5219(11)	3.4731(7)	3.4732(10)
M1–M3	3.4893(7)	3.4914(5)	3.5082(11)	3.4780(7)	3.4765(10)
M2–M3	3.5009(6)	3.4880(6)	3.5211(10)	3.4678(7)	3.4619(10)
M1–M′	3.5953(12)	3.5828(19)	3.5948(17)	–	–
M2–M′	3.5987(12)	3.5933(19)	3.5821(18)	–	–
M3–M′	3.5992(13)	3.5911(18)	3.6055(17)	–	–
M′-O41-M1	119.54(11)	118.66(19)	109.9(2)	–	–
M′-O51-M2	118.81(11)	119.06(19)	110.1(2)	–	–
M′-O61-M3	118.99(10)	119.66(19)	110.3(2)	–	–
M1-O1-M2	118.01(2)	118.52(18)	114.4(2)	112.98(15)	112.58(19)
M1-O1-M3	118.20(10)	118.07(18)	114.0(2)	112.40(15)	112.8(2)
M2-O1-M3	118.24(10)	118.80(18)	114.4(2)	112.48(13)	111.9(2)
M1-O11-M2	107.77(9)	106.92(16)	109.1(2)	109.05(15)	108.01(18)
M1-O31-M3	106.43(9)	107.87(16)	109.0(2)	108.73(15)	108.8(2)
M2-O21-M3	107.18(9)	106.74(16)	109.9(2)	107.77(13)	107.5(2)



7: M = Zr

8: M = Zr, R = Et
9: M = Hf, R = Et
10: M = Zr, R = Me

Scheme 4. Syntheses of **7**–**10**.

0.592(5) Å above it in **10**. This value is close to that for **5** and much higher than for **3**. The Zr–Zr distances of 3.4736(7), 3.4777(7), and 3.4683(7) Å (av. 3.4732 Å) for **8** and 3.4765(10), 3.4732(10), 3.4619(10), 3.4778(10), 3.4816(10), and 3.471(8) Å (av. 3.4738 Å) for **10** are also far from the bonding range. Zr–Cl (av. 2.4536 Å for **8** and 2.4584 and 2.7649 Å for **10**), Zr–O, and all bond angles are typical[22] and similar to those for **3** and **5**. Some of the geometrical data are summarized in Table 2. In both structures the counterion Cl^- and hydroxo group hydrogen atoms of axial EtOH and MeOH form several hydrogen bonds that hold the Cl^- close to the polymetallic cation.

Synthesis and crystal structure of $[Zr_3(\mu_3\text{-O})(\mu,\eta^2\text{-thp})_3(thf)_2(Cl)_7]$: For a deeper understanding of the influence of solvent polarity/coordination ability on the reaction pathway and final product formation, we also studied the reaction of $[Zr(Cl)_3(OMe)(MeOH)_2]$ (**11**) with tetrahydropyran-2-methanol (thpH). Compound **11** was obtained in a direct reaction of $ZrCl_4$ with methanol. This high-yielding synthesis, which was easy to perform, gave product which was possibly oligo- or polymeric and which was observed to be a very good starting material for the syntheses of zirconium alkoxo species by ligand exchange. After its reaction with thpH in a toluene/MeOH mixture (1:1 molar ratio) at room temperature (Scheme 5), workup involving THF recrystallization afforded a neutral, analytically pure sample of $[Zr_3(\mu_3\text{-O})(\mu,\eta^2\text{-thp})_3(thf)_2(Cl)_7]$ (**12**) that could be stored under N_2 for weeks. Complex **12** is insoluble in aliphatic and aromatic hydrocarbons but is easily soluble in THF, CH_3CN, and halogenated solvents.

Both ^1H NMR and IR data showed coordination of the thp^- ligands and the presence of THF molecules in **12**. This was confirmed by the X-ray crystal structure. Unfortunately poor-quality X-ray data prevented dependable geometrical analysis of **12** but we are not expecting any unprecedented values here. The molecular structure of **12** (Scheme 5) consists of discrete trinuclear molecules that, similarly to **3**–**6** and **8**–**10**, comprise a μ_3-O bridged M_3 triangle.

Each thp^- ligand coordinates with central atoms through the oxygen atom of the heterocycle and the μ_2 bridging alkoxo oxygen atom. Analogously to those in **3**, **5**, **8**, and **10** each Zr atom is seven-coordinated but interestingly each of these

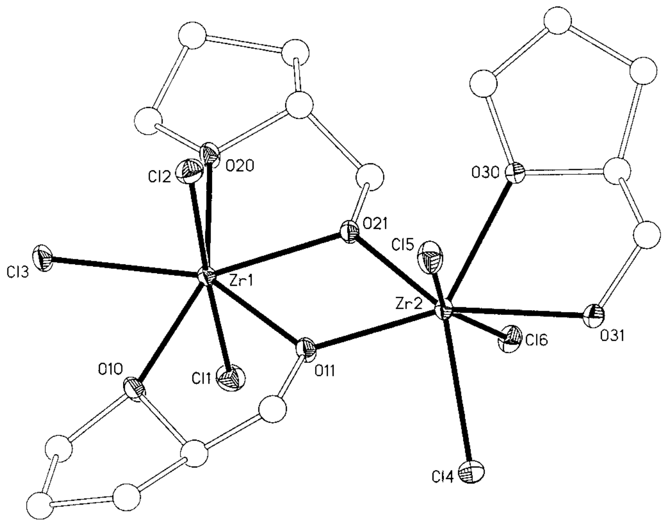


Figure 4. Molecular structure of **7**. Hydrogen atoms and second positions of disordered carbon atoms are omitted for clarity. The displacement ellipsoids are drawn at the 50% probability level. The C atoms are represented by circles of arbitrary radius. Selected bond lengths [Å]: Zr1–Cl1 2.4369(11), Zr1–Cl2 2.4308(11), Zr1–Cl3 2.4664(13), Zr2–Cl4 2.4671(13), Zr2–Cl5 2.4344(11), Zr2–Cl6 2.5164(11), Zr1–O11 2.161(3), Zr1–O10 2.232(3), Zr1–O21 2.173(2), Zr1–O20 2.261(3), Zr2–O11 2.115(2), Zr2–O21 2.124(3), Zr2–O31 2.262(3), Zr2–O30 2.256(3).

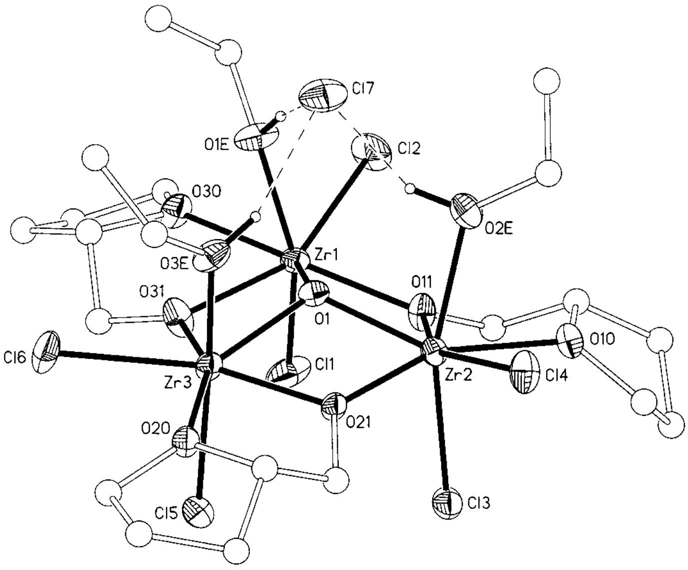


Figure 5. Molecular structure of **8**. Hydrogen atoms and second positions of disordered carbon atoms are omitted for clarity. The displacement ellipsoids are drawn at the 50% probability level.

complexes possesses a different ligand arrangement. Zr1 is surrounded by the μ_3 oxo atom, one oxygen from the ligand heterocycle, two μ_2-bridging alkoxo oxygens, two terminal, mutually *trans*, chlorine atoms, and one THF molecule. Zr2 differs from Zr1 in the orientation of the two terminal chlorine atoms, these being in a mutually *cis* orientation. In turn Zr3 lacks a THF molecule, which is replaced by the additional terminal Cl atom. This causes **12** in the solid state to lose the C_3 symmetry that is typical for the compounds mentioned earlier.

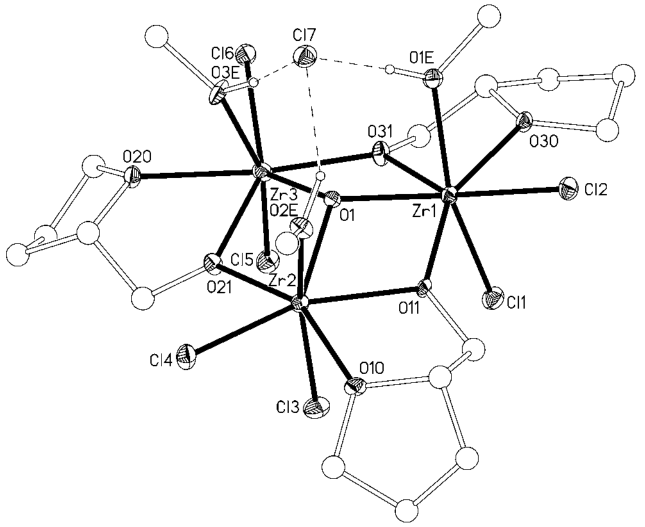
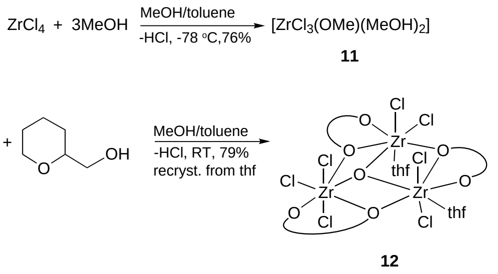


Figure 6. Molecular structure of **10**. The C-bonded H atoms are excluded for clarity. The displacement ellipsoids are drawn at the 50% probability level. The C atoms are represented by circles of arbitrary radius.



Scheme 5. Synthesis of **12**.

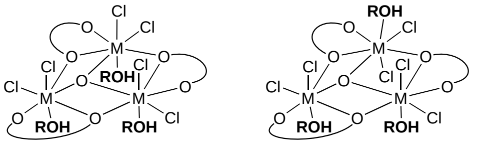
Summary and Conclusion

Schemes 2–5 summarize highly optimized routes to homo- and heterometallic polynuclear alkoxo complexes of Zr and Hf. All the compounds described are of great interest as model intermediates in Ziegler–Natta catalysis.

Incorporation of an alkaline earth metal in **3**–**6** provides additional information about the possible nature of the interaction between precatalyst metal centers and the $MgCl_2$ or $Mg(OR)_2$ catalyst support. It is also clear from the data presented that solvent polarity plays a pivotal role in final product formation. Small differences in the reaction conditions drive the reaction toward the formation of ionic or neutral species, as shown in the syntheses of **7**–**10** and **12**.

Recently we described the syntheses of magnesium bisalkoxides that form open dicubane structures.[16, 18, 25a, 26] Such complexes are reactive species and can interact with different Lewis acids with or without structure retention. These studies are extended herein to another alkaline earth metal, calcium. The composition and reactivity of **2** and **2a** as well as the X-ray crystal structure of **2b** suggest similar open dicubane structures for those compounds. Nevertheless, differences in the coordination preferences of both metals can mean that in case of thffo$^-$ ligand structure assignments are somewhat provisional although they seem rational. Some of our yet unpublished results indicate that, even for magnesium, agglomeration beyond the tetrameric stage is possible.

When considering the formation mechanism for **3**–**6**, our results for compounds **8**–**10** are a good starting point. These homopolymetallic species are geometrically very interesting. They all exhibit C_3 symmetry, thanks to the *syn* position of the three ROH molecules (or alternatively Cl atoms). Another possible isomer with two ROH molecules *syn* and one *anti* is shown in Scheme 6. Although the repulsion of the ROH molecules should be lower for such an isomer we saw no sign of its formation.

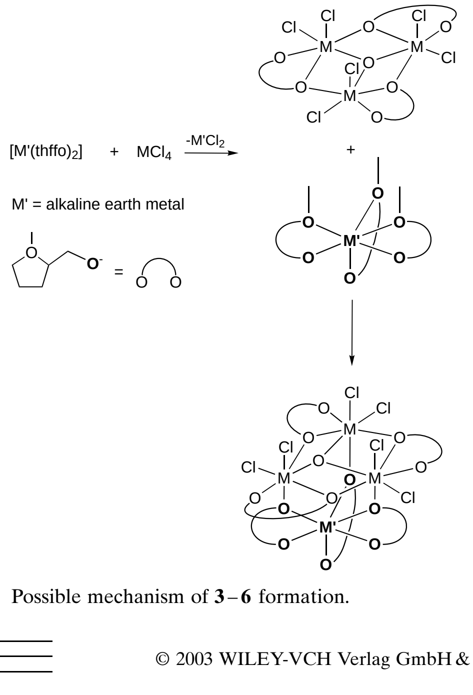


syn, syn, syn *anti, syn, syn*

Scheme 6. Possible isomers of complexes **8**–**10**.

Similar symmetry of the metal core in **3**–**6** and **8**–**10** suggests that formation of **8**–**10** might be the first step for further agglomeration. Scheme 7 shows the possible mechanism of **3**–**6** formation. We believe that in the first step MCl_4 reacts with $[M'(thffo)_2]$, terminating the open dicubane structure. The chlorine atoms in MCl_4 are exchanged by tetrahydrofurfuroxo groups and a dianionic M_3 core with free *syn* positions is formed. $MgCl_2$ is a side-product of this reaction. In the next step the *syn* positions are filled by three tetrahydrofurfuroxo groups of a bulky Mg^{2+}-containing moiety for charge balance. From this perspective the dicationic magnesium moiety might be considered as a tripodal ligand situated at the $M_3(\mu_3\text{-}O)$ core. The entropy effect might be a driving force for such reaction.

It is interesting (and important) to note that the formation of the μ_3-oxo-bridged M_3 subunit is very common. This structure seems extremely stable. We believe that this stability constitutes a major reason why the activity of such compounds in olefin polymerization is lower than that of titanium alkoxo species, which (for simple systems, for example, those containing $Ti(OEt)_4$) prefer motifs other than $M_3(\mu_3\text{-}O)$.[27]. Further investigation of **3**–**6** showed that even with very strong alkylating agents the structure of the M_3 triangle (including the terminal chlorine atoms) remained untouched, proving the high stability of the trinuclear core.[28] This stability prevents any metallic center in such a precatalyst from being activated (for example, by removal of a chlorine atom) and became a polymerization center. It has also been shown that $AlMe_3$ reacts with $[Mg(thffo)_2]$ to form a complex similar to **3**–**6**, namely tetranuclear bimetallic $[Al_3Mg(\mu_3\text{-}O)(thffo)_3(Me)_6]$, which has a tetranuclear $Al_3(\mu_3\text{-}O)$ core[29] capped with the magnesium moiety.



Scheme 7. Possible mechanism of **3**–**6** formation.

Experimental Section

General data: All reactions were conducted under N_2 atmospheres. Chemicals were treated as follows: THF, distilled from CuCl, predried over NaOH, and then distilled from Na/benzophenone; toluene, distilled from Na/benzophenone; CH_2Cl_2, distilled from CaH_2 and then P_2O_5; hexane, distilled from P_2O_5; methanol, ethanol, and CH_3CN, distilled from CaH_2; tetrahydrofurfuryl alcohol (thffoH, Aldrich), 2,3-dihydro-2,2-dimethyl-7-benzofuran alcohol (ddbfoH, Aldrich), and tetrahydropyran-2-methanol (thpH, Aldrich), distilled before use; $[Mg(thffo)_2]$, synthesized and purified as described;[18] $ZrCl_4$ (Lancaster), $HfCl_4$ (Aldrich), and CD_3CN (Cambridge Isotope Laboratories), used as received.

IR spectra were recorded on a Specord M-80 (Karl-Zeiss-Jena) spectrometer. NMR spectra were obtained on a Bruker ESP 300E spectrometer. Microanalyses were conducted in-house with a ASA-1 (GDR, Karl-Zeiss-Jena) instrument.

[Ca(thffo)₂] (2): A Schlenk flask was charged with metallic calcium (0.75 g, 18.39 mmol), thffoH (3.60 mL, 3.79 g, 37.15 mmol), and toluene (60 mL). It was refluxed at 100 °C until the evolution of H_2 had ceased (10–12 h). The solution was allowed to cool to room temperature and the white precipitate was filtered off. The volume was reduced to 20 mL and hexane (40 mL) was added. The white precipitate was filtered off, washed with hexane (3 × 5 mL), and dried by oil pump vacuum to give **2** as a white solid (3.57 g, 14.71 mmol, 80 %). Elemental analysis calcd (%) for $C_{10}H_{18}CaO_4$ (242.33): C 49.56, H 7.49, Ca 16.54; found C 49.66, H 7.50, Ca 16.52.

[Ca(ddbfo)₂] (2a): Metallic calcium (0.75 g, 18.39 mmol), ddbfoH (5.50 mL, 6.05 g, 36.88 mmol), and toluene (60 mL) were combined in a procedure analogous to that for **2**. The identical workup gave **2a** as colorless crystals (5.93 g, 16.18 mmol, 88 %). Elemental analysis calcd (%) for $C_{20}H_{22}CaO_4$ (366.47): C 65.55, H 6.05, Ca 10.94; found C 65.88, H 5.63, Ca 10.49.

[Ca₄(ddbfo)₈(MeOH)₄]·2MeOH·2CH₂Cl₂ (2b): Compound **2a** (2.00 g, 5.45 mmol) was dissolved in a mixture of MeOH (20 mL) and CH_2Cl_2 (20 mL). The mixture was stirred until a clear solution was obtained. Solvent was removed in vacuo until an oil was obtained; hexane (30 mL) was then added. After three weeks colorless crystals of **2b** were formed (1.20 g, 0.66 mmol, 48 %). Elemental analysis calcd (%) for $C_{86}H_{112}Ca_4O_{22}$ (1658.13): C 62.30, H 6.81, Ca 9.67; found C 62.12, H 6.85, Ca 9.78.

[Zr₃Mg(μ₃-O)(μ,η²-thffo)₆(Cl)₆] (3): A Schlenk flask was charged with $ZrCl_4$ (1.86 g, 7.98 mmol), $[Mg(thffo)_2]$ (**1**; 2.50 g, 11.03 mmol), and a mixture of CH_2Cl_2 (30 mL), THF (15 mL), and CH_3CN (30 mL). The solution was refluxed for 2 h. After about 20 min the suspension became clouded. It was cooled and stirred for 12 h at ambient temperature. The white precipitate formed was filtered off, washed with CH_2Cl_2 (3 × 5 mL) and dried by oil pump vacuum to give crude **3** (2.47 g, 2.18 mmol, 82 %) which was recrystallized from CH_3CN to give, after one week, colorless crystals of 2(**3**)·5 CH_3CN (2.50 g, 2.02 mmol, 76 %).^1H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 1.40–1.55$ (m), 1.72–2.18 (m), 3.37–3.57 (m), 3.68–3.85 (m), 3.97–4.18 (m), 4.25–4.50 (m), 4.66–4.77 (m), 4.84–4.92 (m); IR (CsI, Nujol): $\nu = 220$ (vw), 266 (m), 271 (s), 288 (sh), 302 (s), 406 (s), 416 (s), 439 (m), 468 (m), 525 (m), 545 (vs), 553 (vs), 595 (s), 660 (sh), 680 (vs), 797 (vs), 834 (w), 853 (w), 912 (m), 982 (s), 973 (s), 1032 (vs), 1045 (vs), 1130 (w), 1180 (w) cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{54}Cl_6MgO_{13}Zr_3$ (1133.44): C 31.79, H 4.80, Cl 18.77, Mg 2.14, Zr 24.26; found C 31.86, H 4.65, Cl 19.02, Mg 2.15, Zr 24.26.

[Hf$_3$Mg(μ_3-O)(μ,η^2-thffo)$_6$(Cl)$_6$] (4): $HfCl_4$ (2.00 g, 6.24 mmol), **1** (1.96 g, 8.63 mmol), and a mixture of CH_2Cl_2 (30 mL), THF (15 mL), and CH_3CN (30 mL) were combined in a procedure analogous to that for **3**. The identical workup gave **4** as a white powder (2.20 g, 1.58 mmol, 76 %). Crystals were grown from CH_3CN to give 2(**4**)·5CH_3CN (2.15 g, 1.43 mmol, 69 %). ^{1}H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 1.54-1.63$ (m), 1.89–2.10 (m), 3.32–3.51 (m), 3.74–3.90 (m), 4.03–4.12 (m), 4.19–4.48 (m), 4.63–4.77 (m), 4.95–5.03 (m); IR (CsI, Nujol): $\nu = 228$ (vw), 254 (m), 279 (m), 440 (m), 544 (m), 560 (m), 596 (w), 720 (s), 812 (m), 940 (m), 982 (m), 1046 (s), 1076 (s) cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{54}Cl_6Hf_3MgO_{13}$ (1395.24): C 25.83, H 3.90, Cl 15.25, Mg 1.74, Hf 38.38; found C 26.52, H 4.06, Cl 15.42, Mg 1.39, Hf 38.37.

[Zr$_3$Ca(μ_4-O)(μ,η^2-thffo)$_6$(Cl)$_6$] (5): $ZrCl_4$ (1.00 g, 4.29 mmol), **2** (1.44 g, 5.93 mmol), and a mixture of CH_2Cl_2 (30 mL), THF (15 mL), and CH_3CN (30 mL) were combined in a procedure analogous to that for **3**. The identical workup gave **5** as a white powder (1.23 g, 1.07 mmol, 75 %). Crystals grown from CH_2Cl_2 gave **5**·2CH_2Cl_2 (1.26 g, 0.96 mL, 67 %).^{1}H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 1.53-1.63$ (m), 1.75–2.15 (m), 3.34–3.50 (m), 3.64–3.80 (m), 3.92–4.20 (m), 4.25–4.48 (m), 4.63–4.75 (m), 4.96–5.06 (m); IR (CsI, Nujol): $\nu = 228$ (vw), 252 (m), 276 (m), 312 (s), 430 (m), 470 (m), 560 (vs), 600 (s), 642 (s), 666 (s), 700 (m), 732 (s), 816 (s), 922 (s), 940 (s), 984 (vs), 1060 (vs), 1186 (m), 1326 (m) cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{54}CaCl_6O_{13}Zr_3$ (1149.21): C 31.35, H 4.74, Ca 3.49, Cl 18.51, Zr 23.81; found C 30.80, H 4.90, Ca 3.50, Cl 18.72, Zr 23.81. The sample mass was corrected for the presence of 2 equiv of CH_2Cl_2 per complex molecule in the crystals.

[Hf$_3$Ca(μ_4-O)(μ,η^2-thffo)$_6$(Cl)$_6$] (6): $HfCl_4$ (1.00 g, 3.12 mmol), **2** (1.05 g, 4.32 mmol), and a mixture of CH_2Cl_2 (30 mL), THF (15 mL), and CH_3CN (30 mL) were combined in a procedure analogous to that for **3**. The identical workup gave **6** as a white powder (1.17 g, 0.83 mmol, 80 %). ^{1}H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 1.50-1.62$ (m), 1.72–2.22 (m), 3.35–3.48 (m), 3.60–3.88 (m), 3.92–4.14 (m), 4.27–4.45 (m), 4.64–4.77 (m), 5.05–5.20 (m); IR (CsI, Nujol): $\nu = 220$ (vw), 268 (s), 298 (m), 366 (vw), 418 (m), 438 (m), 566 (s), 592 (s), 654 (vs), 728 (s), 808 (vs), 866 (m), 924 (s), 952 (s), 980 (vs), 1076 (vs), 1184 (m) cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{54}CaCl_6Hf_3O_{13}$ (1411.02): C 25.54, H 3.86, Ca 2.84, Cl 15.08, Hf 37.95; found C 25.42, H 3.70, Cl 15.89, Ca 2.80, Hf 37.97.

[Zr$_2$(μ,η^2-thffo)$_2$(η^2-thffoH)(Cl)$_6$] (7): A Schlenk flask was charged with $ZrCl_4$ (1.16 g, 5.00 mmol), thffoH (0.48 mL, 0.51 g, 5.00 mmol), and toluene (60 mL). Evolution of HCl started immediately. The mixture was stirred at room temperature for about 64 h, then with a vacuum applied until an oil was formed. Hexane (40 mL) was added to give, after five weeks, colorless crystals of **7**·2CH_2Cl_2 (1.76 g, 2.03 mmol, 81 %). Elemental analysis calcd (%) for $C_{15}H_{28}Cl_6O_6Zr_2$ (699.55): C 25.75, H 4.03, Cl 30.41, Zr 26.08; found C 25.70, H 3.98, Cl 30.32, Zr 26.18. The sample mass was corrected for the presence of 2 equiv CH_2Cl_2 per complex molecule in the crystals.

[Zr$_3$(μ_3-O)(μ,η^2-thffo)$_3$(EtOH)$_3$(Cl)$_6$]Cl (8): A Schlenk flask was charged with $ZrCl_4$ (1.20 g, 5.15 mmol) and thffoH (0.60 mL, 0.63 g, 6.19 mmol) and cooled to −80 °C (toluene/N_2). A cold (−80 °C) mixture of EtOH (50 mL) and toluene (10 mL) was added. The resulting suspension was stirred at room temperature with an applied vacuum until a clear solution was obtained. Another portion of EtOH (60 mL) and toluene (20 mL) was added and the mixture was refluxed until the evolution of HCl had ceased (10–12 h). The volatiles were removed and the resulting white solid was recrystallized from the mixture of toluene, ethanol, and hexane (2:1:8, by vol.) to give, after five days, **8** as colorless crystals (1.99 g, 2.03 mmol, 79 %). ^{1}H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 1.11$ (t, 3 H; CH_3CH_2OH), 1.85 (m, 4 H; 2,3-HC_4H_7O), 2.44 (brm, 1 H; CH_3CH_2OH), 3.54 (q, 2 H; CH_3CH_2OH), 3.98 (m, 2 H; CH_2), 4.41–4.66 (br, 2 H; 4-HC_4H_7O, 1 H; 1-HC_4H_7O); IR (CsI, Nujol): $\nu = 216$ (w), 228 (w), 292 (s), 322 (vs), 344 (s), 406 (m), 420 (m), 478 (vs), 540 (s), 560 (s), 584 (m), 628 (s), 666 (s), 806 (vs), 866 (s), 918 (vs), 938 (vs), 974 (s), 984 (s), 994 (vs), 1026 (vs), 1042 (s), 1056 (vs), 1088 (m), 3432 (m) cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{45}Cl_7O_{10}Zr_3$ (979.45): C 25.75, H 4.63, Cl 16.34, Zr 27.94; found C 25.68, H 4.62, Cl 16.30, Zr 27.97.

[Hf$_3$(μ_3-O)(μ,η^2-thffo)$_3$(EtOH)$_3$(Cl)$_6$]Cl (9): $HfCl_4$ (1.00 g, 3.12 mmol), thffoH (0.40 mL, 0.42 g, 4.13 mmol), EtOH (50 mL), and toluene (10 mL) were combined in a procedure analogous to that for **8**. The identical workup gave **9** as colorless crystals (1.47 g, 1.19 mmol, 76 %). ^{1}H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 1.11$ (t, 3 H; CH_3CH_2OH), 1.85 (m, 4 H; 2,3-HC_4H_7O), 2.40 (br, 1 H; CH_3CH_2OH), 3.53 (q, 2 H; CH_3CH_2OH), 3.89 (m, 2 H; CH_2), 4.41–4.66 (br, 2 H; 4-HC_4H_7O, 1 H; 1-HC_4H_7O); IR (CsI, Nujol): $\nu = 219$ (w), 228 (w), 295 (s), 320 (vs), 344 (s), 407 (m), 421 (m), 478 (vs), 540 (s), 560 (s), 586 (m), 630 (s), 668 (s), 808 (vs), 868 (s), 920 (vs), 940 (vs), 974 (s), 984 (s), 994 (vs), 1028 (vs), 1044 (s), 1056 (vs), 1088 (m), 3430 (m) cm^{-1}; elemental analysis calcd (%) for $C_{21}H_{45}Cl_7Hf_3O_{10}$ (1241.22): C 20.32, H 3.65, Cl 19.49, Hf 43.14; found C 20.41, H 3.60, Cl 19.30, Hf 43.14.

[Zr$_3$(μ_3–O)(μ,η^2-thffo)$_3$(MeOH)$_3$(Cl)$_6$]Cl (10): $ZrCl_4$ (1.00 g, 4.29 mmol), thffoH (0.42 mL, 0.44 g, 4.33 mmol), MeOH (50 mL), and toluene (10 mL) were combined in a procedure analogous to that for **8**. The identical workup gave **10**·$C_6H_5CH_3$ as colorless crystals (0.97 g, 0.94 mmol, 66 %). ^{1}H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 1.85$ (m, 4 H; 2,3-HC_4H_7O), 2.31 (s, 3 H; CH_3OH), 3.28 (s, 1 H; CH_3OH), 4.17 (m, 2 H; CH_2), 4.54 (br, 2 H; 4-HC_4H_7O, 1 H; 1-HC_4H_7O); IR (CsI, Nujol): $\nu = 288$ (vs), 308 (m), 392 (w), 456 (m), 544 (m), 552 (s), 580 (s), 642 (vs), 724 (m), 808 (vs), 868 (s), 920 (s), 940 (vs), 958 (s), 996 (s), 1024 (vs), 1068 (vs), 1082 (s), 1140 (w), 1192 (w), 1234 (w), 1300 (w) cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{39}Cl_7Zr_3O_{10}\cdot C_6H_5CH_3$ (1029.47): C 29.17, H 4.60, Cl 24.11, Zr 26.58; found C 29.05, H 4.50, Cl 25.85, Zr 26.65.

[Zr(Cl)$_3$(OMe)(MeOH)$_2$] (11): $ZrCl_4$ (1.00 g, 4.29 mmol) was dissolved in cold (−78 °C) methanol (50 mL). Evolution of HCl started immediately and the gas was removed under vacuum. The mixture was next stirred at room temperature under an applied vacuum until an oil was formed. Then MeOH (60 mL) and toluene (30 mL) were added and removal of HCl under oil pump vacuum was continued until an oil was obtained. This procedure was repeated three times over a 72 h period. The volume was then reduced to 20 mL and hexane (40 mL) was added. The white precipitate was filtered off, washed with hexane (3 × 5 mL), and dried under oil pump vacuum to give crude **10** (1.07 g, 3.65 mmol, 85 %) which was recrystallized from THF to give, after 12 d, colorless crystalline **11** (0.95 g, 3.26 mmol, 76 %). IR (CsI, Nujol): $\nu = 210$ (m), 318 (vs), 332 (s), 485 (m), 540 (m), 587 (m), 714 (w), 742 (w), 810 (w), 840 (w), 957 (s), 1137 (m), 3320 (vs) cm^{-1}; elemental analysis calcd (%) for $C_3H_{11}Cl_3O_3Zr$ (292.70): C 12.31, H 3.79, Cl 36.34, Zr 31.17; found C 12.24, H 3.70, Cl 36.30, Zr 31.17.

[Zr$_3$(μ_3-O)(μ,η^2-thp)$_3$(thf)$_2$(Cl)$_7$] (12): A Schlenk flask was charged with **11** (1.00 g, 3.42 mmol), thpH (3.86 mL, 3.97 g, 3.42 mmol), toluene (50 mL), and MeOH (10 mL). The mixture was stirred at room temperature until the evolution of HCl had ceased (10–12 h). The volatiles were removed under vacuum, and the resulting white solid was dissolved in THF. After two weeks colorless crystals of **12** were formed (0.93 g, 0.90 mmol, 79 %). ^{1}H NMR (300 MHz, CD_3CN, 20 °C): $\delta = 1.10$ (m, 2 H; 4-HC_5H_9O), 1.65 (brm, 4 H; $O(CH_2)_2(CH_2)_2$), 1.70 (m, 4 H; 2,3-HC_5H_9O), 3.50 (m, 2 H; 1-HC_5H_9O), 3.76 (m, 2 H; CH_2), 3.80 (brm, 4 H; $O(CH_2)_2(CH_2)_2$), 4.12 (m, 1 H; 5-HC_5H_9O); IR (CsI, Nujol): $\nu = 302$ (vs), 336 (vs), 452 (s), 494 (vs), 566 (s), 608 (s), 666 (s), 690 (s), 780 (s), 826 (w), 876 (s), 934 (vs), 944 (vs), 954 (s), 1006 (vs), 1060 (vs), 1072 (vs), 1108 (s), 1182 (w), 1206 (m), 1268 (w), 1534 (vw), 1560 (vw) cm^{-1}; elemental analysis calcd (%) for $C_{26}H_{49}Cl_7Zr_3O_9$ (1027.50): C 30.39, H 4.81, Cl 24.15, Zr 26.63; found C 31.25, H 5.02, Cl 23.72, Zr 26.63.

X-ray crystallography: Crystal data collection and refinement are summarized in Table 1. Preliminary examinations and intensity data collection were carried out on a Kuma KM4 κ-axis diffractometer with graphite-monochromated $Mo_{K\alpha}$ and with a scintillation counter or CCD camera. All data were corrected for Lorentz and polarization effects. Data reduction and analysis were carried out with the Kuma Diffraction programs.[30, 31] The structures were solved by direct methods[32] and refined by the full-matrix least-squares method on all F^2 data using the SHELXL97 software.[33] After refinement with isotropic displacement parameters for all atoms, absorption correction based on least-squares fitted against $|F_c| - |F_o|$ differences was also applied[34] to the data. Carbon-bonded hydrogen atoms were included in calculated positions and refined in the riding mode using SHELXL97 default parameters. Other hydrogen atoms were located on a difference map and refined isotropically with O–H distances restrained for **10** and free for **8**. All non-hydrogen atoms were refined with anisotropic displacement parameters. In the structures of **3**, **5**, and **7** some chiral carbon atoms were partially disordered and each of them was refined individually in two positions. In the structure of **8** two ethanol molecules were also partially disordered. In the structures of **3** and **4** one CH_3CN molecule was refined with a 0.5 occupancy factor. In the structure of **7** one CH_2Cl_2 molecule was found disordered.

CCDC-182147 (**2b**), CCDC-182148 (**3**), CCDC-182149 (**4**), CCDC-182150 (**5**), CCDC-182151 (**7**), CCDC-182152 (**8**), and CCDC-182153 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from CCDC, 12 Union Road, Cambridge CB21EZ, UK; fax: +441223-336033; or deposit@ccdc.cam.ac.uk).

Acknowledgement

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

---

[1] a) D. S. Breslow, N. R. Newburg, *J. Am. Chem. Soc.* **1957**, *79*, 5072; b) G. Natta, P. Pino, G. Mazzanti, U. Giannini, *J. Am. Chem. Soc.* **1957**, *79*, 2975; c) D. S. Breslow, R. N. Newburg, *J. Am. Chem. Soc.* **1959**, *81*, 81; d) J. C. Chien, *J. Am. Chem. Soc.* **1959**, *81*, 86; e) F. R. W. P. Wild, L. Zsolnai, G. Huttner, H. H. Brintzinger, *J. Organomet. Chem.* **1982**, *232*, 233; f) W. Kaminsky, K. Külper, H. H. Brintzinger, F. R. W. P. Wild, *Angew. Chem.* **1985**, *97*, 507; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 507; g) R. F. Jordan, *Adv. Organomet. Chem.* **1991**, *32*, 325; h) K. B. Sinclair, R. B. Wilson, *Chem. Ind.* **1994**, 857; i) H. H. Brintzinger, D. Fischer, R. Mhlhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143; j) M. Bochmann, *J. Chem. Soc. Dalton Trans.* **1996**, 255; k) W. Kaminsky, *J. Chem. Soc. Dalton Trans.* **1998**, 1413; l) K. Soga, T. Shiono, *Prog. Polym. Sci.* **1997**, *22*, 1503.

[2] a) P. J. Shapiro, E. Bunel, W. P. Schaefer, J. E. Bercaw, *Organometallics* **1990**, *9*, 867; b) P. J. Schapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **1994**, *116*, 4623; c) J. Okuda, *Chem. Ber.* **1990**, *123*, 1649; d) J. A. M. Canich, Eur. Patent Appl. EP 420436-A1, **1991**.

[3] a) G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448; *Angew. Chem. Int. Ed.* **1999**, *38*, 428; b) G. J. P. Britovsek, M. Bruce, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. Mastroianni, S. J. McTavish, C. Redshaw, G. A. Solan, S. Strömberg, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **1999**, *121*, 8728; c) L. V. Cribbs, B. P. Etherton, G. G. Hlatky, S. Wang, *Proc. Ann. Technol. Conf.—Soc. Plast. Eng.* **1998**, *56(2)*, 1871; d) L. Deng, P. Margl, T. Ziegler, *J. Am. Chem. Soc.* **1999**, *121*, 6479; e) S. Mecking, *Angew. Chem.* **2001**, *113*, 550; *Angew. Chem. Int. Ed.* **2001**, *40*, 534.

[4] a) F. G. N. Cloke, T. J. Geldbach, P. B. Hitchcock, J. B. Love, *J. Organomet. Chem.* **1996**, *506*, 343; b) J. D. Scollard, D. H. McConville, *J. Am. Chem. Soc.* **1996**, *118*, 10008; c) R. Baumann, W. M. Davis, R. R. Schrock, *J. Am. Chem. Soc.* **1997**, *119*, 3830; d) R. Baumann, R. Stumpf, W. M. Davis, L.-Ch. Liang, R. R. Schrock, *J. Am. Chem. Soc.* **1999**, *121*, 7822.

[5] A. J. Nielson, M. W. Glenny, C. E. F. Rickard, *J. Chem. Soc. Dalton Trans.* **2001**, 232.

[6] E. B. Tjaden, D. C. Swenson, R. F. Jordan, *Organometallics* **1995**, *14*, 371.

[7] a) R. Fandos, A. Meetsma, J. H. Teuben, *Organometallics* **1991**, *10*, 59; b) P.-J. Sinnema, A. Meetsma, J. H. Teuben, *Organometallics* **1993**, *12*, 184; c) R. Uhrhammer, D. G. Black, T. G. Gardner, J. D. Olsen, R. F. Jordan, *J. Am. Chem. Soc.* **1993**, *115*, 8493; d) C. Floriani, S. Ciurli, A. Chiesi-Villa, C. Guastini, *Angew. Chem.* **1987**, *99*, 86; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 70; e) B. Rieger, *J. Organomet. Chem.* **1991**, *420*, C17; f) D. W. Stephan, F. Guérin, R. E. v. H. Spence, L. Koch, X. Gao, S. J. Brown, J. W. Swabey, Q. Wang, W. Xu, P. Zoricak, D. G. Harrison, *Organometallics* **1999**, *18*, 2046; g) E. Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Chem. Commun.* **2000**, 379.

[8] K. Krohn, I. Vinke, H. Adam, *J. Org. Chem.* **1996**, *61*, 1467.

[9] P. Bedeschi, S. Casolari, A. L. Costa, E. Tagliavini, A. Umani-Ronchi, *Tetrahedron Lett.* **1995**, *36*, 7897.

[10] T. Sawaki, Y. Aoyama, *J. Am. Chem. Soc.* **1999**, *121*, 4793.

[11] a) C. Yu, S. Yoon, H. Choi, K. Beak, *Chem. Commun.* **1997**, 763; b) R. M. Vesteegen, R. P. Sjibesma, E. W. Meijer, *Angew. Chem.* **1999**, *111*, 3095; *Angew. Chem. Int. Ed.* **1999**, *38*, 2917; c) T. Ooi, K. Takaya, T. Miura, H. Maruoka, *Synlett* **2001**, 69.

[12] S. Yamasaki, M. Kanai, M. Shibasaki, *Chem. Eur. J.* **2000**, *6*, 4067, and references therein.

[13] a) A. van der Linden, C. J. Schaverien, N. Meijboom, C. Ganter, A. G. Orpen, *J. Am. Chem. Soc.* **1995**, *117*, 3008; b) R. D. J. Froese, D. G. Musaev, T. Matsubara, K. Morokuma, *J. Am. Chem. Soc.* **1997**, *119*, 7190; c) S. Fokken, T. P. Spaniol, J. Okuda, *Organometallics* **1997**, *16*, 4240.

[14] I.-K. Lee, W. J. Gauthier, J. M. Ball, B. Iyengar, S. Collins, *Organometallics* **1992**, *11*, 2115.

[15] P. Sobota, K. Przybylak, J. Utko, L. B. Jerzykiewicz, A. J. L. Pombeiro, M. F. C. Guedes da Silva, K. Szczegot, *Chem. Eur. J.* **2001**, *7*, 951.

[16] P. Sobota, J. Utko, K. Sztajnowska, J. Ejfler, L. B. Jerzykiewicz, *Inorg. Chem.* **2000**, *39*, 235.

[17] a) S.-B. Samuels, F. J. Karol, US Patent 4918038, **1990**; b) K. D. Schramm, F. J. Karol, US Patent 5070055, **1991**.

[18] Z. Janas, L. B. Jerzykiewicz, P. Sobota, J. Utko, *New J. Chem.* **1999**, 185.

[19] N. Ya. Turova, E. P. Turevskaya, V. G. Kessler, A. I. Yanovsky, Y. T. Struchkov, *J. Chem. Soc. Chem. Commun.* **1993**, 21; b) S. C. Goel, M. A. Matchett, M. Y. Chiang, W. E. Buhro, *J. Am. Chem. Soc.* **1991**, *113*, 1844.

[20] a) W. A. Herrmann, N. W. Huber, O. Runte, *Angew. Chem.* **1995**, *107*, 2371; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2187; b) R. C. Mehrotra, A. Singh, *Chem. Soc. Rev.* **1996**, *1*, 1.

[21] ^1H NMR (300 MHz, $CDCl_3$, 20 °C) of tetrehydrofurfuryl alcohol (thffoH): $\delta = 1.51-1.59 + 1.78-1.89$ (m + m, 4H; 2,3-HC_4H_7O), 3.06 (s, 1H of OH), 3.38–3.58 (m, 2H; CH_2), 3.67–3.78 (m, 2H; 4-HC_4H_7O), 3.89–3.93 (m, 1H; 1-HC_4H_7O).

[22] K. G. Caulton, L. G. Hubert-Pfalzgraf, *Chem. Rev.* **1990**, *90*, 969.

[23] a) Z. A. Starikova, E. P. Turevskaya, N. I. Kozlova, N. Ya. Turova, D. V. Berdyev, A. I. Yanovsky, *Polyhedron* **1999**, *18*, 941; b) K. A. Fleeting, P. O'Brien, A. C. Jones, D. J. Otway, A. J. P. White, D. J. Williams, *J. Chem. Soc. Dalton Trans.* **1999**, 2853; c) W. J. Evans, M. A. Ansari, J. W. Ziller, *Inorg. Chem.* **1999**, *38*, 1160.

[24] E. P. Turevskaya, D. V. Berdyev, N. Ya. Turova, Z. A. Starikova, A. I. Yanovsky, Yu. T. Struchkov, A. I. Belokon, *Polyhedron* **1997**, *16*, 663.

[25] a) P. Sobota, J. Utko, Z. Janas, S. Szafert, *Chem. Commun.* **1996**, 1923; b) P. Sobota, T. Płuziński, T. Lis, *Inorg. Chem.* **1989**, *28*, 2217; c) J. Utko, P. Sobota, T. Lis, K. Majewska, *J. Organomet. Chem.* **1989**, *359*, 295; d) ref. [20a].

[26] a) Z. Janas, P. Sobota, M. Klimowicz, S. Szafert, K. Szczegot, L. B. Jerzykiewicz, *J. Chem. Soc. Dalton Trans.* **1997**, 3897; b) P. Sobota, J. Utko, J. Ejfler, L. B. Jerzykiewicz, *Organometallics* **2000**, *19*, 4929.

[27] E. P. Turevskaya, V. G. Kessler, N. Ya. Turova, A. P. Pisarevsky, A. I. Yanovsky, Y. T. Struchkov, *J. Chem. Soc. Chem. Commun.* **1994**, 2303.

[28] P. Sobota, Sz. Przybylak, J. Utko, L. B. Jerzykiewicz, *Organometallics* **2002**, *21*, 3497.

[29] H. Hatop, M. Ferbinteanu, H. W. Roesky, F. Cimpoesu, M. Schiefer, H.-G. Schmidt, M. Noltemeyer, *Inorg. Chem.* **2002**, *41*, 1022.

[30] *Kuma KM4 Software*, Kuma Diffraction, Wrocław (Poland), **1998**.

[31] *KM4CCD Software*, version 1.161, Kuma Diffraction Instruments GmbH, **1995–1999**.

[32] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467.

[33] G. M. Sheldrick, *SHELXL97, Program for the Refinement of Crystal Structures*, University of Göttingen (Germany), **1997**.

[34] P. Starynowicz, *COSABS99: Program for absorption correction*, University of Wrocław (Poland), **1999**.

Received: April 8, 2002 [F4004]