

# Olefin polymerization behavior of bis(phenoxy-imine) Zr, Ti, and V complexes with $\text{MgCl}_2$ -based cocatalysts

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## Abstract

This contribution reports on the olefin polymerization behavior of phenoxy-imine ligated Zr, Ti, and V complexes **1–10** with  $\text{MgCl}_2/\text{R}_m\text{Al}(\text{OR})_n$  systems. Zr complexes **1–4** combined with  $\text{MgCl}_2/\text{R}_m\text{Al}(\text{OR})_n$  display strikingly high ethylene polymerization activities; indeed, they are some of the highest reported activities for methylalumoxane (MAO)- and borate-free olefin polymerization catalysts (max. 1819 kg-PE/(mmol-cat h), 0.9 MPa ethylene pressure, 50 °C). In addition, when Ti complexes **5–7** are combined with  $\text{MgCl}_2/\text{R}_m\text{Al}(\text{OR})_n$  they exhibit high ethylene polymerization activities (max. 36.3 kg-PE/(mmol-cat h), 0.9 MPa ethylene pressure, 50 °C) and produce polyethylenes with narrow molecular weight distributions ( $M_w/M_n$ ) and ethylene-propylene copolymers with homogeneous structures, representing the first examples of MAO- and borate-free, highly active single-site catalyst systems. The activities exhibited by the Zr and Ti complexes with  $\text{MgCl}_2/\text{R}_m\text{Al}(\text{OR})_n$  are superior or comparable to those obtained with MAO cocatalyst systems. Moreover, V complexes **9** and **10** in association with  $\text{MgCl}_2/\text{R}_m\text{Al}(\text{OR})_n$  demonstrate high activities at elevated temperatures (**9**: 75 °C, 65.1 kg-PE/(mmol-cat h), atmospheric ethylene pressure) and are the first reported examples of highly active, thermally robust single-site V-based olefin polymerization catalysts. All of the polyethylenes formed from the  $\text{MgCl}_2/\text{R}_m\text{Al}(\text{OR})_n$  systems display good polymer morphology, indicating that complexes **1–10** are heterogenized on the surface of the  $\text{MgCl}_2/\text{R}_m\text{Al}(\text{OR})_n$ . These results suggest that  $\text{MgCl}_2/\text{R}_m\text{Al}(\text{OR})_n$  not only works as an excellent cocatalyst, but is also a good support for phenoxy-imine ligated Zr, Ti, and V complexes.

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**Keywords:** Catalysis; Polymerization; Cocatalyst; Magnesium dichloride; Alkylaluminum; Transition metal complex; FI catalysts

## 1. Introduction

The discovery of  $\text{TiCl}_4$ /alkylaluminum/ $\text{MgCl}_2$  catalyst systems ( $\text{MgCl}_2$ -supported  $\text{TiCl}_4$  catalysts) for olefin polymerization at Mitsui Petrochemicals [1] and Montecatini [2] in the late 1960s revolutionized the polyolefin industry, due to the increased cost effectiveness stemming from the simplified production process and the superior material properties of the polyolefins produced [3]. Remarkably, these catalysts display two orders of magnitude greater activities for ethylene polymerization than Ziegler's original  $\text{TiCl}_4$ /alkylaluminum catalysts [4,5]. When we also consider the control of polymer morphology as well as the extremely high productivity described above, then  $\text{MgCl}_2$ -supported  $\text{TiCl}_4$  catalysts have contributed significantly to the enormous growth of polyolefin production. Although these catalysts are the most commonly used catalysts for olefin

polymerization in industry, they are multi-site catalysts that produce complex polymer mixtures with widely varying molecular weights ( $M_w$ ) and microstructures. In addition, their non-uniformity in terms of active sites due to their multi-site nature renders any mechanistic study for elucidating the catalysis and/or the rational design of modified catalysts extremely difficult. While extensive and continuous efforts have been devoted to developing single-site catalysts based on  $\text{MgCl}_2$ -supported  $\text{TiCl}_4$ , no single-site catalysts of this type have been reported so far.

Although important properties such as the structure of the active site and the mode and mechanism of the catalytic action are still a current research topic [6–10], kinetic studies have demonstrated that  $\text{MgCl}_2$  increases the rate constant for chain propagation as well as the number of active sites [4]. These results indicate that  $\text{MgCl}_2$  works not only as a support [11–13], but also as a good cocatalyst [14–16] for titanium chloride species. Therefore, the development of  $\text{MgCl}_2$ -supported  $\text{TiCl}_4$  catalysts implies the discovery of an  $\text{MgCl}_2$  cocatalyst for the titanium chloride species. We have postulated that the cocatalytic performance displayed

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by  $\text{MgCl}_2$  (i.e., the enhancement of the rate constant for chain propagation) originates from an electronic interaction between the active Ti chloride species and  $\text{MgCl}_2$ , presumably through the Cl attached to the Ti and Mg.

Several transition metal complex catalysts have been developed so far, including group 4 metallocene catalysts and  $\text{MgCl}_2$ , which are often described as  $\text{MgCl}_2$ -supported catalyst systems [17–22]. In general, these catalyst systems form polymers with a broad molecular weight distribution ( $M_w/M_n$ ) with low efficiency. Significantly, Kissin et al. [23] have recently reported that a mixture of  $\text{AlEt}_2\text{Cl}$  or  $\text{AlMe}_2\text{Cl}$  with  $\text{MgBr}_2$  (which results in the formation of  $\text{MgCl}_2$ ) can function as an effective cocatalyst for group 4 metallocene catalysts to generate single-site catalysts. However, the activities that they measure are typically lower than those observed with MAO cocatalyst systems. Therefore, the development of highly active, single-site catalysts based on transition metal complexes with  $\text{MgCl}_2$  cocatalysts is a scientific challenge that may provide information on the catalysis of conventional  $\text{MgCl}_2$ -supported  $\text{TiCl}_4$  catalysts.

In our own efforts to develop high-performance non-metallocene olefin polymerization catalysts, we have investigated well-defined transition metal complexes featuring non-symmetric bidentate and tridentate ligands that possess electronically flexible properties. As a consequence, we found new families of transition metal complexes incorporating phenoxy-imine, phenoxy-pyridine, phenoxy-ether, pyrrolide-imine, indolide-imine, imine-pyridine or phenoxy-imine-pyridine chelate ligands, which exhibit high catalytic properties upon activation with an appropriate cocatalyst [24–37]. Among them, in particular bis(phenoxy-imine) early transition metal complexes (named FI catalysts) display unique polymerization catalysis. As disclosed in our patents [38,39] and in a series of papers [40–69], FI catalysts with MAO or with a *i*- $\text{Bu}_3\text{Al}/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$  cocatalyst are capable of producing a variety of distinctive polymers with high efficiency. These include vinyl-terminated low molecular weight PEs ( $M_w$ : 2000; vinyl selectivity >90%) [54], exceptionally high molecular weight PEs (viscosity-average molecular weight,  $M_v > 5,000,000$ ) [44], ethylene/ $\alpha$ -olefin copolymers ( $M_w > 10,000,000$ ) [55] and atactic PPs ( $M_w > 8,000,000$ ) [56], monodisperse [46,47,51,53,61] to controlled multimodal PEs [60] and PPs [58], stereo- and regioirregular high molecular weight poly(higher  $\alpha$ -olefin)s ( $M_w > 700,000$ ) [43,62], highly syndiotactic ( $T_m > 150^\circ\text{C}$ ) [53,61] to highly isotactic PPs ( $T_m > 160^\circ\text{C}$ ) [69] and various polyolefinic block copolymers from ethylene and  $\alpha$ -olefins [46,48,51].

Unlike common group 4 metallocene catalysts, FI catalysts possess O and N heteroatoms in the ligands that can interact electronically with  $\text{MgCl}_2$ . Therefore, we expected that  $\text{MgCl}_2$  could work as a cocatalyst for FI catalysts. Accordingly, the decision was made to investigate  $\text{MgCl}_2$  as a cocatalyst for FI catalysts in the hope of developing additional high-performance FI catalyst systems [70–73].

In this contribution, we describe some new catalyst systems comprised of Zr-, Ti-, and V-FI catalysts and  $\text{MgCl}_2$ -based cocatalysts, which can be used as highly active MAO- and borate-free, supported single-site catalysts for olefin polymerization.

## 2. Experimental

### 2.1. General

All operations were performed under an inert atmosphere using standard Schlenk techniques or in a nitrogen-filled drybox. *n*-Decane (Mitsui Chemicals, Inc.) and toluene (Wako Pure Chemical Industries, Ltd.) were dried over activated  $\text{Al}_2\text{O}_3$ , and degassed with high-purity dry  $\text{N}_2$  prior to use. 2-Ethyl-1-hexanol (Wako Pure Chemical Industries, Ltd.) was dried by bubbling through high-purity dry  $\text{N}_2$ . Anhydrous  $\text{MgCl}_2$  was purchased from Toho Catalyst Co., Ltd. and used as supplied.  $\text{Cp}_2\text{ZrCl}_2$  and  $\text{Cp}_2\text{TiCl}_2$  were obtained from Wako Pure Chemical Industries, Ltd.  $\text{Et}_3\text{Al}$  and *i*- $\text{Bu}_3\text{Al}$  (Tosoh-Akzo Co., Ltd.) were used without further purification. Methylalumoxane was purchased from Albemarle as a 1.2 M toluene solution and used as supplied. Polymerization grade ethylene and propylene gases were obtained from Sumitomo Seika Co., Ltd., and Mitsui Chemicals, Inc., respectively. A  $\text{MgCl}_2/2$ -ethyl-1-hexanol adduct solution was prepared as previously described [71]. Bis(phenoxy-imine) Zr, Ti, and V complexes were synthesized according to slightly modified procedures from the literature [35,40,44,52,72]. All other chemicals were obtained commercially and used as received.

Gel permeation chromatography (GPC) was performed on a Waters 150-C gel permeation chromatograph at  $145^\circ\text{C}$  using three TSKgel columns (two sets of TSKgelGMH<sub>HR</sub>-H(S)HT and TSKgelGMH<sub>6</sub>-HTL) with refractive index detection and calibration versus narrow polystyrene standards. GPC-IR spectra were recorded with a Nicolet Magna560 FT-IR, using a Millipore GPC-150 gel permeation chromatograph at  $140^\circ\text{C}$  equipped with two Plgel-MIXED-A (polystyrene calibration). The propylene contents of the ethylene-propylene copolymers were determined by means of IR analysis using an FT/IR-350 from JASCO Co.

### 2.2. Ethylene polymerization

A representative ethylene polymerization experiment was conducted as follows: toluene (500 ml) was introduced under ethylene atmospheric pressure into a 1000 ml stainless steel reactor equipped with a propeller-like stirrer, and was heated to  $50^\circ\text{C}$  with stirring (150 rpm) using a thermostat. A 1.0 M *i*- $\text{Bu}_3\text{Al}$  solution in toluene (0.8 ml, 0.8 mmol) and a 0.1 M  $\text{MgCl}_2/2$ -ethyl-1-hexanol adduct solution (2.0 ml, 0.2 mmol as Mg, 0.6 mmol as 2-ethyl-1-hexanol) were then added (in that order) to the reactor and stirred for 3 min to

give  $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$ . Subsequently, a  $1.68 \times 10^{-5}$  M toluene solution of a Zr complex (0.95 ml, 0.016  $\mu\text{mol}$ ) was added to the reactor. Ethylene was then pumped into the reactor up to a pressure of 0.9 MPa with vigorous stirring (350 rpm) to initiate polymerization. The ethylene pressure was maintained at 0.9 MPa by a continuous ethylene feed. After 30 min, the polymerization was terminated by the addition of methanol (5 ml). The ethylene supply was closed and the reactor was vented. The resulting mixture was added to acidified methanol (1000 ml containing 5 ml of conc. HCl). The polymer was collected by filtration, washed with methanol ( $2 \times 200$  ml) and dried to constant weight overnight in a vacuum oven at 80 °C.

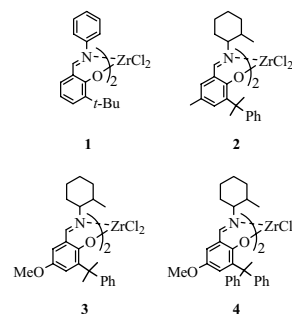
### 2.3. Ethylene–propylene copolymerization

A representative ethylene–propylene polymerization experiment was conducted as follows: toluene (400 ml) was introduced under ethylene at atmospheric pressure to a 1000 ml stainless steel reactor equipped with a propeller-like stirrer at room temperature. Propylene (40 l) was pumped into the reactor with the aid of a gas flow meter (4.1 l/min, 9.75 min) with vigorous stirring (800 rpm). After the solution was heated to 50 °C using a thermostat, ethylene was pumped into the reactor up to 0.9 MPa total pressure. A 1.0 M *i*-Bu<sub>3</sub>Al solution in toluene (4.8 ml, 4.8 mmol) and a 0.1 M  $\text{MgCl}_2/2\text{-ethyl-1-hexanol}$  adduct solution (8.0 ml, 0.8 mmol as Mg, 4.8 mmol as 2-ethyl-1-hexanol) were added (in that order) to the reactor and stirred for 3 min to give  $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$ . Polymerization was initiated by adding a 0.611 M toluene solution of a Ti complex (1.64 ml, 1.0  $\mu\text{mol}$ ) to the reactor. The total pressure was maintained at 0.9 MPa by a continuous ethylene feed. After 30 min, the polymerization was quenched by the addition of methanol (5 ml). The reactor was vented and the resulting mixture was added to acidified methanol (1500 ml containing 5 ml of conc. HCl). The polymer was isolated by filtration, washed with methanol ( $2 \times 200$  ml) and dried to constant weight in a vacuum oven at 130 °C overnight.

## 3. Results and discussion

### 3.1. Potential of $\text{MgCl}_2$ as a cocatalyst for phenoxy-imine ligated Zr complex **1**

A preliminary investigation into the suitability of mechanically-pulverized  $\text{MgCl}_2$  (vibromill; crystallite size 80 Å [74]) as a cocatalyst for ethylene polymerization with bis(phenoxy-imine) Zr complex **1** (Scheme 1, see Section 3.2.) was conducted (50 °C, 0.9 MPa ethylene pressure).  $\text{Et}_3\text{Al}$  was used as an alkylating agent for complex **1** as well as being a scavenger in the polymerization system. The polymerization results are summarized in Table 1,



Scheme 1. Structures of bis(phenoxy-imine) Zr complexes **1–4**.

which also contains the results obtained from **1** with  $\text{Et}_3\text{Al}$  as a comparison.

The results showed how the mixture of complex **1**,  $\text{Et}_3\text{Al}$  and  $\text{MgCl}_2$  catalyzed the polymerization of ethylene. The activity observed (3.4 kg-PE/(mmol-cat h)) is very high for a non-metallocene catalyst system. By contrast, the mixture of **1** and  $\text{Et}_3\text{Al}$  was unreactive towards ethylene under the given conditions. These results suggest that  $\text{MgCl}_2$  has a good potential as a cocatalyst for olefin polymerization with bis(phenoxy-imine) Zr complexes. The  $\text{MgCl}_2$  employed may work as a Lewis acid to generate a cationic active species from the alkylated complex **1** [75] and become an anionic species functioning as a counter anion to the cationic active species. Based on the fact that  $\text{MgCl}_2$  is a poor cocatalyst for  $\text{Cp}_2\text{ZrCl}_2/\text{Et}_3\text{Al}$  under identical conditions (<0.1 kg-PE/(mmol-cat h)), we postulated that an electronic interaction between the cationic active species derived from Zr complex **1** and  $\text{MgCl}_2$  (probably through the O and N heteroatoms in the ligand and Mg) may be responsible for the high activity observed. Such an interaction might be expected to assist the electron transfer between the ligand and the metal, reducing the barrier to ethylene insertion.

### 3.2. Bis(phenoxy-imine) Zr complex with $\text{MgCl}_2$ -based cocatalyst systems

Since the de-alcoholysis of a  $\text{MgCl}_2/\text{alcohol}$  adduct with alkylaluminum produces highly porous  $\text{MgCl}_2$  with a small particle size (which should be a more suitable cocatalyst for phenoxy-imine ligated complexes than mechanically-pulverized  $\text{MgCl}_2$ ), an  $\text{MgCl}_2$ -based cocatalyst,  $\text{MgCl}_2/\text{R}_m\text{Al(OR)}_n$ , was prepared for bis(phenoxy-imine) Zr

Table 1  
Ethylene polymerization results using complex **1**/ $\text{Et}_3\text{Al}$  with and without  $\text{MgCl}_2^a$

Entry	Complex	$\text{MgCl}_2$ (mmol)	Yield (g)	Activity (kg-PE/ (mmol-cat h))	$M_v$ ( $\times 10^{-4}$ )
1	<b>1</b>	1.6	9.10	3.4	70.6
2	<b>1</b>	0	Trace	–	–

<sup>a</sup> Conditions: 50 °C; 0.9 MPa ethylene pressure; solvent, 500 ml toluene; polymerization time, 20 min; complex **1**, 8.0  $\mu\text{mol}$ ;  $\text{Et}_3\text{Al}$ , 0.2 mmol.

complexes **1–4** (Scheme 1) by the de-alcoholysis of a  $\text{MgCl}_2/2\text{-ethyl-1-hexanol}$  adduct using  $i\text{-Bu}_3\text{Al}$  [71].

The treatment of  $\text{MgCl}_2$  with 3.0 eq. of 2-ethyl-1-hexanol in decane at  $140^\circ\text{C}$  formed a  $\text{MgCl}_2/2\text{-ethyl-1-hexanol}$  adduct solution. Subsequent de-alcoholysis with 4.0 eq. of  $i\text{-Bu}_3\text{Al}$  to  $\text{MgCl}_2$  at  $50^\circ\text{C}$  yielded a mixture of  $\text{MgCl}_2$ ,  $i\text{-Bu}_3\text{Al}$ , and  $i\text{-butylaluminum 2-ethyl-1-hexoxide}$ ,  $i\text{-Bu}_m\text{Al(OR)}_n$ , which was used as a cocatalyst. X-ray analysis indicated the formation of  $\text{MgCl}_2$  with a crystallite size of  $28 \text{ \AA}$  as determined by the (1 1 0) reflection [74].

Bis(phenoxy-imine) Zr complexes **1–4** were tested with the above mentioned  $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$  as a cocatalyst to determine their suitability as an ethylene polymerization catalyst. Both  $i\text{-Bu}_3\text{Al}$  and  $i\text{-butylaluminum 2-ethyl-1-hexoxide}$  ( $i\text{-Bu}_m\text{Al(OR)}_n$ ) such as  $i\text{-Bu}_2\text{Al(2-ethyl-1-hexoxide)}$  are expected to act as in situ alkylating agents for the Zr complexes as well as impurity scavengers in a polymerization system. All of the polymerizations were performed at  $50^\circ\text{C}$  under 0.9 MPa pressure of ethylene in toluene. For comparison, we carried out some experiments using MAO as a cocatalyst. The polymerization data are collected in Table 2.

As anticipated, all of the  $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$  systems are highly active ethylene polymerization catalysts. In contrast, the complexes with  $i\text{-Bu}_m\text{Al(OR)}_n$  are poor catalysts ( $0.1 \text{ g} < \text{polymer yield}$ ). The activities obtained with  $\text{MgCl}_2$  systems were in the range of 245–1819 kg-PE/(mmol-cat h), which are some of the highest values for ethylene polymerization catalysts ever reported. The strikingly high activities obtained without using MAO and borate cocatalysts are of great significance. Notably, the activity displayed by complex **3** with  $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$  exceeds that obtained with the MAO cocatalyst system. These results demonstrated that  $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$  is an excellent cocatalyst for bis(phenoxy-imine) Zr complexes, and  $\text{MgCl}_2$  is a crucial component of the cocatalyst, though the possibility cannot be ruled out that the combination of  $\text{MgCl}_2$  and  $i\text{-Bu}_m\text{Al(OR)}_n$  results in a unique cocatalytic performance.

Significantly, the PEs arising from the Zr complexes **1–4**/ $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$  systems show morphologies

with well-defined particles, whereas those with the MAO cocatalyst systems display ill-defined polymer morphologies (Fig. 1).

These facts indicate that the complex exists on the surface of a solid  $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$  cocatalyst, and that polymerization occurred on the surface. Therefore, the Zr complexes with the  $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$  cocatalyst systems were demonstrated to be  $\text{MgCl}_2$ -supported catalyst systems. Since the morphology of the polymer particle can be controlled by the form of the support that was employed, the systems have the potential for control of the polymer morphology.

The PE arising from complex **1** with the  $\text{MgCl}_2$ -based cocatalyst possesses a broad molecular weight distribution ( $M_w/M_n$ : 13.16;  $M_w$ : 51,300). This result suggests that several active species are formed in this catalyst system. However, this is not surprising because we often observe multimodal behavior with Zr-FI catalyst systems, probably due to the presence of structural isomers [60]. In fact, **1** with MAO produced a broad molecular weight distribution PE ( $M_w/M_n$ : 13.36;  $M_w$ : 71,000) under the same conditions. We were not able to determine the molecular weight distributions of the PEs formed with complexes **2–4** with  $\text{MgCl}_2$ -based cocatalysts due to their exceptionally high molecular weights ( $M_v > 4,000,000$ ), which represent some of the highest values reported among PEs produced with complex catalysts.

Considering that the supported Zr complexes display extremely high ethylene polymerization activities and that the structurally related complexes such as mono(phenoxy-imine) Zr complexes and bis(phenoxy) Zr complexes are far less active catalysts than bis(phenoxy-imine) Zr complexes for ethylene polymerization, it seems reasonable that the phenoxy-imine ligand is attached to the Zr metal during the polymerization reaction.

### 3.3. Bis(phenoxy-imine) Ti complex with $\text{MgCl}_2$ -based cocatalyst systems

Ti complexes **5–8** (Scheme 2) proved to be highly active in the presence of  $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$  for the polymer-

Table 2  
Ethylene polymerization results with complexes **1–4** using  $\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$  or MAO as a cocatalyst<sup>a</sup>

Entry	Complex	Cocatalyst	Amount of cocatalyst (mmol)		Yield (g)	Activity (kg-PE/ (mmol-cat h))	$M_v$ ( $\times 10^{-4}$ )
			Mg	Al			
1	<b>1</b>	$\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$	0.20	0.80	1.96	245	9.1
2		MAO	0	1.25	10.29	1286	7.4
3	<b>2</b>	$\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$	0.20	0.80	8.67	1084	410.0
4		MAO	0	1.25	6.02	753	213.0
5	<b>3</b>	$\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$	0.20	0.80	14.55	1819	509.0
6		MAO	0	1.25	13.14	1643	399.0
7	<b>4</b>	$\text{MgCl}_2/i\text{-Bu}_m\text{Al(OR)}_n$	0.20	0.80	8.00	1000	460.0
8		MAO	0	1.25	11.91	1489	298.0

<sup>a</sup> Conditions:  $50^\circ\text{C}$ ; 0.9 MPa ethylene pressure; solvent, 500 ml toluene; polymerization time, 30 min; complex **1–4**, 0.016  $\mu\text{mol}$ .

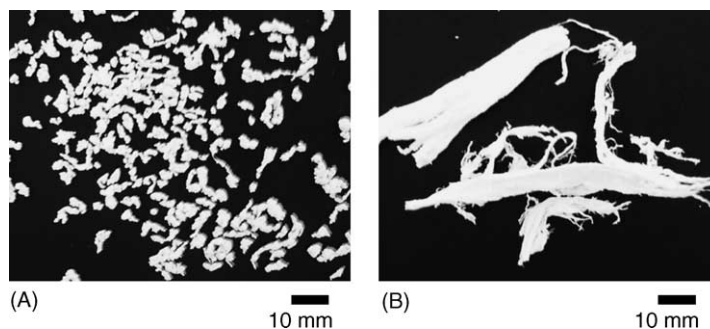
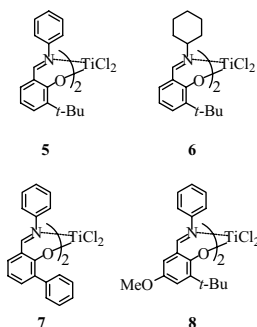


Fig. 1. Photographs of the PEs arising from  $3/\text{MgCl}_2/i\text{-Bu}_m\text{Al}(\text{OR})_n$  (A) and  $3/\text{MAO}$  (B).



Scheme 2. Structures of bis(phenoxy-imine) Ti complexes **5–8**.

ization of ethylene with a steady uptake of ethylene over the 30 min duration of the run [71]. By contrast, in no instance was any PE obtained using **5–8** in the absence of  $\text{MgCl}_2$  (i.e. **5–8** with  $i\text{-Bu}_m\text{Al}(\text{OR})_n$ ), showing that the  $\text{MgCl}_2$  also works as a good cocatalyst for bis(phenoxy-imine) Ti complexes (Table 3).

The activities displayed by the Ti complexes with the  $\text{MgCl}_2$ -based cocatalysts (20.8–36.3 kg-PE/(mmol-cat h)) are very high for Ti-based catalysts. In fact, they are comparable to or exceed those seen with the  $\text{Cp}_2\text{TiCl}_2/\text{MAO}$  catalyst system. It is highly significant that the activities obtained with  $\text{MgCl}_2/i\text{-Bu}_m\text{Al}(\text{OR})_n$  are comparable to those

seen with the MAO cocatalyst system, further confirming the very high potential of  $\text{MgCl}_2$ -based compounds as a cocatalyst.

As expected, the complex **5–8**/ $\text{MgCl}_2$ -based cocatalyst systems produced well-defined PE particles, indicating that the systems are  $\text{MgCl}_2$ -supported Ti catalysts. GPC analyses revealed that the PEs formed from **5–7**/ $\text{MgCl}_2/i\text{-Bu}_m\text{Al}(\text{OR})_n$  possess narrow molecular weight distributions in the range of 2.40–2.67 (MAO cocatalyst: 2.07–2.74), though that arising from **8** has the relatively broad molecular weight distribution of 3.51 (MAO cocatalyst: 4.74). These results suggest that the  $\text{MgCl}_2$ -supported Ti complexes **5–7** are single-site catalysts. Thus, these  $\text{MgCl}_2$ -supported Ti catalysts behave in a manner similar to that of their soluble counterparts. These are the first reported examples of  $\text{MgCl}_2$ -supported non-metallocene single-site catalysts.

Following on from the unprecedented single-site behavior of the Ti complexes with  $\text{MgCl}_2$ -based cocatalyst systems, ethylene-propylene copolymerization with  $7/\text{MgCl}_2/i\text{-Bu}_m\text{Al}(\text{OR})_n$  was carried out at  $50^\circ\text{C}$  for 30 min under 0.9 MPa total pressure. The Ti complex system provided an amorphous copolymer with a propylene content of 29.3 mol% (IR analysis) and a narrow  $M_w/M_n$  of 1.70, which exhibited a high activity of 28.2 kg-PE/(mmol-cat h). GPC-IR analysis indicated the uniform incorporation of

Table 3

Ethylene polymerization results with complexes **5–8** using  $\text{MgCl}_2/i\text{-Bu}_m\text{Al}(\text{OR})_n$  or MAO as a cocatalyst<sup>a</sup>

Entry	Complex	Cocatalyst	Amount of cocatalyst (mmol)		Yield (g)	Activity (kg-PE/(mmol-cat h))	$M_w^b$ ( $\times 10^{-4}$ )	$M_w/M_n^b$
			Mg	Al				
1	<b>5</b>	$\text{MgCl}_2/i\text{-Bu}_m\text{Al}(\text{OR})_n$	0.40	2.40	9.07	36.3	50.9	2.66
2		MAO	0	1.25	11.16	44.6	46.4	2.38
3	<b>6</b>	$\text{MgCl}_2/i\text{-Bu}_m\text{Al}(\text{OR})_n$	0.40	2.40	5.21	20.8	59.6	2.67
4		MAO	0	1.25	5.35	21.4	62.5	2.74
5	<b>7</b>	$\text{MgCl}_2/i\text{-Bu}_m\text{Al}(\text{OR})_n$	0.40	2.40	9.01	36.0	23.1	2.40
6		MAO	0	1.25	24.77	99.1	22.9	2.07
7	<b>8</b>	$\text{MgCl}_2/i\text{-Bu}_m\text{Al}(\text{OR})_n$	0.40	2.40	6.54	26.2	117.0	3.51
8		MAO	0	1.25	17.01	68.0	42.2	4.74

<sup>a</sup> Conditions:  $50^\circ\text{C}$ ; 0.9 MPa ethylene pressure; solvent, 500 ml toluene; polymerization time, 30 min; complex **5–8**, 0.5  $\mu\text{mol}$ .

<sup>b</sup> Determined by GPC.

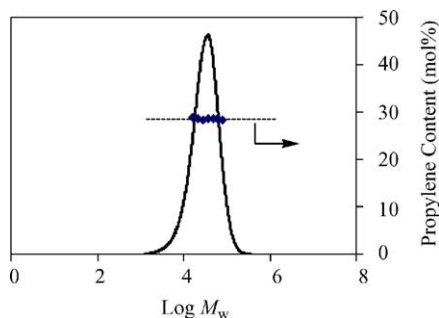


Fig. 2. GPC-IR chart of the ethylene-propylene copolymer produced with  $7/\text{MgCl}_2/i\text{-Bu}_m\text{Al}(\text{OR})_n$ .

propylene (Fig. 2), further confirming the chemically homogeneous catalysis of the system.

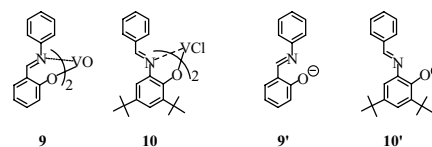
To our knowledge, this is the first example of a transition metal complex with a  $\text{MgCl}_2$ -based cocatalyst that produces a polymer with a narrow distribution of molecular weight and chemical composition. Thus, it has been demonstrated that  $\text{MgCl}_2$ -supported phenoxy-imine ligated Ti complexes can combine high catalytic activity with the production of (co)polymers with narrow molecular weight and composition distributions.

### 3.4. Bis(phenoxy-imine) V complex with $\text{MgCl}_2$ -based cocatalyst systems

V-based olefin polymerization catalysts, such as  $\text{VOCl}_3$  and  $\text{V}(\text{acac})_3$ , in association with alkylaluminum compounds have been recognized as useful single-site catalysts since the 1960s [76], though group 4 metallocene catalysts and constrained-geometry catalysts (CGC) are more recent examples of high-performance single-site catalysts [77–84]. In fact, these V-based catalysts are widely used for the commercial production of ethylene/propylene/diene elastomers (EPDM).

While V-based catalysts possess many desirable properties as single-site catalysts (e.g. the production of high molecular weight polymers, high incorporation ability for  $\alpha$ -olefins and dienes, living polymerization behavior for propylene), they show low catalytic activities (particularly at elevated temperatures) because of catalyst deactivation. Catalyst deactivation processes often include reduction of the V metal (typically to V(II)) and ligand migration, which are induced by alkylaluminum species. Due to this low productivity under practical conditions, a de-ashing process is inevitably necessary in the polymer production, which renders the production process complicated and less environmentally friendly. Therefore, the development of V-based catalyst systems that display high productivity at high process temperatures has been urgently required [85–101].

As already discussed, bis(phenoxy-imine) Zr and Ti complexes are supported on a  $\text{MgCl}_2/\text{R}_m\text{Al}(\text{OR})_n$  surface and the phenoxy-imine ligand remains attached to the metal during the course of the polymerization. With a knowledge of these



Scheme 3. Structures of phenoxy-imine ligated V complexes **9**, **10** and their ligands **9'**, **10'**.

facts, we expected that a phenoxy-imine ligated V complex (Scheme 3) could be a high-activity catalyst at elevated temperatures, since the fixation of a phenoxy-imine ligated V complex on the  $\text{MgCl}_2/\text{R}_m\text{Al}(\text{OR})_n$  surface is expected to curtail the ligand from leaching and that the phenoxy-imine ligand may stabilize the higher oxidation state of V.

The  $\text{MgCl}_2$ -based cocatalyst employed for V compounds,  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ , was synthesized by the de-alcoholysis of a  $\text{MgCl}_2/2$ -ethyl-1-hexanol adduct with  $\text{Et}_3\text{Al}$  using a procedure similar to that used for the de-alcoholysis with  $i\text{-Bu}_3\text{Al}$ .<sup>1</sup> Bis(phenoxy-imine) V complex **9** [102,103] was tested with and without  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  for ethylene polymerization in the presence of  $\text{Et}_2\text{AlCl}$  and ethyl trichloroacetate [104] under atmospheric pressure [72]. The polymerization results are collected in Table 4. For comparison, the results for complex **10**, which has a structurally different phenoxy-imine ligand **10'**, and  $\text{VOCl}_3$  under identical conditions are also included.

A comparison of the activities obtained at 25 °C (entries 1–6) indicated that though all the V compounds examined exhibit somewhat lower activities in the presence of  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ , the polymerization behavior of the catalyst systems is similar to each other. These results suggest that the phenoxy-imine ligands **9'**, **10'** and the  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  that were employed have no significant influence on catalyst productivity under the conditions studied (25 °C; atmospheric pressure).

Complexes **9** and **10** with  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  produced well-defined PE particles, whereas those without  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  formed the type of stringy material that is typically obtained from homogeneous polymerization. These results demonstrate that complexes **9** and **10** are heterogenized on the surface of the solid  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ , in the same way as the bis(phenoxy-imine) Zr and Ti complexes. Thus, V complexes **9** and **10** in conjunction with  $\text{MgCl}_2$ -based cocatalysts are  $\text{MgCl}_2$ -supported V catalysts.

All of the V compounds with  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  provided very high molecular weight PEs ( $M_v > 5,000,000$ ) for which we are unable to determine the molecular weights and molecular weight distributions using GPC analyses. The

<sup>1</sup> Preparation of  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ : Treatment of anhydrous  $\text{MgCl}_2$  (9.52 g, 100 mmol) with 3.0 eq. of 2-ethyl-1-hexanol (39.07 g, 300 mol) in decane (48.5 ml) at 140 °C for 4 h, followed by the dilution of the resulting solution with toluene (900 ml) at rt, afforded a 0.10 M  $\text{MgCl}_2/2$ -ethyl-1-hexanol adduct solution. The dealcoholysis of this solution (8.00 ml, 0.80 mmol as Mg) with a 1.00 M  $\text{Et}_3\text{Al}$  solution in toluene (2.40 ml, 2.40 mmol) for 5 min with stirring yielded  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ .

Table 4  
Ethylene polymerization results with complexes **9**, **10** and  $\text{VOCl}_3^a$

Entry	Catalyst	Cocatalyst	Amount of cocatalyst (mmol)		Temperature ( $^{\circ}\text{C}$ )	Yield (g)	Activity (kg-PE/(mmol-cat h))
			Mg	$\text{Et}_3\text{Al}$			
1	<b>9</b>	–	0	0	25	5.00	20.0
2	<b>10</b>	–	0	0	25	4.18	16.7
3	$\text{VOCl}_3$	–	0	0	25	3.15	12.6
4	<b>9</b>	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$	0.80	2.40	25	4.68	18.7
5	<b>10</b>	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$	0.80	2.40	25	2.83	11.3
6	$\text{VOCl}_3$	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$	0.80	2.40	25	2.07	8.3
7	<b>9</b>	–	0	0	50	3.32	13.3
8	<b>10</b>	–	0	0	50	2.22	8.9
9	$\text{VOCl}_3$	–	0	0	50	2.03	8.1
10	<b>9</b>	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$	0.80	2.40	50	11.53	46.1
11	<b>10</b>	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$	0.80	2.40	50	10.40	41.6
12	$\text{VOCl}_3$	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$	0.80	2.40	50	1.67	6.7
13	<b>9</b>	–	0	0	75	1.23	4.9
14	<b>10</b>	–	0	0	75	1.22	4.9
15	$\text{VOCl}_3$	–	0	0	75	1.39	5.6
16	<b>9</b>	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$	0.80	2.40	75	16.28	65.1
17	<b>10</b>	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$	0.80	2.40	75	10.94	43.8
18	$\text{VOCl}_3$	$\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$	0.80	2.40	75	1.34	5.4

<sup>a</sup> Conditions: atmospheric ethylene pressure; solvent, 400 ml toluene; polymerization time, 15 min; complex **9**, **10** or  $\text{VOCl}_3$ , 1.0  $\mu\text{mol}$ ;  $\text{Et}_2\text{AlCl}$ , 0.4 mmol; ETA, 0.4 mmol.

PE produced with complex **9**/ $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  using  $\text{H}_2$  (25  $^{\circ}\text{C}$ , ethylene/ $\text{H}_2$ , 100/(25 l h)) as a chain transfer agent possessed a narrow molecular weight distribution (2.50), suggesting that the  $\text{MgCl}_2$ -supported V complex **9** is a single-site catalyst. The dependence of catalytic activity on the polymerization temperature (50 and 75  $^{\circ}\text{C}$ ) was studied (Table 4). The data indicated that the activity observed at high temperatures is very dependent on the ligand structure and the presence or absence of  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ .  $\text{VOCl}_3$  showed considerably diminished activity at higher temperatures that was independent of the presence or absence of  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ , suggesting that catalyst deactivation is significant at elevated temperatures, which is probably an intrinsic feature of  $\text{VOCl}_3$ -based catalysts. Although phenoxy-imine ligated complexes **9** and **10** without  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  behaved as thermally-poor catalysts that are similar in behavior to  $\text{VOCl}_3$  catalysts, those with  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  proved to be remarkably effective catalysts. In the case of complex **10**/ $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$ , increasing the temperature afforded a corresponding increase in activity, though some catalyst deactivation occurred at 75  $^{\circ}\text{C}$ . Significantly, complex **9**/ $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  exhibited enhanced activity with increasing temperature and displayed a very high activity of 65.1 kg-PE/(mmol-cat h) at 75  $^{\circ}\text{C}$  with a steady uptake of ethylene. This is of great significance, because higher activity at elevated temperatures is desired for both process and economic considerations for V-based catalysts. These results clearly demonstrate that the phenoxy-imine ligand **9'** plays a role of vital importance in realizing a thermally robust V-based catalyst

system. This has been further confirmed by the fact that  $\text{V}(\text{acac})_3$  with  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  displayed much lower activity at 75  $^{\circ}\text{C}$  compared with that at 25  $^{\circ}\text{C}$  (e.g. 25  $^{\circ}\text{C}$ : 59.0 kg-PE/(mmol-cat h), 75  $^{\circ}\text{C}$ : 8.6 kg-PE/(mmol-cat h)). These results, as well as the single-site behavior of the complex **9** catalyst system, suggest that a combination of phenoxy-imine ligand **9'** and an  $\text{MgCl}_2$ -based compound results in a unique V-based catalyst.

Taking the above mentioned results into consideration, the productivity of complex **9** with the  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  catalyst system was examined over 5–60 min polymerization time at 75  $^{\circ}\text{C}$ . Notably, a steady rate of ethylene uptake ensued over the 60 min duration of the run, and thus the polymer yield increased proportionally with the polymerization time (Fig. 3).

These results suggest that catalyst deactivation is negligible, even at 75  $^{\circ}\text{C}$  and at atmospheric pressure for **9** with the  $\text{MgCl}_2$ -based cocatalyst. Such a thermally robust, long-lived V-based catalyst is unprecedented. In contrast,  $\text{VOCl}_3$  with and without  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  decayed rapidly and became practically inactive after ca. 15 min. These facts show that the combination of the phenoxy-imine ligand **9'** and  $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  affords unusual stability to an otherwise unstable active V center at elevated temperatures. The complex **9**/ $\text{MgCl}_2/\text{Et}_m\text{Al}(\text{OR})_n$  catalyst represents the first example of a highly-active, thermally robust, long-lived V-based catalyst at technical process temperatures.

Considering that V(IV) is readily reduced to the V(II) state (which is one of the common deactivation pathways

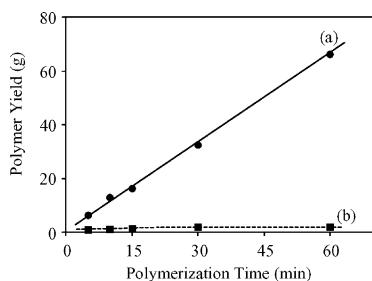


Fig. 3. Plot of polymer yield vs. polymerization time for ethylene polymerization with complex **9**/MgCl<sub>2</sub>/Et<sub>m</sub>Al(OR)<sub>n</sub> and VOCl<sub>3</sub>. Conditions: 75 °C; atmospheric ethylene pressure; solvent, 400–1600 ml toluene; (a) complex **9**, 1.0 μmol; MgCl<sub>2</sub>/Et<sub>m</sub>Al(OR)<sub>n</sub>, 0.8 mmol (Mg); Et<sub>2</sub>AlCl, 0.4 mmol; ETA, 0.4 mmol; (b) VOCl<sub>3</sub>, 1.0 μmol; Et<sub>2</sub>AlCl, 0.4 mmol; ETA, 0.4 mmol.

for V-based catalysts) the phenoxy-imine ligand **9'** may stabilize the higher oxidation state of the V center. In addition, MgCl<sub>2</sub>/Et<sub>m</sub>Al(OR)<sub>n</sub>, which works as a support, probably impedes ligand leaching from the V center, as well as bimolecular deactivation of the V catalyst [85]. Thus, the combination of the phenoxy-imine ligand **9'** and MgCl<sub>2</sub>/Et<sub>m</sub>Al(OR)<sub>n</sub> gave rise to an unprecedented V-based olefin polymerization catalyst system. A theoretical study is in progress in order to elucidate the difference in catalytic performance of **9** and **10** catalyst systems, focusing on the steric and electronic properties of the structurally-different phenoxy-imine ligands **9'** and **10'**.

As an example of an application for this unique catalyst system (complex **9**/MgCl<sub>2</sub>/Et<sub>m</sub>Al(OR)<sub>n</sub>), ethylene-propylene copolymerization was performed at 75 °C. The system formed an amorphous copolymer with a propylene content of 21.3 mol% (<sup>13</sup>C NMR). The copolymer consists of randomly distributed monomer units (PPP: 1.75%, PPE: 4.80%, EPE: 14.16%, PEP: 50.81%, EEP: 24.10%, and EEE: 4.38%), and contains a certain amount of propylene inverted units (3.4%). GPC analysis showed that the copolymer possesses a very high *M<sub>w</sub>* of 697,000 with a relatively broad molecular weight distribution of 4.72. The reason for the formation of the relatively broad molecular weight distribution copolymer is unclear at the present time. Remarkably, the GPC-IR study revealed that the longer copolymer chains possess higher comonomer content (Fig. 4). This

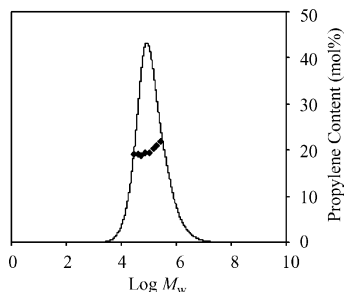


Fig. 4. GPC-IR chart of the ethylene-propylene copolymer arising from **9**/MgCl<sub>2</sub>/Et<sub>m</sub>Al(OR)<sub>n</sub>.

comonomer distribution is rather unexpected but should have beneficial effects on material properties.

The high cocatalytic performance of MgCl<sub>2</sub>-based compounds for bis(phenoxy-imine) complexes have been described so far. It should be pointed out that MgCl<sub>2</sub> is a poor cocatalyst for group 4 metallocene catalysts. On the basis of the results introduced herein, as well as the high cocatalytic performance of MgCl<sub>2</sub> for MgCl<sub>2</sub>-supported TiCl<sub>4</sub> catalysts, it seems reasonable that the high cocatalytic performance of MgCl<sub>2</sub> for bis(phenoxy-imine) complexes originates from an electronic interaction between the O, N heteroatoms in the ligands and MgCl<sub>2</sub>. From these results, MgCl<sub>2</sub>-based compounds are expected to function as good cocatalysts for transition metal complexes possessing heteroatom(s) in the ligand (non-metallocene complexes) [24,105–107]. In fact, the diimine-pyridine ligated Fe complexes developed by Brookhart [109] and Gibson [108] in combination with an MgCl<sub>2</sub>-based compound can be high-activity catalysts for the polymerization of ethylene, which will be discussed elsewhere.

#### 4. Conclusion

In summary, we have introduced a family of new olefin polymerization catalyst systems composed of bis(phenoxy-imine) Zr, Ti or V complexes (Zr-, Ti- or V-FI catalysts) and MgCl<sub>2</sub>-based cocatalysts. These can be strikingly active (Zr-FI catalysts), highly active single-site (Ti-FI catalysts) or highly active, thermally robust, single-site (V-FI catalysts) catalysts for ethylene polymerization. These new catalyst systems behave as MgCl<sub>2</sub>-supported catalysts and thus have the potential for control of polymer morphology in addition to their unique catalysis properties. The results described herein indicate the exceptionally high potential of MgCl<sub>2</sub>-based compounds as cocatalysts and highlight a strategy for developing unique olefin polymerization catalysts by the combination of transition metal complexes having heteroatoms in the ligands (non-metallocene complexes) with MgCl<sub>2</sub>, which is a pivotal component of the industrially-dominant Ziegler-Natta catalysts. It is expected that the chemistry of these compounds will provide an insight into the catalysis of heterogeneous and multi-site Ziegler-Natta catalysts.

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