Four- and five-coordinate magnesium compounds containing ketiminate ligands. Synthesis and characterization of L₂Mg, L₂Mg(LH), and L₂Mg(Py), where L = MeC(O)CHC(NAr)Me

Wen-Yi Lee [a], Hsiang-Hua Hsieh [a], Chun-Chin Hsieh [a], Hon Man Lee [a], Gene-Hsiang Lee [b],
Jui-Hsien Huang [a,*], Tsun-Cheng Wu [c], Shiow-Huey Chuang [c,*]

[a] *Department of Chemistry, National Changhua University of Education, 1 Jing-Der Road, Changhua 50058, Taiwan*
[b] *Department of Chemistry, National Taiwan University, Taipei 106, Taiwan*
[c] *Department of Applied Chemistry, National University of Kaohsiung, Kaohsiung 811, Taiwan*

Abstract

Magnesium complexes containing ketiminate ligands were synthesized and characterized. MgBu₂ reacted readily in toluene with two equiv. of [MeC(O)CHC(NHAr)Me], where Ar = 2,6-diisopropylphenyl, to generate [MeC(O)CHC(NAr)Me]₂Mg (1) in 43% yield. The four-coordinate magnesium compound 1 is very moisture sensitive and acts as a Lewis acid, accepting one equiv. of Lewis base to form five-coordinate magnesium compounds. Compound [MeC(O)CHC(NAr)Me]₂Mg[MeC(O)CHC(NHAr)Me] (2) was obtained in 57% yield from the reaction in toluene of MgBu₂ with three equiv. of [MeC(O)CHC(NHAr)Me]. Treatment of 1 with one equiv. of free ketimine ligands [MeC(O)CHC(NHAr)Me] also led to the formation of 2. The bulky η¹-ketimine of 2 can be replaced with a less bulky Lewis base such as pyridine. Treatment of 1 with excess pyridine in toluene at ambient temperature led to the formation of compound [MeC(O)CHC(NAr)Me]₂Mg[NC₅H₅] (3) as colorless crystalline solids in 51% yield. Compounds 1, 2, and 3 were characterized by NMR and X-ray crystallography. Compounds 2 and 3 showed no activity toward the polymerization of ε-caprolactone at 25 °C after 3 h. However, when the temperature was increased to 70 °C, compounds 2 and 3 efficiently catalyzed polymerization of ε-caprolactone to generate high molecular weight poly-ε-caprolactones. The polydispersity index (PDI) of these poly-ε-caprolactones is in the range 1.57–3.18.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Magnesium; Ketiminate; Caprolactone

1. Introduction

β-Diketiminate ligands [HC(C(R)N(R′))₂]⁻ have been widely studied in transition metal chemistry for over a decade [1]. Metals involved in the chemistry range from main group metals [2] to transition metals [3] and bond to the two nitrogen atoms of β-diketiminate ligands, forming two metal–nitrogen σ-bonds. Bulky ligands can stabilize metal complexes; however, they can also sterically hinder the entrance of reactants into the metal complex reaction centers. Bidentate mono-anionic ketiminate ligands [4] can bind to metals to form a six-membered ring, causing the metal atoms to be surrounded by bulky substituents on one side but leaving the other side open.

Monomeric magnesium compounds [5] containing various ligands have attracted much attention because of their potential uses in chemical vapor deposition (CVD), as dopant precursors [6], and as catalysts in ring-opening polymerization [7]. An advantage to using magnesium for these applications is its low toxicity. In addition, magnesium has a suitable energy level to act as an acceptor for the group III-nitride semiconductors [8]. Reactivity studies

---

* Corresponding author. Tel.: +886 4 7232105x3531; fax: +886 4 7211190.
E-mail address: juihuang@cc.ncue.edu.tw (J.-H. Huang).

using magnesium compounds as catalysts for the ring-opening polymerization of ε-caprolactone and lactides have shown promising results [7a,7d].

We previously reported on the chemistries of aluminum and titanium complexes containing ketiminate ligands [9]. Here we describe the synthesis and structural characterization of a series of magnesium complexes that contain bidentate monoanionic ketiminate ligands. In addition, we explored the catalytic reactivities of two of these compounds towards the ring-opening polymerization of ε-caprolactones.

2. Results and discussion

2.1. Synthesis of compounds 1–3

The reactions of MgBu$_2$ with free ketimine ligands and successive reactions are summarized in Scheme 1. MgBu$_2$ reacted readily with two equiv. of [MeC(O)CHC(N-HAr)Me], where Ar = 2,6-diisopropylphenyl, in toluene at 50 °C for 12 h, with the elimination of two equiv. of butane to yield [MeC(O)CHC(NAr)Me]$_2$Mg (1). Colorless crystals of 1 can be obtained in 43% yield from a saturated heptane solution of 1. Compound 1 was characterized by NMR spectroscopy and X-ray crystallography. The ^{1}H and ^{13}C{^{1}H} NMR spectra of 1 exhibit a single resonance for the methine protons of the ketiminate backbones at δ 4.94 and 98.2, respectively, which are upfield shifts compared to the free ketimine ligands and are similar to the chemical shifts of related aluminum ketiminate compounds [9c]. In addition, compound 1 exhibits only two singlet resonances for the methyl group of the ketiminate backbones,

reflecting a pseudo-C_2 symmetry of the compound in solution at room temperature. Two types of isopropyl resonances are also observed in the ^{1}H NMR spectra, indicating slow rotation of the N–Ar bonds due to the large steric hindrance.

The four-coordinate magnesium compound 1 is very moisture sensitive and acts as a Lewis acid, accepting one equiv. of Lewis base to form five-coordinate magnesium compounds. Compound [MeC(O)CHC(NAr)Me]$_2$Mg[Me-C(O)CHC(NHAr)Me] (2) can be obtained in 57% yield from the reaction in toluene of MgBu$_2$ with three equiv. of [MeC(O)CHC(NHAr)Me]. Treatment of 1 with one equiv. of free ketimine ligands [MeC(O)CHC(NHAr)Me] also leads to the formation of 2. It is noteworthy that compound 2 contains two equiv. of η^2-ketiminate ligands and one equiv. of η^1-ketimine ligand, which acts as a Lewis base and coordinates to magnesium through the oxygen end of the ketiminate backbone. Therefore, we must exercise caution in identifying the chemical shifts for the η^2-ketiminate and η^1-ketimine. A series of ^{1}H, ^{13}C{^{1}H}, proton-coupling ^{13}C, DEPT, and ^{1}H–^{13}C HSQC NMR spectra has been used to identify methyl and isopropyl groups of the ketiminate and ketimine ligands [10]. The characteristic resonances for the methine protons of η^2-ketiminate and η^1-ketimine fragments appeared in a 2:1 ratio at δ 4.82 and 4.89, respectively. The downfield resonance at δ 11.7 represents the resonance of HNCMe for the η^1-ketimine ligand. It is interesting to note that only two methyl resonances are observed at δ 1.28 and 1.37 for the isopropyl fragments of the η^2-ketiminate phenyl substituted rings, despite a bulky ketimine being coordinated at the magnesium center. A reasonable explanation

Ar = 2,6-diisopropylphenyl
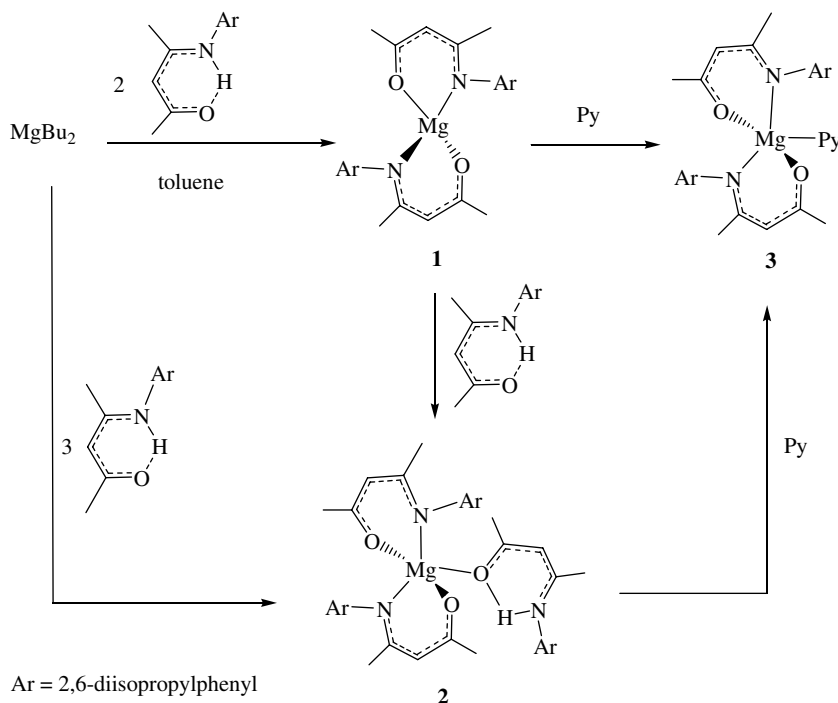
Scheme 1.

for this phenomenon is that in the NMR time scale the Mg–O (ketimine) bond in solution results in a pseudo-C_2 symmetric geometry for compound **2**.

The five-coordinate compound **2** contains a free ketimine ligand that bonds to magnesium through the oxygen atom, demonstrating the Lewis acidity and oxophilicity of the magnesium center in compound **1**. The bulky η^1-ketimine of **2** can be replaced by a less bulky Lewis base such as pyridine. Treatment of **1** with excess pyridine in toluene at ambient temperature led to the formation of compound [MeC(O)CHC(NAr)Me]$_2$Mg[NC$_5$H$_5$] (**3**) as colorless crystalline solids in 51% yield. The same results can be obtained from the reaction of **2** with excess pyridine, and the generated free ketimine can be removed by recrystallizing the resulting mixture in a diethyl ether solution. Compound **3** is relative stable which remain intact after prolonged vacuum dried. Compound **3** was also characterized by NMR spectra and X-ray crystal structure determination. The methine protons of the two ketiminate backbones exhibit a single resonance at δ 4.86, indicating the symmetrical arrangement of the two ketiminate ligands. In the proton-coupling ^{13}C NMR spectra, the methine carbon exhibits a doublet at δ 96.0 with $^1J_{CH} = 155$ Hz. These data reflect the fast rotation of the Mg–N (pyridine) bond in solution, which results in a pseudo-symmetrical structure for compound **3**.

2.2. Thermal properties of compounds 1 and 2

The thermal properties of compounds **1** and **2** were investigated. Compound **1** is relatively thermally unstable, decomposing at 100 °C to yield five-coordinate compound

2 and free ketimine ligands. Compound **2** shows appreciable volatility at 270 °C and 4×10^{-5} bar, which makes it a suitable magnesium or magnesium oxide precursor for liquid injection in CVD and metalorganic chemical vapor deposition (MOCVD) techniques.

2.3. Molecular structures of 1–3

The solid-state structures of compounds **1–3** were determined by X-ray crystallography. Crystallographic data and selected bond lengths and angles are presented in Tables 1 and 2, respectively. The molecular structures of **1–3** are presented in Figs. 1–3.

Very few examples of ketiminate magnesium compounds have been seen in the literature. Matthews et al. published a couple of papers mentioned monomeric and dimeric ketiminate magnesium compounds [11]. Compound **1** exhibits C_2 symmetry and features a highly distorted tetrahedral geometry with the two η^2-ketiminate ligands bonded to the magnesium center. The bond angles of O(1)–Mg(1)–O(1A) and N(1)–Mg(1)–N(1A) are 143.43(10)° and 141.08(8)°, respectively. The η^2-ketiminate ligands coordinate to the magnesium atom with a bite angle of 91.57(6)°, smaller than the angle for regular tetrahedral geometry (109.28°). The bond lengths for the ketiminate backbones O(1A)–C(2), C(3)–C(4), C(2)–C(3), and N(1)–C(4) are in the range 1.280(2)–1.413(2) Å, reflecting partial double bonds in the six-membered Mg-ketiminate ring. The magnesium atom ascends above the ketiminate O(1A)–C(2)–C(3)–C(4)–N(1) plane by 0.3783 Å, and the bond lengths of the magnesium to the oxygen and nitrogen atoms of the ketiminate are Mg(1)–O(1) = 1.8955(15) Å

Table 1
Summary of crystallographic data for compounds **1**, **2**, and **3**

Compound	1	2	3
Formula	C$_{34}$H$_{48}$MgN$_2$O$_2$	C$_{54}$H$_{79}$MgN$_3$O$_3$	C$_{39}$H$_{53}$MgN$_3$O$_2$
Formula weight	541.05	842.51	620.15
T (K)	150(2)	150(1)	150(1)
Space group	Monoclinic	Triclinic	Orthorhombic
Crystal system	$C2/c$	$P\bar{1}$	$Fdd2$
a (Å)	23.751(12)	12.4066(2)	19.0375(7)
b (Å)	12.110(7)	12.6657(2)	24.5278(9)
c (Å)	11.639(6)	18.3241(2)	31.3408(11)
α (°)	90	84.4536(7)	90
β (°)	107.342(10)	77.4041(8)	90
γ (°)	90	64.2184(7)	90
V (Å^3)	3196(3)	2530.39(6)	14634.5(9)
Z	4	2	16
D_{calc} (Mg/m^3)	1.125	1.106	1.126
μ (mm^{-1})	0.086	0.078	0.084
$F(000)$	1176	920	5376
λ (Å)	0.71073	0.71073	0.71073
Number of reflections collected	11 104	40 291	33 021
Number of independent reflections (R_{int})	3636 (0.0702)	11 550 (0.0373)	7952 (0.0613)
Data/restraints/parameters	3636/0/177	11 550/2/551	7952/1/421
Goodness-of-fit on F^2	1.018	1.084	1.239
R_1, wR_2 [$I > 2 \sigma(I)$]	0.0499, 0.1058	0.0777, 0.2127	0.0679, 0.1533
R_1, wR_2 (all data)	0.0688, 0.1610	0.1101, 0.2429	0.0767, 0.1629
Largest difference in peak and hole (e/Å^3)	0.431 and −0.396	0.836 and −0.639	0.284 and −0.288

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1**, **2**, and **3**

Compound 1

Mg(1)–O(1)	1.8955(15)	Mg(1)–N(1)	2.0589(15)
O(1)–Mg(1)–O(1A)	143.43(10)	O(1)–Mg(1)–N(1)	100.46(6)
O(1A)–Mg(1)–N(1)	91.57(6)	O(1)–Mg(1)–N(1A)	91.57(6)
N(1)–Mg(1)–N(1A)	141.08(8)		

Compound 2

Mg–O(1)	1.9633(16)	Mg–O(2)	1.9814(16)
Mg–O(3)	2.0252(17)	Mg–N(2)	2.1594(19)
Mg–N(2)	2.1628(19)		
O(1)–Mg–O(2)	178.62(7)	O(3)–Mg–N(1)	115.14(7)
O(3)–Mg–N(2)	114.33(7)	N(1)–Mg–N(2)	130.50(7)
N(1)–Mg–O(1)	86.25(7)	N(2)–Mg–O(2)	87.04(7)

Compound 3

Mg(1)–O(1)	1.9475(19)	Mg(1)–N(1)	2.135(2)
Mg(1)–N(2)	2.216(4)	Mg(2)–O(2)	1.942(2)
Mg(2)–N(3)	2.152(3)	Mg(2)–N(4)	2.213(4)
O(1)–Mg(1)–O(1A)	174.87(16)	N(1)–Mg(1)–N(2)	117.30(7)
N(1A)–Mg(1)–N(2)	117.30(7)	N(1)–Mg(1)–N(1A)	125.40(15)
O(2)–Mg(2)–O(2A)	179.29(17)	N(3)–Mg(2)–N(3A)	132.84(15)
N(3A)–Mg(2)–N(4)	113.58(7)	N(3)–Mg(2)–N(4)	113.358(7)

Fig. 2. The molecular structure of compound **2**. Thermal ellipsoids were drawn at 30% probabilities, and hydrogen atoms and hexane carbon atoms were omitted for clarity.

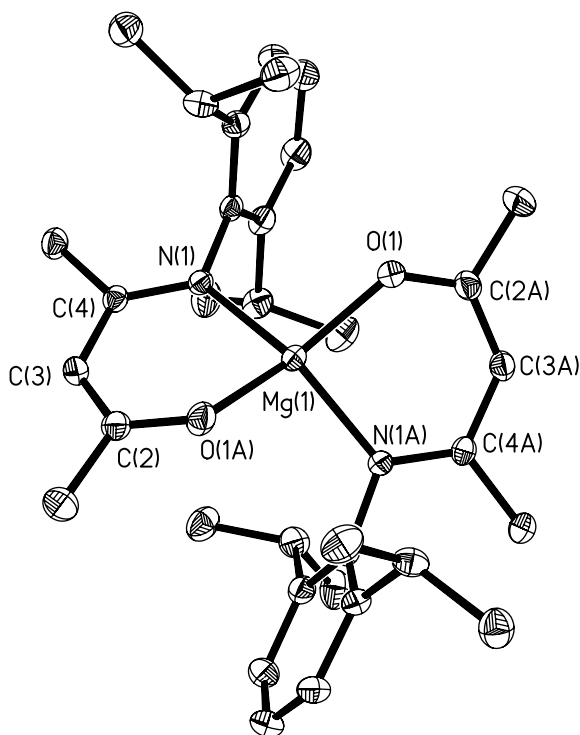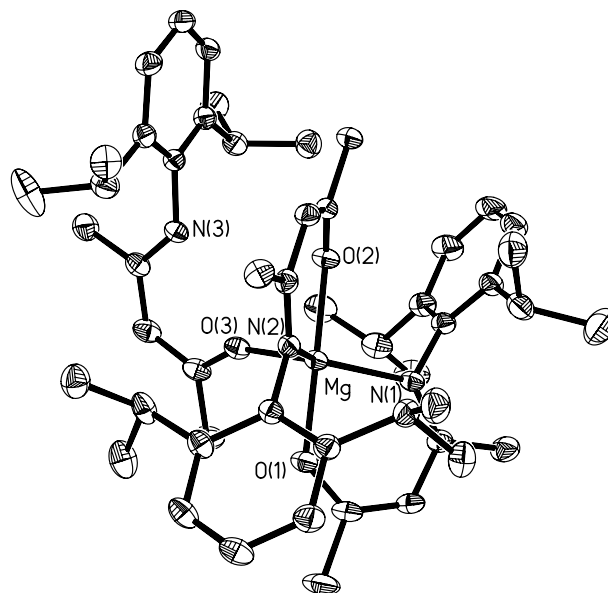

Fig. 1. The molecular structure of compound **1**. Thermal ellipsoids were drawn at 50% probabilities, and hydrogen atoms were omitted for clarity.
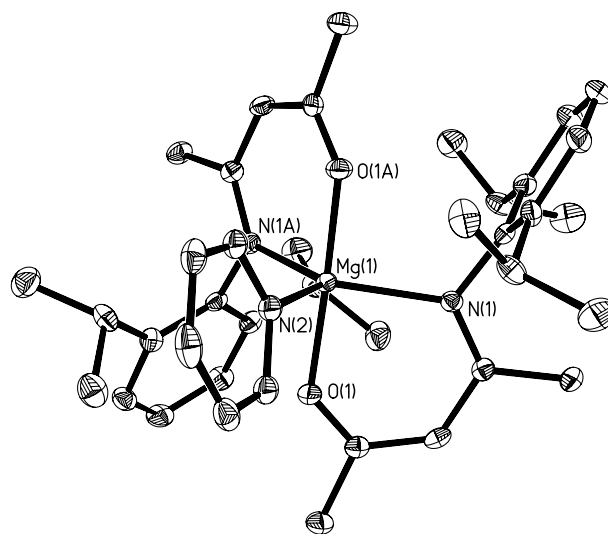

Fig. 3. The molecular structure of compound **3**. Thermal ellipsoids were drawn at 30% probabilities, and hydrogen atoms were omitted for clarity.
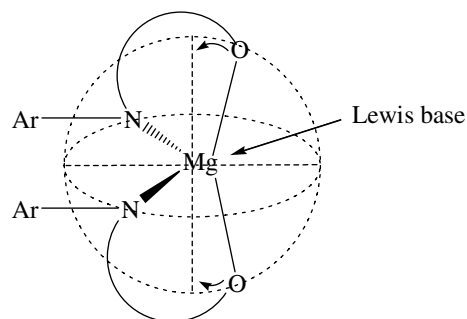
Fig. 4. A schematic drawing for compound **1**, showing the open side of the magnesium atom susceptible for the Lewis base attack.

and Mg(1)–N(1A) = 2.0589(15) Å. Fig. 4 shows how the two nitrogen atoms of the two ketiminate ligands in compound **1** lie in the horizontal circular plane, while the two oxygen atoms of the two ketiminate ligands are located in the perpendicular circular plane. Closer examination of the structure of **1** revealed that the aryl fragments of

the ketiminate protect one side of the magnesium center, leaving the magnesium atom accessible on the other side. As a result, the open side of the magnesium center exhibits a nucleophilicity susceptible to Lewis base attack. As shown in Fig. 4, several structural changes occur when a Lewis base attaches to the magnesium center: (i) the molecular geometry changes from a highly distorted tetrahedral to a trigonal bipyramidal structure, (ii) the two oxygen atoms of the two ketiminate ligands occupy the axial positions and become linear, and (iii) the bite angles of the ketiminate ligands become smaller due to the constrained geometry. The molecular structures of **2** and **3** reflect these phenomena.

Crystals of **2** and **3** were obtained from a saturated toluene solution and a diethyl ether solution, respectively. The unit cell of crystal **2** contains a half molecule of hexane which may come from the dibutylmagnesium solution. The hexane atoms were omitted in the molecular structure of **2** (Fig. 2) for clarity. There are two independent molecules of **3** in a unit cell. However, the molecular structures of these two molecules are similar; therefore, only one of the molecules is shown in Fig. 3. As described previously, Lewis bases attack the magnesium atoms on one side, resulting in the distorted trigonal bipyramidal **2** and **3**. The magnesium atoms in both **2** and **3** exhibit trigonal bipyramidal geometries, with the oxygen atoms of the ketiminate ligands occupying the axial positions [O(1)–Mg–O(2) = 178.62(7)° for **2** and O(1)–Mg(1)–O(1A) = 174.87(16)° for **3**]. The bite angles of the ketiminate ligands with the magnesium atoms vary from 86.25(7)° to 88.44(9)°, very close to those for compound **1**. The Mg–O and Mg–N bond lengths for compounds **2** and **3** are longer than those for compound **1** due to the larger steric congestion.

2.4. Ring-opening polymerization of ε-caprolactone catalyzed by compounds 2 and 3

Ring-opening polymerization of ε-caprolactone was performed using compounds **2** and **3** as catalysts. A summary of the polymerization data are shown in Table 3. Compounds **2** and **3** showed no activity toward the polymerization of ε-caprolactone at 25 °C after 3 h. However, when the temperature was increased to 70 °C, compounds **2** and **3** efficiently catalyzed polymerization of ε-caprolactone to generate high molecular weight poly-ε-caprolactones. The polydispersity index (PDI) of these poly-ε-caprolactones is in the range 1.57–3.18, slightly larger than the poly-ε-caprolactones catalyzed by related magnesium compounds [12].

We have synthesized a series of magnesium compounds **1–3** and found compounds **2** and **3** efficiently catalyzed polymerization of ε-caprolactone to generate high molecular weight poly-ε-caprolactones at 70 °C. We now are investigating the influence of the Lewis bases on the molecular structures and polymerization activity of the five-coordinate magnesium compounds.

Table 3
Ring-opening polymerization of ε-caprolactone catalyzed by compounds **2** and **3**

Entry	Catalyst	[M]/[C]	T (°C)	Yield (%)	M_w[b]	M_n[c]	PDI
1	**2**	100	25	–	–	–	–
2	**2**	50	70	69	38 487	15 287	2.52
3	**2**	100[a]	70	98	125 000	79 428	1.57
4	**2**	150[a]	70	91	105 289	50 393	2.09
5	**2**	200[a]	70	97	161 717	87 586	1.85
6	**3**	100	25	–	–	–	–
7	**3**	50	70	89	59 971	18 854	3.18
8	**3**	100	70	91	68 347	26 359	2.59
9	**3**	150[a]	70	96	118 080	52 843	2.23
10	**3**	200[a]	70	98	105 293	57 697	1.82

–: no reaction was observed.
[a] The solution solidified during the 3-h reaction time.
[b] Weight average molecular weight.
[c] Number average molecular weight.

3. Experimental

3.1. General procedures

All the reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a glove box. Toluene and diethyl ether were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. All solvents were distilled and stored in solvent reservoirs which contained 4 Å molecular sieves and were purged with nitrogen. ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker Avance 300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to the residual proton and ^{13}C of CDCl$_3$ (δ 7.24, 77.0) and C$_6$D$_6$ (δ 7.15, 128.0). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU. [OCMeCHC-MeNH(Ar)] was prepared according to a previously reported procedure [9].

3.2. Synthesis of [OCMeCHCMeN(Ar)]₂Mg (1)

A 100 mL Schlenk flask containing [OCMeCHC-MeNH(Ar)] (1.04 g, 4.00 mmol) was cooled to −78 °C and 20 mL toluene was added. To the toluene solution, MgBu$_2$ (1.0 M, 2.0 mL, 2.00 mmol) was added through a syringe. The solution was warmed to room temperature and heated to 50 °C for 12 h. The resulting solution was vacuum dried and the solid was recrystallized from heptane to yield 0.47 g of white solid in 43% yield. ^1H NMR (C$_6$D$_6$): 1.12 (d, 12H, CHMe*Me*), 1.20 (d, 12H, CHMe*Me*) 1.47 (s, 6H, C*Me*), 1.65 (s, 6H, C*Me*), 3.13 (m, 4H, C*H*Me$_2$), 4.94 (s, 2H, CMeC*H*CMe), 7.10 (m, 6H, phenyl C*H*). ^{13}C NMR (C$_6$D$_6$): 23.2 (q, J_{CH} = 127 Hz, NC*Me*), 24.29 (q, J_{CH} = 126 Hz, CHMe*Me*), 24.34 (q, J_{CH} = 126 Hz, CHMe*Me*), 27.0 (q, J_{CH} = 129 Hz, OC*Me*), 28.4 (d, J_{CH} = 128 Hz, *C*HMe$_2$), 98.2 (d, J_{CH} = 157 Hz, CMe*C*HCMe), 123.8 (d, J_{CH} = 152 Hz, phenyl *C*H), 125.6 (d, J_{CH} = 159 Hz, phenyl *C*H), 141.8 (s, phenyl

C_{ipso}), 144.2 (s, phenyl C_{ipso}), 174.8 (s, C_{ipso}), 184.3 (s, C_{ipso}). A consistent set of elemental analysis data could not be obtained even where pure crystals were used for analysis. We attributed the problem to the air sensitivity of **1**.

3.3. Synthesis of [OCMeCHCMeN(Ar)]₂Mg-[OCMeCHCMeNH(Ar)] (2)

The same procedure for **1** is applied where MgBu₂ (1.0 M, 2.0 mL, 2 mmol) and three equiv. of [OCMeCHC-MeNH(Ar)] (1.556 g, 6.0 mmol) were used. Products were recrystallized from a saturated toluene solution to yield 0.91 g of colorless tetragonal crystals (57%). ^{1}H NMR (C₆D₆): 1.06 (d, 6H, CHMe*Me*), 1.09 (s, 6H, C*Me*), 1.13 (d, 6H, CH*Me*Me), 1.26 (s, 3H, C*Me*), 1.28 (d, 12H, CHMe*Me*), 1.37 (d, 12H, CHMe*Me*), 1.60 (s, 6H, C*Me*), 2.04 (s, 3H, C*Me*), 3.26 (br, 2H, *CH*MeMe), 3.28 (sept, 4H, *CH*MeMe), 4.82 (s, 2H, CMeC*H*CMe), 4.89 (s, 1H, CMeC*H*CMe), 6.97–7.18 (m, 9H, phenyl C*H*), 11.70 (s, 1H, CMeN*H*). ^{13}C NMR (C₆D₆): 19.6 (q, J_{CH} = 129 Hz, C*Me*), 23.6 (q, J_{CH} = 125 Hz, C*Me* and CHMe*Me*), 24.2 (q, J_{CH} = 130 Hz, C*Me*), 24.3 (q, J_{CH} = 127 Hz, CH*Me*Me), 25.0 (q, J_{CH} = 125 Hz, CH*Me*Me), 26.5 (q, J_{CH} = 125 Hz, CHMe*Me*), 27.0 (q, J_{CH} = 127 Hz, C*Me*), 28.3 (d, J_{CH} = 125 Hz, *CH*MeMe and *CH*MeMe), 96.9 (d, J_{CH} = 158 Hz, CMe*C*HCMe), 97.0 (d, J_{CH} = 158 Hz, CMe*C*HCMe), 123.0 (d, J_{CH} = 156 Hz, phenyl *C*H), 123.9 (d, J_{CH} = 158 Hz, phenyl *C*H), 128.3 (d, J_{CH} = 158 Hz, phenyl *C*H), 129.0 (d, J_{CH} = 160 Hz, phenyl *C*H), 133.8 (s, phenyl C_{ipso}), 141.3 (s, phenyl C_{ipso}), 146.0 (s, phenyl C_{ipso}), 148.3 (s, phenyl C_{ipso}), 166.3 (s, C*Me*), 171.8 (s, C*Me*), 181.6 (s, C*Me*), 195.9 (s, C*Me*). Anal. Calc. for MgC₅₁H₇₃N₃O₃: C, 76.53; H, 9.19; N, 5.25. Found: C, 76.78; H, 9.03; N, 5.16%.

3.4. Synthesis of [OCMeCHCMeN(Ar)]₂Mg(C₅H₅N) (3)

A 50 mL Schlenk flask containing **1** (1.08 g, 2.00 mmol) and 20 mL toluene was cooled to 0 °C. To the toluene solution, excess pyridine in 10 mL toluene was added dropwise. The solution was warmed to room temperature and stirred for 6 h. The resulting solution was vacuum dried and the solid was recrystallized from diethyl ether to yield 0.63 g of colorless crystals in 51% yield. ^{1}H NMR (CDCl₃): 0.82 (s, 12H, CHMe*Me*), 1.05 (d, 12H, CHMe*Me*), 1.32 (s, 6H, C*Me*), 1.57 (s, 6H, C*Me*), 2.85 (m, 4H, *CH*Me₂), 4.86 (s, 2H, CMeC*H*CMe), 7.02 (m, 6H, phenyl C*H*), 7.34 (m, 2H, pyridine C*H*), 7.77 (m, 1H, pyridine C*H*), 8.52 (m, 2H, pyridine C*H*). ^{13}C NMR (CDCl₃): 23.6 (q, J_{CH} = 126 Hz, CHMe*Me*), 23.9 (q, J_{CH} = 127 Hz, C*Me*), 24.4 (q, J_{CH} = 125 Hz, CHMe*Me*), 26.2 (q, J_{CH} = 126 Hz, C*Me*), 27.7 (d, J_{CH} = 129 Hz, *CH*Me₂), 96.0 (d, J_{CH} = 155 Hz, CMe*C*HCMe), 122.5 (d, J_{CH} = 154 Hz, pyridine C*H*), 123.4 (d, J_{CH} = 158 Hz, phenyl C*H*), 123.9 (d, J_{CH} = 165 Hz, phenyl C*H*), 137.8 (d, J_{CH} = 160 Hz, pyridine C*H*), 141.1 (s, phenyl C_{ipso}), 147.2 (s, N-C_{ipso}), 150.1 (d, J_{CH} = 183 Hz, pyridine C*H*), 172.2 (s, C*Me*), 182.0 (s, C*Me*). Anal. Calc. for MgC₃₉H₅₃N₃O₂: C, 75.53; H, 8.61; N, 6.78. Found: C, 75.31; H, 8.19; N, 6.32%.

3.5. General polymerization procedure

ε-Caprolactone and catalysts (0.03 g) were dissolved in toluene (5 mL each) in separate flasks. A flask containing catalyst was immersed in an oil bath at desire temperature and then the ε-caprolactone solution was added. The reaction was stirred at a given temperature for 3 h. The polymerization was quenched with excess methanol. The precipitated polymer was then filtered and dried under vacuum.

3.6. Crystallographic structural determination of 1, 2, and 3

Crystal data collection and refinement parameter and bond length and angles are listed in Tables 1 and 2, respectively. The crystals were mounted on capillaries and transferred to a goniostat and were collected at 150 K under nitrogen stream. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo Kα radiation. Structure determinations were performed using the SHELXTL package of programs. All refinements were carried out by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms are included in calculated positions into the refinements.

Appendix A. Supplementary material

CCDC 626116, 626117, and 626118 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.11.015.

References

[1] (a) L. Bourget-Merle, M.F. Lappert, J.R. Severn, Chem. Rev. 102 (2002) 3031–3065;
(b) V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283–315;
(c) O. Kuhl, Coord. Chem. Rev. 248 (2004) 411–427;
(d) M.F. Lappert, J. Organomet. Chem. 600 (2000) 144–158.
[2] (a) H.M. El-Kaderi, A. Xia, M.J. Heeg, C.H. Winter, Organometallics 23 (2004) 3488–3495;
(b) V.C. Gibson, J.A. Segal, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 122 (2000) 7120–7121;

(c) P.J. Bailey, R.A. Coxall, C.M. Dick, S. Fabre, S. Parsons, Organometallics 20 (2001) 798–801;

(d) M.H. Chisholm, J. Gallucci, K. Phomphrai, Inorg. Chem. 41 (2002) 2785–2794;

(e) S.S. Kumar, S. Singh, H.W. Roesky, J. Magull, Inorg. Chem. 44 (2005) 1199–1201;

(f) M.R. Crimmin, I.J. Casely, M.S. Hill, J. Am. Chem. Soc. 127 (2005) 2042–2043;

(g) A.G. Avent, M.R. Crimmin, M.S. Hill, P.B. Hitchcock, Dalton Trans. (2005) 278–284.

[3] (a) R. Andres, E. de Jesus, F.J. de la Mata, J.C. Flores, R. Gomez, J. Organomet. Chem. 690 (2005) 939–943;

(b) D.S. Laitar, C.J.N. Mathison, W.M. Davis, J.P. Sadighi, Inorg. Chem. 42 (2003) 7354–7356;

(c) N.A. Eckert, E.M. Bones, R.J. Lachicotte, P.L. Holland, Inorg. Chem. 42 (2003) 1720–1725;

(d) J.M. Smith, R.J. Lachicotte, P.L. Holland, J. Am. Chem. Soc. 125 (2003) 15752–15753;

(e) P.B. Hitchcock, M.F. Lappert, A.V. Protchenko, Chem. Commun. (2005) 951–953;

(f) G.B. Nikiforov, H.W. Roesky, J. Magull, M. Noltemeyer, H.-G. Schmidt, E.G. Ilyin, Y.B. Kokunov, A. Demsar, Eur. J. Inorg. Chem. (2003) 437–441.

[4] (a) P.L. Franceschini, M. Morstein, H. Berke, H.W. Schmalle, Inorg. Chem. 42 (2003) 7273–7282;

(b) P. Shukla, J.C. Gordon, A.H. Cowley, J.N. Jones, J. Organomet. Chem. 690 (2005) 1366–1371;

(c) L. Kakaliou, W.J. Scanlon, B. Qian, S.W. Baek, M.R. Smith III, D.H. Motry, Inorg. Chem. 38 (1999) 5964–5977.

[5] (a) P. Wei, D.W. Stephan, Organometallics 22 (2003) 601–604;

(b) A. Xia, M.J. Heeg, C.H. Winter, Organometallics 21 (2002) 4718–4725;

(c) R.J. Wehmschulte, B. Twamley, M.A. Khan, Inorg. Chem. 40 (2001) 6004–6008;

(d) M. Gillett-Kunnath, W. Teng, W. Vargas, R. Ruhlandt-Senge, Inorg. Chem. 44 (2005) 4862–4870;

(e) I.L. Fedushkin, A. Alexandra, V.A. Chudakova, G.K. Fukin, S. Dechert, H. Schumann, Eur. J. Inorg. Chem. (2003) 3336–3346.

[6] (a) A.R. Sadique, M.J. Heeg, C.H. Winter, Inorg. Chem. 40 (2001) 6349–6355;

(b) C.H. Winter, J.L. Sebestl, M.J. Heeg, Mater. Res. Soc. Sym. Proc. 37 (1998) 1289–1294.

[7] (a) M.H. Chisholm, N.W. Eilerts, J.C. Huffman, S.S. Iyer, M. Pacold, K. Phomphrai, J. Am. Chem. Soc. 122 (2000) 11845–11854;

(b) Y. Sarazin, M. Schormann, M. Bochmann, Organometallics 23 (2004) 3296–3302;

(c) J. Ejfler, M. Kobylka, L.B. Jerzykiewicz, P. Sobota, Dalton Trans. (2005) 2047–2050;

(d) M.H. Chisholm, J.C. Huffman, K. Phomphrai, J. Chem. Soc., Dalton Trans. (2001) 222–224.

[8] M. Heuken, J. Söllner, W. Taudt, S. Lampe, H. Hamadeh, J. Crystal Growth 170 (1997) 30–38.

[9] (a) P.-C. Kuo, I.-C. Chen, J.-C. Chang, M.T. Lee, C.-H. Hu, C.-H. Hung, H.M. Lee, J.-H. Huang, Eur. J. Inorg. Chem. (2004) 4898–4906;

(b) S.-H. Hsu, J.-C. Chang, C.-L. Lai, C.-H. Hu, H.M. Lee, G.-H. Lee, S.-M. Peng, Inorg. Chem. 43 (2004) 6782–6792;

(c) R.-C. Yu, C.-H. Hung, J.-H. Huang, H.-Y. Lee, J.-T. Chen, Inorg. Chem. 41 (2002) 6450–6455.

[10] A ^{1}H–^{13}C HSQC 2-D NMR spectrum and the assignment for compound **2** was provided in the Supplementary material.

[11] (a) T.S. Ouattara, R.J. Butcher, J.S. Matthews, J. Coord. Chem. (2005) 461–465;

(b) J.S. Matthews, T.S. Ouattara, R.J. Butcher, Acta Crystallogr., Sect. E 61 (2005) m2598–m2600.

[12] T.-L. Yu, C.-C. Wu, C.-C. Chen, B.-H. Huang, J. Wu, C.-C. Lin, Polymer 46 (2005) 5909–5917.