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Magnesium Complexes Containing η^1- and η^3-Pyrrolyl or Ketiminato Ligands: Synthesis, Structural Investigation and ε-Caprolactone Ring-Opening Polymerisation

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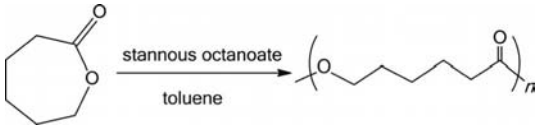
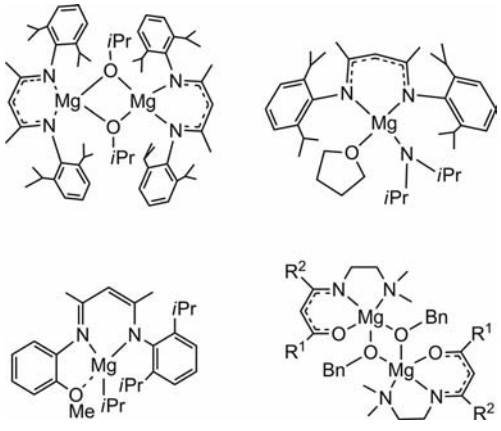
A series of dimeric magnesium derivatives containing substituted pyrrolyl or ketiminato ligands was synthesised and the application of these derivatives for the ring opening polymerisation of ε-caprolactone has been carried out. Reactions of $[Mg\{N(SiMe_3)_2\}]_2$ (**1**) with one equiv. of 2-dimethylaminomethyl pyrrole and 2-diethylaminomethyl pyrrole in toluene generates $[Mg\{C_4H_3N(2\text{-}CH_2NMe_2)\}\{N(SiMe_3)_2\}]_2$ (**2**) and $[Mg\{C_4H_3N(2\text{-}CH_2NEt_2)\}\{N(SiMe_3)_2\}]_2$ (**3**), respectively, in high yield. Similarly, the reaction of **1** with one equiv. of 2-*tert*-butylaminomethyl pyrrole in toluene at room temperature affords $[Mg\{C_4H_3N(2\text{-}CH_2NH\textit{t}Bu)\}\{N(SiMe_3)_2\}]_2$ (**4**). Furthermore, reactions of **1** with one equiv. of HOCMeCHCMeN(C_6H_3-2,6-*i*Pr_2) or HOCMeCHCMeN(C_6H_4-2-OMe) in toluene yielded the dimeric magnesium complexes, $[Mg\{OCMeCHCMeN(C_6H_3\text{-}2,6\text{-}\textit{i}Pr_2)\}\{N(SiMe_3)_2\}]_2$ (**5**) and $[Mg\{OCMeCHCMeN(C_6H_4\text{-}2\text{-}OMe)\}\{N(SiMe_3)_2\}]_2$ (**6**), respectively, in satisfactory yields by means of deamination. All the complexes were characterised by NMR spectroscopy and X-ray diffraction analysis in the solid state. They show moderate reactivity towards the ring opening polymerisation of ε-caprolactone in dichloromethane or tetrahydrofuran.

Introduction

Biodegradable and biocompatible materials[1] have attracted much attention in the past decades due to environmental and energy concerns. Within the field of material science, polyesters[2] are interesting candidates as a consequence of them being both biocompatible and biodegradable under mild conditions, properties that have led to significant investigations into their applications in tissue engineering, drug and gene delivery and even as environmentally friendly packaging materials.[3] Synthetically, polyesters are commonly obtained by either condensation polymerisation of dicarboxylic acids and bifunctional alcohol units or by ring opening polymerisation (ROP) of cyclic esters. The practical uses of the material decide what monomer of the cyclic esters and the catalysts for the polymerisation will be chosen. Polycaprolactone (PCL)[4] is a biodegradable polyester and been used in a wide variety of applications such as in implantable materials, additives for resins, drug delivery devices and sutures etc. PCL is prepared by ring opening polymerisation of ε-caprolactone using catalysts such as stannous octanoate[5,6] (Scheme 1). However, the toxicity of organotin complexes for the catalyst in the formation of PCL has raised concerns about the use of this polymer for medical purposes.[7] Therefore, developing human-friendly catalysts for forming PCL has become an important issue for organometallic chemists. The nontoxic metal-alkoxido compounds of metals such as Ca, Mg, Zn and some alkaline metals[8–10] have been used for the ring opening polymerisation of ε-caprolactone and lactides. Several magnesium ketiminato or diketiminato complexes published in the literature[10c,11] are shown in Scheme 2.



Scheme 1.



Scheme 2.

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We have been working on synthesising main group metal complexes containing monoanionic substituted pyrrolyl or ketiminato ligands.[12] As an extension of our continuous interest in the pyrrolyl ligand system, we report herein the synthesis, characterisation and reactions of magnesium complexes containing substituted pyrrole or ketimine ligands and studies of their reactivity and potential for use as catalysts in ring opening polymerisation.

Results and Discussion

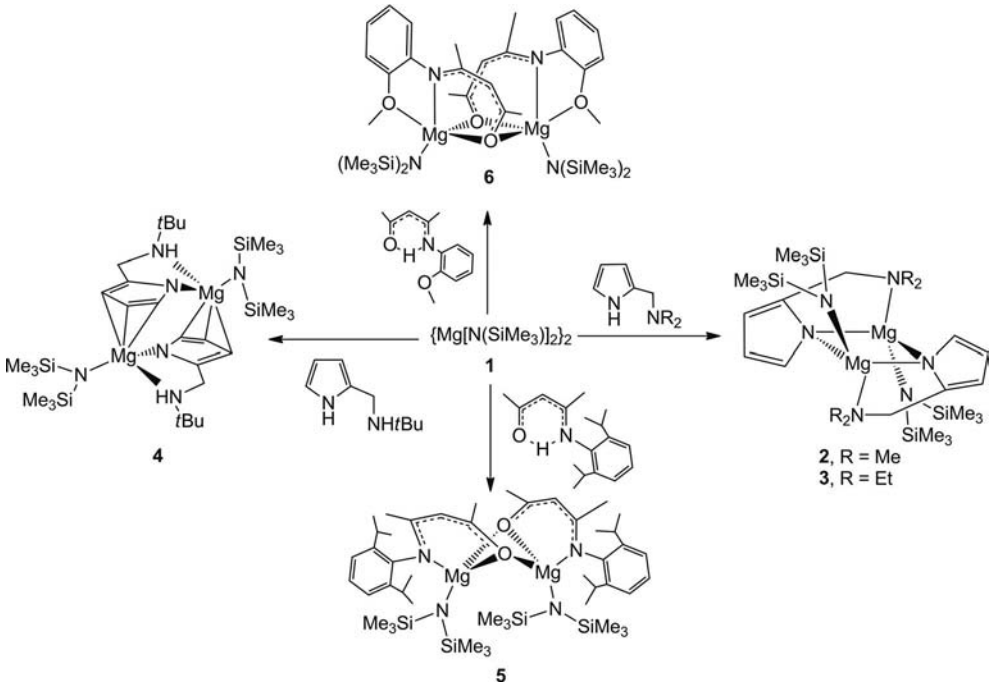
Synthesis and Characterisation

The reactions of complex **1**, $[Mg\{N(SiMe_3)_2\}]_2$,[13] with various ligands are shown in Scheme 3. Reaction of complex **1** with one equiv. of 2-dimethylaminomethyl pyrrole in toluene generates dimeric magnesium $[Mg\{C_4H_3N(2\text{-}CH_2NMe_2)\}\{N(SiMe_3)_2\}]_2$ (**2**) in high yield. The ^1H NMR spectrum of **2** at room temperature shows two doublets at δ = 2.70 and 4.08 ppm for the methylene protons of the CH_2N group and two singlets at δ = 1.78 and 2.03 ppm for the methyl protons of the NMe_2 fragment. The rigidity of the dimeric geometry in solution can be attributed to the splitting. A very small amount of a minor product was observed in the ^1H NMR spectrum of **2**. Variable-temperature NMR spectra of **2** in [D_8]toluene show that the signals resulting from the two methylene protons and two methyl groups are collapsed up to a temperature of 320 K but reappear as two singlets at 370 K, indicating an exchange among inequivalent parts of the coordinated ligand at high temperature. From the ^1H NMR chemical shift differences between the slow limit and coalescence temperatures, the activation energy for the exchange was estimated at ca. 63.8 kJ mol^{-1}.

Similarly, reaction of complex **1** with one equiv. of 2-diethylaminomethyl pyrrole in toluene affords the dimeric magnesium complex $[Mg\{C_4H_3N(2\text{-}CH_2NEt_2)\}\{N(SiMe_3)_2\}]_2$ (**3**) in high yield. Two different geometries were observed by ^1H NMR spectroscopy at room temperature even after repeating crystallisation. The NMR spectrum shows two doublets at δ = 3.19 and 4.05 ppm for the methylene protons of the CH_2N group, four quadruplets at δ = 1.75, 1.99, 2.43 and 2.74 ppm for the methylene protons of the NCH_2Me group and two triplets at δ = 0.55 and 0.83 ppm for the methyl protons of the NCH$_2$*Me* fragment. Most of the NMR signals of the minor component, which can be attributed to a monomeric form, are embedded in the major component signals therefore appearing as a couple of resonances. The molecular structure of **3** could also be verified by ^1H-^{13}C HSQC 2D NMR spectroscopy.

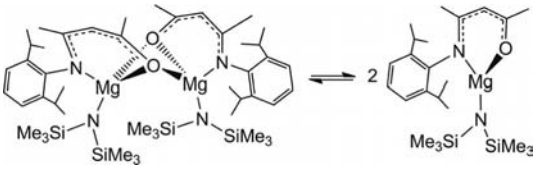
Reaction of complex **1** with one equiv. of 2-*tert*-butylaminomethyl pyrrole in toluene at room temperature generates the dimeric magnesium complex $[Mg\{C_4H_3N(2\text{-}CH_2NHtBu)\}\{N(SiMe_3)_2\}]_2$ (**4**) in 90% yield. The ^1H NMR spectrum of complex **4** shows broad signals for the protons of the *tBu* and CH_2N groups as well as the N*H* component of the CH$_2$NH*t*Bu fragment. A more specific description of the geometry of complex **4** is discussed in the next section. Complex **4** is thermally unstable, slowly decomposing above 350 K to form unidentifiable products.

Similarly, reaction of one equiv. HOCMeCHCMeN(C_6H_3-2,6-*i*Pr$_2$) with **1** in toluene yields the dimeric magnesium complex $[Mg\{OCMeCHCMeN(C_6H_3\text{-}2,6\text{-}iPr_2)\}\{N(SiMe_3)_2\}]_2$ (**5**) in high yield by means of deamination. Even after repeated recrystallisation of complex **5**, the ^1H NMR spectra remain exactly the same and are complicated by the presence of two methine protons for the ketiminato



Scheme 3.

backbone indicating two different magnesium-ketiminato coordination modes in the complexes. After dissolving **5** in benzene, its freezing point depression was obtained using the equation of $\Delta T_f = i \times K_f \times C_m$ (where ΔT_f = freezing point depression; i = the number of individual particles in solution; K_f = the cryoscopic constant; C_m = the molality of the solution). The i value was measured at 1.19, meaning complex **5** dissociates into more particles and a possible dissociation mechanism is shown in Scheme 4 where only 81% of **5** remains as a dimeric structure.



Scheme 4.

Again, reaction of one equiv. of tridentate HOCMeCHCMeN(C_6H_4-2-OMe) with **1** in toluene yields a dimeric magnesium complex [Mg{OCMeCHCMeN(C_6H_4-2-OMe)}{N($SiMe_3$)$_2$}]$_2$ (**6**) in 90% yield by means of deamination. Complex **6** is thermally unstable, decomposing into unidentifiable products above 50 °C. All the ^{1}H NMR resonances of **6** appear as broad signals and no monomeric form was found based on the methine proton signals of the ketiminato backbone. Presumably the methoxy group of the substituted ketiminato ligand participates in stabilising the dimeric magnesium geometry.

Molecular Structures of Complexes 2–6

All the crystals of complexes **2**–**6** were obtained from toluene solutions at –20 °C. We characterised the molecular structures by single-crystal X-ray diffraction studies. The crystallographic data are summarised in Table 3 and selected bond lengths and angles are listed in Table 1. Figures 1 and 2 represent the molecular structures of **2** and **3**, respectively. The unit cell of **2** contains one dimeric magnesium unit as well as an independent toluene molecule. Both **2** and **3** exhibit dimeric architectures comprised of the substituted pyrrolyl frame, a [C_4H_3N(2-CH_2NR_2)] unit bound to two magnesium centres simultaneously projected into a μ_2-η^1-mode through the $N_{pyrrole}$ atoms and an NR_2 fragment from the corresponding ligand. In the dimeric unit, a Mg2N2 square plane is configured by participation of two magnesium and two pyrrole-N atoms, exhibiting a range of bond lengths (2.1588–2.1828 Å) and angles (89.46–90.54°). Even in presence of methyl and ethyl substituents on **2** and **3**, respectively, the lack of influence of steric crowding on the geometries is noticeable. There are some Mg2N2 constructed magnesium complexes as demonstrated earlier[14] but pyrrolyl bridged dimeric units of magnesium have been less well explored.[15]

Table 1. Selected bond lengths [Å] and angles [°] for complexes **2**–**6**.

2			
Mg(1)–N(6)	1.9892(15)	Mg(2)–N(5)	1.9872(15)
Mg(1)–N(1)	2.1588(16)	Mg(2)–N(2)	2.1495(16)
Mg(1)–N(2)	2.1831(16)	Mg(2)–N(1)	2.1924(16)
Mg(1)–N(3)	2.1914(16)	Mg(2)–N(4)	2.1938(16)
N(6)–Mg(1)–N(1)	125.74(7)	N(5)–Mg(2)–N(2)	124.23(7)
N(6)–Mg(1)–N(2)	120.54(7)	N(5)–Mg(2)–N(1)	122.70(6)
N(1)–Mg(1)–N(2)	90.12(6)	N(2)–Mg(2)–N(1)	90.12(6)
N(6)–Mg(1)–N(3)	119.16(7)	N(5)–Mg(2)–N(4)	118.94(7)
N(1)–Mg(1)–N(3)	105.62(6)	N(2)–Mg(2)–N(4)	106.33(6)
N(2)–Mg(1)–N(3)	85.72(6)	N(1)–Mg(2)–N(4)	85.24(6)
Mg(2)–N(2)–Mg(1)	90.11(6)	Mg(1)–N(1)–Mg(2)	89.62(6)
3			
Mg(1)–N(3)	1.9920(10)	Mg(1)–N(2)	2.2256(10)
Mg(1)–N(1)	2.1779(10)	N(1)–Mg(1A)	2.1828(10)
Mg(1)–N(1A)	2.1828(10)		
N(3)–Mg(1)–N(1)	122.50(4)	N(3)–Mg(1)–Mg(1A)	137.90(3)
N(3)–Mg(1)–N(1A)	121.12(4)	N(1)–Mg(1)–Mg(1A)	44.79(3)
N(1)–Mg(1)–N(1A)	89.46(4)	N(1A)–Mg(1)–Mg(1A)	44.67(3)
N(3)–Mg(1)–N(2)	121.66(4)	N(2)–Mg(1)–Mg(1A)	98.99(3)
N(1)–Mg(1)–N(2)	85.40(4)	Mg(1)–N(1)–Mg(1A)	90.54(4)
N(1A)–Mg(1)–N(2)	107.56(4)		
4			
C(1)–Mg(1A)	2.8162(15)	Mg(1)–N(2)	2.2095(13)
C(2)–Mg(1A)	2.3791(15)	Mg(1)–C(2A)	2.3791(15)
C(3)–Mg(1A)	2.6660(15)	Mg(1)–C(3A)	2.6660(15)
Mg(1)–N(3)	1.9963(12)	Mg(1)–C(1A)	2.8162(15)
Mg(1)–N(1)	2.0638(12)		
N(3)–Mg(1)–N(1)	123.39(5)	N(2)–Mg(1)–C(3A)	137.62(5)
N(3)–Mg(1)–N(2)	111.77(5)	C(2A)–Mg(1)–C(3A)	32.21(5)
N(1)–Mg(1)–N(2)	78.64(5)	N(3)–Mg(1)–C(1A)	149.03(5)
N(3)–Mg(1)–C(2A)	119.56(5)	N(1)–Mg(1)–C(1A)	81.30(5)
N(1)–Mg(1)–C(2A)	107.58(5)	N(2)–Mg(1)–C(1A)	89.83(5)
N(2)–Mg(1)–C(2A)	107.86(5)	C(2A)–Mg(1)–C(1A)	29.58(5)
N(3)–Mg(1)–C(3A)	105.03(5)	C(3A)–Mg(1)–C(1A)	48.41(5)
N(1)–Mg(1)–C(3A)	98.35(5)		
5			
Mg(1)–N(2)	2.0109(17)	Mg(1)–O(1A)	2.0404(14)
Mg(1)–O(1)	2.0153(15)	Mg(1)–N(1)	2.1087(17)
O(1)–Mg(1A)	2.0404(14)		
N(2)–Mg(1)–O(1)	124.86(6)	O(1A)–Mg(1)–N(1)	114.89(6)
N(2)–Mg(1)–O(1A)	119.74(6)	O(1)–Mg(1)–N(1)	92.32(6)
O(1)–Mg(1)–O(1A)	79.24(6)	N(2)–Mg(1)–N(1)	117.47(7)
6			
Mg(1)–N(2)	2.036(2)	Mg(1)–O(1)	2.0388(19)
Mg(1)–O(1A)	2.0532(19)	Mg(1)–N(1)	2.150(2)
Mg(1)–O(2)	2.212(2)		
N(2)–Mg(1)–O(1)	126.75(9)	N(2)–Mg(1)–O(1A)	108.30(9)
O(1)–Mg(1)–O(1A)	80.73(8)	N(2)–Mg(1)–N(1)	134.16(10)
O(1)–Mg(1)–N(1)	98.18(8)	O(1A)–Mg(1)–N(1)	85.18(8)
N(2)–Mg(1)–O(2)	91.10(9)	O(1)–Mg(1)–O(2)	96.71(8)
O(1A)–Mg(1)–O(2)	157.67(8)	N(1)–Mg(1)–O(2)	73.17(8)

A representation of the molecular structure of **4** is depicted in Figure 3 and selected bond lengths and angles are listed in Table 1. Single crystal X-ray studies reveal that complex **4** consists of a dimeric framework where the pyrrolyl ring itself binds to two magnesium atoms through its central N-atom and three ring C-atoms into a μ_2-(η^1-η^3)-mode. This is the only example of a μ_2-(η^1-η^3)-mode devel-

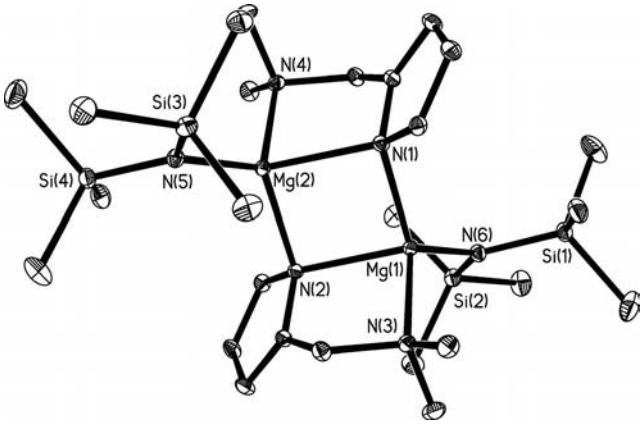


Figure 1. The molecular structure of complex **2** with thermal ellipsoids drawn at the 30% probability level. Toluene molecules and hydrogen atoms are omitted for clarity.

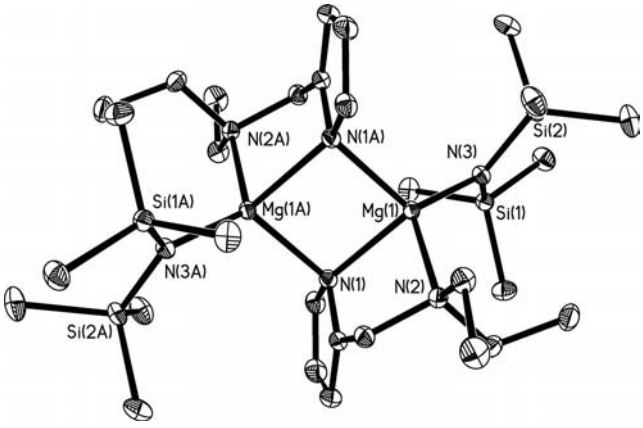


Figure 2. The molecular structure of complex **3** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

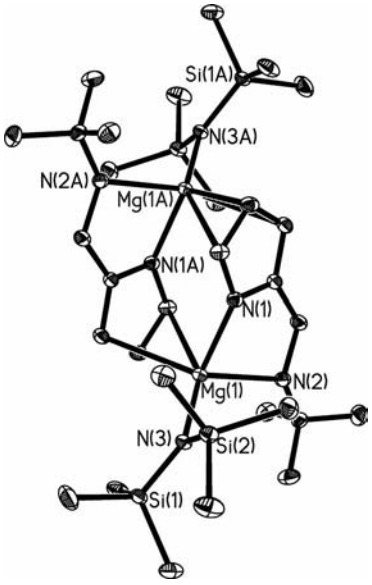


Figure 3. The molecular structure of complex **4** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

oped by a pyrrole ring towards magnesium atoms when considering different binding modes such as μ_2-(η^1-η^n)-, reported many times in the literature.[16] The average Mg–(η^3-Cp) bond length is ca. 2.6204 Å which is comparable with earlier literature values (2.46–2.75 Å).[17] The Mg–$N_{\eta 1\text{-pyrrolyl}}$ bond length in **4** (2.064 Å) is much shorter than in **2** and **3** (2.159–2.183 Å) and this can be attributed to the differences between terminal and bridging nitrogens with magnesium atoms. The $N_{pyrrole}$ and N_{amino} atoms of the substituted pyrrolyl ligands constrain the magnesium atom into forming a five-membered ring having an $N_{pyrrole}$–Mg–N_{amino} bite angle of 78.64(5)°.

Figure 4 shows a perspective drawing of complex **5** and selected bong lengths and angles are summarised in Table 1. The molecular geometry of **5** consists of two tetrahedral magnesium units which are interconnected by equal sharing of two ketiminato oxygen atoms forming a $Mg_2(\mu\text{-}O)_2$ mediated molecular-square with a dihedral angle of 18.5°.[18] The corresponding Mg–$N_{silylamide}$ bong length [2.0109(17) Å] is slightly shorter than Mg–$N_{ketiminato}$ [2.1087(17) Å] presumably due to the delocalisation of the ketiminato nitrogen lone pair electrons in the latter.

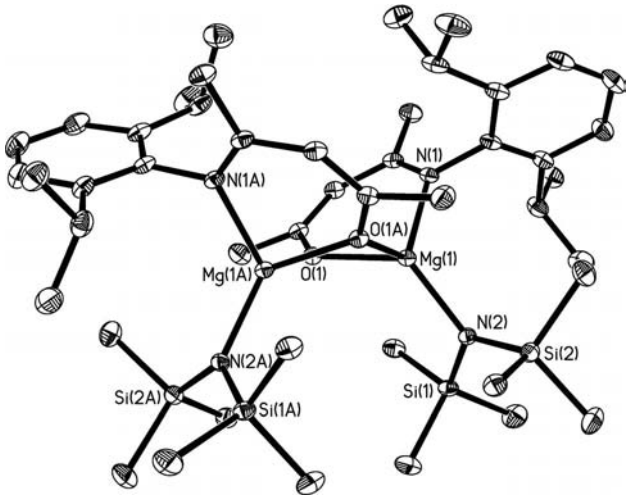


Figure 4. The molecular structure of complex **5** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Complex **6** features a dimeric magnesium unit as shown in Figure 5 and corresponding bond lengths and angles are listed in Table 1. The molecular geometry of **6** can be described as consisting of two edge-sharing trigonal bipyramidals (TBP)[19] in which a pair of magnesium and ketiminato backbone oxygen atoms form a $Mg_2(\mu\text{-}O)_2$ square plane. The compound features a centrosymmetric dimer in which each magnesium possesses a trigonal bipyramidal geometry. The trigonal plane is developed from participation of N_{amido}, $N_{ketiminato}$ backbone and bridging oxygen atom from another ketiminato tridentate precursor. The axial sites are occupied by $O_{ketiminato}$ backbone atoms and methoxy substituents. The related Mg–N and Mg–O bond lengths in **6** are slightly longer than those in **5**.

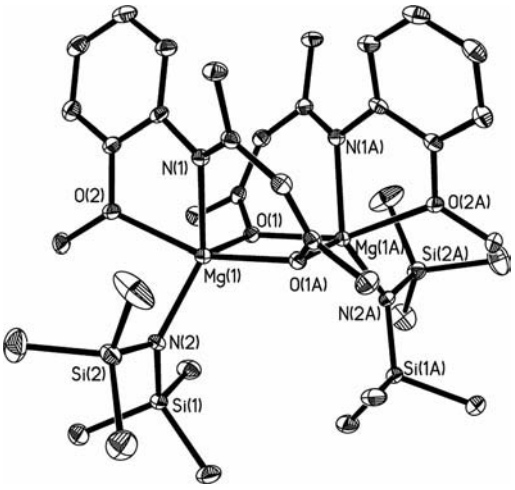


Figure 5. The molecular structure of complex **6** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

monitored by ^{1}H NMR spectroscopy and the ligand redistribution rate estimated at ca. 1.78×10^{-4} s^{-1} based on the decreasing concentration of **2** vs. time as shown in Figure 6.

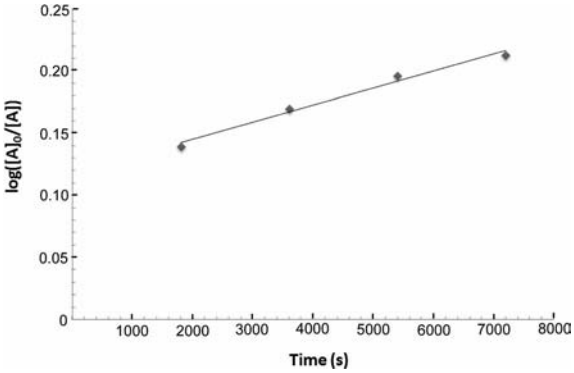
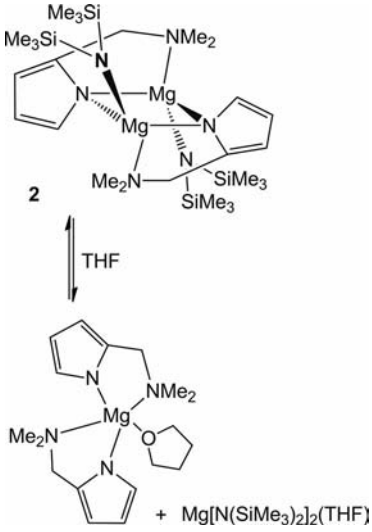


Figure 6. The correlation diagram of the concentration changes of **2** vs. time. $[A]_o$ = the initial concentration of **2**. [A] = the concentration of **2** at time *t*.

Ligand Redistribution Study of Complex 2 in THF

While dissolving the dimeric magnesium complex **2** in C_6H_6 and adding excess THF (tetrahydrofuran), ligand redistribution ensues to form the monomeric magnesium complexes $Mg[C_4H_3N(2\text{-}CH_2NMe_2)]_2(THF)$[20] and $Mg[N(SiMe_3)_2]_2(THF)$ as shown in Scheme 5. The reaction was



Scheme 5.

Ring-Opening Polymerisation of ε-Caprolactone

The results of ring opening polymerisation of ε-caprolactone using complexes **2**–**6** as catalysts are shown in Table 2. The bidentate pyrrolyl ligand mediated dimeric complexes **2**–**4** possess noticeable activity towards the ring opening polymerisation of ε-caprolactone showing a conversion of over 95% within 30 min at room temperature. It is worthy of note that the polymerisation rate resulting from **4** is faster than that due to **3** or **2**. In the solid state, complexes **2**–**4** possess dimeric geometries while in solution they manifest as a mixture of monomer and dimer at room temperature. The monomer/dimer ratio of complexes **2**–**4** in solution follow the sequence of **4** > **3** > **2**, according to ^{1}H NMR spectroscopy. As a result, the more monomeric ratio favours a faster ring opening polymerisation rate and consequently a higher activity.

Complex **5** apparently shows better catalytic activity towards **ε**-caprolactone polymerisation than **6** (entry 4–7). The possible reason might be due to it having a higher monomeric ratio in solution than **6**. Another perspective is that the methoxy substituent in **6** may decelerate **ε**-caprolactone monomer binding to the magnesium centre which also worsens the polymerisation rate.

Table 2. Ring opening polymerisation of ε-caprolactone using complexes **2**–**6** as initiators (monomer/catalyst ratio = 100:1; T = 25 °C).

Entry	Cat.	Solvent	Time [min]	Yield [%][a]	Activity[b]	M_n[c]	M_w[c]	M_n/M_w[d]
1	**2**	CH_2Cl_2	30	94.44	359	59,000	78,000	1.31
2	**3**	CH_2Cl_2	8	95.60	1362	80,000	115,000	1.44
3	**4**	CH_2Cl_2	5	99.00	2257	94,000	125,000	1.32
4	**5**	CH_2Cl_2	30	94.12	357	68,000	95,000	1.40
5	**5**	THF	10	95.33	1089	127,000	170,000	1.35
6	**6**	CH_2Cl_2	60	97.50	186	14,000	25,000	1.77
7	**6**	THF	20	95.64	545	68,000	118,000	1.74

[a] Yield (%) = [product (g) − initiator (g)]/monomer (g). [b] Activity = Product (g)/initiator (mol); time is given in minutes. [c] Obtained directly from GPC data. [d] M_n/M_w = weight average molecular weight/number average molecular weight.

Conclusions

The reactivities of $[Mg\{N(SiMe_3)_2\}]_2$ with substituted pyrrole and ketimine have been carried out in toluene and a series of dimeric magnesium complexes **2**–**6** were obtained and fully characterised. The pyrrolyl ligand, $C_4H_3N(2\text{-}CH_2NMe_2)$ functions as a bidentate ligand binding magnesium atoms in μ-η^1 mode whereas $C_4H_3N(2\text{-}CH_2NHtBu)$ dominates as a bidentate μ-η^1,η^3-ligand. All the complexes, when applied to ε-caprolactone for ring opening polymerisation, show moderate reactivity. Furthermore, it is noteworthy that the polymerisation rate of the corresponding substrates follows the sequence **4** > **3** > **2**. The development of pyrrolyl-linked anionic ligands with group IVB metals is in progress and generating increasing interest.

Experimental Section

General Procedure: All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or a glove box. Toluene, diethyl ether and tetrahydrofuran were dried by heating to reflux over sodium benzophenone ketyl. CH_2Cl_2 was dried with P_2O_5. All solvents were distilled and stored in solvent reservoirs which contained molecular sieves (4 Å) and were purged with nitrogen. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were recorded in ppm relative to the residual protons and ^{13}C of $CDCl_3$ (δ = 7.24, 77.0) and C_6D_6 (δ = 7.15, 128.0). Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyser at the Instrument Centre, NCHU. Due to the air and moisture sensitivity of the materials, the analyical data of some metal complexes are not within the error ranges even after several attempts were made. The ligands and magnesium compounds such as $C_4H_3NH(2\text{-}CH_2NMe_2)$, $C_4H_3NH(2\text{-}CH_2NEt_2)$, $C_4H_3NH(2\text{-}CH_2NHtBu)$,[21] HOCMeCHCMeNAr (Ar = C_6H_3-2,6-iPr$_2$ or C_6H_4-2-OMe)[12f,22] and $[Mg\{N(SiMe_3)_2\}]_2$ (**1**)[13] were prepared according to a previously reported procedure. All chemicals (Aldrich, Acros) were used as received.

$[Mg\{C_4H_3N(2\text{-}CH_2NMe_2)\}\{N(SiMe_3)_2\}]_2$ (2): To a solution of **1** (1.38 g, 2.0 mmol) in toluene (20 mL) was added a $C_4H_3NH(2\text{-}CH_2NMe_2)$ (0.50 g, 4.0 mmol) toluene solution (10 mL) dropwise at 0 °C. The mixture was stirred at room temperature for 1 h and changed from colourless to pale yellow. Volatiles were removed under vacuum and the solid was recrystallised from a toluene solution to yield 1.04 g of a white solid in 85% yield. ^1H NMR (C_6D_6): δ = 0.19 (s, 36 H, NSi*Me*$_3$), 1.78 (s, 6 H, N*Me*), 2.03 (s, 6 H, N*Me*), 2.70 (d, 2 H, C*H*$_2$N), 4.08 (d, 2 H, C*H*$_2$N), 6.30 (br., 2 H, pyrrolyl C*H*), 6.47 (br., 2 H, pyrrolyl C*H*), 6.94 (br., 2 H, pyrrolyl C*H*) ppm. ^{13}C NMR (C_6D_6): δ = 6.38 (q, $J_{C,H}$ = 121 Hz, NSi*Me*$_3$), 44.87 (q, $J_{C,H}$ = 131 Hz, N*Me*), 47.05 (q, $J_{C,H}$ = 138 Hz, N*Me*), 59.54 (t, $J_{C,H}$ = 137 Hz, *C*H$_2$N), 111.75 (d, $J_{C,H}$ = 167 Hz, pyrrolyl *C*H), 111.86 (d, $J_{C,H}$ = 168 Hz, pyrrolyl *C*H), 131.81 (d, $J_{C,H}$ = 178 Hz, pyrrolyl *C*H), 138.30 (s, C_{ipso}) ppm. $C_{26}H_{58}Mg_2N_6Si_4$ (615.73): calcd. C 50.72, H 9.50, N 13.65; found C 49.77, H 8.64, N 13.18.

$[Mg\{C_4H_3N(2\text{-}CH_2NEt_2)\}\{N(SiMe_3)_2\}]_2$ (3): A similar procedure for the preparation of complex **2** was followed. Compound **1** (1.38 g, 2.0 mmol) and $C_4H_3NH(2\text{-}CH_2NEt_2)$ (0.61 g, 4.0 mmol) were used and 1.17 g of a yellow solid was obtained (87% yield). ^1H NMR ([D$_8$]toluene): δ = 0.11 (s, 36 H, NSi*Me*$_3$), 0.55 (t, 6 H, NCH$_2$*Me*), 0.83 (t, 6 H, NCH$_2$*Me*), 1.75 (q, 2 H, NC*H*$_2$Me), 1.99 (q, 2 H, NC*H*$_2$Me), 2.43 (q, 2 H, NC*H*$_2$Me), 2.74 (q, 2 H, NC*H*$_2$Me), 3.19 (d, 2 H, C*H*$_2$N), 4.05 (d, 2 H, C*H*$_2$N), 6.20 (s, 2 H, pyrrolyl CH), 6.30 (s, 2 H, pyrrolyl CH) ppm. ^{13}C NMR ([D$_8$]-toluene): δ = 5.74 (q, $J_{C,H}$ = 118 Hz, NCH$_2$*Me*), 5.89 (q, $J_{C,H}$ = 115 Hz, NSi*Me*$_3$), 10.32 (q, $J_{C,H}$ = 125 Hz, NCH$_2$*Me*), 44.59 (t, $J_{C,H}$ = 119 Hz, N*C*H$_2$Me), 46.12 (t, $J_{C,H}$ = 121 Hz, N*C*H$_2$Me), 54.10 (t, $J_{C,H}$ = 130 Hz, *C*H$_2$N), 108.76 (d, $J_{C,H}$ = 166 Hz, pyrrolyl *C*H), 110.55 (d, $J_{C,H}$ = 171 Hz, pyrrolyl *C*H), 132.44 (d, $J_{C,H}$ = 177 Hz, pyrrolyl *C*H), 138.31 (s, C_{ipso}) ppm. $C_{30}H_{66}Mg_2N_6Si_4$ (671.84): calcd. C 53.63, H 9.90, N 12.51; found C 52.67, H 10.15, N 11.69.

$[Mg\{C_4H_3N(2\text{-}CH_2NHtBu)\}\{N(SiMe_3)_2\}]_2$ (4): A similar procedure for the preparation of complex **2** were used. Compound **1** (1.38 g, 2.0 mmol) and $C_4H_3NH(2\text{-}CH_2NHtBu)$ (0.56 g, 4.0 mmol) were used and 1.18 g of a yellow solid was obtained (90% yield). ^1H NMR (C_6D_6): δ = 0.43 (s, 36 H, NSi*Me*$_3$), 0.88 (s, 18 H, N*tBu*), 1.38 (br., 2 H, N*H*), 3.58 (br., 4 H, C*H*$_2$N), 6.27 (s, 2 H, pyrrolyl C*H*), 6.35 (s, 2 H, pyrrolyl C*H*), 6.81 (br., 2 H, pyrrolyl C*H*) ppm. ^{13}C NMR (C_6D_6): δ = 6.23 (NSi*Me*$_3$), 28.54 (N*tBu*), 41.77 (*C*H$_2$N), 52.75 (NC_{ipso}), 101.96 (pyrrolyl *C*H), 131.22 (pyrrolyl *C*H), 131.41 (pyrrolyl CH), 142.61 (C_{ipso}) ppm. $C_{30}H_{66}Mg_2N_6Si_4$ (671.84): calcd. C 53.63, H 9.90, N 12.51; found C 52.57, H 9.69, N 11.88.

$[Mg\{OCMeCHCMeN(C_6H_3\text{-}2,6\text{-}iPr_2)\}\{N(SiMe_3)_2\}]_2$ (5): To a solution of **1** (1.38 g, 2.0 mmol) in toluene (20 mL) was added a HOCMeCHCMeN(C_6H_3-2,6-iPr$_2$) (1.02 g, 4.0 mmol) toluene solution (10 mL) dropwise at 0 °C. The mixture was stirred at room temperature for 1 h and changed from colourless to pale yellow. Volatiles were removed under vacuum and the solid was recrystallised from a toluene solution to yield 1.49 g of a white solid in 85% yield. Complex **5** exists in both monomeric and dimeric forms, making it complicated to differentiate the NMR spectra. Characteristic proton and carbon resonances of the methine fragment of the ketiminato backbone are at δ = 5.21 and 4.88 ppm, and 103.4 and 97.6 ppm, respectively. $C_{46}H_{84}Mg_2N_4O_2Si_4$ (886.14): calcd. C 62.35, H 9.55, N 6.32; found C 63.17, H 10.13, N 5.87.

$[Mg\{OCMeCHCMeN(C_6H_4\text{-}2\text{-}OMe)\}\{N(SiMe_3)_2\}]_2$ (6): A similar procedure for the preparation of complex **5** were used. Compound **1** (1.38 g, 2.0 mmol) and HOCMeCHCMeN(C_6H_4-2-OMe) (0.86 g, 4.0 mmol) were used and 1.40 g of a yellow solid was obtained (90% yield). ^1H NMR (C_6D_6): δ = 0.29 (s, 36 H, NSi*Me*$_3$), 1.69 (br., 6 H, CHMe*Me*), 1.83 (br., 6 H, CH*Me*Me), 3.58 (s, 6 H, O*Me*), 5.08 (s, 2 H, CMeC*H*CMe), 6.49–6.88 (br., 8 H, phenyl C*H*) ppm.

Crystallographic Structural Determination of 2–6: Single crystals of **2**·toluene, **3**, **4**, **5** and **6** were mounted on a glass fibre using epoxy resin and transferred to the goniostat. Data were collected on a Bruker SMART CCD diffractometer equipped with graphite-monochromated Mo-K_α radiation. Due to the air-sensitivity of these crystals, complexes were covered with oil and transferred to the N_2 stream of the diffractometer prior to data collection. The structures were solved by direct and difference Fourier methods and refined by full-matrix least-squares on F^2. All nonhydrogen atoms were refined with anisotropic displacement parameters. Absorption corrections were performed with the program SADABS[23] and crystallographic computing was performed using the SHELXTL[24] package of programs. The toluene solvent is located about an inversion centre and was refined with soft restraints and constraints and its carbon atoms were refined with isotropic displacement parameters. A summary of crystal data collection and refinement parameters for all compounds is given in Table 3.

CCDC-830342 (for **2**), -830338 (for **3**), -830340 (for **4**), -830339 (for **5**), and -830341 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of

Table 3. Crystallographic data for complexes **2**–**6**.

	2·toluene	**3**	**4**	**5**	**6**
Formula	$C_{33}H_{66}Mg_2N_6Si_4$	$C_{30}H_{66}Mg_2N_6Si_4$	$C_{30}H_{66}Mg_2N_6Si_4$	$C_{46}H_{84}Mg_2N_4O_2Si_4$	$C_{36}H_{64}Mg_2N_4O_4Si_4$
Fw	707.90	671.87	671.87	886.15	777.89
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$C2/c$	$Pbcn$
a [Å]	22.4035(4)	9.3547(4)	9.5446(10)	11.130(3)	22.149(4)
b [Å]	15.6037(3)	10.8897(4)	14.1127(10)	22.444(7)	12.194(2)
c [Å]	12.7094(2)	10.8930(4)	15.5764(17)	21.331(5)	16.073(3)
α [°]	90	99.237(2)	90	90	90
β [°]	103.2730(10)	99.103(2)	101.290(3)	98.431(6)	90
γ [°]	90	110.628(2)	90	90	90
V [Å^3], Z	4324.24(13), 4	996.97(7), 1	2057.5(3), 2	5271(3), 4	4341.0(13), 4
$D_{calcd.}$ [Mg m^3]	1.087	1.119	1.084	1.117	1.190
Absorption coeff. [mm^{-1}]	0.195	0.208	0.202	0.174	0.206
T [K]	150(2)	150(2)	150(2)	150(2)	150(2)
F(000)	1544	368	736	1936	1680
Reflections collected	34711	21423	30739	20695	59133
Independent reflections	10454 (R_{int} = 0.0476)	5228 (R_{int} = 0. 0190)	4978 (R_{int} = 0.0331)	6374 (R_{int} = 0.0923)	4986 (R_{int} = 0.1879)
Data/restraints/parameters	10454/0/423	5228/0/198	4978/0/203	6374/0/274	4986/0/235
Goodness of fit on F^2	1.018	1.073	1.071	0.936	1.002
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0429, wR_2 = 0.0990	R_1 = 0.0295, wR_2 = 0.0843	R_1 = 0.0357, wR_2 = 0.1023	R_1 = 0.0456, wR_2 = 0.1021	R_1 = 0.0489, wR_2 = 0.0998
R indices (all data)	R_1 = 0.0911, wR_2 = 0.1163	R_1 = 0.0373, wR_2 = 0.0878	R_1 = 0.0441, wR_2 = 0.1079	R_1 = 0.0933, wR_2 = 0.1153	R_1 = 0.1117, wR_2 = 0.1266
Largest diff. peak/hole [e Å^{-3}]	0.313/–0.289	0.341/–0.183	0.427/–0.470	0.424/–0.385	0.309/–0.439

charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Polymerisation: All the polymerisations were carried out in dichloromethane or tetrahydrofuran in a nitrogen-filled Schlenk tube. Considering a typical method, the initiator was first dissolved in solvent (5 mL), followed by the addition of ε-caprolactone. The resultant mixture was then stirred at the selected temperature for a period of time to produce a gel- or solid-like polymer. The process continued until the mixture was gradually quenched with acidified water (3% CH_3COOH) and the resultant solid washed with hexane. It was dried to form a product in satisfactory yield. The molecular weights of the polymers were determined by using gel permeation chromatography (GPC) (Instrument: Waters, RI 2414, pump 1515).

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[1] a) R. Arshhady (Ed.), *Biodegradable Polymers: Concepts, Criteria, Definitions in Biodegradable Polymers*, PBM Series 2, Citus Books, London, UK, **2003**; b) M. Vert, J. Feijen, A. Albertsson, G. Scott, E. Chiellini (Eds.), *Biodegradable Polymers and Plastics*, The Royal Society of Chemistry (RSC), Cambridge, U. K., **1992**.

[2] a) J. Scheirs, T. E. Long (Eds.), *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*, Wiley, **2003**; b) G. Scott, D. Gilead (Eds.), *Degradable Polymers: Principles and Applications*, 2nd ed., Springer, **2003**; c) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147–6176.

[3] a) A. C. Albertsson, I. K. Varma, *Biomacromolecules* **2003**, *4*, 1466–1486; b) R. E. Drumright, P. R. Gruber, D. E. Henton, *Adv. Mater.* **2000**, *12*, 1841–1846; c) R. Auras, B. Harte, S. Selke, *Macromol. Biosci.* **2004**, *4*, 835–864; d) H. Tsuji, *Macromol. Biosci.* **2005**, *5*, 569–597; e) K. E. Uhrich, S. M. Cannizzaro, R. S. Langer, K. M. Shakesheff, *Chem. Rev.* **1999**, *99*, 3181–3198.

[4] a) M. Labet, W. Thielemans, *Chem. Soc. Rev.* **2009**, *38*, 3484–3504; b) V. R. Sinha, K. Bansal, R. Kaushik, R. Kumria, A. Trehan, *Int. J. Pharm.* **2004**, *278*, 1–23; c) C. X. F. Lam, S. H. Teoh, D. W. Hutmacher, *Polym. Int.* **2007**, *56*, 718–728; d) R. Chandra, R. Rustgi, *Prog. Polym. Sci.* **1998**, *23*, 1273–1335.

[5] a) M. Ryner, K. Stridsberg, A. C. Albertsson, H. von Schenck, M. Svensson, *Macromolecules* **2001**, *34*, 3877–3881; b) H. R. Kricheldorf, I. Kreiser-Saunders, A. Stricker, *Macromolecules* **2000**, *33*, 702–709; c) A. Kowalski, A. Duda, S. Penczek, *Macromol. Rapid Commun.* **1998**, *19*, 567–572; d) H. R. Kricheldorf, I. Kreisersaunders, C. Boettcher, *Polymer* **1995**, *36*, 1253–1259.

[6] A. J. Nijenhuis, D. W. Grijpma, A. J. Pennings, *Macromolecules* **1992**, *25*, 6419–6424.

[7] M. Gajda, A. Jancso, *Organotins, formation, use, speciation and toxicology*, in: *Metal ions in life sciences*, **2010**, RSC publishing, Cambridge, U.K..

[8] a) S.-M. Ho, C.-S. Hsiao, A. Datta, C.-H. Hung, L.-C. Chang, T.-Y. Lee, J.-H. Huang, *Inorg. Chem.* **2009**, *48*, 8004–8011; b) Z. Zhong, P. J. Dijkstra, C. Birg, M. Westerhausen, J. Feijen, *Macromolecules* **2001**, *34*, 3863–3868.

[9] a) V. Poirier, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Dalton Trans.* **2009**, 9820–9827; b) M.-Y. Shen, Y.-L. Peng, W.-C. Hung, C.-C. Lin, *Dalton Trans.* **2009**, 9906–9913; c) C.-C. Chang, M. S. Ameerunisha, *Coord. Chem. Rev.* **1999**, *189*, 199–278.

[10] a) A. Garces, L. F. Sanchez-Barba, C. Alonso-Moreno, M. Fajardo, J. Fernandez-Baeza, A. Otero, A. Lara-Sanchez, I. Lopez-Solera, A. M. Rodriguez, *Inorg. Chem.* **2010**, *49*, 2859–2871; b) M. H. Chisholm, J. Gallucci, K. Phomphrai, *Inorg. Chem.* **2002**, *41*, 2785–2794; c) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238; d) T. R. Jensen, L. E. Breyfogle, M. A. Hillmyer, W. B. Tolman, *Chem. Commun.* **2004**, 2504–2505.

[11] a) V. C. Gibson, J. A. Segal, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2000**, *122*, 7120–7121; b) A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White, D. J. Williams, *Dalton*

Trans. **2004**, 570–578; c) H.-Y. Tang, H.-Y. Chen, J.-H. Huang, C.-C. Lin, *Macromolecules* **2007**, *40*, 8855–8860.

[12] 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) J.-C. Chang, C.-H. Hung, J.-H. Huang, *Organometallics* **2001**, *20*, 4445–4447; c) C.-Y. Lin, H. M. Lee, J.-H. Huang, *J. Organomet. Chem.* **2007**, *692*, 3718–3722; d) C.-Y. Lin, C.-F. Tsai, H.-J. Chen, C.-H. Hung, R.-C. Yu, P.-C. Kuo, H. M. Lee, J.-H. Huang, *Chem. Eur. J.* **2006**, *12*, 3067–3073; e) Y.-C. Chen, C.-Y. Lin, C.-Y. Li, J.-H. Huang, L.-C. Chang, T.-Y. Lee, *Chem. Eur. J.* **2008**, *14*, 9747–9753; f) R.-C. Yu, C.-H. Hung, J.-H. Huang, H.-Y. Lee, J.-T. Chen, *Inorg. Chem.* **2002**, *41*, 6450–6455; g) J.-H. Huang, H.-J. Chen, J.-C. Chang, C.-C. Zhou, G.-H. Lee, S.-M. Peng, *Organometallics* **2001**, *20*, 2647–2650.

[13] M. Westerhausen, *Coord. Chem. Rev.* **1998**, *176*, 157–210.

[14] a) H. Sachdev, C. Wagner, V. Huch, M. Veith, *J. Chem. Soc., Dalton Trans.* **2002**, 4709–4713; b) E. Hevia, A. R. Kennedy, R. E. Mulvey, S. Weatherstone, *Angew. Chem. Int. Ed.* **2004**, *43*, 1709–1712; c) A. W. Duff, P. B. H. Hitchcock, M. F. Lappert, R. G. Taylor, J. A. Segal, *J. Organomet. Chem.* **1985**, *293*, 271–283; d) A. G. Barrett, I. J. Casely, M. R. Crimmin, M. S. Hill, J. R. Lachs, M. F. Mahon, P. A. Procopiou, *Inorg. Chem.* **2009**, *48*, 4445–4453.

[15] J. Lewinski, M. Dranka, I. Kraszewska, W. Sliwinskia, I. Justyniak, *Chem. Commun.* **2005**, 4935–4937.

[16] a) D. Jacoby, S. Isoz, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *J. Am. Chem. Soc.* **1995**, *117*, 2805–2816; b) L. Bonomo, E. Solari, R. Scopelliti, C. Floriani, N. Re, *J. Am. Chem. Soc.* **2000**, *122*, 5312–5326; c) S. De Angelis, E. Solan, C. Flonani, A. Chiesi-Villa, C. Rizzoli, *J. Am. Chem. Soc.* **1994**, *116*, 5702–5713; d) S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, *J. Chem. Soc., Dalton Trans.* **1994**, 2467–2469; e) J. Jubb, S. Gambarotta, R. Duchateau, J. H. Teuben, *J. Chem. Soc., Chem. Commun.* **1994**, 2641–2642.

[17] a) A. J. Arduengo, F. Davidson, R. Krafczyk, W. J. Marshall, M. Tamm, *Organometallics* **1998**, *17*, 3375–3382; b) H. Schumann, J. Gottfriedsen, M. Glanz, S. Dechert, J. Demtschuk, *J. Organomet. Chem.* **2001**, *617*, 588–600; c) H. R. Damrau, A. Geyer, M.-H. Prosenc, A. Weeber, F. Schaper, H.-H. Brintzinger, *J. Organomet. Chem.* **1998**, *553*, 331–343.

[18] a) F. Corazza, C. Floriani, A. Chiesi-Villa, C. Guastini, S. Ciurli, *J. Chem. Soc., Dalton Trans.* **1988**, 2341–2345; b) J. S. Matthews, T. S. Ouattara, R. J. Butcher, *Acta Crystallogr., Sect. E* **2005**, *61*, m2598; c) B. Sedai, M. J. Heeg, C. H. Winter, *J. Organomet. Chem.* **2008**, *693*, 3495–3503.

[19] a) W.-C. Hung, C.-C. Lin, *Inorg. Chem.* **2009**, *48*, 728–734; b) M. Marsch, K. Harms, W. Massa, G. Boche, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 696–697; c) L. F. Sánchez-Barba, D. L. Hughes, S. M. Humphrey, M. Bochmann, *Organometallics* **2006**, *25*, 1012–1020; d) J. Wu, Y.-Z. Chen, W.-C. Hung, C.-C. Lin, *Organometallics* **2008**, *27*, 4970–4978.

[20] L.-F. Hsueh, *Thesis*, National Changhua University of Education, Taiwan, **2008**.

[21] W. Herz, K. Dittmer, S. J. Cristol, *J. Am. Chem. Soc.* **1947**, *69*, 1698–1700.

[22] H.-H. Hsieh, *Thesis*, National Changhua University of Education, Taiwan, **2008**.

[23] *SADABS*, Area-Detector Absorption Correction, Bruker AXS Inc., Madison, WI, **2004**.

[24] a) G. M. Sheldrick, *SHELX97 – Programs for Crystal Structure Analysis: Structure Determination (SHELXS)*, University of Göttingen, Germany, **1997**; b) G. M. Sheldrick, *SHELX97 – Programs for Crystal Structure Analysis: Refinement (SHELXL)*, University of Göttingen, Germany, **1997**.

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