Synthesis and characterization of lithium and yttrium complexes containing tridentate pyrrolyl ligands. Single-crystal X-ray structures of {Li[C$_4$H$_2$N(CH$_2$NMe$_2$)$_2$-2,5]}$_2$ (1) and {[C$_4$H$_2$N(CH$_2$NMe$_2$)$_2$-2,5]YCl$_2$(μ-Cl)·Li(OEt$_2$)$_2$}$_2$ (2) and ring-opening polymerization of ε-caprolactone

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Abstract

The lithiated pyrrolyl ligand, {Li[C$_4$H$_2$N(CH$_2$NMe$_2$)$_2$-2,5]}$_2$ (1) was synthesized and structurally characterized. Reaction of 1 with YCl$_3$ in the molar ratio 1:1 in diethyl ether at room temperature afforded a di-yttrium di-lithium tetranuclear complex, {[C$_4$H$_2$N(CH$_2$NMe$_2$)$_2$-2,5]YCl$_2$(μ-Cl)·Li(OEt$_2$)$_2$}$_2$ (2) in 87% yield. Compounds 1 and 2 were characterized by NMR spectroscopy and single crystal X-ray crystallography. Compound 1 shows high reactivity for the ring-opening polymerization of ε-caprolactone.
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Keywords: Lithium; Yttrium; Pyrrolyl; Ring-open polymerization

1. Introduction

Among the ancillary ligand systems, cyclopentadienyl (Cp) ligands have been widely used in the organometallic complexes as ancillary ligands and are well studied [1]. However, there is considerable interest in developing the chemistry of metal complexes bearing non-Cp ligand systems, such as alkoxides [2], amide [3], and β-diketiminato chelate [4] and bulky salicylaldiminato ligands [5]. Several nice reviews summarized the currently used non-Cp ancillary ligand systems [6]. As we know that metal and ancillary ligands are the two major variable parameters for composing an active catalyst. Metals used for composing organometallic catalysts cover the whole periodic table, including main group [7] and transition metals [8]. Much work on lanthanide metal complexes

[9] has been reported and expanded the application to ring-opening polymerization of some heterocyclic monomers such as caprolactone and lactide [10]. We have been using substituted pyrrolyl molecules as speculating ligands and some reactions of pyrrolyl metal complexes with small organic molecules have been described [11]. Herein, we report the synthesis and characterization of the lithiated substituted pyrrolyl ligand and its corresponding yttrium complex. The ring-opening polymerization of ε-caprolactone using substituted pyrrolyl complexes will also be discussed.

2. Experimental

2.1. General procedure

All reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques or in a

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glove box. Toluene, diethyl ether, and tetrahydrofuran 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 on a Bruker AC 200 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 Analyzer at the Instrument Center, NCHU. $[C_4H_3N(CH_2NMe_2)_2\text{-}2,5]$ was prepared according to previously reported procedure [12]. YCl_3 (Strem) and n-BuLi (Aldrich) were used as received.

2.2. Synthesis of {Li[$C_4H_2N(CH_2NMe_2)_2$-2,5]}$_2$ (1)

A n-BuLi hexane solution (83.8 mmol, 2.5 M, 33.2 mL) was added dropwise to a heptane (50 mL) solution of $[C_4H_3N(CH_2NMe_2)_2\text{-}2,5]$ (15.0 g, 82.9 mmol) at 0 °C under nitrogen. The solution became cloudy while the n-BuLi solution was added. The milky white suspension was stirred at room temperature for 3 h, and the solid was isolated via filtration and dried under vacuum to generate 10.0 g of desired lithium salt in 65% yield. The white solid can be recrystallized from a saturated diethyl ether solution to yield colorless crystals. ^1H NMR ($CDCl_3$): δ 2.11 (s, 24H, N*Me*$_2$), 3.02 (s, 4H, C*H*$_2$NMe$_2$), 3.80 (s, 4H, C*H*$_2$NMe$_2$), 5.93 (s, 4H, C$_4$*H*$_2$N). ^1H NMR (toluene-d^8): δ 1.75 (s, 24H, N*Me*$_2$), 2.82 (s, 4H, C*H*$_2$NMe$_2$), 3.71 (s, 4H, C*H*$_2$NMe$_2$), 6.15 (s, 4H, C$_4$*H*$_2$N). ^{13}C NMR ($CDCl_3$): δ 43.2 (q, $J_{CH} = 117$ Hz, *C*H$_3$), 46.3 (q, $J_{CH} = 117$ Hz, *C*H$_3$), 61.2 (t, $J_{CH} = 132$ Hz, *C*H$_2$), 104.7 (d, $J_{CH} = 164$ Hz, *C*H), 138.4 (s, C_{ipso}). ^{13}C NMR (toluene-d^8): δ 42.6 (q, $J_{CH} = 117$ Hz, *C*H$_3$), 45.8 (q, $J_{CH} = 117$ Hz, *C*H$_3$), 61.6 (t, $J_{CH} = 132$ Hz, *C*H$_2$), 106.3 (d, $J_{CH} = 164$ Hz, *C*H), 137.5 (s, C_{ipso}). Anal. Calc. for $C_{20}H_{36}N_6Li_2$: C, 64.16; H, 9.69; N, 22.45. Found: C, 64.11; H, 9.84; N, 22.68.

2.3. Synthesis of {[$C_4H_2N(CH_2NMe_2)_2$-2,5]YCl$_2$-(μ-Cl)·Li(OEt$_2$)$_2$}$_2$ (2)

To a 50 mL Schlenk flask charged with 20 mL diethyl ether and YCl_3 (3.0 g, 15.38 mmol) was added dropwise with a Li[$C_4H_2N(CH_2NMe_2)_2$-2,5] (2.88 g, 15.4 mmol)/diethyl ether (20 mL) solution at −78 °C with stirring. The mixture was stirred at room temperature for 12 h and the resulting suspension was filtered through Celite. The filtrate was dried under vacuum to remove volatiles and the resulting solid was recrystallized from a diethyl ether solution to generate 5.64 g of 2 in 87% yield. Crystals suitable for X-ray structure analysis were obtained from a saturated diethyl ether solution upon standing

at −20 °C for several days. ^1H NMR ($CDCl_3$): 1.19 (t, 24H, OCH$_2$C*H*$_3$), 2.55 (s, 24H, N*Me*$_2$), 3.56 (q, 16H, OC*H*$_2$CH$_3$), 3.73 (s, 8H, C*H*$_2$N), 5.76 (m, 4H, C$_4$*H*$_2$N). ^{13}C NMR ($CDCl_3$): 14.9 (q, $J_{CH} = 126$ Hz, OCH$_2$*C*H$_3$), 47.2 (q, $J_{CH} = 138$ Hz, N*Me*$_2$), 62.9 (t, $J_{CH} = 137$ Hz, *C*H$_2$N), 65.6 (t, $J_{CH} = 140$ Hz, O*C*H$_2$CH$_3$), 102.0 (d, $J_{CH} = 165$ Hz, pyrrole CH), 135.6 (s, C_{ipso}). Due to the presence of small amount of lithium chloride in the product, the results of elemental analyses were found lower than expected even after repeating recrystallization in several attempts.

2.4. Single crystal X-ray structure determination

A single crystal was sealed in a glass capillary and transferred to a goniostat. Data collections were preformed at 298 K for compound 1 and 2. Data were collected on a Bruker SMART CCD diffractometer with graphite-monochromated Mo Kα radiation. Structure determinations were made using the SHELXTL package of programs. All refinements were carried out by

Table 1
The summary of crystallographic data for compounds 1 and 2

	1	2
Formula	$C_{20}H_{36}Li_2N_6$	$C_{36}H_{76}Y_2Li_2N_6O_4Cl_6$
f_w	374.43	1061.43
Temperature (K)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.9786(13)	11.8100(16)
b (Å)	9.7764(10)	13.4322(18)
c (Å)	18.9299(19)	17.106(2)
β (°)	94.217(2)	108.477(2)
Volume (Å^3)/Z	2395.4(4) /4	2573.7(6)/2
Density (calc.) (Mg/m^3)	1.038	1.370
Absorption coefficient (mm^{-1})	0.063	2.594
F(000)	816	1104
Crystal size (mm)	$0.42 \times 0.36 \times 0.35$	$0.60 \times 0.50 \times 0.35$
θ range (°)	2.16–27.53	2.37–27.53
No. of reflections collected	15,011	15,501
No. of independent reflections (R_{int})	5465 (0.0379)	5799 (0.0898)
Max. and min. transmission	0.9486 and 0.7374	0.9486 and 0.4544
No. of data/restraints/parameters	5465/0/253	5799/62/284
Goodness-of-fit on F^2	0.772	0.821
Final R indices $[I > 2\sigma(I)]$		
R_1[a]	0.0371	0.0569
wR_2[b]	0.0428	0.1190
R indices (all data)		
R_1[a]	0.1397	0.1125
wR_2[b]	0.0471	0.1291
Largest diff. peak and hole (e Å^{-3})	0.121 and −0.100	1.316 and −1.021

[a] $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$.
[b] $R_2 = [\sum[\omega(F_o^2 - F_c^2)] / \sum[\omega(F_o^2)^2]^2]^{1/2}$.

full-matrix least squares using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were included at calculated positions. The crystal data are summarized in Table 1. In **2**, some of carbon atoms show disorder. The dual-site disorder pairs: for C(9) and C(12) were fixed at a 0.5/0.5 ratio; for C(13) and C(14) were fixed at a 0.7/0.3 ratio; for C(15) and C(16) were fixed at 0.6/0.4 ratio.

2.5. Polymerization

Typically, a 50 mL Schlenk flask containing a toluene or THF solution (20 mL) of compounds **1** or **2** and a magnetic stirring bar under nitrogen, was added ε-caprolactone by a syringe, and the mixture was stirred at room temperature. The mixture was quenched with excess of methanol and solid was isolated by filtration, dried under vacuum.

3. Results and discussion

3.1. Synthesis and characterization of {Li[C$_4$H$_2$N(CH$_2$NMe$_2$)$_2$-2,5]}$_2$ (1) and {[C$_4$H$_2$N(CH$_2$NMe$_2$)$_2$-2,5]YCl$_2$(μ-Cl)·Li(OEt$_2$)}$_2$ (2)

The lithiated substituted pyrrolyl ligand **1** was obtained by adding n-BuLi to the heptane solution of [C$_4$H$_2$NH(CH$_2$NMe$_2$)$_2$-2,5] (Scheme 1). The air and moisture sensitive compound **1** could be isolated in 65% yield which decomposes readily while exposed to air. Although compound **1** reacts slowly with CDCl$_3$ resulting unidentified compounds, the ^{1}H and ^{13}C NMR spectra of **1** in CDCl$_3$ can be recorded. The ^{1}H

NMR spectra of **1** show that the methylene fragments appear as two broad resonances at δ 3.02 and 3.80 while the methyl groups at δ 2.11 as a broad resonance. However, the two broad resonances, indeed, indicated to presume the quick fluxional behavior of compound **1**. Therefore, variable temperature ^{1}H NMR spectra were drawn for compound **1** in toluene-d^8 from 230 to 340 K (see Fig. 1). At higher temperature compound **1** exhibits one resonance at δ 3.27 for symmetry-equivalent methylene protons of the substituted pyrrolyl ligands. Gradual lowering of the NMR probe temperature resulted in broadening of this resonance and then splitting into two doublets at δ 3.73 and 2.80. The activation energy for the fluxionality of compound **1** was estimated to be ca. 13.8 kcal/mol from the coalescence behavior [13]. A pluasible fluxional equilibria of compound **1** is shown in Scheme 2.

Reaction of **1** with one equivalent of YCl$_3$ in diethyl ether at room temperature afforded a diyttrium compound **2**, {[C$_4$H$_2$N(CH$_2$NMe$_2$)$_2$-2,5]YCl$_2$(μ-Cl)·Li(OEt$_2$)}$_2$ in 87% yield (Scheme 1). Compound **2** could be isolated directly from a diethyl ether solution after recrystallization. The presence of a triplet at δ 3.56 and a quartet at δ 1.19 in the ^{1}H NMR spectrum of **2** signify the presence of two equivalent of diethyl ether coordinated to Li (X-ray, see below). Attempts to remove this diethyl ether molecules by heating the solids under vacuum led only to the formation of less soluble compounds. Presumably, the coordinated diethyl ethers were removed from the core structure of **2** and less soluble polymeric yttrium compounds were formed. The proton resonances of methylene and methyl groups of the tridentate pyrrolyl ligands of 2 appeared as singlet at δ 3.73 and 2.55 justifying the symmetrical arrangement of the ligands. Compound **2** is very moisture and
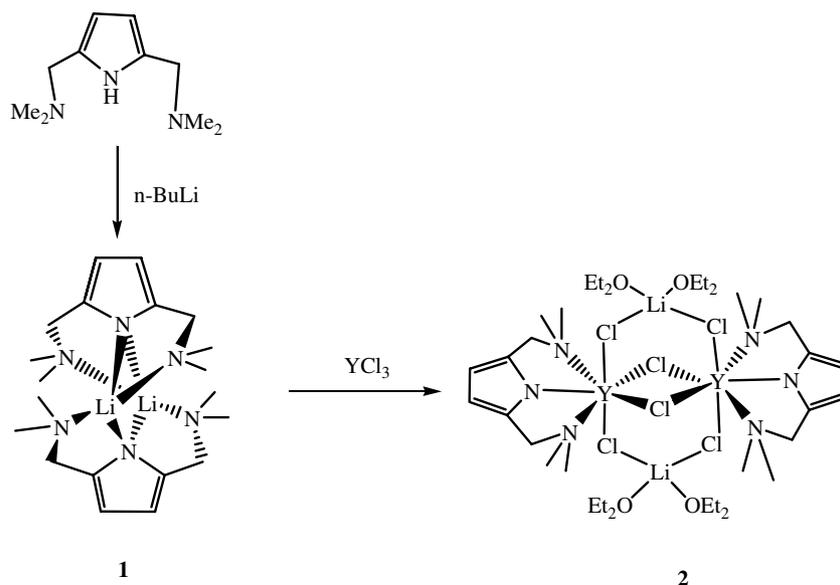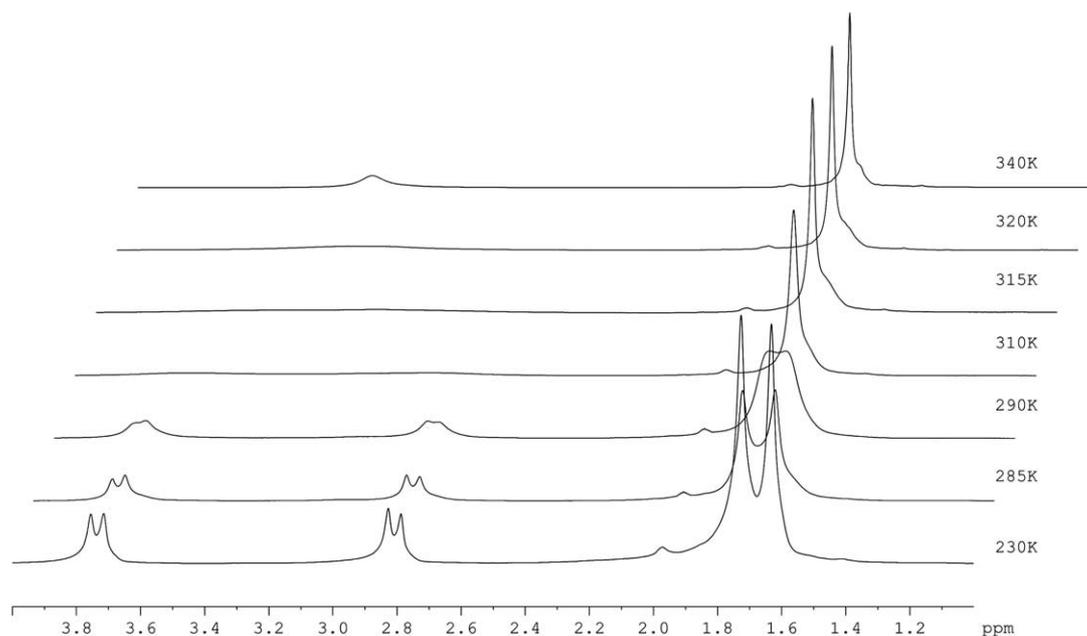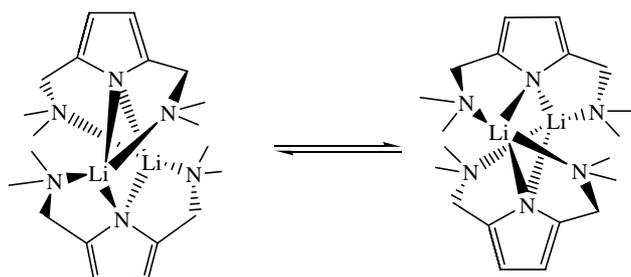

Scheme 1.

Fig. 1. Variable temperature NMR spectra of compound **1** in toluene-*d*[8] at a 300 MHZ NMR spectrometer.

Scheme 2.

Fig. 2. The molecular structure of compound **1**, showing 50% thermal ellipsoids probability. All the hydrogen atoms are omitted for clarity.

air sensitive, which readily decomposed to un-identified product when exposed to air.

Attempts to synthesize yttrium alkyl or alkoxide compounds by reacting **2** with alkyl lithium or lithium alkoxide reagents resulted in the reformation of lithiated pyrrolyl compound **1**.

3.2. Molecular structure of {Li[C₄H₂N(CH₂NMe₂)₂-2,5]}₂ (1)

The molecular structures of η^1-pyrrolyl lithium complexes have been reported in the literature [14]. Suitable crystals of compound **1** were grown from a saturated diethyl ether solution for structure determination. The molecular structure of the lithiated pyrrolyl compound is shown in Fig. 2 and selected bond distances and angles are listed in Table 2. The substituted pyrrolyl ligands act as tridentate ligands, with the nitrogen atoms of the two pyrrolyl bridged between the two lithium atoms forming a four-membered ring core structure. A schematic drawing the molecular geometry is shown in Fig. 3 with the view looking down the two lithium ions. The two lithium
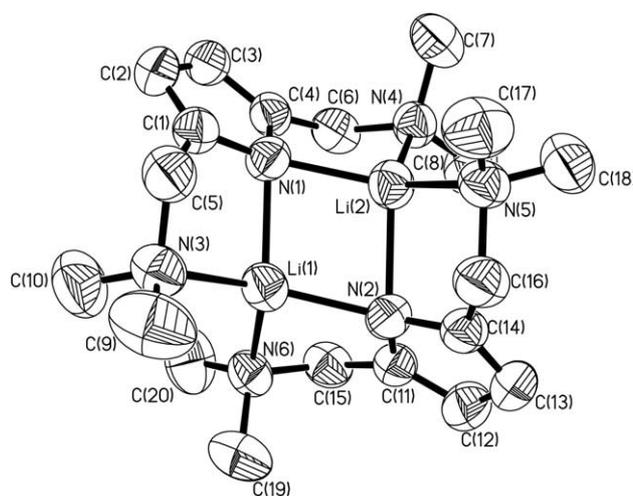
ions can be described as distorted tetrahedral geometries. The two nitrogen atoms of pyrrolyl fragments bind the two lithium atoms in an unsymmetric manner, with the Li–N bond distances in the ranges of 2.030(3)–2.110(3) Å. The N(dimethylamino)–Li–N(pyrrolyl) bite angles in **1** are smaller than a normal sp³ bond angle of 109.28°, ranges from 87.28(12)° to 90.50(12)°, due to the formation of ring constraint.

3.3. Molecular structure of {[C₄H₂N(CH₂NMe₂)₂-2,5] YCl₂(μ-Cl)·Li(OEt₂)₂}₂ (2)

Molecular structures of dimeric yttrium complexes containing variety of ligands have been characterized

Table 2
Selected bond distances (Å) and bond angles (°) for compounds **1** and **2**

1

Li(1)–N(1)	2.079(3)
Li(1)–N(3)	2.134(3)
Li(2)–N(1)	2.033(3)
Li(2)–N(4)	2.094(3)
Li(1)–Li(2)	2.591(4)
Li(1)–N(2)	2.030(3)
Li(1)–N(6)	2.105(3)
Li(2)–N(2)	2.110(3)
Li(2)–N(5)	2.121(3)
N(2)–Li(1)–N(6)	87.28(13)
N(2)–Li(1)–N(3)	139.13(16)
N(6)–Li(1)N(3)	117.32(14)
N(1)–Li(2)–N(2)	100.91(13)
N(1)–Li(2)–N(5)	135.45(16)
N(2)–Li(2)–N(5)	90.50(12)
Li(1)–N(2)–Li(2)	77.46(12)
N(2)–Li(1)–N(1)	102.07(13)
N(1)–Li(1)–N(6)	127.99(16)
N(1)–Li(1)–N(3)	88.16(13)
N(1)–Li(2)–N(4)	89.83(13)
N(2)–Li(2)–N(4)	119.73(15)
N(4)–Li(2)–N(5)	121.38(15)
Li(1)–N(1)–Li(2)	78.11(12)

2

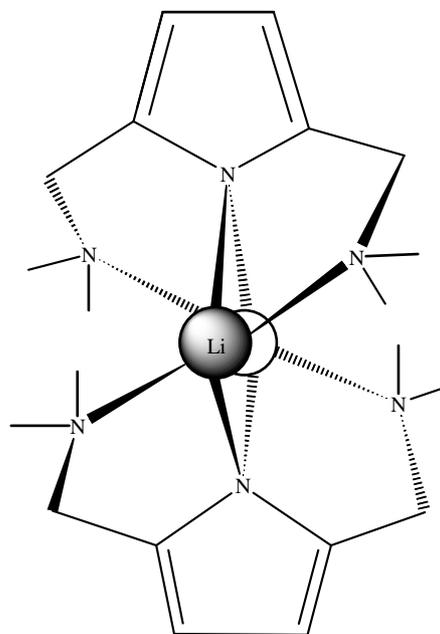|	
Y(1)–N(1)	2.269(4)
Y(1)–Cl(4)	2.639(2)
Y(1)–N(2)	2.658(5)
Y(1)–Cl(2)#1	2.7432(15)
Li(1)–O(2)	2.061(13)
Li(1)–Cl(4)#1	2.389(12)
Y(1)–Cl(3)	2.6349(15)
Y(1)–N(3)	2.654(4)
Y(1)–Cl(2)	2.7294(15)
Li(1)–O(1)	1.900(14)
Li(1)–Cl(3)	2.366(10)
N(1)–Y(1)–Cl(4)	92.66(12)
N(1)–Y(1)–N(3)	65.55(16)
Cl(3)–Y(1)–Cl(2)	93.43(5)
N(3)–Y(1)–Cl(2)	77.90(11)
O(1)–Li(1)–O(2)	108.6(6)
O(2)–Li(1)–Cl(3)	100.1(4)
O(2)–Li(1)–Cl(4)#1	108.7(6)
Y(1)–Cl(2)–Y(1)#1	103.56(5)
N(1)–Y(1)–Cl(3)	90.27(12)
Cl(3)–Y(1)–Cl(4)	176.96(5)
N(1)–Y(1)–N(2)	66.26(16)
Cl(4)–Y(1)–Cl(2)	84.75(5)
N(2)–Y(1)–Cl(2)	149.09(12)
O(1)–Li(1)–Cl(3)	109.2(6)
O(1)–Li(1)–Cl(4)#1	107.2(5)
Cl(3)–Li(1)–Cl(4)#1	122.3(5)

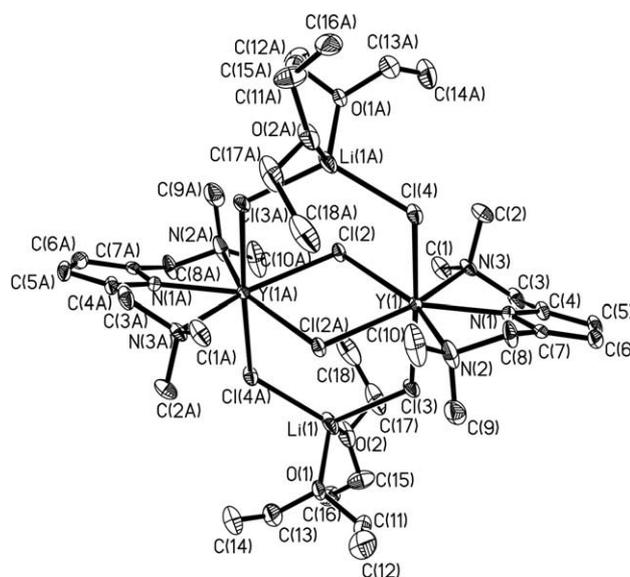Fig. 3. A schematic drawing of the molecular geometry of compound **1** with the view looking down the two lithium ions.

Fig. 4. The molecular structure of compound **2**, showing 30% thermal ellipsoids probability. All hydrogen atoms are omitted for clarity.

in the literature [15]. Molecules of compound **2** suitable for X-ray structure analysis were obtained from a saturated diethyl ether solution. The molecular structure of the substituted pyrrolyl yttrium compound **2** is shown in Fig. 4 and selected bond distances and angles are listed in Table 2. The molecular structure of **2** comprises of a central symmetrical geometry consisting of two seven-coordinate yttrium atoms, which are bridged by two chlorine atoms and two lithium atoms. The two lithium ions can be viewed as counter ions inserted into the diyttrium geometry and coordinated to more electron-rich chlorine atoms to stabilize the whole structure. The two chlorine atoms, Cl(3) and Cl(4), here can be considered as terminal atoms. A Cambridge Structure Database structure search shows that the general Y–Cl(terminal) bond distances are in the range of 2.60 Å,

Table 3
Ring-opening polymerization of ε-caprolactone using compounds **1**[a] and **2**[b]

Entry	Catalyst	[M]/[C]	Time	Mn (g/mol)	PDI	Yield
1	**1**	50	20 min[c]	89,400	1.95	96
2	**1**	100	7 min[c]	105,300	2.42	97
3	**1**	150	4 min[c]	101,300	2.60	98
4	**1**	200	3 min[c]	38,300	3.82	99
5	**1**	250	2 min[c]	11,400	2.18	95
6	**2**	100	24 h	–	–	–
7	**2**	200	24 h	–	–	–

[a] Reactions were carried in 20 mL toluene at room temperature.
[b] Reactions were carried in 20 mL THF at room temperature.
[c] The time for solution solidified.

and Y–Cl(bridge) bond distances are in the range of 2.70 Å. The two seven-coordinated yttrium atoms are both surrounded by a tridentate pyrrolyl ligand, two terminal chorine atoms, and two bridged chlorine atoms. The two terminal chlorine atoms of one yttrium coordination sphere are linked to the two chlorine atoms of the other yttrium's coordination sphere through lithium atoms. The geometry of seven-coordinated yttrium is best described as a pentagonal bipyramidal geometry with the two terminal chorine atoms being in the apical positions where the Cl(3)–Y–Cl(4) bond angle is 176.96(5)°. The pentagonal geometry, formed by the two bridged chlorine atoms and the three nitrogen atoms of the substituted pyrrolyl ligand, can be viewed as two skewed planes (N(3)–N(1)–N(2)–Y(1) vs. Y(1)–Cl(2)–Cl(2A)) with the dihedral angle of. The σ-bonded Y(1)–N(1) bond distance is 2.269(4)Å while the two coordinate-bonded Y(1)–N(2) and Y(1)–N(3) bond distances are at 2.658(5) and 2.654(4) Å, respectively.

3.4. Polymerization study

Compounds **1** and **2** have been studied as the catalysts for the ring-opening polymerization of ε-caprolactone and the results are shown in Table 3. The lithiated compound **1** exhibits high reactivity toward the ε-caprolactone polymerization, however, the PDI of the polycaprolactone is large. The large PDI value may be attributed to the fast initiating reaction by compound **1** and slow propagation. Compound **2** show no activity toward the ε-caprolactone polymerization even at higher temperature (50 °C). This may be due to the inertness of yttrium halide bonds. Currently we are working on synthesizing new lithium and yttrium complexes and studying the reactivity of these new complexes.

Acknowledgments

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 263808 and 263809. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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