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A facile route to lithium complexes supported by β-ketoiminate ligands and their reactivity

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ABSTRACT

Several β-ketoiminate lithium complexes $Li_2(L)_2 \cdot 2(THF)$ (**6**–**10**) were conveniently synthesized by using 1 equiv. of *n*-BuLi with 1 equiv. of β-ketoiminate ligands (**1**–**5**) in THF-hexane at 60 °C. All the new complexes have been characterized by NMR and IR spectroscopy. Complexes (**8**–**10**) were determined by single crystal X-ray diffraction. All the lithium complexes showed high activity for the ring-opening polymerization (ROP) of L-lactide to give the polyesters with relative narrow molecular weight distributions (Mw/Mn = 1.42–1.87). Complex **10** showed the highest activity toward ROP of L-LA. Moreover, the results proved that the polymerization initiated by complex **10** proceeded in a controllable fashion.

1. Introduction

Various chelating N or O containing moieties have been explored, such as amidinates [1–5], guanidinates [1,4,6–9], β-diketiminates [10–12], and bridged bisphenolate [13–15], etc. β-ketoiminates, as one of the members, have attracted increasing attention in organometallic chemistry, since their steric and electronic properties can be easily tuned by an appropriate choice of starting materials used in their synthesis. A variety of complexes of main and d-block metals with these ligands have been found wide applications in homogeneous catalysis including organic synthesis and polymerization of non-polar and polar monomers [16–24]. The lanthanide alkoxide complexes stabilized by monoanionic *N*-aryloxo-functionalized β-ketoiminates ligands are well known to be active catalysts in various transformations, such as the ring-opening polymerization of lactones and lactides [25] and organic reactions [26].

The synthesis of the lanthanide aryloxide complexes supported by a dianionic *N*-aryloxo-functionalized β-ketoiminate and their activity for ring-opening polymerization of L-lactide have been reported [25]. Several main group derivatives supported by β-ketoiminate ligands have also been synthesized [23,26–29], but no papers have been found to concern the application of the first group metals compounds in homogeneous catalysis for the ROP of L-lactide. However, the preparation and application of lithium catalysts/initiators such as, alkyl lithium, alkoxy lithium and bimetallic lithium compounds for the ROP of cyclic esters have developed [30,31]. Besides, the bimetallic complexes containing alkali metals have recently been found to be more active than the corresponding mononuclear partner, which was the cooperation between metals existed in the reactions [32–35]. In this connection we start the project on the synthesis of the first group metals stabilized by monoanionic β-ketoiminate ligands and their catalytic activity in hopes to assess the potential applications of β-ketoiminate ligands in design of organometallic catalysts.

It was found that the lithium complexes could be conveniently synthesized by the reaction of *n*-BuLi with β-ketoiminates and these complexes were found to be active catalysts for the ROP of L-lactide.

2. Experimental section

2.1. General remarks

All manipulations and reactions were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone

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ketyl prior to use. L-lactide was recrystallized twice. ($C_6H_5NC(CH_3)CHC(Ph)O$) (**1**) (LH), 2,6-Me-$C_6H_5NC(CH_3)CHC(Ph)O$ (**2**) ($L^{2,6\text{-}Me}H$), 2,6-^{i}Pr-$C_6H_5NC(CH_3)CHC(Ph)O$ (**3**) ($L^{2,6\text{-}iPr}H$), *p*-Cl-$C_6H_5NC(CH_3)CHC(Ph)O$ (**4**) ($L^{p\text{-}Cl}H$) and *p*-CH_3O–$C_6H_5NC(CH_3)CHC(Ph)O$ (**5**) ($L^{p\text{-}MeO}H$) were prepared according to the published procedures [36–38].

Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. ^{1}H NMR and ^{13}C NMR spectra of complexes **1**–**5** were recorded on a 300 MHz instrument in a $CDCl_3$ solution, while complexes **6**–**10** were recorded on a 400 MHz instrument in a THF-d_8 solution. Melting points were determined in sealed Ar-filled capillary tubes, and are not corrected. Molecular weight and molecular weight distribution (PDI) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL-GPC 50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL/min at 40 °C.

2.2. Syntheses of β-ketoiminate ligands

To a stirred solution of 1-phenylbutane-1, 3-dione (20 mmol) in dried toluene were added the aniline (20 mmol) and p-toluenesulfonic acid (ca. 20 mg) as a catalyst at room temperature. The mixture was heated and refluxed, and the water formed was removed azotropically using a Dean–Stark apparatus for 24 h. Evaporation of toluene gave yellow solid or oil. The crude product was purified by recrystallization from hexane. Light yellow or yellow solids were obtained, and they were characterized.

2.2.1. ($C_6H_5NHC(CH_3)CHCO(Ph)$) (**1**)

Yield = 83%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): 13.09 (s, 1H), 7.91 (d, J = 1.5 Hz, 2H), 7.40 (dd, J = 23.0 Hz, 6.9 Hz, 6H), 7.19 (d, J = 7.1 Hz, 2H), 5.90 (s, 1H), 2.14 (d, J = 5.7 Hz, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 188.76 (C=O), 162.99 (C–N), 139.83 (Carom), 138.45 (Carom), 130.71 (Carom), 128.97 (Carom), 128.10 (Carom), 126.89 (Carom), 125.55 (Carom), 124.49 (Ph-C), 94.60 (CHCO(Ph)), 20.21 (CH_3–CN).

2.2.2. 2,6-Me-$C_6H_5NHC(CH_3)CHCO(Ph)$ ($L^{2,6\text{-}Me}H$) (**2**)

Yield = 72%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): 12.53 (s, 1H), 7.94 (s, 2H), 7.45 (s, 3H), 7.13 (s, 3H), 5.93 (s, 1H), 3.48 (s, 3H), 2.25 (s, 6H); ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 188.76 (C=O), 165.06 (C–N), 163.92 (Carom), 136.70 (Carom), 136.17 (Carom), 130.98 (Carom), 128.45 (Carom), 128.02 (Carom), 127.72 (Carom), 127.27 (Ph-C), 92.47 (CHCO(Ph)), 24.45 (CH_3–CN), 19.70 (2,6-$(CH_3)_2$–C_6H_3), 18.52 (2,6-$(CH_3)_2$–C_6H_2).

2.2.3. 2,6-^{i}Pr-$C_6H_5NHC(CH_3)CHCO(Ph)$ ($L^{2,6\text{-}iPr}H$) (**3**)

Yield = 86%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): 12.66 (s, 1H), 7.96 (d, J = 0.5 Hz, 2H), 7.56–6.99 (m, 6H), 5.91 (s, 1H), 3.19–2.83 (m, 2H), 1.79 (s, 3H), 1.20 (dd, J = 17.2 Hz, 6.7 Hz, 12H). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 188.46 (C=O), 165.23 (C–N), 146.02 (Carom), 139.93 (Carom), 133.40 (Carom), 130.61 (Carom), 128.27 (Carom), 128.09 (Carom), 126.97 (Carom), 123.48 (Ph-C), 92.39 (CHCO(Ph)), 28.59 (CH-^{i}Pr), 24.69 (CH_3-^{i}Pr), 22.77 (CH_3-^{i}Pr), 19.93 (CH_3–CN).

2.2.4. *p*-Cl-$C_6H_5NHC(CH_3)CHC(Ph)O$ ($L^{p\text{-}Cl}H$) (**4**)

Yield = 65%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): 13.08 (s, 1H), 8.00–7.74 (m, 2H), 7.41 (dd, J = 31.2 Hz, 6.9 Hz, 5H), 7.13 (d, J = 7.9 Hz, 2H), 5.93 (s, 1H), 2.15 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 188.95 (C=O), 161.69 (C–N), 130.09 (Carom), 131.06 (Carom), 129.29 (Carom), 128.30 (Carom), 127.06 (Carom), 125.89 (Ph-C), 94.65 (CHCO(Ph)), 20.38 (CH_3–CN).

2.2.5. *p*-MeO-$C_6H_5NHC(CH_3)CHC(Ph)O$ ($L^{p\text{-}MeO}H$) (**5**)

Yield = 60%. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, δ [ppm]): 12.80(s, 1H), 7.92 (d, J = 2.3 Hz, 2H), 7.44 (s, 3H), 7.22–7.03 (m, 2H), 7.00–6.80 (m, 2H), 5.87 (s, 1H), 3.81 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C, δ [ppm]): 188.95 (C=O), 162.81 (C–N), 111.73–153.38 (Carom), 94.91 (CHCO(Ph)), 56.20 (2-OCH_3-C_6H_4), 20.95 (CH_3–CN).

2.3. Synthesis of complexes **6**–**10**

In an inert atmosphere, β-ketoiminate ligands (1 equiv.) were dissolved in anhydrous THF at room temperature. *n*-BuLi (1 equiv.) was added to the rapidly stirring solution in ice bath. Raising the temperature to room temperature, the complexes were isolated as yellow crystals in good yield after stirring for 4 h and workup from the concentrated THF solution.

2.3.1. $Li_2(L)_2\cdot 2(THF)$ (**6**)

Following the general procedure, from **LH** (237 mg, 1.0 mmol) and *n*-BuLi (2.6 M in hexane, 385 μL, 1.0 mmol) was obtained 478.3 mg of **6** as yellow crystals from concentrated tetrahydrofuran-cyclohexane solution at room temperature for two days (66%). m.p.: 254.5–255.0 °C (dec.). (Found: C, 77.82; H, 7.89; N, 6.40; $C_{48}H_{58}N_2Li_2O_4$ (740.96) requires C, 77.74; H, 7.83; N, 6.48. IR (KBr,cm^{-1}): 3057 (w, $\tilde{\nu}_{C\text{-}H}$), 1618 (s, $\tilde{\nu}_{C=O}$), 1549 (m), 1520 (m, $\tilde{\nu}_{C=N}$), 1434 (s), 1380 (w, δ_{C-H}), 1327 (s), 1158 (s), 1093 (w), 1068 (m), 1026 (m). ^{1}H NMR (400 MHz, THF-d_8, 25 °C, δ [ppm]): 7.71 (d, J = 7.2 Hz, 2H), 7.22 (*t*, J = 7.5 Hz, 2H), 7.12 (dd, J = 14.2 Hz, 7.1 Hz, 3H), 6.95 (s, 1H), 6.80 (d, J = 7.5 Hz, 2H), 5.49 (s, 1H), 1.82 (s, 3H). ^{13}C NMR (100.6 MHz, THF-d_8, 25 °C, δ [ppm]): 174.59, 167.91, 154.49, 144.24, 129.42, 128.58, 128.26, 127.19, 123.42, 122.83, 95.34, 22.66.

2.3.2. $Li_2(L^{2,6\text{-}Me})_2\cdot 2(THF)$ (**7**)

The synthesis of complex **7** was carried out in the same way as that described for complex **6**, but $\mathbf{L^{2,6\text{-}Me}H}$ (265 mg, 1.0 mmol) was used instead of **LH**. Light-yellow crystals were obtained from a mixture of THF/hexane solution (15 mL/1 mL) at room temperature over a few days (0.44 g, 57%). m.p.: 310.3–312.0 °C (dec.); (Found: C, 77.91; H, 8.36; N, 3.55; $C_{50}H_{64}N_2Li_2O_4$ (770.96) requires C, 77.83; H, 8.30; N, 3.63. IR (KBr, cm^{-1}): 3066 (w, $\tilde{\nu}_{C-H}$), 1600 (s, $\tilde{\nu}_{C=O}$), 1589 (s), 1504 (s, $\tilde{\nu}_{C=N}$), 1426 (w), 1383 (w, δ_{C-H}), 1319 (s), 1281 (m), 1088 (m), 1027 (m). ^{1}H NMR (400 MHz, THF-d_8, 25 °C, δ [ppm]): 7.58 (d, J = 7.1 Hz, 2H), 7.12–7.00 (m, 3H), 7.00–6.81 (m, 3H), 5.65 (s, 1H), 2.10 (s, 6H), 1.65 (s, 3H). ^{13}C NMR (100.6 MHz, THF-d_8, 25 °C, δ [ppm]): 173.52, 168.34, 151.88, 143.65, 129.78, 128.78, 128.65, 128.35, 127.03, 123.16, 94.58, 22.63, 18.82.

2.3.3. $Li_2(L^{2,6\text{-}ipr})_2\cdot 2(THF)$ (**8**)

Complex **7** was synthesized following a similar procedure in **6**–**7**: except [(PhCO)CH(CH_3CN-(H)(2,6-i-$Pr_2C_6H_5$)] ($\mathbf{L^{2,6\text{-}ipr}H}$) (322 mg, 1 mmol) was used. Yellow crystals of complex **8** were obtained from concentrated tetrahydrofuran-cyclohexane solution at room temperature for one day (55%). m.p.: 178.5–179.0 °C (dec.). Anal. Calc. For $C_{52}H_{68}Li_2N_2O_4$: C, 78.10; H, 8.51; N, 3.50. Found: C, 78.15; H, 8.60; N, 3.45. IR (KBr, cm^{-1}): 3088 (w, $\tilde{\nu}_{C\text{-}H}$), 1598 (s, $\tilde{\nu}_{C=O}$), 1576 (s), 1515 (w, $\tilde{\nu}_{C=N}$), 1456 (w), 1383 (w, $\delta_{C\text{-}H}$), 1316 (s), 1239 (w), 1177 (m). ^{1}H NMR (400 MHz, THF-d_8, 25 °C, δ [ppm]): 7.62 (s, 2H), 7.15–7.08 (m, 3H), 6.94 (d, J = 7.5 Hz, 3H), 5.64 (s, 1H), 3.20–3.17 (m, 2H), 1.27 (s, 3H), 1.09 (dd, J = 29.4 Hz, 3.4 Hz, 12H). ^{13}C NMR (100.6 MHz, THF-d_8, 25 °C, δ [ppm]): 167.59, 141.68, 140.55, 138.58, 138.25, 128.27, 127.03, 125.34, 123.90, 110.41, 94.10, 28.41, 24.75, 24.52, 23.83.

2.3.4. $Li_2(L^{p\text{-}Cl})_2\cdot 2(THF)$ (**9**)

The synthesis of complex **9** was carried out in the same way as that described for complex **6**, but [(phCO)CH(CH_3CN-(H)(*p*-Cl-

Table 1
Crystallographic data for complexes **8**–**10**.

Complex	**8**	**9**	**10**
Formula	$C_{52}H_{68}Li_2N_2O_4$	$C_{40}H_{42}Cl_2Li_2N_2O_4$	$C_{42}H_{48}Li_2N_2O_6$
F_w	798.96	699.54	690.70
T(K)	293(2)	293(2)	293(2)
Crystal system	Tetragonal	Triclinic	Monoclinic
Space group	I 41/a	$P-1$	P 21/c
a (Å)	25.8829(12)	10.7407(8)	11.6613(9)
b (Å)	25.8829(12)	12.0863(7)	8.4971(8)
c (Å)	14.2083(19)	15.3976(10)	19.2270(11)
α (deg)	90	92.443(5)	90
β (deg)	90	97.514(6)	91.384(7)
γ (deg)	90	107.357(6)	90
V (Å^3)	9518.5(14)	1884.4(2)	1904.6(3)
Z	8	2	2
D_{calc}	1.115	1.233	1.204
μ (mm^{-1})	0.068	0.214	0.079
F (000)	3456	736	736
Θ_{max}(°)	25.50	25.50	25.49
Reflections collected	11370	14238	8409
Independent reflections	4416	7003	3539
Observed reflections	3036	4016	2777
Parameters refined	273	469	246
$R(I > 2\sigma(I))$	0.0648	0.0690	0.0488
wR_2 (all data)	0.1796	0.2215	0.1310
GOF on F^2	1.067	1.022	1.034

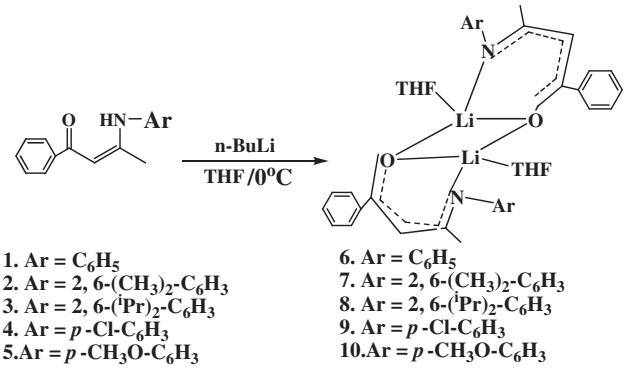
C_6H_5)] (**L$^{p\text{-Cl}}$H**) (272 mg, 1 mmol) was used. Yellow crystals of compound **9** were obtained from concentrated tetrahydrofuran-cyclohexane solution at room temperature for one day (60%). m.p.: 275.2–276.5 °C (dec.). Anal. Calc. For $C_{40}H_{42}Cl_2Li_2N_2O_4$: C, 68.62; H, 6.00; N, 4.00. Found: C, 68.70; H, 6.09; N, 3.96. IR (KBr, cm^{-1}): 3080 (w, $\tilde{\nu}_{C\text{-}H}$), 1623 (m, $\tilde{\nu}_{C=O}$), 1520 (m, $\tilde{\nu}_{C=N}$), 1326 (m, $\delta_{C\text{-}H}$), 1289 (w), 1157 (m). ^{1}H NMR (400 MHz, THF-d_8, 25 °C, δ [ppm]): 7.72 (s, 2H), 7.37–7.00 (m, 5H), 6.65 (d, J = 6.6 Hz, 2H), 5.31 (s, 1H), 1.76(s, 3H). ^{13}C NMR (100.6 MHz, THF-d_8, 25 °C, δ [ppm]): 163.73, 153.22, 144.33, 144.24, 129.40, 128.91, 128.27, 127.24, 125.00, 95.49, 22.58.

2.3.5. $Li_2(L^{p\text{-}MeO})_2\cdot 2(THF)$ (**10**)

The synthesis of complex **10** was carried out in the same way as that described for complex **6**, but [(phCO)CH(CH_3CN-(H)(p-CH_3O–C_6H_5)] (**L$^{p\text{-MeO}}$H**) (267 mg, 1 mmol) was used. Yellow crystals of compound **10** were obtained from concentrated tetrahydrofuran-cyclohexane solution at room temperature for one day (52%). m.p.: 194.0–195.2 °C (dec.). Anal. Calc. For $C_{42}H_{48}Li_2N_2O_6$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.40; H, 6.35; N, 5.20. IR (KBr, cm^{-1}): 3062 (w, $\tilde{\nu}_{C\text{-}H}$), 1609 (s, $\tilde{\nu}_{C=O}$), 1576 (m), 1507 (s, $\tilde{\nu}_{C=N}$), 1383 (w, $\delta_{C\text{-}H}$), 1249 (s), 1157 (w), 1070 (m). ^{1}H NMR (400 MHz, THF-d_8, 25 °C, δ [ppm]): 7.71 (d, J = 6.5 Hz, 2H), 7.16–7.14 (m, 3H), 6.81 (d, J = 9.2 Hz, 2H), 6.73 (d, J = 6.8 Hz, 2H), 5.47 (s, 1H), 3.78 (s, 3H OCH_3), 2.06 (s, 3H). ^{13}C NMR (100.6 MHz, THF-d_8, 25 °C, δ [ppm]): 163.40, 132.85, 131.42, 128.97, 128.32, 128.00, 127.38, 124.11, 115.10, 114.80, 93.75, 55.77, 22.64.

2.4. General procedure for the polymerization reaction

The ring-opening polymerization of L-lactide initiated by complexes **6**–**10**, and a typical polymerization procedure is as follows: A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the desired amount of L-lactide and THF. The contents of the flask were then stirred until L-lactide was dissolved, then a solution of the initiator in THF was added using a syringe. The mixture was stirred vigorously for the desired time, during which an increase in the viscosity was observed. The reaction mixture was quenched by the addition of ethanol and then poured into ethanol to precipitate the polymer. The polymer was dried under a vacuum and weighed.



Scheme 1. Synthesis of complexes **6**–**10**.

2.5. X-ray crystallography

Suitable single crystals of complexes **8**, **9** and **10** were sealed in a thin-walled glass capillary for determination of the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in the ω scan mode using MoKα radiation (λ = 0.71070 Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using the SHELEXL-97 programs [39].

3. Results and discussion

3.1. Syntheses of complexes **6**–**10**

The β-ketoiminate ligands, LH (**1**), L$^{2,6\text{-Me}}$H (**2**), L$^{2,6\text{-iPr}}$H (**3**), L$^{p\text{-Cl}}$H (**4**) and L$^{p\text{-MeO}}$H (**5**) were synthesized by the published method [38].

The reaction of 1 equiv. of n-BuLi with 1 equiv. of β-ketoiminate ligands were tried at 0 °C and then raising the temperature to room temperature led in the isolation of the desired lithium complexes **6**–**10** (Scheme 1).

Complexes **6**–**10** were characterized by standard analytical/spectroscopic techniques. The IR spectra of **6**–**10** exhibited strong absorptions near 1550 and 1510 cm^{-1}, indicative of the partial C=N character of the β-ketoiminate ligands. ^{1}H NMR spectrum of **6**–**10** revealed signals assigned to the corresponding ligand. The formations of **8**–**10** were further confirmed by single-crystal structure analysis. An attempt to determine the molecular structures of **6** and **7** were unsuccessful, due to the poor quality and weak diffraction of the crystals. Complexes **6**–**10** are sensitive to air and moisture. They have good solubility in THF except complex **8**.

3.2. Molecular structures of complexes **8**–**10**

To provide complete structural information for these new lithium complexes, single-crystal X-ray structural analyses were carried out for complexes **6**–**10**. Crystals suitable for an X-ray structure determination of complexes **8**–**10** were obtained from a

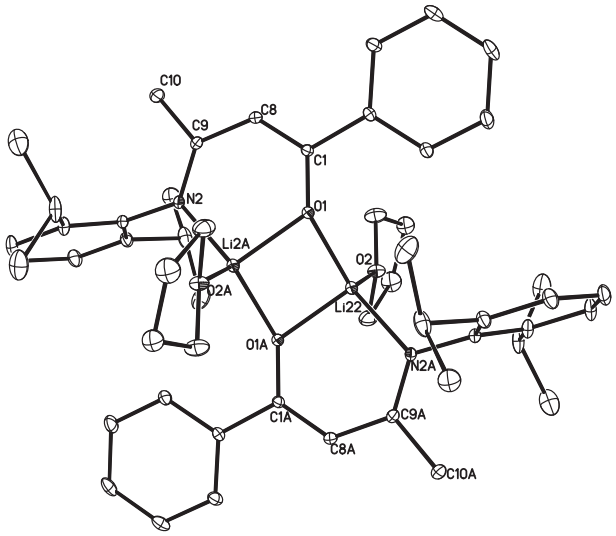


Fig. 1. ORTEP diagram of complex $Li_2(L^{2,6\text{-ipr}})_2 \cdot 2(THF)$ **8** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity (#1 $-x+1, -y+1, -z+2$).

THF solution at room temperature. X-ray diffraction analyses showed that complexes **8**–**10** are dimeric structure and all crystallizes with two THF molecules in the unit cell. The molecular structure of complexes **8**–**10** was shown in Figs. 1–3, their selected bond lengths and bond angles are listed in Table 2. Each β-ketoiminate ligand binds to a Li atom in the typical chelating fashion, with the O–Li–N angles of 131.6 (3), 112.8 (2) and 95.94 (18)o for **8**, 95.2 (2), 106.1 (3), 140.0 (3) for **9** and 128.22 (16), 94.06 (13), 116.69 (15) for **10** (Table 2). In the unit cell of complexes **8**, **9** and **10** crystallize with two THF molecules, the Li atom is four-coordinated by two oxygen atoms from two different β-ketoiminate ligands, one nitrogen atom from one β-ketoiminate ligand and one oxygen atom from one solvated THF molecule. The coordination geometry around the Li metal can be best described as a distorted pseudo-tetrahedron, which is different from those for cubane Li_4O_4 β-ketoiminate complexes [29]. The cubane Li_4O_4 structures of reported complexes are comprised of four lithium atoms and four ligands, e.g. $[\{Pr^iNCMeCHCMeOLi \cdot OP(NMe_2)_3\}_2]$ and $[(Pr^iNCMeCHCMeOLi)_4]$ [29]. The O (1), O (2), O (4), O (5) and N (2) atoms can be considered to occupy equatorial positions, O (3) and N (1) atoms occupy axial positions with the angle of O(3)–Li–N(1) being distorted away from the idealized 180° to 167.78 (8)o for **8**, 148.8 (3) o to 95.1 (2)o for **9** and 128.2 (16)o to 94.1 (3)o for **10**. The average

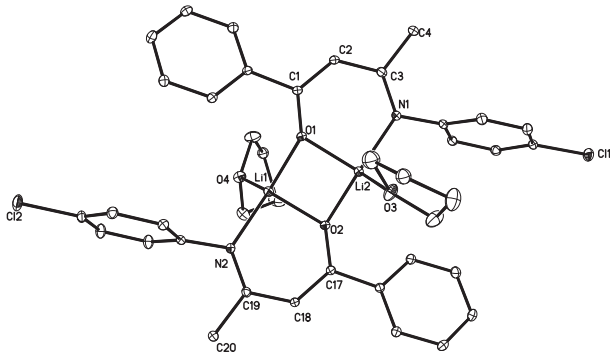


Fig. 2. ORTEP diagram of complex $Li_2(L_2^{p\text{-Cl}})_2 \cdot 2(THF)$ **9** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity.

Li–O distance of 1.912 (5) Å for **8**, 1.902 (6) for **9** are shorter than in $[\{Pr^iNCMeCHCMeOLi \cdot OP(NMe_2)_{32}]$ (1.918 (5) Å) [29], but the average Li–O distance of 1.919 (3) for **10** is similar with the complex $[\{Pr^iNCMeCHCMeOLi \cdot OP(NMe_2)_{32}]$ (1.918 (5) Å) [29]. The average Li–N distance of **8** (2.020 Å), **9** (2.020 Å) and 1.989 Å are longer than the complex $[(Pr^iNCMeCHCMeOLi)_4]$ (1.977 (8) Å) [29]. This may be also attributed to the steric demand resulted from the different bond length between these complexes, which are in accordance with the corresponding bond lengths in the Schiff base complex of lithium [31], and the other lithium β-ketoiminate complexes [31,40–43], when the differences in the steric demand among these complexes are considered. The bond parameters revealed a π-electron delocalization within the β-ketoiminate moieties.

3.3. Ring-opening polymerization of L-lactide (L-LA) by complexes **6**–**10**

To further explore the relationship between the structures of the catalysts and their catalytic properties and behaviors, complexes **6**–**10** were examined in the ROP of L-lactide. As expected, the β-ketoiminate lithium complexes were efficient initiators in the ROP of L-lactide. The representative polymerization results are shown in Table 3. It is clear that L-lactide polymerization can be initiated by all of the β-ketoiminate lithium complexes. Among the five complexes, **10** showed the highest activity toward ROP of L-LA (Table 3, entries **1**–**27**). To compare with lithium complexes supported by bridged bis-phenolate ligands reported [44,45], complexes **6**–**10** show higher reactivity but less controllability in the ROP of L-lactide.

As shown in Table 3, the polymerization medium also has a profound effect on the catalytic activity and the molecular weight

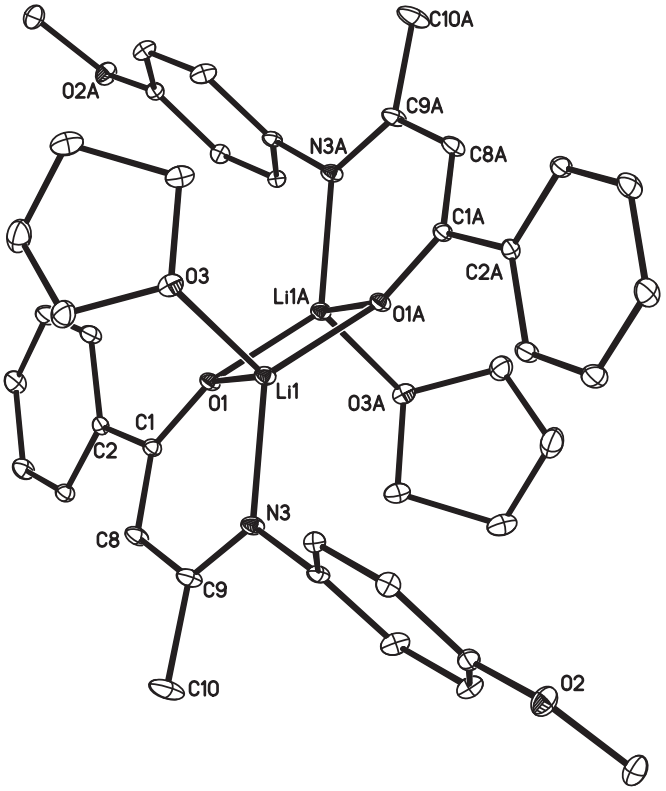


Fig. 3. ORTEP diagram of complex $Li_2(L_2^{p\text{-CH3O}})_2 \cdot 2(THF)$ **10** showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level and hydrogen atoms are omitted for clarity (#1 $-x, -y+1, -z$).

Table 2
Selected bond lengths (Å) and bond angles (°) of complexes **8**–**10**.

Complex **8**			
O(1)–Li(22)#1	1.879(4)	O(1)-Li(22)	1.892(4)
O(2)–Li(22)	1.965(5)	N(2)-Li(22)#1	2.020(4)
Li(22)#1–O(1)–Li(22)	85.22(19)	N(2)#1-Li(22)-Li(22)#1	124.6(3)
O(2)–Li(22)–Li(22)#1	118.0(3)	O(1)-Li(22)-Li(22)#1	47.18(14)
O(1)#1–Li(22)–Li(22)#1	47.60(14)	O(2)-Li(22)-N(2)#1	112.8(2)
O(1)–Li(22)–N(2)#1	131.6(3)	O(1)#1-Li(22)-N(2)#1	95.94(18)
O(1)–Li(22)–O(2)	107.5(2)	O(1)#1–Li(22)–O(2)	109.5(2)
Complex **9**			
O(1)–Li(2)	1.891(6)	O(1)–Li(1)	1.911(6)
O(2)–Li(1)	1.891(6)	O(2)–Li(2)	1.917(6)
N(1)–Li(2)	2.036(6)	N(2)–Li(1)	2.009(6)
Li(2)–O(1)–Li(1)	88.1(2)	Li(1)–O(2)–Li(2)	87.9(2)
O(2)–Li(1)–O(1)	92.0(3)	O(2)–Li(1)–O(4)	112.0(3)
O(1)–Li(1)–O(4)	110.1(3)	O(2)–Li(1)–N(2)	95.0(2)
O(1)–Li(1)–N(2)	140.1(3)	O(4)–Li(1)–N(2)	103.3(3)
O(2)–Li(1)–Li(2)	46.44(18)	O(1)–Li(1)–Li(2)	45.63(18)
O(4)–Li(1)–Li(2)	122.4(3)	N(2)–Li(1)–Li(2)	127.2(3)
O(1)–Li(2)–O(2)	91.9(3)	O(1)–Li(2)–O(3)	114.0(3)
O(2)–Li(2)–O(3)	106.2(3)	O(1)–Li(2)–N(1)	94.9(2)
O(2)–Li(2)–N(1)	140.8(3)	O(3)–Li(2)–N(1)	106.1(3)
O(1)–Li(2)–Li(1)	46.27(18)	O(2)–Li(2)–Li(1)	45.64(18)
O(3)–Li(2)–Li(1)	118.3(3)	N(1)–Li(2)–Li(1)	129.4(3)
Complex **10**			
O(1)–Li(1)#1	1.892(3)	O(1)–Li(1)	1.902(3)
O(3)–Li(1)	1.963(3)	N(3)–Li(1)	1.987(3)
Li(1)#1–O(1)–Li(1)	83.65(13)	O(1)#1–Li(1)–O(1)	96.42(13)
O(1)#1–Li(1)–O(3)	109.14(14)	O(1)–Li(1)–O(3)	104.87(13)
O(1)#1–Li(1)–N(3)	128.22(16)	O(1)–Li(1)–N(3)	94.06(13)
O(3)–Li(1)–N(3)	116.69(15)	O(1)#1–Li(1)–Li(1)#1	48.34(10)
O(1)–Li(1)–Li(1)#1	48.01(10)	O(3)–Li(1)–Li(1)#1	116.02(18)
N(3)–Li(1)–Li(1)#1	121.06(19)		

Symmetry transformations used to generate equivalent atoms for **8**: #1 $-x+1, -y+1, z+2$; **10**: #1 $-x, -y+1, -z$.

of the resultant polymers. It was found that complex **10** showed greater activity in THF than in toluene (Table 3, entries **24**–**26** and **52**–**34**). The reaction time played an important role in the ROP of L-LA. For example, when complex **10** was used, the yield increased with the prolonger of the reaction time, and decreased when prolonging the reaction time over 30 min (Table 3, entries **25** and **28**–**31**). The reason may be that the monomer had been converted completely after the transesterification reactions for 30 min (Table 3, entries **28**–**31**). The molecular weights obtained by GPC followed the trend of the yield when the reaction time prolonged, while the molecular weight distributions remained almost unchanged (1.46–1.52), indicating a controllable polymerization of **10**.

Table 3
Polymerization of L-LA Initiated by complexes **6**–**10**.[a]

Entry	Init	$[M]_0/[I]_0$	Temp (°C)	Conv (%)[b]	Mn_n(Calcd)[c] (10^4)	Mn_n(10^4)[d]	PDI
1	**6**	100:1	20	96	1.38	9.28	1.54
2	**6**	200:1	20	91	2.62	6.44	1.58
3	**6**	300:1	20	83	3.59	5.70	1.56
4	**6**	400:1	20	75	4.32	5.00	1.55
5	**6**	500:1	20	72	5.20	5.11	1.53
6	**7**	100:1	20	88	1.27	1.65	1.49
7	**7**	200:1	20	94	2.71	3.34	1.53
8	**7**	300:1	20	91	3.94	5.81	1.51
9	**7**	400:1	20	87	5.02	6.17	1.42
10	**7**	500:1	20	78	5.62	5.01	1.48
12	**8**	100:1	20	91	1.31	3.82	1.50
13	**8**	200:1	20	92	2.65	5.14	1.48
14	**8**	300:1	20	80	3.46	5.26	1.44
15	**8**	400:1	20	78	4.50	4.81	1.43
16	**8**	500:1	20	65	4.68	1.93	1.42
17	**9**	200:1	20	85	2.45	3.91	1.48
18	**9**	300:1	20	80	3.46	3.09	1.65
19	**9**	400:1	20	60	3.46	2.59	1.60
20	**9**	500:1	20	60	4.32	2.44	1.52
21	**9**	800:1	20	41	4.73	1.75	1.53
22	**10**	100:1	20	93	1.34	8.94	1.62
23	**10**	200:1	20	92	2.65	8.14	1.53
24	**10**	300:1	20	90	3.89	8.60	1.50
25	**10**	400:1	20	82	4.72	7.29	1.50
26	**10**	500:1	20	78	5.62	6.31	1.50
27	**10**	800:1	20	56	6.46	4.98	1.45
28	**10**	400:1	30	98	5.65	7.61	1.46
29	**10**	400:1	60	94	5.42	6.17	1.51
30	**10**	400:1	90	81	4.67	5.17	1.51
31	**10**	400:1	120	74	4.27	5.14	1.52
32	**10**[e]	300:1	20	81	3.50	4.41	1.51
33	**10**[e]	400:1	20	76	4.38	3.97	1.53
34	**10**[e]	500:1	20	71	5.12	3.54	1.57

[a] General polymerization conditions:THF solution, $[V]_{sol}/[V]_{mono} = 10:1$, $t = 20$ min for L-LA.
[b] Conv: weight of polymer obtained/weight of monomer used.
[c] Mn_n (Calcd) $= M_{mono} \times [M]_0/[I]_0 \times$ Conv.
[d] Measured by GPC relative to polystyrene standards.
[e] Solvent: toluene.

4. Conclusion

Five β-ketoiminate ligands (**1**–**5**) were synthesized and their lithium complexes (**6**–**10**) were convenient prepared by reaction with *n*-BuLi, respectively. All complexes were found to be active catalysts for the ROP of L-LA to give the polyesters with high molecular weights and relative narrow molecular weight distributions. Among the five lithium complexes, complex 1**0** showed the highest activity toward ROP of L-LA. Moreover, the results proved that the polymerization initiated by **10** proceeded in a controllable fashion. The study on the sign of main group catalysts with β-ketoiminate ligands is going on in our laboratory.

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Appendix A. Supplementary data

CCDC 903670, 884416 and 903669 contain the supplementary crystallographic data for this paper. These data can be obtained free

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

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