



# Syntheses, characterization of N-functionalized benzyl zinc, cadmium and manganese (II) compounds

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## ABSTRACT

Treatment of  $[\text{LiL} \cdot \text{TMEDA}]$  (**1**)  $\{\text{L} = [2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{CH}(\text{SiMe}_3)]^-\}$  with half equivalent of  $\text{ZnCl}_2$ ,  $\text{CdCl}_2$  or  $\text{MnCl}_2$  in diethyl ether gave the crystalline compound  $[\text{ML}_2]$   $\{\text{M} = \text{Zn}$  (**2**),  $\text{Cd}$  (**3**) and  $\text{Mn}$  (**4**) $\}$ , respectively. Reaction of **1** with one equivalent of  $\text{ZnCl}_2$  in diethyl ether afforded the crystalline compound  $[\text{Zn}(\text{Cl})\text{L} \cdot \text{TMEDA}]$  (**5**) in good yield. An eight-membered cyclic homoleptic binuclear compound  $[\text{ZnL}']_2$  (**6**)  $\{\text{L}' = [(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{CH})_2\text{SiMe}_2]^{2-}\}$  was prepared from the reaction of  $(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{CH}_2)_2\text{SiMe}_2$  (**B'**) with two equivalents of *n*-BuLi and one equivalent of  $\text{ZnCl}_2$ . All of the crystalline compounds **1–6** were well characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectroscopy, elemental analyses and single crystal X-ray crystallography. In addition, moderate activity for the polymerization of *rac*-lactide to poly(lactic acid) (PLA) was found in compounds **2** and **5**, and all the resulting polylactides are most predominantly heterotactic-rich.

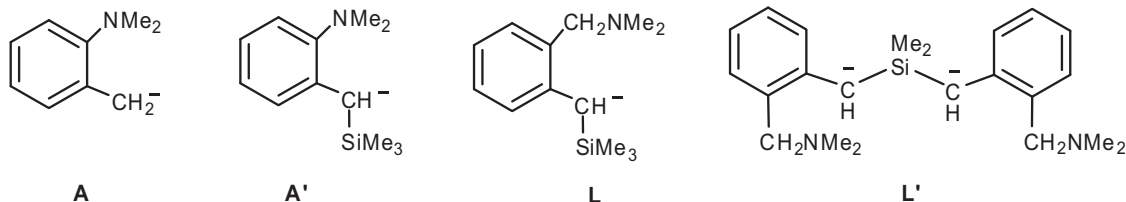
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## 1. Introduction

Transition metal alkyl compounds are well known and play an important role in the chemistry of simple organic compounds because the properties of alkyl groups have been imparted by the transition metals [1]. Zinc and cadmium metal alkyl adducts with nitrogenous bases were firstly reported by Thiele in 1962 [2], then zinc and cadmium metal(II) compounds with alkyl and amido ligands extensively appeared in the literature [3–15]. For organo-manganese (II) compounds having alkyl and amido ligands,

were used in direct *ortho*-metalation of anisole or cyclic ethers (tetrahydrofuran; tetrahydropyran) adjacent to oxygen [17] and bimetallic sodium-manganese base was a useful reagent for cleavage and capture chemistry of tetrahydrofuran [18,19].

Organometallic compounds based on N-functionalized benzyl anion ligand **A** [20–26] or silyl-substituted benzyl anion ligand **A'** have been well documented [27–30], whereas organometallic compounds based on the ligand **L**  $\{\text{L} = [2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{CH}(\text{SiMe}_3)]^-\}$  are rarely reported. The sole example is the lithium compound co-crystallized with *n*-BuLi to form a ladder structure [31].



Cahiez and his co-workers compiled an authoritative review in 2009 [16]. Alkyl compounds have attracted increasing attention due to their use in the deprotonative metalation for the regioselective functionalization of aromatic compounds, cyclic ethers or ethylene. For example, bimetallic alkyl lithium cadmates or lithium zincates

Herein, we report the synthesis and structural characterization of a series of lithium, zinc, cadmium and manganese compounds based on **L** and the novel zinc compound with the dimethylsilyl group bridged dianion ligand **L'**  $\{\text{L}' = [(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{CH})_2\text{SiMe}_2]^{2-}\}$ .

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The catalytic behaviors in ring-opening polymerization of *rac*-lactide were also presented for the zinc compounds **2** and **5**.

## 2. Experimental

### 2.1. General comments

All manipulations were carried out under nitrogen atmosphere in flamed Schlenk-type glassware on a dual manifold Schlenk line. Solvents purchased from commercial sources were distilled over standard drying agents under nitrogen from alkali metals directly and stored over 4 Å molecular sieves. All the chemicals used were of reagent grade, obtained from Aldrich. *N,N,N,N*-tetramethylethylenediamine (TMEDA) were distilled from KOH prior to use. *rac*-Lactide was recrystallized with dry toluene and sublimed twice under vacuum at 50 °C. Melting points were determined in sealed capillaries under argon on an electrothermal apparatus and are uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker DRX 300 (300.1 MHz for <sup>1</sup>H, 75.5 MHz for <sup>13</sup>C) instrument and referenced internally to the residual solvent resonances (chemical shift data in δ). All NMR spectra (<sup>1</sup>H, <sup>13</sup>C) were measured at 298 K and all <sup>13</sup>C NMR spectra were proton-decoupled. The homonuclear decoupled <sup>1</sup>H NMR spectrum were recorded on a Bruker AV 400 spectrometer at 400. Elemental analyses were performed on a Vario EL-III instrument. X-ray single crystal structures were determined on a Bruker Smart CCD APEX area detector. Gel permeation chromatography (GPC) analyses were carried out on a Waters 1515 Breeze Gel Permeation Chromatograph equipped with differential refractive index detectors. The GPC columns were eluted with tetrahydrofuran with 1 mL/min rate at 25 °C and were calibrated with monodisperse polystyrene standards.

### 2.2. Synthesis of 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SiMe<sub>3</sub> (**B**)

To a solution of 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> (12.7 g, 85.2 mmol) and TMEDA (9.9 g, 12.7 mL, 85.2 mmol) in diethyl ether (100 mL) was added dropwise *n*-BuLi (2.5 M, 34.1 mL, 85.2 mmol) in hexane at 0 °C. The mixture was slowly allowed to warm to ambient temperature and stirred for 8 h. ClSiMe<sub>3</sub> (10.9 mL, 9.3 g, 85.2 mmol) was added dropwise via a syringe at 0 °C. The reaction mixture was stirred overnight, and then water (10 mL) was added. The aqueous phase was separated and extracted with diethyl ether (15 mL × 3). The combined organic phase was dried over MgSO<sub>4</sub> and rotary evaporated under reduced pressure. Compound **B** (17.4 g, 91%) was obtained as a colorless liquid by distillation under reduced pressure (bp 72–74 °C, 5 Pa). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.16 (s, 6H, NMe<sub>2</sub>), 2.37 (s, 2H, CH<sub>2</sub>SiMe<sub>3</sub>), 3.34 (s, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 0.07 (s, 9H, SiMe<sub>3</sub>) 7.04–7.37 (m, 4H, Ar-H), <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -1.2 (SiMe<sub>3</sub>), 21.5 (CH<sub>2</sub>SiMe<sub>3</sub>), 48.6 (NMe<sub>2</sub>), 62.2 (CH<sub>2</sub>NMe<sub>2</sub>), 123.7, 126.0, 126.5, 131.8, 135.1, 140.3 (Ar-C).

### 2.3. Synthesis of (2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>SiMe<sub>2</sub> (**B'**)

From 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> (6.41 g, 42.6 mmol), TMEDA (6.3 mL, 42.6 mmol), *n*-BuLi (2.5 M, 17.1 mL, 42.6 mmol) and Cl<sub>2</sub>SiMe<sub>2</sub> (2.6 mL, 21.3 mol), using the procedure similar to that for **B**, there was obtained pale yellow liquid of **B'** (5.43 g, 71%, bp 118–120 °C, 5 Pa). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ -0.03 (6H, SiMe<sub>2</sub>), 2.33 (s, 2H, CH<sub>2</sub>SiMe<sub>2</sub>), 2.37 (s, 2H, CH<sub>2</sub>SiMe<sub>2</sub>), 2.11 (s, 6H, NMe<sub>2</sub>), 2.19 (s, 6H, NMe<sub>2</sub>), 3.24 (s, 4H, CH<sub>2</sub>NMe<sub>2</sub>), 6.94–7.25 (m, 8H, Ar-H), <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -1.57 (SiMe<sub>2</sub>), 22.7 (CH<sub>2</sub>SiMe<sub>2</sub>), 46.7 (NMe<sub>2</sub>), 63.6 (CH<sub>2</sub>NMe<sub>2</sub>), 125.1, 128.1, 130.3, 131.5, 136.5, 140.6 (Ar-C).

### 2.4. Synthesis of [2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH(SiMe<sub>3</sub>)Li·TMEDA] (**1**)

*n*-BuLi (31.7 mmol, 12.7 mL, 2.5 M in hexane) was added dropwise to solution of **B** (7.11 g, 31.7 mmol) and TMEDA (3.72 g, 31.7 mmol) in hexane (40 mL) at 0 °C. The solution became yellow and was stirred at room temperature for 8 h. The yellow precipitate was collected by filtration and dried *in vacuo* to give the yellow solid which was recrystallized from a saturated hexane solution to yield pale yellow crystals of **1** (8.20 g, 75%). Mp: 91–93 °C. *Anal.* Calc. for C<sub>19</sub>H<sub>38</sub>N<sub>3</sub>SiLi: C, 66.44; H, 11.21; N, 12.13. Found: C, 66.32; H, 11.06; N, 12.31%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.09 (s, 9H, SiMe<sub>3</sub>), 2.06 (s, 18H, NMe<sub>2</sub> and Me of TMEDA), 2.11 (t, 4H, CH<sub>2</sub> of TMEDA), 2.15 (s, 2H, CH<sub>2</sub>SiMe<sub>3</sub>), 3.34 (s, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 7.04–7.37 (m, 4H, Ar-H), <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 1.73 (SiMe<sub>3</sub>), 21.2 (CH<sub>2</sub>SiMe<sub>3</sub>), 45.9 (CH<sub>3</sub> of TMEDA), 48.1 (NMe<sub>2</sub>), 56.2 (CH<sub>2</sub> of TMEDA), 63.2 (CH<sub>2</sub>NMe<sub>2</sub>), 126.2, 127.5, 128.7, 131.8, 135.8, 140.1 (Ar-C).

### 2.5. Synthesis of [{2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH(SiMe<sub>3</sub>)<sub>2</sub>Zn] (**2**)

ZnCl<sub>2</sub> (0.21 g, 1.5 mmol) was added to a yellow solution of **1** (1.04 g, 3.0 mmol) in diethyl ether (20 mL) at -78 °C. The resulting mixture was warmed up to room temperature slowly and stirred for 12 h. The white precipitate was filtered off. The filtrate was concentrated to ca. 10 mL *in vacuo* and set aside yielding colorless crystals of **2** (0.62 g, 81%). Mp: 134–136 °C. *Anal.* Calc. for C<sub>26</sub>H<sub>44</sub>N<sub>2</sub>Si<sub>2</sub>Zn: C, 61.69, H, 8.76, N, 5.53. Found: C, 61.54, H, 8.69, N, 5.71%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.09 [s, 18H, SiMe<sub>3</sub>], 1.43, 1.47 (s, 2H, CHSiMe<sub>3</sub>), 2.55, 2.68 (s, 12H, NMe<sub>2</sub>), 3.53, 3.57 (s, 4H, CH<sub>2</sub>NMe<sub>2</sub>), 6.95–7.34 (m, 8H, Ar-H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 2.49 (SiMe<sub>3</sub>), 31.5 (CHSiMe<sub>3</sub>), 56.3 (NMe<sub>2</sub>), 67.4 (CH<sub>2</sub>NMe<sub>2</sub>), 119.1, 125.3, 129.3, 131.8, 133.3, 138.9, 149.8, 151.4 (Ar-C).

### 2.6. Synthesis of [{2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH(SiMe<sub>3</sub>)<sub>2</sub>Cd] (**3**)

From CdCl<sub>2</sub> (0.27 g, 1.5 mmol) and **1** (1.03 g, 3.0 mmol), using the procedure similar to that for **2**, there were obtained colorless crystals of **3** (0.61 g, 72%) by recrystallization from hexane/tetrahydrofuran (1:2). Mp: 135–137 °C. *Anal.* Calc. for C<sub>26</sub>H<sub>44</sub>N<sub>2</sub>Si<sub>2</sub>Cd: C, 56.45, H, 8.02, N, 5.06. Found: C, 56.27, H, 8.15, N, 4.91%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.06 (s, 18H, SiMe<sub>3</sub>), 1.85 (s, 2H, CHSiMe<sub>3</sub>), 2.21 (s, 6H, NMe<sub>2</sub>), 2.24 (s, 6H, NMe<sub>2</sub>), 2.54 (s, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 2.58 (s, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 6.62–7.24 (m, 8H, Ar-H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ 4.5 (SiMe<sub>3</sub>), 31.9 (CHSiMe<sub>3</sub>), 67.4 (CH<sub>2</sub>NMe<sub>2</sub>), 50.3 (NMe<sub>2</sub>), 123.7, 126.4, 129.4, 131.8, 132.9, 133.7, 134.7, 151.7, 153.8 (Ar-C).

### 2.7. Synthesis of [{2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH(SiMe<sub>3</sub>)<sub>2</sub>Mn] (**4**)

From MnCl<sub>2</sub> (0.19 g, 1.5 mmol) and **1** (1.03 g, 3.0 mmol), using the procedure similar to that for **2**, there were obtained yellow crystals of **4** (0.54 g, 72%) by recrystallization from hexane/tetrahydrofuran (1:2). Mp: 128–130 °C. *Anal.* Calc. for C<sub>26</sub>H<sub>44</sub>MnN<sub>2</sub>Si<sub>2</sub>: C, 62.99, H, 8.95, N, 5.65. Found: C, 62.83; H, 8.81; N, 5.79%.

### 2.8. Synthesis of [2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH(SiMe<sub>3</sub>)Zn(Cl)·TMEDA] (**5**)

From ZnCl<sub>2</sub> (0.41 g, 3.0 mmol) and **1** (1.04 g, 3.0 mmol), using the procedure similar to that for **2**, there was obtained colorless crystals of **5** (1.1 g, 81%). Mp: 146–148 °C. *Anal.* Calc. for C<sub>19</sub>H<sub>38</sub>ClN<sub>3</sub>SiZn: C, 52.16, H, 8.76, N, 9.61. Found: C, 52.04, H, 8.63, N, 9.76%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.59 (s, 9H, SiMe<sub>3</sub>), 1.88 (s, 9H, NMe<sub>2</sub> and NMe<sub>2</sub> of TMEDA), 2.01 (s, 9H, NMe<sub>2</sub> and NMe<sub>2</sub> of TMEDA), 2.24 (t, 4H, CH<sub>2</sub> of TMEDA), 3.43 (s, 2H, CH<sub>2</sub>NMe<sub>2</sub>), 7.09–7.42 (m, 4H, Ar-H); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>): δ -0.27 (SiMe<sub>3</sub>), 31.5 (CHSiMe<sub>3</sub>), 45.6 (NMe<sub>2</sub>), 47.7 (NMe<sub>2</sub> of TMEDA), 53.1 (CH<sub>2</sub> of TMEDA), 67.8 (CH<sub>2</sub>NMe<sub>2</sub>), 122.9, 127.2, 129.7, 138.9, 142.5 (Ar-C).

### 2.9. Synthesis of [(2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH)<sub>2</sub>SiMe<sub>2</sub>Zn]<sub>2</sub> (**6**)

*n*-BuLi (4.1 mL, 10.3 mmol, 2.5 M, in hexane solution) was added dropwise to a solution of (2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>SiMe<sub>2</sub> (**B'**) (1.81 g, 5.1 mmol) and TMEDA (1.54 mL, 10.2 mmol) in tetrahydrofuran (30 mL) at 0 °C. The solution became yellow and was stirred at room temperature for 12 h, and the yellow solid was isolated via filtration and dried under vacuum to generate lithium salt 1.78 g (3.0 mmol), which was redissolved in tetrahydrofuran (30 mL). ZnCl<sub>2</sub> (0.41 g, 3.0 mmol) was added to in several portions to the above solution at −78 °C. The resulting mixture was warmed up to room temperature slowly and stirred for 15 h. The white precipitate was filtered off and the volatiles were removed *in vacuo*. The residue was extracted with hexane / tetrahydrofuran (1:2) and filtered. The filtrate was concentrated *in vacuo* to ca. 15 mL and set aside to afford colorless crystals of **6** (0.92 g, 74%). Mp: 136–138 °C. Anal. Calc. for C<sub>44</sub>H<sub>64</sub>N<sub>4</sub>Si<sub>2</sub>Zn<sub>2</sub>: C, 63.21; H, 7.72; N, 6.70. Found: C, 63.09, H, 7.66, N, 6.77%. <sup>1</sup>HNMR (C<sub>6</sub>D<sub>6</sub>): δ 0.19 (s, 12H, SiMe<sub>2</sub>), 1.81 (s, 2H, CHSiMe<sub>3</sub>), 1.87 (s, 2H, CHSiMe<sub>3</sub>), 2.38 (s, 12H, NMe<sub>2</sub>), 2.45 (s, 12H, NMe<sub>2</sub>), 3.48 (s, 8H, CH<sub>2</sub>NMe<sub>2</sub>), 6.98–7.43 (m, 16H, Ar-H); <sup>13</sup>CNMR (C<sub>6</sub>D<sub>6</sub>): δ −0.75 (SiMe<sub>2</sub>), 30.2 (CHSiMe<sub>2</sub>), 46.3 (NMe<sub>2</sub>), 61.1 (CH<sub>2</sub>NMe<sub>2</sub>), 112.9, 114.7, 128.7, 129.4, 131.8, 133.8, 138.4, 139.9, 150.1, 151.8 (Ar-C).

### 2.10. Typical polymerization procedure

A Schlenk tube previously dried at 150 °C and cooled under nitrogen, and then the Schlenk flask was charged with 1.0 mmol of *rac*-lactide in toluene (5 mL) containing a prescribed amount of benzyl alcohol. To this solution was added a solution of 0.01 mmol of catalyst in 0.5 mL of toluene ([lactide]/[metal] = 100). The mixture was immediately stirred with a magnetic stir bar at room temperature or 70 °C. After the desired time, the reaction was quenched by adding acidified methanol (ca. 1 mL of 1.2 M CH<sub>3</sub>COOH solution) and the polymer was precipitated with excess methanol (50 mL). The polymer was filtered and then dried under vacuum to constant weight.

### 2.11. X-ray crystallography

Data collection for compounds **1–6** was performed with Mo Kα radiation (λ = 0.71073 Å) by using a Bruker Smart Apex CCD diffractometer at 298(2) or 213(2) K. Crystals were coated in oil

and then directly mounted on the diffractometer under a stream of cold nitrogen gas. The crystal data and summary of X-ray data collection are presented in Table 1. A total of *N* reflections were collected in the ω scan mode. Corrections were applied for Lorentz and polarization effects as well as absorption by using multiscans (SADABS) [32]. The structure was solved by direct methods (SHELXS-97) [33]. Then, the remaining non-hydrogen atoms were obtained from the successive difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were constrained to parent sites, by using a riding mode (SHELXTL) [34].

## 3. Results and discussion

### 3.1. Synthesis and characterization of compounds **1–5**

The general synthetic routes for the compounds **1–5** are illustrated in Scheme 1. Treatment of 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub> with one equivalent of *n*-BuLi in the presence of TMEDA in diethyl ether, and addition of ClSiMe<sub>3</sub>, gave compound **B** (**B** = 2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SiMe<sub>3</sub>) as a colorless liquid in 91% yield by distillation under reduced pressure (bp 72–74 °C, 5 Pa). Metalation of **B** by equivalent *n*-BuLi and TMEDA in hexane gave pale yellow crystalline lithium compound **1** in good yield as highly air and moisture sensitive liquid.

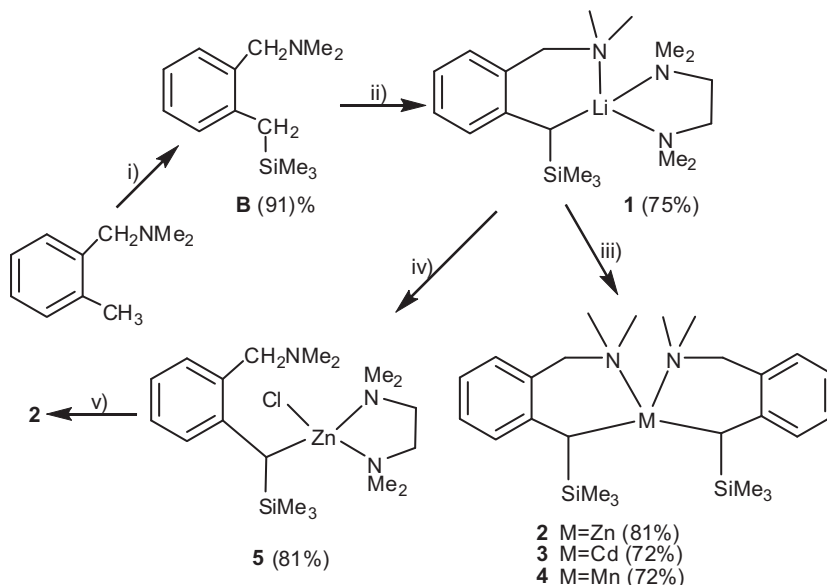
The compounds **2–5** were prepared from the reaction of **1** and the corresponding anhydrous ZnCl<sub>2</sub>, CdCl<sub>2</sub> or MnCl<sub>2</sub> (Scheme 1). Thus, treatment of **1** with anhydrous ZnCl<sub>2</sub>, CdCl<sub>2</sub> or MnCl<sub>2</sub> in a 2:1 M ratio in diethyl ether or tetrahydrofuran at −78 °C afforded compound **2**, **3** or **4** with the general formula [M(L)<sub>2</sub>] [M = Zn (**2**), Cd (**3**), Mn (**4**)] in good yield, respectively. The single crystals suitable for X-ray diffraction studies of compounds **2**, **3** or **4** were obtained from recrystallization in hexane/tetrahydrofuran. However compound **5** was obtained by treatment of compound **1** with anhydrous ZnCl<sub>2</sub> in a 1:1 M ratio and recrystallization from diethyl ether. Attempts for the synthesis of the compound LMCl (M = Cd or Mn) from the reaction of **1** with equal molar ratio of CdCl<sub>2</sub> or MnCl<sub>2</sub> via a similar procedure were failed.

### 3.2. Molecular structures of compounds **1–5**

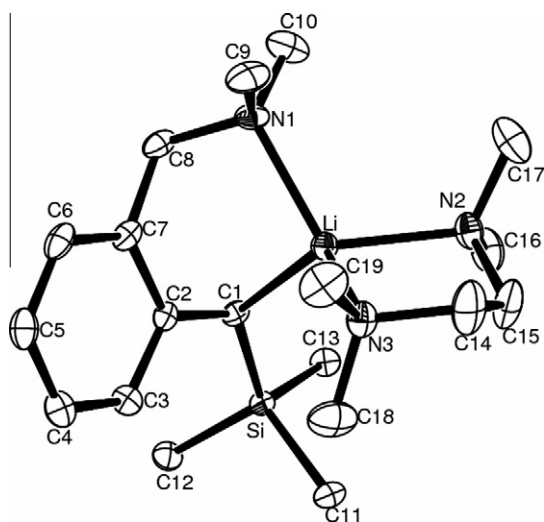
The molecular structure of the crystalline lithium compound **1** is illustrated in Fig. 1, and selected bond lengths and angles are

**Table 1**  
Crystallographic data and structure refinement for compounds **1–6**.

Complex	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>
Formula	C <sub>19</sub> H <sub>38</sub> LiN <sub>3</sub> Si	C <sub>26</sub> H <sub>44</sub> ZnN <sub>2</sub> Si <sub>2</sub>	C <sub>26</sub> H <sub>44</sub> CdN <sub>2</sub> Si <sub>2</sub>	C <sub>26</sub> H <sub>44</sub> MnN <sub>2</sub> Si <sub>2</sub>	C <sub>19</sub> H <sub>38</sub> ClN <sub>3</sub> SiZn	C <sub>44</sub> H <sub>64</sub> N <sub>4</sub> Si <sub>2</sub> Zn <sub>2</sub>
Fw	343.55	506.18	553.21	495.75	437.43	835.92
Crystal system	monoclinic	orthorhombic	orthorhombic	orthorhombic	triclinic	tetragonal
Space group	P2(1)/n	Pna2(1)	Pca2(1)	Pca2(1)	Pī	P4
<i>a</i> (Å)	10.136(8)	18.657(8)	15.546(3)	15.247(2)	9.780(4)	16.395(4)
<i>b</i> (Å)	17.141(13)	9.410(4)	10.231(2)	10.1992(15)	10.114(4)	16.395(4)
<i>c</i> (Å)	13.030(8)	16.443(8)	18.107(3)	18.139(3)	14.050(3)	8.452(4)
α (°)	90.00	90.00	90.00	90.00	87.59(4)	90.00
β (°)	91.08(9)	90.00	90.00	90.00	74.75(4)	90.00
γ (°)	90.00	90.00	90.00	90.00	62.86(4)	90.00
<i>V</i> (Å <sup>3</sup> )	2263(3)	2887(2)	2879.9(10)	2820.7(7)	1188.3(7)	2271.9(12)
<i>Z</i>	4	4	4	4	2	4
<i>D</i> <sub>calc</sub> (g cm <sup>−3</sup> )	1.008	1.165	1.276	1.167	1.223	1.222
μ (mm <sup>−1</sup> )	0.108	0.949	0.856	0.568	1.203	1.141
<i>F</i> (000)	760	1088	1160	1068	468	888
Reflections collected	9194	10 128	10 304	11 103	4919	9337
Independent reflections	3975	3305	4201	4907	4099	3951
<i>R</i> <sub>int</sub>	0.0510	0.1056	0.0291	0.0265	0.0169	0.0289
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> ≥ 2σ( <i>I</i> )]	0.0995, 0.1950	0.0556, 0.1136	0.0382, 0.0772	0.0385, 0.0869	0.0374, 0.0953	0.0531, 0.1451
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1255, 0.2069	0.1024, 0.1345	0.0403, 0.0790	0.0407, 0.0879	0.0414, 0.0975	0.0547, 0.1464
Goodness of fit	1.209	0.992	1.106	1.084	1.063	1.097
<i>F</i> <sup>2</sup> Largest difference in peak and hole (e Å <sup>−3</sup> )	0.489 to −0.264	0.328 to −0.279	0.666 to −0.672	0.468 to −0.170	0.774 to −0.446	0.764 to −0.501



**Scheme 1.** Reagents and conditions: (i)  $n\text{-BuLi}$ , TMEDA,  $\text{ClSiMe}_3$ , diethyl ether or hexane,  $0^\circ\text{C}$ ; (ii)  $n\text{-BuLi}$ , TMEDA, diethyl ether or hexane,  $0^\circ\text{C}$ ; (iii)  $\text{MCl}_2$  (0.5 equiv.), ( $\text{M} = \text{Zn}$ ,  $\text{Cd}$ ,  $\text{Mn}$ ), diethyl ether or tetrahydrofuran,  $-78^\circ\text{C}$ ; (iv)  $\text{ZnCl}_2$  (1 equiv.), diethyl ether or tetrahydrofuran,  $-78^\circ\text{C}$ ; (v) compound **1** (1 equiv.), diethyl ether,  $-78^\circ\text{C}$ .



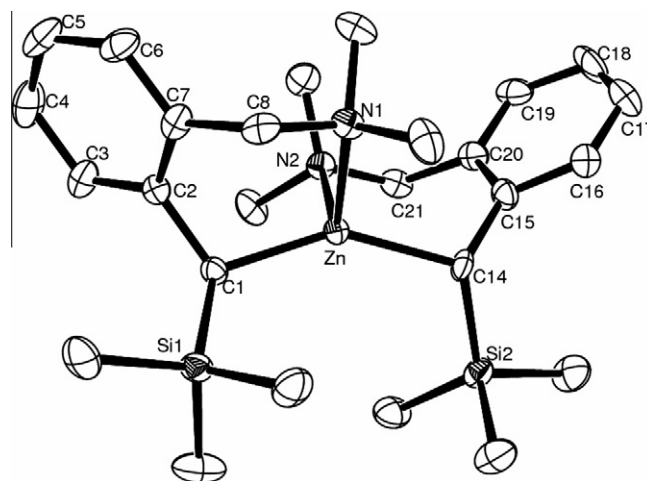
**Fig. 1.** Molecular structure of compound **1** showing thermal ellipsoids is plotted at 20% probability level, hydrogen atoms are omitted for clarity.

**Table 2**  
Selected bond lengths [Å] and angles [ $^\circ$ ] for **1**.

Bond lengths			
Li–C1	2.298(8)	Li–N1	2.139(8)
Li–N2	2.130(8)	Li–N3	2.200(8)
Si–C1	1.829(4)	N1–C8	1.478(6)
Bond angles			
N2–Li–N1	113.0(3)	N2–Li–N3	86.1(3)
N1–Li–N3	120.7(4)	C1–Li–N2	122.0(4)
N1–Li–C1	95.9(3)	N3–Li–C1	121.3(3)
C8–N1–Li	103.2(3)	C2–C1–Li	84.6(3)

listed in Table 2. The TMEDA-solvated lithium compound (**1**) exhibits a monomeric structure in which the lithium atom and the ligand form a six-membered cycle.

The molecular structure of the solvated-free compound **2** is illustrated in Fig. 2 and selected bond lengths and angles are listed



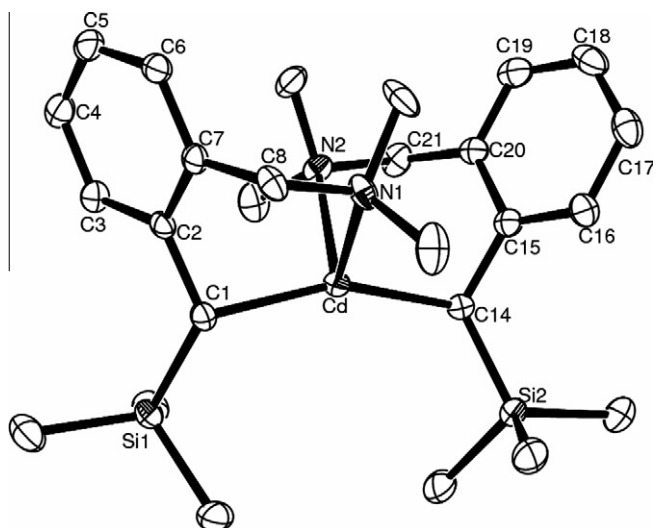
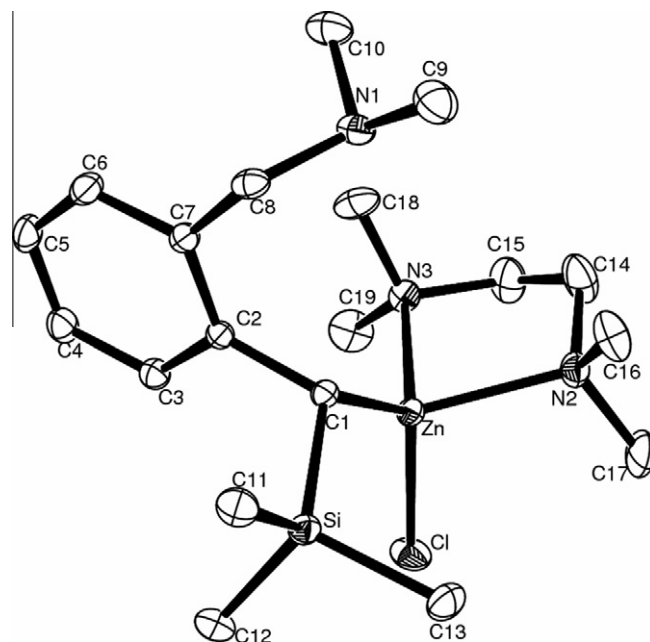
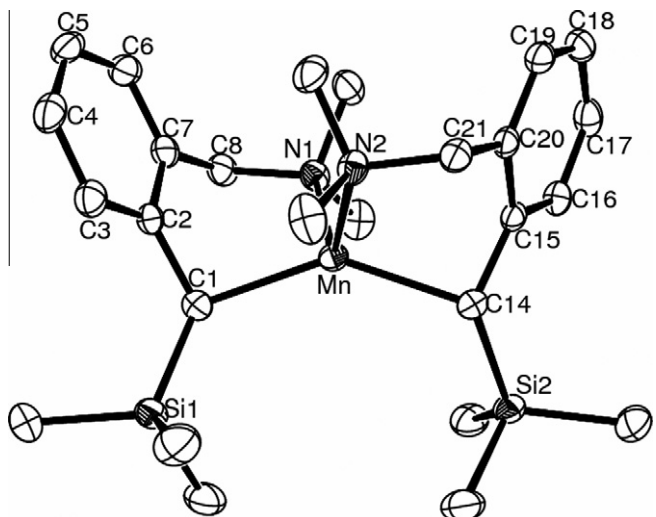
**Fig. 2.** Molecular structure of compound **2** showing thermal ellipsoids is plotted at 20% probability level, hydrogen atoms are omitted for clarity.

in Table 3. To the best of our knowledge, **2** is the only example for the solvated-free neutral benzylzinc compound. The core structure of **2** is a spirocycle [6,6] built by two ligands and zinc atom with the latter as the spiro union, of which zinc atom and each of the ligands form a twist boat-shaped six-membered ring. The bond lengths 2.002(9) and 2.043(9) Å of Zn–C1 and Zn–C14 are shorter than those [2.041(4) and 2.050(4) Å] of the reported benzylzinc compound [ $\text{Zn}\{\text{CH}(\text{SiMe}_3)\text{Ph}\}_2\cdot\text{TMEDA}$ ] [26], respectively.

The molecular structures of compounds **3** and **4** which are very similar to compound **2** are illustrated in Figs. 3 and 4, respectively, and selected bond lengths and angles are presented in Table 3. To the best of our knowledge, compound **3** is the only case for the solvated-free neutral benzyl cadmium compound. Cadmium atom and two the bulky ligands form a twist boat-shaped six-membered ring. The bond lengths 2.227(5) and 2.220(6) Å of Cd–C1 and Cd–C14 are longer than those [2.002(9) and 2.043(9) Å] in the compound **2**, respectively. The bond angle  $158.1^\circ$  (2) of C1CdC14 is wider than that [ $146.8^\circ$ ] in the compound **2**.

**Table 3**Selected bond lengths (Å) and angles (°) for **2**, **3** and **4**.

2		3		4	
<i>Bond lengths</i>					
Zn–C1	2.002(9)	Cd–C1	2.227(5)	Mn–C1	2.185(3)
Zn–C14	2.043(9)	Cd–C14	2.220(6)	Mn–C14	2.197(3)
Zn–N1	2.235(10)	Cd–N1	2.524(5)	Mn–N1	2.285(2)
Zn–N2	2.361(9)	Cd–N2	2.535(4)	Mn–N2	2.283(2)
N1–C8	1.517(16)	N1–C8	1.486(7)	N1–C8	1.501(4)
N2–C21	1.437(16)	N2–C21	1.478(7)	N2–C21	1.496(3)
<i>Bond angles</i>					
C1–Zn–C14	146.8(3)	C1–Cd–C14	158.1(2)	C1–Mn–C14	141.9(11)
C1–Zn–N1	96.6(4)	C1–Cd–N1	83.6(18)	C1–Mn–N1	89.0(10)
C1–Zn–N2	104.1(4)	C1–Cd–N2	109.8(19)	C1–Mn–N2	112.6(10)
C14–Zn–N1	102.6(4)	C14–Cd–N1	110.7(19)	C14–Mn–N1	112.0(9)
C14–Zn–N2	95.1(4)	C14–Cd–N2	83.8(18)	C14–Mn–N2	88.8(9)
N1–Zn–N2	108.8(2)	N1–Cd–N2	102.7(17)	N1–Mn–N2	112.0(9)
C8–N1–Zn	106.9(8)	C8–N1–Cd	109.2(3)	C8–N1–Mn	109.7(17)
C2–C1–Zn	108.4(6)	C2–C1–Cd	101.3(3)	C2–C1–Mn	97.7(16)
C21–N2–Zn	103.6(8)	C21–N2–Cd	109.0(3)	C21–N2–Mn	110.2(16)
C15–C14–Zn	108.8(7)	C15–C14–Cd	103.0(3)	C15–C14–Mn	95.8(16)

**Fig. 3.** Molecular structure of compound **3** showing thermal ellipsoids is plotted at 20% probability level, hydrogen atoms are omitted for clarity.**Fig. 5.** Molecular structure of compound **5** showing thermal ellipsoids is plotted at 20% probability level, hydrogen atoms are omitted for clarity.**Fig. 4.** Molecular structure of compound **4** showing thermal ellipsoids is plotted at 20% probability level, hydrogen atoms are omitted for clarity.

For compound **4**, the four-coordinated manganese atom is wrapped by two C atoms and two N atoms of two ligands forming the distorted tetrahedral coordination geometry composed by two six-membered rings, which were puckered rather than in a *trans* arrangement. The bond lengths of Mn–C1[2.185(3) Å] and

**Table 4**Selected bond lengths (Å) and angles (°) for **5**.

<i>Bond lengths</i>			
Zn–C(1)	2.006(3)	Zn–Cl	2.2497(17)
Zn–N2	2.172(2)	Zn–N3	2.136(2)
Si–C1	1.856(3)		
<i>Bond angles</i>			
C(1)–Zn–N3	118.42(10)	C(1)–Zn–N2	115.13(10)
N3–Zn–N2	84.04(9)	C(1)–Zn–Cl	123.62(8)
Cl–Zn–N3	103.89(8)	Cl–Zn–N2	104.13(8)
C(2)–C(1)–Zn	111.65(16)	Si–C(1)–Zn	111.67(13)

Mn–C14 [2.197(3) Å] are longer than that [2.002(9) and 2.043(9) Å] of the compound **2**, respectively. The bond angle  $141.94^\circ$  (11) of C1MnC14 is narrower than that  $[146.8^\circ]$  of the compound **2**.

Compound **5** was isolated by crystallization from diethyl ether as a colorless crystalline solid in good yield. The molecular structure of compound **5** is illustrated in Fig. 5, and selected bond lengths and angles are presented in Table 4. The TMEDA-solvated heteroleptic zinc compound **5** is a monomer, in which zinc atom is surrounded by one C atom of the ligand unit and two N atoms from TMEDA molecule and one Cl atom. Unexpectedly, the amino group on the ligand does not take part in the coordination and the coordination mode is similar to that reported benzylzinc compound  $[\text{Zn}(\text{Cl})\text{CH}(\text{SiMe}_3)\text{Ph}\cdot\text{TMEDA}]$  [25]. The bond lengths of Zn–C(1) 2.006(3) Å, Zn–Cl 2.249(17) Å, Zn–N2 2.173(2) Å and Zn–N3 2.136(2) Å are close to those of the reported compound, [2.011(4), 2.252(2), 2.170(4) and 2.130(4) Å] [25], respectively.

### 3.3. Synthesis and characterization of compound **6**

Using a similar procedure as for **B**, compound **B'** [**B'** = (2-Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>SiMe<sub>2</sub>] was synthesized from the reaction of *N,N*-dimethyl-*o*-methylbenzylamine with *n*-BuLi, TMEDA, and then Cl<sub>2</sub>SiMe<sub>2</sub>. Metalation of **B'** with two equivalents of *n*-BuLi in tetrahydrofuran yielded the corresponding benzyl lithium compound, which reacted directly with equivalent anhydrous ZnCl<sub>2</sub> in tetrahydrofuran at  $-78^\circ\text{C}$  affording compound  $[\text{L}'\text{Zn}]_2$  (**6**). The compound **6** was isolated by recrystallization from tetrahydrofuran/hexane (2:1) as colorless crystals in 74% yield as shown in Scheme 2. Attempts for synthesis of cadmium or manganese compound based on **L'** were not successful.

### 3.4. Molecular structure of compound **6**

The molecular structure of **6** is illustrated in Fig. 6. Centrosymmetric crystalline bimetallic zinc compound **6** exists as a dimer in solid state. The central eight-membered ZnC1SiC13Zn'C1'Si'C13' ring is flanked by four twist boat-shaped six-membered rings built by two zinc atoms and four 2-(*N,N*-dimethylaminomethyl)benzyl units. The average distance of Zn–C [ $2.0200 \pm 0.0075$  Å] is slightly shorter than that in compound **2** [ $2.0234 \pm 0.0205$  Å]. The geometry of the flanked six-membered cycles is similar to that of compound **2**, and selected bond lengths and angles of **6** are listed in Table 5.

### 3.5. Polymerization reactions of *rac*-lactide for compounds **2** and **5**

In the view of zinc initiators based on aliphatic alkyl amide compounds have been extensively used in the ring-opening

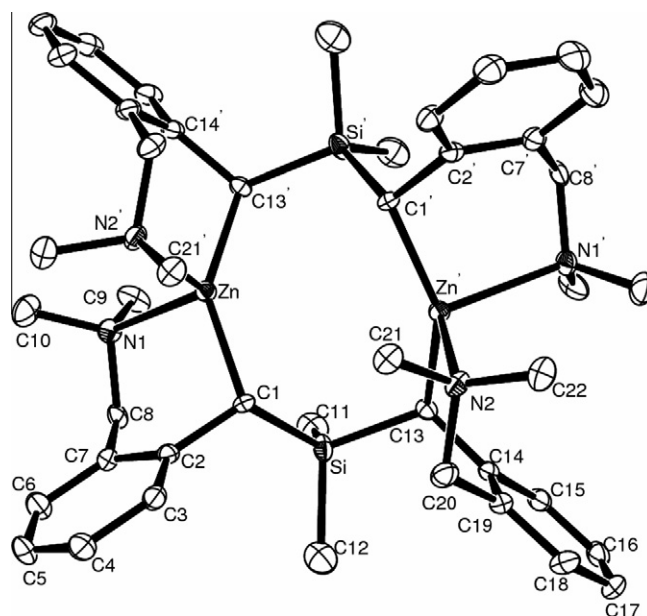
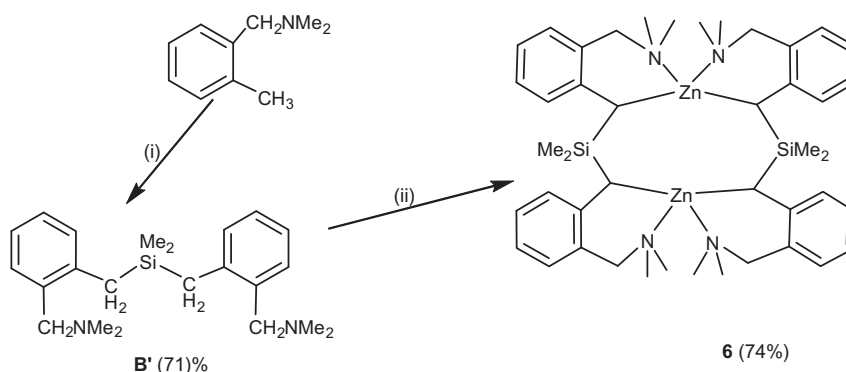


Fig. 6. Molecular structure of compound **6** showing thermal ellipsoids is plotted at 20% probability level, hydrogen atoms are omitted for clarity.

Table 5  
Selected bond lengths (Å) and angles ( $^\circ$ ) for **6**.

Bond lengths			
Zn–C1	2.027(4)	Zn–C13'	2.012(5)
Zn–N1	2.320(4)	Zn–N2'	2.339(5)
C1–Si	1.873(5)	Si–C13	1.890(5)
C2–C1	1.510(7)	C8–N1	1.489(8)
Bond angles			
13'–Zn–C1	143.9(2)	C13'–Zn–N1	104.80(18)
C1–Zn–N1	96.39(17)	C13'–Zn–N2'	95.53(18)
C1–Zn–N2'	106.57(17)	N1–Zn–N2'	105.62(17)
Zn–Zn'–C1'	30.45(2)	Zn'–Zn–C13'	82.80(1)
C2–C1–Zn	106.6(3)	C8–N1–Zn	105.3(3)
C20–N2–Zn'	106.0(3)	Si–C1–Zn	119.1(2)

polymerization (ROP) of lactide [35–41]. Hence, the highly hindered *N*-functionalized benzyl zinc compounds **2** and **5** were used as initiators for catalytic ring-opening polymerization of *rac*-lactide. Polymerizations were carried out in Schlenk flask under nitrogen atmosphere strictly free of moisture and oxygen in toluene, as well as the polymerization factors of molar ratio of  $[\text{LM}]/[\text{LA}]$  (100 or 200) and reaction temperature (room temperature or  $70^\circ\text{C}$ )



Scheme 2. Reagents and conditions: (i) *n*-BuLi, TMEDA, Cl<sub>2</sub>SiMe<sub>2</sub> (0.5 equiv.), diethyl ether or hexane,  $0^\circ\text{C}$ ; (ii) *n*-BuLi (2 equiv.), TMEDA (2 equiv.), ZnCl<sub>2</sub>, tetrahydrofuran,  $-78^\circ\text{C}$ .



**Table 6***rac*-Lactide polymerization data for the compounds **2** and **5**.

Entry	Catalyst	[LA]/[C] <sup>a</sup>	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>	<i>Mn</i> (g/mol) <sup>c</sup>	<i>Mw/Mn</i> <sup>c</sup>	<i>P<sub>r</sub></i> <sup>d</sup>
1	<b>2</b>	100:1	25	14	11	–	–	–
2	<b>2</b>	100:1	70	6	86	11 497	1.39	0.56
3	<b>2</b>	200:1	70	6	53	11 729	1.50	0.60
4	<b>5</b>	100:1	25	14	12	–	–	–
5	<b>5</b>	100:1	70	6	89	9531	1.46	0.64
6	<b>5</b>	200:1	70	6	81	18 206	1.38	0.63

<sup>a</sup> Benzyl alcohol.<sup>b</sup> The yields were calculated according to the mass of the polymer was precipitated by the addition of MeOH and was collected by filtration and dried.<sup>c</sup> Determined by gel-permeation chromatography, calibrated with polystyrene standards in tetrahydrofuran.<sup>d</sup> *P<sub>r</sub>* is the probability of racemic linkages between monomer units and is determined from the methine region (5.30–5.00 ppm) of the homonuclear decoupled <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> at 25 °C. *P<sub>r</sub>* = 2I<sub>1</sub>/(I<sub>1</sub> + I<sub>2</sub>), with I<sub>1</sub> = 5.20–5.25 ppm, I<sub>2</sub> = 5.13–5.20 ppm [42–47].

were tested, Compounds **2** and **5** exhibited very similar activity for the ROP of *rac*-lactide. The details are summarized in Table 6.

Compound **2** initiated polymerization of *rac*-lactide at room temperature in toluene in the presence of benzyl alcohol and gave only 11% of yield (entry 1). Prolongation of the reaction time did not improve the yield. As expected, an increase in the temperature to 70 °C yielded 86% in 6 h with a medium broad polydispersity index [36] (*Mn* = 11 497, *Mw/Mn* = 1.39, entry 2). With the molar ratio of monomer: initiator from 100:1 to 200:1, molecular weight of the polymers and the molecular weight distribution were almost unchanged (*Mn* = 11 729, *Mw/Mn* = 1.50, entry 3) while only 53% of yield was obtained.

Compound **5** showed similar catalytic activity with compound **2**. Compound **5** catalyzed *rac*-lactide to polylactide with 12% or 89% yield at room temperature or 70 °C (entries 4 and 5), respectively. Good yield (81%), However, when the molar ratio of monomer: initiator increased to 200:1, a significantly higher molecular weight polymer (*Mn* = 18 206) and the narrower molecular weight distribution (*Mw/Mn* = 1.38, entry 6) were observed.

All the resulting polylactides are most predominantly heterotactic-rich under our conditions examined, as determined by the methine region of the homonuclear decoupled <sup>1</sup>H NMR experiments in the region of 5.30–5.00 ppm [42–47].

#### 4. Conclusions

Six sterically hindered N-functionalized benzyl metal(II) compounds [LiL-TMEDA] (**1**), [ML<sub>2</sub>] [M = Zn (**2**), Cd (**3**) or Mn (**4**)], [LZnCl-TMEDA] (**5**) and [Zn L']<sub>2</sub> (**6**) were obtained. Each of the compounds **1–6** has been characterized by microanalysis, multinuclear NMR spectra at ambient temperature and X-ray single crystal study. Compound **2** or **3** would be the only sample for solvated-free homoleptic neutral benzylzinc or benzylcadmium compound, respectively. Compounds ZnL<sub>2</sub> (**2**) and [LZn(Cl)-TMEDA] (**5**) exhibited moderate activity for the ring-opening polymerization of *rac*-lactide in toluene in the presence of benzyl alcohol at 70 °C. All the resulting polylactides are most predominantly heterotactic-rich.

#### Acknowledgements

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#### Appendix A. Supplementary material

CCDC 797568, 797569, 797570, 797571, 797572 and 797573 contain the supplementary crystallographic data for compounds **1**, **2**, **3**, **4**, **5** and **6**, respectively. These data can be obtained free

of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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