Inorganica Chimica Acta 388 (2012) 127–134

Contents lists available at SciVerse ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

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

Bin Jia, Xuehong Wei *, Hongbo Tong, Meisu Zhou, Diansheng Liu *

Institute of Applied Chemistry, Shanxi University, Taiyuan 030006, PR China

ARTICLE INFO

Article history:
Received 14 June 2011
Received in revised form 8 February 2012
Accepted 13 February 2012
Available online 23 February 2012

Keywords:
Zinc
Cadmium
Manganese (II)
Benzyl
rac-Lactide

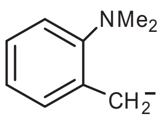
ABSTRACT

Treatment of [Li**L**·TMEDA] (**1**) {**L** = [2-$Me_2NCH_2C_6H_4CH(SiMe_3)]^-$} with half equivalent of $ZnCl_2$, $CdCl_2$ or $MnCl_2$ in diethyl ether gave the crystalline compound [M**L**$_2$] {M = Zn (**2**), Cd (**3**) and Mn (**4**)}, respectively. Reaction of **1** with one equivalent of $ZnCl_2$ in diethyl ether afforded the crystalline compound [Zn(Cl)**L**·TMEDA] (**5**) in good yield. An eight-membered cyclic homoleptic binuclear compound [Zn**L′**]$_2$ (**6**) {**L′** = $[(2\text{-}Me_2NCH_2C_6H_4CH)_2SiMe_2]^{2-}$} was prepared from the reaction of $(2\text{-}Me_2NCH_2C_6H_4CH_2)_2SiMe_2$ (**B′**) with two equivalents of *n*-BuLi and one equivalent of $ZnCl_2$. All of the crystalline compounds **1**–**6** were well characterized by ^1H NMR, ^{13}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.

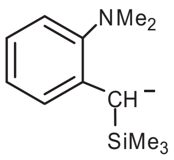
1. Introduction

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

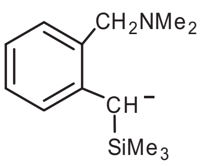
Organometallic compounds based on N-functionalized benzyl anion ligand **A** [20–26] or silyl-substituted benzyl anion ligand **A′** have been documented [27–30], whereas organometallic compounds based on the ligand **L** {**L** = [2-$Me_2NCH_2C_6H_4CH(SiMe_3)]^-$} are rarely reported. The sole example is the lithium compound co-crystallized with *n*-BuLi to form a ladder structure [31]. 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 dimethylsily group bridged dianion ligand **L′** {**L′** = $[(2\text{-}Me_2NCH_2C_6H_4CH)_2SiMe_2]^{2-}$}.



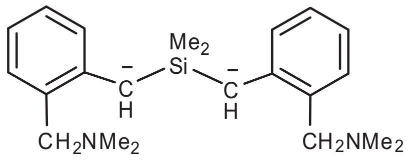
A



A'



L



L'

---

* Corresponding authors. Tel.: +86 351 701 8390; fax: +86 351 701 1688 (D. Liu).
E-mail addresses: xhwei@sxu.edu.cn (X. Wei), dsliu@sxu.edu.cn (D. Liu).

0020-1693/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2012.02.022

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. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX 300 (300.1 MHz for ^1H, 75.5 MHz for ^{13}C) instrument and referenced internally to the residual solvent resonances (chemical shift data in δ). All NMR spectra (^1H, ^{13}C) were measured at 298 K and all ^{13}C NMR spectra were proton-decoupled. The homonuclear decoupled ^1H 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-$Me_2NCH_2C_6H_4CH_2SiMe_3$ (***B***)

To a solution of 2-$Me_2NCH_2C_6H_4CH_3$ (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. $ClSiMe_3$ (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 $MgSO_4$ 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). ^1HNMR ($CDCl_3$): δ 2.16 (s, 6H, N*Me*$_2$, 2.37 (s, 2H, C*H*$_2$SiMe$_3$), 3.34 (s, 2H, C*H*$_2$NMe$_2$), 0.07 (s, 9H, SiMe$_3$) 7.04–7.37 (m, 4H, Ar–*H*), ^{13}C NMR ($CDCl_3$): δ −1.2 (Si*Me*$_3$), 21.5 (*C*H$_2$SiMe$_3$), 48.6 (N*Me*$_2$), 62.2 (*C*H$_2$NMe$_2$), 123.7, 126.0, 126.5, 131.8, 135.1, 140.3 (Ar–*C*).

2.3. Synthesis of $(2\text{-}Me_2NCH_2C_6H_4CH_2)_2SiMe_2$ (***B′***)

From 2-$Me_2NCH_2C_6H_4CH_3$ (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_2SiMe_2 (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). ^1HNMR ($CDCl_3$): δ −0.03 (6H, Si*Me*$_2$), 2.33 (s, 2H, C*H*$_2$SiMe$_2$), 2.37 (s, 2H, C*H*$_2$SiMe$_2$), 2.11 (s, 6H, N*Me*$_2$), 2.19 (s, 6H, N*Me*$_2$), 3.24 (s, 4H, C*H*$_2$NMe$_2$), 6.94–7.25 (m, 8H, Ar–*H*), ^{13}C NMR ($CDCl_3$): δ −1.57 (Si*Me*$_2$), 22.7 (*C*H$_2$SiMe$_2$), 46.7 (N*Me*$_2$), 63.6 (*C*H$_2$NMe$_2$), 125.1, 128.1, 130.3, 131.5, 136.5, 140.6 (Ar–*C*).

2.4. Synthesis of [2-$Me_2NCH_2C_6H_4CH(SiMe_3)Li\cdot$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 $C_{19}H_{38}N_3SiLi$: C, 66.44; H, 11.21; N, 12.13. Found: C, 66.32; H, 11.06; N, 12.31%. ^1HNMR (C_6D_6): δ 0.09 (s, 9H, Si*Me*$_3$), 2.06 (s, 18H, N*Me*$_2$ and *Me* of TMEDA), 2.11 (t, 4H, C*H*$_2$ of TMEDA), 2.15 (s, 2H, C*H*$_2$SiMe$_3$), 3.34 (s, 2H, C*H*$_2$NMe$_2$), 7.04–7.37 (m, 4H, Ar–*H*), ^{13}C NMR (C_6D_6): δ 1.73 (Si*Me*$_3$), 21.2 (*C*H$_2$SiMe$_3$), 45.9 (*C*H$_3$ of TMEDA), 48.1 (N*Me*$_2$), 56.2 (*C*H$_2$ of TMEDA), 63.2 (*C*H$_2$NMe$_2$), 126.2, 127.5, 128.7, 131.8, 135.8, 140.1 (Ar–*C*).

2.5. Synthesis of [{2-$Me_2NCH_2C_6H_4CH(SiMe_3)$}$_2$Zn] (***2***)

$ZnCl_2$ (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 $C_{26}H_{44}N_2Si_2Zn$: C, 61.69, H, 8.76, N, 5.53. Found: C, 61.54, H, 8.69, N, 5.71%. ^1HNMR (C_6D_6): δ 0.09 [s, 18H, Si*Me*$_3$], 1.43, 1.47 (s, 2H, C*H*SiMe$_3$), 2.55, 2.68 (s, 12H, N*Me*$_2$), 3.53, 3.57 (s, 4H, C*H*$_2$NMe$_2$), 6.95–7.34 (m, 8H, Ar–*H*); ^{13}CNMR (C_6D_6): δ 2.49 (Si*Me*$_3$), 31.5(*C*HSiMe$_3$), 56.3 (N*Me*$_2$), 67.4 (*C*H$_2$NMe$_2$), 119.1, 125.3, 129.3, 131.8, 133.3, 138.9, 149.8, 151.4 (Ar–*C*).

2.6. Synthesis of [{2-$Me_2NCH_2C_6H_4CH(SiMe_3)$}$_2$Cd] (***3***)

From $CdCl_2$ (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/tetrohydrofuran (1:2). Mp: 135–137 °C. *Anal.* Calc. for $C_{26}H_{44}N_2Si_2Cd$: C, 56.45, H, 8.02, N, 5.06. Found: C, 56.27, H, 8.15, N, 4.91%. ^1HNMR (C_6D_6): δ 0.06 (s, 18H, Si*Me*$_3$), 1.85 (s, 2H, C*H*SiMe$_3$), 2.21(s, 6H, N*Me*$_2$), 2.24(s, 6H, N*Me*$_2$), 2.54(s, 2H, C*H*$_2$NMe$_2$), 2.58 (s, 2H, C*H*$_2$NMe$_2$), 6.62–7.24 (m, 8H, Ar–*H*); ^{13}CNMR (C_6D_6): δ 4.5 (Si*Me*$_3$), 31.9 *C*H(SiMe$_3$), 67.4 (*C*H$_2$NMe$_2$), 50.3 (N*Me*$_2$), 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-$Me_2NCH_2C_6H_4CH(SiMe_3)$}$_2$Mn] (***4***)

From $MnCl_2$ (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/tetrohydrofuran (1:2). Mp: 128–130 °C. *Anal.* Calc. for $C_{26}H_{44}MnN_2Si_2$: C, 62.99, H, 8.95, N, 5.65. Found: C, 62.83; H, 8.81; N, 5.79%.

2.8. Synthesis of [2-$Me_2NCH_2C_6H_4CH(SiMe_3)Zn(Cl)\cdot$TMEDA] (***5***)

From $ZnCl_2$ (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 $C_{19}H_{38}ClN_3SiZn$: C, 52.16, H, 8.76, N, 9.61. Found: C, 52.04, H, 8.63, N, 9.76%. ^1HNMR (C_6D_6): δ 0.59 (s, 9H, Si*Me*$_3$), 1.88 (s, 9H, N*Me*$_2$ and N*Me*$_2$ of TMEDA), 2.01 (s, 9H, N*Me*$_2$ and N*Me*$_2$ of TMEDA), 2.24 (t, 4H, C*H*$_2$ of TMEDA), 3.43 (s, 2H, C*H*$_2$NMe$_2$), 7.09–7.42 (m, 4H, Ar–*H*); ^{13}CNMR (C_6D_6): δ −0.27 (Si*Me*$_3$), 31.5 (*C*HSiMe$_3$), 45.6 (N*Me*$_2$), 47.7 (N*Me*$_2$ of TMEDA), 53.1 (*C*H$_2$ of TMEDA), 67.8 (*C*H$_2$NMe$_2$), 122.9, 127.2, 129.7, 138.9, 142.5 (Ar–*C*).