Inorganic Chemistry Communications 14 (2011) 1737–1741

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Zinc complexes of chiral ligands obtained from methylbenzylamine

María Frutos Pastor, Todd J.J. Whitehorne, Paul O. Oguadinma, Frank Schaper *

Département chimie, Université de Montréal, Montréal, Québec, Canada H3C 3J7

ARTICLE INFO

Article history:
Received 29 April 2011
Accepted 26 July 2011
Available online 2 August 2011

Keywords:
Schiff base ligand
Zinc complexes
Chiral ligands
Lactide polymerization

ABSTRACT

Condensation of *S*-methylbenzylamine with 2 equiv. of 2,4-*tert*-butylphenol yielded the chiral tridentate ligand **2**H_2, which formed the dimetallic complex (**2**)(k-N,(μ-O)$_2$ZnEt)((μ-O)$_2$ZnEt), **3**, upon reaction with $ZnEt_2$. Reaction of the chiral Schiff base ligand, **4**H, obtained from condensation of salicylaldehyde and *S*-methylbenzylamine, with $ZnEt_2$ yielded (**4**)$_2$Zn, 5, or (**4**)ZnEt, **6**, respectively. Deprotonation of **4**H with NaH afforded tetrameric {(**4**)Na}$_4$, **7**. Complexes **3**, **5** and **7** were characterized by single crystal diffraction studies and tested as initiators in the polymerization of *rac*-lactide. Complexes **3** and **5** showed only low to moderate activity. All complexes yielded essentially atactic polymers with minor contents of heterotactic enchainment.

While the utility of chiral ligands in asymmetric catalysis is undoubted, enantiopure ligands often require elaborate synthesis and/or are highly expensive. In recent years, we and others became interested in the selective polymerization of *rac*-lactide [1–7]. Given the potential applications of polylactide (PLA) for disposable packaging, low costs of the catalyst are a prerequisite for potential applications. We thus investigated the performance of enantiopure complexes with ligands based on methyl-benzylamine, one of the cheapest sources of chirality available, in *rac*-lactide polymerization. Harder and our group reported the synthesis of a diketimine ligand with *N,N'-S*-methylbenzylamine substituents [8,9]. *Rac*-lactide polymerizations catalyzed by the corresponding Zn alkoxide complex **1** (Scheme 1), however, yielded heterotactic PLA due to the prevalence of chain-end control in diketiminate zinc alkoxide complexes [6]. In the following we present the preparation of several metal complexes bearing simple, chiral *N,N,O*- and *N,O*-ligands, based on *S*-methylbenzylamine. Unfortunately, none of the obtained complexes displayed any selectivity when applied in *rac*-lactide polymerization.

(N,O,O)-ligand. The tridentate ligand **2**H_2 was obtained by condensation of 2,4-ditertbutylphenol, *S*-methylbenzylamine and formaldehyde, in adaption of literature procedures (Scheme 2) [10,11]. Similar compounds with different chiral *N*-substituents have been reported previously and employed as ligands for Zr [12] and V complexes [13]. **2**H_2 was obtained as a yellow oil, in good yields and reasonable purity (one spot TLC, >90% estimated from NMR), and proved to be soluble in most organic solvents (hexane, toluene, methanol, ethanol, diethyl ether, dichloromethane etc.). The molecular formula was confirmed by HR–MS, but we were unable to remove the remaining impurities by column chromatography (SiO_2, Al_2O_3), recrystallization or adaptation of the reaction conditions. While the obtained purity was sufficient for subsequent reaction, no analytically pure sample could be obtained (ΔC ≈ 1%).

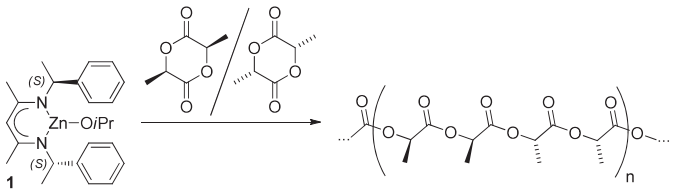
Silvernail et al. obtained related bis(phenolato)amine complexes LZn (lacking a chiral *N*-substituent) as dimers {LZn}$_2$ by reaction of LH_2 with one equivalent of Zn{N(SiMe$_3$)$_2$}$_2$ [14]. Identical reactions with **2**H_2, however, gave only unresolved product mixtures. Reaction of **2**H_2 with $ZnEt_2$ yielded the bimetallic zinc complex **2**(ZnEt)$_2$, **3** (Scheme 2). While the four NCH_2 protons in the free ligand **2**H_2 appeared as two doublets due to the fast inversion of the nitrogen center, coordination to zinc prevents this inversion in **3** and the NCH_2 protons split consequently into four doublets. Complex **3** did not undergo further protonation reactions with alcohols.

In the crystal structure of **3** (Fig. 1, Table 1), one zinc atom is found in a tetrahedral environment, coordinated by two phenolates, an ethyl group and the bridging amine. The second zinc ethyl group is likewise coordinated to the two bridging phenolates and thus adopts a trigonal–planar coordination geometry with Σ X—Zn1/3—X = 360°, despite the reduced O—Zn1/3—O bite angle of 85°, and without apparent intermolecular interactions. Zn—O, but not Zn—C bond lengths are shorter by 0.08(1) Å for trigonal–planar Zn1/3 than for tetrahedral Zn2/4, which can be attributed to the increased Lewis acidity of the three-coordinated Zn center and the involvement of p–p donation from oxygen. Zn2/4—O and Zn2/4—N bond lengths in **3** are slightly longer (0.05 and 0.14 Å, respectively) than the corresponding bond lengths in {LZn}$_2$ dimers obtained by Silvernail et al. [14], indicating a slightly more strained structure for **3**, but are well at the longer end of the range generally observed in tetrahedral zinc complexes (Zn—OAr: 1.99(4) Å, $n = 61$; Zn—NR_3: 2.04(7) Å, $n = 221$) [15].

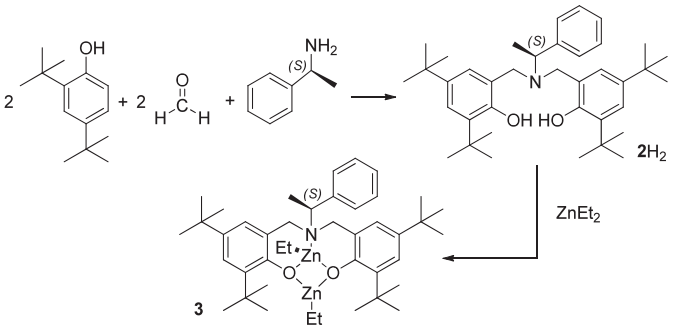
Bimetallic **3** was obtained even in the presence of excess **2**H_2 and under variation of reaction conditions (solvent, order of reagent addition, etc.). A reduced lability of the second Zn ethyl group towards protonation

* Corresponding author.
E-mail address: Frank.Schaper@umontreal.ca (F. Schaper).

1387-7003/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.inoche.2011.07.018



Scheme 1. Lactide polymerization with **1**.



Scheme 2. Synthesis of complex **3**.

by alcohols has been noted before by us and others [6,16–18], but it was nevertheless unexpected for a bidentate diphenolate ligand. Some rational for the preferred formation of a dinuclear zinc complex can be obtained from the crystal structure of **3**: it seems likely that the putative intermediate of the reaction between **2**H_2 and $ZnEt_2$, (**2**H)ZnEt, would adopt a structure comparable to **3**, in which the three-coordinated ZnEt fragment is replaced by hydrogen (Fig. 2). Protonation of the second ethyl group would thus be hindered by the stable tetrahedral coordination geometry of the zinc center and the hydrogen bonding between O1 and O2, which places the hydrogen pointing away from the ethyl group and might explain its low reactivity towards protonation.

(N,O)-ligand. The bidentate ligand **4**H was obtained following reported procedures [19]. Reaction of **4**H with $Zn\{N(SiMe_3)_2\}_2$ afforded the homoleptic complex $(\mathbf{4})_2Zn$, **5** [20–22], independent from reaction conditions and in the presence of excess $Zn\{N(SiMe_3)_2\}_2$ (Scheme 3). Reaction of **4**H with $ZnEt_2$ was more controlled and yielded the heteroleptic complex (**4**)ZnEt, **6** (Scheme 3). Attempts to react the second Zn ethyl group with isopropanol or benzyl alcohol yielded, however, again the homoleptic complex **5**. Formation of **5** most likely proceeds by way of a pre-equilibrium between **6**, **5** and $ZnEt_2$, which

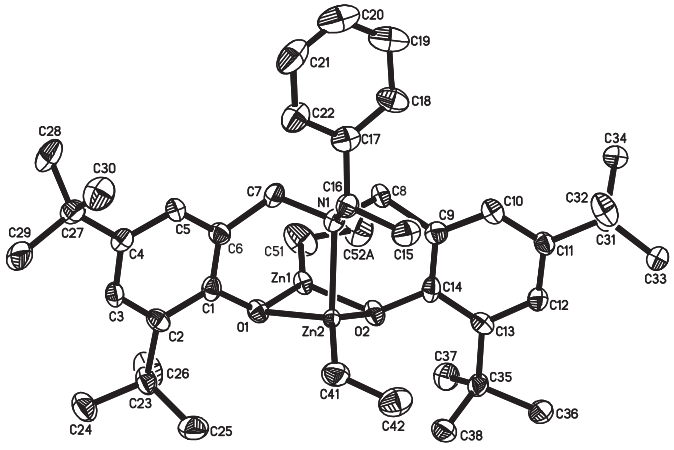


Fig. 1. X-ray structure of **3**. Hydrogen atoms, minor part of disordered atom C52 and the second independent molecule are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

Table 1
Bond distances [Å] and angles [°] in the X-ray structure of complex **3**.

Zn2/4—N[a]	2.191(5); 2.188(5)
Zn1/3—O[b]	1.933(4)–1.987(4)
Zn2/4—O[a]	2.037(4)–2.062(4)
Zn1/3—C51/151[b]	1.944(7); 1.953(7)
Zn2/4—C41/141[a]	1.962(6); 1.953(6)
O—Zn1/3—O[b]	84.9(2); 84.6(2)
O—Zn2/4—O[a]	80.4(2); 81.1(2)
N—Zn2/4—O[a]	89.3(2)–90.0(2)

[a] Tetrahedral zinc center: Zn2, Zn3.
[b] Trigonal–planar zinc center: Zn1, Zn4.

favors the heteroleptic complex **6**. Upon addition of alcohol, $ZnEt_2$ is removed from the equilibrium in the form of Zn(O*i*Pr)Et and **6** is transformed into **5**. NMR-scale experiments showed complete conversion of equimolar mixtures of **5** and $ZnEt_2$ into the heteroleptic complex **6** in 30 min, demonstrating the accessibility of the proposed pre-equilibrium.

Complex **5** was further characterized by an X-ray diffraction(Table 2, Fig. 3). The asymmetric unit contains two independent molecules of essentially identical geometry. The coordination geometry around the Zn centers is distorted tetrahedral due to the reduced N—Zn—O bite angle (95–97°). Both independent molecules adopt a Δ-configuration. The same relative configuration was observed in a previous room-temperature X-ray diffraction study of the Λ,*R*,*R*-enantiomer of **5** [21]. The stereoselectivity of bis(*N*-1-phenylethylsalicylideneiminato) zinc complexes to adopt a Λ,*R*,*R* or a Δ,*S*,*S* configuration [20–22] was previously attributed to a steric preference of the methyl group to occupy an axial position (predicted from NMR data) [20]. However, none of the crystal structures displays the methyl group in this position (although the situation might be different in solution). Based on X-ray data, attractive hydrogen bonding between the methyl group and oxygen and CH–π interactions (i.e. C15—O1 and C9H—(C25–C27) in Fig. 3) have been offered as explanation for the observed stereoselectivity [21]. The hydrogen bonding is, however, rather weak (d(C—O) = 3.4 Å) and there is no indication that comparable interactions would be absent in the Δ,*S*,*S* diastereomer. Furthermore, crystal structures of compounds similar to **5**, but carrying additional nitro, dichloro or methoxy substituents on the phenol [22,23], might not show any hydrogen bonding (d(C—O)>4 Å), but conserve the selectivity for Λ,*R*,*R* configurations. These structures display to varying degrees π-stacking interactions between phenol and the phenyl substituent (interplanar distances of 3.3–3.5 Å), which are sterically only possible in the Λ,*R*,*R* or Δ,*S*,*S* configuration. We propose that these interactions, albeit absent in the solid state for **5**, are at least partially responsible for the observed stereoselectivity. It should be noted that π-stacking between phenol and phenyl also places the methyl group in the axial position, predicted from NMR data for these compounds [20].

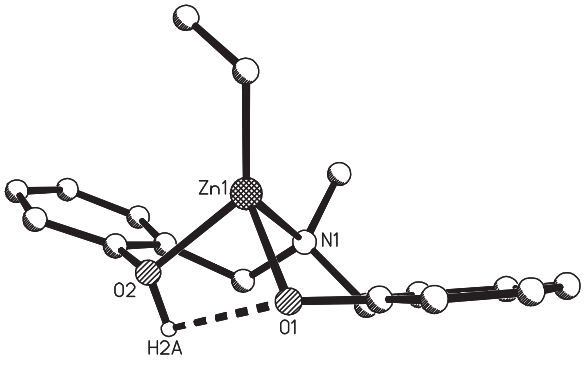
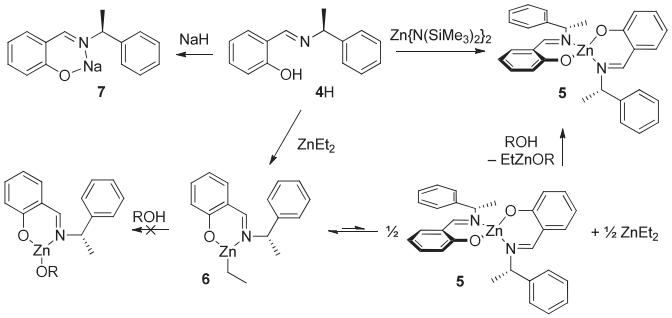


Fig. 2. Potential structure of intermediate (**2**H)ZnEt. O1—H2A = 2.5 Å.



Scheme 3. Synthesis of **5** and **6**.

For the sake of comparison, a more ionic compound, the sodium salt (**4**)Na, **7**, was prepared in slight variation from reported procedures by a simple reaction of **4**H with NaH [24]. Complex **7** crystallizes as a cubic tetramer (Fig. 4, Table 2), essentially isostructural to the structure of the diethyl ether adduct of its *R,R,R,R*-enantiomer [24]. While sodium was described as four-coordinated in the reported diethyl ether adduct, in **7** short Na—C_{Ph} distances of 2.8 to 3.0 Å are found to the meta position of the phenylethyl substituent. These are notably smaller than the sum of the vdW radii of Na and C (4.0 Å) and in the normal range observed for Na–π interactions. Coordination geometry around Na1, Na2 and Na4 is thus best described as distorted square–pyramidal, with the O, N and C atom of the same ligand in the equatorial plane. The absence of a sixth ligand leads to an increase of the X—Na—O angles to the apical oxygen atom (N: 109–134°, C: 109–129°). For Na3, short intermolecular distances to a second phenyl ring (d(Na3—C14a/C15a) = 3.7 Å) complete an octahedral coordination and C/N—Na3—O angles closer to ideal geometry (89° and 96°, respectively) are observed.

Lactide polymerization. Complexes **3**, **5** and **7** were tested for potential enantioselectivity in *rac*-lactide polymerization (Table 3). Complex **3** proved inactive in initiating lactide polymerizations in $CDCl_3$ at ambient temperature, but prolonged reaction times at 50 °C led to essentially complete conversion. Low rates of insertion into Zn ethyl groups have been observed before [25] and, given the low rate of polymerization, neither insertion in Zn—OAr nor activation of **3** by trace impurities can be excluded. The polymer microstructure showed a slight, but notable bias for heterotacticity, typically observed for tetrahedral zinc complexes due to a chain-end control mechanism. The value is higher than that observed for Zn(O*i*Pr)$_2$, which yields atactic PLA ($P_r = 0.50$) [26]. While this indicates that the ligand remains coordinated to Zn in the active species, its function seems to be limited to providing moderate steric bulk without any chiral induction from the methylbenzyl substituent.

Bischelate complex **5** proved to be inactive towards lactide polymerization even at 50 °C. Under forcing conditions (molten monomer, 180 °C), polymerization was achieved in 30 min, but we cannot exclude that catalyst decomposition precedes initiation under these conditions. The obtained polymer was atactic, with a negligible heterotactic bias. This lack of reactivity seems to be related to the steric saturation of the zinc center, which prevents insertion into the Zn—OAr group. The sodium salt **7**, on the other hand, effectively initiated lactide polymerization in $CDCl_3$ at ambient temperature, leading to 85% monomer conversion in 2 h. Not surprisingly, the use of an enantiopure initiator, which might not remain bound to the sodium counter cation, did not affect the polymer microstructure and essentially atactic PLA was obtained.

Table 2
Bond distances [Å] and angles [°] in the X-ray structures of complexes **5** and **7**.

	5 (M = Zn)	7 (M = Na)
M—N	2.012(2)–2.020(2)	2.399(1)–2.459(1)
M—O [a]	1.926(2)–1.948(2)	2.259(1)–2.293(1)
M—O		2.306(1)–2.441(2)
N—M—O[b]	94.91(9)–97.41(9)	75.93(4)–78.81(4)
N—M—O[c]	110.85(8)–113.69(7)	96.56(4)–164.60(5)
N—M—N	126.62(7); 124.80(9)	
O—M—O	111.16(7); 118.71(10)	83.10(4)–97.46(4)

[a] **7**: Oxygen is part of the six-membered metallacycle, e.g. Na3, N3, C49–C51, O3.
[b] Ligand bite angles, e.g. **5**: O1—Zn1—N1; **7**: N3—Na3—O3.
[c] Angles between N and O atoms of different ligands.

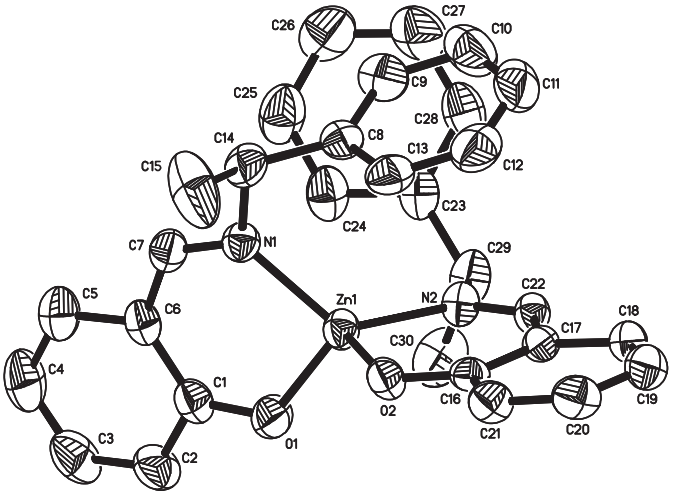


Fig. 3. X-ray structure of Δ,*S,S*-**5**. Hydrogen atoms and the second independent molecule are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

In summary, incorporation of enantiopure *S*-methylbenzylamine is a very economic way to enantiopure metal complexes containing a chiral center. Asymmetric induction from the chiral center, however, was not observed in *rac*-lactide polymerizations, which might be related to the small steric differences between methyl and phenyl close to the metal center and/or to the high degree of flexibility provided by rotation around the N-C single bond.

Experimental section. All reactions, except ligand synthesis, were carried out under nitrogen atmosphere using Schlenk or glove box techniques. Solvents were dried by passage through activated aluminum oxide (MBraun SPS) and de-oxygenated by repeated extraction with nitrogen. C_6D_6 was distilled from Na and de-oxygenated by three freeze–pump–thaw cycles. $CDCl_3$ was dried over activated molecular sieves. All other chemicals were obtained from commercial suppliers and used as

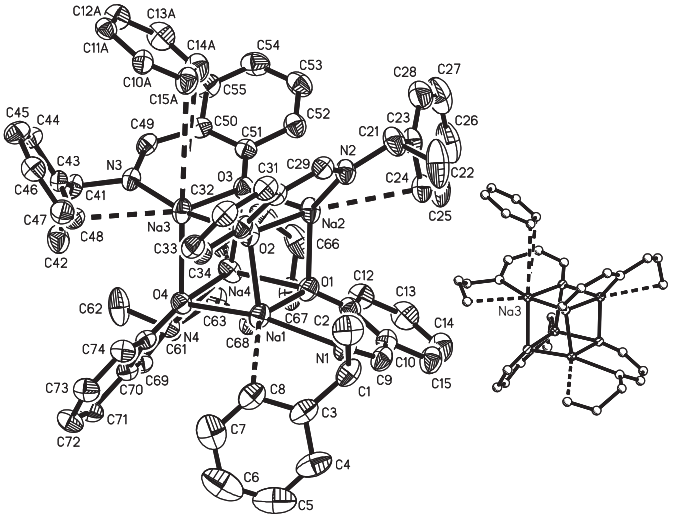


Fig. 4. X-ray structure of **7**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Atoms C10a–C15a are generated by $x - 1, y, z$.

Table 3
Rac-lactide polymerization results.

Initiator	[Lactide]/initiator	T	Time	Conversion	P_r[a]
3	200:1	23 °C	2 h	–	–
3	100:1	50 °C	20 h	91%	0.59
5	100:1	23 °C	2 h	–	–
5	100:1	50 °C	24 h	–	–
5	100:1	180 °C[b]	0.5 h	95%	0.52
7	200:1	23 °C	2 h	85%	0.56

Conditions: $CDCl_3$, [lactide]/[initiator] = 100:1, [initiator] = $5–7 \cdot 10^{-6}$ M.
[a] P_r is the probability for alternating monomer insertion, determined from decoupled ^{1}H NMR: $P_r = 2 \cdot I_1/(I_1 + I_2)$, with I_1 = 5.20–5.25 ppm (*rmr*, *mmr*/*rmm*), I_2 = 5.13–5.20 ppm (*mmr*/*rmm*, *mmm*, *mrm*) [25].
[b] No solvent.

received. Elemental analyses were performed by the Laboratoire d'Analyse Élémentaire (Université de Montréal). NMR spectra were recorded on a Bruker DRX 400 MHz spectrometer and referenced to residual solvent (C_6D_6, ^{1}H: δ 7.15, ^{13}C: δ 128.02; $CDCl_3$, ^{1}H: δ 7.26, ^{13}C: δ 77.0).

2,2'-({[(1*S*)-1-phenylethyl]imino}dimethanediyl)bis(2,4-di-*tert*-butylphenol), 2H₂. A mixture of 2,4-di-*tert*-butylphenol (10.0 g, 49 mmol), formaldehyde (3.7 mL, 37% in water, 49 mmol) and *S*-1-phenyethylamine (2.9 g, 24 mmol) in water (30 mL) was heated to reflux for 18 h. After cooling to room temperature, two phases formed. The crude reaction mixture was extracted twice with hexane. The combined organic phases were washed with water, dried over Na_2SO_4 and evaporated, to yield a light-yellow sticky solid in ca. 90% purity (13.1 g, 97%).

^{1}H-RMN ($CDCl_3$, 300 MHz): 7.42–7.26 (m, 5H, Ph), 7.20 (d, *J* = 2 Hz, 2H, Ph), 6.91 (d, *J* = 2 Hz, 2H, Ph), 4.12 (q, *J* = 7 Hz, 1H, C*H*(CH_3)Ph), 3.63 (bs, 4H, CH_2N), 1.52 (d, *J* = 7 Hz, 3H, CH(C*H*$_3$)Ph), 1.42 (s, 18 H, *t*Bu), 1.25 (s, 18 H, *t*Bu). ^{1}H-RMN (C_6D_6, 300 MHz): 7.54 (bs, 2H, Ph), 7.47 (d, *J* = 2 Hz, 2H, Ph), 7.28–7.10 (m, 3H, Ph), 6.93 (d, *J* = 2 Hz, 2H, Ph), 4.06 (q, *J* = 7 Hz, 1H, C*H*(CH_3)Ph), 3.55 (d, *J* = 14 Hz, 2H, CH_2N), 3.33 (d, *J* = 14 Hz, 2H, CH_2N), 1.61 (s, 18 H, *t*Bu), 1.33 (s, 18 H, *t*Bu), 1.10 (d, *J* = 7 Hz, 3H, CH(C*H*$_3$)Ph). ^{13}C-RMN ($CDCl_3$, 75 MHz): δ 152.3 (Ph), 141.4 (Ph), 140.0 (Ph), 135.9 (Ph), 128.6 (Ph), 128.4 (Ph), 127.8 (Ph), 127.4 (Ph), 125.1 (Ph), 123.5 (Ph), 121.5 (Ph), 56.2 (CH_2), 52.1 (CH_2), 34.9 (*C*(CH_3)$_3$), 34.1 (*C*(CH_3)$_3$), 31.6 (C(*C*H$_3$)$_3$), 29.6 (*C*(CH_3)$_3$), 11.3 (*C*H(CH_3)Ph), 1.03 (*C*H(CH_3)Ph). HR–MS: calcd. for $C_{38}H_{56}NO_2$ (MH^+): 558.4306. Found: 558.4304.

(2)(ZnEt)₂, 3. To a solution of $ZnEt_2$ (22 mg, 0.18 mmol) in hexane (1 mL) were added a solution of **2**H$_2$ (0.10 g, 0.18 mmol) in hexane (3 mL). After 3 h of stirring, the solvent is removed by decantation and the remaining solid washed with hexane. Recrystallization from a toluene/hexane mixture yielded 51 mg (77%) of colorless crystals.

^{1}H NMR (C_6D_6, 300 MHz): 7.56 (d, *J* = 3 Hz, 1H, Ph), 7.50 (d, *J* = 2 Hz, 1H, Ph), 7.30 (d, *J* = 7 Hz, 2H, Ph), 7.20–7.11 (m, 3H, Ph), 6.96 (d, *J* = 2 Hz, 1H, Ph), 6.95 (d, *J* = 2 Hz, 1H, Ph), 4.05 (q, *J* = 7 Hz, 1H, C*H*(Me)Ph), 4.08 (d, *J* = 15 Hz, 1H, NCH_2), 3.85 (d, *J* = 15 Hz, 1H, NCH_2), 3.84 (d, *J* = 15 Hz, 1H, NCH_2), 3.53 (d, *J* = 15 Hz, 1H, NCH_2), 1.66 (s, 9 H, *t*Bu), 1.64 (s, 9 H, *t*Bu), 1.43 (t, *J* = 8 Hz, 3 H, $ZnCH_2CH_3$), 1.39 (d, *J* = 7 Hz, 3H, CH(*Me*)Ph), 1.35 (s, 9 H, *t*Bu), 1.33 (s, 9 H, *t*Bu), 1.07 (t, *J* = 8 Hz, 3 H), 0.58 (q, *J* = 8 Hz , 2H, $ZnCH_2$), 0.57 (q, *J* = 8 Hz, 2H, $ZnCH_2$). ^{13}C NMR (C_6D_6, 75 MHz): δ 159.6 (Ph), 158.7 (Ph), 130.6 (Ph), 128.6 (Ph), 126.5 (Ph), 125.3 (Ph), 125.1 (Ph), 124.5 (Ph), 64.7 (*C*H(CH_3)Ph), 62.5 (NCH_2), 58.7 (NCH_2), 35.8 (*C*(CH_3)$_3$), 35.7, (*C*(CH_3)$_3$), 34.4 (*C*(CH_3)$_3$), 34.3 (*C*(CH_3)$_3$), 32.0 (C(*C*H$_3$)$_3$), 30.8 (C(*C*H$_3$)$_3$), 21.3 (CH(*C*H$_3$)Ph), 12.9 ($ZnCH_2CH_3$), 11.6 ($ZnCH_2CH_3$), 0.92 ($ZnCH_2CH_3$), 0.25 ($ZnCH_2CH_3$). Anal. calcd. for $C_{42}H_{63}NO_2Zn_2$: C, 67.73; H, 8.53; N, 1.88. Found: C, 68.08; H, 8.12; N, 1.84.

Ligand 4H. Following a previous procedure [19], a mixture of salicylaldehyde (1.0 g, 8.3 mmol), *S*-1-phenylethylamine (1.0 g, 8.3 mmol) and Na_2SO_4 (4 g) as a drying agent in dry methanol (50 mL) are heated to reflux for 6 h. The reaction mixture is filtered and the solvent removed to yield a yellow oil, which is washed with cold methanol and dried under vacuum to yield 1.8 g (90%) of **4**H.

^{1}H-RMN (C_6D_6, 400 MHz): δ 13.76 (s, 1H, O*H*), 7.82 (s, 1H, N = C*H*), 7.22–7.06 (m, 7H, Ph), 6.89 (dd, *J* = 2 Hz, *J* = 8 Hz, 1H, *m*-Ph), 6.70 (td, *J* = 7 Hz, *J* = 1 Hz, 1H, *p*-Ph), 4.04 (q, *J* = 7 Hz, 1H, C*H*(CH_3)Ph), 1.32 (d, *J* = 7 Hz, 3H, CH(C*H*$_3$)Ph). C-RMN (C_6D_6, 101 MHz): δ 169.39 (N = *C*H), 161.02 (Ph), 143.77 (Ph), 132.24 (Ph), 131.34 (Ph), 128.63 (Ph), 127.22 (Ph), 126.35 (Ph), 118.79 (Ph), 118.58 (Ph), 116.93 (Ph), 68.41 (*C*H(CH_3)Ph), 24.93 (CH(*C*H$_3$)Ph). Anal. calcd. for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.05; H, 6.85; N, 6.18.

(4)₂Zn, 5. a) A solution of **4**H (100 mg, 0.44 mmol) in toluene (6 mL) was added to $Zn\{N(SiMe_3)_2\}_2$ (171 mg, 0.44 mmol). After 5 h stirring at ambient temperature, the solution is concentrated to 1/3 of its volume and the product precipitated by addition of hexanes (4 mL). Decantation of the solvent, washing with hexane and drying yielded 107 mg (95%) of **5** as a slightly yellow powder, which could be further purified by recrystallization from toluene/hexane.

b) To a solution of $ZnEt_2$ (100 mg, 1.1 mmol) in diethyl ether was added a solution of **4**H (500 mg, 2.2 mmol) in diethyl ether. After 20 h stirring at ambient temperature, the solvent was decanted from the formed precipitate, which was washed with hexane and recrystallized from toluene/hexane (208 mg, 37%).

^{1}H NMR (C_6D_6, 400 MHz): 7.52 (s, 2H, N = C*H*), 7.26–6.74 (m, 4H, Ph), 6.91 (d, *J* = 7 Hz, 2 H, Ph), 6.85 (t, *J* = 7 Hz, 4H, Ph), 6.81 (d, *J* = 7 Hz, 2H, Ph), 6.74 (d, *J* = 7 Hz, 4H, Ph), 6.57 (t, *J* = 7 Hz, 2 H, Ph), 3.81 (q, *J* = 7 Hz, 2H, C*H*(CH_3)Ph), 1.28 (d, *J* = 6 Hz, 6H, CH(C*H*$_3$)Ph). ^{13}C NMR (C_6D_6, 101 MHz): δ 171.7 (N = *C*H), 169.0 (Ph), 140.7 (Ph), 136.2 (Ph), 135.3 (Ph), 129.3 (Ph), 128.7 (Ph), 125.7 (Ph), 124.0 (Ph), 118.9 (Ph), 114.2 (Ph), 69.4 (*C*H(CH_3)Ph), 22.0 (CH(*C*H$_3$)Ph). Anal. calcd. for $C_{30}H_{30}O_2N_2$: C, 69.84; H, 5.86; N, 5.43. Found: C, 69.90; H, 5.77; N, 5.25.

(4)ZnEt, 6. To a solution of $ZnEt_2$ (57 mg, 0.47 mmol) in toluene (1 mL) was added a solution of **4**H (100 mg, 0.41 mmol) in toluene (1 mL). After stirring for 5 h at ambient temperature, the solution is concentrated under vacuum. The slightly yellow precipitate formed is washed with hexane to yield a colorless powder (94 mg, 71%).

^{1}H-RMN (C_6D_6, 400 MHz): δ 7.71 (s, 1H, N = C*H*), 7.28 (d, *J* = 8 Hz, 2H, Ph), 7.19–7.10 (m, 4H, Ph), 7.05 (t, *J* = 7 Hz, 1H, Ph), 6.73 (dd, *J* = 2 Hz, *J* = 10 Hz, 1H, Ph), 6.58 (td, *J* = 10 Hz, *J* = 2 Hz, 1H, Ph), 4.28 (q, *J* = 7 Hz, 1H, C*H*(CH_3)Ph), 1.68 (d, *J* = 7 Hz, 3H, CH(C*H*$_3$)Ph), 1.24 (t, *J* = 8 Hz, 3 H, $ZnCH_2CH_3$), 0.28 (q, *J* = 8 Hz, 2 H, $ZnCH_2CH_3$). ^{13}C-RMN (C_6D_6, 101 MHz): δ 168.95 (N = *C*H), 167.27 (Ph), 141.97 (Ph), 135.56 (Ph), 134.29 (Ph), 128.63 (Ph), 127.63 (Ph), 127.31 (Ph), 122.68 (Ph), 121.07 (Ph), 116.93 (Ph), 68.34 (*C*H(CH_3)Ph), 22.40 (CH(*C*H$_3$)Ph), 12.79 ($ZnCH_2CH_3$), −0.61 ($ZnCH_2CH_3$). Anal. calcd. for $C_{17}H_{19}NOZn$: C, 64.06, H, 6.01, N, 4.39. Found: C, 63.90, H, 6.15, N, 4.44.

(4)Na, 7. To a suspension of NaH (0.02 g, 0.9 mmol) in toluene, a solution of **4**H (0.2 g, 0.9 mmol) in toluene was added. After 4 h of stirring at ambient temperature, the solution was filtered and the solvent removed by evaporation. Recrystallization from toluene/hexane yielded 170 mg (78%) of **7**.

^{1}H NMR (C_6D_6, 400 MHz): δ 7.89 (s, 1 H, N = C*H*), 7.24 (td, *J* = 8 Hz, *J* = 2 Hz, 1H, Ph), 7.18–7.12 (m, 4 Hz, Ph), 6.86 (dd, *J* = 2 Hz, *J* = 7 Hz, 2 H, Ph), 6.70 (t, *J* = 7 Hz, 1H, Ph), 5.73 (d, *J* = 8 Hz, 1H, Ph), 3.78 (q, *J* = 7 Hz, 1H, C*H*(CH_3)Ph), 1.12 (d, *J* = 7 Hz, 3H, CH(C*H*$_3$)Ph). ^{13}C-RMN (C_6D_6, 101 MHz): δ 171.2 (N = *C*H), 165.9 (Ph), 144.9 (Ph), 137.0 (Ph), 132.7 (Ph), 129.7 (Ph), 127.5 (Ph), 126.5 (Ph), 123.5 (Ph), 123.0 (Ph), 112.4 (Ph), 69.9 (*C*H(CH_3)Ph), 22.7 (CH(*C*H$_3$)Ph). Anal. calcd. for $C_{15}H_{14}NONa$: C, 72.86; H, 5.71; N, 5.66. Found: C, 72.52; H, 5.67; N, 5.62.

X-ray diffraction studies. Data sets for **5** and **7** were recorded on a Bruker SMART 6000 diffractometer with Helios optics, equipped with a rotating anode source for Cu Kα radiation (λ = 1.54178 Å). Data for **3** was collected on a Bruker Smart APEX2 with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). Cell refinement and data reduction

Table 4
Details of X-ray structures studies.

	3	**5**	**7**
Formula	$C_{42}H_{63}NO_2Zn_2$	$C_{30}H_{28}N_2O_2Zn$	$C_{60}H_{56}N_4O_4Na_4$
Mw (g/mol); $d_{calcd.}$ (g/cm^3)	744.67; 1.238	513.91; 1.315	989.05; 1.245
T (K); *F*(000)	200; 796	150; 2144	150; 2080
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Space group	*P*1	$\mathbf{P2_12_12_1}$	$\mathbf{P2_12_12_1}$
a (Å)	10.5215(7)	9.890(1)	10.0993(2)
b (Å)	11.4562(8)	17.737(2)	21.9355(5)
c (Å)	16.8967(11)	29.588(3)	23.8247(5)
α (°)	88.579(1)	90	90
β (°)	89.501(1)	90	90
γ (°)	78.849(1)	90	90
V (Å^3); Z	1997.6(2); 2	5190.1(10); 8	5278.0(2); 4
θ range (°); completeness	2.6–89.4; 1.0	2.9–72.0; 1.0	2.7–72.3; 0.99
Collected refl.; R_{sigma}	40932; 0.070	67349; 0.027	68375; 0.019
Independent refl.; R_{int}	18172; 0.037	10084; 0.038	10358; 0.033
μ (mm^{-1})	1.720	1.535	0.902
$I>2\sigma(I)$: $R1(F)$; $wR(F^2)$	0.047; 0.103	0.031; 0.080	0.030; 0.082
All data: $R1(F)$; $wR(F^2)$	0.066; 0.110	0.034; 0.081	0.032;0.083
GoF(F^2); flack	0.93; 0.00(3)	1.04; 0.00(2)	1.02; 0.00(3)
Res. elec. dens.	0.45; −0.27	0.33; −0.27	0.14; −0.21

were performed using APEX2 [27]. Absorption corrections were applied using SADABS [28]. Structures were solved by direct methods using SHELXS97 and refined on F^2 by full-matrix least squares using SHELXL97 [29]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined on calculated positions using a riding model. For further details see Table 4 and the supp. information.

Acknowledgments

We like to thank Elena Nadezhina and Francine Bélanger for assistance with the combustion analyses, and Alexandra Furtos and Marie-Christine Tang for assistance with mass spectroscopy. Funding was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Centre in Green Chemistry and Catalysis (CCVC/CCGC).

Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.07.018.

References

[1] M.J. Stanford, A.P. Dove, Chem. Soc. Rev. 39 (2010) 486.
[2] C.A. Wheaton, P.G. Hayes, B.J. Ireland, Dalton Trans. (2009) 4832.
[3] R.H. Platel, L.M. Hodgson, C.K. Williams, Polym. Rev. 48 (2008) 11.
[4] M.H. Chisholm, Z. Zhou, J. Mater. Chem. 14 (2004) 3081.
[5] O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, Chem. Rev. 104 (2004) 6147.
[6] F. Drouin, P.O. Oguadinma, T.J.J. Whitehorne, R. E. Prud'homme, F. Schaper, Organometallics 29 (2010) 2139.
[7] F. Drouin, T.J.J. Whitehorne, F. Schaper, Dalton Trans. 40 (2011) 1396.
[8] F. Buch, S. Harder, Z. Naturforsch, B: Chem. Sci. 63 (2008) 169.
[9] P.O. Oguadinma, F. Schaper, Organometallics 28 (2009) 4089.
[10] E.Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, Organometallics 20 (2001) 3017.
[11] F.M. Kerton, S. Holloway, A. Power, R.G. Soper, K. Sheridan, J.M. Lynam, A.C. Whitwood, C.E. Willans, Can. J. Chem. 86 (2008) 435.
[12] S. Groysman, I. Goldberg, M. Kol, E. Genizi, Z. Goldschmidt, Inorg. Chim. Acta 345 (2003) 137.
[13] S. Barroso, P. Adão, F. Madeira, M.T. Duarte, J.C. Pessoa, A.M. Martins, Inorg. Chem. 49 (2010) 7452.
[14] C.M. Silvernail, L.J. Yao, L.M.R. Hill, M.A. Hillmyer, W.B. Tolman, Inorg. Chem. 46 (2007) 6565.
[15] F.H. Allen, Acta Crystallogr, Sect. B: Struct. Sci. B58 (2002) 380.
[16] R.J. Herolds, L. Aggarwal, V. Neff, Can. J. Chem. 41 (1963) 1368.
[17] M. Cheng, D.R. Moore, J.J. Reczek, B.M. Chamberlain, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 8738.
[18] G. Labourdette, D.J. Lee, B.O. Patrick, M.B. Ezhova, P. Mehrkhodavandi, Organometallics 28 (2009) 1309.
[19] A.L. Iglesias, G. Aguirre, R. Somanathan, M. Parra-Hake, Polyhedron 23 (2004) 3051.
[20] M.J. O'Connor, R.E. Ernst, J.E. Schoenborn, R.H. Holm, J. Am. Chem. Soc. 90 (1968) 1744.
[21] H. Sakiyama, H. Okawa, N. Matsumoto, S. Kida, J. Chem. Soc., Dalton Trans. (1990) 2935.
[22] C. Evans, D. Luneau, J. Chem. Soc., Dalton Trans. (2002) 83.
[23] T. Akitsu, Polyhedron 26 (2007) 2527.
[24] R. Fischer, H. Görls, D. Walther, Z. Anorg. Allg. Chem. 630 (2004) 1387.
[25] B.M. Chamberlain, M. Cheng, D.R. Moore, T.M. Ovitt, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 3229.
[26] J. Claverie, Université de Québec à Montréal, Canada, Personal Communication (2009).
[27] APEX2, Release 2.1-0, Bruker AXS Inc, Madison, USA, 2006.
[28] G.M. Sheldrick, SADABS, Bruker AXS Inc, Madison, USA, 1996 2004.
[29] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.