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Journal of Organometallic Chemistry 693 (2008) 1861–1869
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and structures of some sterically hindered zinc complexes containing 6-membered ZnNCCCN and ZnOCCCN rings

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Received 16 January 2008; received in revised form 13 February 2008; accepted 14 February 2008
Available online 20 February 2008

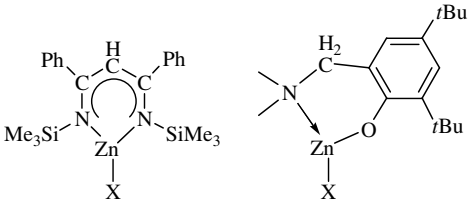
Abstract

Zinc β-diketiminates containing the *N*,*N*′-chelating ligand $[\{N(SiMe_3)C(Ph)\}_2CH]^-$ (≡LL$^-$) $[Zn(LL)(\mu\text{-}Cl)]_2$ (**1**) and [ZnEt(LL)thf] (**2**) were prepared from $2ZnCl_2 + [Li(LL)]_2$ and $ZnEt_2 + H(LL)$, respectively. The new phenols 2-(*N*-R-piperazinyl-*N*′-methyl)-4,6-di-*tert*-butylphenol [R = Ph (**3a**), Me (**3b**)] and 2,2-[μ-*N*,*N*′-piperazindiyldimethyl]-bis(4,6-di-*tert*-butylphenol) (**4**) were obtained from 2,4-tBu_2-C_6H_3OH, $(CH_2O)_n$ and the appropriate piperazine. Zinc phenoxides **5**, **7** and **8** were derived from $2ZnEt_2$ with 2(**3a**), 2(**3b**) and **4**, respectively. Controlled methanolysis of **5** furnished the bis(phenoxo)zinc compound $Zn[OC_6H_2tBu_2\text{-}2,4\text{-}\{CH_2N(CH_2CH_2)_2NPh\}\text{-}6]_2$ (**6**). The X-ray structures of the crystalline zinc compounds **1**, **2**, **5**, **6**, **7** and **8**, are presented; each of **5**–**8** contains two ZnOCCCN six-membered rings. The centrosymmetric molecule **1** has a rhomboidal $(ZnCl)_2$ core with exceptionally different Zn–Cl and Zn–Cl′ bond lengths of 2.248(1) and 2.509(1) Å, respectively. None of **1**, **2** or **5**–**8** was an effective catalyst for the copolymerisation of an oxirane and CO_2.

Keywords: Zinc; β-Diketiminate; Phenoxide; X-ray structure; Copolymerisation catalysis

1. Introduction

Recently, we reported on the synthesis and structures of some bimetallic diamides derived from the 1,2-benzene-bis(neopentylamido) ligand (L^{2-}), including the zinc-containing complexes $[Li(thf)_4][\{Zn(\mu\text{-}L)\}_3(\mu_3\text{-}Cl)]$, $[\{Li(OEt_2)\text{-}(\mu\text{-}L)Zn\}_2(\mu\text{-}L)]$, $[Li(OEt_2)(\mu\text{-}L)Zn(\mu\text{-}L)Zn(LH)\}]$ and the paramagnetic $[Li(thf)_4][Zn(L)(L^{\cdot-})]$ [1]. That study was part of an exploratory programme to identify compounds which might be active catalysts for the copolymerisation of an oxirane and carbon dioxide or the related catalytic ring-opening polymerisation of lactide. Two classes of zinc *N*,*N*′- or *O*,*N*′-chelate compounds and their potential for the oxirane/CO_2 copolymerisation are the focus of the present investigation. These have a ZnNCCCN or ZnOCCCN cyclic core, the β-diketiminates or 2-dialkylaminophenolates of formulae **A** or **B**, respectively. A recent paper by Gibson and coworkers identified metal complexes such as these as potential catalysts for such processes [2].



The use of zinc-based catalysts for the copolymerisation of an oxirane (including propylene oxide) and carbon dioxide has a long history, as expounded in the 2004 review of

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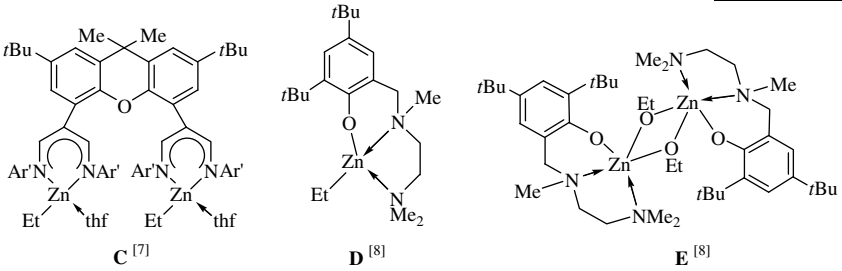
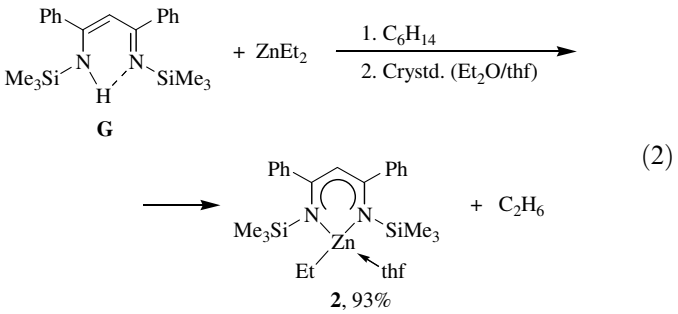
doi:10.1016/j.jorganchem.2008.02.012

Coates and Moore [3]. Among the landmarks were heterogeneous systems based on $ZnEt_2/H_2O$ [4a], $ZnEt_2/C_6H_4(OH)_2$-1,3 [4b], $ZnEt_2/PhCH_2CH_2NH_2$ [4c] and $Zn(OH)_2/(CH_2)_3(CO_2H)_2$-1,3 [4d].

The use of single-site catalysts for such copolymerisations are of more recent date, starting (1995) from zinc aryloxides such as $[Zn(OC_6H_2tBu_3\text{-}2,4,6)_2(thf)_2]$ and $[\{Zn(OC_6H_3F_2\text{-}2,6)(\mu\text{-}OC_6H_3F_2\text{-}2,6)(thf)\}_2]$ [5]. Coates and coworkers showed that certain β-diketiminatozinc complexes, including the binuclear complex $[\{Zn(L')(\mu\text{-}OMe)\}_2]$ [$L' = N(C_6H_3Me_2\text{-}2,6)C(Me)C(CN)C(Me)N(C_6H_3iPr_2\text{-}2,6)$] [6a], were highly active living copolymerisation (CO_2, cyclohexene oxide) catalysts [6]. A very recent paper dealing with such copolymerisations featured dinuclear zinc complexes containing β-diiminato binding sites such as **C** ($Ar' = C_6H_3Me_2$-2,3) [7]. Highly active catalysts for the controlled polymerisation of lactide were the crystalline complexes **D** and **E** [8]. Synthesis and structures of a series of binuclear zinc alkyl, aryl and aryloxide complexes, which were suggested as potential precursors for catalysts of such processes, has been reported recently [9].



C [7] **D** [8] **E** [8]



G **2**, 93% (2)

Compounds **1** and **2** were characterised by microanalysis, ^1H and ^{13}C NMR spectra and EI mass spectra, and single crystal X-ray diffraction. Surprisingly, the binuclear zinc chloride complex **1** was resistant to $Li[N(SiMe_3)_2]$ or $KOtBu$ in refluxing thf for 10 min. Likewise, the zinc ethyl compound **2** proved to be unresponsive to attack by $HN(SiMe_3)_2$, but *i*PrOH yielded a gel containing (by ^1H NMR spectroscopy) a significant proportion of the β-diketimine **G**.

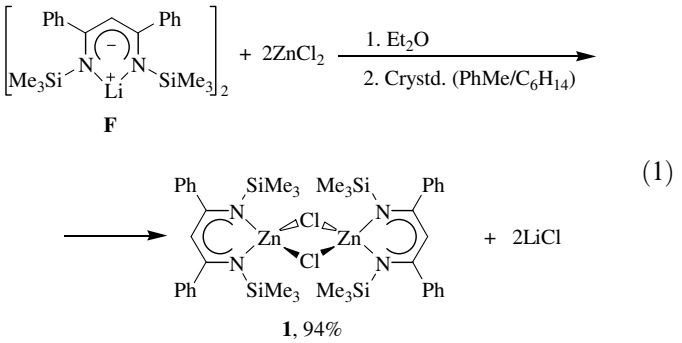
The dimeric structure of complex **1** has been confirmed by the X-ray diffraction study. It is noteworthy that while β-diketiminatozinc chloride and bromide with a "nacnac" type ligand were regarded as dimeric [6b], their structures had not been proved (the unsolvated Et derivative was a monomer having a 3-coordinate planar Zn atom [6b]). The centrosymmetric molecule **1** (Fig. 1) has a rhomboidal $(ZnCl)_2$ core with clearly different Zn–Cl and Zn–Cl′ bond lengths of 2.248(1) and 2.509(1) Å, respectively; these distances may be compared with the 2.328(9) and 2.332(8) Å reported for the more symmetrically bridged $[Zn(CCl_2CF_3)(\mu\text{-}Cl)(OEt_2)]_2$ [12a]. Even in a highly sterically crowded complex with an NPPN chelating ligand $[\{Zn(\mu\text{-}Cl)(NPPN)\}_2]$ [$NPPN = N(C_6H_3iPr_2\text{-}2,6)P(Ph)P(nBu)(Ph)N(C_6H_3iPr_2\text{-}2,6)$] the difference in bridging Zn–Cl bond lengths [2.3011(8) and 2.4124(9) Å] was not so pronounced [12b]. The coordination environment of each Zn atom in **1** can be described as trigonal pyramidal with the N1, N2 and Cl atoms in equatorial positions (the sum of N1–Zn–N2 [100.36(13)°], N1–Zn–Cl [127.12(10)°] and N2–Zn–Cl [125.28(9)°] angles is 352.8°) and the Cl′ atom in the axial position.

The molecular structure of the crystalline compound **2** is shown in Fig. 2. The zinc atom adopts a trigonal pyramidal coordination environment with the N1, N2 and the α-ethyl carbon (C22) atoms in equatorial positions (the sum of the

2. Results and discussion

2.1. β-Diketiminatozinc complexes

The crystalline β-diketiminatozinc compounds **1** and **2** were obtained in high yield by a salt-(**1**) or alkane-(**2**) elimination procedure, as summarised in Eqs. (1) and (2), respectively. The starting materials, the lithium β-diketiminate **F** [10] (for **1**) or the β-diketimine **G** [10] (for **2**), have been used by our group as precursors for a wide range of metal β-diketiminates [11]



F **1**, 94% (1)

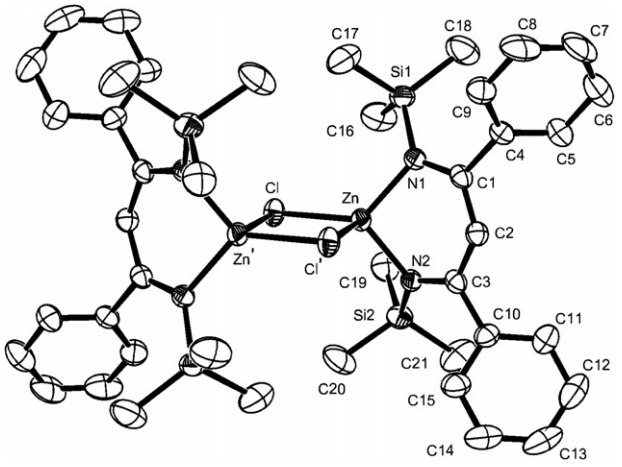


Fig. 1. ORTEP representation of the molecular structure of **1** (50% ellipsoids; H atoms omitted). Symmetry transformation to generate equivalent atoms: $-x$, $-y$, $-z$.

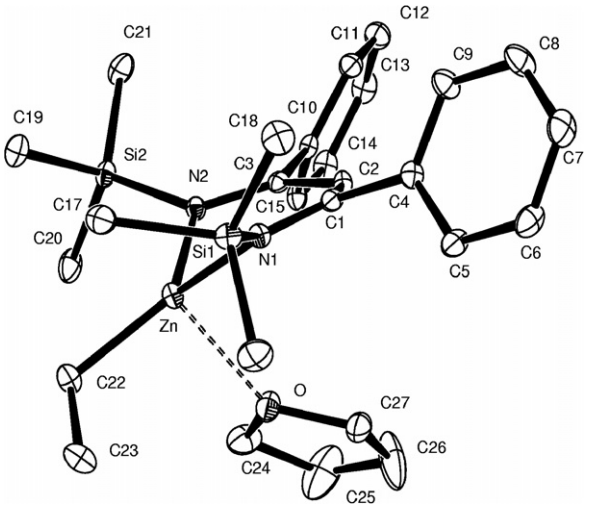


Fig. 2. ORTEP representation of the molecular structure of **2** (20% ellipsoids; H atoms omitted).

N1–Zn–N2 [95.85(9)°], N1–Zn–C22 [133.06(12)°] and N2–Zn–C22 [127.79(11)°] angles is 356.7°) and the O atom of the thf moiety in the axial position. Such a geometry around a Zn atom is similar to that of a recently reported ZnEt complex of a binucleating β-diketiminato ligand with a pyridine donor ligand in place of thf in **2** [13]. The Zn–C and Zn–O distances of 1.984(3) and 2.332(2) Å, respectively, are similar to the 1.988(7) and 1.985(9) Å (Zn–C) and 2.323(5) and 2.240(5) Å (Zn–O) found in [ZnEt{μ-N(H)$C_6H_2Me_3$-2,4,6}(thf)]$_2$ [14]. This rather long Zn–O distance in **2** [it is significantly longer than those in complex **8** at 2.165(2) Å] suggests that the bonding between the Zn atom and the thf ligand is weak.

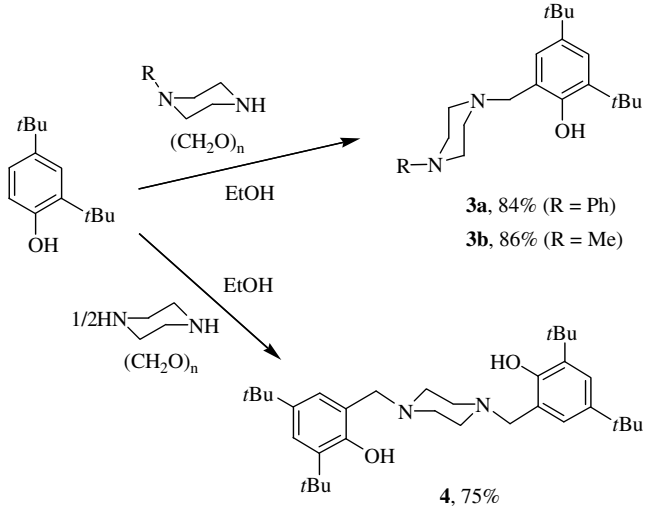
Selected geometric parameters for the boat-shaped ZnN1C1C2C3N2 ring for compounds **1** and **2** are listed in Table 1; the atoms Zn and C2 are *ca.* 0.82 (**1**) or 0.72 (**2**) and *ca.* 0.115 (**1**) or 0.105 Å (**2**) out of the C1N1C3N2 plane, respectively. The atoms Si1 and Si2 are 0.65 and 0.86 Å (**1**) or 0.89 and 0.71 Å (**2**) on the same side of this plane.

Table 1
Selected bond lengths (Å) and angles (°) for the ZnN1C1C2C3N2 moiety of **1** and **2**

	1	**2**
Bond lengths		
Zn1–N1	1.965(3)	2.019(2)
Zn1–N2	1.957(3)	2.021(2)
N1–C1	1.336(5)	1.328(4)
N2–C3	1.339(5)	1.332(4)
C1–C2	1.407(6)	1.398(4)
C2–C3	1.417(5)	1.413(4)
Bond angles		
N1–Zn1–N2	100.36(13)	95.85(9)
Zn1–N1–C1	110.1(3)	115.54(18)
Zn1–N2–C3	110.2(2)	114.83(18)
N1–C1–C2	125.9(3)	126.0(3)
N2–C3–C2	124.2(4)	125.3(2)
C1–C2–C3	128.7(4)	128.1(3)

2.2. 2-(Piperazinyl-N-methyl)-4,6-di-tert-butyl-phenoxozinc compounds and their phenolic precursors

The 2-(piperazinyl-*N*-methyl)-4,6-di-*tert*-butyl-phenols **3a** and **3b** were prepared in good yield as shown in outline in Scheme 1. The detailed procedure was related to that used previously for 2-[$Me_2NCH_2CH_2N(Me)CH_2$]-4,6-$Bu^t_2C_6H_2OH$ [8], except that in place of *N*,*N*,*N*′-trimethylethylenediamine used for the latter, for **3a** and **3b** the appropriate 1-hydrocarbylpiperazine was employed. For **3a** and **3b** this involved (i) heating under reflux equimolar portions of the three reagents (slight excess of paraformaldehyde) in ethanol, (ii) adding aqueous HBr (and washing the resulting salts with ethanol), (iii) neutralising with Na[HCO_3] and (iv) extracting with chloroform. The



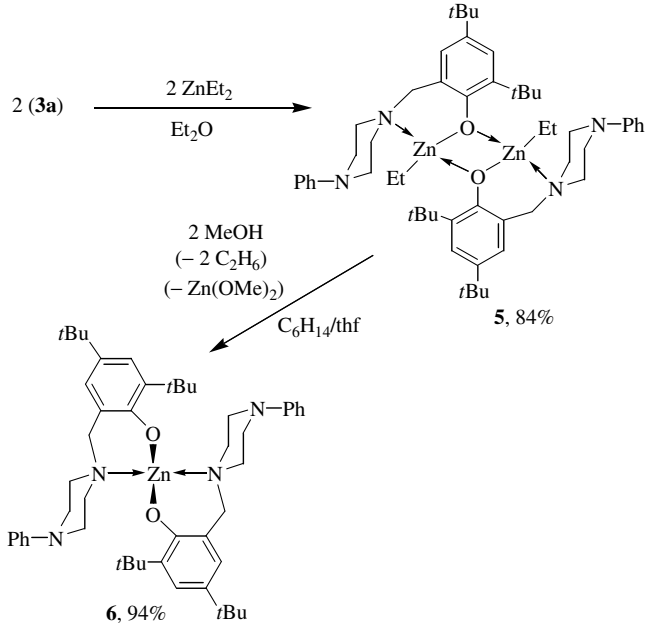
Scheme 1.

corresponding diphenol **4** having a piperazine-*N*,*N*′-dimethylene bridge, was obtained in an analogous fashion using a 2:2:1 molar ratio of the phenol, $(CH_2O)_n$ and piperazine, Scheme 1.

Reaction of the phenol **3a** with an equimolar portion of diethylzinc in diethyl ether afforded the dinuclear ethylzinc phenoxide **5**, which upon methanolysis, using a stoichiometric quantity of MeOH (**5** + 2MeOH), in thf/hexane furnished the mononuclear zinc phenoxide-thf adduct **6**, Scheme 2; the presumed co-product, $Zn(OMe)_2$, was not isolated and the 94% cited yield is based on the ligand.

Using a procedure similar to that for **5**, the analogue **7** was obtained from **3b** and diethylzinc, Eq. (3). Likewise, the bis(phenol) **4** and $2ZnEt_2$ were the source of the piperazine-*N*,*N*′-dimethylene bridged bis(phenoxoethylzinc) complex **8**, Eq. (4). Each of the crystalline compounds **5**–**8** (**8** being isolated diastereoselectively as *meso*-), obtained in good yield, contains two *O*,*N*-chelating $[OCCC(H)_2N\overset{\frown}{}]^-$ ligands bonded to the zinc atom (**6**) or atoms (**5**, **7**, **8**) (*cf*., **B**) in a terminal (**6**, **8**) or bridging (**5**, **7**) fashion; for **8**, the two zinc atoms are *N*,*N*′-joined by the *N*,*N*′-disubstituted piperazine.

The molecular structures of the crystalline centrosymmetric compounds **5** (Fig. 3) and **7** (Fig. 4) are similar. Each has a fused pentacyclic core built around a central ZnOZn'O' rhomboid with the angle at the zinc atoms narrower than that at the oxygen atoms. The rhomboid is flanked by the twist boat-shaped six-membered ZnOC1C6C7N1 rings (C7 and O1 out of the plane), the C1 and C6 atoms of which are part of the aromatic C1–C6 ring; the N1 atom is a member of a piperazine ring, the N2 atom of which has a pendant phenyl (C20–C25; **5**) or methyl (C20; **7**) substituent. Selected geometrical parameters for **5** and **7** are given in Table 2



Scheme 2.

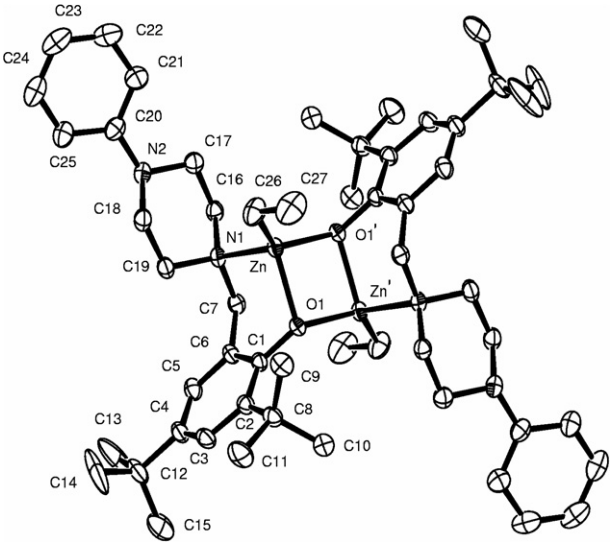


Fig. 3. ORTEP representation of the molecular structure of **5** (50% ellipsoids; H atoms omitted). Symmetry transformation to generate equivalent atoms: $-x+1$, $-y+1$, $-z+1$.

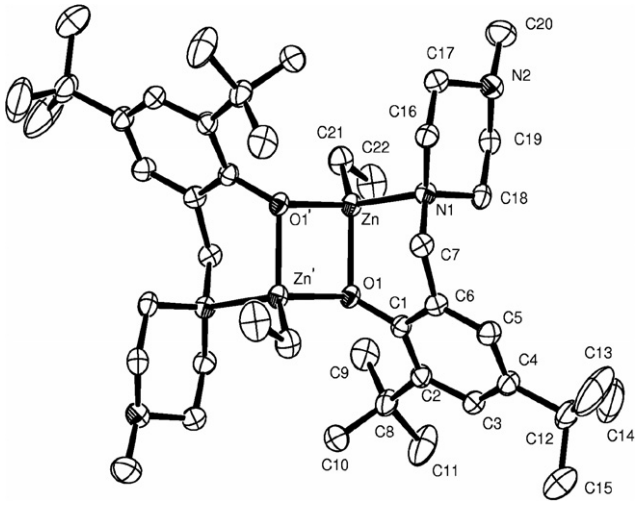
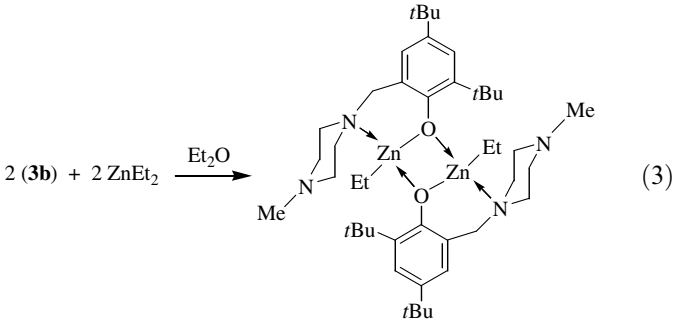


Fig. 4. ORTEP representation of the molecular structure of **7** (50% ellipsoids; H atoms omitted). Symmetry transformation to generate equivalent atoms: $-x+2$, $-y$, $-z+1$.

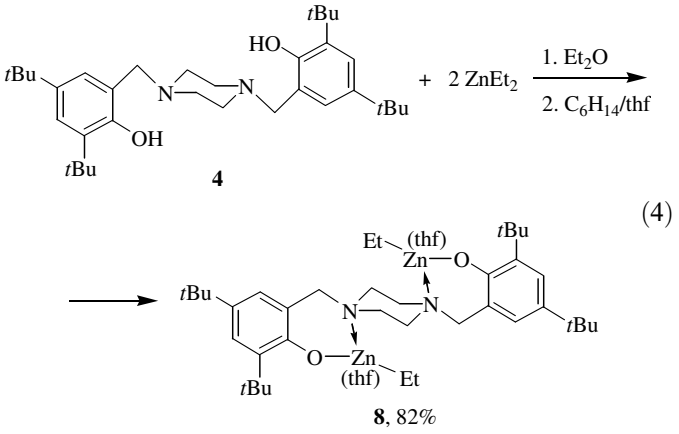


(3)

Table 2
Selected bond lengths (Å) and angles (°) for **5** and **7**

	5[a]	**7**[b]		**5**[a]	**7**[b]
Bond lengths					
Zn–O1	2.063(2)	2.055(2)	N1–C7	1.505(4)	1.504(4)
Zn–O1′	2.056(2)	2.084(2)	C7–C4	1.499(4)	1.503(4)
Zn–C26	1.982(3)		C6–C1	1.405(4)	1.402(4)
Zn–C21		1.982(3)	C1–O1	1.373(3)	1.369(3)
Zn–N1	2.199(2)	2.164(2)			
Bond angles					
Zn–O1–Zn′	95.60(7)	95.09(8)	N1–C7–C6	110.4(2)	111.2(2)
O1–Zn–O1′	84.40(7)	84.91(8)	C7–C6–C1	119.5(2)	120.5(3)
C26–Zn–O1	125.1(1)		C6–C1–O1	118.0(2)	118.1(3)
C21–Zn–O1		128.3(1)	C1–O1–Zn	115.8(2)	119.7(2)
C26–Zn–O1′	128.8(1)		C1–O1–Zn′	125.9(2)	123.2(2)
C21–Zn–O1′		114.9(1)	Zn–N1–C7	104.6(2)	104.5(2)
C26–Zn–N1	118.3(1)		O1–Zn–N1	91.23(8)	91.67(8)
C21–Zn–N1		123.8(1)	O1′–Zn–N1	104.6(1)	98.77(8)

Symmetry transformations to generate equivalent atoms.
[a] $-x+1,-y+1,-z+1$.
[b] $-x+2,-y,-z+1$.



The molecular structure of the crystalline compound **6** is illustrated in Fig. 5 (selected geometric parameters are listed in Table 3). The molecule **6** has the zinc atom at the spiro centre of two *N*,*O*-centred 2,4-di-*tert*-butyl-6-{*N*′-phenyl-*N*-(piperazinyl)methyl}phenoxo ligands; each of the two boat-shaped ZnOCCCN rings has a carbon atom (C7 or C32) and an oxygen atom (O1 or O2) out of the plane of the remaining four atoms. All the four Zn–O and Zn–N distances in the diphenoxo complex **6** are shorter than the corresponding distances in the phenoxo-ethylzinc compounds **5**, **7** and **8**. This fact (together with the ease of ligand redistribution reaction upon methanolysis of **5**) suggests that the steric bulk of this type of *N*,*O*-centred ligand is not sufficient to stabilise mixed-ligand phenoxo/alkoxo zinc complexes.

The molecular structure of the crystalline compound **8** is shown in Fig. 6 (selected geometrical parameters are listed in Table 3). The molecule is centrosymmetric about the mid-point of the bridging piperazine ring. Its nitrogen atoms provide one of the four donor sites to the Zn and Zn′ atoms, each (*e.g.*, Zn) also bound to a thf ligand (via O2), an ethyl group (via C18) and the O1 atom of the

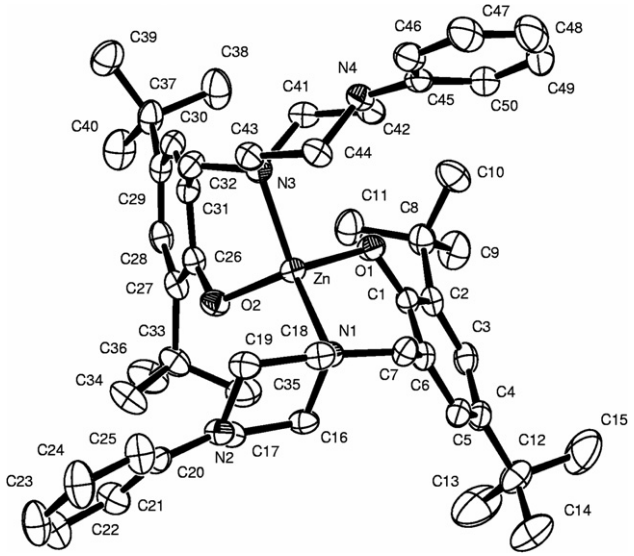


Fig. 5. ORTEP representation of the molecular structure of **6** (50% ellipsoids; H atoms omitted).

Table 3
Selected bond lengths (Å) and angles (°) for **6** and **8**

Complex **6**		Complex **8**	
Bond lengths			
Zn–O1	1.9182(12)	Zn–O1	1.926(2)
Zn–O2	1.9111(12)	Zn–O2	2.165(2)
Zn–N1	2.0914(14)	Zn–C18	1.978(3)
Zn–N3	2.0982(14)	Zn–N	2.147(2)
Bond angles			
N1–Zn–O1	99.47(5)	O1–Zn–N	95.79(8)
N3–Zn–O2	98.66(5)	C18–Zn–O1	128.54(12)
N1–Zn–N3	133.40(5)	C18–Zn–N	125.76(11)
O1–Zn–O2	120.36(5)	O1–Zn–O2	93.53(8)
		C18–Zn–O2	109.43(13)
		O2–Zn–N	94.95(8)

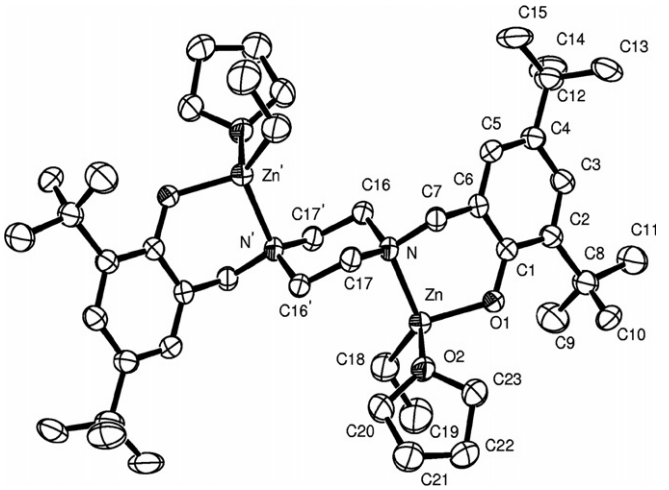


Fig. 6. ORTEP representation of the molecular structure of **8** (50% ellipsoids; H atoms omitted). Symmetry transformation to generate equivalent atoms: $-x+1$, $-y+1$, $-z+1$.

six-membered boat-shaped (C7 and C1 out of the plane) ZnNC7C6C1O1 ring.

Each of the new zinc compounds **1**, **2** and **5**–**8** was examined for catalytic activity for the copolymerisation of propene oxide (PO), cyclohexene oxide (CHO) or a 1:1 PO/CHO mixture and carbon dioxide at relatively low pressures (40–50 bar, 80 °C). With the β-diketiminates **1** and **2** the catalytic activity was low, while with the phenoxides only in the case of complex **5** a small CO_2 uptake was observed; however no polymer was isolated.

In conclusion, six new zinc complexes containing bulky β-diketiminato and 2-(piperazinyl-*N*-methyl)-4,6-di-*tert*-butylphenoxo ligands were prepared as potential catalyst precursors for copolymerisation of cyclohexene oxide and carbon dioxide; in the event none of compounds **5**–**8** showed significant activity. An attempted synthesis of a mixed-ligand zinc alkoxide (which is considered as an active catalyst) from *N*,*N*′-bis(trimethylsilyl)-β-diketiminatozinc chloride (**1**) and ethyl (**2**) was unsuccessful due to the inertness of the Zn–Cl bond in the former or the lability of the β-diketiminato-zinc bond in the latter. The amino-functionalised phenoxo ligands in complexes **5**, **7** and **8** were not sufficiently bulky to stabilise mixed-ligand phenoxo/alkoxo compounds as evident from the formation of the homoleptic zinc phenoxide **6** (Scheme 2).

3. Experimental

3.1. General details

Experiments involving zinc compounds were performed under an atmosphere of argon, or in a vacuum, using Schlenk apparatus and vacuum line techniques. The solvents used were reagent grade or better and were freshly distilled under dry nitrogen gas and freeze/thaw degassed prior to use. The drying agents employed were sodium benzophenone (C_6H_6, Et_2O, PhMe and thf) or sodium-potassium alloy (C_5H_{12}, C_6H_{14}). $[Li\{N(SiMe_3)C(Ph)_2CH\}]_2$ and $H[\{N(SiMe_3)C(Ph)\}_2CH]$ were prepared as described in the literature [10]; other chemicals were commercial samples. The NMR spectra were recorded in C_6D_6 or C_7D_8 at 298 K using a Bruker DPX 300 instrument and referenced internally to residual solvent resonances. Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were determined on an electrothermal apparatus (Philip Harris). Elemental analyses were by Medac. Ltd.

Copolymerisation experiments were carried out in 5 mL pressure vessels and were conducted with 100 mg of catalyst. The catalyst was loaded into the vessels in a glovebox and sealed. Subsequently, 2 mL of epoxide (PO, CHO or a 1:1 PO/CHO mixture) was added. The vessels were loaded with 25 bars of carbon dioxide gas and heated to 80 °C. The pressure and the temperature of the vessels were monitored in time for 4 h. The copolymerisations were in batch mode; the pressure at reaction temperature was in the range of 40–50 bar. A pressure decrease was interpreted as evidence for the coupling of carbon dioxide and epoxides. After the reaction was completed, the reactors were cooled down, and the volatile compounds of the reaction mixture were removed; the solid residue was analysed for its polymer content.

3.2. Preparation of $[Zn\{(N(SiMe_3)C(Ph))_2CH\}(\mu\text{-}Cl)]_2 \cdot PhMe$ (**1**)

A solution of $[Li\{(N(SiMe_3)C(Ph))_2CH\}]_2$ (3.01 g, 8.09 mmol) in diethyl ether (50 cm^3) was added to a stirred suspension of zinc chloride (1.10 g, 8.09 mmol) in Et_2O (20 cm^3) at ambient temperature. The mixture was set aside for 16 h, toluene (10 cm^3) was added and the mixture was filtered. Volatiles were removed from the filtrate in vacuo yielding compound **1** (3.54 g, 94%). X-ray quality crystals were obtained from a mixture of toluene and pentane after cooling at −30 °C for 2 d. Compound **1**, m.p. 160 °C ($C_{49}H_{66}Cl_2N_4Si_4Zn_2$ requires: C, 57.4; H, 6.49; N, 5.47. Found: C, 56.6; H, 6.41; N, 5.60.); ^1H NMR (C_7D_8): δ 0.22 [s, 18H, $Si(CH_3)_3$], 2.10 (s, ∼1.5H, Ph*Me*), 5.39 (s, 1H, CH), 7.03 (m, 6H, Ph; overlapped with ∼2H, *Ph*Me), 7.36 (m, 4H, Ph); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.41 [$Si(CH_3)_3$], 106.3 (CH); 128.0, 128.2, 129.1, 145.7 (C_6H_5); 178.5 (s, *C*Ph) [signals for PhMe solvate molecule: 21.4 (Ph*Me*); 125.6, 128.5, 129.3, 137.8 (*Ph*Me)]; EI-MS (M denotes the monomer) (*m*/*z*, assignment): 466, $[M+H_2]^+$, 365 $[M-ZnCl]^+$.

3.3. Preparation of $[Zn\{(N(SiMe_3)C(Ph))_2CH\}Et(thf)]$ (**2**)

The β-diketimine $H[\{N(SiMe_3)C(Ph)\}_2CH]$ (3.22 g, 8.79 mmol) in hexane (50 cm^3) was added to a stirred solution of diethylzinc (8.79 cm^3, 8.79 mmol, in 1 M hexane) at ambient temperature. Volatiles were removed after 3 h and

the residue was dissolved in a mixture of Et_2O and thf. After 1 d at –30 °C, X-ray quality crystals of **2** (4.35 g, 93%) were collected ($C_{27}H_{42}N_2OSi_2Zn$ requires: C, 60.9; H, 7.95; N, 5.26. Found: C, 60.8; H, 7.34; N, 5.67%.); ^{1}H NMR (C_7D_8): δ 0.08 [s, 18H, $Si(CH_3)$], 0.85 (q, 2H, CH_2CH_3), 1.72 (t, 3H, CH_2CH_3), 1.40 (m, thf), 3.57 (m, thf), 5.32 (s, 1H, CH), 6.98–7.40 (m, 6H, Ph), 7.28–7.33 (m, 4H, Ph); $^{13}C\{^1H\}$ NMR (C_7D_8): δ 3.11 [$Si(CH_3)_3$], 5.7 (CH_2CH_3), 13.4 (CH_2CH_3), 25.8 (thf), 67.8 (thf), 105.8 (CH); 127.8, 128.2, 128.7, 146.3 (Ph); 176.3 (s, *C*Ph); EI-MS (M denotes parent) (*m*/*z*, assignment): 429 $[M-Et-thf]^+$, 350 $[M-Zn-Et-Me]^+$.

3.4. Preparation of 2-(N-phenylpiperazinyl-N′-methyl)−4,6-di-tert-butyl-phenol (*3a*)

1-Phenylpiperazine (8.11 g, 50 mmol), paraformaldehyde (1.81 g, 60 mmol based on HCHO) and 2,4-$Bu^t_2C_6H_3OH$ (10.32 g, 50 mmol) were dissolved in ethanol (50 cm^3). The solution was heated under reflux for 20 h, then cooled to *ca.* 20 °C. Hydrobromic acid (8 cm^3 of a 48% aqueous solution) was added. The resultant gel was freed from volatiles in vacuo. The residue was washed with ethanol, thereby removing its original yellow colouration. The colourless solid was dissolved in water, and then neutralised by addition of aqueous $Na[HCO_3]$, and finally extracted into chloroform. The extract was dried ($MgSO_4$) and solvent removed in vacuo, thus affording colourless crystals of **3a** (15.98 g, 84%) ($C_{25}H_{36}N_2O$ requires: C, 78.9; H, 9.53; N, 7.36. Found: C, 78.65; H, 9.26; N, 7.15%.), m.p. 160–161 °C. ^{1}H NMR(C_6D_6): δ 1.33 [s, 9H, $C(CH_3)_3$], 1.71 [s, 9H, $C(CH_3)_3$], 2.11 (br, 4H, NCH_2), 2.70 (br, 4H, NCH_2), 3.28 (s, 2H, $CH_2C_6H_5$), 6.60 (d, 2H, C_6H_5), 6.87 (t, 1H, *p*-C_6H_5), 6.88 (s, 1H, C_6H_2), 7.12 (t, 2H, C_6H_5), 7.50 (s, 1H, C_6H_2), 10.92 (s, 1H, OH); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 30.0 (CH_3), 32.0 (CH_3), 35.4 (CH_3); 49.1, 54.4 (CH_2N); 63.5 (CH_2C_6); 116.7, 120.15, 120.4, 120.9, 123.3, 123.8, 129.3, 136.15, 140.9, 155.0 (C_6H_5, C_6H_2); EI-MS (M denotes parent) (*m*/*z*, assignment): 380 (40%, $[M]^+$), 162 (100%, $[PhN(CH_2CH_2)_2NH]^+$).

3.5. Preparation of 2-(N-methylpiperazinyl-N′-methyl)-4,6-di-tert-butyl-phenol (*3b*)

From 1-methylpiperazine (4.96 g, 50 mmol), paraformaldehyde (1.80 g, 60 mmol based on HCHO), and 2,4-$Bu^t_2C_6H_3OH$ (10.32 g, 50 mmol), using the procedure similar to that for **3a**, there were obtained colourless crystals of **3b** (13.69 g, 86%) ($C_{20}H_{34}N_2O$ requires C, 75.4; H, 10.76; N, 8.80. Found: C, 75.6; H, 10.43; N, 8.68%.), m.p. 112–113 °C. ^{1}H NMR (C_6D_6): δ 1.37 [s, 9H, $C(CH_3)_3$], 1.73 [s, 9H, $C(CH_3)_3$], 1.95 (s, 3H, CH_3N), 2.11–2.66 [br, 8H, $N(CH_2CH_2)_2N$], 3.73 (s, 2H, CH_2C_6), 6.96 (s, 1H, C_6H_2), 7.34 (s, 1H, C_6H_2), 10.92 (s, 1H, OH); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 30.0 $(CH_3)_3$, 34.3 $(CH_3)_3$, 35.3 $(CH_3)_3$, 45.7 (CH_3N); 52.4, 54.9 [$N(CH_2CH_2)_2N$]; 62.3 (CH_2C_6); 121.1, 123.6, 135.9, 140.6, 155.1 (C_6H_2); EI-MS (M denotes parent) (*m*/*z*, assignment): 319 (75%, $[M]^+$), 100 (85%, $[MeN(CH_2CH_2)_2NH]^+$), 58 (100%, $[Bu^tH]^+$).

3.6. Preparation of 2,2-[μ-(N,N′-pirerazindiyl)dimethyl]-bis(4,6-di-tert-butyl-phenol) (*4*)

From piperazine (2.13 g, 25 mmol), paraformaldehyde (1.80 g, 60 mmol based on HCHO), and 2,4-$Bu^t_2C_6H_3OH$ (10.32 g, 50 mmol), using a procedure similar to that of **3a**, there were obtained colourless crystals of **4** (9.80 g, 75%) ($C_{34}H_{54}N_2O_2$ requires C, 78.1; H, 10.41; N, 5.36. Found: C, 78.0; H, 10.32; N, 5.24.), m.p. 236–238 °C, ^{1}H NMR (C_6D_6): δ 1.38 [s, 18H, $C(CH_3)_3$], 1.72 [s, 18H, $C(CH_3)_3$], 2.07 [br, 8H, $N(CH_2CH_2)_2N$], 3.14 (s, 4H, CH_2C_6), 6.82 (s, 2H, C_6H_2), 7.46 (s, 2H, C_6H_2), 10.70 (s, 2H, OH); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 29.95 (CH_3), 31.9 (CH_3), 34.3 (CH_3), 35.3 (CH_3), 51.8 [$N(CH_2CH_2)_2N$], 61.9 (CH_2C_6); 120.8, 123.2, 123.7, 135.95, 140.9, 154.8 (C_6H_2); EI-MS (M denotes parent) (*m*/*z*, assignment): 523 (30%, $[M]^+$), 508 (45%, $[M-Me]^+$), 219 (100%, $[M-MeN(CH_2CH_2)_2NH]^+$), 85 (75%, $[MeN(CH_2CH_2)_2NH]^+$).

3.7. Preparation of bis[ethyl{μ-4,6-di-tert-butyl-2-(N-phenylpiperazinyl-N′-methyl)phenoxo}zinc] (*5*)

Diethylzinc (3.26 cm^3 of a 1 M solution in Et_2O, 3.26 mmol) was added dropwise to a solution of the phenol **3a** (1.24 g, 3.26 mmol) in Et_2O (40 cm^3) at −35 °C. The mixture was allowed to warm with stirring to ambient temperature for 16 h, then filtered. The colourless precipitate was washed with hexane and then extracted into thf/hexane. The extract was concentrated in vacuo and stored at −25 °C to afford colourless crystals of **5** (1.30 g, 84%) ($C_{27}H_{40}N_2OZn$ requires C, 68.4; H, 8.51; N, 5.91. Found: C, 67.9; H, 8.43; N, 5.68%.), m.p. 129 °C (decomp). ^{1}H NMR (C_6D_6): δ 0.47 (q, 2H, CH_3CH_2), 1.30 (t, 3H, CH_3CH_2), 1.40 [s, 9H, $(CH_3)_3$], 1.71 [s, 9H, $(CH_3)_3$], 2.58–3.00 [br, 8H, $(CH_2CH_2)_2$], 3.88 (s, 2H, CH_2C_6), 6.88 (d, 2H, C_6H_5), 6.81 (br, 1H, C_6H_5), 6.94 (s, 1H, C_6H_2), 7.14 (t, 2H, C_6H_5), 7.60 (s, 1H, C_6H_2); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 3.43 (CH_3CH_2), 13.02 (CH_3CH_2), 31.4 [$(CH_3)_3$], 31.9 [$(CH_3)_3$], 34.2 [$C(CH_3)_3$], 35.8 [$C(CH_3)_3$]; 47.0, 47.9, 52.1, 54.4 [$N(CH_2CH_2)_2N$]; 63.5 (CH_2C_6); 116.4, 120.3, 125.45, 127.1, 129.4, 139.0, 139.5, 150.9, 159.8 (Ph, C_6H_2).

3.8. Preparation of bis[4,6-di-tert-butyl-2-(N-phenylpiperazinyl-N′-methyl)phenoxo]zinc (*6*)

Methanol (5.20 cm^3, of a 0.5 M solution in C_6H_{14}, 2.60 mmol) was added dropwise to a stirred solution of **5** (1.23 g, 1.30 mmol) in thf/hexane (35 cm^3) at −78 °C. The mixture was allowed to warm to ambient temperature during 4 h. Volatiles were removed in vacuo and the residue was extracted with thf/hexane. The extract was concentrated to *ca.* 15 cm^3 and stored at 0 °C, yielding colourless

crystals of the zinc phenoxide **6** (1.01 g, 94%) ($C_{50}H_{70}N_4O_2Zn$ requires C, 72.8; H, 8.56; N, 6.80. Found: C, 72.5; H, 8.32; N, 6.63%.). ^{1}H NMR (C_6D_6): δ 1.42 (s, 18H, CH_3), 1.62 (s, 18H, CH_3), 2.83–3.10 [br, 16H, $(CH_2CH_2)_2$], 3.75 (s, 4H, CH_2C_6), 6.70 (d, 4H, C_6H_5), 6.84 (t, 2H, C_6H_5), 6.89 (s, 2H, C_6H_2), 7.12 (t, 4H, C_6H_5), 7.59 (s, 2H, C_6H_2); ^{13}C{^{1}H} NMR (C_6D_6): δ 30.3 (CH_3), 32.3 (CH_3), 34.2 [$C(CH_3)_3$], 35.5 [$C(CH_3)_3$]; 46.4, 47.65, 53.5, 55.0, [$N(CH_2CH_2)_2N$]; 64.7 (CH_2C_6); 116.4, 119.1, 120.5, 124.9, 125.9, 129.9, 135.8, 138.1, 150.7, 163.5 (Ph, C_6H_2).

3.9. Preparation of bis[ethyl{μ-4,6-di-tert-butyl-2-(N-methylpiperazinyl-N′-methyl)phenoxo}zinc] (7)

Compound **7** (1.19 g, 87%) ($C_{44}H_{76}N_4O_2Zn_2$ requires C, 64.4; H, 9.30; N, 6.80. Found: C, 64.1; H, 9.23; N, 6.89%.) was obtained from the phenol **3b** (1.06 g, 3.33 mmol) and an equimolar portion of diethylzinc (3.33 cm^3 of a 1 M solution in Et_2O, 3.33 mmol), using a procedure similar to that for the zinc complex **5**. ^{1}H NMR (C_6D_6): δ 0.51 (q, 2H, CH_3CH_2), 1.30 (t, 3H, CH_3CH_2), 1.39 [s, 9H, $(CH_3)_3$], 1.45 [s, 9H, $(CH_3)_3$], 1.97 (s, 3H, CH_3N), 2.08–2.16 [br, 8H, $(CH_2CH_2)_2$], 3.56 (s, 2H, CH_2C_6), 6.99 (s, 1H, C_6H_2), 7.54 (s, 1H, C_6H_2); ^{13}C{^{1}H} NMR: δ 3.43 (CH_3CH_2), 13.02 (CH_3CH_2), 29.8 [$(CH_3)_3$], 32.0 [$(CH_3)_3$], 34.05 [$C(CH_3)_3$], 35.6 [$C(CH_3)_3$], 46.1 (CH_3N); 53.9, 55.2 [$N(CH_2CH_2)_2N$]; 65.3 (CH_2C_6); 119.4, 124.7, 126.2, 135.7, 137.7, 162.1 (C_6H_2). X-ray-quality crystals of **7** · 2(thf) were obtained by recrystallisation from thf/hexane.

3.10. Preparation of [2,2-{(μ-N,N′-piperazindiyl)dimethyl}-bis{(4,6-di-tert-butyl-phenoxo)ethyl(thf)zinc}] (8)

Compound **8** (1.50 g, 82%) ($C_{46}H_{78}N_2O_4Zn_2$ requires C, 64.7; H, 9.21; N, 3.28. Found: C, 64.7; H, 9.20; N, 3.51%.) was obtained from the bis(phenol) **4** (1.12 g, 2.14 mmol) and diethylzinc (4.28 cm^3 of a 1 M solution in Et_2O, 4.28 mmol) using a procedure similar to those for the zinc complexes **5** and **7**. ^{1}H NMR (C_6D_6, C_5D_5N): δ 0.59 (q, 4H, CH_3C H_2), 1.30 (t, 4H, CH_3CH_2), 1.43 [s, 18H, $(CH_3)_3$], 1.49 (t, 8H, thf), 1.82 [s, 18H, $(CH_3)_3$], 2.14–2.38 [br, 8H, $N(CH_2CH_2)_2N$], 3.40 (s, 4H, CH_2C_6), 3.55 (t, 8H, thf), 6.75 (s, 2H, CH_2C_6), 7.62 (s, 2H, CH_2C_6); ^{13}C{^{1}H} NMR (C_6D_6, C_5D_5N): δ 3.65 (CH_3CH_2), 13.8 (CH_3CH_2), 23.65 (thf), 30.7 [$(CH_3)_3$], 31.9 [$(CH_3)_3$], 34.3 [$(CH_3)_3$], 35.3 [$C(CH_3)_3$], 51.8 [$N(CH_2CH_2)_2N$], 61.9 (CH_2C_6), 6.5 (thf); 122.3, 123.3, 125.2, 133.55, 142.5, 158.9 (C_6H_2). X-ray quality crystals of **8** were isolated as a bis-thf solvate.

3.11. X-ray crystallographic studies

Diffraction data were collected on a Nonius Kappa CCD diffractometer using monochromated Mo Kα radiation, λ 0.71073 Å at 173(2) K. Crystals were coated in oil and then directly mounted on the diffractometer under a steam of cold nitrogen gas. The structures were refined on all F^2 using SHELXL-97 [15]; absorption corrections were applied using MULTISCAN. In **1**, the poorly defined toluene solvate molecule was disordered across a twofold rotation axis and was refined with constraints. The molecule **5** lies

Table 4
Crystal data and structure refinement for **1**, **2**, **5**, **6**, **7** and **8**

Compound	**1**	**2**	**5**	**6**	**7**	**8**
Formula	$C_{42}H_{58}Cl_2N_4Si_4Zn_2$ · C_7H_8	$C_{27}H_{42}N_2OSi_2Zn$	$C_{54}H_{80}N_4O_2Zn_2$	$C_{50}H_{70}N_4O_2Zn$ · C_4H_8O	$C_{44}H_{76}N_4O_2Zn_2$ · $(C_4H_8O)_2$	$C_{46}H_{78}N_2O_4Zn_2$ · $(C_4H_8O)_2$
M	1025.06	532.18	947.96	896.57	968.04	998.05
Crystal system	Monoclinic	Orthorhombic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$Pbca$ (no. 61)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/c$ (no.14)
a (Å)	24.0729(10)	11.7351(2)	9.6763(2)	9.9905(1)	8.7705(1)	11.0444(2)
b (Å)	12.3641(5)	16.2542(2)	11.1045(3)	13.2993(2)	19.2908(20)	19.2560(3)
c (Å)	21.3953(6)	30.6042(5)	12.5991(4)	19.9840(3)	15.5111(2)	13.4883(3)
α (°)	90	90	81.006(1)	80.325(1)	90	90
β (°)	122.020(2)	90	86.528(1)	77.611(1)	91.066(1)	90.489(1)
γ (°)	90	90	76.839(2)	78.217(1)	90	90
U (Å)	5399.3(3)	5837.6(2)	1301.57(6)	2517.20(6)	2623.87(5)	2868.47(9)
Z	4	8	1	2	2	2
Absorption coefficient (mm^{-1})	1.11	0.94	0.96	0.53	0.96	0.88
Unique reflections, R_{int}	4748, 0.050	4598, 0.061	4579, 0.064	8842, 0.036	4901, 0.049	5048, 0.044
Reflections with $I > 2\sigma(I)$	3730	3797	4062	8153	4442	4348
Final R indices $[I > 2\sigma(I)]$ R_1, wR_2	0.052, 0.125	0.040, 0.088	0.044, 0.113	0.035, 0.090	0.050, 0.135	0.042, 0.114
R indices (all data) R_1, wR_2	0.070, 0.136	0.054, 0.095	0.052, 0.118	0.039, 0.094	0.056, 0.140	0.051, 0.122

on a crystallographic inversion centre; there was disorder in one of the *tert*-butyl groups which was included with SAD1 constraints. Further details are found in Table 4.

Acknowledgements

We thank the BASF for financial support (J.D.F. and X.H.W.). We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury.

Appendix A. Supplementary material

CCDC 289172, 654543, 654544, 654545, 654546 and 654547 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.02.012.

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