Zinc Guanidinate Complexes and Their Application in Ring-Opening Polymerisation Catalysis

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Keywords: Guanidinate / N ligands / O ligands / Ring-opening polymerisation / Zinc

The insertion reaction between 1 equiv. of carbodiimide, R′N=C=NR′, and the zinc bis(amide) $[Zn\{N(SiMe_3)_2\}_2]$ affords the homoleptic zinc(II) guanidinate compounds $[Zn\{(Me_3Si)_2NC(NR')_2\}_2]$ (**3**, R′ = *i*Pr; **4**, R′ = Cy) in preference to the monosubstituted compounds. Compound **3** also results from the protonation reaction of 1 equiv. of the neutral guanidine $(Me_3Si)_2NC(N\mathit{i}Pr)(NH\mathit{i}Pr)$ (**2**) with $[Zn\{N(SiMe_3)_2\}_2]$ or $ZnMe_2$. In contrast, the *N*-dimethylguanidine analogue $Me_2NC(N\mathit{i}Pr)(NH\mathit{i}Pr)$ (**1**) reacts cleanly with 1 equiv. of $ZnMe_2$ to afford the dimeric species $[Zn\{Me_2NC(N\mathit{i}Pr)_2\}Me]_2$ (**5**). Attempted protonation of the Zn–C bond in **5** with 2,6-di-*tert*-butylphenol resulted in preferential reaction at the Zn–N bond and formation of the mixed (aryloxo)methyl complex $[Zn(OAr)Me\cdot\{Me_2NC(N\mathit{i}Pr)(NH\mathit{i}Pr)\}]$ (**6**), isolated as the guanidine adduct. Heating of **6**, in an attempt to promote methane elimination, afforded a small amount of the dimetallic complex $[\{Zn(OAr)\}_2(\mu\text{-}\{Me_2NC(N\mathit{i}Pr)_2\})(\mu\text{-}NMe_2)]$ (**7**) as a result of the extrusion of NMe_2^- from the guanidine-based ligand. The amine-elimination reaction between $[Zn\{N(SiMe_3)_2\}_2]$ and 1 equiv. of 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) proceeds smoothly to afford the mixed (guanidinate)(amide) complex $[Zn(hpp)\{N(SiMe_3)_2\}]_2$ (**8**), which forms a dimer in the solid state. Crystal structures of compounds **3**–**8** are reported and a preliminary study of the activity of **8** in the ring-opening polymerisation of lactide is described.
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Introduction

There has been a great deal of recent interest in the metal-catalysed ring-opening polymerisation (ROP) of cyclic esters, in particular lactide (LA),[1] as benefits over polymers derived from petrochemical sources include the renewable source of feedstock and the biocompatibility of the resultant polyester material.[2] Well-defined metal catalysts have generally allowed a greater control over the selectivity of the polymerisation process to be achieved, and structure-activity correlation studies associated with the ancillary ligands have been the focus of many of the recent developments in this area. As a consequence, many novel metal alkoxide and amide species have been synthesised and shown to be active catalysts for this process, where monomer insertion into the metal−oxygen or metal−nitrogen bond initiates polymerisation, and propagation ideally occurs in a controlled fashion to furnish stereoregular polylactide (PLA).

Anionic, *N*,*N*′-chelating ligands have thus far proved to be one of the most promising classes of supporting group in metal-catalysed lactide polymerisation. In particular, the β-diketiminate anion,[3] in combination with a zinc centre containing a reactive Zn−X bond, has been pursued in this area, exhibiting varying degrees of activity and selectivity dependant on the nature of the X group (Figure 1).[4,5] In general, it has been found that compounds containing a Zn−OR group, especially when R is a small alkyl group such as isopropyl, are significantly more active than those containing the amide group $[N(SiMe_3)_2]^-$, most likely due to a sluggish insertion of the first monomer into the sterically crowded Zn−N linkage. A recent report has also noted that structurally related bis(phosphanyl)methyl complexes of zinc are also active for the ROP of lactide,[6] although in these cases no evidence of "living" behaviour was observed.

A related class of chelating *N*,*N*′-donor ligands that has received attention in this area is the amidinate anion, $[RC(NR')_2]^-$,[7,8] where the metallacycle formed upon complexation to a metal atom differs principally from β-diketiminate compounds in the number of constituent atoms (i.e. 4 vs. 5). A range of different metals have been investigated including Fe,[9] Sn,[10] and the lanthanides[11] where, as for the β-diketiminate complexes, the coordination sphere is usually completed by either alkoxide or amide substituents at which initial reaction with the monomer is considered to take place (Figure 2). A notable exception is the series of homoleptic lanthanide complexes $[Ln\{RC(NCy)_2\}_3]$ (R = Me, Ln = Nd, Gd, Yb; R = Ph, Ln = Nd, Yb),[12] which are reported to be highly active for the ROP of ε-caprolactone, presumably initiating at one of the M−N

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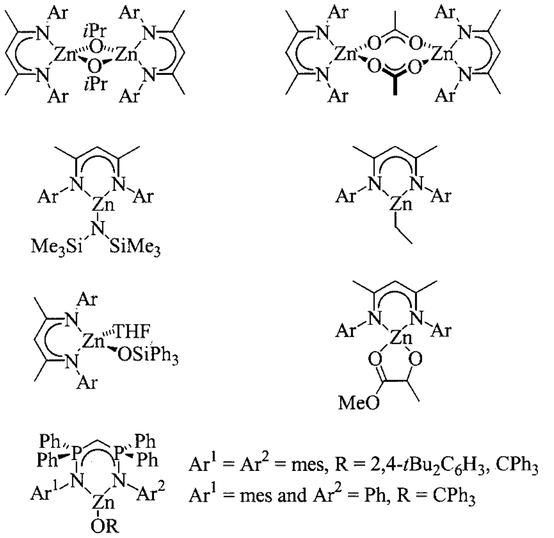
DOI: 10.1002/ejic.200400031

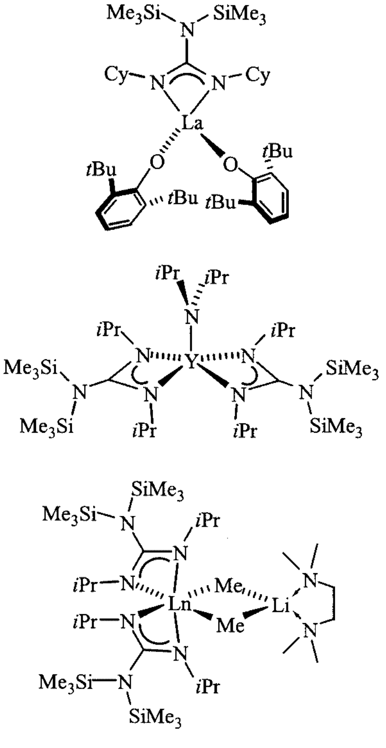


$Ar^1 = Ar^2 =$ mes, R = 2,4-$tBu_2C_6H_3$, CPh_3
$Ar^1 =$ mes and $Ar^2 =$ Ph, R = CPh_3

Figure 1. Zinc complexes, supported by β-diketiminate and related ligands, that are active for the ring-opening polymerisation of lactide

metal−amidinate bonds. Extension of this area to include the closely related guanidinate anions, $[R_2NC(NR')_2]^-$,[13] has focussed mainly on the lanthanides, with catalytic activity observed with examples of both mono-,[14] and bis(ligand)[15] complexes (Figure 3).

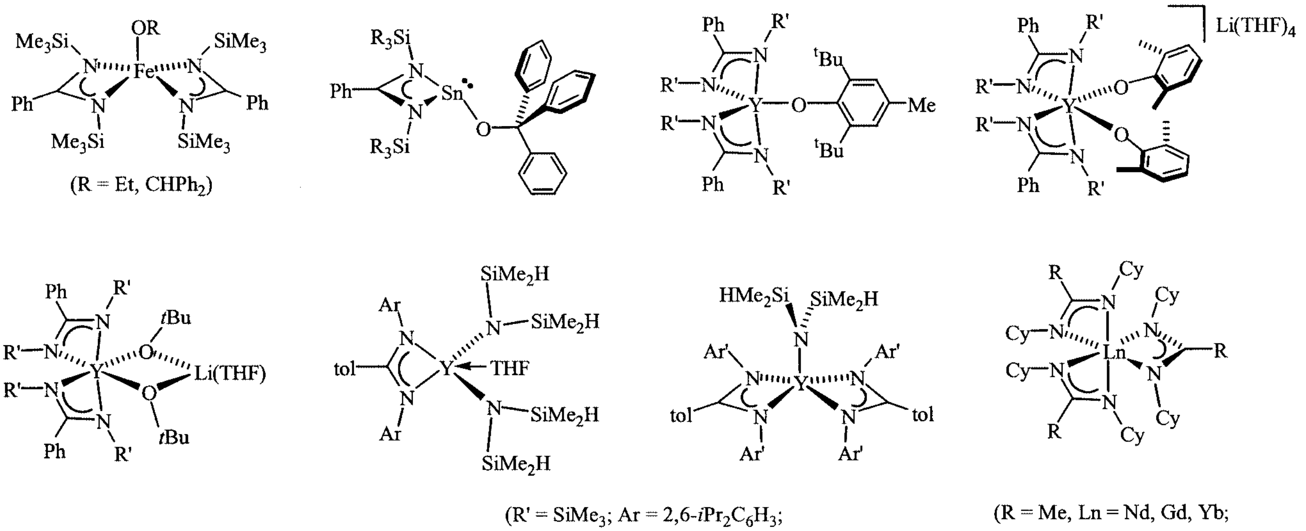
Considering the potential for combining an active Zn−X (where X = alkoxide, amide) component with a supporting amidinate or guanidinate ligand set, it came as a surprise to us that no accounts have appeared on the investigation of zinc amidinate and guanidinate complexes as catalysts in this area. Indeed, very few amidine or amidinate complexes of zinc have been reported, with a few notable exceptions being the $[ZnBr_2L_2]$ adduct, where L = neutral *N,N'*-di-*p*-tolylformamidine,[16] and the bis(benzamidinate) complex $[Zn\{PhC(NSiMe_3)_2\}_2]$.[17] A report of the reaction between alkylzinc compounds and amidines to afford Zn(amidinate)$_2$ complexes appeared as unpublished results that, to the best of our knowledge, were never expounded upon.[7]



(Ln = Yb, Nd)

Figure 3. Metal complexes, supported by guanidinate ligands, that are active for ring-opening polymerisation

Recently, the synthesis of tolylformamidinate complexes of zinc was investigated, although the only products forthcoming from the study were cluster species incorporating oxygen.[18] Wheatley and co-workers have investigated mixed Zn/Li species containing *N,N'*-diphenylbenzamidin-



(R = Et, $CHPh_2$)

(R' = $SiMe_3$; Ar = 2,6-$iPr_2C_6H_3$; Ar' = 2,6-$Et_2C_6H_3$)

(R = Me, Ln = Nd, Gd, Yb; R = Ph, Ln = Nd, Yb)

Figure 2. Metal complexes, supported by amidinate ligands, that are active for ring-opening polymerisation

ate and reported the reactivity with dry oxygen gas to afford similar oligomeric structures.[19] In contrast, a recent review did not report any zinc complexes containing anionic guanidinate ligands in the literature.[13] During the course of our work, we have developed several areas of research based around amidinate[20] and guanidinate chemistry,[21,22] and wish to report the results from a study into the synthesis and catalytic application of guanidinate-containing zinc complexes.

Results and Discussion

An atom-efficient route that has been employed in the synthesis of metal guanidinate complexes is the insertion of a carbodiimide into an existing metal−amide bond,[14,23] first reported by Lappert and co-workers in 1970.[24] The stoichiometric reaction between R′N=C=NR′ (R′ = *i*Pr, Cy) and $[Zn\{N(SiMe_3)_2\}_2]$ was therefore investigated as a potential route to mono(guanidinato)zinc−amide complexes (Scheme 1). However, after the appropriate workup, the only product isolated from the reaction for each of the carbodiimides investigated was the homoleptic, bis(guanidinate) complex $[Zn\{(Me_3Si)_2NC(NR')_2\}_2]$ (**3**, R′ = *i*Pr; **4**, R′ = Cy), resulting from insertion of a molecule of carbodiimide into *both* zinc−amide bonds. Compounds **3** and **4** can be purified by crystallisation from hexane at −30 °C affording colourless crystals in moderate yield. The molecular structures are illustrated in Figures 4 and 5, crystal data are summarised in the Exp. Sect. and selected bond lengths and angles in Table 1.

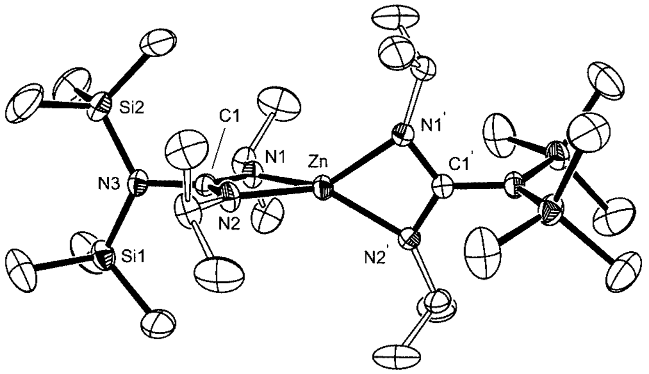
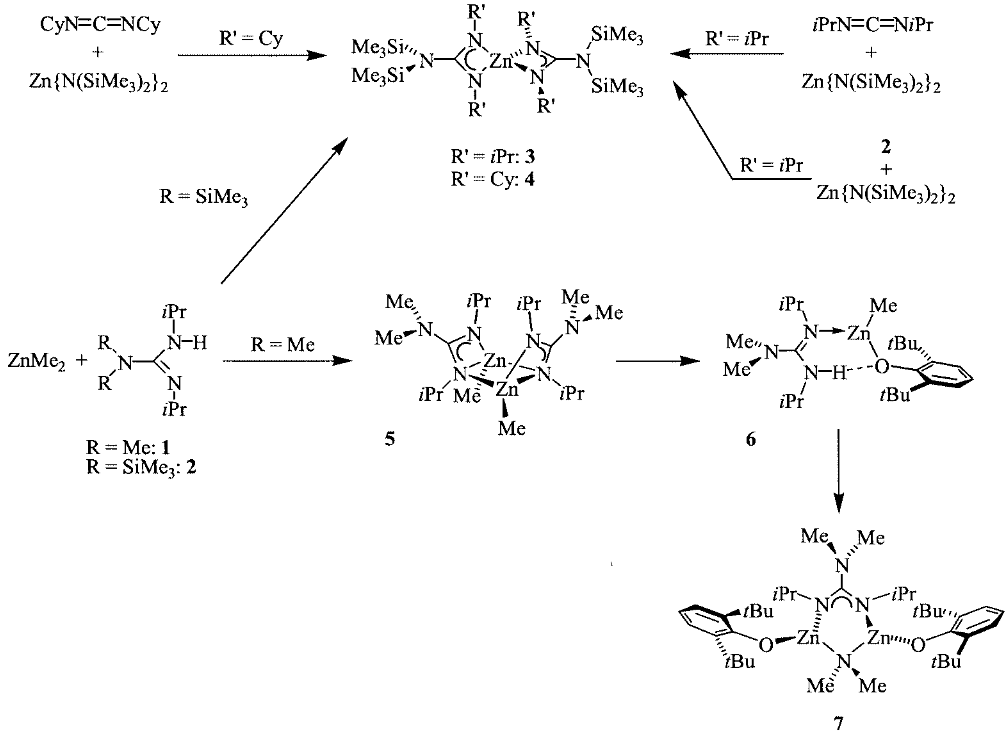


Figure 4. Molecular structure of $[Zn\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2]$ (**3**) with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms omitted for clarity

Compounds **3** and **4** are monomeric in the solid state, with the metal coordination sphere consisting of two η^2-guanidinate ligands in a "flattened" tetrahedral geometry. The angles at the metal atom are in the range 66.23(8)−139.32(13)° and 66.03(12)−135.93(12)° for **3** and **4**, respectively, where the lowest value is a consequence of the small bite angle of the ligand. The four-membered metallacycles are essentially planar (largest deviation: **3**, 0.015 Å; **4**, 0 Å) with an angle of 84.06° and 86.95° between the "ZnNCN" least-squares planes for **3** and **4**, respectively. The carbon−nitrogen distances are consistent with delocalisation across the "CN_2" fragment of the metallacycle, and the $C-N(SiMe_3)_2$ distances [**3**, 1.428(3) Å; **4**, 1.430(5) Å] and large angles between the "CN_2" and "NSi_2" moieties



Scheme 1. Summary of the synthesis of zinc guanidinate complexes **3**−**7**

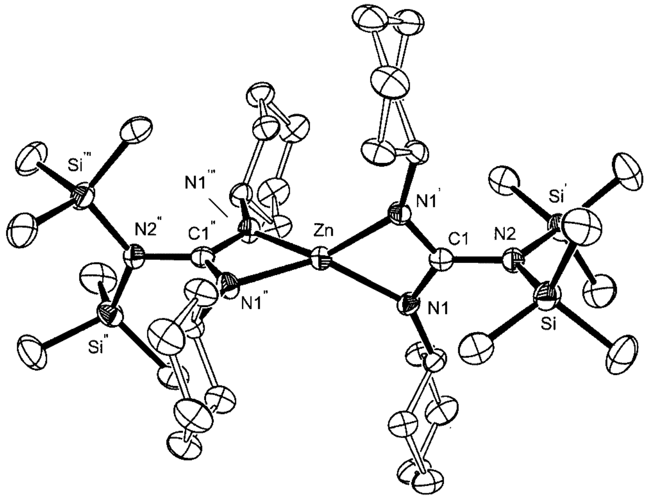


Figure 5. Molecular structure of $[\mathrm{Zn}\{(\mathrm{Me_3Si})_2\mathrm{NC}(\mathrm{NCy})_2\}_2]$ (**4**) with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms omitted for clarity

Table 1. Selected bond lengths [Å] and angles [°] for **3** and **4**

3[a]			
Zn−N(1)	2.011(2)	Zn−N(2)	2.021(2)
C(1)−N(1)	1.325(3)	N(3)−Si(1)	1.753(2)
C(1)−N(2)	1.326(3)	N(3)−Si(2)	1.752(2)
C(1)−N(3)	1.428(3)		
N(1)−Zn−N(2)	66.23(8)	N(1)−Zn−N(1′)	134.89(12)
N(1)−Zn−N(2′)	132.05(9)	N(2)−Zn−N(2′)	139.32(13)
N(1)−C(1)−N(2)	112.3(2)		

4[b]			
Zn−N(1)	2.006(2)	C(1)−N(1)	1.322(3)
N(2)−Si	1.7590(15)	C(1)−N(2)	1.430(5)
N(1)−Zn−N(1′)	66.03(12)	N(1′)−Zn−N(1‴)	135.93(12)
N(1)−Zn−N(1‴)	133.45(13)	N(1)−C(1)−N(1′)	111.5(3)

[a] Symmetry elements for **3**: ′ $-x + 1, y, -z + 1/2$. [b] Symmetry elements for **4**: ′ $-x + 5/4, y, -z + 1/4$; ″ $-x + 5/4, -y + 1/4, z$; ‴ $x, -y + 1/4, -z + 1/4$.

[**3**, 87.61°; **4**, 81.46°] are consistent with a single bond with possible N−Si π-interactions.[25]

An alternative approach to the targeted mono(guanidinate) complexes was subsequently investigated, namely the reaction between dimethylzinc and 1 equiv. of the (neutral) guanidine, predicted to proceed by protonolysis of the zinc−carbon linkage. The ligand precursors, $[\mathrm{R_2NC}\{\mathrm{NR'}\}\{\mathrm{NHR'}\}]$, were prepared from the reaction between the lithium diamide $\mathrm{LiNR_2}$ (R = $\mathrm{SiMe_3}$, Me) and *i*PrN=C=N*i*Pr, followed by quenching of the intermediate lithium salt with a stoichiometric amount of water, to afford $[\mathrm{Me_2NC}(\mathrm{N}i\mathrm{Pr})(\mathrm{NH}i\mathrm{Pr})]$ (**1**) and $[(\mathrm{Me_3Si})_2\mathrm{NC}(\mathrm{N}i\mathrm{Pr})(\mathrm{NH}i\mathrm{Pr})]$ (**2**).[26] The compounds were isolated as colourless and yellow liquids, respectively, and were used without further purification. The reaction between **2** and $[\mathrm{Zn}\{\mathrm{N}(\mathrm{SiMe_3})_2\}_2]$ or $\mathrm{ZnMe_2}$ in a 1:1 ratio did not proceed to the mono(ligand) complex, but afforded only the bis(guanidinate) species **3** after the appropriate workup (Scheme 1). In contrast, the reaction of the dimethylamino analogue **1** with $\mathrm{ZnMe_2}$ afforded colourless crystals of **5** suitable for an X-ray diffraction study. The molecular structure is illustrated in Figure 6, crystal data are summarised in the Exp. Sect. and selected bond lengths and angles in Table 2.

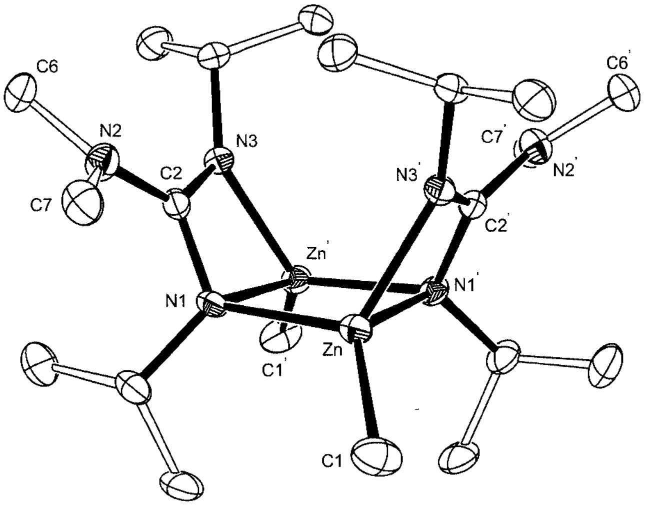


Figure 6. Molecular structure of $[\mathrm{Zn}\{\mathrm{Me_2NC}(\mathrm{N}i\mathrm{Pr})_2\}\mathrm{Me}]_2$ (**5**) with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms omitted for clarity

Table 2. Selected bond lengths [Å] and angles [°] for **5** and **6**

5[a]			
Zn−N(1)	2.101(3)	Zn−N(1′)	2.201(3)
Zn−N(3′)	2.063(3)	Zn−C(1)	1.987(5)
C(2)−N(1)	1.393(6)	N(2)−C(6)	1.462(6)
C(2)−N(3)	1.314(5)	N(2)−C(7)	1.461(6)
C(2)−N(2)	1.357(5)		
N(1′)−Zn−N(3′)	63.50(16)	N(1′)−Zn−N(1)	91.80(12)
N(1′)−Zn−C(1)	130.9(2)	N(3′)−Zn−C(1)	126.05(18)
N(3′)−Zn−N(1)	109.42(16)	N(1)−Zn−C(1)	119.74(19)
N(1)−C(2)−N(3)	112.2(4)		

6			
Zn−O	1.9511(15)	Zn−C(24)	1.955(2)
Zn−N(1)	1.9952(18)	C(1)−N(1)	1.324(3)
C(1)−N(2)	1.353(3)	C(1)−N(3)	1.373(3)
O−C(10)	1.358(3)	H(2A)···O	2.83
O−Zn−C(24)	120.79(9)	O−Zn−N(1)	107.78(7)
N(1)−Zn−C(24)	131.30(9)	Zn−O−C(10)	110.96(12)
C(1)−N(1)−Zn	125.04(15)	C(2)−N(1)−Zn	114.34(13)
C(1)−N(1)−C(2)	119.45(18)	C(1)−N(3)−C(8)	123.0(2)
C(1)−N(3)−C(9)	121.6(2)	C(8)−N(3)−C(9)	115.1(2)

[a] Symmetry elements for **5**: ′ $-x, -y + 1, z$.

Compound **5** crystallised as the dimeric compound $[\mathrm{Zn}\{\mathrm{Me_2NC}(\mathrm{N}i\mathrm{Pr})_2\}\mathrm{Me}]_2$, with a $\mu,\eta^2{:}\eta^1$-coordination mode of the guanidinate ligand, resulting in an essentially planar $\mathrm{Zn_2N_2}$ ring (largest deviation from least-squares plane: 0.041 Å). Whilst this type of coordination has not previously been observed for monoanionic guanidinate ligands,[27] related tricyclic core structures have been reported for amidinate complexes of lithium,[28−30] magnesium[31] and iron,[32] and we have also observed this structural motif in a recently reported lithium phospha(III)guanidinate complex.[33] In contrast to the majority of these structures which contain crystallographic inversion symmetry, a non-centrosymmetric structure is observed for compound **5**, with a *syn* arrangement of the ligands about the central Zn_2N_2 ring.[29,31] The zinc atoms are present in a distorted tetrahedral geometry [angles in the range 63.50(16)−130.9(2)°], with the "ZnNCN" metallacycle at an angle of 66.19° to the central Zn_2N_2 plane. Examination of the Zn−N bond lengths in **5** suggests a strong association of the monomeric units in the solid state. Indeed, if we consider the dimer as consisting of two [Zn(guanidinate)-Me] fragments, based solely upon metal−nitrogen distances there is an apparent stronger interaction between the ligand of one unit and the metal of another [Zn−N(1) = 2.101(3) Å], than within the chelating guanidinate itself [Zn−N(1′) = 2.201(3) Å]. In all cases the Zn−N distances are significantly longer than in the homoleptic compounds **3** (av. 2.016 Å) and **4** (2.006 Å), despite a reduced angle between the NR_2 plane and the metallacycle in **5** (31.60°) that allows contribution from a zwitterionic resonance to the overall bonding.[25] In agreement with this postulate, the C(2)−N(2) bond length of **5** [1.357(5) Å] is intermediate between the value expected for C−N single and C=N double bonds, and is significantly shorter than the corresponding bonds in **3** [1.428(3) Å] and **4** [1.430(5) Å].

Transformation of the zinc−methyl group to a Zn−O linkage, desirable for applications in ROP, was attempted by reaction with 2,6-di-*tert*-butylphenol (Scheme 1). It was anticipated that the steric bulk of the alkyl substituents positioned about the resultant metal−oxygen bond would disfavour a bridging coordination mode for the aryloxide and promote a low aggregation within the final product. The reaction was performed at room temperature and after the appropriate workup colourless crystals of **6** were obtained. The molecular structure is illustrated in Figure 7, crystal data are summarised in the Exp. Sect. and selected bond lengths and angles in Table 2.

The molecular structure of **6** shows retention of the zinc−methyl group and incorporation of the aryloxide ligand in an overall monomeric, distorted trigonal planar zinc complex (Σ_{angles} at Zn: 359.57°). The coordination sphere of the zinc atom is completed by the *neutral* form of the guanidine ligand, $Me_2NC(N\textit{i}Pr)(NH\textit{i}Pr)$ (**1**), bonding through the N_{imino} atom,[34] such that the "CN_2" component is essentially coplanar with the ZnMeON metallacycle [max. deviation at C(1) 0.15 Å]. This arrangement is likely governed by the formation of an intramolecular hydrogen bond between the amino-NH and the aryloxide-O atoms [H(2a)···O 2.83 Å] which results in a widening of the angle between the N(1) and C(24) atoms at the zinc atom from the ideal trigonal planar angle to 131.30(9)°.

Despite coordinating as a neutral ligand in **6**, the Zn−N bond [1.9952(18) Å] is shorter than those observed in **5** (av. 2.12 Å) where it binds as an anionic ligand, reflecting the reduction in coordination number at the metal centre. This shortening may also be enhanced by the intramolecular H-bond noted above. The Zn−O bond [1.9511(15) Å] is relatively long in comparison to related three- and four-coordinate zinc complexes containing this and the similarly substituted 2,4,6-$\textit{t}Bu_3C_6H_2$ aryloxide groups [range: 1.818(1)−1.923(5) Å], and the angle at the oxygen atom [110.96(12)°] is by far the smallest observed [range: 124.04(14)−155.7(10)°].[35] These data suggest that there is a reduced π-donation from the oxygen to the zinc atom in **6** compared with the other examples cited, caused by the localisation of electron density in the hydrogen bond to the amino NH group.

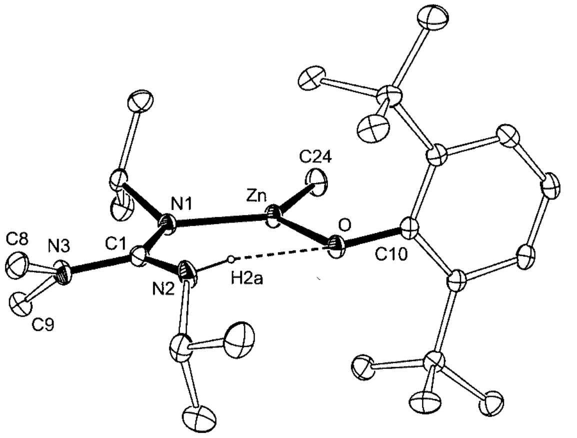


Figure 7. Molecular structure of [Zn(OAr)Me·{$Me_2NC(N\textit{i}Pr)(NH\textit{i}Pr)$}] (**6**) with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms, except H(2a), omitted for clarity

The EI^+ mass spectrum of **6** indicates that, as predicted under these experimental conditions, dissociation of the guanidine occurs resulting in a signal at *m/z* (%)= 284 (72) equivalent to the "Zn(OAr)Me" fragment. Slightly more unexpected was the observation of a peak at *m/z* (%) = 439 (38) in the same spectrum, corresponding to the monomeric form of the target complex, "Zn{$Me_2NC(N\textit{i}Pr)_2$}(OAr)". This fragment must arise as a result of protonation of the methyl group by the NH functionality, with loss of methane, and prompted us to investigate the thermal stability of **6** in the expectation that, under the correct conditions, reactivity could be promoted at the Zn−C bond. Thus, a mixture of **5** and 1 equiv. of HOAr was heated in toluene, and the resultant solid crystallised from hexane at −30 °C, affording a small number of colourless crystals of **7** that were analysed by NMR spectroscopy and X-ray diffraction. The X-ray diffraction study was performed on representative crystals of **7** to determine the nature of the product; the molecular structure is illustrated in Figures 8 and 9, crystal data are summarised in the Exp. Sect. and selected bond lengths and angles in Table 3.

Compound **7** is a dimetallic zinc complex where the metal atoms are joined by bridging guanidinate and amide groups to generate a six-membered metallacycle. Each zinc atom is also bound by an aryloxide ligand, giving an overall distorted trigonal-planar geometry with the sum of the angles at Zn(1) and Zn(2) equal to 359.54° and 359.37°, respec-

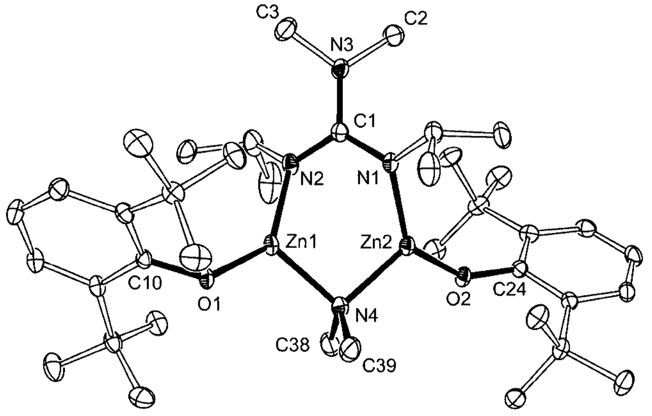


Figure 8. Molecular structure of [{Zn(OAr)}$_2$(μ-{Me$_2$NC(N*i*Pr)$_2$})(μ-NMe$_2$)] (**7**) with thermal ellipsoids drawn at the 20% probability level; hydrogen atoms omitted for clarity

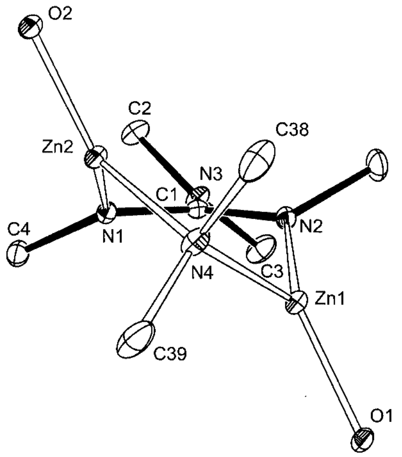


Figure 9. Core of [{Zn(OAr)}$_2$(μ-{Me$_2$NC(N*i*Pr)$_2$})(μ-NMe$_2$)] (**7**) along the approximate N(4)−C(1)−N(3) vector, illustrating the "half-chair" geometry of the metallacycle, and the distribution of the ligand substituents

Table 3. Selected bond lengths [Å] and angles [°] for **7** and **8**

	7		
Zn(1)−N(2)	1.950(3)	Zn(2)−N(1)	1.946(3)
Zn(1)−O(1)	1.846(2)	Zn(2)−O(2)	1.840(2)
Zn(1)−N(4)	1.990(3)	Zn(2)−N(4)	1.982(3)
C(1)−N(1)	1.352(5)	C(1)−N(2)	1.336(5)
C(1)−N(3)	1.361(5)	N(4)−C(38)	1.470(6)
N(4)−C(39)	1.461(6)		
O(1)−Zn(1)−N(2)	135.79(12)	O(2)−Zn(2)−N(1)	134.73(12)
O(1)−Zn(1)−N(4)	111.24(12)	O(2)−Zn(2)−N(4)	111.50(13)
N(2)−Zn(1)−N(4)	112.51(13)	N(1)−Zn(2)−N(4)	113.14(13)
N(1)−C(1)−N(2)	119.3(3)		
	8[a]		
Zn−N(1)	2.1879(18)	Zn−N(2)	2.0486(19)
Zn−N(1′)	2.0831(19)	Zn−N(4)	1.9177(18)
C(1)−N(1)	1.380(3)	N(4)−Si(1)	1.707(2)
C(1)−N(2)	1.318(3)	N(4)−Si(2)	1.702(2)
C(1)−N(3)	1.349(3)		
N(1)−Zn−N(2)	64.20(7)	N(1)−Zn−N(1′)	92.88(7)
N(1)−Zn−N(4)	131.93(8)	N(2)−Zn−N(4)	125.11(8)
N(2)−Zn−N(1′)	104.61(7)	N(1′)−Zn−N(4)	122.41(8)
Zn−N(1)−Zn′	87.12(7)	N(1)−C(1)−N(2)	113.37(19)

[a] Symmetry elements for **8**: ′ $-x + 1$, $-y$, $-z + 1$.

tively. Overall, the metallacycle adopts a half-chair conformation (Figure 9) with a twist angle of 34.56° between the planes defined by Zn(1)−N(4)−Zn(2) and N(1)−C(1)−N(2). Both the guanidinate and amide bridge symmetrically between the two metal atoms.

Whilst a number of examples of bridging acyclic guanidinates have been reported between Pd, Fe and the s-block metals,[36] by far the most common coordination mode involves chelating to the metal atom,[13] rationalised in terms of the ligand donor orbital pointing towards the "mouth" of the ligand. The C−N distances within the guanidinate ligand (av. 1.35 Å) signify delocalisation of the R$_2$N lone pair into the core of the ligand, typically observed for this substitution pattern of nitrogen substituents. The average Zn−N$_{\text{amide}}$ distance in **7** (1.963 Å) is shorter than that found to the bridging amide group in the homoleptic series [Zn(NR$_2$)(μ-NR$_2$)]$_2$ (R = Ph,[37] 2.03 Å; R = CH$_2$Ph,[38] 2.04 Å; R = CH$_2$*i*Pr,[39] 2.03 Å], a possible consequence of the greater electron-withdrawing ability of the ArO$^-$ ligand. The Zn−O bond lengths (av. 1.843 Å) are within the range associated with this substituent (vide supra), although the angle at the oxygen atom varies significantly between the two ligands [Zn(1)−O(1)−C(10) 130.0(2)°, Zn(2)−O(2)−C(24) 140.9(2)°] indicating the "soft" character of this angle.

Recently, we[21,22] and others[25,40] have utilised the commercially available bicyclic guanidine 1,3,4,6,7,8-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine (hppH) as a ligand precursor in the coordination chemistry of transition-metal and main-group complexes. The major difference of this system in comparison with acyclic guanidinates is that the constraint of the amide substituent and the amidine "CN$_2$" components of the molecule in the cyclic framework is predicted to enhance electron donation to a metal centre by increasing the contribution to the overall bonding from a zwitterionic resonance form. A potential complication in the application of the anionic ligand [hpp]$^-$ in molecular catalysis that arises from the bicyclic nature of the ligand is the propensity to adopt a bridging coordination mode to different metal centres, extensively exploited by Cotton and others in the support of many dimetallic systems.[30,41] Indeed, we have observed that the stoichiometric reaction between neutral hppH and ZnMe$_2$ affords the fully characterised, trimetallic complex [Zn$_3$(hpp)$_4$Me$_2$] containing both two-coordinate [μ-hpp]$^-$ and three-coordinate [κ^{1,2}*N*-κ^3*N*′-hpp]$^-$ bonding modes; this will be described fully in a forthcoming publication.[42]

In contrast to the reactions between acyclic guanidines and [Zn{N(SiMe$_3$)$_2$}$_2$], the reaction with hppH proceeds smoothly at room temperature to afford the mono(guanidinate) species [Zn(hpp){N(SiMe$_3$)$_2$}]$_n$ (**8**) in excellent yield. Low-temperature (−30 °C) crystallisation from a concentrated hexane solution affords colourless crystals suitable for an X-ray diffraction study. The molecular structure is illustrated in Figure 10, crystal data are summarised in the Exp. Sect. and selected bond lengths and angles in Table 3.

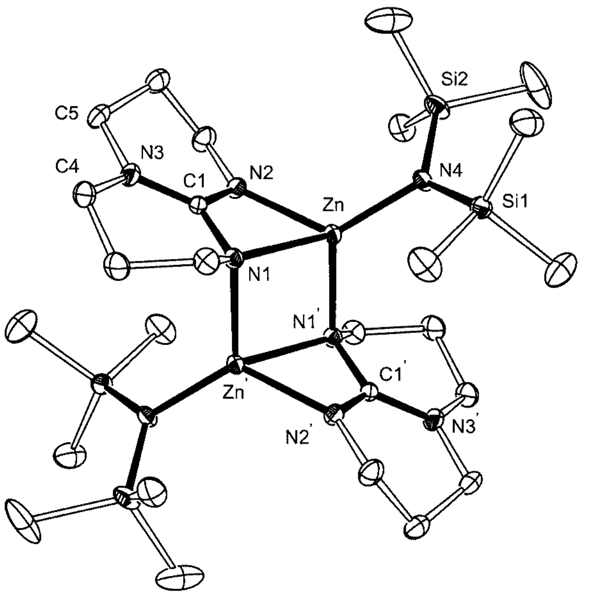


Figure 10. Molecular structure of $[Zn(hpp)\{N(SiMe_3)_2\}]_2$ (**8**) with thermal ellipsoids drawn at the 30% probability level; hydrogen atoms omitted for clarity

Compound **8** crystallised as the dimeric compound $[Zn(hpp)\{N(SiMe_3)_2\}]_2$, with a previously unreported $\mu,\eta^2:\eta^1$-coordination mode for the $[hpp]^-$ anion. Unlike the molecular structure of **5**, complex **8** exists as a centrosymmetric dimer with an *anti* arrangement of ligands about the central Zn_2N_2 metallacycle, a likely consequence of the different steric requirements of the ligands at the zinc centre. The Zn_2N_2 core of the molecule is perfectly planar and forms an angle of 72.9° to the essentially planar ZnN_2C metallacycle (largest deviation from least-squares plane 0.075 Å). The resultant geometry at the zinc centre is therefore best described as distorted tetrahedral with bond angles in the range 64.20(7)° (corresponding to the bite angle of the ligand) to 131.93(8)°.

As in **5**, a strong interaction between the two "monomeric" $[Zn(hpp)\{N(SiMe_3)_2\}]$ units is indicated by the shorter Zn−N(1′) distance [2.0831(19) Å] compared with Zn−N(1) [2.1879(18) Å]. The remaining Zn−N bond of the chelating $[hpp]^-$ anion is shorter [2.0486(19) Å], a probable combination of increased electron donation from $[hpp]^-$ [angle between N(1)−C(1)−N(2) and C(4)−N(3)−C(5) planes 4.57°] and a more electron-deficient zinc atom arising from the presence of the amide vs. the methyl substituent. The $Zn-N_{amide}$ distance [1.9177(18) Å] is slightly longer than the value in related, three-coordinate β-diketiminate[43] and (imine)(oxazoline)[44] zinc amides [1.896(2) and 1.883(3) Å, respectively], which may reflect a weaker bond, more reactive to ROP.

Preliminary NMR investigations of the catalytic activity of **8** towards the ring-opening of D,L-lactide (LA) was performed in CD_2Cl_2 and [D$_8$]toluene. In contrast to many zinc complexes incorporating the relatively bulky $N(SiMe_3)_2$ group, where initiation is reported as being slow,[4] the immediate reaction of **8** to generate a new species (> 98% in ca. 2 min) was observed, as judged by a shift of the $N(Si\mathit{Me_3})_2$ resonance from $\delta = -0.02$ ppm to $\delta = 0.05$ ppm (CD_2Cl_2). The progress of the reaction was monitored by ^{1}H NMR spectroscopy, clearly indicating that 45−85 equiv. of LA were polymerised to polylactide (PLA) with more than 95% conversion in less than 2 h. Assuming the rate of initiation is much greater than the rate of propagation, leading to all zinc centres being activated prior to further insertion of monomer, integration of the $N(Si\mathit{Me_3})_2$ end-group signal versus either the methine or methyl resonances of the growing polymer chain will allow an approximate value of the molecular weight to be calculated. From the ^{1}H NMR spectra of the polymerisation reactions performed with **8**, this appeared to be a reasonable approximation (vide supra), and a graph of molecular weight vs. conversion was therefore plotted (Figure 11). The straight-line relationships generated for different monomer concentrations and solvents present good evidence that the polymerisation proceeds in a "well-behaved" fashion. In addition, after 18 h at room temperature, a sample of **8** and LA (45 equiv.) that had progressed to more than 98% conversion was able to initiate the polymerisation of a further 50 equiv. of LA in CD_2Cl_2. The fresh monomer was converted into PLA over a period of 2 h, demonstrating the stability of the propagating species over time and providing further indication of the controlled nature of the polymerisation. There was no evidence for a tacticity bias in the ^{1}H NMR spectrum of the PLA produced by **8**, as indicated by selective decoupling of the methine protons.

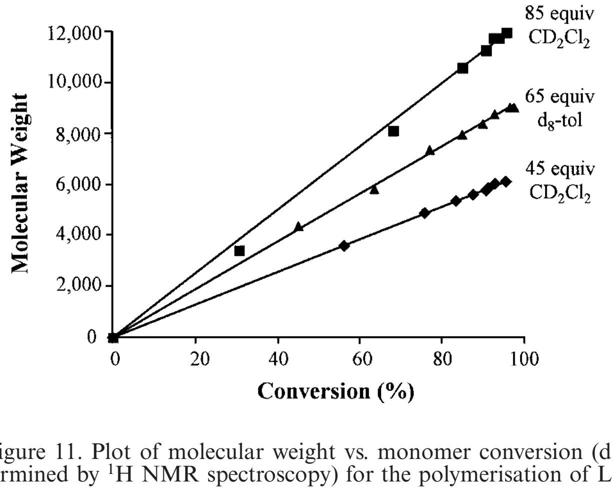


Figure 11. Plot of molecular weight vs. monomer conversion (determined by ^{1}H NMR spectroscopy) for the polymerisation of LA with **8**

Conclusion

We have demonstrated that the synthesis of mono(guanidinate) complexes of zinc is beleaguered with difficulties, and the nature of the product can be highly dependant on the synthetic protocol employed and substitution pattern of the nitrogen groups contained within the ligand precursor. Initial attempts at formation of the mono(ligand) amide only afforded the homoleptic Zn^{II} guanidinate products **3** and **4** under a variety of conditions. Assuming a stepwise reaction pathway is in operation, proceeding by initial formation of one guanidinate anion at the metal atom, this mono(ligand) product evidently activates the metal−amide bond to further insertion relative to the Zn−N bond of the bis(amide) starting material.

An interesting contrast was noted in the protonation reactivity between $ZnMe_2$ and the neutral diisopropylguanidines $R_2NC(N\mathit{i}Pr)(NH\mathit{i}Pr)$ (R = $SiMe_3$ and Me), where a similar steric environment at the metal atom is anticipated as the metal-bound nitrogen atoms are substituted by isopropyl groups in each instance. Changing the nitrogen substituents of the NR_2 moiety from trimethylsilyl to methyl, however, arrested multiple protonation of the dialkylzinc and provided a clean and efficient route to the first example of a mono(guanidinate) compound **5** of zinc. It has been previously demonstrated in guanidinate chemistry of aluminium that, despite being remote from the metal centre, the nature of the R substituents can strongly influence the distribution of electron density within the $[R_2NC\{NR'\}_2]^-$ anion and the potential therefore exists to "tune" the reactivity of the metal centre.[25] In general, the larger, more electron-withdrawing silyl substituents will reduce the extent of electron donation through the $N_{amino}-C$ bond by disfavouring delocalisation of the N_{amino} lone-pair into the framework of the ligand. The smaller, electron-donating methyl groups, however, allow the NR_2 and CN_2 components of the ligand to approach coplanarity, thus providing the correct orbital alignment for interaction between the nitrogen lone-pair and the empty p-orbital of the sp^2-carbon atom. The result is the potential for greater electron donation for the anion derived from **1** compared with **2**, which is apparently sufficient to prevent activation of the zinc−methyl bond to further protonation in compound **5**. It is curious to note that in **5**, the usually highly reactive $Zn-CH_3$ bond is even resistant to protonation from a bulky phenol derivative and that the acidic proton preferentially reacts at one of the Zn−N bonds of the guanidinate, affording the mixed methyl(aryloxide) compound **6**.

The molecular structure of **6** confirms retention of the neutral ligand at the zinc centre and reveals an intramolecular hydrogen bond to the aryloxide-O atom. Comparison of the Zn−O bond with other examples of compounds containing the same ligand indicates that the bond in **6** is exceptionally long and angular. This is in agreement with the oxygen lone-pairs participating in the hydrogen bond to the NH group, with the result being consistent with a lower Zn−O bond order than noted in previous examples of zinc complexes incorporating this ligand.

Attempts to promote methane elimination by heating a mixture of **5** and ArOH met with partial success. Loss of the zinc−methyl group was achieved with concomitant conversion of the neutral guanidine ligand to the anionic guanidinate and retention of the aryloxide substituent. However, the guanidinate ligand was found to be unstable under the conditions employed, as indicated by the isolation of a small amount of the dimetallic species $[\{Zn(OAr)\}_2(\mu\text{-}\{Me_2NC(N\mathit{i}Pr)_2\})(\mu\text{-}NMe_2)]$ (**7**), formed by amide extrusion from the guanidine or guanidinate ligand. As this product was only isolated in low yield, and as such may represent only a minor component of the product mixture, detailed mechanistic studies into its formation were not carried out. However further work in this area is merited due to the possible implications that such a process has in metal-catalysed guanylation of amines and transamination of guanidines,[45] and C=N metathesis of carbodiimides.[46]

Building on the observation that the introduction of a more electron-donating guanidinate ligand caused multiple protonation at the metal centre to be effectively "shut down" during the synthesis of **5**, we turned our attention to the potentially more strongly electron-donating anion $[hpp]^-$. It has been shown that constraining the NR_2 and CN_2 components in the bicyclic framework of this compound promotes an increased contribution from a zwitterionic resonance form, manifested in shorter Ti−N distances in a series of titanium compounds incorporating the $[hpp]^-$ anion in comparison to acyclic amidinates and guanidinates.[21] Thus, synthesis of $[Zn(hpp)\{N(SiMe_3)_2\}]_2$ (**8**), containing the desired combination of a supporting ancillary guanidinate and reactive zinc−amide bond, was achieved. Compound **8** was found to be active in the small-scale polymerisation of lactide and analysis of the NMR spectroscopic data indicated a well-behaved system.

Overall we have therefore exploited the observation that, in order to prevent the formation of homoleptic Zn^{II} guanidinate compounds, more electron-donating guanidinate anions must be employed. Eventually, the correct combination of ligands was found in **8** and we proved the concept that this compound is an active catalyst for the well-behaved ROP of lactide. The application of **8** in the polymerisation of related monomers and an in-depth study of the structure of the polymeric material will be published in due course.

Experimental Section

General Remarks: All manipulations were carried out under dry nitrogen using standard Schlenk and cannula techniques, or in a conventional nitrogen-filled glovebox operating at < 1 ppm oxygen. Solvents were dried with appropriate drying agents, degassed, and stored over a potassium mirror or activated molecular sieves prior to use. $R'N=C=NR'$ (R′ = *i*Pr, Cy; Aldrich), $LiNMe_2$ (Fluka), $LiN(SiMe_3)_2$ (Aldrich) and $ZnMe_2$ (ca. 2 M solution in toluene; Fluka) were obtained commercially and used as received, unless stated otherwise. The compound $[Zn\{N(SiMe_3)_2\}_2]$ was synthesised from the reaction between $ZnBr_2$ and 2 equiv. of $LiN(SiMe_3)_2$. The crude product was extracted into hexane and used without further purification. Elemental analyses were performed by S. Boyer at The University of North London. NMR spectra were recorded with a Bruker Avance DPX 300 MHz spectrometer. Coupling constants are quoted in Hertz.

$Me_2NC(N\textit{i}Pr)(NH\textit{i}Pr)$ (1): A slurry of lithium dimethylamide (5.00 g, 98.00 mmol) in Et_2O (100 mL) was cooled to 0 °C and a solution of diisopropylcarbodiimide (12.40 g, 98.00 mmol) in Et_2O (50 mL) was added dropwise with a cannula. The mixture was allowed to warm to room temperature to afford a cloudy yellow solution, that was stirred for a further 14 h under ambient conditions. Degassed water (1.8 mL, 100.00 mmol) was subsequently added dropwise with a syringe causing the formation of a clear yellow solution and a white precipitate. The mixture was filtered through Celite and the volatiles were removed to afford a pale-yellow liquid that was used without further purification. Yield: 11.75 g (70%). ^{1}H NMR ($CDCl_3$, 298 K): δ = 3.37 (sept, $^3J_{H,H}$ = 6.4, 1 H, C*H*Me$_2$), 3.25 (sept, $^3J_{H,H}$ = 6.3, 1 H, C*H*Me$_2$), 2.67 (s, 6 H, N*Me$_2$*), 1.03 (d, $^3J_{H,H}$ = 6.3, 6 H, CH*Me$_2$*), 1.02 (d, $^3J_{H,H}$ = 6.3, 6 H, CH*Me$_2$*) ppm; N*H* signal not observed. ^{13}C NMR ($CDCl_3$, 298 K): δ = 155.8 (*C*N$_3$), 47.3 (*C*HMe$_2$), 45.9 (*C*HMe$_2$), 39.0 (N*Me$_2$*), 25.1 (CH*Me$_2$*), 23.6 (CH*Me$_2$*) ppm.

$(Me_3Si)_2NC(N\textit{i}Pr)(NH\textit{i}Pr)$ (2): Compound **2** was synthesised using a similar procedure to that outlined for the synthesis of **1**, using lithium bis(trimethylsilyl)amide (2.50 g, 14.94 mmol), diisopropylcarbodiimide (1.89 g, 14.94 mmol) and water (0.27 g, 14.94 mmol). The compound was isolated as a colourless liquid and was used without further purification. Yield: 3.21 g (75%). ^{1}H NMR ($CDCl_3$, 298 K): δ = 3.79 (br. sept, $^3J_{H,H}$ = 6.0, 1 H, C*H*Me$_2$), 3.64 (br. sept, $^3J_{H,H}$ = 5.6, 1 H, C*H*Me$_2$), 1.08 (br. d, $^3J_{H,H}$ = 5.9, 6 H, CH*Me$_2$*), 1.04 (br. d, $^3J_{H,H}$ = 5.8, 6 H, CH*Me$_2$*), 1.15 (s, 18 H, Si*Me$_3$*) ppm; N*H* signal not observed. ^{13}C NMR ($CDCl_3$, 298 K): δ = 147.5 (*C*N$_3$), 47.3 (*C*HMe$_2$), 42.0 (*C*HMe$_2$), 24.9 (CH*Me$_2$*), 22.7 (CH*Me$_2$*), 1.6 (Si*Me$_3$*) ppm.

$[Zn\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2]$ (3). Method 1: A solution of dimethylzinc (0.9 mL of a 2 M solution in toluene, 1.80 mmol) was further diluted with an additional 20 mL of toluene and cooled to −78 °C. A solution of **2** (0.50 g, 1.74 mmol) in toluene (40 mL) was added dropwise with a cannula and the resultant colourless solution was allowed to warm to room temperature and stirred for 14 h. The mixture was filtered and cooled to −30 °C to afford colourless crystals of $[Zn\{(Me_3Si)_2NC(N\textit{i}Pr)_2\}_2]$. Yield: 0.45 g (48%). $C_{26}H_{64}N_6Si_4Zn$ (638.56): calcd. C 48.91, H 10.10, N 13.16; found C 48.99, H 9.99, N 13.07. ^{1}H NMR (C_6D_6, 298 K): δ = 3.70 (sept, $^3J_{H,H}$ = 6.1, 4 H, C*H*Me$_2$), 1.17 (d, $^3J_{H,H}$ = 6.2, 24 H, CH*Me$_2$*), 0.30 (2, 36 H, Si*Me$_3$*) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 165.2 (*C*N$_3$), 44.7 (*C*HMe$_2$), 27.0 (CH*Me$_2$*), 2.3 (Si*Me$_3$*) ppm. MS (EI$^+$): *m*/*z* = 636 [M]$^+$, 621 [M − Me]$^+$. **Method 2:** A solution of **2** (0.37 g, 1.29 mmol) in toluene (20 mL) was added dropwise at room temperature to a toluene (25 mL) solution of $[Zn\{N(SiMe_3)_2\}_2]$ (0.50 g, 1.29 mmol) with a cannula. No visible change was observed. The reaction mixture was stirred at room temperature for 18 h, after which time the volatiles were removed to afford a sticky white solid. ^{1}H NMR spectra indicated a 1:1 mixture of **3** (identified from the chemical shift values in comparison with an authentic sample) and unchanged $[Zn\{N(SiMe_3)_2\}_2]$. No further purification was attempted.

$[Zn\{(Me_3Si)_2NC(NCy)_2\}_2]$ (4): A solution of CyN=C=NCy (0.27 g, 1.29 mmol) in toluene (25 mL) was added dropwise to a stirred solution of $[Zn\{N(SiMe_3)_2\}_2]$ (0.50 g, 1.29 mmol) in toluene (25 mL) at room temperature. No visible change was observed, and the resultant colourless solution was stirred at ambient conditions for 16 h. Removal of the volatiles in vacuo afforded crude **2** as a white solid that was crystallised from toluene at −30 °C as analytically pure colourless crystals. Yield: 0.32 g (62%) based on CyN=C=NCy. $C_{38}H_{80}N_6Si_4Zn$ (798.81): calcd. C 57.14, H 10.09, N 10.52; found C 57.05, H 10.09, N 10.56. ^{1}H NMR (C_6D_6, 298 K): δ = 3.37 (m, 4 H, *Cy*), 1.91−1.24 (m, 44 H, *Cy*), 0.33 (s, 36 H, Si*Me$_3$*) ppm.

An analogous reaction procedure using *i*PrN=C=N*i*Pr afforded a colourless crystalline material that analysed for **3**.

$[Zn\{Me_2NC(N\textit{i}Pr)_2\}Me]_2$ (5): A solution of **1** (1.00 g, 5.84 mmol) in toluene (30 mL) was added at room temperature to a solution of dimethylzinc (2.9 mL of a 2 M solution in toluene, 5.80 mmol) that had been further diluted by 50 mL of toluene. Evolution of a gas was observed and the resultant clear yellow solution was stirred under ambient conditions for 12 h. Removal of the volatiles afforded a pale-yellow solid that could be used without further purification. Analytically pure samples were obtained by crystallisation from hexane at −30 °C. Yield 0.98 g (67%). $C_{10}H_{23}N_3Zn$ (501.37): calcd. C 47.91, H 9.25, N 16.76; found C 47.73, H 9.37, N 16.86. ^{1}H NMR (C_6D_6, 298 K): δ = 3.41 (sept, $^3J_{H,H}$ = 6.1, 2 H, C*H*Me$_2$), 2.47 (s, 6 H, N*Me$_2$*), 1.12 (br. d, 12 H, CH*Me$_2$*), −0.12 (s, 3 H, Zn*Me*) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 166.5 (*C*N$_3$), 47.2 (*C*HMe$_2$), 40.0 (N*Me$_2$*), 25.7 (br., CH*Me$_2$*), −11.2 (Zn*Me*) ppm. MS (EI$^+$): *m*/*z* = 404 $[\{Me_2NC(N\textit{i}Pr)_2\}_2Zn]^+$, 360 $[\{Me_2NC(N\textit{i}Pr)_2\}_2Zn - NMe_2]^+$, 234 $[\{Me_2NC(N\textit{i}Pr)_2\}Zn]^+$.

$[Zn(OAr)Me\cdot\{Me_2NC(N\textit{i}Pr)(NH\textit{i}Pr)\}]$ (6): A solution of 2,6-di-*tert*-butylphenol (0.41 g, 2.00 mmol) in toluene (20 mL) was added dropwise at room temperature to a solution of **5** (0.50 g, 2.00 mmol) in toluene (30 mL). The resultant clear, pale-yellow solution was stirred at room temperature for 12 h, after which time the volatile component was removed in vacuo to afford a pale-yellow solid. Crystallisation from hexane afforded **6** as colourless crystals. Despite repeated crystallisations, a persistent, unidentified impurity was observed during the preparation of **6**. As such, accurate analysis was not obtained and the NMR spectroscopic data are reported for the major component, which corresponds to **6**. Yield: 0.43 g (46%) calculated for **6**. $C_{24}H_{45}N_3OZn$ (457.00): calcd. C 63.07, H 9.92, N 9.19; found C 56.74, H 9.39, N 6.73. ^{1}H NMR (C_6D_6, 298 K): δ = 7.46 (d, $^3J_{H,H}$ = 7.8, 2 H, *m*-C$_6$H$_3$), 6.92 (t, $^3J_{H,H}$ = 7.7, 1 H, *p*-C$_6$H$_3$), 3.29 (sept, $^3J_{H,H}$ = 6.5, 1 H, C*H*Me$_2$), 3.08 (br. sept, 1 H, C*H*Me$_2$), 2.19 (br. s, 6 H, N*Me$_2$*), 1.72 (s, 18 H, C*Me$_3$*), 1.17 (br. d, $^3J_{H,H}$ = 6.4, CH*Me$_2$*), 0.99 (br. d, $^3J_{H,H}$ = 6.0, CH*Me$_2$*), −0.33 (s, 3 H, Zn*Me*) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 165.7 (*C*N$_3$), 139.0 (*C*), 128.3 (*C*), 125.3 (*C*H), 115.9 (*C*H), 50.1 (br., *C*HMe$_2$), 45.6 (*C*HMe$_2$), 39.8 (N*Me$_2$*), 35.5 (*C*Me$_3$), 32.4 (C*Me$_3$*), 24.9 (CH*Me$_2$*), 22.7 (CH*Me$_2$*), −8.8 (Zn*Me*) ppm. IR (nujol mull, KBr): $\tilde{\nu}$ = 3234 (m), 3140 (m), 1596 (s), 1518 (s), 1404 (s), 1365 (s), 1349 (m), 1318 (m), 1254 (s), 1243 (s), 1198 (w), 1183 (w), 1171 (w), 1136 (w), 1122 (m), 1102 (m), 1064 (w), 1047 (m), 975 (w), 938 (w), 881 (w), 853 (m), 814 (m), 752 (s), 686 (m), 634 (w) cm^{-1}.

$[\{Zn(OAr)\}_2(\mu\text{-}\{Me_2NC(N\textit{i}Pr)_2\})(\mu\text{-}NMe_2)]$ (7): 2,6-Di-*tert*-butylphenol (0.41 g, 2.00 mmol) in toluene (20 mL) was added dropwise at room temperature to a solution of **5** (0.50 g, 2.00 mmol) in toluene (30 mL). The resultant clear, pale-yellow solution was heated at 75 °C for 3 d, after which time a clear colourless solution had formed. The volatiles were removed to afford a waxy solid that was redissolved in hexane. Cooling of this solution to −30 °C afforded a small number of colourless crystals suitable for an X-ray analysis. ^{1}H NMR (C_6D_6, 298 K): δ = 7.36 (d, $^3J_{H,H}$ = 7.7, 4 H, *m*-C$_6$H$_3$), 6.86 (t, $^3J_{H,H}$ = 7.7, 2 H, *p*-C$_6$H$_3$), 2.98 (sept, $^3J_{H,H}$ = 6.4, 2 H, C*H*Me$_2$), 2.73 (s, 6 H, N*Me$_2$*), 2.16 (s, 6 H, N*Me$_2$*), 1.63 (s, 36 H, C*Me$_3$*), 0.87 (d, $^3J_{H,H}$ = 6.4, 12 H, CH*Me$_2$*) ppm. ^{13}C NMR (C_6D_6, 298 K): δ = 169.8 (*C*N$_3$), 165.6 (*C*), 138.2 (*C*), 125.1 (*C*H), 115.9 (*C*H), 48.6 (*C*HMe$_2$), 44.2 (N*Me$_2$*), 40.2 (N*Me$_2$*), 35.6 (*C*Me$_3$), 31.8 (C*Me$_3$*), 26.1 (CH*Me$_2$*) ppm.

Table 4. Crystal structure and refinement data for **3**−**8**

	3	**4**	**5**	**6**	**7**	**8**
Empirical formula	$C_{26}H_{64}N_6Si_4Zn$	$C_{38}H_{80}N_6Si_4Zn$	$C_{20}H_{46}N_6Zn_2$	$C_{24}H_{45}N_3OZn$	$C_{39}H_{68}N_4O_2Zn_2$	$C_{26}H_{60}N_8Si_4Zn_2$
Formula mass	638.56	798.81	501.37	457.00	755.71	727.92
Temperature [K]	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal size [mm]	0.40 × 0.35 × 0.20	0.20 × 0.15 × 0.10	0.30 × 0.10 × 0.05	0.30 × 0.30 × 0.25	0.10 × 0.10 × 0.02	0.40 × 0.30 × 0.05
Crystal system	monoclinic	orthorhombic	orthorhombic	triclinic	monoclinic	monoclinic
Space group	*C*2/*c* (No. 15)	*Fddd* (No. 70)	*Fdd*2 (No. 43)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a [Å]	17.3585(4)	9.8360(3)	21.5372(11)	10.5249(2)	9.7245(2)	10.6494(2)
b [Å]	8.7203(2)	30.3263(9)	27.5586(15)	10.5294(2)	27.4359(6)	11.4158(4)
c [Å]	26.1372(6)	32.0293(9)	8.8220(4)	13.2813(3)	16.0939(2)	15.7858(4)
α [°]	90	90	90	78.008(1)	90	90
β [°]	94.137(1)	90	90	73.935(1)	104.185(1)	100.008(1)
γ [°]	90	90	90	66.487(1)	90	90
V [Å^3]	3946.11(16)	9554.0(5)	5236.2(5)	1288.99(5)	4162.94(14)	1889.90(7)
Z	4	8	8	2	4	2
D_c [Mg·m^{-3}]	1.08	1.11	1.27	1.18	1.21	1.28
Absorption coefficient [mm^{-1}]	0.77	0.65	1.85	0.97	1.19	1.42
θ range for data collection [°]	3.78 to 25.60	3.85 to 25.00	4.28 to 25.02	3.79 to 24.72	3.72 to 25.02	3.80 to 24.73
Reflection collected	11770	10132	14344	16240	61410	11043
Independent reflections	3509 (R_{int} = 0.060)	2079 (R_{int} = 0.0481)	2233 (R_{int} = 0.065)	4347 (R_{int} = 0.050)	7332 (R_{int} = 0.082)	3205 (R_{int} = 0.048)
Reflection with $I > 2\sigma(I)$	2836	1714	2077	3700	5443	2780
Data/restraints/parameters	3509/0/168	2079/0/113	2233/1/128	4347/0/269	7332/0/428	3205/0/181
Goodness-of-fit on F^2	1.017	1.060	1.050	1.018	1.060	1.044
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.043, wR_2 = 0.102	R_1 = 0.044, wR_2 = 0.099	R_1 = 0.038, wR_2 = 0.087	R_1 = 0.035, wR_2 = 0.075	R_1 = 0.051, wR_2 = 0.105	R_1 = 0.030, wR_2 = 0.069
R indices (all data)	R_1 = 0.059, wR_2 = 0.110	R_1 = 0.058, wR_2 = 0.107	R_1 = 0.044, wR_2 = 0.090	R_1 = 0.046, wR_2 = 0.079	R_1 = 0.079, wR_2 = 0.117	R_1 = 0.039, wR_2 = 0.072
Largest diff. peak/hole [e·Å^{-3}]	0.28/−0.30	0.58/−0.47	0.37/−0.38	0.27/−0.36	0.69/−0.42	0.34/−0.42

[Zn(hpp){N(SiMe$_3$)$_2$}]$_2$ (8): A solution of hppH (0.18 g, 1.29 mmol) in toluene (20 mL) was added dropwise to a toluene solution (25 mL) of [Zn{N(SiMe$_3$)$_2$}$_2$] (0.50 g, 1.29 mmol) at room temperature. No visible change was observed. The solution was stirred at room temperature for 18 h, after which time the volatile components were removed in vacuo to afford [Zn(hpp)N(SiMe$_3$)$_2$]$_2$ as a white powder. Yield: 0.43 g (90%). Analytically pure samples for applications in polymerisation experiments were obtained by recrystallisation of a sample of **7** from hexane at −30 °C, affording colourless parallelepipedal crystals. $C_{26}H_{60}N_8Si_4Zn_2$ (727.92): calcd. C 42.90, H 8.31, N 15.39; found C 43.05, H 8.20, N 15.27. ^{1}H NMR (C$_6$D$_6$, 298 K): δ = 3.22 (m, 8 H, hpp-C*H$_2$*), 2.52 (t, $^3J_{H,H}$ = 6.4, 8 H, hpp-C*H$_2$*), 1.61 (quint, $^3J_{H,H}$ = 5.9, 8 H, hpp-C*H$_2$*), 0.36 (s, 36 H, Si*Me$_3$*) ppm. ^{13}C NMR (C$_6$D$_6$, 298 K): δ = 161.6 (*C*N$_3$), 47.9 (hpp-*C*H$_2$), 43.7 (hpp-*C*H$_2$), 23.8 (hpp-*C*H$_2$), 5.6 (Si*Me$_3$*) ppm. MS (EI$^+$): *m*/*z* = 347 [(hpp)Zn{N(SiMe$_3$)$_2$ − Me]$^+$.

X-ray Crystallographic Study: Details of the crystal data, intensity collection and refinement for complexes **3**−**8** are listed in Table 4. Crystals were covered with oil and suitable single crystals were selected under a microscope and mounted on a Kappa CCD diffractometer. The structures were refined with SHELXL-97.[47] Additional features are: [Zn{(Me$_3$Si)$_2$NC(N*i*Pr)$_2$}$_2$] (**3**): The molecule lies on a twofold rotation axis. [Zn{(Me$_3$Si)$_2$NC(NCy)$_2$}$_2$] (**4**): The molecule lies on a site of crystallographic 222 symmetry. [Zn{Me$_2$NC(N*i*Pr)$_2$}Me]$_2$ (**5**): The molecule lies on a twofold rotation axis. [Zn(OAr)Me{Me$_2$NC(N*i*Pr)(NH*i*Pr)}] (**6**): H on N(2) freely refined; all other H atoms riding. [Zn(hpp){N(SiMe$_3$)$_2$}]$_2$ (**8**): The molecule lies on a crystallographic inversion centre. CCDC-199300 (**3**), -199299 (**4**), -228536 (**5**), -228537 (**6**), -228538 (**7**) and -199301 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44 -1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the University of Sussex for additional financial support. We also wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury.

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Received January 15, 2004
Early View Article
Published Online May 5, 2004