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Synthesis of C_2 and C_s symmetric zinc complexes supported by bis(phosphinimino)methyl ligands and their use in ring opening polymerisation catalysis

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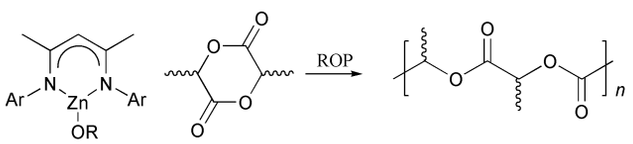
Synthetic routes to zinc complexes supported by sterically demanding bis(phosphinimino)methyl ligands are reported. Two aryl-substituted ligand precursors have been utilised, $[CH_2(Ph_2P{=}NC_6H_2Me_3\text{-}2,4,6)_2]$, **1**, and $[CH_2(Ph_2P{=}NPh)(Ph_2P{=}NC_6H_2Me_3\text{-}2,4,6)]$, **2**. The second of these is the first example of an asymmetric bis(phosphinimino)methane. These ligands are converted to three-coordinate RZnX complexes (R = **1**; X = Me, $N(SiMe_3)_2$; R = **2**; X = Me) with either C_2 or C_s symmetry in solution by reaction with either $ZnMe_2$ or $Zn[N(SiMe_3)_2]_2$ in toluene. All three derivatives have been shown to exist as three-coordinate monomers in the solid state by X-ray diffraction analysis. Protonolysis of these compounds with the bulky phenol 2,4-$^tBu_2C_6H_3OH$ or triphenylmethanol resulted in the isolation of a series of three-coordinate aryloxy or alkoxyzinc derivatives. In contrast, reaction with less sterically demanding alcohols resulted in protonation of the bis(phosphinimino)methyl ligand. A similar result was obtained from reaction of RZnMe (R = **1**) and triphenylsilanol and the product is the first example of a bis(triorganosiloxy)zinc compound to be structurally characterised. All the compounds have been examined for activity in ring opening polymerisation catalysis of *rac*-lactide. The aryloxy and triphenylmethoxy derivatives are active catalysts; however, no evidence of true 'living' behaviour or stereocontrol of diastereomer insertion has been observed.

Introduction

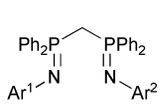
Several recent reports have described the synthesis of three- and four-coordinate zinc complexes supported by sterically demanding β-diketiminate ligands.[1] Much of this work is motivated by a drive toward the realisation of metalorganic catalysts that will affect ring opening polymerisation (ROP) of cyclic ethers or esters and exert some level of stereocontrol upon successive monomer coordination and insertion.[2] Among the most prominent are the alkoxyzinc β-diketiminate complexes, **I**, first reported by Coates and coworkers and demonstrated to effect remarkable stereospecific monomer insertion in the living ROP of D,L-lactide.[1a] The biocompatible polyester poly(lactide) (PLA) has been identified as a particularly important material due to the renewable nature of its feedstock. As the monomer is most commonly available in racemic form, the tacticity and mechanical properties of the resultant polymer are dependent upon the relative rates of diastereomer insertion and the resultant sequence of stereocentres after ROP.[3,4]



I DL-lactide polylactide

For example, polymerisation of *rac*-lactide by **I** when R = ^{i}Pr and Ar = 2,6-diisopropylphenyl results in heterotactic PLA, containing successive pairs of -(*RR*)- and -(*SS*)- stereosequences. This alternating enchainment of D- and L-lactide has been attributed to a chain end control mechanism in which the sterically demanding β-diketiminate ligand amplifies the influence of the sterogenic centre of the last inserted monomer.[1a]

Our current efforts in this area are prompted by these observations and are a continuation of our program of study that seeks to apply bulky and kinetically stabilising ligand systems to the 'taming' of reactive metal centres.[5–7] Historically, heteroatom-substituted methyl ligands, $(X)_nH_{3-n}C^-$ [*e.g.* X = R_3Si, n = 1–3;[8] X = R_2P(III), R_2P(V), n = 1,2[9]], have been at the forefront of such an approach and we were struck by the resemblance of the β-diketiminate ligand of **I** to anions produced by the deprotonation of bis(diphenylphosphinimino)methanes in which the phosphinimino nitrogen atoms bear aryl substituents with comparable steric demands. We were also intrigued to discover whether variation in catalyst symmetry would affect any observed stereocontrol in ROP. Similar principles have been effective in the design of catalysts for living α-olefin polymerisation where, for example, isospecific insertion of propylene has been achieved by judicious design of catalysts with overall C_2, C_s or C_1 symmetry.[10] A similar approach utilising unsymmetrical β-diketiminate ligands has very recently been described for living CO_2/epoxide polymerisation.[1e] We now wish to describe the application of the bis(diphenylphosphinimino)-methyls derived from the symmetrical methane **1** and the unsymmetrical methane **2** to the synthesis of three-coordinate zinc alkoxides with overall C_2 or C_s symmetry, and our preliminary observations of their use in the ring opening polymerisation of racemic lactide.



1; $Ar^1 = Ar^2$ = 2,4,6-trimethylphenyl
2; Ar^1= 2,4,6-trimethylphenyl; Ar^2 = phenyl

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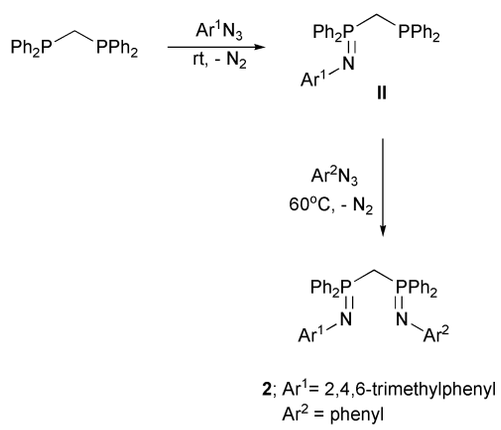
Results and discussion

The bis(mesityl)-substituted bis(diphenylphosphinimino)-methane **1** was synthesised according to the method reported by Bochmann and coworkers in which bis(diphenylphosphino)-methane (dppm) is oxidised with two equivalents of mesityl azide at 60 °C.[11] The unsymmetrical compound **2** may be synthesised by careful oxidation of dppm with a single equivalent of mesityl azide at room temperature followed by addition of a toluene solution of phenyl azide and heating to 60 °C (Scheme 1).



Scheme 1

Although the intermediate phosphiniminophosphine **II** was not isolated, its formation was inferred from the molecular ion at *m*/*z* 518 observed in the 70 eV mass spectrum of a sample taken from the reaction mixture prior to addition of phenyl azide. The $^{31}P\{^{1}H\}$ NMR spectrum of the same sample indicated quantitative consumption of dppm and showed two doublet signals typical of an AX spin pattern at −7.4 and −4.9 ppm, with a homonuclear $^{2}J_{PP}$ coupling of 7.3 Hz. Compound **2** was isolated as a pale yellow powder after washing with pentane and could be obtained as analytically pure, pale yellow crystals after crystallisation from diethyl ether. Its formation was apparent from the appearance of a molecular ion peak at *m*/*z* 608 in the mass spectrum and the observation of a pair of doublets at −9.5 and 0.5 ppm ($^{2}J_{PP}$ = 18.2 Hz) as the only peaks in the $^{31}P\{^{1}H\}$ NMR spectrum. Compounds analogous to the intermediate **II** have been reported previously and have been shown, upon careful oxidation with the appropriate chalcogen, to yield asymmetric disubstituted methane derivatives containing both iminophosphino and chalcogenophosphino functions [*i.e.* $CH_2(Ph_2P{=}NR)(Ph_2P{=}E)$; E = O, S].[12] Compound **2** is, however, to the best of our knowledge, the first example of a bis(phosphinimino)methane bearing dissimilar nitrogen-bound substituents. The unsymmetrical structure was confirmed by a single crystal X-ray diffraction analysis performed on a sample crystallised by slow evaporation of a diethyl ether solution in the open atmosphere. The molecular structure of **2** along with the numbering scheme used is illustrated in Fig. 1; selected bond lengths and angles are given in Table 1 and details of the X-ray analysis are given in Table 3 (see Experimental). The structure consists of pairs of molecules that are hydrogen bonded through the mesityl-bound nitrogen to a water molecule lying on a crystallographic 2-fold axis. The P=N [P(1)–N(1) 1.573(2) Å] bond of the mesityl-containing molecular fragment is slightly longer than that of the corresponding phenyl-linked P(2)–N(2) measurement [1.555(3) Å], reflecting the additional intermolecular interaction. Both distances are, however, comparable to values determined in other structurally characterised phosphiniminomethanes and bis(phosphinimino)methanes.[13]

The zinc methyl compounds [{$CH(Ph_2P{=}NC_6H_2Me_3$-2,4,6)$_2$}-ZnMe], **3**, and [{$CH(Ph_2P{=}NPh)(Ph_2P{=}NC_6H_2Me_3$-2,4,6)}-ZnMe], **4**, were obtained straightforwardly by room temperature addition of one equivalent of dimethylzinc to toluene solutions of **1** and **2**, respectively. Reaction under these conditions resulted in the generation of one equivalent of methane and the isolation of **3** and **4** in high yield as colourless, air-sensitive crystalline solids after crystallisation from toluene (Scheme 2).

Table 1 Selected bond lengths (Å) and angles (°) for compounds **2**–**5**

	2	**3**[a]	**4**[a]	**5**
Zn–N(1)	—	1.988(4)	2.011(3)	1.977(4)
Zn–N(2)	—	1.992(5)	2.028(3)	1.994(4)
Zn–C	—	1.932(7)	1.951(4)	1.907(4)[b]
P(1)–N(1)	1.573(3)	1.606(5)	1.609(3)	1.634(4)
P(2)–N(2)	1.555(3)	1.611(5)	1.628(3)	1.629(4)
P(1)–C(1)	1.816(4)	1.715(6)	1.719(4)	1.717(5)
P(2)–C(1)	1.820(3)	1.705(6)	1.722(4)	1.699(5)
N(1)–Zn–C	—	121.7(3)	123.5(16)	123.56(17)[c]
N(2)–Zn–C	—	134.0(3)	132.2(16)	128.14(17)[d]
N(1)–Zn–N(2)	—	104.3(2)	103.94(12)	108.29(16)
Zn–N(1)–P(1)	—	122.1(3)	107.84(16)	111.5(2)
Zn–N(2)–P(2)	—	114.5(3)	106.63(16)	120.1(2)
N(1)–P(1)–C(1)	106.37(15)	110.8(3)	106.97(16)	115.2(2)
N(2)–P(2)–C(1)	106.95(15)	112.3(3)	107.66(17)	109.5(2)
P(1)–C(1)–P(2)	122.25(19)	133.2(4)	129.9(2)	123.7(3)

[a] Values given for Zn(1)-containing molecule only. [b] Value for Zn–N(3). [c] Value for N(1)–Zn–N(3). [d] Value for N(2)–Zn–N(3).

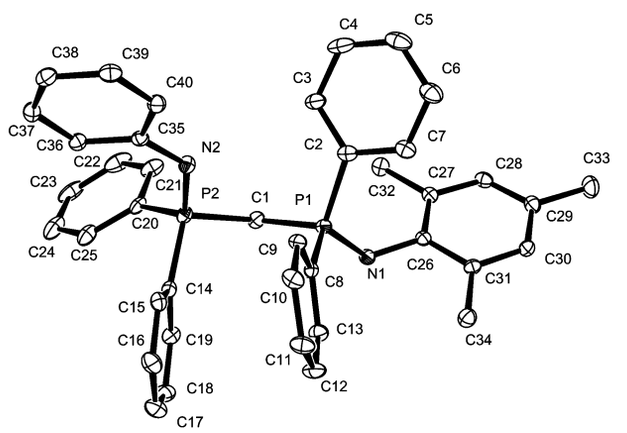
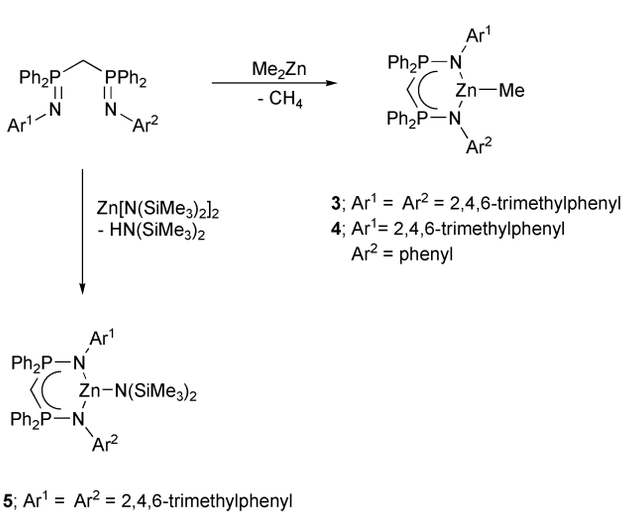


Fig. 1 Molecular structure of **2**. Water of crystallisation and H atoms omitted for clarity (20% probability ellipsoids).

The amidozinc derivative [{$CH(Ph_2P{=}NC_6H_2Me_3$-2,4,6)$_2$}-$ZnN(SiMe_3)_2$], **5**, was obtained similarly by addition of a toluene solution of **1** to $Zn[N(SiMe_3)_2]_2$. Compounds **3**–**5** have been completely characterised by microanalysis, mass spectrometry



Scheme 2

and multinuclear NMR spectroscopy. C_2 symmetry in solution was deduced from the simplicity of the collated NMR data for compounds **3** and **5**. The respective $^{31}P\{^1H\}$ NMR spectra consisted of singlets at 29.1 and 33.1 ppm, representing downfield shifts of 44.2 and 48.2 ppm from the resonance observed for free **1**. In the $^{13}C\{^1H\}$ NMR spectra the methanide carbon centres in both **3** and **5** appear as triplets centred at 16.0 and 17.7 ppm, respectively, with associated $^1J_{PC}$ values of 143.5 and 134.2 Hz for coupling to the two equivalent phosphorus nuclei. The asymmetric chelate structure of **4** is evident from the observation of two doublets ($^2J_{PP}$ = 8.5 Hz) in the $^{31}P\{^1H\}$ NMR spectrum which display similar downfield chemical shifts of 23.7 and 26.1 ppm. The identity of the bis(phosphinimino)methyl derivatives **3**, **4**, and **5** was confirmed by X-ray diffraction analysis and the molecular structures are illustrated in Figs. 2, 3 and 4 respectively. Selected bond lengths and angles are given in Table 1 and details of the X-ray analyses presented in Table 3.

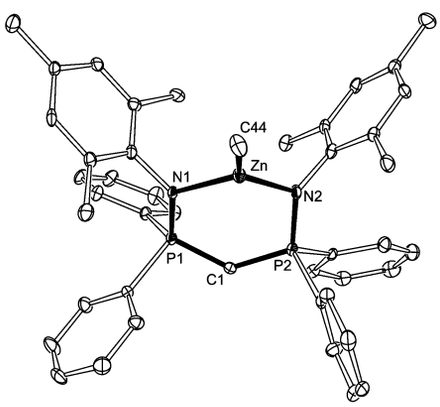


Fig. 2 Molecular structure of the Zn(1)-containing molecule of **3**. H atoms omitted for clarity (20% probability ellipsoids).

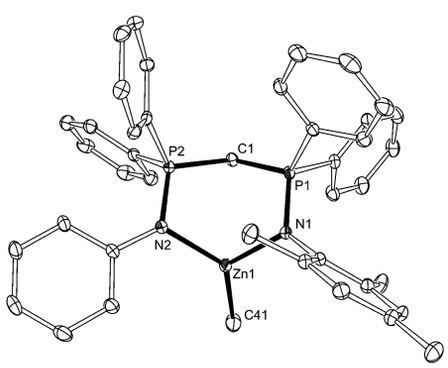


Fig. 3 Molecular structure of the Zn(1)-containing molecule of **4**. H atoms omitted for clarity (20% probability ellipsoids).

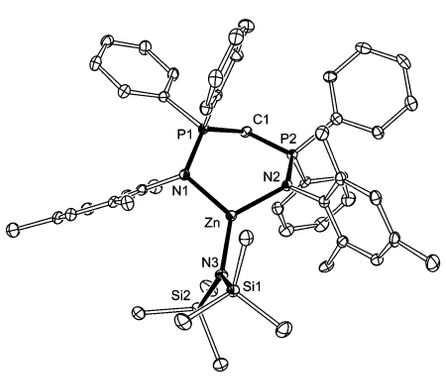


Fig. 4 Molecular structure of **5**. H atoms omitted for clarity (20% probability ellipsoids).

The crystal structures of both **3** and **4** contain two independent molecules of similar geometry. In each case the molecular parameters discussed relate to the Zn(1)-containing molecule. As in the analogous trimethylsilyl-substituted complex [ZnMe{$HC(Ph_2P{=}NSiMe_3)_2$}][14] and in several of the recently described alkyl and dialkylamido zinc derivatives of bulky β-diketiminate ligands,[1] all three compounds are monomeric and comprise a six-membered metallacyclic structure in which the ligand behaves as a bidentate chelate and the zinc centres are three coordinate. All three molecules contain zinc in a distorted trigonal planar environment. The high degree of coplanarity is indicated by the sums of angles subtended by the bonds around zinc which are 360.0(8), 359.6(6) and 360.0(6)° for **3**, **4** and **5** respectively. The increased steric demands of the bulky $(Me_3Si)_2N$ group of **5** cause the N–P–C–P–N–Zn chelate to adopt a twist-boat form which minimises interaction with the mesityl substituents while the methyl derivatives **3** and **4** take on distorted boat conformations (Fig. 5). This distortion is rather more pronounced in the two independent molecules of **4** and decreases the Zn(1)–C(1) separation to less than 2.8 Å. A number of structurally characterised bis(diphenylphosphinimino)methyl complexes have been shown to contain direct metal to methanide carbon bonds.[15] The distortion observed in **4** (and also compound **8**, *vide infra*) indicate that the reduced steric demands introduced by replacement of a mesityl substituent by phenyl are sufficient to allow a similar interaction to develop in zinc derivatives of **2**. This interaction is best regarded as electrostatic in origin, given the closed shell configuration of the Zn^{2+} ion. Comparable distortions have not been observed in metal derivatives of β-diketiminate ligands where charge is delocalised *via* planar sp^2 carbon rather than the tetrahedral P(v) centres of anions derived from **1** and **2**. As a consequence the central carbon atom of such bis(diphenylphosphinimino)methyl ligands exhibits a higher degree of carbanionic character. Recent calculations performed on the square planar nickel complex [NiBr{$HC(Ph_2P{=}NC_6H_3{}^iPr_2$-2,6)$_2$}] have shown that comparable negative charge resides on the methanide carbon centre and the nitrogen donors of the ligand chelate.[11b] The ligand frameworks of **3**, **4** and **5** nevertheless provide evidence for considerable delocalisation of charge *via* the P–N linkages. The P–C(1) bonds are shortened in comparison to typical P–C σ bonds while the P–N bond distances are elongated compared to the corresponding values in **2** (Table 1) and other structurally characterised bis(phosphinimino)-methanes [*e.g.* for $H_2C(Ph_2P{=}NSiMe_3)_2$ P–C(1) = 1.825(1), P–N = 1.536(2) Å; P–C–P = 124.94(15)°].[13a] The decreased Zn–C(1) distance of **4** is also accompanied by a lengthening of the Zn(1)–N(1) and Zn(1)–N(2) bond lengths [2.011(3), 2.028(3) Å] in comparison to the analogous measurements in **3** [1.988(4), 1.992(5) Å]. These values are, however, longer than those usually observed in β-diketiminato derivatives of zinc bearing similar co-ligands {*e.g.* in [$HC(CMeNC_6H_3{}^iPr_2$-2,6)$_2$ZnMe],[1d] the Zn–N distances are 1.940(18) and 1.9428(18) Å while in the analogous $(Me_3Si)_2N$ derivative they are 1.949(2) Å [1a]} but shorter than in the three-coordinate bis(3-*tert*-butylpyrazolyl)hydroborato derivative [{η^2-BH_2(3-^{t}Bupz)$_2$}ZnC$(CH_3)_3$] [2.040(5), 2.045(6) Å].[16]

Synthesis of bis(diphenylphosphinimino)methylzinc alkoxides

Three-coordinate alkoxyzinc β-diketiminates have been successfully applied in the living ROP of D,L-lactide.[1] We thus sought to investigate conditions under which analogous complexes supported by bis(diphenylphosphinimino)methyl ligands could be prepared from compounds **3**–**5**. Attempted protonolysis of **3** with a single equivalent of 2,6-di-*tert*-butyl phenol in toluene gave no reaction even under reflux conditions due, most likely, to the extremely hindered nature of the phenolic hydroxy group. Conversely, treatment of **3** with equimolar quantities of either 2,4-di-*tert*-butylphenol or triphenylmethanol in toluene

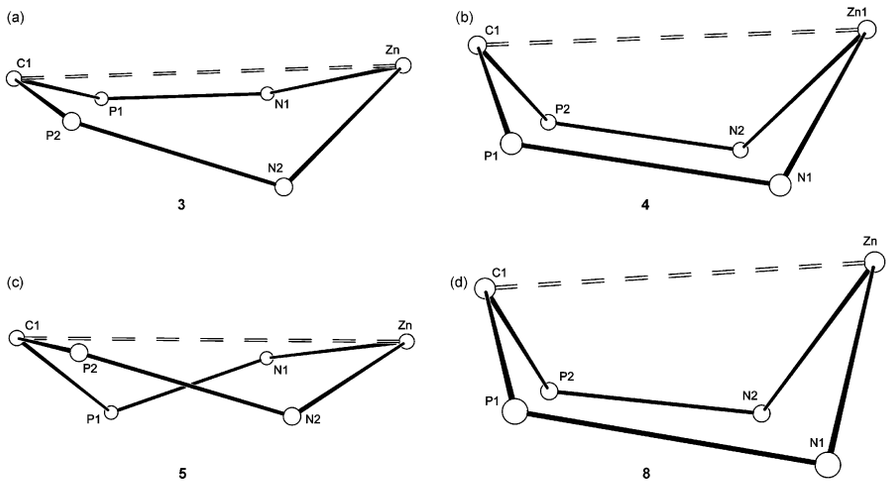
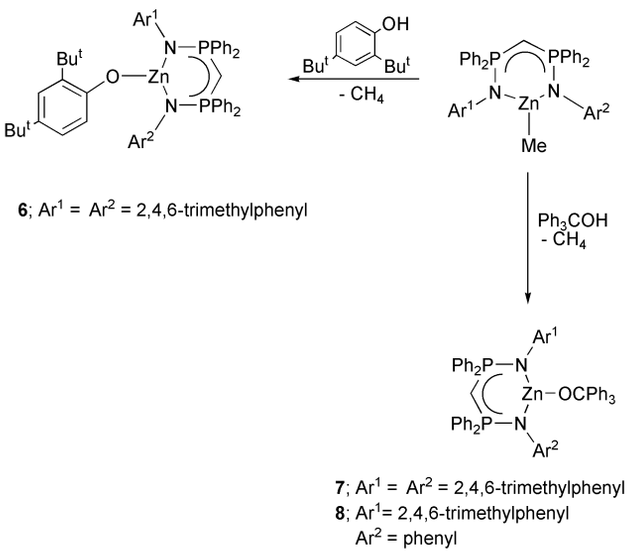


Fig. 5 N–P–C–P–N–Zn chelate cores of (a) **3**, (b) **4**, (c) **5** and (d) **8**, showing the respective boat and twist-boat conformations. For **3**, **4** and **8** (boat conformation) the respective angles defined by the P(1)–C(1)–P(2) and N(1)–Zn–N(2) least square planes and the P(1)–N(1)–P(2)–N(2) plane are for **3**: 14.84, 37.06°; **4**: 48.63, 59.56°; and **8**: 57.69, 71.36°. For **5** (twist-boat) the angle between the least squares planes defined by P(1)–C(1)–P(2)–N(2) and Zn–N(1)–N(2)–P(1) is 42.15°.



Scheme 3

at room temperature resulted in the clean elimination of a single equivalent of methane and the formation of the zinc aryloxy and alkoxy derivatives **6** and **7** in good yield (Scheme 3).

Compounds **6** and **7** displayed similar spectroscopic features to those described for the C_2 symmetric precursors **3** and **5**. In both cases retention of a symmetrical chelated $[CH(Ph_2PNC_6H_2Me_3\text{-}2,4,6)_2]^-$ anion was confirmed by the observation of a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at 33.0 ppm for **6** and 32.6 ppm for **7**. Similar treatment of **4** with Ph_3COH also provided the asymmetrically chelated alkoxyzinc derivative **8** which was identified by the observation of two doublets, at 28.1 and 27.0 ppm ($^2J_{PP}$ = 7.8 Hz), in the $^{31}P\{^1H\}$ NMR spectrum.

The molecular structures of compounds **6**–**8** were determined by single crystal X-ray diffraction studies. These confirmed the monomeric nature of all three compounds. The results are illustrated in Figs. 6–8 and selected bond lengths and angles are given in Table 2. A summary of the crystallographic analyses is provided in Table 4 (see Experimental). An approximately planar, distorted trigonal N_2ZnO coordination environment was confirmed for compounds **6**, **7** and **8** with respective sums of angles around the metal of 358.7, 358.7 and 356.85°. The slightly increased perturbation to planar coordination that is indicated by the last of these figures may be attributed to the pronounced boat conformation adopted by the

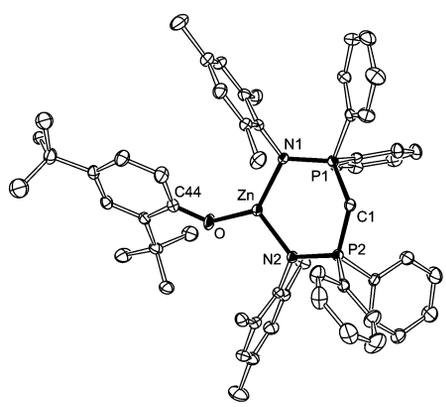


Fig. 6 Molecular structure of **6**. H atoms omitted for clarity (30% probability ellipsoids).

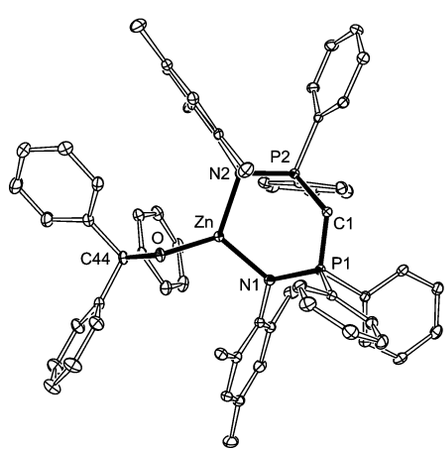


Fig. 7 Molecular structure of **7**. H atoms omitted for clarity (20% probability ellipsoids).

chelate ligand in **8**. This permits a close Zn–C(1) contact of 2.464(4) Å [Fig. 5(d)], which is considerably shorter than that observed in the parent methyl derivative **4** and, most likely, a result of the increased electronegativity of the triphenylmethoxy substituent. Comparable effects upon the individual P–N, P–C and Zn–N bond lengths around the chelate ring are also observed. The Zn–N [1.928(3), 1.937(2) Å] and Zn–O [1.837(3) Å] bonds of the aryloxy derivative **6** are notably shorter than in any of the other compounds discussed while

Table 2 Selected bond lengths (Å) and angles (°) for compounds **6**–**9**

	6	**7**	**8**	**9**
Zn–N(1)	1.928(3)	1.988(3)	2.034(3)	2.067(3)
Zn–N(2)	1.937(2)	1.970(3)	2.010(3)	2.081(3)
Zn–O	1.837(3)	1.859(2)	1.846(3)	1.894(3)[a]
				1.887(3)[b]
P(1)–N(1)	1.630(3)	1.635(5)	1.611(3)	1.590(4)
P(2)–N(2)	1.637(3)	1.634(3)	1.619(3)	1.594(4)
P(1)–C(1)	1.712(3)	1.700(3)	1.737(4)	1.816(5)
P(2)–C(1)	1.709(3)	1.716(3)	1.728(3)	1.814(4)
N(1)–Zn–O	130.98(11)	122.13(11)	115.06(12)	115.71(13)[c]
				103.60(13)[d]
N(2)–Zn–O	113.53(12)	124.68(11)	135.92(12)	102.42(13)[e]
				114.60(13)[f]
N(1)–Zn–N(2)	114.19(11)	111.93(11)	105.87(13)	102.13(13)
Zn–N(1)–P(1)	114.44(14)	120.52(15)	98.78(15)	121.92(18)
Zn–N(2)–P(2)	122.76(16)	108.26(14)	100.01(14)	128.39(19)
N(1)–P(1)–C(1)	114.92(16)	108.92(15)	105.74(17)	109.8(2)
N(2)–P(2)–C(1)	110.75(15)	116.56(15)	105.25(17)	111.0(2)
P(1)–C(1)–P(2)	127.7(2)	124.6(2)	127.7(2)	123.7(3)
Zn–O–C	133.9(3)	125.6(2)	128.3(2)	163.03(19)[g]
				168.5(2)[h]

[a] Zn–O(1). [b] Zn–O(2). [c] N(1)–Zn–O(1). [d] N(1)–Zn–O(2). [e] N(2)–Zn–O(1). [f] N(2)–Zn–O(2). [g] Zn–O(1)–Si(1). [h] Zn–O(2)–Si(2).

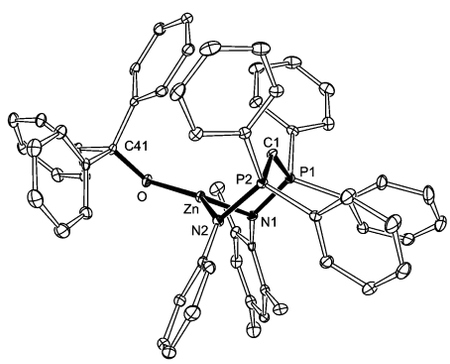
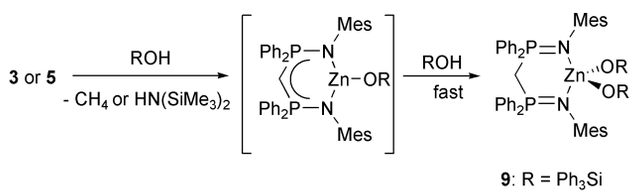


Fig. 8 Molecular structure of **8**. H atoms omitted for clarity (20% probability ellipsoids).

this latter distance is also less than that observed in previously characterised three-coordinate zinc derivatives bearing terminal phenolic substituents. For example in $[(2,6\text{-}^{t}Bu_2PhO)_2Zn(PMePh_2)]$, the Zn–O measurements are 1.844(4) and 1.864(4) Å.[17] The Zn–O–C(44) angle [133.9(3)°] in **6** is also wider than those of the triphenylmethoxy derivatives **7** and **8**, suggesting some level of O pπ to Zn pπ bonding. Aryloxyzinc complexes have been discussed in this context previously.[18]

The work of Coates and Chisholm has demonstrated that zinc β-diketiminate derivatives bearing larger co-ligands than isopropoxide or *tert*-butoxide are inferior for ROP of *rac*-lactide.[1a,c] This is believed to be associated with a slow rate of initiation which results in polymers with broad molecular weight distributions and higher than expected molecular weights. The putative initiating aryloxy and triphenylmethoxy groups of compounds **6**, **7** and **8** were therefore judged to be excessively bulky. Attempts to synthesise compounds bearing smaller alkoxy substituents using the protolytic strategy outlined in Scheme 3 have, however, proved unsuccessful. Treatment of **3** or **5** with stoichiometric quantities of methanol, isopropanol or phenol resulted in protonation of the bis(phosphinimino)methyl ligand in addition to the desired elimination of methane or hexamethyldisilazane. This was demonstrated most clearly by the observation of free bis(phophinimino)-methane **1** at −16.4 ppm in the $^{31}P\{^{1}H\}$ NMR spectra of the crude isolated materials. These spectra also indicated that approximately half of the starting **3** remained unreacted. It appears likely therefore that in these cases protonation of the desired alkoxide is more rapid than of **3** itself leading to the formation of dialkoxyzinc derivatives further coordinated by the neutral bis(phosphinimino)methane **1** (Scheme 4 and see the siloxy derivative below). This behaviour is probably related to the size of the hydroxy-bearing reactant that is insufficiently bulky to prevent rapid protonolysis of the target compounds. A similar outcome has previously been observed from reactions of alcohols and alkylzinc compounds supported by insufficiently bulky β-diketiminate and tris(pyrazolyl)borate ligands.[1a,16]



Scheme 4

Chisholm *et al.* have reported that trialkylsiloxyzinc β-diketiminates and tris(pyrazolyl)borates are also active in the polymerisation of cyclic ethers and esters.[19] As an extension to the current study we therefore targeted analogous compounds supported by bis(diphenylphosphinimino)methyl ligands. Reaction of **3** with a single equivalent of triphenylsilanol resulted in protonation of the bis(phosphiminimo)methyl ligand in an identical fashion to that outlined above. We have been able to isolate the product of this reaction however, the bis(triphenylsiloxy)zinc derivative **9**, which was separated from unreacted **3** by fractional crystallisation and identified as a mononuclear bis(triphenylsiloxy)zinc complex by an X-ray diffraction analysis. The molecular structure is shown in Fig. 9 and selected bond distances and angles are given in Table 2. Compound **9** is the first bis(triorganosiloxy)zinc compound to have been structurally characterised.[20] The distorted tetrahedral coordination at zinc is provided by two terminal $OSiPh_3$ fragments and a single molecule of the bis(diphenylphosphinimino)methane **1**. The lengths of the Zn–O bonds in **9** [1.894(3), 1.887(3) Å] are somewhat longer than in the only other structurally characterised compounds containing terminal (non-bridging) Zn–O–Si linkages, the tris(pyrazolyl)borato derivatives $[\{\eta^3\text{-}HB(3\text{-}^{t}Bupz)_3\}ZnOSiMe_3]$ [1.829(2) Å] and $[\{\eta^3\text{-}HB(3\text{-}^{t}Bupz)(3,5(CF_3)_2pz)_2\}ZnOSiMe_3]$ [1.792(2) Å].[19] The Zn–O–Si angles observed in both of these compounds [175.0(1) and 175.9(2)°, respectively] are also wider than either the Zn–O(1)–Si(1) [163.03(19)°] or Zn–O(2)–Si(2) [168.5(2)°] angles in **9**. This is

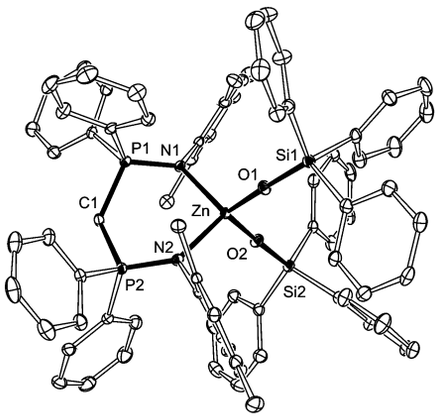


Fig. 9 Molecular structure of **9**. H atoms omitted for clarity (20% probability ellipsoids).

probably a reflection of the more crowded and asymmetric coordination environment provided by the bis(phosphinimino)methane and triphenylsiloxy co-ligands.

Polymerisation studies

We have conducted preliminary experiments to investigate the utility of the zinc complexes **3**–**9** in the polymerisation of *rac*-lactide. Attempts to initiate ring opening polymersiation of 100 equivalents of monomer at room temperature in CH_2Cl_2 (the conditions reported to give the highest degree of stereocontrol for complexes **I**) in all cases have been unsuccessful and gave no appreciable evidence of polymer formation even over a period of several weeks (<1% by ^{1}H NMR). These reactions were repeated in toluene solution at 60 °C. The methyl derivatives **3** and **4**, the amide **5** and the siloxide **9** were also inactive under these conditions. The aryloxy derivative **6** and both the triphenylmethoxy derivatives **7** and **8**, however, are active for the ROP of *rac*-lactide requiring 4, 5, and 2 h, respectively, to effect >95% conversion of 100 equivalents of monomer. This activity is lower than that reported for other zinc-based systems,[1] but comparable to a recently reported Sn(II) catalyst,[21] while the enhanced rate of monomer consumption in **8** is most likely related to the decreased steric demands of the unsymmetrical ligand. These data, taken in isolation, however, are an unreliable indicator of the nature of the polymerisation process. The molecular weights of the isolated polymers determined by gel permeation chromatography are, in general, higher than expected for a genuine living process in which each molecule of zinc catalyst mediates the growth of an individual polymer chain. The observed polydispersities were also somewhat erratic, ranging from effectively monodisperse (M_w/M_n = 1.1) to values in excess of 2 for reactions undertaken with ostensibly identical reagents and conditions. This behavior may be associated with the relatively large initiating groups of **6**–**8** effectively inhibiting monomer coordination. Similar observations have been made previously with regard to catalysts based on zinc β-diketiminato derivatives,[1] and Sn(II) triphenylmethoxides supported by sterically demanding amidinate ligands.[22] The observed activity may therefore be initiated by minor impurities in either the catalyst or monomer inputs. Room temperature addition of a single equivalent of *rac*-lactide to **6**, **7**, or **8** in C_6D_6 in an NMR tube resulted in complete monomer consumption (by ^{1}H NMR) and the appearance of several new peaks in the ^{31}P{^{1}H} NMR spectrum, including resonances close to those attributed to the free ligands **1** and **2**. Although this observation could arise from hydrolysis by adventitious moisture in the monomer precursor, the inactivity of all the compounds under study in CH_2Cl_2 and of **3**, **4** and **5** at elevated temperatures mitigates against this [our lactide (Aldrich) was sublimed prior to use and its integrity ensured by storage in a drybox for the duration of this study]. The above noted carbanionic character of the PCP bridgehead carbon centre may also direct the behaviour of these systems. For example, the closely related compound [ZnMe{HC(Ph_2P=$NSiMe_3$)$_2$}] has been reported to react with cumulenes such as adamantyl isocyanate by nucleophilic addition of the methanide to the isocyanate carbon to form a new C–C bond.[14] Further studies are therefore in progress to establish the initial products from reaction of the present zinc complexes with enantiopure lactide and other simple organic molecules. A fundamental requirement of these and similar zinc complexes is that the ligand remains bound as an innocent spectator during chain growth. Although reaction at the methanide centre need not preclude the possibility of stereoselective insertion, any behaviour of this nature will require a re-evaluation of the mode of action of the active species. We have noted no evidence for a tacticity bias from analysis of the poly(lactide) derived from ring opening by **6**, **7** or **8** by selective decoupling of the methine protons in the ^{1}H NMR. In all cases the data indicate the formation of effectively atactic poly(lactide).[23]

We are continuing to develop the chemistry of related ligands (both symmetrical and unsymmetrical) bearing more sterically demanding aryl substituents and are pursuing metathetical routes to low-coordinate metal complexes bearing less bulky alkoxy substituents.

Experimental

All reactions were conducted under an atmosphere of dry argon and manipulated either on a double manifold vacuum line or in a dinitrogen-filled drybox operating at less than 1 ppm of O_2. Toluene was purified by distillation from molten sodium. Zn[N($SiMe_3$)$_2$]$_2$,[24] mesityl azide,[11] phenyl azide[25] and **1**[11] were synthesised by literature procedures. NMR spectra were recorded at 300.1 (^{1}H), 75.5 (^{13}C), 99.4 (^{29}Si), and 121.5 (^{31}P) MHz in C_6D_6 unless otherwise stated; intensities of the quaternary and ^{29}Si signals were enhanced by polarisation transfer. Chemical shifts of ^{1}H and ^{13}C NMR were referenced internally to residual solvent resonances. ^{31}P NMR were referenced externally to H_3PO_4 (85% aqueous solution). Mass spectra were obtained at 70 eV; in assignments, mes = 2,4,6-trimethylphenyl. Elemental analyses were performed by SACS at the University of North London.

[CH_2(Ph_2P=NPh)(Ph_2P=$NC_6H_2Me_3$-2,4,6)] 2

A toluene (20 mL) solution of mesityl azide (2.51 g, 15.6 mmol) was added at room temperature to a toluene (30 mL) solution of dppm (6.00 g, 15.6 mmol) causing immediate gas evolution. This was stirred for 14 h at room temperature before a toluene (20 mL) solution of phenyl azide (1.86 g, 15.6 mmol) was added and the yellow solution heated to 60 °C for 6 h. *In vacuo* removal of volatiles yielded a yellow tar, which was triturated with pentane to produce a pale yellow powder. Crystallisation from diethyl ether at room temperature gave **2** as pale yellow microcrystals (8.10 g, 85%) A sample of **2** recrystallised in diethyl ether on the bench top provided pale yellow single crystals suitable for X-ray diffraction that proved to be a hemi-water solvate. Anal. calc. for $C_{40}H_{38}N_2P_2$: C 78.91, H 6.30, N 4.60. Found: C 78.87, H 6.26, 4.52%. ^{1}H NMR ($CDCl_3$, 298 K): δ 1.98 (s, 6H, *o*-Me), 2.18 (s, 3H, *p*-Me), 3.53 (t, 2H, PCH_2, $^2J_{PH}$ = 16.8 Hz), 6.46 (d, 2H, *o*-Ph), 6.71 (s, 2H, *m*-mes) 6.93–7.86 (m, *ca.* 23H, *m*,*p*-Ph, *o*,*m*,*p*-PhP). ^{13}C{^{1}H} NMR ($CDCl_3$, 298 K): δ 21.9 (*o*-Me), 27.7 (*p*-Me), 31.4 (CH_2P,), 117.5 (*p*-Ph), 122.8 (Ar), 123.1 (Ar), 128.1 (d, PhP, J_{PC} = 12.8 Hz), 128.9 (Ar), 129.7 (Ar), 130.3 (Ar), 131.4 (Ar), 131.6 (Ar), 132.0 (d, PhP, J_{PC} = 12.8 Hz), 132.7 (d, PhP, J_{PC} = 10.6 Hz), 134.8 (Ar), 137.3 (*o*-mes), 144.0 (i-mes), 151.2 (i-Ph). ^{31}P{^{1}H} NMR (298 K): δ −9.5, 0.5 ($^2J_{PP}$ = 18.2 Hz). MS: *m*/*z* 608 [15%, M^+], 474 [20, $Ph_2PCH_2Ph_2PNPh$], 398 [100, $PhPCH_2Ph_2PNPh$], 367

[25], 318 [40, Ph_2PNmes], 290 [65, CH_2Ph_2PNPh], 276 [35, Ph_2PNPh], 241 [10, PhPNmes], 199 [30, PhPNPh], 183 [60], 121 [40, $mesH_2$], 77 [20, Ph].

[{CH(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}ZnMe] 3

A solution of $ZnMe_2$ in toluene (3.08 mmol, 1.4 mL of a 2.0 M solution, Acros) was added at room temperature to a solution of **1** (2.0 g, 3.08 mmol) in toluene (20 mL). After initial gas evolution had subsided, the pale yellow solution was stirred for 14 h. The solution was concentrated to incipient crystallisation, warmed to redissolve precipitated solids and then allowed to cool slowly to provide large pale yellow crystals of **3**·$(C_7H_8)_{0.25}$ suitable for X-ray diffraction analysis (1.76 g, 76%). Anal. calc. for $C_{44}H_{46}N_2P_2Zn(C_7H_8)_{0.25}$: C 72.95, H 6.44, N 3.72. Found: C 72.71, H 6.59, 3.73%. ^{1}H NMR (298 K): δ −0.59 (s, 3H, ZnMe), 1.52 (s, 1H, CH), 2.11 (s, 6H, *p*-Me), 2.15 (s, 12H, *o*-Me), 6.74 (s, 4H, *m*-mes), 6.95–7.05 (m, 12H, *m*,*p*-Ph), 7.74–7.80 (m, 8H, *o*-Ph). ^{13}C{^{1}H} NMR (298 K): δ −16.6 (ZnMe), 16.0 (t, CH_2P, $^1J_{PC}$ = 143.5 Hz), 20.8 (*p*-Me), 21.1 (*o*-Me), 127.8 (*o*-mes), 129.3 (*o*-Ph), 130.5 (*p*-Ph), 131.9 (*m*-mes), 132.8 (*m*-Ph), 135.9 (*p*-mes), 136.8 (dd, i-Ph, $^1J_{PC}$ = 90.6 Hz), 143.5 (i-mes). ^{31}P{^{1}H} NMR (298 K): δ 29.1. MS: *m*/*z* 729 [2%, M^+], 713 [8, $M^+ - CH_4$], 440 [30, Ph_2PCH_2PNmes], 332 [14, CH_3Ph_2PNmes], 319 [20, $Ph_2PNmesH$], 210 [35], 183 [20], 164 [5, PNmes], 143 [50, HNmes], 91 [100, NPh], 65 [20, Zn].

[{CH(Ph$_2$PNPh)(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)}ZnMe] 4

Compound **4** was synthesised in an analogous fashion from **2** (1.50 g, 2.47 mmol) and $ZnMe_2$ (2.47 mmol, 1.23 mL, of 2.0 M solution in toluene) and isolated as pale yellow crystals suitable for X-ray analysis after crystallisation from toluene (0.97 g, 57%). Anal. calc. for $C_{41}H_{40}N_2P_2Zn(C_7H_8)_{0.5}$: C 72.80, H 6.05, N 3.82. Found: C 72.82, H 5.97, N 3.80%. ^{1}H NMR (298 K): δ −0.68 (s, 3H, ZnMe), 1.34 (s, 1H, CH), 1.56 (s, 6H, *o*-Me), 1.98 (s, 3H, *p*-Me), 6.44 (d, 2H, *o*-Ph), 6.87–7.18 (m, 23H, *m*-mes, *m*,*p*-Ph, *o*,*m*-PhP), 7.65 (m, 4H, *p*-PhP). ^{13}C{^{1}H} NMR (298 K): δ −13.8 (ZnMe), 19.1 (CH_2P), 20.7 (*o*-Me), 21.5 (*p*-Me), 125.3 (*o*-mes), 127.5 (d, *o*-PhP, $^2J_{PC}$ = 11.3 Hz), 128.2 (Ar), 128.3 (d, *o*-PhP, $^2J_{PC}$ = 11.3 Hz), 128.5 (Ar), 128.7 (Ar), 129.0 (Ar), 130.3 (Ar), 131.0 (Ar), 131.8 (d, *m*-PhP, $^3J_{PC}$ = 9.8 Hz), 132.5 (d, *m*-PhP, $^3J_{PC}$ = 9.8 Hz), 133.3 (Ar), 135.6 (*p*-mes), 135.7 (dd, i-PhP, $^1J_{PC}$ = 90.6 Hz), 142.2 (i-Ph), 148.9 (i-mes). ^{31}P{^{1}H} NMR (298 K): δ 23.7, 26.1 ($^2J_{PP}$ = 8.5 Hz). MS: *m*/*z* 687 [30%, M^+], 671 [100, $M^+ - CH_4$], 487 [10], 370 [15], 330 [30], 290 [20], 198 [20], 183 [70], 122 [50], 77 [25].

[{CH(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}ZnN(SiMe$_3$)$_2$] 5

A solution of $Zn[N(SiMe_3)_2]_2$ (2.0 g, 5.20 mmol) in toluene (10 mL) was added at room temperature to a solution of **1** (3.38 g, 5.20 mmol) in toluene (25 mL) and the resulting pale yellow solution stirred for 14 h. Volatiles were removed *in vacuo* and the pale yellow solid produced crystallised by slow cooling of a warm saturated solution to room temperature to afford **5** as large colourless crystals suitable for X-ray diffraction analysis (3.89 g, 86%). Anal. calc. for $C_{49}H_{61}N_3P_2Si_2Zn$: C 67.22, H 7.04, N 4.80. Found: C 67.70, H 7.41, 4.41%. ^{1}H NMR (298 K): δ 0.19 (s, 18H, $SiMe_3$), 1.89 (s, 1H, CH), 2.10 (s, 6H, *p*-Me), 2.12 (s, 12H, *o*-Me), 6.70 (s, 4H, *m*-mes), 6.98 (m, 12H, *m*,*p*-Ph), 7.79 (m, 8H, *o*-Ph). ^{13}C{^{1}H} NMR (298 K): δ 5.5 ($SiMe_3$), 17.7 (t, CH_2P, $^1J_{PC}$ = 134.4 Hz), 20.7 (*p*-Me), 21.7 (*o*-Me), 125.6 (*o*-mes), 127.6 (dd, *o*-Ph, $^2J_{PC}$ = 5.7 Hz), 130.4 (*m*-mes), 130.7 (*p*-Ph), 133.4 (t, *m*-Ph, J_{CP} = 4.74 Hz) 136.3 (dd, i-Ph, $^1J_{PC}$ = 95.8 Hz), 136.4 (*p*-mes), 143.0 (i-mes). ^{31}P{^{1}H} NMR (298 K): δ 33.1. ^{29}Si{^{1}H} NMR (298 K): δ −4.4. MS: *m*/*z* 874 [2%, M^+], 858 [5, $M^+ - CH_4$], 712 [40], 440 [15, Ph_2PCH_2PNmes], 330 [25, $CHPh_2PNmes$], 319 [15, $Ph_2PNmesH$], 240 [15], 183 [30], 164 [15, PNmes], 146 [30], 91 [100, NPh].

[{CH(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}ZnOC$_6$H$_3$^{t}Bu$_2$-2,4] 6

A solution of 2,4-di-*tert*-butylphenol (0.28 g, 1.37 mmol) in toluene (10 mL) was added at room temperature to a solution of **3** (1.0 g, 1.37 mmol) in toluene (20 mL). The pale yellow solution was stirred for 14 h before concentration to incipient crystallisation. Warming to dissolve precipitated solids followed by slow cooling to room temperature afforded **6** as large colourless crystals suitable for an X-ray diffraction study (0.98 g, 78%). Anal. calc. for $C_{57}H_{64}N_2P_2OZn$: C 74.38, H 7.02, N 3.04. Found: C 74.35, H 7.09, 2.95%. ^{1}H NMR (298 K): δ 1.32 (s, 9H, ^{t}Bu), 1.51 (s, 9H, ^{t}Bu), 1.70 (s, 1H, CH), 2.10 (s, 6H, *p*-Me), 2.13 (s, 12H, *o*-Me), 6.05 (d, 1H, 6-$C_6H_3{}^tBu_2O$), 6.67 (s, 4H, *m*-mes), 6.75 (d, 1H, 4-$C_6H_3{}^tBu_2O$) 6.96 (m, 12H, *m*,*p*-Ph), 7.19 (s, 1H, 3-$C_6H_3{}^tBu_2O$), 7.75 (m, 8H, *o*-Ph). ^{13}C{^{1}H} NMR (298 K): δ 18.6 (CH_2P), 20.7 (*p*-Me), 21.5 (*o*-Me), 29.9 [$C(CH_3)_3$], 32.2 [$C(CH_3)_3$], 34.0 [$C(CH_3)_3$], 35.3 [$C(CH_3)_3$], 120.0 (Ar), 122.7 (Ar), 123.0 (Ar), 129.9 (Ar), 130.9 (Ar), 132.8 (Ar), 132.9 (Ar), 133.0 (Ar), 134.6 (Ar), 135.9 (Ar), 136.8 (*p*-mes), 142.1 (i-mes) 162.1 (i-$C_6H_3{}^tBu_2O$). ^{31}P{^{1}H} NMR (298 K): δ 33.0. MS: *m*/*z* 918 [15%, M^+], 713 [80], 517 [10], 440 [65, Ph_2PCH_2PNmes], 332 [25, CH_3Ph_2PNmes], 319 [45, $Ph_2PNmesH$], 240 [40], 191 [100], 134 [40], 91 [85, NPh], 57 [65].

[{CH(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}ZnOCPh$_3$] 7

Compound **7** was synthesised by the same general method as that outlined for **6** from **3** (1.0 g, 1.37 mmol) and triphenylmethanol (0.36 g, 1.37 mmol). Crystallisation from toluene at room temperature afforded **7**·(C_7H_8) as large colourless crystals suitable for an X-ray diffraction analysis (1.03 g, 70%). Anal. calc. for $C_{69}H_{66}N_2P_2OZn$: C 77.70, H 6.25, N 2.63. Found: C 77.67, H 6.30, N 2.52%. ^{1}H NMR (298 K): δ 1.72 (s, 1H, CH), 2.13 (s, 12H, *o*-Me), 2.13 (s, 6H, *p*-Me), 6.67 (s, 4H, *m*-mes), 6.96–7.31 (m, 27H, *m*,*p*-PhP, *o*,*m*,*p*-PhCO), 7.67 (m, 8H, *o*-PhP). ^{13}C{^{1}H} NMR (298 K): δ 17.6 (CH_2P), 21.0 (*p*-Me), 22.1 (*o*-Me), 83.7 (O*C*Ph), 125.6 (Ar), 125.9 (Ar), 127.9 (Ar), 128.8 (Ar), 130.0 (Ar), 131.0 (Ar), 132.6 (Ar), 133.3 (Ar), 135.1 (Ar), 136.4 (*p*-mes), 142.9 (i-mes) 154.7 (i-O*C*Ph). ^{31}P{^{1}H} NMR (298 K): δ 32.6. MS: *m*/*z* 973 [1%, M^+], 895 [1, M − PhH], 840 [2], 714 [5, $CH(Ph_2PNmes)Zn$], 650 [5, $CH_2(Ph_2PNmes)$], 440 [15, Ph_2PCH_2PNmes], 332 [10, CH_3Ph_2PNmes], 260 [45], 183 [70], 91 [100, HNPh].

[{CH(Ph$_2$PNPh)(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)}ZnOCPh$_3$] 8

Compound **8** was synthesised by the same general method outlined for **6** from **4** (1.0 g, 1.45 mmol) and triphenylmethanol (0.38 g, 1.45 mmol). Crystallisation from warm toluene provided **8** as colourless crystals suitable for an X-ray diffraction study (0.70 g, 51%). Anal. calc. for $C_{59}H_{52}N_2P_2OZn$: C 76.00, H 5.63, N 3.01. Found: C 76.08, H 5.62, N 2.98%. ^{1}H NMR (298 K): δ 1.71 (s, 1H, CH), 1.97 (s, 6H, *o*-Me), 2.17 (s, 3H, *p*-Me), 6.30 (d, 2H, *o*-Ph), 6.81–7.14 (m, 32H, *m*-mes, *m*,*p*-Ph, *o*,*m*-PhP), 7.84 (m, 8H, *o*-PhP). ^{13}C{^{1}H} NMR (298 K): δ 18.9 (CH_2P), 20.5 (*o*-Me), 21.2 (*p*-Me), 82.9 (O*C*Ph), 125.8 (Ar), 126.9 (Ar), 128.3 (Ar), 128.4 (Ar), 128.5 (Ar), 128.7 (Ar), 129.0 (Ar), 129.3 (Ar), 130.4 (Ar), 131.3 (Ar), 131.6 (Ar), 132.4 (Ar), 133.4 (Ar), 135.6 (Ar), 135.7 (Ar), 141.5 (i-Ph), 142.3 (i-mes), 154.7 (O*C*Ph). ^{31}P{^{1}H} NMR (298 K): δ 28.1, 27.0 ($^2J_{PP}$ = 7.3 Hz). MS: *m*/*z* 670 [80%], 593 [10], 398 [10], 330 [15], 290 [25], 243 [20], 183 [100], 105 [85], 77 [75].

[{CH$_2$(Ph$_2$PNC$_6$H$_2$Me$_3$-2,4,6)$_2$}Zn(OSiPh$_3$)$_2$] 9

A solution of triphenylsilanol (0.57 g, 2.07 mmol) in toluene (20 mL) was added to a solution of **3** (1.50 g, 2.07 mmol) in toluene (25 mL) at room temperature. The yellow solution was stirred for 14 h before removal of solvent to provide a pale yellow solid. ^{31}P{^{1}H} NMR of this displayed an approximate 1:1 mix of unreacted **3** and a signal characteristic of the

Table 3 Selected crystallographic and data collection parameters for compounds **2**–**5**

	2	**3**	**4**	**5**
Chemical formula	$C_{40}H_{38}N_2P_2{\cdot}½(H_2O)$	$C_{44}H_{46}N_2P_2Zn{\cdot}¼(C_7H_8)$	$C_{41}H_{40}N_2P_2Zn{\cdot}½(C_7H_8)$	$C_{49}H_{61}N_3P_2Si_2Zn$
Formula weight	617.67	753.17	734.13	875.5
T/K	173(2)	173(2)	173(2)	173(2)
Crystal system	Orthorhombic	Triclinic	Monoclinic	Monoclinic
Space group	*Fdd*2 (no.43)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no.14)	$P2_1/c$ (no.14)
a/Å	26.6838(6)	11.2619(5)	25.6605(3)	12.2060(2)
b/Å	53.8252(14)	18.4588(13)	14.7185(2)	19.8779(4)
c/Å	9.4022(2)	20.2548(13)	20.5047(2)	19.7239(5)
α/°	90	112.223(2)	90	90
β/°	90	95.261(4)	98.474(1)	100.129(1)
γ/°	90	92.019(4)	90	90
Z	16	4	8	4
V/Å^3	13 504.0(5)	3870.2(4)	7659.8(2)	4711.0(2)
D_c/Mg m^{-3}	1.22	1.29	1.27	1.23
μ/mm^{-1}	0.16	0.75	0.76	0.68
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.043, 0.088	0.065, 0.124	0.057, 0.136	0.065, 0.143
$R1$, $wR2$ (all data)	0.058, 0.095	0.110, 0.141	0.089, 0.152	0.090, 0.155
Measured/independent reflections/R_{int}	10 024/4977/0.050	20 269/9360/0.104	61 498/13 600/0.062	31 199/7435/0.094
Reflections with $I > 2\sigma(I)$	4217	6313	9703	5775

Table 4 Selected crystallographic and data collection parameters for compounds **6**–**9**

	6	**7**	**8**	**9**
Chemical formula	$C_{57}H_{64}N_2P_2OZn$	$C_{62}H_{58}N_2OP_2Zn{\cdot}C_7H_8$	$C_{59}H_{52}N_2P_2OZn$	$C_{79}H_{74}N_2O_2P_2Si_2Zn{\cdot}2(C_7H_8)$
Formula weight	920.41	1066.55	932.34	1451.16
T/K	173(2)	173(2)	173(2)	173(2)
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/c$ (no.14)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no.14)
a/Å	12.9453(7)	12.8791(2)	10.4249(3)	12.7106(3)
b/Å	14.0557(9)	26.6119(5)	12.5215(3)	21.5304(4)
c/Å	15.6630(9)	16.6536(4)	19.3876(5)	29.7106(8)
α/°	94.210(2)	90	96.599(1)	90
β/°	106.701(3)	100.941(1)	94.940(1)	101.289(1)
γ/°	110.514(3)	90	106.035(1)	90
Z	2	4	2	4
V/Å^3	2508.0(3)	5604.1(2)	2397.7(1)	7973.4(3)
D_c/Mg m^{-3}	1.22	1.264	1.29	1.21
μ/mm^{-1}	0.59	0.54	0.62	0.43
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.048, 0.094	0.049, 0.103	0.050, 0.093	0.059, 0.137
$R1$,$wR2$ (all data)	0.07, 0.106	0.074, 0.113	0.078, 0.103	0.092, 0.154
Measured/independent reflections/R_{int}	13 734/6926/0.053	27 200/7853/0.064	20 170/6629/0.100	33 679/10 993/0.072
Reflections with $I > 2\sigma(I)$	5141	5919	4927	7871

protonated **1**. Compound **9**·$(C_7H_8)_2$ was isolated by fractional crystallisation from toluene at room temperature as colourless needles suitable for an X-ray diffraction analysis (0.40 g, 27% based upon Ph_3SiOH). Anal. calc. for $C_{93}H_{90}N_2P_2O_2Si_2Zn$: C 76.97, H 6.26, N 1.93. Found: C 76.87, H 6.19, N 1.84%. ^{1}H NMR (298 K): δ 2.19 (s, 12H, *o*-Me), 2.25 (s, 6H, *p*-Me), 3.91 (t, 2H, CH_2P), 6.74–6.67 (s, 4H, *m*-mes), 6.92–7.42 (m, 27H, *m*,*p*-PhP, *o*,*m*,*p*-PhSiO), 7.76 (m, 8H, *o*-PhP). ^{13}C{^{1}H} NMR (298 K): δ 21.6 (*o*-Me), 22.7 (*p*-Me), 29.1 (PCH_2), 125.8 (Ar), 126.7 (Ar), 127.5 (Ar), 128.3 (Ar), 128.7 (Ar), 129.0 (Ar), 129.3 (Ar), 129.4 (Ar), 130.1 (Ar), 131.3 (Ar), 131.6 (Ar), 132.1 (Ar), 133.1 (Ar), 135.6 (Ar), 136.6 (Ar), 137.1 (Ar), 141.9 (i-Ph), 142.0 (i-mes), 149.9 (OSi*Ph*). ^{31}P{^{1}H} NMR (298 K): δ −16.4. MS: *m*/*z* 988 [3%], 911 [2], 854 [2], 790 [7], 712 [100], 672 [20], 635 [15], 580 [15], 475 [15], 440 [45], 332 [80], 276 [20], 240 [50], 183 [65], 77 [35].

Typical polymerisation procedure

rac-Lactide (typically 0.5 g) was combined with the zinc complex (0.001 equivalents) in a 25 mL ampoule with a Teflon Youngs' stopcock. Toluene (12 mL) was then added and the sealed ampoule heated to 60 °C. Monomer conversion was monitored by integration of monomer *vs.* polymer methine resonances in the ^{1}H NMR ($CDCl_3$) by withdrawal of 0.5 mL aliquots, quenching with methanol (*ca.* 0.1 mL) and removal of volatiles.

Crystal structure determinations

Data were collected at 173 K on an Nonius Kappa CCD diffractometer, λ(Mo Kα) = 0.71073 Å; details are given in Tables 3 and 4. The structures were solved by direct methods (SHELXS-97)[26] and refined by full matrix least squares (SHELXL-97)[27] with non-H atoms anisotropic and H atoms included in riding mode except in **2** where the hydrogen atoms on C(1) and on the oxygen atom were located on a difference map and freely refined. In **6** the C(54) ^{t}Bu group was disordered and was refined with SADI distance constraints and with the lower occupancy sites isotropic. In **9** there were three independent, poorly defined molecules of toluene solvate. All three were disordered, with one on a general position and two on inversion centres. For all three, C atoms were left isotropic and H atoms omitted, and SADI constraints were applied. A semi-empirical absorption correction was applied in **3**, **4**, **5**, **6**, **7** and **9**.

CCDC reference numbers 190727–190734.

See http://www.rsc.org/suppdata/dt/b2/b207358g/ for crystallographic data in CIF or other electronic format.

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