Cationic organozinc complexes of a *bis*(phosphinimine) pincer ligand: synthesis, structural and polymerization studies†

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Cationic organozinc complexes of a neutral *bis*(phosphinimine) pincer ligand (**L**) have been prepared and structurally characterized. This recently introduced ligand was constructed from a dibenzofuran (dbf) framework with symmetric attachment of phosphinimine groups at the 4 and 6 positions. Starting from protonated derivatives [**L**H][B(C_6F_5)$_4$] (**1a**), [**L**H][BPh_4] (**1b**), or [**L**H$_2$][BPh_4]$_2$ (**1c**), the complexes [**L**ZnCH_3][B(C_6F_5)$_4$] (**2a**), [**L**ZnCH_3][BPh_4] (**2b**), and [**L**ZnOAc][BPh_4] (**3**), were prepared *via* protonolysis of an appropriate alkylzinc precursor. The complex [**L**ZnPh][BPh_4] (**4**) is generated as a side-product in the synthesis of **2b**. Solid-state structural studies have revealed the compounds to be charge separated cationic zinc species with 3-coordinate trigonal planar geometry. Preliminary studies have shown these complexes to be inactive for the polymerization of lactide. Upon modification of the initiating group to a methyl-(*S*)-lactate, however, complex [**L**ZnOCH(Me)CO_2Me][B(C_6F_5)$_4$] (**5**) demonstrated significant polymerization activity at 60 °C. Additionally, NMR and mass spectrometry data confirmed a coordination-insertion mechanism was operative for this catalyst.

Introduction

The design and synthesis of new ligand architectures for the stabilization of reactive metal complexes has become an increasingly important goal of many researchers.[1] The development of highly modular pincer-type ligands is especially topical, whereby the electronic and steric properties of such ligands can be readily modified to suit the needs of a particular application.[2] In addition to electronics and sterics, the effect of ligand bite angle is an important consideration, and thus, numerous frameworks with various bite angles are often explored.[3]

Much recent work, often done in the context of lactone polymerization catalysis, has involved the preparation of zinc complexes of a wide variety of anionic ligand frameworks,[4] such as β-diketiminates,[5] phenolates,[6] and tris-pyrazolylborates.[7] Due to the strong electron donating abilities and highly modular nature of the phosphinimine functionality, transition metal complexes of phosphinimine frameworks are beginning to receive increased attention.[8] However, zinc complexes of phosphinimine-based ligands are still uncommon. Additionally, the field of lactone polymerization is dominated by anionic ligand ancillaries, while neutral frameworks remain underexplored.[9] Thus, the study of zinc complexes bearing neutral phosphinimine-based ligands is of fundamental interest.

Structurally characterized tricoordinate cationic zinc species are surprisingly rare, with presently only a handful of examples in the literature.[10] This pioneering work was accomplished by Bochmann *et al.*, who have shown that low coordinate cationic zinc species are readily isolable in the presence of Lewis bases, which serve to coordinatively saturate the metal centre.[11] Intriguingly, coordinatively unsaturated cationic zinc complexes were formed in the absence of excess Lewis base when a neutral, chelating diazadiene ligand was employed.[10] Since this time, a handful of others have reported structurally characterized zinc cations, but all of these are coordinatively saturated.[12]

We have chosen to continue our exploration of the *bis*(phosphinimine) dbf based ligand architecture, previously shown to be capable of stabilizing cationic butyl-magnesium species with excellent properties for the ring-opening polymerization of ε-caprolactone.[13] The rigidity of the architecture, coupled with the modular nature of the phosphinimine functionality, make this an ideal framework for the preparation of reactive species with controlled steric and electronic properties. Previous work examined cationic zinc complexes of a directly related mono(phosphinimine) ligand.[14] However, direct structural characterization of fully separated ion pairs was not achieved in that case. Herein, we demonstrate how utilization of a neutral *bis*(phosphinimine) ligand allows isolation of three-coordinate cationic zinc species. Several examples of such compounds have been prepared and structurally characterized.

Results and discussion

Synthesis of complexes

Starting from the neutral bis(phosphinimine) ligand 4,6-(MesN=PPh_2)$_2$dibenzofuran (**L**), protonation of the phosphinimine nitrogen atoms can be carried out, as described in a previous article,[13] to give [**L**H][B(C_6F_5)$_4$] (**1a**), [**L**H][BPh_4] (**1b**), or [**L**H$_2$][BPh_4]$_2$ (**1c**). Reaction of an alkylzinc precursor with the appropriate protonated ligand derivative in the absence of coordinating solvent gives complexes of the general form [**L**ZnR][A], (A = BPh_4^-, $B(C_6F_5)_4^-$). In this way, the compounds

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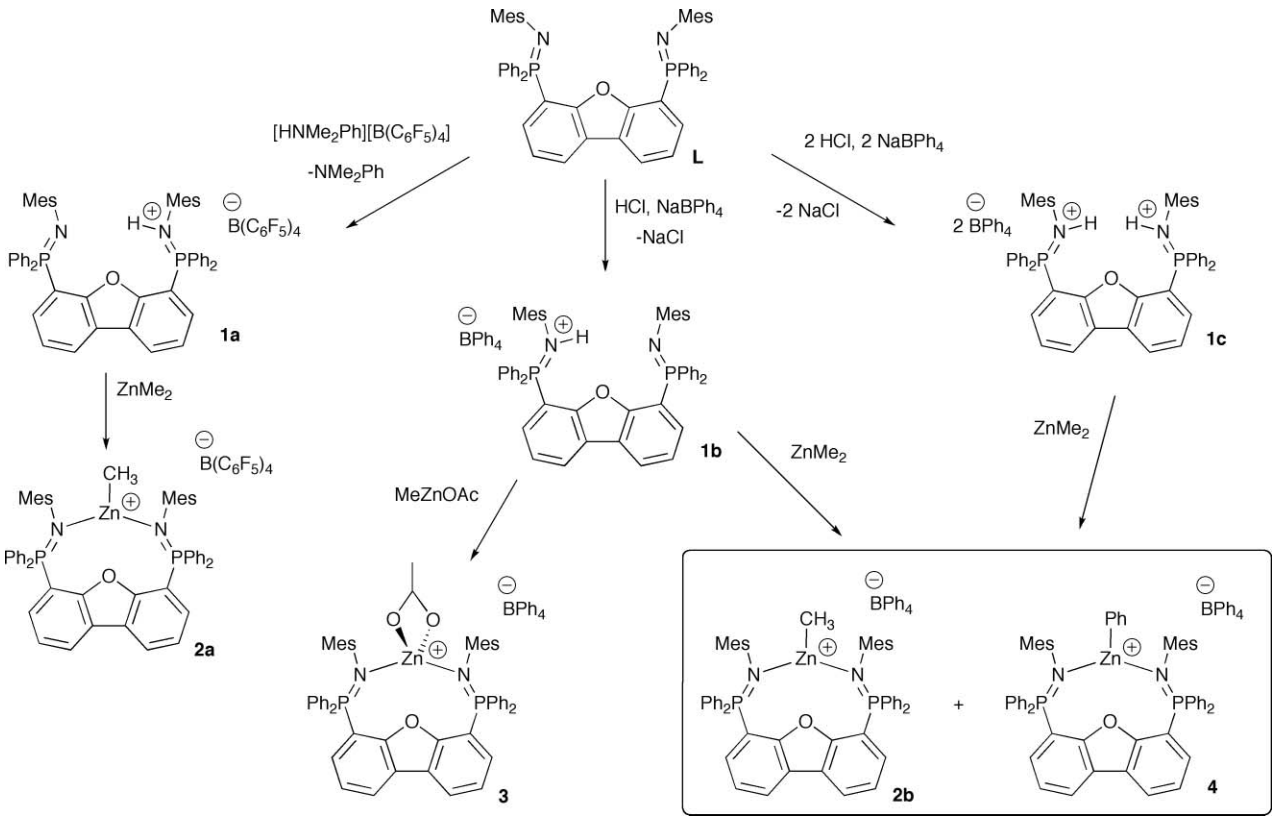


Scheme 1 Synthesis of cationic zinc complexes **2a**, **2b**, **3** and **4** from protonated derivatives of the neutral bis(phosphinimine) ligand.

[**L**ZnCH$_3$][B(C$_6$F$_5$)$_4$] (**2a**), [**L**ZnCH$_3$][BPh$_4$] (**2b**), [**L**ZnOAc][BPh$_4$] (**3**), and [**L**ZnPh][BPh$_4$] (**4**) were synthesized (Scheme 1).

Reaction of **1a** with a single equivalent of ZnMe$_2$ is facile, giving immediate effervescence of methane and complete conversion to a single product in under 5 min. Complex **2a** has a single unique phosphorus nucleus which resonates in the ^{31}P{^{1}H} NMR spectrum at δ 23.4 (C$_6$D$_5$Br solvent), approximately 41 ppm downfield of the free ligand.[15] This downfield shift is a clear indication of coordinated phosphinimine, while the presence of only a single phosphorus environment implies that the cation of **2a** is C_2 or C_s symmetric on the NMR timescale, with both phosphinimine donors bound to the zinc centre. The mesityl groups are also equivalent, with *ortho* and *para* methyls resonating at δ 1.34 and 2.05 in the ^{1}H NMR spectrum, respectively. The ^{11}B and ^{19}F NMR spectra show typical resonances associated with the B(C$_6$F$_5$)$_4^-$ anion, and do not suggest significant interaction between anion and cation components in solution.[16] In the ^{1}H NMR spectrum of this compound, a signal at δ –0.48 which integrates as 3H is attributed to a single zinc-methyl group. All other spectroscopic signatures and elemental analysis data are consistent with the proposed compound. Unfortunately, in our hands this compound was immune to repeated crystallization attempts, and thus the solid-state structure could not be ascertained.

In an attempt to garner detailed structural information about the complex, the tetraphenylborate anion was employed with the aim of promoting crystallinity. Reaction of **1b** with dimethylzinc proceeded rapidly, giving complete consumption of **1b** in less than 5 min at ambient temperature. Interestingly, the reaction generated a mixture of two products, with the major complex, identified as **2b**, resonating in the ^{31}P{^{1}H} NMR spectrum at δ 23.7 (C$_6$D$_5$Br solvent). A single by-product resonates slightly downfield at δ 24.3. This compound was revealed to be the phenyl substituted compound **4**, by isolation of single crystals and determination of the solid-state structure (*vide infra*). Under the conditions employed, the reaction gave the two species in approximately a 7 to 1 ratio, as determined by integration of the ^{1}H NMR resonances. The zinc-methyl of **2b** appears at δ –0.49 ppm in the ^{1}H NMR spectrum, while the mesityl *ortho* and *para* methyls resonate at δ 1.33 and δ 2.04, respectively. All resonances closely match those for the cation of **2a**, suggesting that the nature of the cation is unaffected by the choice of anion.

In the ^{1}H NMR spectrum of the isolated mixture of **2b** and **4**, only the mesityl component of the ligand gives rise to clearly resolved resonances for the two different compounds. This is not surprising given the close proximity of the mesityl groups to the zinc-phenyl in **4** and the zinc-methyl in **2b**. All remaining protons resonate with nearly identical chemical shifts (C$_6$D$_5$Br). The *ortho* and *para* methyl groups of the by-product appear at δ 1.03 and 2.09, respectively. Due to the similar properties of these two species, separation and purification could not be achieved. While the mechanism for the formation of **4** is currently not understood in great detail, the origin of the phenyl group is certainly the tetraphenylborate anion, which is known to be more chemically labile than the B(C$_6$F$_5$)$_4^-$ anion, and thus, more prone to aryl abstraction.[17,18] *In situ* observation of ^{11}B NMR spectra of the reaction mixture shows, in addition to a peak at δ –5.6 attributed to the tetraphenylborate anion, a signal at δ –10.4 corresponding to a methyltriphenylborate anion. This observation, as well as

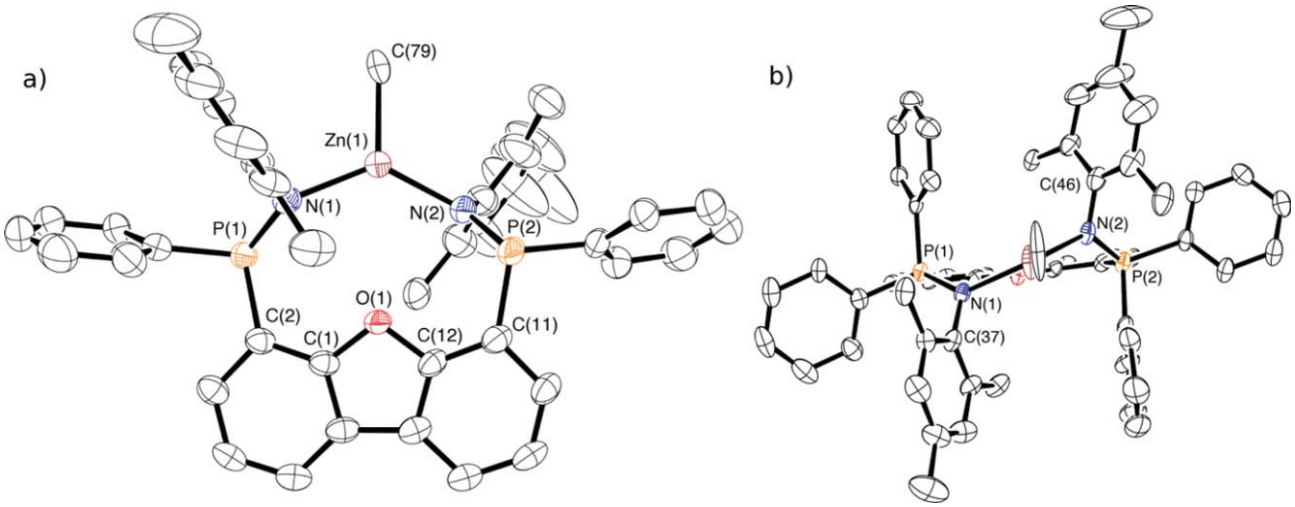


Fig. 1 (a) Solid-state structure of the cation of **2b**, showing 30% thermal ellipsoids, with hydrogen atoms and disordered positions omitted for clarity. One phenyl ring from each PPh_2 group has also been omitted for clarity. (b) Alternate view of the solid-state structure of **2b**, depicting the pseudo-C_2 symmetry of the complex geometry, and the steric crowding between the mesityl groups and the dibenzofuran backbone.

the absence of a by-product in the synthesis of **1a**, lends further support to this conclusion.

Single crystals suitable for X-ray structural analysis were obtained at ambient temperature from a solution containing a mixture of **2b** and **4** in a mixture of benzene and bromobenzene. Determination of the structure revealed the identity of the crystals to be **2b**·0.5C_6H_6; the solid-state structure is depicted in Fig. 1. Compound **2b** was found to be a well-defined ion pair with no close cation–anion contacts. The zinc atom exhibits trigonal planar coordination geometry. The zinc centre is bound to the two nitrogen atoms in a pseudo-symmetric way, and does not interact notably with the dibenzofuran oxygen atom (the two atoms are separated by a distance which is greater than 2.91 Å, the sum of their Van der Waals radii[19] [Zn(1)–O(1) = 3.239(2) Å]). Zinc–nitrogen bond lengths of 2.033(4) and 2.044(4) Å, and a zinc–carbon distance of 2.034(9) Å, are typical of Zn–N and Zn–C single bonds observed in previous studies (Table 1).[10,14]

For zinc to be bound in this bidentate manner, the σ-symmetric orbitals of the phosphinimine nitrogen atoms must be orientated toward one another, but away from the dibenzofuran backbone (Fig. 1(a)). This requirement is achieved through orientation of each mesityl group such that one *ortho*-methyl closely approaches the oxygen of the dbf moiety, while the other remains in close proximity to the zinc centre, thereby maintaining a high level of steric protection. Rotational freedom about the C_{dbf}–P and P–N bonds are the major factors which allow this geometry to occur. Rotation about the former positions the nitrogen atoms at an ideal relative separation [C(1)–C(2)–P(1)–N(1) = −37.4(4)°; C(12)–C(11)–P(2)–N(2) = −41.0(4)°], while the latter influences the location and direction of the σ-donating lone pairs [C(2)–P(1)–N(1)–C(37) = −102.6(3)°; C(11)–P(2)–N(2)–C(46) = −89.2(4)°]. These rotations occur in both phosphinimines almost equally but in opposite directions, yielding a complex which is pseudo-C_2-symmetric, thereby placing the zinc centre within an axially chiral binding pocket (Fig. 1(b)). The opposite enantiomer is generated by a centre of inversion within the unit cell, and thus the compound exists as a racemic mixture in the solid-state. The notable distortion from trigonal planarity at zinc is a result of the obtuse bite angle of the ligand [N(1)–Zn(1)–N(2) = 131.8(1)°]. Achieving a sharper bite angle would require further rotation about the P–N bond, which cannot be achieved due to the steric repulsion between the mesityl *ortho*-methyl groups and the dbf backbone.

Table 1 Selected bond lengths (Å), bond angles (°), and torsion angles (°) for complex **2b**

Bond lengths/Å			
Zn(1)–N(1)	2.044(4)	Zn(1)–N(2)	2.033(4)
Zn(1)–C(79)	2.034(9)	P(1)–N(1)	1.611(4)
P(2)–N(2)	1.603(3)		
Bond angles/°			
N(1)–Zn(1)–C(79)	114.2(4)	N(2)–Zn(1)–C(79)	113.5(4)
N(1)–Zn(1)–N(2)	131.8(1)	P(1)–N(1)–Zn(1)	130.9(2)
C(37)–N(1)–Zn(1)	110.1(3)	P(1)–N(1)–C(37)	118.8(3)
P(2)–N(2)–Zn(1)	127.2(2)	C(46)–N(2)–Zn(1)	114.2(3)
P(2)–N(2)–C(46)	118.5(3)		
Torsion angles/°			
C(1)–C(2)–P(1)–N(1)	−37.4(4)		
C(12)–C(11)–P(2)–N(2)	−41.0(4)		
C(2)–P(1)–N(1)–C(37)	−102.6(3)		
C(11)–P(2)–N(2)–C(46)	−89.2(4)		

The nearest contact between the tetraphenylborate anion and the zinc centre exists at the *para* position of an approaching phenyl ring, which at 5.461(6) Å, is clearly indicative of a separated ion pair. The methyl group bound to zinc is disordered over two positions, with a concomitant two-site disorder in the position of the approaching phenyl group of the anion. These disordered structures exist in a 7 : 3 ratio with the major one depicted in Fig. 1. The secondary position of the disordered phenyl ring is slightly closer to the zinc centre [C_{anion}–Zn(1) = 5.20(1) Å], suggesting that this disorder may be caused by an interplay between electrostatic cation–anion attraction and steric repulsion between the ions.

With the possibility of generating a dicationic zinc species through double protonolysis, the doubly protonated ligand derivative **1c** was reacted with a single equivalent of dimethylzinc. The material isolated from this reaction was again found to be a mixture of **2b** and **4**, but with a significant enhancement in the proportion of the phenyl-substituted species **4**, which accounted for 45% of the total material. From this mixture, single crystals of **4** were isolated, and the solid-state structure was obtained, confirming its identity. The X-ray crystal structure of **4** is shown in Fig. 2. The zinc atom exists as a distorted trigonal planar, three-coordinate cation. The ligand coordinates in an orientation analogous to that observed in the structure of **2b**, with pseudo-C_2-symmetry and no binding to the dbf oxygen atom [Zn(1)–O(1) = 3.207(2) Å]. Zinc–nitrogen bond distances are shortened slightly, by an average of 0.024(8) Å [Zn(1)–N(1) = 2.016(2), Zn(1)–N(2) = 2.012(2) Å], (Table 2) an observation which is consistent with its position downfield of **2b** in the $^{31}P\{^{1}H\}$ NMR spectrum. These findings suggest that less donation to zinc from phenyl is compensated for by tighter binding of the ligand. The nitrogen atoms are positioned in similar locations to that in **2b**, [C(1)–C(2)–P(1)–N(1) = 42.5(3)°, C(12)–C(11)–P(2)–N(2) = 46.0(3)°], and likewise the lone pairs on the nitrogen atoms are oriented in approximately the same direction, [C(2)–P(1)–N(1)–C(25) = 99.2(2)°, C(11)–P(2)–N(2)–C(46) = 94.7(2)°]. The bite angle in this complex thus remains very wide, and is, in fact, slightly greater than that observed for **2b** [N(1)–Zn(1)–N(2) = 133.1(1)°]. The closest Zn–C_{anion} contact is 6.384(3) Å, and as such, the compound can be regarded as a separated ion pair.

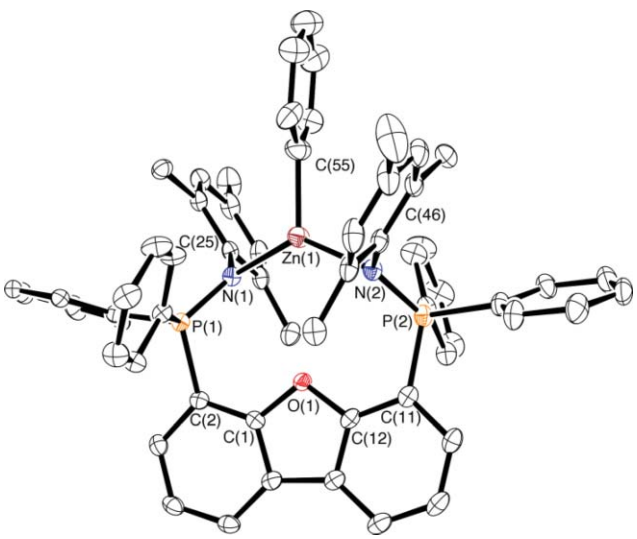


Fig. 2 Solid-state structure of the cation of **4**. Ellipsoids drawn at the 30% probability level and solvent molecules and H-atoms have been omitted for clarity.

The ability to utilize the above synthetic methodology for the preparation of zinc complexes bearing non-alkyl functionalities would give these cationic zinc compounds a wider range of potential applications. Since our research interests lie specifically in the field of lactone polymerization, alkoxides are an especially desirable target.[4] Attempts to generate alkoxides by reaction of **2a** or **2b** with an appropriate alcohol, or by reaction of **1a** or **1b** with zinc alkoxide precursors of the form RZnOR′ have thus far

Table 2 Selected bond lengths (Å), bond angles (°), and torsion angles (°) for complex **4**

Bond lengths/Å			
Zn(1)–N(1)	2.016(2)	Zn(1)–N(2)	2.012(2)
Zn(1)–C(55)	1.943(4)	P(1)–N(1)	1.598(2)
P(2)–N(2)	1.599(2)		
Bond angles/°			
N(2)–Zn(1)–C(55)	111.6(1)	N(1)–Zn(1)–C(55)	115.2(1)
N(1)–Zn(1)–N(2)	133.1(1)	P(1)–N(1)–Zn(1)	130.1(1)
C(25)–N(1)–Zn(1)	109.0(2)	P(1)–N(1)–C(25)	120.4(2)
P(2)–N(2)–Zn(1)	129.3(1)	C(46)–N(2)–Zn(1)	110.4(2)
P(2)–N(2)–C(46)	120.2(2)		
Torsion angles/°			
C(1)–C(2)–P(1)–N(1)	42.5(3)		
C(12)–C(11)–P(2)–N(2)	46.0(3)		
C(2)–P(1)–N(1)–C(25)	99.2(2)		
C(11)–P(2)–N(2)–C(46)	94.7(2)		

met with little success, presumably due to the inherent stability of such precursors. However, a proof of concept for this approach was demonstrated by reaction of MeZnOAc with **1b**. When these reagents were combined the reaction proceeded rapidly, and in under 5 min complete conversion to complex [**L**ZnOAc][BPh_4], **3**, was realized. Contrary to that observed in the related reaction of **1b** with dimethylzinc, only a single product was generated, which resonates at δ 28.3 in the $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_5Br), significantly downfield from that of the methylzinc cations (**2a** and **2b**) and the phenylzinc cation **4** discussed previously. All other spectroscopic signatures are similar, clearly indicating either C_2 or C_s symmetry, and suggesting no notable cation–anion interactions on the NMR timescale. The acetate methyl group resonates at δ 1.80 in the ^{1}H NMR spectrum, and cleanly integrates as 3H confirming the anticipated ratio of one acetate group per ligand.

Single crystals of **3** suitable for X-ray diffraction (Fig. 3) were obtained by slowly cooling a solution of the compound in a mixture of benzene and bromobenzene (1 : 1) from 100 °C to

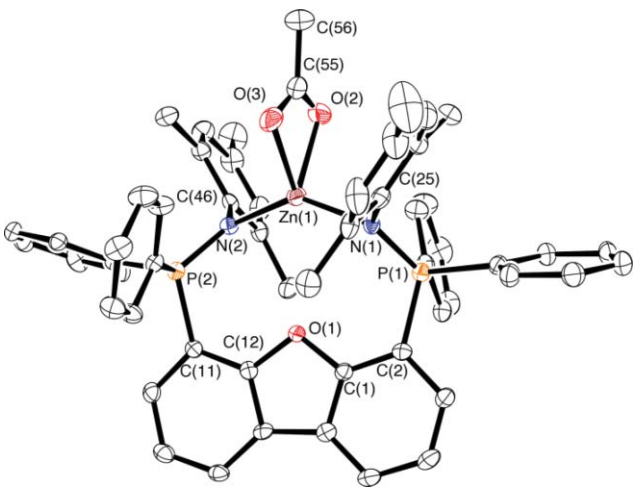


Fig. 3 Solid-state structure of the cation of **3** drawn with 30% thermal ellipsoids. Hydrogen atoms and solvent molecules have been removed for clarity.

Table 3 Selected bond lengths (Å), bond angles (°), and torsion angles (°) for complex **3**

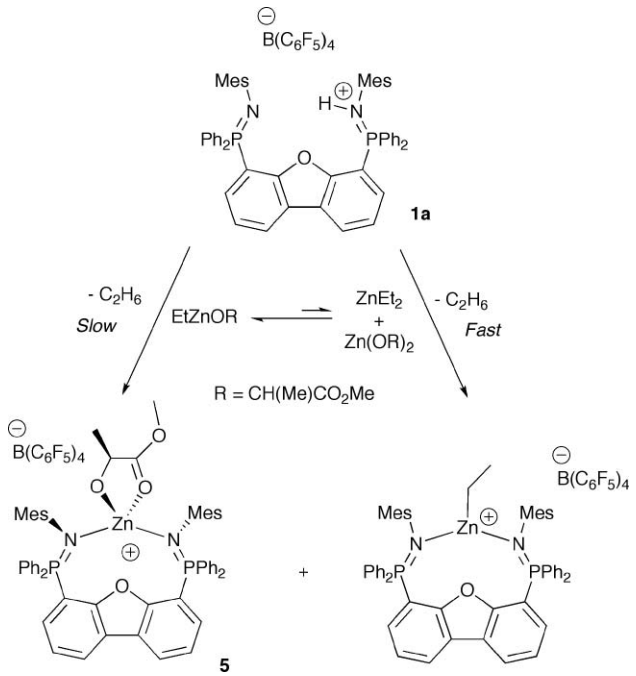
Bond lengths/Å			
Zn(1)–N(1)	1.972(3)	Zn(1)–N(2)	1.971(3)
Zn(1)–O(2)	2.089(3)	Zn(1)–O(3)	2.082(3)
P(1)–N(1)	1.606(3)	P(2)–N(2)	1.614(3)
Bond angles/°			
N(1)–Zn(1)–O(2)	104.8(1)	N(1)–Zn(1)–O(3)	102.0(1)
N(2)–Zn(1)–O(2)	106.1(1)	N(2)–Zn(1)–O(3)	111.5(1)
N(1)–Zn(1)–N(2)	141.7(1)	O(2)–Zn(1)–O(3)	63.8(2)
P(1)–N(1)–Zn(1)	128.2(2)	C(25)–N(1)–Zn(1)	113.1(2)
P(1)–N(1)–C(25)	118.6(2)	P(2)–N(2)–Zn(1)	127.7(2)
C(46)–N(2)–Zn(1)	113.4(2)	P(2)–N(2)–C(46)	119.0(2)
Torsion angles/°			
C(1)–C(2)–P(1)–N(1)	46.3(3)		
C(12)–C(11)–P(2)–N(2)	42.5(3)		
C(2)–P(1)–N(1)–C(25)	94.1(4)		
C(11)–P(2)–N(2)–C(46)	96.3(3)		

ambient temperature. The nearest Zn–C_{anion} contact distance in the structure is 6.229(3) Å, again indicative of a separated ion pair in the solid-state. Contrary to the solid-state structures of **2b** and **4**, the zinc centre in this compound is four-coordinate, with highly distorted tetrahedral geometry on account of the wide bite angle of **L** and the acute bite angle of the chelating acetate moiety [O(2)–Zn(1)–O(3) = 63.8(2)°] (Table 3). The acetate oxygen atoms bind to zinc at nearly equal distances, with an average bond length of 2.086(4) Å. At 1.972(3) and 1.971(3) Å the zinc–nitrogen bond distances are noticeably shorter in this complex. As for **4**, the shortened bonds are likely a result of reduced electron donation from the acetate to zinc, which is compensated for by tighter binding of the ligand. The ligand adopts a similar orientation as that elucidated for the structures of **2a** and **4**, but with a substantially different bite angle, which is widened by approximately 10° [N(1)–Zn(1)–N(2) = 141.7(1)°]. This increase in ligand bite angle stems from very subtle changes in the geometry of the ligand, and is primarily due to a shift in the position of the zinc atom slightly further into the binding pocket. As a consequence, the zinc centre sits marginally closer to the dbf oxygen atom (Zn(1)–O(1) = 3.06 Å), but at a distance still outside the range of a bonding interaction. The shortened zinc–nitrogen bond distances are consistent with the noted downfield shift in the $^{31}P\{^{1}H\}$ NMR spectrum, all of which suggest a greater partial positive charge on the zinc atom and increased donation of electron density from the phosphinimine functionalities.

Lactide polymerization studies

Preliminary studies of **2a** and **3** as catalysts for the ring opening polymerization of lactide have unfortunately revealed these compounds to be inactive under moderate conditions (60 °C). Exposure to more harsh reaction conditions (100 °C) in the presence of a lactide monomer resulted in catalyst decomposition. Since the methyl and acetate groups of **2a** and **3**, respectively, are known to be poor initiating groups for this transformation,[20] the result is not particularly surprising. As mentioned above, simple alkoxide analogues could not be prepared, and thus, it was difficult to determine whether the lack of activity was due to the nature of the initiating group, or an inherent property of the catalyst system itself. To further probe this question, we prepared a complex that bears a methyl-(*S*)-lactate initiating group, which was expected to serve as an excellent model for the growing polymer chain. In addition, this species is a close approximation of the product resulting from a single lactide insertion into the Zn–C bond of complex **2a**.

By reaction of **1a** with 1.1 equivalent of EtZn-methyl-(*S*)-lactate, 85% of **1a** was converted to **5**, with the remainder being converted to a by-product which we propose to be [**L**ZnEt][$B(C_6F_5)_4$] (Scheme 2). Heteroleptic zinc species of the form RZnOR are known to exist in a complex equilibrium, with disproportionation giving rise to small concentrations of homoleptic ZnR_2 in solution.[21] Because **1a** reacts significantly faster with $ZnEt_2$ than with EtZn-methyl-(*S*)-lactate, some formation of the [**L**ZnEt][$B(C_6F_5)_4$] by-product was expected. Separation and purification of the two complexes could not be achieved, thus, studies assessing the utility of **5** as a lactide polymerization catalyst were undertaken using an 85 : 15 mixture of these two species.



Scheme 2 Generation of complex **5** and the by-product [**L**ZnEt][$B(C_6F_5)_4$] by reaction of **1a** with EtZnOCH(Me)CO_2Me.

At ambient temperature in bromobenzene-d_5, complex **5** exhibits two broad, but distinct, resonances at δ 24.5 and 25.1 in the $^{31}P\{^{1}H\}$ NMR spectrum (Fig. 4). This observation is a direct consequence of the asymmetric nature of the methyl-(*S*)-lactate group, which breaks the C_2 symmetry of the ligand observed in the solid-state. Upon warming to 50 °C, these peaks coalesce into one signal at δ 25.0, which sharpens further at 70 °C. This dynamic behaviour suggests rapid rotation of the methyl-(*S*)-lactate group on the NMR timescale at elevated temperatures. At 50 °C, a quartet at δ 4.28, a doublet at δ 1.29, and a singlet at δ 2.78 attributed to the methine, methyl and CO_2CH_3 of the methyl-(*S*)-lactate group, respectively, are observed in the ^{1}H NMR spectrum.

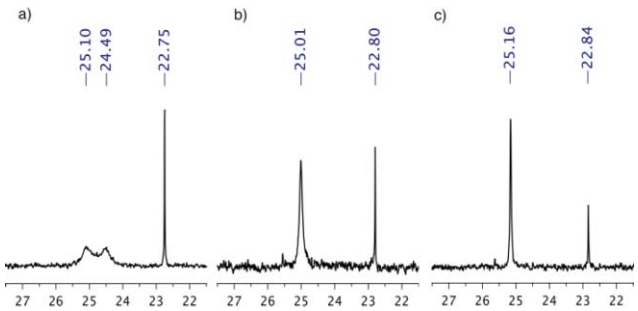


Fig. 4 $^{31}P\{^{1}H\}$ NMR spectra of the methyl-(*S*)-lactate complex **5** and the **L**ZnEt side product in C_6D_5Br solution at: ambient temperature (a), 50 °C (b), and 70 °C (c).

Interestingly, the mesityl *ortho*-methyls are split into two separate resonances at δ 1.74 and 1.70, suggesting restricted rotation about the N–C bonds.

While complex **5** was found to catalyze the ROP of *rac*-lactide extremely slowly at ambient temperature, significantly enhanced activity was noted under conditions which were relatively mild. A coordination-insertion mechanism is evident upon *in situ* observation of polymerization of 10 equiv of *rac*-lactide at 50 °C in $CDCl_3$ solution. After 30 min at 50 °C, complex **5** was completely converted into a new species, presumably the product of one or more insertions of lactide monomer, which resonates slightly downfield (δ 25.5) in the $^{31}P\{^{1}H\}$ NMR spectrum. A concomitant change of the methyl-(*S*)-lactate end group is observed in the ^{1}H NMR spectrum, with replacement of the O–CH_3 resonance at δ 2.7, by a new peak at δ 3.5. After complete loss of the resonances associated with **5**, observation of the methine resonances in the ^{1}H NMR spectrum indicates 36% consumption of monomer (approximately 4 equivalents), suggesting comparable rates of initiation *versus* propagation for this catalyst system. It is important to note that the [**L**ZnEt][$B(C_6F_5)_4$] impurity shows no reactivity toward the lactide monomer under these conditions.

In situ observation of polymerization of 50 equivalents of *rac*-lactide was carried out in C_6D_5Br solvent at 60 °C. Under these conditions ($[LA]_0 = 0.25$ M), it was found that 90% conversion to atactic polylactide was achieved in 3.5 h. Isolated polymer samples were obtained from larger scale polymerizations conducted under identical experimental conditions. The methyl-(*S*)-lactate end group is clearly observed in the ^{1}H NMR spectrum of the isolated polymer, providing further evidence for a coordination-insertion mechanism. Additionally, MALDI-TOF analysis detected oligomer fragments consistent with the presence of methyl-(*S*)-lactate end groups. Peaks are separated by $m/z = 72$, suggesting significant rates of intrachain transesterification. Despite the likely transesterification side-reactions, however, analysis of the polymer samples revealed reasonable molecular weight control. Specifically, samples produced using a monomer to initiator ratio of 50 : 1, as described above, had PDI values ranging from 1.2–1.3, with molecular weights of 18 000 g mol^{-1}, approximately triple the expected value.

Related cationic ethylzinc catalysts only exhibited activity for the polymerization of lactide at much higher temperatures (≥100 °C), and polymer molecular weight was poorly controlled.[14] By comparison, complex **5** represents a substantial improvement on that preliminary finding. While the activity of this compound is modest compared with many known classes of neutral zinc catalysts,[4] it represents a new family of lactide polymerization catalyst with significant potential for future development.

Conclusions

A sterically demanding dbf *bis*(phosphinimine) ligand has allowed the preparation of coordinatively and electronically unsaturated cationic zinc species. A general and versatile methodology for the synthesis of these cationic compounds has been developed, whereby it was demonstrated that methylzinc, phenylzinc, zinc acetate and zinc methyl-(*S*)-lactate compounds can all be obtained. By utilizing a tetraphenylborate counterion, materials were generated from which single crystals suitable for X-ray diffraction could readily be prepared, facilitating the solid-state structural characterization of these compounds. It was found that in each case the ligand adopts a well defined orientation which is pseudo-C_2-symmetric in the solid-state, and the zinc centre is thus placed in an axially chiral binding pocket. While complexes **2a**, **2b**, **3**, and **4** are inactive for polymerization of lactide, incorporation of a methyl-(*S*)-lactate initiating group in complex **5** enhanced the polymerization properties whereby **5** exhibited notable activity at 60 °C. Although the ligand was shown to adopt a C_2-symmetric conformation in the solid-state, complex **5** generated only atactic polylactide when used to polymerize *rac*-lactide.

Future work will further explore this catalytic system, focusing on fine tuning the steric and electronic properties of this highly modular ligand framework, with the aim of enhancing polymerization activity while inhibiting transesterification side reactions. Additionally, P-chiral derivatives of the ligand will be studied in hopes of achieving stereochemically controlled polymerization of *rac*-lactide.

Experimental

General considerations

All manipulations of air-sensitive materials and reagents were conducted using high-vacuum techniques under a purified argon atmosphere or in a glove box (MBraun Labmaster 130). All solvents were purified using an MBraun solvent purification system (MB-SPS), stored in teflon-sealed glass vessels over sodium benzophenone ketyl (THF and ether), CaH_2 (DCM, bromobenzene) or "titanocene" (pentane, benzene and toluene), and distilled prior to use. Deuterated solvents (Cambridge Isotopes) were dried over sodium benzophenone ketyl (benzene-d_6, toluene-d_8, and bromobenzene-d_5) or CaH_2 ($CDCl_3$), degassed *via* three freeze–pump–thaw cycles, distilled under vacuum and stored in glass bombs under argon. The compounds **L**, **1a**, **1b**, and **1c** were prepared as previously reported.[13] MeZnOAc was prepared by a known literature procedure *via* a ligand scrambling route.[22] *Rac*-lactide was purchased from Alfa Aesar and was recrystallized from toluene and sublimed twice prior to use. All other materials were obtained from commercial sources in high purity (Sigma-Aldrich, Acros Organics) and used without additional purification. NMR spectra (^{1}H (300.13 MHz), $^{13}C\{^{1}H\}$ (75.47 MHz), $^{31}P\{^{1}H\}$ (121.48 MHz), ^{19}F (282.42 MHz), and ^{11}B (96.29 MHz)) were collected using a Bruker Avance II NMR spectrometer equipped with a variable-temperature unit. Spectra were collected at ambient

temperature unless otherwise noted and referenced to either $SiMe_4$ through the residual solvent resonance(s) (^1H and $^{13}C\{^1H\}$), or an external standard (85% H_3PO_4 ($^{31}P\{^1H\}$), trifluorotoluene (^{19}F), or boron trifluoride diethyl etherate (^{11}B)). ^1H and $^{13}C\{^1H\}$ NMR peak assignments were facilitated by COSY, DEPT-90, and HSQC experiments. X-Ray crystal structures were collected using a Bruker AXS SMART APEX II single crystal X-ray diffractometer (Mo Kα ($\lambda = 0.71073$ Å)). Elemental analyses were performed using an Elementar Vario Microcube instrument. GPC data were collected on a Viscotek Triple Detector GPC System outfitted with a model 270 Dual Detector Platform (Four Capillary Viscometer and Light Scattering Detector) and a Refractive Index Detector. Samples were run in THF at a concentration of 1 mg mL^{-1}. MALDI-TOF data were collected using an Applied BioSystems Voyager Elite instrument.

Synthesis

[4,6-(MesN=PPh$_2$)$_2$dibenzofuran·ZnMe]$^+$[B(C$_6$F$_5$)$_4$]$^-$, 2a. An excess of 1.2 M dimethylzinc in toluene (65 μL, 0.0780 mmol) was added to a solution of **1a** (100 mg, 0.0674 mmol) in bromobenzene (2 mL). Effervescence of methane was immediately observed. After allowing the mixture to stand for 30 min at ambient temperature, the product was precipitated as a red/orange oil by addition of pentane (5 mL). The mother liquor was decanted, the resulting oil was washed twice with 1 mL of pentane, then once with 2 mL of a 1 : 2 benzene–pentane mixture and dried *in vacuo*, giving the material as a pale yellow powder in 92.0% yield (96.6 mg, 0.0618 mmol). ^1H NMR (C_6D_5Br): δ 7.87 (d, 2H, $^3J_{HH} = 7.6$ Hz, 1,9-dbf), 7.32–7.19 (ov m, 4H, *p*-Ph obscured by solvent), 7.19–7.06 (ov m, 10H, *o*-Ph + 2,8-dbf), 6.99 (td, 8H, $^3J_{HH} = 7.6$ Hz, $^4J_{PH} = 3.2$ Hz, *m*-Ph), 6.77 (dd, 2H, $^3J_{PH} = 11.8$ Hz, $^3J_{HH} = 7.6$ Hz, 3,7-dbf), 6.41 (s, 4H, *m*-mesityl), 2.05 (s, 6H, *p*-CH_3 mesityl), 1.34 (s, 12H, *o*-CH_3 mesityl), –0.48 (s, 3H, CH_3Zn); $^{11}B\{^1H\}$ NMR (C_6D_5Br): δ –17.7; ^{19}F NMR (C_6D_5Br): δ 133.22 (d, 8F, *o*-C_6F_5), 163.68 (t, 4F, *p*-C_6F_5), 167.47 (t, 8F, *m*-C_6F_5); $^{31}P\{^1H\}$ NMR (C_6D_5Br): δ 23.4 (s); $^{13}C\{^1H\}$ NMR (C_6D_5Br): δ 157.60 (s, aromatic C), 150.23 (br s, C_6F_5), 147.06 (br s, C_6F_5), 139.99 (br s, C_6F_5), 138.29 (d, $J_{PC} = 7.9$ Hz, aromatic C), 136.55 (d, $J_{PC} = 6.0$ Hz, aromatic C), 135.00 (br s, C_6F_5), 134.39 (d, $J_{PC} = 4.1$ Hz, aromatic C), 134.12 (d, $^4J_{CP} = 2.6$ Hz, *p*-Ph), 132.84 (d, $^2J_{CP} = 10.0$ Hz, *o*-Ph), 132.36 (d, $^2J_{CP} = 6.8$ Hz, 3,7-dbf), 129.81 (s, *m*-mesityl), 129.49 (d, $^3J_{CP} = 12.4$ Hz, *m*-Ph), 127.13 (d, $^4J_{CP} = 2.3$ Hz, 1,9-dbf), 124.09 (d, $^3J_{CP} = 10.5$ Hz, 2,8-dbf), 123.96 (d, $J_{CP} = 8.9$ Hz, aromatic C), 114.75 (d, $^1J_{PC} = 92.0$ Hz, 4,6-dbf), 20.75 (s, *p*-*C*H$_3$ mesityl), 19.04 (s, *o*-*C*H$_3$ mesityl); *ipso*-Ph not observed. Anal. Calcd. (%) for $C_{79}H_{51}BF_{20}N_2OP_2Zn·C_6H_5Br$: C: 59.38; H: 3.28; N: 1.63; found: C: 59.44; H: 3.29; N: 1.71.

[4,6-(MesN=PPh$_2$)$_2$dibenzofuran·Zn(Me/Ph)]$^+$[BPh$_4$]$^-$, 2b/4. Method A: a small excess of dimethylzinc (0.160 mL of a 1.2 M solution in toluene, 0.192 mmol) was added to a solution of **1b** (200 mg, 0.178 mmol) in bromobenzene (1 mL). Immediate evolution of methane gas was observed, with a concomitant colour change of the solution from pale yellow to pale orange. Within 15 min at ambient temperature, the reaction products crystallized from solution. The mother liquor was decanted from the white crystalline material, which was washed with benzene (3 × 1 mL) and pentane (2 × 1 mL), and dried *in vacuo*, giving an overall yield of 89% (191 mg, 0.159 mmol). The material was found to contain 87% **2b** and 13% **4**, by integration of the *ortho* methyl groups in the ^1H NMR spectrum.

Method B: a slight excess of dimethylzinc (0.050 mL of a 1.2 M solution in toluene, 0.060 mmol) was added to a suspension of **1c** (80.7 mg, 0.0559 mmol) in bromobenzene (1 mL). All material dissolved within 1 min, and the resulting yellow solution was left to stand for 30 min. Within this time, the reaction products crystallized from solution. The mother liquor was decanted from the resulting white crystalline material, which was then washed with benzene (3 × 1 mL) and pentane (2 × 1 mL), and dried *in vacuo*, affording an overall 64% yield (42.7 mg, 0.0355 mmol). The material was found to contain 55% **2b** and 45% **4**, by integration of the *ortho* methyl groups in the ^1H NMR spectrum.

NMR data are reported for material isolated from method B (55% **2b**, 45% **4**). ^1H NMR (C_6D_5Br): δ 7.83 (br m, 8H, *o*-BPh_4), 7.70 (d, 2H, $^3J_{HH} = 7.8$ Hz, 1,9-dbf), 7.25–7.00 (ov m, 20H, *o*-Ph + *p*-Ph + *m*-BPh_4, partially obscured by solvent resonance), 7.00–6.83 (ov m, 14H, *p*-BPh_4 + *m*-Ph + 2,8-dbf, partially obscured by solvent resonances), 6.70 (dd, 2H, $^3J_{PH} = 12.0$ Hz, $^3J_{HH} = 7.5$ Hz, 3,7-dbf), 6.40 (s, 2.2H, *m*-mesityl of **2b**), 6.37 (s, 1.8 H, *m*-mesityl of **4**), 2.08 (s, 2.7H, *p*-CH_3 mesityl of **4**), 2.04 (s, 3.3H, *p*-CH_3 mesityl of **2b**), 1.33 (s, 6.6H, *o*-CH_3 mesityl of **2b**), 1.03 (s, 5.4H, *o*-CH_3 mesityl of **4**), –0.49 (s, 1.65H, ZnCH_3); $^{31}P\{^1H\}$ NMR (C_6D_5Br): δ 23.6 (**2b**), 24.2 (**4**); $^{11}B\{^1H\}$ NMR (C_6D_5Br): δ –5.55. Compound solubility and purity did not permit the collection and assignment of $^{13}C\{^1H\}$ NMR data.

[4,6-(MesN=PPh$_2$)$_2$dibenzofuran·ZnOAc]$^+$[BPh$_4$]$^-$, 3. Complex **3** was prepared similarly to **2a**, by reaction of **1b** (200 mg, 0.178 mmol) and MeZnOAc (25 mg, 0.179 mmol). After combining the reagents in bromobenzene (1 mL), the resulting cloudy solution promptly clarified to give a yellow solution. After standing for 15 min at ambient temperature the product crystallized. The mother liquor was decanted, the white crystalline material was washed with benzene and pentane, and after drying under vacuum for 24 h, complex **3** was isolated in 99% yield (220 mg, 0.176 mmol). ^1H NMR (C_6D_5Br): δ 7.83 (br s, 8H, *o*-BPh_4), 7.68 (d, 2H, $^3J_{HH} = 7.9$ Hz, 1,9-dbf), 7.27–7.09 (m, 12H, *o*-Ph + *p*-Ph, partially obscured by solvent signal), 7.05 (t, 8H, $^3J_{HH} = 7.3$ Hz, *m*-BPh_4), 7.01–6.93 (m, 10H, *m*-Ph + 2,-8-dbf, partially obscured by solvent signal), 6.93–6.84 (m, 4H, *p*-BPh_4, partially obscured by solvent), 6.71 (dd, 2H, $^3J_{PH} = 12.2$ Hz, $^3J_{HH} = 7.9$ Hz, 3,7-dbf), 6.41 (s, 4H, *m*-mesityl), 1.97 (d, 6H, $^4J_{HH} = 2.0$ Hz, *p*-CH_3 mesityl), 1.80 (s, 3H, CO_2CH_3), 1.40 (s, 12H, *o*-CH_3 mesityl); $^{31}P\{^1H\}$ NMR (C_6D_5Br): δ 28.34; $^{11}B\{^1H\}$ NMR (C_6D_5Br): δ –5.55; $^{13}C\{^1H\}$ NMR (C_6D_5Br): δ 185.02 (s, *C*O_2CH$_3$), 164.80 (q, $^1J_{BC} = 49.2$ Hz, *ipso*-BPh_4), 138.46 (d, $J_{CP} = 8.0$ Hz, aromatic C), 136.89 (q, $^2J_{BC} = 1.3$ Hz, *o*-BPh_4), 136.42 (d, $J_{CP} = 5.7$ Hz, aromatic C), 134.66 (d, $J_{CP} = 3.8$ Hz, aromatic C), 134.26 (s, *p*-Ph), 133.41 (d, $^3J_{CP} = 10.3$ Hz, *m*-Ph), 132.38 (d, $^2J_{CP} = 10.4$ Hz, 3,7-dbf), 131.45 (d, obscured by solvent, *o*-Ph), 130.04 (s, *m*-mesityl), 129.44 (d, $^3J_{CP} = 12.9$ Hz, *m*-Ph), 128.27 (s, 1,9-dbf), 125.86 (q, $^3J_{BC} = 2.7$ Hz, *m*-BPh_4), 121.93 (s, *p*-BPh_4), 113.76 (d, $^1J_{PC} = 92.6$ Hz, 4,6-dbf), 21.20 (s, CO_2CH_3), 20.80 (s, *p*-*C*H$_3$ mesityl), 18.59 (s, *o*-*C*H$_3$ mesityl). Signals for four quaternary carbons were not observed. Anal. Calcd. (%) for $C_{80}H_{71}BN_2O_3P_2Zn·2\ C_6H_6$: C: 78.77; H: 5.96; N: 2.00; found: C: 78.58; H: 5.94; N: 2.11.

Table 4 Crystal data and structure refinement for **2b**, **3**, and **4**

Complex	**2b**·0.5C_6H_6	**3**·2 C_6H_6	**4**·1.5C_6H_5Br
Empirical formula	$C_{82}H_{74}BN_2OP_2Zn$	$C_{92}H_{83}BN_2O_3P_2Zn$	$C_{93}H_{80.5}BBr_{1.5}N_2OP_2Zn$
Formula weight	1241.55	1402.76	1500.10
T/K	173(2)	173(2)	173(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/c$
a/Å	11.435(1)	17.878(1)	17.7836(9)
b/Å	15.818(1)	21.687(1)	21.818(1)
c/Å	19.206(2)	19.846(1)	19.887(1)
α/°	86.685(1)	90	90
β/°	75.823(1)	101.083(1)	100.504(1)
γ/°	82.763(1)	90	90
V/Å^3	3340.0(5)	7551.5(8)	7587.0(7)
Z	2	4	4
ρ_c/Mg m^{-3}	1.235	1.165	1.245
μ/mm^{-1}	0.464	0.416	0.941
Crystal size/mm	0.26 × 0.15 × 0.13	0.42 × 0.20 × 0.03	0.56 × 0.52 × 0.39
Theta range/°	2.58 to 25.03	2.58 to 25.03	2.08 to 25.03
Reflns. collected	40 680	90 217	90 928
Independent reflns.	11 774	13 330	13 399
GOF on F^2	1.032	1.019	1.051
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0662$	$R_1 = 0.0620$	$R_1 = 0.0492$
	w$R_2 = 0.1554$	w$R_2 = 0.1378$	w$R_2 = 0.1337$
R indices (all data)	$R_1 = 0.1351$	$R_1 = 0.1138$	$R_1 = 0.0634$
	w$R_2 = 0.1883$	w$R_2 = 0.1544$	w$R_2 = 0.1410$

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. w$R_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$. w $= 1/[\sigma^2(F_o^2) + (mP)^2 + nP]$, where $P = (F_o^2 + 2F_c^2)/3$.

[4,6-(MesN=PPh$_2$)$_2$dibenzofuran·ZnOCH(Me)CO$_2$Me]$^+$ [B(C$_6$F$_5$)$_4$]$^-$, 5. Complex **5** was prepared by reaction of **1a** (200 mg, 0.135 mmol) with a slight excess of EtZnOCH(Me)CO_2Me (29.3 mg, 0.148 mmol). The reagents were combined with bromobenzene (2 mL) in a Teflon sealed vial and heated to 80 °C for 2 h with stirring. After cooling to ambient temperature, the product was precipitated as a red/orange oil by addition of pentane (5 mL). The mother liquor was decanted, the material washed with a 1 : 1 mixture of benzene and pentane (3 × 2 mL) and then dried *in vacuo*, giving a pale red/orange powder in 62% yield (139 mg, 0.0842 mmol). The material was found to be contaminated with approximately 15% [**L**ZnEt][B(C_6F_5)$_4$]. ^{1}H NMR (C_6D_5Br, 50 °C): δ 7.94 (d, 2H, $^3J_{HH}$ = 7.7 Hz, 1,9-dbf), 7.40–7.10 (ov m, 14H, *o*-Ph + *p*-Ph + 2,8-dbf), 7.10–6.95 (ov m, 8H, *m*-Ph obscured by solvent), 6.85 (dd, $^3J_{PH}$ = 11.7 Hz, $^3J_{HH}$ = 7.2 Hz, 3,7-dbf), 6.39 (s, 4H, *o*-CH_3 mesityl), 4.28 (q, 1H, $^3J_{HH}$ = 6.7 Hz, OC*H*MeCO$_2$Me), 2.78 (s, 3H, OCHMeCO$_2$*Me*), 1.97 (d, 6H, $^4J_{HH}$ = 2.0 Hz, *p*-CH_3 mesityl), 1.74 (s, 6H, *o*-CH_3 mesityl), 1.70 (s, 6H, *o*-CH_3 mesityl), 1.29 (d, 3H, $^3J_{HH}$ = 6.9 Hz, OCH*Me*CO$_2$Me); ^{31}P{^{1}H} NMR (C_6D_5Br, 50 °C): δ 25.0 (s), 22.8 (s, **L**ZnEt side product); ^{11}B{^{1}H} NMR ($CDCl_3$, 50 °C): δ −16.5 (br s); ^{19}F{^{1}H} NMR ($CDCl_3$, 50 °C): δ −132.44 (br s, 8F, *o*-C_6F_5), −163.66 (br t, 4F, *p*-C_6F_5), −167.24 (t, 8F, *m*-C_6F_5).

X-Ray structure determinations†

X-Ray diffraction data were collected on a Bruker AXS Smart Apex II X-ray diffractometer (Mo Kα (λ = 0.71073 Å)) (Table 4). Suitable crystals of the complexes were mounted on a glass fiber in Paratone oil and flash frozen to −100 °C. For all data sets, a full hemisphere of data was collected. Structures were solved using direct methods and refined using full-matrix least squares procedures on F^2 with SHELXTL.[23] Except where noted, non-hydrogen atoms were refined anisotropically, and hydrogen atoms were included in calculated positions as spheres riding on their parent atoms, with thermal parameters fixed at 1.5 times the U_{eq} of the parent atom for methyl groups and 1.2 times the U_{eq} of the parent atoms for all others.

ROP of *rac*-lactide

***In situ* polymerization.** In a J-Young NMR tube, 4.1 mg (0.0025 mmol) of **5** and 18.0 mg (0.125 mmol) of *rac*-lactide were combined with 0.50 mL of bromobenzene-d_5. The tube was sealed and heated to 60 °C until conversion reached 90% (3.5 h). Conversion was determined by integration of the methine region of the ^{1}H NMR spectrum. *In situ* observation of polymerization of 10 equivalents at 50 °C followed the same methodology.

Large scale polymerization. In a Teflon sealed vial, 28.9 mg (0.0175 mmol) of **5** and 126 mg (0.874 mmol) of *rac*-lactide were combined with 3.50 mL of bromobenzene. After 3.5 h the reaction was quenched by addition of excess methanol (~5 mL). All solvents were then removed *in vacuo*, and the crude material was reconstituted in methylene chloride. The polymer was then precipitated by addition of methanol (5 mL) and isolated by centrifugation and decanting the solvent, followed by drying *in vacuo* for 2 h.

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