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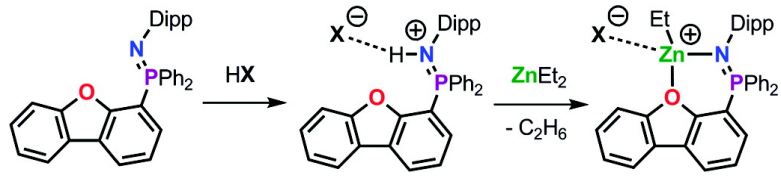

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Activated Zinc Complexes Supported by a Neutral, Phosphinimine-Containing Ligand: Synthesis and Efficacy for the Polymerization of Lactide

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*Summary: A general approach for the synthesis of cationic zinc complexes supported by neutral ancillary ligands has been developed and exploited to prepare [**L**H][B(C$_6$F$_5$)$_4$] (**L** = 4-(2,6-^{i}Pr$_2$-C$_6$H$_3$NPPh$_2$)dbf), **1a**, and [**L**H][SO$_3$CF$_3$], **1b**) using [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] and triflic acid, respectively. Reactions of **1a** and **1b** with diethylzinc afforded the corresponding complexes [LZnEt][B(C$_6$F$_5$)$_4$], **2a**, and [LZnEt(OSO$_2$CF$_3$)], **2b**. Both zinc complexes have exhibited notable activities for the catalytic polymerization of L-lactide.*

Polylactide has received growing attention in recent years as an environmentally friendly, potentially carbon neutral alternative to conventional polyolefins. Consequently, the development of new single-site metal catalysts for the ring-opening polymerization of lactide has seen tremendous growth over the past decade.[1] Several important families of single-site zinc catalysts have been developed that exhibit high polymerization activity;[2] however, these studies have predominantly employed neutral catalyst species supported by anionic ancillary ligands. A handful of recent studies have considered the use of neutral ligands,[3] though very few cationic species have been successfully applied to lactide polymerization.[2e,4] This is surprising given that borane-activated ion-pairs have realized significant success in the field of olefin polymerization catalysis.[5] For these reasons, we were motivated to prepare sterically and electronically unsaturated zinc complexes of the form [LZnR]$^+$ as homogeneous catalysts for lactide polymerization. Such activated species might be expected to show enhanced activity due to more facile coordination of lactide to the metal center.[6] To the best of our knowledge, the results reported herein constitute the first single-site cationic zinc species supported by neutral ligands to be used for the polymerization of lactide.

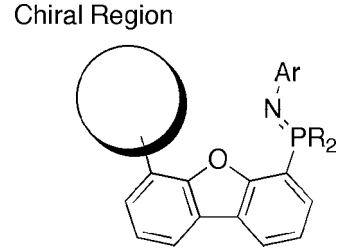

Figure 1. General structure of ligand **L**, to which a chiral group will be added in future generations of catalyst design.

A novel neutral ligand (**L**) has been designed whereby a single phosphinimine substituent is attached at the 4 position of dibenzofuran (dbf). This ligand is intended to coordinate in a bidentate manner through the phosphinimine nitrogen and the oxygen of the dbf backbone to afford six-membered metallacycles. The modular phosphinimine functionality, which allows for a high degree of steric and electronic tunability, is also chemically robust and serves as an excellent electron donor.[7] In addition, the ^{31}P NMR handle is particularly useful, as the phosphinimine is highly sensitive to the chemical environment, exhibiting large downfield shifts upon coordination to a Lewis acid. As the dbf backbone can be easily substituted at the 6 position,[8] we envision developing enantioselective catalysts by installation of chiral functionalities at this site (Figure 1).

The general ligand framework is easily synthesized by reaction of the phosphine precursor, generated according to a modified literature procedure,[9] with an appropriate aryl-azide

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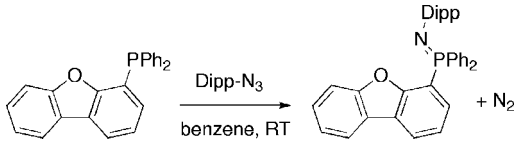
Scheme 1. Synthesis of Ligand L



under standard Staudinger conditions.[10] Specifically, the Dipp (2,6-diisopropylphenyl)-substituted ligand, which has been isolated as an analytically pure white powder in 79% yield, has been employed in the present work (Scheme 1). Ligand **L** gives rise to a single resonance at δ −13.4 in the $^{31}P\{^1H\}$ NMR (benzene-d_6) spectrum, and an overall C_s symmetry is observed. The isopropyl groups are chemically equivalent on the NMR time scale, as evidenced by a single isopropyl methyl resonance at δ 1.06 and 24.37 in the ^1H and $^{13}C\{^1H\}$ NMR spectra, respectively.

X-ray quality single crystals of **L** were readily obtained, and its molecular structure was determined crystallographically (Figure 2). The ligand binding geometry can be roughly defined by measurement of two torsion angles, which measure the rotation about the P1−C2 and P1−N1 bonds. An ideal six-membered chelate ring would have C1−C2−P1−N1 and C2−P1−N1−C25 torsion angles of 0° and 180°, respectively. The solid state structure of the free ligand, however, exhibits corresponding torsion angles of 168.0(2)° and 155.7(2)°. The significant rotation about the P1−C2 bond is likely a result of steric interactions between the dbf backbone and the bulky Dipp group of the phosphinimine functionality.

Protonated derivatives of **L** were prepared by reaction with the anilinium acid $[HNMe_2Ph][B(C_6F_5)_4]$ to give $[\mathbf{L}H][B(C_6F_5)_4]$,[11] **1a**, and triflic acid to afford $[\mathbf{L}H][SO_3CF_3]$, **1b** (Scheme 2). Both compounds were isolated as analytically pure, thermally stable white solids in excellent yield (97% and 85%, respectively). The conjugate base byproduct either can be removed, as in the case of **1a**, or is itself a weakly coordinating anion, as happens with **1b**.[12]

Compound **1a** exhibits a $^{31}P\{^1H\}$ NMR resonance at δ 36.1 in a 1:1 benzene-d_6/bromobenzene-d_5 solvent mixture, which is shifted 49.4 ppm downfield relative to the neutral ligand. The acidic proton appears as a doublet at δ 4.96 in the ^1H NMR spectrum, with a $^2J_{PH}$ of 9.3 Hz. This coupling is similar to that reported for related aminophosphonium salts and is thus indicative of a two-bond separation between the hydrogen and

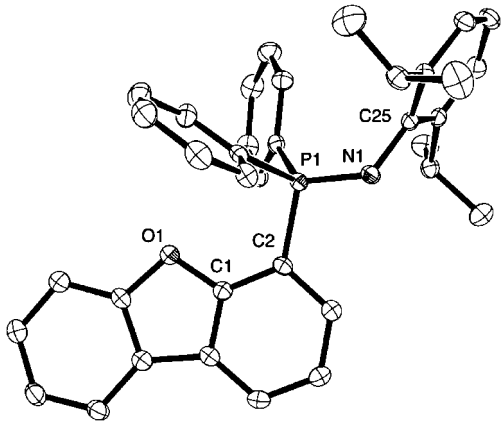
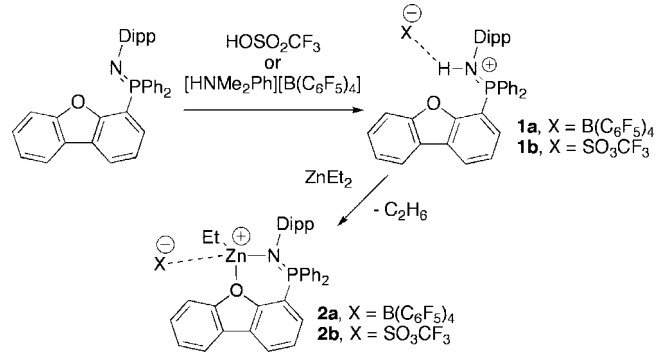


Figure 2. Molecular structure of neutral ligand **L** (depicted with 30% probability ellipsoids, H atoms are omitted for clarity). Selected bond distances (Å) and angles (deg): P(1)−N(1) = 1.559(2), N(1)−P(1)−C(2) = 106.9(1), C(25)−N(1)−P(1) = 127.2(2).

Scheme 2. Synthesis of Protonated Ligand Derivatives 1a and 1b and Zinc Complexes 2a and 2b



phosphorus atoms.[13] The molecule retains C_s symmetry upon protonation, as evidenced by a single isopropyl methyl doublet at 0.56 ppm in the ^1H NMR spectrum. The borate anion exhibits the expected ^{19}F NMR spectrum, with *ortho*, *para*, and *meta* fluorine environments resonating at −131.6, −162.4, and −166.2 ppm, respectively. These resonances do not differ significantly from those of the anilinium salt precursor and are consistent with a noncoordinating anion.[14] Similar spectroscopic signatures were observed for triflate derivative **1b**, which gives rise to a single $^{31}P\{^1H\}$ NMR resonance at δ 33.5 (a 46.9 ppm downfield shift relative to the neutral ligand). Likewise, **1b** also retains C_s symmetry in solution.

In an effort to unambiguously locate the acidic proton, the solid state structure of **1b** was determined (Figure 3). It was located from the electron density map and refined freely. A significant hydrogen-bonding interaction between the triflate anion and H1n is noted (N1−O4 = 2.789(2) Å). Further evidence for the protonation of the phosphinimine nitrogen is provided by a P−N bond (P1−N1 = 1.633(2) Å) elongation of 0.07 Å, relative to that observed in the neutral structure. The torsion angles about the C−P (C1−C2−P1−N1 = 64.9(2)°) and P−N bonds (C2−P1−N1−C25 = −34.6(2)°) are both distorted from ideal chelate geometry. However, unlike the neutral analogue, the major distortion is rotation about the P−N bond, which is presumably due to the cation−anion hydrogen-bonding interaction.

Bochmann et al. have previously reported the synthesis of cationic zinc complexes prepared from a protonated diazadiene ligand;[15] the present work utilizes a similar methodology, which

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(12) Synthesis of **1a**: Under an argon atmosphere, neutral ligand **L** (0.098 g, 0.186 mmol) was combined with 1 equiv of the anilinium activator $[HNMe_2Ph][B(C_6F_5)_4]$ (0.150 g, 0.187 mmol) in 2 mL of benzene. Immediately upon combining the reagents, the formation of a pale yellow oil was observed. The reaction mixture was allowed to stir for 5 min at ambient temperature, and then the benzene was decanted. The remaining oil was washed twice with pentane and dried under vacuum to afford protonated ligand **1a** as a white powder in 97% yield (0.217 g, 0.180 mmol). Synthesis of **1b** was performed in an analogous manner. See the Supporting Information for full details of the synthesis and characterization of both compounds.

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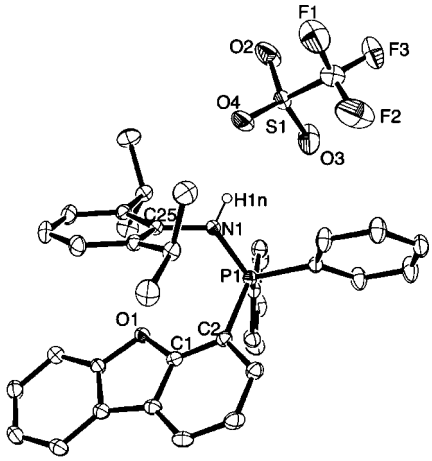

Figure 3. Molecular structure of **1b**·0.5C_6H_6 (30% probability ellipsoids, benzene solvent molecule and all H atoms except H1n are omitted for clarity). Selected bond distances (Å) and angles (deg): P1−N1 = 1.633(2), N1−O4 = 2.789(2), N1−P1−C2 = 109.59(8), C25−N1−P1= 126.83(13), C25−N1−H1n = 116(2), P1−N1−H1n = 116(2), N1−H1n−O4 = 166(2).

to the best of our knowledge represents only the second example of such a synthetic route. The isolation of the protonated ligand prior to complexation is necessary because diethylzinc does not bind to the ligand to form the requisite neutral complex, and thus, a one-pot synthesis does not afford the desired cationic species as cleanly as the stepwise procedure described herein. In addition, the one-pot reaction of a neutral ligand with EtZnCl and $K[B(C_6F_5)_4]$ does not generate the desired cationic zinc species as a salt metathesis product.

Reaction of **1a** or **1b** with diethylzinc occurs via an alkane elimination pathway with loss of ethane and concomitant generation of complexes [**L**ZnEt][$B(C_6F_5)_4$], **2a**, and [**L**ZnEt-(OSO_2CF_3)], **2b**, respectively.[16] The formation of ethane was corroborated by observation of effervescence and a resonance at δ 0.80 in the ^{1}H NMR spectra of both complexes. This signal disappeared completely upon exposure of the samples to three freeze−pump−thaw cycles. Complexes **2a** and **2b** were isolated as well-behaved white solids in good yield (87% and 83%, respectively) and were established to be indefinitely stable if stored under an inert atmosphere. Similar to **1a** and **1b**, complexes **2a** and **2b** exhibit downfield $^{31}P\{^1H\}$ NMR signals of δ 30.1 and 26.9 in 1:1 benzene-d_6/bromobenzene-d_5 solvent, indicative of tight phosphinimine binding to the zinc center. Both complexes exhibit the anticipated methyl (**2a**, δ 1.00; **2b**, δ 1.36) and methylene (**2a**, δ 0.73; **2b**, δ 0.80) ^{1}H NMR resonances, which integrate as 3H and 2H, respectively, and are thus consistent with the presence of a single ethyl group. The ^{19}F NMR spectrum of **2a** changes very little compared with the protonated precursor (δ −131.6, −162.4, −166.2). Specifically, the ^{19}F NMR spectrum of **2a** is consistent with a noncoordinating $B(C_6F_5)_4^-$ anion with no indication of fluorine atom or C_6F_5 transfer to the metal center, even after prolonged periods in solution at elevated temperature. Likewise, no evidence was observed for close Zn−F contacts in solution. Thus, complex **2a** is best described as a fully separated ion-pair. While the synthesis of cationic metal complexes using anilinium salts is well established, to the best of our knowledge the only previous example of isolation of a protonated ligand prior to reaction with a metal alkyl is that of the diazadiene ligand (*vide supra*).[15]

Although repeated attempts to grow X-ray quality crystals of **2a** were unsuccessful, the molecular structure of **2b** has been crystallographically established (Figure 4). Unsurprisingly, the crystal data reveal that the more strongly coordinating triflate anion is bound to the zinc center. A high degree of disorder exists in the structure, necessitating the modeling of the zinc atom, the ethyl group, and the dbf portion of the ligand together as a 66:34 disorder over two sites. This disorder appears to result from an interplay between the steric interaction of the ethyl group and ligand versus binding strength of the zinc center and the oxygen atom of the dbf framework. The major component of the disorder has a geometry in which the ethyl group is rotated away from the Dipp group, resulting in a long Zn−O interaction (Zn−O1 = 2.60(1) Å). In the less abundant component, the ethyl group is rotated toward the Dipp group in a more sterically encumbered position, but the Zn−O bond distance is substantially shorter (Znb−O1b = 2.08(2) Å). Interestingly, there is a widening of the N−Zn−C_{ethyl} bond angle in the minor component (N−Zn−C37 = 131.6(2)°; N−Znb−C37b = 138.8(5)°), rather than the opposite effect, which would be expected from stronger coordination of the oxygen atom. This can be attributed to the enhanced steric repulsion between the ethyl and Dipp groups. These observations suggest that while the Zn−O interaction is not as strong as the Zn−N bonding, it is likely to play a key role in the chemistry of the system. For both components, torsion angles about the C−P (N1−P1−C2−C1 = 20(2)°) and P−N bonds (C2−P1−N1−C25 = −156.1(6)°) are close to ideal.

While the solid state structure of **2b** indicates that the triflate anion is coordinated to zinc (Zn−O4 = 2.069(4) Å), it is anticipated that it should be highly susceptible to displacement,[17] a phenomenon that has been successful for generating cationic supramolecular materials of late transition metals.[18] Thus, while the complex should not be considered a true ion-pair, we view it as more accurately described as "activated".

Preliminary investigations of the reactivity of **2a** and **2b** toward the catalytic ring-opening polymerization of L-lactide have been undertaken. Polymerization experiments were performed on an NMR scale in 1:1 benzene-d_6/bromobenzene-d_5 solvent, and conversions were determined by integration of the lactide ^{1}H NMR methine resonance. With an initial 1 M concentration of L-lactide and a 1% catalyst loading, complex **2a** gave 90% conversion after 6 h at 100 °C, while **2b** required 9 h to reach 85% conversion under the same conditions, as determined by *in situ* NMR analysis. We suggest that the reduced activity of **2b** compared with **2a** is likely a direct result of competitive coordination of the triflate anion, a conclusion that is consistent with the observed coordination of the anion in the crystal structure of the complex. Material isolated from preparative ring-opening polymerization (ROP) experiments was

(16) Synthesis of **2a**: Under an argon atmosphere, a slight excess of diethylzinc (21 μL, 0.127 mmol) was added to a solution of **1a** (150 mg, 0.124 mmol) in 5 mL of toluene. The reaction mixture was heated to 100 °C for 16 h, and the solvent was then removed under vacuum. The crude product was dissolved in a minimum amount of bromobenzene and precipitated as a pale yellow oil by addition of pentane. The solvent was decanted, and the oil was washed twice with pentane and dried under vacuum to yield **2a** as a white powder in 87% yield (141 mg, 0.108 mmol). The synthesis of **2b** was performed in an analogous manner. See the Supporting Information for full details of the synthesis and characterization of both compounds. .

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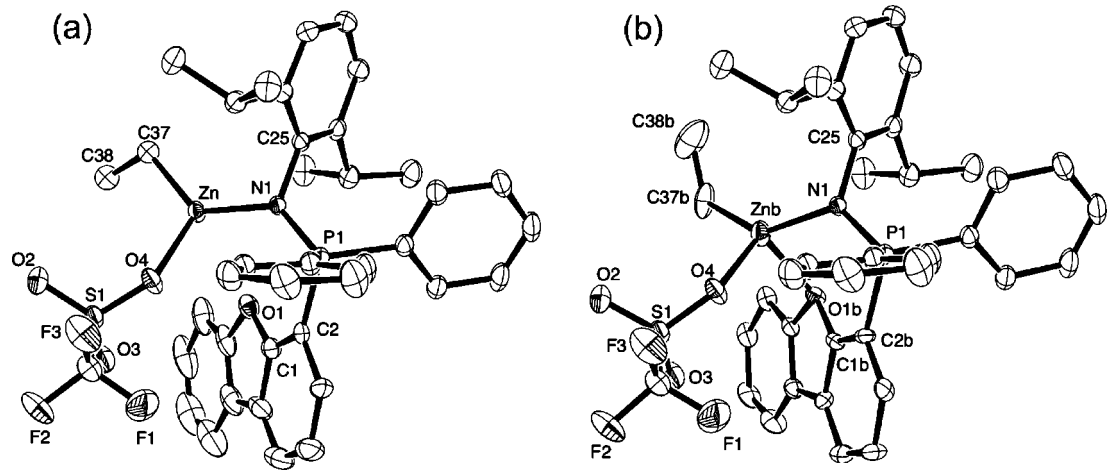

Figure 4. Molecular structure of the activated zinc complex, **2b**, where (a) is the major component and (b) is the minor component of the disorder (30% probability ellipsoids, H atoms are omitted for clarity). Atoms that are not disordered are shown in the images of both components, including the entire phosphinimine subunit and the coordinated triflate anion. Atoms of these components are thus given the same labels in both figures. Selected bond distances (Å) and angles (deg): Zn−O1 = 2.60(1), Znb−O1b = 2.08(2), Zn−N1 = 1.942(4), Znb−N1 = 2.008(8), Zn−O4 = 2.069(4), Znb−O4 = 1.983(8), Zn−C37 = 1.962(6), Znb−C37b = 1.95(1), P1−N1 = 1.606(2), P1−N1−Zn = 131.3(1), P1−N1−Znb = 123.8(2), N−Zn−C37 = 131.6(2), N−Znb−C37b = 138.8(5).

analyzed by gel-permeation chromatography. These data, which exhibit bimodal distributions, are similar for material isolated from both catalysts. The molecular weights are lower than expected, ranging from an estimated 2500 to 5000 g mol^{-1} for the higher molecular weight components. Such results imply significant rates of transesterification side reactions. The bimodality suggests both inter- and intrachain transesterification mechanisms may be operative.[19] Overall, the activities of these complexes are mediocre when compared with the well-known neutral zinc alkoxide catalyst systems,[2] but are more active than some previously reported neutral zinc alkyl species.[2e,f,h] Additionally, **2a** and **2b** exhibit substantially better activity than previously reported cationic zinc amide[4a] and cationic aluminum alkoxide[4c] species, which are inactive toward the ROP of lactide. Since alkyl initiating groups generally give reduced activity compared with alkoxide functionalities, future work will focus on the development of routes to analogous cationic zinc alkoxide complexes.

The protonation of neutral electron donors prior to metal complexation is an underdeveloped strategy, and we believe such a methodology holds significant promise for the development of sterically and electronically unsaturated complexes. Most notably, this approach allows a divalent metal center to be activated toward monomer insertion while still retaining an initiator group for the ring-opening polymerization of cyclic esters, such as lactide. As such, we have reported two activated, phosphinimine-stabilized zinc complexes and their preparation from aminophosphonium salts. While both zinc compounds are catalytically active for the polymerization of L-lactide at elevated temperature, the perfluorophenylborate ion pair **2a** is significantly more active, suggesting that competitive coordination of the triflate anion reduces the reactivity of **2b**. Ongoing efforts are focused on the synthesis and isolation of related cationic zinc alkoxide species. Further work will attempt to determine the exact nature of the catalytically active species in both systems, including a study of how readily the triflate anion of **2b** can be displaced by Lewis bases. In summary, this study represents the first example of a cationic zinc complex functioning as a single-site catalyst for the ring-opening polymerization of lactide.

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Supporting Information Available: Experimental and X-ray crystallographic data in PDF format and CIF files are available free of charge via the Internet at http://pubs.acs.org.

OM801034K

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