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Toward Stereoselective Lactide Polymerization Catalysts: Cationic Zinc Complexes Supported by a Chiral Phosphinimine Scaffold

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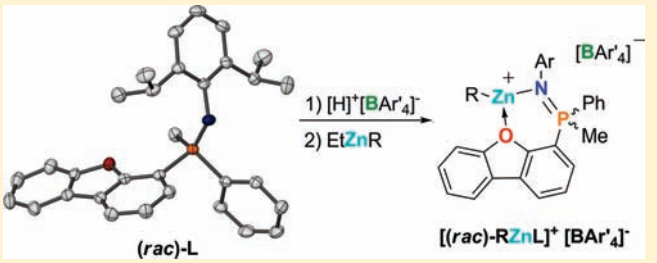
Supporting Information

ABSTRACT: The *P*-stereogenic phosphinimine ligands (dbf)-MePhP═NAr (**7**: Ar = Dipp; **8**: Ar = Mes; dbf = dibenzofuran, Dipp = 2,6-diisopropylphenyl, Mes = 2,4,6-trimethylphenyl) were synthesized as racemates via reactions of the parent phosphines (*rac*)-(dbf)MePhP (**6**) with organoazides. The ligands **7** and **8** were protonated by Brønsted acids to afford the aminophosphonium borate salts [(**7**)-H][BAr_4] (**9**: Ar = C_6F_5; **11**: Ar = Ph) and [(**8**)-H][BAr_4] (**10**: Ar = C_6F_5; **12**: Ar = Ph). The protonated ligands **9** and **10** were active toward alkane elimination reactions with diethylzinc and ethyl-[methyl-(*S*)-lactate]zinc to give the heteroleptic complexes [{(dbf)MePhP═NAr}ZnR][$B(C_6F_5)_4$] (Ar = Dipp, **13**: R = Et; **15**: R = methyl-(*S*)-lactate; Ar = Mes, **14**: R = Et; **16**: R = methyl-(*S*)-lactate). By contrast, reaction of the tetraphenylborate derivative **11** with diethylzinc yielded a phenyl transfer product, [(dbf)MePhP═NDipp]$ZnPh_2$ (**17**). Complex **15** was found to catalyze the ring-opening polymerization of *rac*-lactide.



INTRODUCTION

Polylactide (PLA) has received significant attention in the past decade as a useful material that is biodegradable and available from lactic acid feedstock, a renewable resource derived from wheat, corn, or sugar beets.[1] The polyester itself has a broad range of practical applications, ranging from packaging material and drug delivery systems to biomaterials (e.g., surgical sutures and bone screws) and microelectronics.[2] PLA is obtained synthetically via the ring-opening polymerization (ROP) of lactide, the cyclic diester of lactic acid.

A number of suitable catalyst systems for the polymerization of lactide have been developed.[1,3] However, there exists great potential for next-generation catalysts of enhanced efficiency. Desirable targets include catalysts capable of better stereocontrol, as stereoregular PLA polymers exhibit improved physical properties, such as increased crystallinity and melting points, when compared to their amorphous, low-melting, atactic analogues. Additionally, catalysts that can operate at ambient temperature would be desirable from an energy usage standpoint. Industrially, PLA is usually generated by using an ill-defined tin catalyst operating at >150 °C in a melt polymerization protocol.[4] Catalysts that function at lower temperatures are more energy efficient and may improve the kinetics of polymerization by reducing undesirable competing reactions, such as chain transfer or transesterification. Thus, significant challenges remain for the chemist in this area of PLA synthesis.

Several ligand frameworks for single-site PLA catalysts have been investigated, the most common of which are β-diketiminates,[5] phenolates,[6] and tris-pyrazolylborates.[7] These ancillaries have been used to support a variety of metals, including Ca, Mg, Zn, Al, and Ga, among others. Recently, our group has developed cationic Zn[8] and Mg[9] complexes, stabilized by dibenzofuran based chelates. Notably, some of these species exhibit extremely high catalytic activity at ambient temperature.[8b,c,9]

It has been demonstrated that catalysts containing chiral ligands often give better control over the stereoselectivity of the polymerization reaction via enantiomorphic site-control (monomer insertion is dictated by the stereochemistry of the catalyst) or chain-end control (each insertion step is controlled by the stereochemistry of the previously inserted monomer) mechanisms, although these two mechanisms are often intertwined and may operate cooperatively in some cases.[10] Catalysts capable of enantiomorphic site control can selectively polymerize predominantly one enantiomer of lactide to give isotactic PLA.[11] This mechanism provides access to a crystalline high-melting stereocomplex[12] of *D* and *L* polymer chains in the case of a racemic catalyst. Under chain-end control, a chiral catalyst may afford heterotactic PLA, which is also a high-melting material when compared to atactic PLA. With these possibilities in mind, we explored the synthesis of chiral phosphinimine ligands based on our recently established dbf framework. Herein, we report the synthesis of chiral phosphinimine ligands (dbf)MePhP═NDipp (**7**) and (dbf)MePhP═NMes (**8**), their protonation with Brønsted acids to form aminophosphonium salts, and subsequent reactions with organozinc reagents to form cationic zinc complexes. One of the obtained complexes was also investigated for its behavior toward the ROP of *rac*-lactide.

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EXPERIMENTAL SECTION

Reagents and General Procedures. All manipulations of air- and moisture-sensitive materials and reagents were performed under an atmosphere of dry argon using standard vacuum line techniques or in a glovebox. All solvents used for air-sensitive materials were first purified using an MBraun solvent purification system (SPS), stored in PTFE-sealed glass vessels over sodium benzophenone ketyl (THF and ether), CaH_2 (CH_2Cl_2, bromobenzene) or "titanocene" (pentane, benzene, and toluene), and distilled prior to use. Deuterated solvents were dried over sodium benzophenone ketyl or CaH_2, degassed via three freeze−pump−thaw cycles, distilled under vacuum and stored over 4 Å molecular sieves in glass bombs under argon. NMR spectra were recorded at ambient temperature (ca. 20 °C) with a Bruker AV II NMR spectrometer (300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 121.48 MHz for ^{31}P, 282.42 MHz for ^{19}F, and 96.29 MHz for ^{11}B). Chemical shifts are reported in parts per million relative to the external standards TMS (^{1}H), 85% H_3PO_4 (^{31}P), trifluorotoluene (^{19}F), and boron trifluoride diethyl etherate (^{11}B); residual H-containing species in CD_2Cl_2 (δ = 5.32 ppm) or $CDCl_3$ (δ = 7.27 ppm) were used as internal references (^{1}H). Assignments were aided by the use of ^{13}C{^{1}H}-DEPT and ^{1}H-^{13}C{^{1}H}-HSQC experiments (s = singlet, d = doublet, t = triplet, q = quartet, sp = septet, m = multiplet, br = broad, ov = overlapping signals). Elemental analyses were performed using an Elementar Vario Microcube instrument. The reagents $[H(Et_2O)_2][B(C_6F_5)_4]$,[13] $DippN_3$ and $MesN_3$,[14] and (*S*)-Me-$O_2CC(H)(Me)OZnEt$[15] were prepared according to literature methods. *Rac*-lactide was purchased from Alfa Aesar and purified by recrystallization from toluene (2 times), followed by sublimation. Flash chromatographic purification was run on silica gel (230−400 mesh, as received and without activation) using a fritted column (3 × 45 cm). GPC data were collected on a Viscotek Triple Detection 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 tetrahydrofuran (THF) at a concentration of 1 mg/mL. Molecular weights were determined relative to polystyrene standards, and scaled using a Mark−Houwink parameter of 0.58. MALDI-TOF data were collected using an Applied BioSystems Voyager Elite instrument.

$(BH_3)PPh(OMen)_2$ (OMen = (−)-mentholate) (1) and (BH_3)-PPh(dbf)$_2$ (2). The reagent 4-lithium-dibenzofuran[16] was prepared by modifying the literature method: To a cold (−78 °C) solution of dibenzofuran (1.68 g, 10 mmol) in THF (20 mL), *n*-BuLi (6.3 mL, 10 mmol, 1.6 M in hexane) was added dropwise. The cold bath was then removed, and the red solution was allowed to stir at ambient temperature for 30 min. The resulting dark red solution was added dropwise via syringe to a cold (−78 °C) solution of dichlorophenylphosphine (1.3 mL, 10 mmol) in THF (40 mL). (−)-Menthol (1.56 g, 10 mmol) in THF (10 mL) and pyridine (0.8 mL, 10 mmol) was subsequently added. A white solid was observed to form during the course of the addition. The cold bath was again removed, and the reaction mixture was stirred for 10 h. After removal of the solid by filtration, a cold (0 °C) solution of BH_3·THF (30 mL, 30 mmol, 1 M in THF) was slowly added, and the solution was stirred at ambient temperature for 1 h. The reaction was quenched with 100 mL of 1 N HCl. The organic layer was separated, and the aqueous phase was extracted with ether (3 × 10 mL). The combined organic fractions were washed with brine and dried over $MgSO_4$. After removal of the volatiles, the residue was mounted on a silica column and eluted with benzene/hexanes (1:1), giving **1** (0.75 g, 35%) and **2** (0.99 g, 45%) as the major products. **1**: ^{1}H NMR ($CDCl_3$): 7.87−7.81 (m, 2H, Ph), 7.51−7.46 (m, 3H, Ph), 4.24 (m, 1H, OC*H*), 4.00 (m, 1H, OC*H*), 2.28 (br d, $^3J_{HH}$ = 12.0 Hz, 1H), 2.21 (dsp $^5J_{HP}$ = 2.0 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, C*H*Me$_2$), 2.04 (br d, $^3J_{HH}$ = 12.0 Hz, 1H, OMen ring), 1.85 (dsp, $^5J_{HP}$ = 2.0 Hz, $^3J_{HH}$ = 7.0 Hz, 1H, C*H*Me$_2$), 1.69−1.56 (m, 5H, OMen ring), 1.55−1.26 (m, 5H, OMen ring), 1.19 (q, $^3J_{HH}$ = 12.0 Hz, 2H, OMen ring), 1.03−0.91 (ov m, 10H, OMen ring + Me + BH_3), 0.90−0.79 (ov m, 7H, Me and OMen ring), 0.67 (d, $^3J_{HH}$ = 6.9 Hz, 3H, Me), 0.62 (d, $^3J_{HH}$ = 6.9 Hz, 3H, Me). ^{13}C{^{1}H}NMR ($CDCl_3$): δ 133.78 (d, $^1J_{CP}$ = 80.0 Hz, *C*P), 132.10 (d, $^4J_{CP}$ = 2.3 Hz, *p*-Ph), 130.57 (d, $^2J_{CP}$ = 13.6 Hz, *o*-Ph), 128.47 (s, Ph), 128.32 (s, Ph), 80.01 (d, $^2J_{CP}$ = 4.1 Hz, OC), 79.59 (d, $^2J_{CP}$ = 6.8 Hz, OC), 48.99 (m, OMen), 44.12 (s, OMen), 43.57 (s, OMen), 34.27 (s, OMen), 34.15 (s, OMen), 31.69 (s, OMen), 31.59 (s, OMen), 25.58 (s, OMen), 25.26 (s, OMen), 23.00 (s, OMen), 22.85 (s, OMen), 22.25 (s, OMen), 22.18 (s, OMen), 21.38 (s, CH_3), 21.18 (s, CH_3), 16.12 (s, CH_3), 15.89 (s, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 129.50 (m). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −41.88 (d, $^1J_{PB}$ = 86.7 Hz). **2**: ^{1}H NMR ($CDCl_3$): δ 8.16−7.80 (m, 4H, 1,9-dbf), 7.52−7.26 (m, 13H, 2,3,7,8-dbf and Ph), 7.21−6.18 (m, 2H, 6-dbf), 1.55 (br, 3H, B*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.31 (s, aromatic *C*), 156.01 (s, aromatic *C*), 134.25 (d, $^1J_{CP}$ = 21.1 Hz, aromatic *C*), 133.60 (d, J_{CP} = 10.6 Hz, aromatic *C*), 132.60 (d, J_{CP} = 10.6 Hz, aromatic *C*), 131.83 (d, J_{CP} = 1.5 Hz, aromatic *C*), 131.53 (d, J_{CP} = 2.2 Hz, aromatic *C*), 129.36 (s, aromatic *C*), 128.65 (d, J_{CP} = 10.5 Hz, aromatic *C*), 128.50 (s, aromatic *C*), 127.66 (s, aromatic *C*), 124.96 (d, J_{CP} = 2.2 Hz, aromatic *C*), 124.58 (d, J_{CP} = 5.2 Hz, aromatic *C*), 123.33 (d, J_{CP} = 2.2 Hz, aromatic *C*), 123.20 (s, aromatic *C*), 122.94 (s, aromatic *C*), 121.81 (s, aromatic *C*), 120.80 (s, aromatic *C*), 112.47 (d, $^1J_{CP}$ = 30.9 Hz, aromatic *C*), 111.93 (s, aromatic *C*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 12.60 (br). ^{11}B{^{1}H} NMR ($CDCl_3$): δ −37.56 (br).

(OMen)PhPCl (3). Lithium *l*-menthoxide[17] [50 mmol, prepared from (−)-menthol (7.8 g, 50 mmol) and *n*-BuLi (31.2 mL, 50 mmol, 1.6 M in hexanes) in THF (100 mL) at 0 °C] was added dropwise to a solution of dichlorophenylphosphine (1.4 mL, 10 mmol) in THF (200 mL) at −78 °C. The solution was allowed to slowly warm to ambient temperature over a 15 h period. Removal of the volatiles under vacuum afforded an oily colorless solid. Benzene (50 mL) was added, and the solid was removed by filtration. The benzene was removed in vacuo to give a colorless oil (**3**) (>98% purity as determined by ^{31}P{^{1}H} NMR spectroscopy) in quantitative yield (14.8 g). ^{1}H NMR ($CDCl_3$, integration values are reported for each diasteromer): δ 7.79 (m, 4H, Ph), 7.49 (m, 6H, Ph), 4.05 (m, 1H, OC*H*), 3.94 (m, 1H, OC*H*), 2.32−2.29 (br m, 3H, OMen), 2.02 (m, 1H, OMen), 1.71 (d, 4H, $^3J_{HH}$ = 11.0 Hz, OMen), 1.45 (ov m, 4H, OMen), 1.30−1.04 (ov m, 4H, OMen), 0.99−0.8 (ov m, 20H, OMen). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 142.38 (d, $^1J_{CP}$ = 30.2 Hz, P*C*), 131.49 (s, *m*-Ph), 131.46 (s, *m*-Ph), 129.94 (d, $^2J_{CP}$ = 16.0 Hz, *o*-Ph), 129.59 (d, $^2J_{CP}$ = 16.0 Hz, *o*-Ph), 128.76 (s, *p*-Ph), 128.67 (s, *p*-Ph), 82.55 (d, $^2J_{CP}$ = 13.6 Hz, OCH), 80.20 (d, $^2J_{CP}$ = 11.3 Hz OCH), 48.99 (m, OMen), 43.25 (m, CH_2), 34.29 (s, CH_2), 31.96 (s, OMen), 31.93 (s, OMen), 25.60 (s, OMen), 25.50 (s, OMen), 23.12 (s, CH_2), 23.10 (s, CH_2), 22.33 (s, CH_3), 22.29 (s, CH_3), 21.28 (s, CH_3), 21.20 (s, CH_3), 15.98 (s, CH_3), 15.94 (s, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 177.58 (s), 174.59 (s).

(OMen)(dbf)PhP(BH_3) (4a, 4b). To a cold (−78 °C) solution of compound **3** (5.38 g, 18 mmol) in THF (50 mL) a solution of 4-lithium-dibenzofuran (18 mmol) in THF (50 mL) was slowly added via syringe. The resultant yellow solution was allowed to slowly rise to ambient temperature over 10 h, before being cooled to 0 °C. A solution of BH_3·THF (18 mL, 18 mmol, 1 M in THF) was injected, and the mixture was stirred at ambient temperature for 1 h. Distilled water (15 mL) was added very slowly to quench the reaction. The organic layer was separated, and the aqueous phase was extracted with hexanes (3 × 10 mL). The combined organic fractions were washed with brine and dried over $MgSO_4$. The volatiles were removed in vacuo, and the residue subjected to column separation. Elution with benzene/hexanes (1:1) afforded a 1:1 mixture of **4a** and **4b** (7.45 g, 93%). ^{1}H NMR ($CDCl_3$, integration values are reported for each diasteromer): δ 8.13 (m, 2H, 1,9-dbf), 8.04−1.82 (br m, 8H, dbf), 7.55−7.35 (br m, 14H, Ph + dbf), 4.42 (br, 2H, OC*H*), 2.21 (d, $^3J_{HH}$ = 12.0 Hz, 1H, OMen), 2.06 (m, 2H, OMen), 1.83 (sp, $^3J_{HH}$ = 6.9 Hz, 1H, C*H*Me$_2$), 1.80−1.33 (br ov m, 12H, OMen), 1.28−0.63 (ov m, 23H, Omen + B*H*$_3$), 0.42 (d, $^3J_{HH}$ = 5.4 Hz,

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3H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 156.35 (s, aromatic *C*), 156.27 (s, aromatic *C*), 133.56 (d, $^1J_{CP}$ = 51.3 Hz, PC), 132.62 (d, $^1J_{CP}$ = 53.6 Hz, PC), 131.56 (ov m, aromatic *C*), 128.54 (s, aromatic *C*), 128.50 (s, aromatic *C*), 128.37 (d, J_{CP} = 3.0 Hz, aromatic *C*), 127.77 (s, aromatic *C*), 125.01 (ov m, aromatic *C*), 123.39 (s, aromatic *C*), 123.30 (s, aromatic *C*), 123.23 (s, aromatic *C*), 122.95 (s, aromatic *C*), 122.82 (s, aromatic *C*), 122.68 (s, aromatic *C*), 120.82 (d, J_{CP} = 2.3 Hz, aromatic *C*), 118.20 (s, aromatic *C*), 117.40 (s, aromatic *C*), 116.55 (s, aromatic *C*), 112.14 (d, J_{CP} = 9.8 Hz, aromatic *C*), 80.62 (d, $^2J_{CP}$ = 3.0 Hz, OCH), 80.5 (d, $^2J_{CP}$ = 3.0 Hz, OCH), 49.18 (s, OCHCH(*i*-Pr)CH_2), 49.09 (s, OCHCH(*i*-Pr)CH_2), 43.79 (s, CH_2), 43.08 (s, CH_2), 34.34 (s, CH_2), 34.27 (s, CH_2), 31.72 (s, $CH_2CH(Me)CH_2$), 31.61 (s, $CH_2CH(Me)CH_2$), 25.71 (s, $CHMe_2$), 25.29 (s, $CHMe_2$), 22.93 (s, CH_2), 22.31 (s, Me), 22.23 (s, Me), 21.32 (s, Me), 21.16 (s, Me), 15.73 (s, Me), 15.40 (s, Me). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 99.36 (s). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −39.79 (br). Anal. Calcd for $C_{28}H_{34}BO_2P$: C, 75.68; H, 7.71. Found: C, 75.84; H, 7.40. X-ray quality crystals of **4** were obtained from a saturated solution of the compound in hexanes.

4-(BH_3)PPhMe-dbf (5). To a stirred solution of **4a,4b** (1.83 g, 4.1 mmol) in benzene (30 mL) MeLi (2.57 mL, 4.1 mmol, 1.6 M in diethyl ether) was added dropwise, and the resulting mixture was stirred for an additional 10 h at ambient temperature. To the resulting light yellow solution acidic water (10 mL 0.5 N HCl) was added, and the organic layer was separated. Workup was performed as described for compound **4a,4b** (using diethyl ether instead of benzene), followed by flash chromatographic purification (eluted with benzene/hexanes 1:4). Compound **5** was obtained as a colorless oil (1.16 g, 93%). ^1H NMR ($CDCl_3$): δ 8.12 (d, $^3J_{HH}$ = 8.0 Hz, 1H, 6-dbf), 7.98 (q, $^3J_{HH}$ = 6.0 Hz, 2H, dbf), 7.83 (m, 2H, dbf), 7.59−7.37 (m, 7H, dbf + Ph), 2.24 (d, $^2J_{PH}$ = 11.0 Hz, 3H, CH_3), 1.20 (br, 3H, BH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.16 (d, J_{CP} = 2.0 Hz, aromatic *C*), 156.08 (s, aromatic *C*), 132.78 (d, $^2J_{CP}$ = 12.8 Hz, aromatic *C*), 131.81 (d, J_{CP} = 9.8 Hz, aromatic *C*), 131.26 (d, J_{CP} = 3.0 Hz, aromatic *C*), 130.71 (s, aromatic *C*), 129.94 (s, aromatic *C*), 128.88 (d, J_{CP} = 9.8 Hz, aromatic *C*), 127.93 (s, aromatic *C*), 124.85 (d, J_{CP} = 4.5 Hz, aromatic *C*), 124.64 (d, J_{CP} = 2.0 Hz, aromatic *C*), 123.56 (s, aromatic *C*), 123.47 (s, aromatic *C*), 123.32 (s, aromatic *C*), 121.06 (s, aromatic *C*), 113.64 (d, $^1J_{CP}$ = 52.8 Hz, PC), 112.02 (s, aromatic *C*), 11.26 (d, $^1J_{CP}$ = 41.5 Hz, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 8.04 and 7.47 (ov). $^{11}B\{^1H\}$ NMR ($CDCl_3$): δ −37.53 and −38.08 (ov).

4-PPhMe-dbf (6). A solution of compound **5** (369 mg, 1.2 mmol) in diethylamine (8 mL) was heated to 40 °C for 10 h. After removing the volatiles in vacuo, NMR spectroscopy showed the only compounds present were **6** and $HNEt_2 \cdot BH_3$. A flash column (benzene:hexanes 1:2) separation resulted in the isolation of compound **6** as a colorless oil in 91% purity (the phosphine oxide was present as a 9% impurity as determined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy). No further purification attempts were made. ^1H NMR (C_6D_6): δ 7.62−7.59 (m, 2H, 1,9-dbf), 7.55−7.49 (m, 2H, dbf), 7.31−7.26 (m, 2H, dbf), 7.09−7.04 (m. 6H, dbf + Ph), 1.65 (d, $^2J_{HP}$ = 4.5 Hz, 3H, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 158.78 (d, $^2J_{CP}$ = 11.3 Hz, aromatic *C*), 156.85 (s, aromatic *C*), 139.58 (d, $^2J_{CP}$ = 12.8 Hz, aromatic *C*), 133.13 (d, $^2J_{CP}$ = 19.6 Hz, aromatic *C*), 130.85 (d, $^2J_{CP}$ = 9.0 Hz, aromatic *C*), 129.14 (s, aromatic *C*), 129.06 (s, aromatic *C*), 127.78 (s, aromatic *C*), 124.87 (s, aromatic *C*), 124.70 (s, aromatic *C*), 124.58 (s, aromatic *C*), 124.50 (d, J_{CP} = 2.3 Hz, aromatic *C*), 123.86 (d, J_{CP} = 6.8 Hz, aromatic *C*), 123.30 (s, aromatic *C*), 121.39 (d, $^1J_{CP}$ = 24.9 Hz), 112.45 (s, aromatic *C*), 11.64 (d, $^1J_{CP}$ = 14.34 Hz, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6): δ −35.95 (s) . Because of the minor oxidation of compound **6** upon column workup, fresh samples of **6** were prepared in situ and used directly in the synthesis of **7** and **8**, without prior removal of the $HNEt_2 \cdot BH_3$ byproduct.

(dbf)MePhP═NDipp (7). A solution of **5** (1.16 g, 4.0 mmol) in diethylamine (8 mL) was heated to 40 °C with stirring for 10 h. The volatiles were removed under vacuum, and the residue was dissolved in benzene (15 mL). Next, $DippN_3$ (1.0 g, 4.9 mmol) was slowly added. The resulting light yellow solution was stirred for 12 h, and the volatiles were removed in vacuo. To the resultant oily residue, pentane (10 mL) was added and, upon sonication, the beige solid **7** was isolated (1.2 g, 69%). ^1H NMR (CD_2Cl_2): δ 8.14 (d, $^3J_{HH}$ = 7.8 Hz, 1H, dbf), 8.18 (d, $^3J_{HH}$ = 7.5 Hz, 1H, dbf), 7.96−7.78 (m, 3H, dbf), 7.50−7.36 (m, 7H, dbf + Ph), 6.93 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *o*-dipp), 6.74 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *p*-dipp), 3.34 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, $CHMe_2$), 2.35 (d, $^2J_{HP}$ = 12.9 Hz, 3H PCH_3), 0.98 (ov d, $^3J_{HH}$ = 7.5 Hz, 6H, $CHMe_2$), 0.94 (ov d, $^3J_{HH}$ = 7.5 Hz, 6H, $CHMe_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 156.52 (s, aromatic *C*), 156.12 (d, $^3J_{CP}$ = 4.5 Hz, dbf), 144.88 (s, aromatic *C*), 143.19 (d, J_{CP} = 6.8 Hz, aromatic *C*), 135.89 (s, aromatic *C*), 134.48 (s, aromatic *C*), 131.58 (m. aromatic *C*), 131.10 (d, J_{CP} = 9.8 Hz, aromatic *C*), 128.93 (d, $^2J_{CP}$ = 12.1 Hz, aromatic *C*), 128.18 (s, aromatic *C*), 125.18 (d, $^3J_{CP}$ = 6.8 Hz, aromatic *C*), 124.50 (d, $^4J_{CP}$ = 2.3 Hz, dbf), 123.82 (s, aromatic *C*), 123.75 (s, aromatic *C*), 123.42 (d, $^3J_{CP}$ = 9.8 Hz, aromatic *C*), 122.93 (d, J_{CP} = 2.3 Hz, aromatic *C*), 121.31 (s, aromatic *C*), 119.98 (s, aromatic *C*), 119.49 (d, $^3J_{CP}$ = 3.0 Hz, aromatic *C*), 118.68 (s, aromatic *C*), 28.89 (s, $CHMe_2$), 23.95 (s, $CHMe_2$), 17.09 (d, $^1J_{CP}$ = 69.4 Hz, PCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −13.33 (s). Anal. Calcd for $C_{31}H_{32}NOP$: C, 79.97; H, 6.93; N, 3.01. Found: C, 79.80; H, 6.97; N, 2.97. X-ray quality crystals of **7** were obtained from a layered solution of the compound in benzene and pentane.

(dbf)MePhP═NMes (8). Compound **8** was prepared by an analogous procedure to that utilized for **7** [**5** (1.80 g, 5.92 mmol) and $MesN_3$ (1.24 g, 7.6 mmol)]. (Yield 1.90 g, 76%). ^1H NMR (CD_2Cl_2): δ 8.16−8.07 (m, 2H, 1,9-dbf), 8.00 (d, $^3J_{HH}$ = 7.8 Hz, 1H, 6-dbf), 7.89 (m, 2H, dbf), 7.46 (m, 7H, dbf + Ph), 6.75 (s, 2H, Mes), 2.36 (d, $^2J_{HP}$ = 13.0 Hz, 3H, P*Me*), 2.19 (s, 3H, *p*-*Me*), 2.07 (s, 6H, o-*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 156.50 (s, dbf), 156.06 (d, J_{CP} = 3.8 Hz, aromatic *C*), 145.37 (s, aromatic *C*), 136.41 (s, aromatic *C*), 135.00 (s, aromatic *C*), 132.62 (d, $^3J_{CP}$ = 7.5 Hz, aromatic *C*), 131.59 (m, aromatic *C*), 131.06 (d, $^3J_{CP}$ = 9.8 Hz, aromatic *C*), 128.98 (s, aromatic *C*), 128.81 (m, aromatic *C*), 128.18 (s, aromatic *C*), 127.70 (d, $^3J_{CP}$ = 3.8 Hz, aromatic *C*), 125.16 (d, J_{CP} = 6.8 Hz, aromatic *C*), 124.52 (d, $^4J_{CP}$ = 1.5 Hz, aromatic *C*), 123.78 (s, aromatic *C*), 123.42 (d, $^3J_{CP}$ = 9.8 Hz, aromatic *C*), 121.33 (s, aromatic *C*), 120.44 (s, aromatic *C*), 119.13 (s, aromatic *C*), 112.24 (s, aromatic *C*), 21.14 (s, *o*-CH_3), 20.85 (s, *p*-CH_3), 17.14 (d, $^1J_{CP}$ *J* = 65.7 Hz, PCH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ −10.46 (s). Anal. Calcd for $C_{28}H_{26}NOP$: C, 79.41; H, 6.19; N, 3.31. Found: C, 78.99; H, 6.16; N, 3.37. Crystals of **8** suitable for X-ray diffraction studies were obtained from a layered solution of the compound in benzene and pentane.

[(dbf)MePhP═NHDipp][$B(C_6F_5)_4$] (9). Compound **7** (0.216 g, 0.465 mmol) and $[H(Et_2O)_2][B(C_6F_5)_4]$ (0.385 g, 0.465 mmol) were dissolved in benzene (10 mL) and stirred for 30 min at ambient temperature, resulting in a biphasic mixture. The supernatant layer was removed by pipet, leaving an oil that was washed with pentane (3 × 4 mL). The thick residue was subjected to vacuum, resulting in the isolation of a white solid (0.485 g, 91%). ^1H NMR (CD_2Cl_2): δ 8.47 (d, $^3J_{HH}$ = 7.8 Hz, 1H, dbf), 8.12 (d, $^3J_{HH}$ = 7.8 Hz, 1H, dbf), 7.88 (m, 1H, dbf), 7.75−7.52 (m, 9H, dbf + Ph), 7.34 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *p*-Dipp), 7.17 (d, $^3J_{HH}$ = 7.5 Hz, 2H, *m*-Dipp), 5.11 (d, $^2J_{HP}$ = 9.0 Hz, 1H, N*H*), 2.95 (sp, $^3J_{HH}$ = 6.9 Hz, 2H, $CHMe_2$), 2.56 (d, $^2J_{HP}$ = 12.3 Hz, 3H, PCH_3), 1.02 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CHMe_2$), 0.93 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CHMe_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 157.01 (s, dbf-quaternary), 156.76 (s, dbf-quaternary), 150.29 (br, C_6F_5), 148.29 (s, dbf), 148.24 (s, dbf), 147.11 (br, C_6F_5), 140.38 (br, C_6F_5), 138.45 (br, C_6F_5), 137.15 (br, C_6F_5), 136.80 (d, J_{CP} = 3.0 Hz, aromatic *C*), 135.19 (br, C_6F_5), 132.32 (d, $^2J_{CP}$ = 11.0 Hz, aromatic *C*), 131.09 (d, $^2J_{CP}$ = 14.0 Hz, aromatic *C*), 130.58 (d, J_{CP} = 2.3 Hz, aromatic *C*), 130.04 (m, aromatic *C*), 129.59 (d, J_{CP} = 3.0 Hz, aromatic *C*), 128.22 (d, J_{CP} = 5.2 Hz, aromatic *C*), 127.26 (d, J_{CP} = 6.8 Hz, aromatic *C*), 125.40 (d, J_{CP} = 2.0 Hz), 125.00 (d, J_{CP} = 11.0 Hz, aromatic *C*), 122.44 (s, aromatic *C*),

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122.23 (s, aromatic *C*), 121.40 (s, aromatic *C*), 120.01 (s, aromatic *C*), 112.42 (s, aromatic *C*), 106.76 (s, aromatic *C*), 105.43 (s, aromatic *C*), 29.78 (s, *C*HMe$_2$), 23.74 (s, CH*Me*$_2$), 10.84 (d, $^1J_{PC}$ = 71.7 Hz, P*C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 38.00 (s). ^{19}F NMR (CD_2Cl_2): δ −132.20 (br, 8F, *o*-C_6F_5), −162.82 (t, $^3J_{FF}$ = 21.2 Hz, 4F, *p*-C_6F_5), −166.67 (br, 8F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −16.68 (br s). Anal. Calcd for $C_{55}H_{33}BF_{20}NOP$: C, 57.66; H, 2.90; N, 1.22. Found: C, 57.63; H, 2.88; N, 1.24. X-ray quality crystals of **9** were grown from a solution of the compound in CH_2Cl_2 and pentane.

[(dbf)MePhP═NHMes][B(C$_6$F$_5$)$_4$] (10). The synthetic procedure for compound **10** follows that given for **9**. Compound **8** (0.282 g, 0.665 mmol) and $[H(Et_2O)_2][B(C_6F_5)_4]$ (0.551 g, 0.665 mmol) were reacted to give compound **10** (0.690 g, 94%). ^1H NMR (CD_2Cl_2): δ 8.45 (m, 1H, dbf), 8.10 (d, $^3J_{HH}$ = 7.5 Hz, 1H, dbf), 7.85−7.75 (m, 3H, dbf), 7.66−7.51 (m, 7H, dbf + Ph), 6.88 (s, 2H, *m*-Mes), 5.07 (br, 1H, N*H*), 2.49 (d, $^2J_{HP}$ = 13.0 Hz, 3H, P*Me*), 2.22 (s, 3H, *p*-*Me*), 2.02 (s, 6H, o-*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 156.90 (d, J_{CP} = 2.0 Hz, dbf-quaternary), 156.72 (s, dbf-quaternary), 150.32 (br, C_6F_5), 147.06 (br, C_6F_5), 140.35 (br, C_6F_5), 139.37 (d, J_{CP} = 2.0 Hz, aromatic *C*), 138.50 (br, C_6F_5), 137.22 (br ov d, $^2J_{CP}$ = 4.0, aromatic *C* + C_6F_5), 136.45 (d, J_{CP} = 3.0 Hz, aromatic *C*), 135.21 (br, C_6F_5), 132.26 (d, $^2J_{CP}$ = 11.0 Hz, aromatic *C*), 130.89 (m, aromatic *C*), 129.87 (m, aromatic *C*), 129.32 (d, J_{CP} = 3.0 Hz, aromatic *C*), 128.86 (s, aromatic *C*), 127.11 (d, J_{CP} = 7.5 Hz, aromatic *C*), 125.25 (s, aromatic *C*), 124.85 (d, $^2J_{CP}$ = 12.0 Hz, aromatic *C*), 122.72 (s, aromatic *C*), 122.61 (s, aromatic *C*), 122.15 (s, aromatic *C*), 121.33 (s, aromatic *C*), 112.46 (s, aromatic *C*), 107.83 (s, aromatic *C*), 106.50 (s, aromatic *C*), 20.99 (s, *p*-Me), 19.74 (s, *o*-Me), 10.60 (d, $^1J_{CP}$ = 72 Hz, P*C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 35.92 (s). ^{19}F NMR (CD_2Cl_2): δ −132.25 (br, 8F, *o*-C_6F_5), −162.81 (t, $^3J_{FF}$ = 21.2 Hz, 4F, *p*-C_6F_5), −166.66 (br t, $^3J_{FF}$ = 21.2 Hz, 8F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −16.65 (s). Anal. Calcd for $C_{52}H_{27}BF_{20}NOP$: C, 56.60; H, 2.47; N, 1.27. Found: C, 56.92; H, 2.76; N, 1.24.

[(dbf)MePhP═NHDipp][B(C$_6$H$_5$)$_4$] (11). Compound **7** (0.180 g, 0.387 mmol) was dissolved in methanol (2 mL), to which $HCl_{(aq)}$ (1 N, 0.4 mL) was added. With stirring, $NaBPh_4$ (0.135 g, 0.387 mmol) in methanol (1 mL) was added and a white precipitate formed immediately. The solid was isolated by filtration, washed with methanol and dried in vacuo to yield **11** (0.277 g, 91%). ^1H NMR (CD_2Cl_2): δ 8.39 (d, $^3J_{HH}$ = 7.8 Hz, 1H, dbf), 8.10 (d, $^3J_{HH}$ = 7.2 Hz, 1H, dbf), 7.81 (t, $^3J_{HH}$ = 7.5 Hz, 1H, dbf), 7.62−7.49 (m, 8H, dbf + Ph), 7.36−7.24 (ov m, 10H, Ph), 7.15 (d, $^3J_{HH}$ = 7.8 Hz, 2H, *m*-Dipp), 6.97 (t, $^3J_{HH}$ = 6.0 Hz, 8H, *m*-Ph), 6.80 (t, $^3J_{HH}$ = 7.2 Hz, 4H, *p*-Ph), 3.40 (s, 1H, N*H*), 2.86 (sp, $^3J_{HH}$ = 6.6 Hz, 2H, C*H*Me$_2$), 1.95 (d, $^2J_{HP}$ = 12.9 Hz, 3H, P*C*H$_3$), 0.98 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$), 0.90 (d, $^3J_{HH}$ = 6.6 Hz, 6H, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 164.63 (q, 1:1:1:1, $^1J_{BC}$ = 49.1, *ipso*-BPh_4^-), 156.78 (s, dbf), 156.62 (s, dbf), 148.30 (d, $^3J_{CP}$ = 3.0 Hz, dbf), 136.47 (s, dbf), 136.34 (d, $^3J_{CP}$ = 3.0 Hz, dbf), 132.40 (d, $^3J_{CP}$ = 11.3 Hz, aromatic *C*), 130.90 (s, aromatic *C*), 130.72 (m, aromatic *C*), 130.24 (s, aromatic *C*), 129.79 (s, aromatic *C*), 129.18 (s, dbf), 128.52 (d, $^3J_{CP}$ = 5.3 Hz, aromatic *C*), 126.80 (d, $^3J_{CP}$ = 7.5 Hz, aromatic *C*), 126.21 (m, Ph), 125.15 (m, aromatic *C*), 124.86 (d, $^3J_{CP}$ = 3.8 Hz, aromatic *C*), 122.50 (s, aromatic *C*), 122.27 (s, Ph), 122.13 (s, dbf), 121.59 (s, aromatic *C*), 29.59 (s, *C*HMe$_2$), 23.85 (d, J_{CP} = 3.0 Hz, CH*Me*$_2$), 10.06 (d, $^1J_{CP}$ = 70.9 Hz, P*C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 37.95 (s). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −6.53 (br s). Anal. Calcd for $C_{55}H_{53}BNOP$: C, 84.07; H, 6.80; N, 1.78. Found: C, 84.34; H, 7.13; N, 1.81. Single crystals of **11** suitable for X-ray analysis were obtained from a concentrated solution of the compound in CH_2Cl_2 and pentane.

[(dbf)MePhP═NHMes][B(C$_6$H$_5$)$_4$] (12). Compound **12** was prepared by a procedure analogous to that used for **11**. Reaction of **9** (0.656 g, 1.55 mol) with $NaBPh_4$ (0.530 g, 1.55 mmol) yielded **12** 1.08 g (90%). ^1H NMR (CD_2Cl_2): δ 8.39 (d, $^3J_{HH}$ = 7.8 Hz, 1H, dbf), 8.10 (d, $^3J_{HH}$ = 7.5 Hz, 1H, dbf), 7.80 (s, 1H, dbf), 7.61−7.45 (m, 8H, dbf + Ph), 7.33 (s, 9H, Ph), 6.96 (t, $^3J_{HH}$ = 7.5 Hz, 8H, *m*-Ph), 6.87 (s, 2H, *m*-Mes), 6.81 (t, $^3J_{HH}$ = 7.2 Hz, 4H, *p*-Ph), 4.82 (br s, 1H, N*H*), 2.24 (s, 3H, *p*-*Me*), 1.99 (d, $^2J_{HP}$ = 12.9 Hz, 3H, P*C*H$_3$), 1.95 (s, 6H, *o*-*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 164.58 (q, 1:1:1:1, $^1J_{BC}$ = 49.1 Hz, *ipso*-BPh_4^-), 156.72 (s, dbf), 156.57 (s, dbf), 139.26 (d, $^3J_{CP}$ = 2.3 Hz, dbf), 137.44 (d, $^3J_{CP}$ = 3.0 Hz, dbf), 136.49 (s, aromatic *C*), 136.16 (d, $^3J_{CP}$ = 3.0 Hz, aromatic *C*), 132.33 (d, $^2J_{CP}$ = 12.1 Hz, aromatic *C*), 130.68 (m, aromatic *C*), 129.67 (s, aromatic *C*), 129.56 (d, $^3J_{CP}$ = 3.8 Hz, aromatic *C*), 129.09 (d, $^3J_{CP}$ = 2.7 Hz, aromatic *C*), 126.69 (d, $^3J_{CP}$ = 6.8 Hz, aromatic *C*), 126.20 (m, aromatic *C*), 125.07 (s, aromatic *C*), 124.82 (d, $^2J_{CP}$ = 11.3 Hz, aromatic *C*), 122.63 (s, aromatic *C*), 122.32 (s, aromatic *C*), 122.06 (s, aromatic *C*), 120.96 (s, aromatic *C*), 112.46 (s, aromatic *C*), 107.36 (s, aromatic *C*), 106.03 (s, aromatic *C*), 21.05 (s, *p*-*C*H$_3$), 19.78 (s, o-CH$_3$), 10.00 (d, $^1J_{CP}$ = 70.2 Hz, P*C*H$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 37.27. $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −6.53 (s). Anal. Calcd for $C_{52}H_{47}BNOP$: C, 83.98; H, 6.37; N, 1.88. Found: C, 83.70; H, 6.20; N, 1.87. Single crystals of **12** suitable for X-ray analysis were obtained from a solution of the compound in CH_2Cl_2 and pentane.

[{(dbf)MePhP═NDipp}ZnEt][B(C$_6$F$_5$)$_4$] (13). In a J-Young tube, compound **9** (0.83 g, 0.072 mmol) and an excess of diethylzinc (0.1 mL) were dissolved in C_6D_5Br (0.5 mL). The tube was immersed in liquid N_2, evacuated (10^{-2} Torr), and heated to 100 °C. Monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy indicated it had proceeded to completion after 6 h. All volatiles were removed in vacuo, and the residue was successively washed with benzene (0.5 × 3 mL) and pentane (1 × 3 mL), and then dried under vacuum. Complex **13** was isolated as an analytically pure white solid (0.78 g, 87%). ^1H NMR (CD_2Cl_2): δ 8.46 (d, $^3J_{HH}$ = 7.8 Hz, 1H, dbf), 8.16 (d, $^3J_{HH}$ = 6.6 Hz, 1H, dbf), 7.78 (s, 1H, dbf), 7.71−7.50 (m, 9H, dbf + Ph), 7.24 (br, 2H, *m*-Dipp), 7.11 (br, 1H, *p*-Dipp), 3.35 (sp, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*Me$_2$), 2.84 (sp, $^3J_{HH}$ = 6.6 Hz, 1H, C*H*Me$_2$), 2.28 (d, $^2J_{HP}$ = 12.6 Hz, 3H, P*C*H$_3$), 1.22 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C*H*$_3$), 1.09 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C*H*$_3$), 1.00 (t, $^3J_{HH}$ = 7.8 Hz, 3H, CH$_2$C*H*$_3$), 0.86 (ov m, 5H, C*H*$_3$ and C*H*$_2$CH$_3$), 0.73 (d, $^3J_{HH}$ = 6.6 Hz, 3H, C*H*$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 156.43 (s, dbf), 156.23 (s, dbf), 150.26 (br, C_6F_5), 146.95 (br ov m, C_6F_5 + aromatic *C*), 140.40 (br, C_6F_5), 138.46 (br, C_6F_5), 137.14 (br, C_6F_5), 135.94 (s, aromatic *C*), 135.26 (br, C_6F_5), 131.78 (d, $^3J_{CP}$ = 9.0 Hz, aromatic *C*), 131.16 (d, $^2J_{CP}$ = 12.8 Hz, aromatic *C*), 130.14 (m, aromatic *C*), 128.76 (s, aromatic *C*), 128.42 (s, aromatic *C*), 127.06 (d, $^3J_{CP}$ = 6.8 Hz, aromatic *C*), 126.42 (s, aromatic *C*), 126.02 (s, aromatic *C*), 125.90 (s, aromatic *C*), 125.75 (s, aromatic *C*), 125.50 (s, aromatic *C*), 125.04 (s, aromatic *C*), 122.67 (s, aromatic *C*), 122.49 (s, aromatic *C*), 112.18 (s, aromatic *C*), 111.36 (s, aromatic *C*), 110.04 (s, aromatic *C*), 29.63 (s, *C*HMe$_2$), 29.35 (s, *C*HMe$_2$), 26.10 (s, CH*Me*$_2$), 25.82 (s, CH*Me*$_2$), 22.30 (d, $^1J_{CP}$ = 28.7 Hz, P*C*H$_3$), 10.79 (s, CH$_2$*C*H$_3$), 4.49 (s, *C*H$_2$CH$_3$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 32.66. ^{19}F NMR (CD_2Cl_2): δ −133.05 (br, 8F, *o*-C_6F_5), −163.67 (t, $^3J_{FF}$ = 19.8 Hz, 4F, *p*-C_6F_5), −167.52 (t, $^3J_{FF}$ = 19.8 Hz, 8F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −16.67 (br s). Anal. Calcd for $C_{57}H_{37}BF_{20}NOPZn$: C, 55.25; H, 3.01; N, 1.13. Found: C, 55.61; H, 3.14; N, 1.30.

[{(dbf)MePhP═NMes}ZnEt][B(C$_6$F$_5$)$_4$] (14). Complex **14** was prepared by a procedure similar to that described for complex **13**. Using **10** (0.13 g, 1.176 mmol) and excess diethylzinc, **14** was obtained as a white solid (0.10 g, 73%). ^1H NMR (C_6D_5Br): δ 7.95 (d, $^3J_{HH}$ = 7.8 Hz, 1H, dbf), 7.72 (d, $^3J_{HH}$ = 7.5 Hz, 1H, dbf), 7.43−7.04 (m, 10H, dbf + Ph), 6.72 (s, 1H, *m*-Mes), 6.55 (s, 1H, *m*-Mes), 2.15 (s, 3H, *o*-*Me*), 2.04 (d, $^3J_{HH}$ = 2.0 Hz, 3H, *o*-*Me*), 1.63 (d, $^2J_{HP}$ = 12.3 Hz, 3H, P*C*H$_3$), 1.47 (s, 3H, *p*-*Me*), 0.81 (t, $^3J_{HH}$ = 7.8 Hz, 3H, CH$_2$C*H*$_3$), 0.23 (q, $^3J_{HH}$ = 7.8 Hz, 2H, C*H*$_2$CH$_3$). $^{13}C\{^1H\}$ NMR (C_6D_5Br): δ 156.02 (s, dbf), 155.48 (s, dbf), 150.23 (br, C_6F_5), 147.05 (br, C_6F_5), 140.10 (br, C_6F_5), 138.28 (br, C_6F_5), 137.65 (d, $^3J_{CP}$ = 7.5 Hz, aromatic *C*), 136.85 (br, C_6F_5), 135.50 (d, $^3J_{CP}$ = 4.0 Hz, aromatic *C*), 135.06 (br ov m, C_6F_5), 134.63 (ov s, aromatic *C*), 131.85 (ov s, aromatic *C*), 130.32 (d, $^3J_{CP}$ = 9.8 Hz, aromatic *C*), 127.34 (d, $^3J_{CP}$ = 5.0 Hz, aromatic *C*), 125.22 (s, aromatic *C*), 124.70 (d, $^2J_{CP}$ = 11.0 Hz, aromatic *C*), 122.75 (ov s, aromatic *C*),

Table 1. Crystallographic Data for Compounds 4, 7, 8, 9, 11, 12, and 17

	4	7	8	9	11	12·CH_2Cl_2	17
chemical formula	$C_{28}H_{34}BO_2P$	$C_{31}H_{32}NOP$	$C_{28}H_{26}NOP$	$C_{55}H_{33}BF_{20}NOP$	$C_{55}H_{53}B$ NOP	$C_{53}H_{49}BCl_2NOP$	$C_{43}H_{42}NOPZn$
formula weight	444.33	465.55	423.47	1145.60	785.76	828.61	685.12
crystal system	triclinic	triclinic	triclinic	triclinic	monoclinic	triclinic	monoclinic
space group	$P1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a [Å]	10.1381(9)	9.2839(8)	8.8919(9)	12.425(1)	9.865(2)	10.506(2)	12.079(2)
b [Å]	10.9317(9)	10.4980(7)	9.587(1)	12.448(1)	22.917(5)	11.375(2)	18.919(3)
c [Å]	23.438(2)	13.7598(8)	13.748(1)	16.291(1)	23.616(5)	18.371(3)	15.912(3)
α [deg]	78.951(1)	96.530(1)	81.417(1)	77.596(1)	90	81.683(2)	90
β [deg]	80.774(1)	101.059(1)	77.165(1)	85.955(1)	97.384	88.606(2)	96.948(2)
γ [deg]	89.706(1)	100.442(1)	84.327(1)	89.218(1)	90	83.530(2)	90
V [Å^3]	2515.5(4)	1279.0(2)	1127.3(2)	2454.7(3)	5295(2)	2158.3(6)	3609(1)
Z	4	2	2	2	4	2	4
D_{calcd} [g cm^{-3}]	1.173	1.209	1.248	1.550	0.986	1.275	1.261
μ [mm^{-1}]	0.131	0.131	0.142	0.175	0.086	0.228	0.758
R_{int}	0.0318	0.0431	0.0362	0.0449	0.1013	0.0446	0.0325
GOF on F^2	0.971	1.009	1.041	1.039	0.969	1.081	1.078
R_1 [$I > 2\sigma(I)$][a]	0.0416	0.0375	0.0353	0.0359	0.0702	0.0477	0.0266
wR_2 (all data)[a]	0.1076	0.0941	0.1017	0.0974	0.2095	0.1387	0.0778

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; w$R_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

122.13 (s, aromatic *C*), 121.93 (s, aromatic *C*), 112.18 (s, aromatic *C*), 111.13 (s, aromatic *C*), 110.88 (s, aromatic *C*), 20.74 (s, *o-Me*), 20.55 (s, *o-Me*), 19.83 (s, *p-Me*), 11.34 (s, CH_2CH_3)), 10.18 (d, $^1J_{CP}$ = 68.0 Hz, PCH_3), 2.00 (s, CH_2CH_3). Four aromatic C signals obscured by solvent. $^{31}P\{^1H\}$ NMR (C_6D_5Br): δ 31.78 (s). ^{19}F NMR (CD_2Cl_2): δ −132.26 (br, 8F, *o*-C_6F_5), −162.86 (t, $^3J_{FF}$ = 19.7 Hz, 4F, *p*-C_6F_5), −166.70 (t, $^3J_{FF}$ = 19.7 Hz, 8F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −16.68 (br s). Anal. Calcd for $C_{54}H_{31}BF_{20}NOPZn$: C, 54.18; H, 2.61; N, 1.17. Found: C, 54.61; H, 2.54; N, 1.20.

[{(dbf)MePhP═NDipp}Zn(OCH(Me)CO_2Me)][B(C_6F_5)$_4$] (15). A procedure similar to that described for complex **13** was used for the reaction of **9** (0.114 g, 0.1 mmol) with $MeO_2CC(H)(Me)OZnEt$ (0.217 mg, 0.11 mmol) to afford complex **15** (0.106 g, 81%). ^1H NMR (CD_2Cl_2): δ 8.49 (d, $^3J_{HH}$ = 6.0 Hz, 1H, dbf), 8.14 (d, $^3J_{HH}$ = 7.5 Hz, 1H, dbf), 7.86 (d, $^3J_{HH}$ = 3.0 Hz, 1H, dbf), 7.73−7.15 (m, ov, 12H, dbf + Ph + *m*-Dipp + *o*-Dipp), 3.92 (br, 1H, $CHCH_3$), 3.4 (d, $^3J_{HP}$ = 9.9 Hz, 3H, OCH_3), 3.19 (sp, $^3J_{HH}$ = 6.6 Hz, 1H, $CHMe_2$), 2.77 (sp, $^3J_{HH}$ = 6.6 Hz, 1H, $CHMe_2$), 2.42 (d, $^2J_{HP}$ = 12.9 Hz, 3H, PCH_3), 1.26 (d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHMe_2$), 1.20 (d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHMe_2$), 1.04 (d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHMe_2$), 0.93 (d, $^3J_{HH}$ = 6.8 Hz, 3H, $CHCH_3$), 0.66 (d, $^3J_{HH}$ = 6.6 Hz, 3H, $CHMe_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 156.63 (s, aromatic *C*), 150.63 (br, C_6F_5), 148.70 (s, aromatic *C*), 148.34 (s, aromatic *C*), 147.38 (br, C_6F_5), 140.38 (br, C_6F_5), 138.36 (br, C_6F_5), 137.13 (br, C_6F_5), 136.55 (s, aromatic *C*), 135.15 (br, C_6F_5), 132.86 (d, $^3J_{CP}$ = 11.3 Hz, aromatic *C*), 132.02 (s, aromatic *C*), 131.18 (m, aromatic *C*), 129.98 (s, aromatic *C*), 129.50 (s, aromatic *C*), 127.50 (s, aromatic *C*), 126.42 (s, aromatic *C*), 125.32 (s, aromatic *C*), 124.86 (d, $^3J_{CP}$ = 12.0 Hz, aromatic *C*), 122.60 (s, aromatic *C*), 122.18 (s, aromatic *C*), 121.61 (s, aromatic *C*), 112.36 (s, aromatic *C*), 41.69 (d, $^3J_{CP}$ = 6.0 Hz, O*Me*), 29.35 (s, $CHMe_2$), 26.39 (s, $CHMe_2$), 26.18 (s, $CHMe_2$), 23.78 (s, $CHMe$), 23.41 (s, $CHMe_2$), 23.05 (s, $CHMe_2$), 11.46 (d, $^1J_{CP}$ = 74.0 Hz, PCH_3). *C*HMe signal obscured by solvent. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.68 (s). ^{19}F NMR (CD_2Cl_2): δ −132.14 (br, 8F, *o*-C_6F_5), −162.70 (t, $^3J_{FF}$ = 19.8 Hz, 4F, *p*-C_6F_5), −166.56 (br t, $^3J_{FF}$ = 16.9 Hz, 8F, *m*-C_6F_5). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −16.66 (br s). Anal. Calcd for $C_{59}H_{38}BF_{20}NO_4PZn$: C, 54.01; H, 2.92; N, 1.07. Found: C, 53.49; H, 2.97; N, 1.22.

[(dbf)MePhP═NDipp]$ZnPh_2$ (17). Compound **11** (0.785 g, 0.1 mmol) and excess diethylzinc (0.1 mL) were stirred in dichloromethane (1 mL) for 15 min. Removal of the volatiles in vacuo, followed by recrystallization of the crude material from CH_2Cl_2 and *n*-heptane afforded analytically pure colorless crystals of **17** (0.62 g, 91%). ^1H NMR (CD_2Cl_2): δ 8.20 (d, $^3J_{HH}$ = 7.5 Hz, 1H, dbf), 8.0 (d, $^3J_{HH}$ = 8.4 Hz, 1H, dbf), 7.64−7.39 (m, 10H, dbf + Ph), 6.96 (s, 13H, Ph + *m*-Dipp + *p*-Dipp), 3.52 (sp, $^3J_{HH}$ = 6.6 Hz, 2H, $CHMe_2$), 2.23 (d, $^2J_{HP}$ = 13.2 Hz, 3H, PCH_3), 1.02 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CHMe_2$), 0.91 (d, $^3J_{HH}$ = 6.9 Hz, 6H, $CHMe_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 157.91 (br s, aromatic *C*), 157.08 (s, dbf), 156.56 (s, dbf), 145.18 (d, $^3J_{CP}$ = 6.0 Hz, aromatic *C*), 142.61 (s, aromatic *C*), 138.94 (s, aromatic *C*), 133.09 (s, aromatic *C*), 132.10 (d, $^3J_{CP}$ = 9.0 Hz, aromatic *C*), 131.42 (d, $^3J_{CP}$ = 6.0 Hz, aromatic *C*), 130.84 (s, aromatic *C*), 129.68 (d, $^2J_{CP}$ = 12.8 Hz, aromatic *C*), 128.85 (s, aromatic *C*), 128.62 (s, aromatic *C*), 127.05 (s, Ph), 126.11 (s, aromatic *C*), 125.86 (s, aromatic *C*), 124.05 (s, aromatic *C*), 123.90 (s, aromatic *C*), 123.30 (s, aromatic *C*), 121.47 (s, aromatic *C*), 114.66 (d, $^1J_{CP}$ = 96.6 Hz, aromatic *C*), 112.40 (s, aromatic *C*), 29.19 (s, $CHMe_2$), 24.61 (s, $CHMe_2$), 17.48 (d, $^1J_{CP}$ = 67.9 Hz, PCH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 16.70 (s). Anal. Calcd for $C_{43}H_{42}NOPZn$: C, 75.38; H, 6.18; N, 2.04. Found: C, 75.68; H, 6.18; N, 2.19. Single crystals of **17** suitable for X-ray analysis were obtained from a concentrated solution of the complex in CH_2Cl_2 and pentane.

In Situ Polymerization Studies. In a typical synthesis of PLA, compound **15** (3.3 mg, 2.5 μmol) and *rac*-lactide (36 mg, 0.25 mmol) were dissolved in 0.5 mL of C_6D_5Br in a J-Young tube. The tube was heated to 100 °C until conversion reached 90% (9 h). Conversion was determined by integration of the methine region of the ^1H NMR spectrum.

Polymerization Experiments. In a PTFE-sealed bomb, *rac*-lactide (216 mg, 1.5 mmol) and complex **15** (9.8 mg, 7.5 μmol, monomer/catalyst = 200:1 or 6.6 mg, 5 μmol, monomer/catalyst = 300:1 or 4.9 mg, 3.75 μmol, monomer/catalyst = 400:1) were dissolved in bromobenzene (1.5 mL). The vessel was heated to 100 °C for 9 h, and the reaction was then quenched by addition of excess cold methanol (3 mL). All volatiles were then removed in vacuo, and the crude material was redissolved in methylene chloride. The polymer was then precipitated by addition of cold methanol (3 mL), followed by solvent decantation,

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and drying under vacuum (9×10^{-3} Torr) for 20 h. (Yield: 74%, 69%, and 69% for ratios of 200, 300, and 400, respectively).

Polymerization of Sequential Batches of Monomer. An initial monomer/catalyst ratio of 200:1 was used to polymerize *rac*-lactide in situ. After 9 h of heating at 100 °C, another batch of *rac*-lactide (216 mg, 1.5 mmol) was added. The tube was then heated for another 9 h. The polymer was isolated similarly as described in the large scale procedure (yield: 66%).

X-ray Crystallography. A suitable crystal of each compound was coated in Paratone oil and mounted on a glass fiber. X-ray data were collected at 173 K with ω and φ scans on a Bruker Smart Apex II diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) and Bruker SMART software.[18] Unit cell parameters were calculated and refined from the full data set. Cell refinement and data reduction were performed using the Bruker APEX2 and SAINT programs, respectively.[19] Reflections were scaled and corrected for absorption effects using SADABS.[20] The structures were solved by direct methods with SHELXS[21] and refined by full-matrix least-squares techniques against F^2 using SHELXL.[22] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms (except the N-*H* atoms in **9**, **11**, and **12**, which were located from the electron density maps and refined freely) were placed in calculated positions and refined using the riding model.

Crystal data are summarized in Table 1. No special considerations were required for the refinement of compounds **4**, **7**, **8**, **9**, **12**, and **17**. The unit cell of compound **11** contained a molecule of heavily disordered dichloromethane, for which no suitable model could be found. The electron density related to this molecule was removed from the reflection data using SQUEEZE (PLATON),[23] leaving a void of about 300 Å^3.

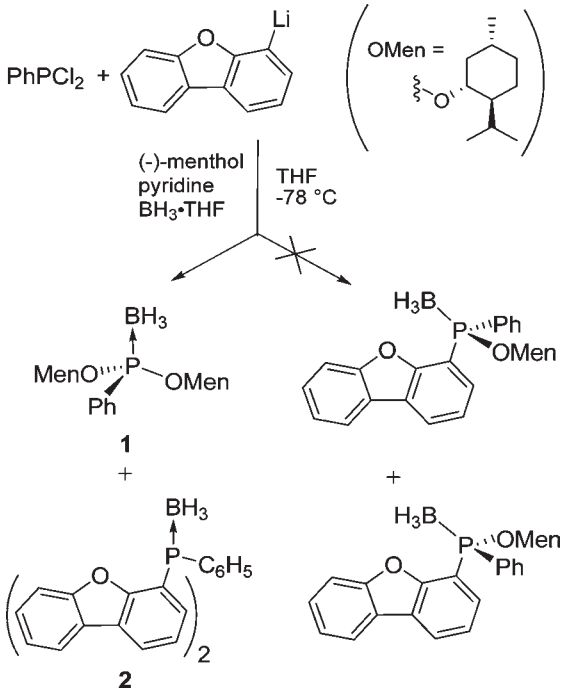
RESULTS AND DISCUSSION

Synthesis of Phosphinimine Ligands 7 and 8. There are several methods available for the preparation of *P*-stereogenic tertiary phosphines.[24] The most widely used techniques, however, are those of Jugé[25] and Imamoto,[26] which make use of phosphine-borane intermediates, as well as chiral resolving agents. (−)-Menthol was selected as a suitable resolution reagent because of its low cost and availability from the chiral pool. Although the synthesis of a new racemic ligand is itself a valuable achievement, we have also made attempts to prepare enantiopure versions via chiral resolution. Few examples of stereogenic ligands supporting zinc catalysts for the synthesis of PLA are known. Several recent examples include chiral *N,N,O* ligands based on a diaminophenoxy framework, as reported by the groups of Mehrkhodavandi and Darensbourg,[27] and a chiral β-diketiminate system described by Schaper and co-workers.[15]

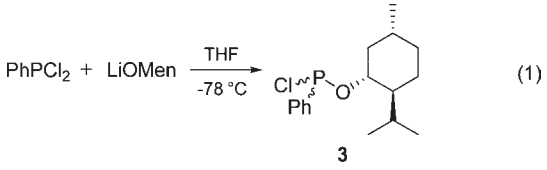
We adopted Imamoto's synthetic route[26] (Scheme 1) in an attempt to prepare the phosphinite-borane adduct 4-[(BH_3)-PPh(OMen)]dbf, as a pair of diastereomers. In a one-pot reaction, 4-lithio-dibenzofuran[16] was reacted with dichlorophenylphosphine followed by (−)-menthol and pyridine and finally $BH_3\cdot$THF. However, the phosphonite borane $(BH_3)PPh(OMen)_2$ (**1**) and the phosphine borane $(BH_3)PPh(dbf)_2$ (**2**) were isolated as the major products of the reaction as white solids. The parent phosphines of **1** and **2**, $(OMen)_2PPh$[28] and $(dbf)_2PPh$,[29] have both been previously reported, though to the best of our knowledge **1** and **2** are new compounds. As expected, the $^{31}P\{^1H\}$ NMR resonance for compound **1** is much further downfield than **2** (**1**: δ 129.50; **2**: δ 12.60).

The synthesis was thus undertaken in a stepwise fashion. When 4-lithiodibenzofuran was reacted with an equimolar quantity of

Scheme 1



dichlorophenylphosphine, the only products observed were the disubstituted compound $(dbf)_2PhP$ and unreacted $PhPCl_2$. No trace of the desired monosubstituted phosphine (dbf)PhPCl was detected, even when the lithium reagent was slowly added to a solution of dichlorophenylphosphine. By contrast, when the bulkier reagent lithium *l*-menthoxide[17] was reacted with dichlorophenylphosphine in a similar manner, pure (OMen)PhPCl (**3**) was obtained as a colorless oil in quantitative yield (eq 1). Multinuclear NMR spectroscopy clearly indicates that phosphine **3** was obtained as a 1:1 mixture of diastereomers: the $^{31}P\{^1H\}$ NMR spectrum exhibits two signals at δ 177.58 and 174.59 resulting from the two unique phosphorus environments.



(1)

Compound **3** was reacted with 4-lithiodibenzofuran, followed by $BH_3\cdot$THF, producing diastereomeric phosphine-borane adducts **4a** and **4b** in a 1:1 ratio (eq 2). We then subjected **4a** and **4b** to column chromatography (silica gel, elution with 4:1 hexanes/benzene). While this afforded analytically pure **4a**/**4b**, separation of the two diastereomers was not achieved. Both the $^{31}P\{^1H\}$ NMR and $^{11}B\{^1H\}$ NMR spectra were broad, but the $^{13}C\{^1H\}$ NMR peaks associated with the (−)-mentholate group were observed as closely spaced pairs.

Interestingly, X-ray quality single crystals containing both diastereomers were obtained, and the crystal structures of **4a** and **4b** were determined. Both isomers had very similar metrical parameters, with the exception of the absolute

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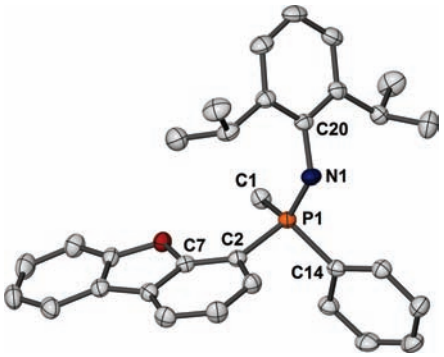
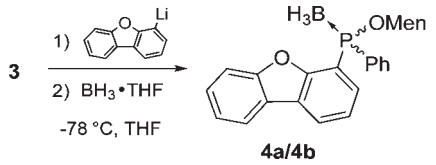


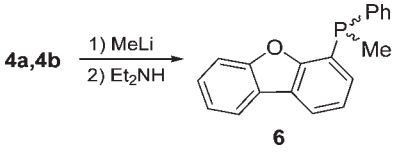
Figure 1. Thermal ellipsoid plot of **7** (50% probability). Hydrogen atoms are omitted for clarity.

configuration at phosphorus (see Supporting Information for details).



(2)

The **4a**,**4b** mixture was further reacted with methyllithium in benzene to replace the (−)-mentholate substituents, yielding the intermediate 4-(BH_3)PPhMe-dbf (**5**) as a colorless oil. By contrast, a similar reaction with *t*-butyllithium did not afford the expected *t*-butyl-substituted analogue, presumably because of steric reasons. The $^{31}P\{^1H\}$ NMR spectrum exhibited two overlapping resonances at δ 8.04 and 7.47. Compound **5** was treated with excess diethylamine to remove the borane protecting group, yielding the racemic phosphine 4-PPhMe-dbf (**6**) as a colorless, air-sensitive oil (eq 3) with a $^{31}P\{^1H\}$ chemical shift of δ −35.95 (sharp singlet). This crude product was deemed to be suitable for use in subsequent synthetic steps without the need for further purification.



(3)

Although chiral resolution was not achieved, the large (−)mentholate moiety allowed the convenient stepwise introduction of dbf and methyl substituents at phosphorus. Having installed these desired organic functionalities, phosphinimine derivatives of **6** were pursued by its reaction with aryl azides under standard Staudinger conditions.[30] The ambient temperature reaction of **6** with $DippN_3$ or $MesN_3$ in benzene produced (dbf)MePhP═NDipp (**7**) or (dbf)MePhP═NMes (**8**), respectively, in reasonable yields (**7**: 79%; **8**: 76%). NMR spectra of the phosphinimines are consistent with the expected structures; notably the $^{31}P\{^1H\}$ NMR resonances of **7** and **8** are shifted downfield by about 20 and 25 ppm, respectively, upon oxidation of the phosphorus(III) center of **6**.[8,9] X-ray quality single crystals of both **7** and **8** were obtained from layered solutions of the compounds in benzene and pentane. Both structures are similar; a thermal ellipsoid plot of ligand **7** is depicted in Figure 1 as a representation of the two racemic compounds. Selected metrical parameters for both **7** and **8** are listed in Table 2. The solid-state structures confirmed the connectivity of the atoms and correlated well with the solution NMR spectra. The P═N bond lengths of 1.551(1) Å and 1.556(1) Å for **7** and **8**, respectively, agree exceptionally well with the value of 1.559(2) Å in the related ligand (dbf)Ph_2P═NDipp.[8a]

Protonation Reactions. Protonation of the phosphinimine compounds **7** and **8** was performed as described elsewhere,[8,9] to allow for the synthesis of metal complexes via an alkane elimination route.[8,9] The salts [(**7**)-H][$B(C_6F_5)_4$] (**9**), [(**8**)-H][$B(C_6F_5)_4$] (**10**), [(**7**)-H][BPh_4] (**11**), and [(**8**)-H][BPh_4] (**12**) were obtained upon reaction with appropriate Brønsted acids (Scheme 2). The derivatives **11** and **12**, containing the $[BPh_4]^-$ anion, were prepared after having obtained the $[B(C_6F_5)_4]^-$ analogues **9** and **10**, in an attempt to increase the crystallinity of the resulting metal complexes (vide infra). These ionic species, all of which were isolated as well-behaved white solids in excellent yields, have different solubilities compared to the parent phosphinimines; **9** and **10** are soluble in aromatic solvents, while **11** and **12** are only soluble in halogenated solvents, such as bromobenzene and dichloromethane. The $^{31}P\{^1H\}$ NMR spectra of compounds **9**−**12** reveal an expected downfield shift: the resonances of **9**−**12** appear in the range of δ 35 to 38 (cf. δ −18 and −10 for **7** and **8**, respectively). The ^1H and ^{19}F NMR data indicate single aryl environments for the borate anions, which suggests there are no tight ion pairs formed in solution (e.g., arene π − cation interactions). Single crystals of **9**, **11**, and **12** were obtained from layered CH_2Cl_2/pentane solutions. X-ray diffraction studies confirmed the expected structures (see Supporting Information for further details), and no evidence for close cation−anion interactions was observed.

Formation of Zinc Complexes. With the protonated ligands **9** and **10** in hand, their reactivity toward organometallic reagents was investigated. Zinc complexes are particularly attractive for catalysis in light of the low cost and toxicity of the metal. Our group has previously been successful in preparing zinc complexes of dbf-supported phosphinimine ligands which are active lactide polymerization catalysts,[8] and so we pursued the chemistry of these new ligands with the requisite organozinc species. Solutions of **9** or **10** in bromobenzene were treated with excess diethylzinc and heated to 100 °C. In both cases, ethane gas evolution was observed both visually and by a diagnostic resonance at δ 0.80 in the ^1H NMR spectrum of the reaction mixture. After workup, the cationic zinc complexes [{(dbf)MePhP═NAr}Zn-Et][$B(C_6F_5)_4$] (**13**: Ar = Dipp, **14**: Ar = Mes) were obtained as white solids in 87 and 73% yield, respectively (Scheme 3). $^{31}P\{^1H\}$ NMR spectra of complexes **13** and **14** exhibit resonances at δ 33.66 and 31.78, respectively, consistent with ligation of the phosphinimine nitrogen atoms to the zinc centers.

In previous work, we demonstrated that the presence of an R = methyl-(*S*)-lactate group in complexes of the type [LZnR][BAr_4] enhances their catalytic competence,[8b,c] and therefore we sought the preparation of methyl-(*S*)-lactate-functionalized zinc complexes of these new chiral ligands. The complex [{(dbf)MePhP═NDipp}Zn(OCH(Me)CO_2Me)][$B(C_6F_5)_4$] (**15**) was cleanly isolated as a white solid in 81% yield from the reaction of **9** and EtZn-methyl-(*S*)-lactate in bromobenzene at 100 °C for 6 h, and features a single $^{31}P\{^1H\}$ NMR resonance at δ 41.68. Although **15** exists as a mixture of two diastereomers, there is no difference in the ^{31}P chemical shifts. Surprisingly, the preparation of Mes analogue **16** did not proceed cleanly. The desired product was formed in 80% yield, but was contaminated with complex **14**,

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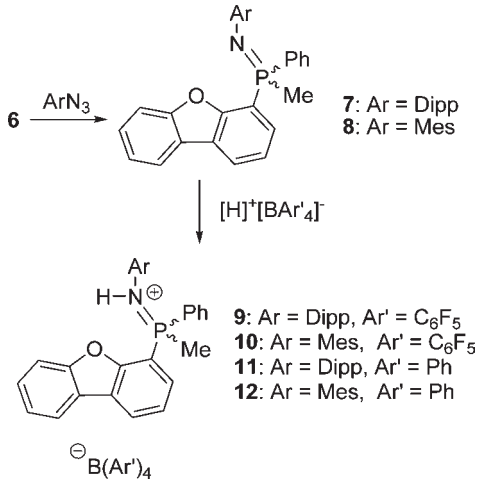
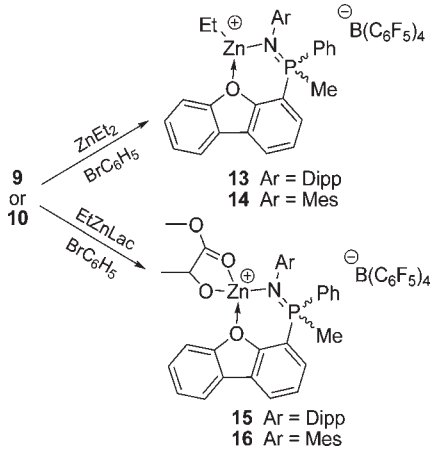
Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for Compounds 7, 8, 9, 11, and 12

	7	8	9	11	12
P1−C1	1.798(1)	1.804(1)	1.787(2)	1.780(3)	1.786(2)
P1−C2	1.817(2)	1.810(1)	1.787(1)	1.784(3)	1.789(2)
P1−C14	1.805(1)	1.816(1)	1.780(1)	1.778(3)	1.780(2)
P1−N1	1.551(1)	1.556(1)	1.639(1)	1.628(2)	1.640(1)
N1−C20	1.409(2)	1.401(2)	1.460(2)	1.467(4)	1.451(2)
C1−P1−C2	107.54(7)	106.57(6)	107.16(7)	107.9(1)	107.93(9)
C1−P1−N1	116.72(7)	116.18(6)	113.64(7)	105.7(1)	114.13(8)
C1−P1−C14	107.11(7)	107.46(6)	109.55(7)	110.7(1)	109.50(9)
N1−P1−C14	108.97(6)	114.35(6)	106.57(7)	110.3(1)	106.26(8)
C2−P1−C14	101.99(6)	101.85(5)	108.92(7)	110.4(1)	110.24(8)
N1−P1−C2	113.34(6)	109.21(6)	110.94(7)	111.7(1)	108.76(7)
P1−N1−C20	130.1(1)	128.4(1)	126.4(1)	127.3(2)	124.7(1)
C7−C2−P1−N1	119.4(1)	174.6(1)	71.(1)	56.7(2)	62.1(2)
C2−P1−N1−C20	105.8(1)	139.5(1)	38.0(1)	89.4(3)	32.9(2)

Scheme 2



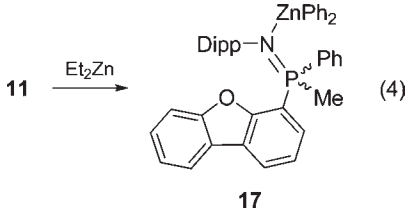
Scheme 3



along with other unidentified impurities. All of the cationic zinc complexes had NMR features consistent with a separated ion pair (e.g., symmetrical borate anions, no perturbations of ^{11}B or ^{19}F NMR chemical shifts compared to the protonated ligands **9**−**12**).

In our hands, complexes **13**−**16** were not sufficiently crystalline to provide X-ray quality single crystals for structural analysis. In an attempt to circumvent this problem, the protonated tetraphenylborate derivatives **11** and **12** were used in reactions with organozinc reagents. However, these compounds were found to possess significantly different chemical behavior than **9** or **10**. The Dipp-substituted compound **11** reacted with diethylzinc in dichloromethane at ambient temperature to afford the unexpected phenyl transfer product [{(dbf)MePhP═NAr}$ZnPh_2$] (**17**) in 91% yield (eq 4). The identity of the boron-containing product(s) from this reaction were not determined. Crystallization of complex **17** from a CH_2Cl_2/pentane solution afforded X-ray quality crystals; a structure determination revealed an adduct between $ZnPh_2$ and the neutral ligand **7**, which is coordinated in an *N*-monodentate fashion (see Supporting Information for further details).

Protonated ligand **12** reacted with diethylzinc to yield intractable mixtures, as did reactions between **11** or **12** and EtZn-methyl-(*S*)-lactate. It is clear from these experiments that the perfluorinated $[B(C_6F_5)_4]^-$ containing analogues feature superior chemical stability and are thus far more suitable for potential catalytic applications.



Polymerization of Lactide Using Complex 15. The $[B(C_6F_5)_4]^-$ salts **13** and **15** were selected for the ring-opening polymerization of *rac*-lactide. The ethylzinc complex **13** was virtually inactive toward ROP of *rac*-lactide even under relatively harsh conditions. In situ NMR tube reactions of *rac*-lactide with **13** (M:I = 100:1, [M] = 0.5 M) at 100 °C showed only 9% conversion

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Table 3. GPC Data for PLA Samples Prepared Using Complex 15

M:I	isolated yield (%)	calc. M_n ($\times 10^3$)	M_n ($\times 10^3$)	M_w($\times 10^3$)	PDI
200	74	28.9	17.3	34.2	1.98
300	69	43.3	21.4	40.5	1.89
400	69	57.7	27.1	49.1	1.81
200 + 200	66	57.7	35.7	68.9	1.93

after 3 h. This is in accord with previous observations that a metal-bound ethyl substituent is a poor initiating group.[1b,5e,8b] By contrast, the methyl-(*S*)-lactate-substituted complex **15** was much more active: in situ polymerization, using the same conditions as for **13**, yielded 90% conversion in 9 h.

To further probe this system, the polymerization of 10 equiv of *rac*-lactide was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. During the course of the reaction, the catalyst resonance remained unchanged, yielding no evidence of an insertion product. MALDI-TOF analysis of a polymer sample, made from M:I = 50:1 at 100 °C, revealed a set of major peaks corresponding to cyclic oligomers $[(C_3H_4O_2)_nNa^+$, 671 to 2183]. The peak separation of $m/z = 72$ indicates transesterification.[31] A small percentage of molecular ions corresponded to oligomers of the formula H-(OCHMeCO)$_n$OMe·Na, suggesting coordination−insertion products.

GPC analysis of polymers made with various catalyst loadings demonstrated that the experimental molecular weights are slightly lower than the calculated values, and also substantially higher than samples produced by earlier-reported monosubstituted dibenzofuran catalysts (Table 3):[8a] M_n values ranged from about 17 000 to 36 000 g/mol. The PDI values of 1.81−1.98 indicate broad molecular weight distributions, providing further evidence of transesterification. The effect of adding a second batch of monomer was investigated by polymerizing 200 equiv of *rac*-lactide for 9 h, and then adding another 200 equiv of monomer. The resulting polymer had the highest number- and weight-average molecular weight values of all the conditions investigated. Thus, chain termination does not appear to be competitive with propagation under these conditions.

To probe the stereochemical outcome of the polymerization of *rac*-lactide, homodecoupled $^1H\{^1H\}$ NMR spectra of several polymer samples, prepared at 80 and 60 °C, were recorded and the P_r values calculated by integration of the methine region. In both cases $P_r = 0.49$, indicating essentially atactic polymer chains. This is perhaps unsurprising given the prior evidence for substantial transesterification during the chain growth process. The development of more active catalysts, featuring stronger electron donation and steric protection from the ligand, that reduce the time and temperature of polymerization is expected to help overcome this issue.

CONCLUSIONS

Compounds **7** and **8**, the first chiral monophosphinimine ligands featuring a dbf framework, have been prepared and characterized. The protonated ligands **9** and **10** were suitable for use in alkane elimination reactions with organozinc reagents to form potential catalysts for the stereocontrolled synthesis of PLA. Furthermore, reactions of *rac*-lactide with the racemic Zn metal complex **15** have demonstrated its competence as a catalyst for the ROP of *rac*-lactide. Our previous work in the area of lactide polymerization catalysts has shown that for achiral dbf-based ligands, the monophosphinimine variants furnish less active metal catalysts than the 4,6-disubstituted ligands. Hence, we are now focusing on the preparation of pincer-type ligands featuring two optically active phosphinimine groups, and a future account will describe these endeavors.

ASSOCIATED CONTENT

Supporting Information. Thermal ellipsoid plots and structural discussion of compounds **4**, **9**, and **17**, and CIF files giving X-ray crystallographic data for **4**, **7**, **8**, **9**, **11**, **12**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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