Supporting Information for

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

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Crystal Structures of Compounds 4, 9, 11 and 17

A molecule of compound **4a** is depicted in Figure S1, as representative of both diastereomers. The solid-state structure confirmed the connectivity of the compound as well as its racemic nature. The metrical parameters of compound **4** are in the typical ranges for similar compounds. For instance, the P–B distance of 1.883(3) Å matches the values of 1.88(2) – 1.907(8) Å, observed in the related series of phosphine-boranes (OMen)PhP(BH_3)Ar (Ar = 2-methylphenyl, 2-ethylphenyl, 2-isopropylphenyl, 1-tetralin) reported by Imamato and coworkers.[1] The phosphorus centre exhibits distorted tetrahedral geometry, as evidenced by the bond angles about P, which range from 100.4(1) – 116.2(1) °.

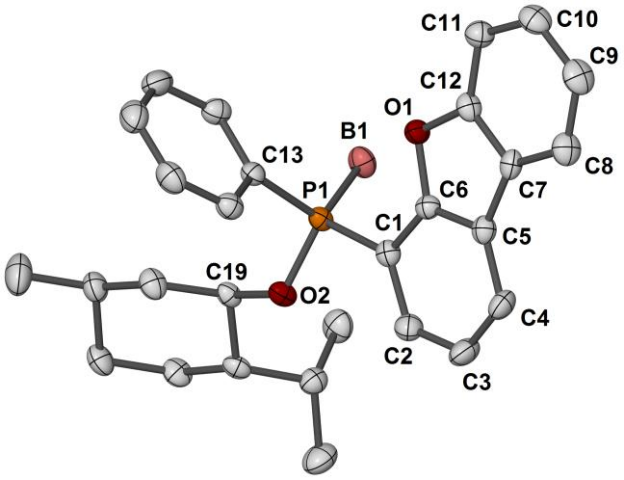

Figure S1. Thermal ellipsoid plot of **4a** (50% probability). Hydrogen atoms and isomer **4b** are omitted for clarity. Selected bond lengths (Å) and angles (deg): P1–B1 1.883(3), P1–O2 1.604(2), P1–C1 1.791(3), P1–C13 1.807(3); C1–P1–O2 100.4(1), C13–P1–O2 104.7(1), C1–P1–C13 105.3(1), B1–P1–O2, 115.9(1) B1–P1–C1 112.7(1), B1–P1–C13 116.2(1).

The compounds **9**, **11** and **12** exhibited similar solid state structures, and a representative thermal ellipsoid plot of compound **9** is depicted in Figure S2. Selected bond lengths, bond angles and torsion angles are listed in Table 2 of the main text. The N–H protons were located in the Fourier difference map and refined; the P=N bond distances lengthened by ca. 5% with respect to the neutral ligands **7** and **8**. This has also been observed for related dbf-supported phosphinimine ligands.[2,3]

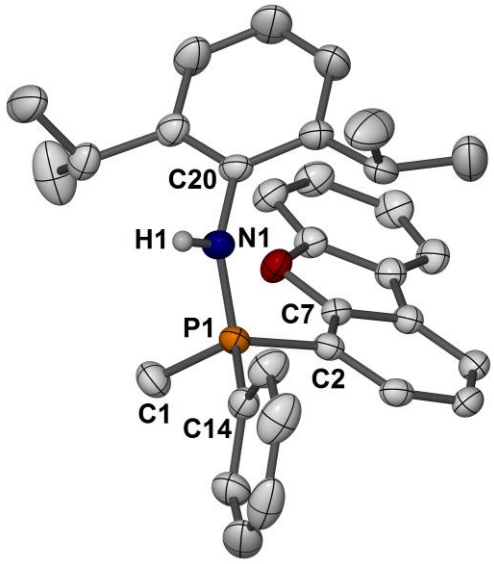

Figure S2. Thermal ellipsoid plot of **9** (50% probability). Carbon-bound hydrogen atoms and the $[B(C_6F_5)_4]^-$ anion are omitted for clarity.

The solid-state structure of complex **17** reveals an adduct between $ZnPh_2$ and the neutral ligand **7**, which is coordinated in an *N*-monodentate fashion. The Zn center features a nearly ideal trigonal planar geometry (Σ<(Zn) = 359.93°), and there is no interaction between the metal center and the dibenzofuran oxygen atom (Figure S3). The nitrogen atom is also nearly trigonal planar (Σ<(N) = 356.54 °), and the P–N distance (1.598(1) Å) is only slightly longer (ca. 3%) than that observed in **7** (1.551(1) Å)**.**

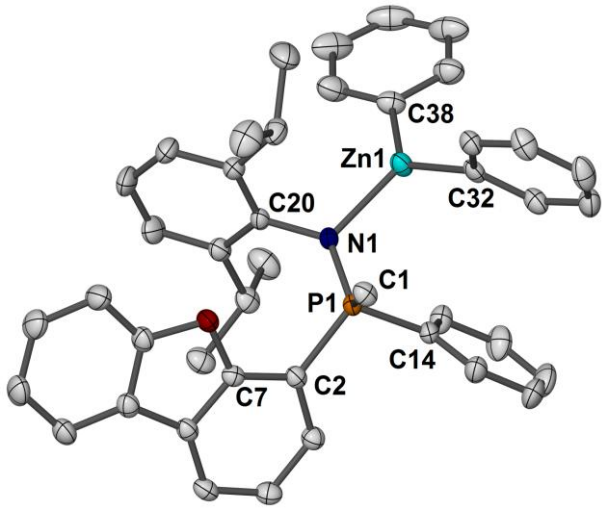

Figure S3. Thermal ellipsoid plot of complex **17** (50% probability). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zn1–N1 2.073(1), Zn1–C32 1.992(1), Zn1–C38 1.973(1), P1–C1 1.797(1), P1–C2 1.805(1), P1–C14 1.793(1), P1–N1 1.598(1), N1–C20 1.439(2); N1–Zn1–C32 112.49(5), N1–Zn1–C38 117.02(5), C32–Zn1–C38 130.42(6), P1–N1–Zn1 115.22(6), C20–N1–Zn1 118.87(8), P1–N1–C20 122.45(9).

References

1. Wada, Y.; Imamoto, T.; Tsuruta, H.; Yamaguchi, K.; Gridnev, I. D. *Adv. Synth. Catal.* **2004**, *346*, 777-788.
2. (a) Wheaton, C. A.; Ireland, B. J.; Hayes, P. G. *Organometallics* **2009**, *28*, 1282-1285. (b) Wheaton, C. A.; Hayes, P. G. *Dalton Trans.* **2010**, *39*, 3861-3869. (c) Wheaton, C. A.; Hayes, P. G. *Chem. Commun.* **2010**, *46*, 8404-8406.
3. Ireland, B. J.; Wheaton, C. A.; Hayes, P. G. *Organometallics*, **2010**, *29*, 1079-1084.