



Note

Electron deficient zinc complexes: Enhanced lactide polymerization activity achieved through rational ligand design

Craig A. Wheaton, Paul G. Hayes*

Department of Chemistry and Biochemistry, University of Lethbridge, 4401 University Drive, Lethbridge, Alberta, Canada T1K 3M4

ARTICLE INFO

Article history:

Received 6 October 2011

Received in revised form

5 January 2012

Accepted 6 January 2012

Keywords:

Zinc

Phosphinimine

Poly(lactic acid)

Ring-opening polymerization

Cationic

ABSTRACT

Modification of a neutral bis(phosphinimine) pincer ligand, whereby alkyl groups were placed at the P and N positions of the phosphinimine moieties, has been performed. A cationic zinc-lactate complex of this ligand displays enhanced activity relative to the previous generation catalyst for the polymerization of *rac*-lactide.

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1. Introduction

Interest in the use of poly(lactic acid) (PLA) as an eco-friendly commodity polymer has grown substantially over the past decade [1]. This is because lactide (LA) feedstocks are derived from renewable resources, while PLA is biodegradable. This interest has promoted increasingly intensive research in the area of LA polymerization catalysis [2]. While organocatalysts [3] and a wide variety of metal-based catalysts [4] have been developed, much work has been specifically devoted to the preparation of alkoxides of Zn(II) and the alkaline earth metals (most commonly Mg(II) and Ca(II)). Prior to 2009, virtually all such LA polymerization catalysts were neutral complexes stabilized by formally anionic ancillary ligands, and this continues to be the focus of most recent work [5]. Recently, however, we have pursued cationic zinc complexes for LA polymerization catalysis [6].

Since our initial reports, there have been several other accounts of cationic Zn(II), Mg(II) and Ca(II) complexes used for the ROP of LA [7], but these tend to suffer drawbacks ranging from poor activity to poor control to ill-defined polymerization mechanisms. A notable exception is a cationic calcium complex recently reported by Mountford and co-workers, which displays both excellent control and activity for the ROP of *rac*-LA at ambient temperature [8].

Our initial foray into the field utilized a mono(phosphinimine) ancillary ligand with a rigid dibenzofuran (dbf) backbone, but zinc-

alkyl complexes thereof proved to be relatively poor catalysts [6a]. Substantial improvements in activity were realized by employing a bis(phosphinimine) pincer ligand [6b]. Further tuning of the steric bulk gave the ligand 4,6-(*p*-^{*i*}PrPh–N=PPh₂)-dbf (**L^{Pipp}**), from which the first cationic metal complex capable of rapid and controlled LA polymerization at ambient temperature was produced [6c]. These preceding studies clearly demonstrate catalyst activity is highly dependent on both ligand steric bulk and the Lewis acidity of the metal center.

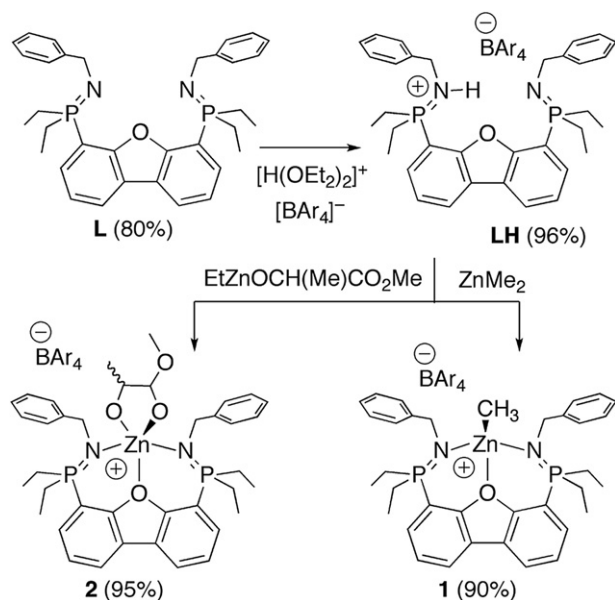
Herein we report our next generation cationic zinc catalyst, in which the ligand scaffold has been modified by installation of alkyl substituents on the phosphinimine groups (Scheme 1). Specifically, ethyl replaces phenyl at P and benzyl replaces para-isopropylphenyl (Pipp) at N. This was expected to render the metal center more sterically accessible, while simultaneously providing better moderation of metal center Lewis acidity by enhancing the electron donating capacity of the ligand. Such a less electropositive metal center was targeted in hopes of achieving a level of Lewis acidity somewhere between that of our previous cationic zinc catalysts and the more commonly studied neutral zinc catalysts. The effect of these modifications has been studied, with the major outcome being a marked enhancement in polymerization activity, as discussed below.

2. Results and discussion

Preparation of the bis(phosphine) precursor dbf(PET₂)₂ was targeted due to its reduced bulk relative to the known dbf(P^{*i*}Pr₂)₂ and dbf(PPh₂)₂ analogs. Efficient dilithiation of dibenzofuran was

* Corresponding author. Tel.: +1 403 329 2313; fax: +1 403 329 2057.

E-mail address: p.hayes@uleth.ca (P.G. Hayes).



Scheme 1. Synthesis of zinc-alkyl (**1**) and zinc-lactate (**2**) complexes of a bis(phosphinimine) pincer ligand (Ar = m -(CF₃)₂-C₆H₃).

achieved using 2.0 equiv of ^tBuLi, rather than significant excesses of ^{sec}BuLi or ⁿBuLi employed in previous reports (see ESI) [9]. This novel bis(phosphine) compound exhibits one sharp signal in the ³¹P{¹H} NMR spectrum (C₆D₆) at δ –19.01.

Synthesis of **L** from dbf(PET₂)₂ and benzyl-azide under standard Staudinger conditions [10] was highly exothermic and proceeded to completion within minutes at ambient temperature. Work-up is straightforward and efficient, with high yield of analytically pure crystalline material produced by simple addition of excess pentane to the reaction mixture. A single peak appears in the ³¹P{¹H} NMR spectrum (C₆D₆) at δ 14.4. Single crystals of **L** were grown from a toluene solution of the compound at –35 °C, and an X-ray crystal structure was obtained (Fig. 1). The P–N bond lengths are similar to those of related bis(phosphinimine) ligands [P(1)–N(1) = 1.568(1) Å; P(2)–N(2) = 1.550(2) Å] [6c,11].

As demonstrated in our previous work, and in the work of Bochmann et al. [12], the synthesis of cationic zinc complexes is most effectively performed by first protonating the ligand with an appropriate Brønsted acid. Reaction of **L** with [H(OEt₂)₂][B(m -(CF₃)₂-C₆H₃)₄] rapidly generated [LH][B(m -(CF₃)₂-C₆H₃)₄], which was isolated in 96% yield as an analytically pure light yellow powder.

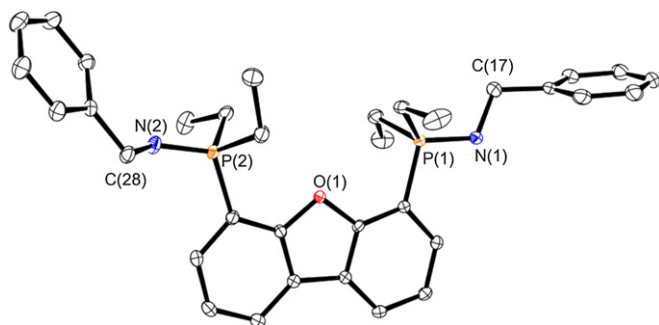


Fig. 1. X-ray crystal structure of **L** with hydrogen atoms omitted and thermal ellipsoids drawn at the 30% probability level. Selected bond distances (Å) and angles (°): P(1)–N(1), 1.568(1); P(2)–N(2), 1.550(2); N(1)–C(17), 1.462(2); N(2)–C(28), 1.448(3); P(1)–N(1)–C(17), 117.1(1); P(2)–N(2)–C(28), 126.9(1).

Methylzinc complex **1** was effortlessly prepared by reacting [LH][B(m -(CF₃)₂-C₆H₃)₄] with ZnMe₂ at ambient temperature for 1 h, to afford a pure white powder in 90% yield. A single peak in the ³¹P{¹H} NMR spectrum (δ 46.6, CD₂Cl₂) is indicative of symmetry-related phosphinimines in solution. The ZnCH₃ resonates in the ¹H NMR spectrum at δ –0.95, which is typical of cationic methylzinc complexes [6].

Synthesis of zinc-lactate complex **2** was performed by reaction of [LH][B(m -(CF₃)₂-C₆H₃)₄] with EtZn(methyl-L-lactate) in toluene solvent at 100 °C for 60 min. This proved much more efficient than the preparation of our previous Zn–lactate complexes [6c], with 95% yield of crystalline material achieved without the need for further purification. Notably, complex **2** was synthesized in an overall yield of 64% in four steps from dibenzofuran. Characteristic peaks of the lactate moiety appear in the ¹H NMR spectrum at δ 4.66 (CH), 3.69 (O–CH₃), and 1.41 (C–CH₃). Despite the presence of the asymmetric lactate moiety, a single resonance is observed at ambient temperature in the ³¹P{¹H} NMR spectrum (δ 46.8). At –60 °C, the spectrum displays two distinct peaks (δ 46.8, 46.3), indicating a fluxional process which we propose is a simple intramolecular rearrangement involving rotation of the lactate moiety.

Large single crystals of complex **2** suitable for X-ray diffraction were grown from CH₂Cl₂ solvent, and the solid-state crystal structure was determined (Fig. 2). As expected, the ancillary ligand coordinates to the metal center in a tridentate fashion and the methyl-lactate moiety binds in a bidentate manner, resulting in a 5-coordinate, distorted trigonal bipyramidal geometry. The phosphinimine groups [Zn(1)–N(1) = 2.013(1) Å, Zn(1)–N(2) = 2.009(2) Å] and the formally anionic oxygen atom [Zn(1)–O(2) = 1.923(2) Å] prove to be the strongest donors, occupying the equatorial sites. The sum of angles

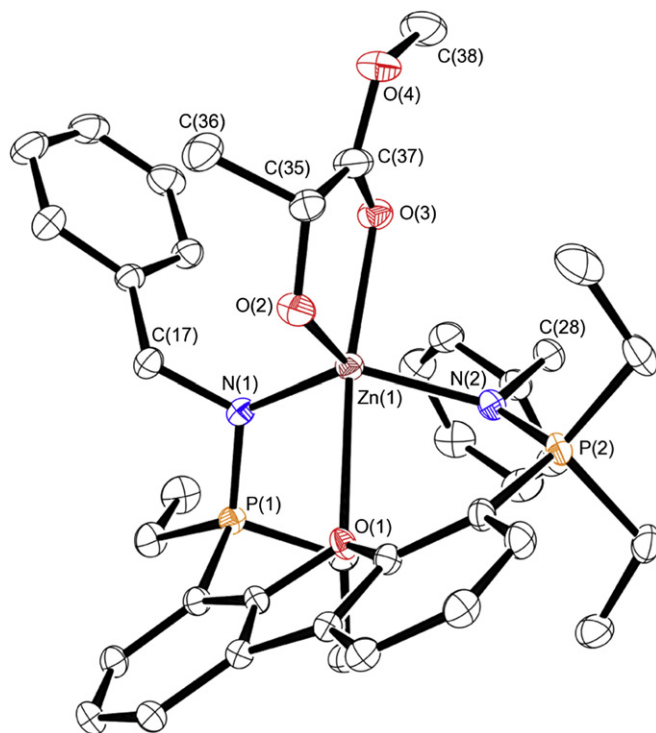


Fig. 2. X-ray crystal structure of the cation of **2**, with hydrogen atoms omitted for clarity and thermal ellipsoids drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Zn(1)–N(1), 2.013(1); Zn(1)–N(2), 2.009(2); Zn(1)–O(2), 1.923(2); Zn(1)–O(3), 2.173(1); Zn(1)–O(1), 2.525(1); P(1)–N(1), 1.608(2); P(2)–N(2), 1.605(1); N(1)–Zn(1)–N(2), 131.35(6); N(1)–Zn(1)–O(2), 109.06(6); N(2)–Zn(1)–O(2), 116.10(6); O(1)–Zn(1)–O(3), 168.57(5); N(1)–Zn(1)–O(3), 108.05(6); N(1)–Zn(1)–O(1), 83.25(5).

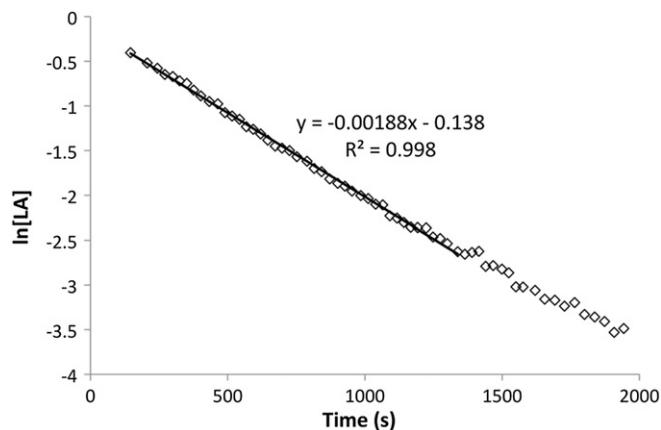


Fig. 3. Plot of $\ln[\text{LA}]$ versus time for polymerization of 200 equiv *rac*-LA. $[\text{LA}]_0 = 1 \text{ M}$, CD_2Cl_2 , 25°C .

about these positions is $356.5(1)^\circ$. Correspondingly, the neutral oxygen-donors occupy the axial sites, wherein the interaction with the lactate carbonyl lies within the expected range $[\text{Zn}(1)–\text{O}(3) = 2.173(1) \text{ \AA}]$, while that of the dbf oxygen is relatively long $[\text{Zn}(1)–\text{O}(1) = 2.525(1) \text{ \AA}]$. The angle between these groups is distorted somewhat from the ideal 180° $[\text{O}(1)–\text{Zn}(1)–\text{O}(2) = 168.57(5)^\circ]$, presumably due to steric repulsion of a nearby benzyl group. Interestingly, the interaction with the dbf oxygen is $0.189(5) \text{ \AA}$ longer than that observed in our previous generation catalyst $[\text{L}^{\text{Pipp}}\text{ZnLactate}][\text{B}(m\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$ [6c], which we attribute to decreased Lewis acidity of the metal center.

The efficacy of both complexes for ROP of *rac*-LA was investigated, and unsurprisingly complex **1** was inactive. However, complex **2** is extremely active for the polymerization of *rac*-LA, giving 90% conversion of 200 equiv of monomer to atactic PLA ($P_r = 0.50$) in less than 20 min at 25°C . Examination of the reaction kinetics by *in situ* NMR studies revealed well-behaved first-order monomer consumption with an observed rate constant of $1.88(1) \times 10^{-3} \text{ s}^{-1}$ and no notable induction period (Fig. 3). This rate is greater than the related complex of L^{Pipp} by a factor of 2.2 (measured under identical conditions) [6c]. Furthermore, a MALDI-ToF mass-spectrum was obtained for a polymer sample prepared from a 2% catalyst loading. Mass peaks are consistent with polymer chains bearing a methyl-lactate end group ($\text{H}–[\text{OCH}(\text{Me})\text{CO}]_n–\text{OCH}(\text{Me})\text{CO}_2\text{Me}$), indicating a coordination-insertion mechanism rather than a cationic process. However, peaks are separated by 72 amu, suggesting appreciable rates of transesterification. The lack of stereochemical control is not due to an epimerization process, as we have observed that **2** polymerizes *L*-LA to give isotactic PLLA.

Table 1
Molecular weight data for PLA samples prepared using different concentrations of catalyst **2**.^a

$[\text{LA}]_0/[\mathbf{2}]$	Time (min)	Isolated yield (%)	Calc. M_n (kg mol^{-1}) ^b	M_n (kg mol^{-1}) ^c	M_w (kg mol^{-1})	PDI
100	20	90	13.1	10.2	12.6	1.25
200	30	96	27.8	18.9	23.5	1.24
300	45	96	41.6	17.3	24.2	1.39
400	60	92	53.1	19.7	28.3	1.43
500	75	71	51.3	23.4	31.0	1.32
400 ^d	90	99	57.2	20.0	31.5	1.57

^a $[\text{LA}]_0 = 1 \text{ M}$, CH_2Cl_2 , 25°C .

^b Calculated using $M_n = ([[\text{LA}]_0/[\mathbf{2}]] \times 144.13 \times \text{conversion}) + 104.1$.

^c Molecular weights determined by GPC in THF at 40°C , and corrected by the accepted Mark–Houwink parameter of 0.58 due to the use of PS standards [13].

^d Sequential polymerization of two portions of 200 equiv of *rac*-LA, the second portion being added after 60 min.

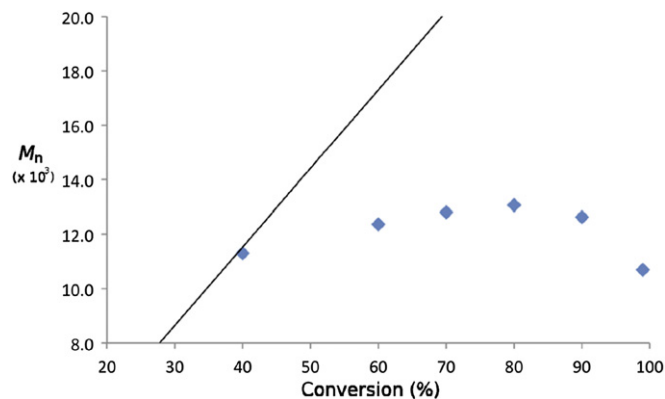


Fig. 4. Plot of M_n versus conversion for the polymerization of *rac*-LA catalyzed by complex **2** ($[\text{LA}]_0/[\mathbf{2}] = 200$, $[\text{LA}]_0 = 1 \text{ M}$, CH_2Cl_2 , 25°C). Theoretical molecular weights are represented by the straight line.

GPC analysis of PLA samples prepared at various catalyst loadings of **2** was undertaken. At higher catalyst loadings ($[\text{LA}]_0/[\mathbf{2}] = 100$ and 200), good molecular weight control was achieved, yielding PLAs with a relatively low polydispersity (1.24–1.25) and M_n values that closely match theoretical values (Table 1). Further reduction of catalyst loading ($[\text{LA}]_0/[\mathbf{2}] = 300$, 400, and 500) resulted in significantly lower than expected M_n and higher polydispersities ($\text{PDI} = 1.39\text{--}1.43$). We attribute this decreased control to appreciable rates of intermolecular transesterification. Catalyst decomposition is an unlikely cause of broadened PDIs at lower catalyst concentration, as we have found **2** to consume additional monomer at a similar rate after complete consumption of the initial portion of *rac*-LA. Specifically, after polymerization of 200 equiv of *rac*-LA for a duration of 90 min (~ 15 half-lives), addition of a further 200 equiv of monomer resulted in continued polymerization, giving PLA with molecular weights similar to those measured for single step polymerization of 400 equiv (Table 1).

In an attempt to improve our understanding of the polymerization process, a variety of samples were prepared under identical conditions ($[\text{LA}]_0 = 1 \text{ M}$, $[\text{LA}]_0/[\mathbf{2}] = 200$) and quenched at different stages of completion. A plot of M_n versus conversion gives a curve rather than the expected straight line (Fig. 4). During the early stages (40–60% conversion) the polymerization is well controlled ($\text{PDI} = 1.11\text{--}1.13$), while in the latter stages, the M_n values begin to drop off relative to the expected values, with a concomitant increase in M_w and PDI (see ESI). An increase in the rate of intermolecular transesterification relative to propagation account for increased PDIs in the later stages of polymerization. The cause of decreasing M_n is less obvious, but most likely attributed to intramolecular transesterification. Such catalyst back-biting would give rise to a lower molecular weight fraction that may be lost upon work-up of the polymer. To verify, GPC studies of an unpurified polymer sample ($[\text{LA}]_0/[\mathbf{2}] = 100$, $[\text{LA}]_0 = 1 \text{ M}$, CH_2Cl_2 , 25°C) were undertaken, indicating the presence of a substantial amount of low molecular weight oligomer ($M_n = 1.25 \text{ kg mol}^{-1}$; $\text{PDI} = 1.03$). The high molecular weight portion closely matched the corresponding purified polymer sample ($M_n = 18.9 \text{ kg mol}^{-1}$; $\text{PDI} = 1.16$). This observation suggests intramolecular transesterification to be a major cause of lower than expected molecular weights.

3. Conclusions

In summary, a modified bis(phosphinimine) ligand has been prepared, which bears alkyl substituents at both the P and N

positions. From this, cationic zinc-alkyl (**1**) and zinc-lactate (**2**) complexes were efficiently prepared. Complex **2** is among the most active yet observed for ROP of lactide by a cationic metal complex. This result further demonstrates the efficacy of cationic zinc species for this process, and highlights the necessity of a strongly electron-donating ligand to stabilize the highly electropositive metal. However, relatively poor molecular weight control remains an issue, which future studies will aim to address.

4. Experimental

4.1. Synthesis of compounds

4.1.1. 4,6-(Bn-N=PEt₂)₂dbf (**L**)

A solution of benzyl-azide (177 mg, 1.33 mmol) was added dropwise to a stirring solution of dbf(PEt₂)₂ (218 mg, 0.633 mmol) in benzene (2 mL). The resulting yellow solution was left to stand at ambient temperature for 30 min. The solution was concentrated to a volume of 1 mL, and 10 mL of pentane was added, causing the solution to become cloudy. Cooling to –35 °C for 19 h resulted in the formation of yellow crystals. The mother liquor was decanted and the crystals were washed with pentane (3 × 1 mL) and dried *in vacuo*, giving **L** in 80% yield (279 mg, 0.503 mmol). ¹H NMR (C₆D₆): δ 8.24 (dd, 2H, ³J_{PH} = 11.0 Hz, ³J_{HH} = 7.6 Hz, 3,7-dbf), 7.88 (d, 4H, ³J_{HH} = 7.1 Hz, *o*-CH₂Ph), 7.56 (d, 2H, ³J_{HH} = 7.6 Hz, 1,9-dbf), 7.40 (t, 4H, ³J_{HH} = 7.7 Hz, *m*-CH₂Ph), 7.22 (t, 2H, ³J_{HH} = 7.3 Hz, *p*-CH₂Ph), 7.13 (td, 2H, ³J_{HH} = 7.6 Hz, ⁴J_{PH} = 1.1 Hz, 2,8-dbf), 4.73 (d, 4H, ³J_{PH} = 18.4 Hz, CH₂Ph), 2.10–1.85 (ov m, 8H, PCH₂CH₃), 0.95 (dt, 12H, ³J_{PH} = 16.8 Hz, ³J_{HH} = 7.6 Hz, PCH₂CH₃). ³¹P{¹H} NMR (C₆D₆): δ 14.43. Anal. Calcd. (%) for C₃₄H₄₀N₂O₂P₂: C: 73.63; H: 7.27; N: 5.05; found: C: 73.47; H: 7.00; N: 5.12.

4.1.2. [LH⁺][B(m-(CF₃)₂-C₆H₃)₄][–] (**LH**)

L (320 mg, 0.577 mmol) and [H(OEt)₂]⁺[B(m-(CF₃)₂-C₆H₃)₄][–] (584 mg, 0.577 mmol) were combined in a 20 mL glass vial with 2 mL of benzene. The resulting mixture was stirred briefly, giving a clear red solution, and left to stand for 5 min. Addition of 2 mL of pentane resulted in precipitation of a red oil. The supernatant was decanted, the oil was washed with pentane (3 × 2 mL) and dried *in vacuo*, affording **LH** as a pale yellow powder in 96% yield (783 mg, 0.552 mmol). ¹H NMR (CD₂Cl₂): δ 8.26 (d, 2H, ³J_{HH} = 7.3 Hz, 1,9-dbf), 7.75 (br s, 8H, *o*-BAR₄^F), 7.65–7.50 (ov m, 8H, *p*-BAR₄^F + 3,7-dbf + 2,8-dbf), 7.26–7.10 (ov m, 10H, *o*- + *m*- + *p*-CH₂Ph), 5.45 (br s, 1H, NH), 4.03 (d, 4H, ³J_{HH} = 16.5 Hz, CH₂Ph), 2.50–2.15 (ov m, 8H, PCH₂CH₃), 1.10 (dt, 12H, ³J_{PH} = 18.9 Hz, ³J_{HH} = 7.6 Hz, PCH₂CH₃). ³¹P{¹H} NMR (CD₂Cl₂): δ 39.53 (s). ¹⁹F{¹H} NMR (CD₂Cl₂): δ –62.82 (s). ¹¹B{¹H} NMR (CD₂Cl₂): δ –6.60 (s). Anal. Calcd. (%) for C₆₆H₅₃BF₂₄N₂O₂P₂: C: 55.87; H: 3.77; N: 1.97; found: C: 55.74; H: 3.87; N: 2.26.

4.1.3. [LZnCH₃]⁺[B(m-(CF₃)₂-C₆H₃)₄][–] (**1**)

A 1.2 M solution of dimethylzinc in toluene (120 μL, 144 mmol) was added to a solution of **LH** (200 mg, 141 mmol) in bromobenzene (1 mL). The solution was left to stand for 1 h, then 2 mL of pentane were added, precipitating the product as a red oil. The supernatant was decanted, the material was washed with pentane (3 × 1 mL) and then dried *in vacuo*, giving **1** as an off-white powder in 90.0% yield (190 mg, 127 mmol). ¹H NMR (CD₂Cl₂): δ 8.34 (dt, 2H, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.1 Hz, 1,9-dbf), 7.73 (br s, 8H, *o*-BAR₄^F), 7.64 (td, 2H, ³J_{HH} = 7.7 Hz, ⁴J_{PH} = 2.4 Hz, 2,8-dbf), 7.56 (br s, 4H, *p*-BAR₄^F), 7.53 (ddd, 2H, ³J_{PH} = 10.4 Hz, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.1 Hz), 7.19–7.13 (ov m, 6H, *m*- + *p*-CH₂Ph), 7.07–7.01 (m, 4H, *o*-CH₂Ph), 4.00 (d, 4H, ³J_{PH} = 19.2 Hz, CH₂Ph), 2.30 (dq, 8H, ²J_{PH} = 11.8 Hz, ³J_{HH} = 7.7 Hz, PCH₂CH₃), 1.07 (dt, 12H, ³J_{PH} = 18.7 Hz, ³J_{HH} = 7.6 Hz, PCH₂CH₃), –0.95 (s, 3H, ZnCH₃). ³¹P{¹H} NMR (CD₂Cl₂): δ 46.60 (s).

¹⁹F{¹H} NMR (CD₂Cl₂): δ –62.84 (s). ¹¹B{¹H} NMR (CD₂Cl₂): δ –6.61 (s). Anal. Calcd. (%) for C₆₇H₅₅BF₂₄N₂O₂P₂Zn: C: 53.71; H: 3.70; N: 1.87; found: C: 53.35; H: 3.54; N: 2.20.

4.1.4. [LZnOCH(Me)CO₂Me⁺][B(m-(CF₃)₂-C₆H₃)₄][–] (**2**)

LH (400 mg, 282 mmol) and ethylzinc-lactate (55.7 mg, 282 mmol) were dissolved in 5 mL of bromobenzene and sealed in a glass bomb. The solution was heated to 100 °C for 1 h and cooled to ambient temperature. The solution was transferred to a glass vial and concentrated to 2 mL *in vacuo*. Addition of 4 mL of pentane caused the precipitation of the product as a pale yellow powder. The supernatant was decanted and the solid was washed with a 1:1 benzene/pentane mixture (2 mL) and pentane (2 × 2 mL) and dried *in vacuo*, giving **2** in an overall yield of 95% (423 mg, 267 mmol). ¹H NMR (CD₂Cl₂): δ 8.35 (dt, 2H, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.2 Hz, 1,9-dbf), 7.73 (s, 8H, *o*-BAR₄^F), 7.61 (td, 2H, ³J_{HH} = 7.7 Hz, ⁴J_{PH} = 2.4 Hz, 2,8-dbf), 7.55 (s, 4H, *p*-BAR₄^F), 7.48 (ddd, 2H, ³J_{PH} = 9.5 Hz, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.2 Hz, 3,7-dbf), 7.18–7.08 (ov m, 6H, *m*- + *p*-CH₂Ph), 7.05–6.98 (ov m, 4H, *o*-CH₂Ph), 4.66 (q, 1H, ³J_{HH} = 6.8 Hz, OCH(CH₃)CO₂CH₃), 3.98 (d, 4H, ³J_{PH} = 23.1 Hz, CH₂Ph), 3.69 (s, 3H, OCH(CH₃)CO₂CH₃), 2.45–2.24 (ov m, 8H, PCH₂CH₃), 1.41 (d, 3H, ³J_{HH} = 6.8 Hz, OCH(CH₃)CO₂CH₃), 1.04 (q, 6H, ³J_{PH} = 7.5 Hz, ³J_{HH} = 7.5 Hz, PCH₂CH₃), 0.98 (q, 6H, ³J_{PH} = 7.5 Hz, ³J_{HH} = 7.5 Hz, PCH₂CH₃). ³¹P{¹H} NMR (CD₂Cl₂): δ 46.8 (s). ¹⁹F{¹H} NMR (CD₂Cl₂): δ –62.8 (s). ¹¹B{¹H} NMR (CD₂Cl₂): δ –6.6 (s). Anal. Calcd. (%) for C₇₀H₅₉BF₂₄N₂O₄P₂Zn: C: 53.00; H: 3.75; N: 1.77; found: C: 53.13; H: 3.92; N: 2.09.

4.2. X-ray crystallography data

4.2.1. Crystal data for **L**

C₃₄H₄₀N₂O₂P₂, FW = 554.62, crystal size 0.32 × 0.32 × 0.12, triclinic, space group *P*–1, *a* = 10.863(1) Å, *b* = 11.126(2) Å, *c* = 13.923(2) Å, α = 72.388(1)°, β = 88.627(2)°, γ = 69.792(1)°, *V* = 1499.1(3) Å³, *Z* = 2, *D*_c = 1.229 g cm^{–3}, *F*(000) = 592, Mo Kα radiation (λ = 0.71073 Å), *T* = 173(2) K, μ = 0.174 mm^{–1}. 20286 reflections, 6118 unique (*R*_{int} = 0.0225) were used in all calculations. *R*₁ (*I* > 2σ(*I*)) = 0.0357, *wR*₂ (*I* > 2σ(*I*)) = 0.0940.

4.2.2. Crystal data for **2**

C₇₀H₅₉BF₂₄N₂O₄P₂Zn, FW = 1586.31, crystal size 0.52 × 0.33 × 0.27, triclinic, space group *P*–1, *a* = 15.019(2) Å, *b* = 15.453(2) Å, *c* = 16.072(2) Å, α = 104.979(1)°, β = 101.291(1)°, γ = 95.363(1)°, *V* = 3492.5(8) Å³, *Z* = 2, *D*_c = 1.508 g cm^{–3}, *F*(000) = 1612, Mo Kα radiation (λ = 0.71073 Å), *T* = 173(2) K, μ = 0.512 mm^{–1}. 47,147 reflections, 14,217 unique (*R*_{int} = 0.0184) were used in all calculations. *R*₁ (*I* > 2σ(*I*)) = 0.0340, *wR*₂ (*I* > 2σ(*I*)) = 0.0904.

Acknowledgments

P.G.H. thanks NSERC, CFI, Canada School of Energy and Environment and GreenCentre Canada for financial support. C.A.W. acknowledges NSERC and the Alberta Ingenuity Fund (Alberta Innovates) for student awards. Thanks to Yun Yang of GreenCentre Canada for GPC measurements.

Appendix. Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.jorganchem.2012.01.004.

References

- [1] (a) D.R. Dodds, R.A. Gross, *Science* 318 (2007) 1250–1251;
(b) R. Gross, B. Kalra, *Science* 297 (2002) 803–807;
(c) Y. Kimura, *Polym. J.* 41 (2009) 797–807.
- [2] For selected recent reviews see: (a) M.J. Stanford, A.P. Dove, *Chem. Soc. Rev.* 39 (2010) 486–494;
(b) C.A. Wheaton, P.G. Hayes, B.J. Ireland, *Dalton Trans.* (2009) 4832–4846;
(c) H.R. Kricheldorf, *Chem. Rev.* 109 (2009) 5579–5594;
(d) J. Wu, T. Yu, C. Chen, C. Lin, *Coord. Chem. Rev.* 250 (2006) 602–626;
(e) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* 104 (2004) 6147–6176.
- [3] For selected examples see: (a) S. Koeller, J. Kadota, A. Deffieux, F. Peruch, S. Massip, J.-M. Leger, J.-P. Desvergne, B. Bibal, *J. Am. Chem. Soc.* 131 (2009) 15088–15089;
(b) C. Bonduelle, B. Martín-Vaca, F.P. Cossío, D. Bourissou, *Chem.—Eur. J.* 14 (2008) 5304–5312;
(c) L. Zhang, F. Nederberg, J. Messman, R. Pratt, J. Hedrick, C. Wade, *J. Am. Chem. Soc.* 129 (2007) 12610–12611;
(d) F. Nederberg, E. Connor, M. Moller, T. Glauser, J. Hedrick, *Angew. Chem. Int. Ed.* 40 (2001) 2712–2715.
- [4] For selected examples see: (a) A. Pietrangelo, S.C. Knight, A.K. Gupta, L.J. Yao, M.A. Hillmyer, W.B. Tolman, *J. Am. Chem. Soc.* 132 (2010) 11649–11657;
(b) A. Otero, J. Fernandez-Baeza, A. Lara-Sanchez, C. Alonso-Moreno, I. Marquez-Segovia, L.F. Sanchez-Barba, A.M. Rodriguez, *Angew. Chem. Int. Ed.* 48 (2009) 2176–2179;
(c) A.F. Douglas, B.O. Patrick, P. Mehrkhodavandi, *Angew. Chem. Int. Ed.* 47 (2008) 2290–2293;
(d) H.Y. Ma, T.P. Spaniol, J. Okuda, *Angew. Chem. Int. Ed.* 45 (2006) 7818–7821;
(e) A.P. Dove, V.C. Gibson, E.L. Marshall, H.S. Rzepa, A.J.P. White, D.J. Williams, *J. Am. Chem. Soc.* 128 (2006) 9834–9843;
(f) Z.Y. Zhong, P.J. Dijkstra, J. Feijen, *J. Am. Chem. Soc.* 125 (2003) 11291–11298.
- [5] For selected examples see: (a) V. Poirier, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Dalton Trans.* (2009) 9820–9827;
(b) M.H. Chisholm, N.W. Eilerts, J.C. Huffman, S.S. Iyer, M. Pacold, K. Phomphrai, *J. Am. Chem. Soc.* 122 (2000) 11845–11854;
(c) B.M. Chamberlain, M. Cheng, D.R. Moore, T.M. Ovitt, E.B. Lobkovsky, G.W. Coates, *J. Am. Chem. Soc.* 123 (2001) 3229–3238;
(d) M. Chisholm, J. Gallucci, K. Phomphrai, *Chem. Commun.* (2003) 48–49;
(e) H. Chen, H. Tang, C. Lin, *Macromolecules* 39 (2006) 3745–3752;
(f) G. Labourdette, D.J. Lee, B.O. Patrick, M.B. Ezhova, P. Mehrkhodavandi, *Organometallics* 28 (2009) 1309–1319;
(g) A. Garces, L.F. Sanchez-Barba, C. Alonso-Moreno, M. Fajardo, J. Fernandez-Baeza, A. Otero, A. Lara-Sanchez, I. Lopez-Solera, A. Maria Rodriguez, *Inorg. Chem.* 49 (2010) 2859–2871;
(h) F. Drouin, P.O. Oguadinma, T.J.J. Whitehorn, R.E. Prud'homme, F. Schaper, *Organometallics* 29 (2010) 2139–2147;
(i) C.K. Williams, L.E. Breyfogle, S.K. Choi, W. Nam, V.G. Young, M.A. Hillmyer, W.B. Tolman, *J. Am. Chem. Soc.* 125 (2003) 11350–11359;
(j) E.L. Marshall, V.C. Gibson, H.S. Rzepa, *J. Am. Chem. Soc.* 127 (2005) 6048–6051.
- [6] (a) C.A. Wheaton, B.J. Ireland, P.G. Hayes, *Organometallics* 28 (2009) 1282–1285;
(b) C.A. Wheaton, P.G. Hayes, *Dalton Trans.* 39 (2010) 3861–3869;
(c) C.A. Wheaton, P.G. Hayes, *Chem. Commun.* 46 (2010) 8404–8406.
- [7] (a) Y. Sarazin, B. Liu, T. Roisnel, L. Maron, J.-F. Carpentier, *J. Am. Chem. Soc.* 133 (2011) 9069–9087;
(b) Y. Sarazin, V. Poirier, T. Roisnel, J.-F. Carpentier, *Eur. J. Inorg. Chem.* (2010) 3423–3428;
(c) J. Börner, U. Flörke, K. Huber, A. Döring, D. Kuckling, S. Herres-Pawlis, *Chem.—Eur. J.* 15 (2009) 2362–2376.
- [8] M.G. Cushion, P. Mountford, *Chem. Commun.* 47 (2011) 2276–2278.
- [9] (a) G. Asensio, A.B. Cuenca, M.A. Esteruelas, M. Medio-Simon, M. Olivan, M. Valencia, *Inorg. Chem.* 49 (2010) 8665–8667;
(b) M. Kranenberg, Y.E.M. van der Burgt, P.C.J. Kamer, P.W.N.M. van Leeuwen, K. Goubitz, J. Fraanje, *Organometallics* 14 (1995) 3081–3089.
- [10] (a) A. Charafeddine, W. Dayoub, H. Chapuis, P. Strazewski, *Chem.—Eur. J.* 13 (2007) 5566–5584;
(b) S. Bräse, C. Gil, K. Knepper, V. Zimmermann, *Angew. Chem. Int. Ed.* 44 (2005) 5188–5240.
- [11] B.J. Ireland, C.A. Wheaton, P.G. Hayes, *Organometallics* 29 (2010) 1079–1084.
- [12] (a) M.D. Hannant, M. Schormann, M. Bochmann, *J. Chem. Soc. Dalton Trans.* (2002) 4071–4073;
(b) M. Hannant, M. Schormann, D. Hughes, M. Bochmann, *Inorg. Chim. Acta* 358 (2005) 1683–1691.
- [13] T. Biela, A. Duda, S. Penczek, *Macromol. Symp.* 183 (2002) 1–10.