Enhanced Reactivity of Aluminum Complexes Containing P-Bridged Biphenolate Ligands in Ring-Opening Polymerization Catalysis

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Aluminum complexes containing \([\text{RPO}(2-O-3,5-tBu_2C_6H_3)_2]^{2-}\) \([R = tBu (3a), Ph (3b)]\) have been synthesized, structurally characterized, and their reactivity studied in comparison with those of their \([\text{RPO}(2-O-3,5-tBu_2C_6H_3)_2]^{2-}\) \([R = tBu (2a), Ph (2b)]\) analogs. Treating AlMe_3 with one equiv of H_2[3a-b] in THF at 0°C affords quantitatively \([3a-b]AlMe\), subsequent reactions of which with benzyl alcohol in THF at 25°C generate \([3a-b]Al(\mu_2-OCH_2Ph)_2\). The methyl \([3a-b]AlMe\) and the benzylxide \([3a-b]Al(\mu_2-OCH_2Ph)_2\) are all active for catalytic ring-opening polymerization (ROP) of ε-caprolactone and rac-lactide (rac-LA). Controlled experiments reveal that \([3a]Al(\mu_2-OCH_2Ph)_2\) is competent in living polymerization. Kinetic studies indicate that \([3a]AlMe\), in the presence of benzyl alcohol, catalyzes ROP of rac-LA at a rate faster than \([3b]AlMe\) and \([2a]AlMe(THF)\) by a factor of 1.8 and 23.6, respectively, highlighting the profound reactivity enhancement in ROP catalysis by varying the P-substituents of these biphenoxy complexes of aluminum.

Keywords: aluminum, biphenolate, ring-opening polymerization, lactone, lactide, catalyst

INTRODUCTION

The search for efficient catalyst precursors or initiators for catalytic ring-opening polymerization (ROP) of cyclic esters continues to constitute an active area of exploratory chemistry (Kamber et al., 2007; Thomas, 2010; Hillmyer and Tolman, 2014; Sarazin and Carpentier, 2015). In this regard, metal complexes containing chelating biphenoxy ligands have attracted significant attention. These complexes are intriguing as their catalytic activities are finely tunable by judiciously varying the peripheral substituents on the two phenolate rings and/or the bridge in between. While most studies concentrate on metal complexes of tetradoentate biphenoxy ligands such as ONNO (Ovitt and Coates, 2000; Zhong et al., 2002; Hormnirun et al., 2006; Zelikoff et al., 2009; Chen et al., 2012; Gao et al., 2015; Jones et al., 2015; Kirk et al., 2016; MacDonald et al., 2016; McKeown et al., 2016; Robert et al., 2017; Pang et al., 2018), OSSO (Buffet and Okuda, 2011; Buffet et al., 2011), ONSO (Stopper et al., 2012), and ONOX \((X = OR, NR_2)\) (Alcazar-Roman et al., 2003; Gendler et al., 2006, Tang and Gibson, 2007; Phomphrai et al., 2010; Wichmann et al., 2012) as exemplified in Figure 1, parallel research centered upon tridentate counterparts is relatively rare (Chmura et al., 2006; Chang and Liang, 2007; Hsu and Liang, 2010; Liang et al., 2011, 2013a,b,c,d,e; Huang et al., 2013; Klitzke et al., 2014a,b; Chang et al., 2016).
It has been documented that complexes of tridentate OOO (Huang et al., 2013), ONO (1a-c) (Liang et al., 2013a,b,c,d,e), and OPO (2a-b) (Chang and Liang, 2007; Hsu and Liang, 2010; Liang et al., 2011; Chang et al., 2016) are active catalyst precursors for ROP of \(\varepsilon\)-caprolactone (\(\varepsilon\)-CL) or lactides (LAs). Studies on complexes of 1 and 2 have revealed that substituents at the pnictogen donor have decisive impacts on ROP catalysis if living polymerization is the goal. Of note are aluminum complexes of 2a that polymerize \(\varepsilon\)-CL and rac-LA in a living manner to produce well-defined poly(\(\varepsilon\)-caprolactone) (PCL) and poly(rac-lactide) (PLA), respectively (Chang et al., 2016). In contrast, analogous complexes of 1a give instead low molecular weight oligo(\(\varepsilon\)-caprolactone) or PCL with a somewhat broad molecular weight distribution (Liang et al., 2013b). Constitutionally, complexes of 1a and 2a are much alike as both are pnictogen biphenolate derivatives carrying a pnictogen-bound tert-butyl group. Having an extra benzylic methylene moiety in each arm, however, the former ligand, upon complexation, forms 6-membered chelating rings that are therefore less rigid than the 5-membered chelating rings derived from the latter. In an effort to better understand the effects of chelating ring size (Lee et al., 2017) and ligand rigidity (Liang et al., 2003a,b, 2005a,b, 2006; Huang and Liang, 2004; MacLachlan and Fryzuk, 2005; Liang, 2006; MacLachlan et al., 2007; Hung et al., 2014) on ROP catalysis, we turn our attention to the oxidative forms of 2 that would persist with the same rigidity but enlarge the chelating rings to be 6-membered. Such biphenolate phosphinoxide derivatives O'O are distinguished from the ether-bridged OOO types that are intrinsically more flexible in ligand backbone and lack of the opportunities of changing substituents at the bridge donor. Note that complexes of O'O types of ligands are relatively undeveloped (Tanke et al., 1991; Siefert et al., 2000; Paine et al., 2004; He et al., 2008; Zhang et al., 2013; Taniyama et al., 2014). In this contribution, we aim to demonstrate the syntheses of the first examples of O'O complexes of aluminum and their enhanced catalytic activities in comparison with those of 2 with respect to ROP of \(\varepsilon\)-CL and rac-LA.

**RESULTS AND DISCUSSION**

**Ligand Synthesis**

The protio ligand precursor \(\text{H}_2[3b]\) is known (Siefert et al., 2000). Its tert-butyl analog \(\text{H}_2[3a]\) can be readily prepared as an off-white solid in high yield from oxidation of \(\text{H}_2[2a]\) with hydrogen peroxide in THF under ambient conditions. Its solution NMR data are consistent with a structure having time-averaged \(C_5\) symmetry. The diagnostic signals of this compound involve the downfield shift of its phosphorus atom at 65 ppm in comparison with that of \(\text{H}_2[2a]\) at −60 ppm (Hsu and Liang, 2010) and the singlet resonance of its hydroxy protons at 12.19 ppm in comparison with the doublet resonance of those in \(\text{H}_2[2a]\) at 7.61 ppm with \(J_{\text{HP}} = 12\) Hz (Hsu and Liang, 2010). The lack of \(\text{OH} \cdots \text{P}\) internuclear coupling and the downfield shift of the hydroxy protons in \(\text{H}_2[3a]\) are apparently a consequence of the 6-membered OH \cdots \text{O}=\text{P} hydrogen bonding. Such intramolecular hydrogen bonding is also confirmed by the solid state structure of \(\text{H}_2[3a]\) established by an X-ray diffraction study (Figure S1, Table S1).
**Synthesis and Characterization of Aluminum Complexes**

Protonolysis of AlMe₃ with one equiv of H₂[3a-b] in THF at 0°C yields nearly quantitative [3a-b]AlMe (Figure 2). Interestingly, these methyl complexes are not THF-bound as evidenced by their ¹H NMR spectra. This result is reminiscent of 4-coordinate [1a-c]AlMe (Liang et al., 2013b) but in contrast to 5-coordinate [2a-b]AlMe (Chang et al., 2016), ascribable to the hardness similarity of O (from phosphinoxide in 3) to N (from 1) rather than P (from 2) in consideration of the distinct preferences of these hard and soft donors to bind to a hard aluminum (Fryzuk et al., 1996, 1998; Liang et al., 2004, 2010; Lee and Liang, 2005, 2009; Su and Liang, 2018). As a result, the solution structures of [3a-b]AlMe and [1a-c]AlMe should be much alike. Subsequent reactions of either isolated or in situ prepared [3a-b]AlMe with one equiv of benzyl alcohol in THF at 25°C afford [{3a-b}Al(µ₂-OCH₂Ph)]₂ as colorless crystals.

The solution NMR data of [3a-b]AlMe and [{3a-b}Al(µ₂-OCH₂Ph)]₂ are indicative of a mirror plane symmetry that makes the two phenolate rings in 3 chemically equivalent as evidenced by the observation of two distinct singlet resonances for arylated tert-butyl groups in the ¹H NMR spectra. The methylene groups in the benzylxide ligands of [{3a-b}Al(µ₂-OCH₂Ph)]₂ exhibit a singlet resonance in the ¹H NMR spectra at ca. 5.7 ppm, a chemical shift that is similar to that found for [{2a-b}Al(µ₂-OCH₂Ph)]₂ (Chang et al., 2016). A ¹H NMR NOE difference experiment of [{3a}Al(µ₂-OCH₂Ph)]₂ was conducted with selective irradiation on the methylene groups, resulting in NOE enhancements of 5.14% for the arylated tert-butyl groups ortho to the phenolate oxygen atoms and 3.21% for the P-bound tert-butyl group. Note that these tert-butyl groups are spatially far away from each other due to the inherent geometry of the facially tridentate 3a. The concurrent NOE enhancements on these tert-butyl groups thus strongly implicate a dimeric structure of [{3a}Al(µ₂-OCH₂Ph)]₂ in solution. Consistent with the oxidized characteristics of the phosphorus atom in phosphinoxide derivatives, the ³¹P chemical shifts of [3a-b]AlMe and [{3a-b}Al(µ₂-OCH₂Ph)]₂ are significantly downfield shifted from those of their corresponding analogs of 2 (Chang et al., 2016).

An attempt to characterize [3a]AlMe by X-ray crystallography led instead to the structure of [3a]Al₂Me₄ that is an O-bound AlMe₃ adduct of [3a]AlMe (Figure 3). We attribute this unexpected result to unintentional imbalance of reaction stoichiometry that gives a trace amount of highly crystalline [3a]AlMe•AlMe₃. Following this lead, we attempted the reactions of [3a]AlMe with one equiv of AlMe₃ or H₂[3a] with two equiv of AlMe₃. Unfortunately, these reactions result ultimately in a mixture of equal molar [3a]AlMe and AlMe₃ as evidenced by ¹H and ³¹P[¹H] NMR spectra of reaction aliquots. Subsequent attempts to crystallographically characterize [3a]AlMe have thus far been unsuccessful. Nevertheless, the structure of [3a]AlMe•AlMe₃ confirms the 4-coordinate nature for the aluminum center of the [3a]AlMe moiety that has a distorted tetrahedral coordination core similar to [1a-c]AlMe (Liang et al., 2013b). The bond distances and angles of [3a]AlMe•AlMe₃ are unexceptional.

Colorless crystals of [{3a}Al(µ₂-OCH₂Ph)]₂ suitable for X-ray diffraction analysis were grown by layering pentane on top of a concentrated THF solution at −35°C. Figure 4 depicts its solid state structure. Consistent with the NOE study, this complex is a dimer, composed of two [3a]Al(OCH₂Ph) units bridged with the benzylxide ligands. With the coordination of the facially tridentate 3a, the aluminum atoms in [{3a}Al(µ₂-OCH₂Ph)]₂ are therefore 5-coordinate. Its coordination geometry is best described as distorted trigonal bipyramidal, having the phosphinoxide donor and one of the bridging benzylxide ligands disposed at the axial positions [O(3)-Al(1)-O(4A) =

![Diagram](image-url)
The axial Al-OCH$_2$Ph bond distances of 1.8726 Å are longer than those disposed equatorially [1.8372 (17) Å]. This indicates that the equatorial benzyloxide ligands are more anionic in nature whereas those at the axial positions are more cationic. Consistent with this result, [2a]AlMe(THF), though constitutionally different, holds a methyl ligand equatorially, and a THF axially (Chang et al., 2016).

The P-bound tert-butyl groups in [2a]AlMe(THF) and [(2a)Al(µ$_2$-OCH$_2$Ph)$_2$] are known to sterically repulse their equatorial methyl and benzyloxide ligands away from the ideal positions with the P-Al-C and P-Al-O angles of 105.51(12)$^\circ$ and 107.25(9)$^\circ$, respectively (Chang et al., 2016). Such steric repulsion is apparently eased by moving the tert-butyl-bound phosphorus atom to the β position in [(3a)Al(µ$_2$-OCH$_2$Ph)$_2$] as evidenced by the O(3)-Al(1)-O(4) angle of 90.14(8)$^\circ$. With the incorporation of the rigid o-phenylene backbone and the 6-membered chelating rings in [(3a)Al(µ$_2$-OCH$_2$Ph)$_2$], the O(1)-Al(1)-O(3) [92.52(8)$^\circ$] and O(2)-Al(1)-O(3) [94.74(8)$^\circ$] angles are notably wider than the corresponding angles [80.35(9)$^\circ$ and 84.17(9)$^\circ$] in the 5-membered chelating rings of [(2a)Al(µ$_2$-OCH$_2$Ph)$_2$] (Chang et al., 2016). As such, the tert-butyl groups ortho to the phenolate oxygen atoms in the former are spatially closer to the axial benzyloxide ligands than those in the latter. This should in principle encourage dissociation of the datively bonded benzyloxide ligands and formation of transient mononuclear [(3a)Al(µOCH$_2$Ph)] for subsequent substrate coordination. The similarity of Al(1)-O(4A) distance [1.8726(17) Å] to that in [(2a)Al(µ$_2$-OCH$_2$Ph)$_2$] [1.8782(2) Å] (Chang et al., 2016) implicates surprisingly little difference in trans influence invoked by P=O and P for axial benzyloxide ligand dissociation from these aluminum complexes.

**Catalytic Ring-Opening Polymerization**

Similar to aluminum derivatives of 1 (Liang et al., 2013b) and 2 (Chang et al., 2016), complexes [3a-b]AlMe and [(3a-b)Al(µ$_2$-OCH$_2$Ph)$_2$] are all active for catalytic ROP of ε-CL and rac-CL. To establish parallel comparison on reactivity of these pnicogen derivatives, the catalysis of [3a]AlMe and [(3a)Al(µ$_2$-OCH$_2$Ph)$_2$] was examined under conditions identical to those employed for [1]AlMe (Liang et al., 2013b), [2a]AlMe(THF) (Chang et al., 2016), and [(2a)Al(µ$_2$-OCH$_2$Ph)$_2$] (Chang et al., 2016). To simplify tabulated discussion and to make consistency with other mononuclear species, the benzyloxide complexes are presented as a monomer. **Table 1** summarizes their catalytic activities with ε-CL. In the presence of one equiv of benzyl alcohol, [3a]AlMe reacts slightly faster than [3b]AlMe with 100 equiv of ε-CL under the conditions employed (entry 1 vs. 3) though both reactions complete in 2 h (entries 2 and 4). The observed number averaged molecular weights (Mn’s), however, are generally smaller than those expected. Studies on Mn’s of these PCLs by $^1$H NMR spectroscopy also give similar results (entry 2, 5.1 kg/mol; entry 4, 9.5 kg/mol). Both [3a]AlMe and [3b]AlMe are more reactive than [2a]AlMe(THF) and [2b]AlMe(THF) (entries 1 and 3 vs. 5 and 6) due apparently to the discrepancy of 3 and 2 that invokes THF coordination and...
retards ROP. Though [1a]AlMe, [2a]AlMe(THF), and [3a]AlMe are all tert-butylated at their pnictogen atom, the polydispersity indexes (PDIs) of PCLs produced from [2a]AlMe(THF) and [3a]AlMe are smaller than those from [1a]AlMe (entries 1–2 and 5 vs. 7–8). All in all, [3a]AlMe is therefore a superior catalyst precursor to [2a]AlMe(THF) that in turn outperforms [1a]AlMe in this catalysis. These results underscore the decisive role that the biphenolate bridges play in ROP catalysis.

Similar to that generated in situ, [3a]Al(OCH2Ph) finishes polymerization of 100 equiv of ε-CL in toluene at 70°C in 2 h, producing quantitatively PCL having comparable Mn and PDI (entry 9 vs. 2). End group analysis by 1H NMR spectroscopy reveals a benzyl ester functionality, implicating that this ROP proceeds with a coordination-insertion mechanism that involves ε-CL coordination to the transient monomeric [3a]Al(OCH2Ph) (vide supra) followed by insertion of this ε-CL into the Al-OCH2Ph bond, allowing ε-CL to ring-open by cleaving its acyl-oxygen bond for chain propagation. Consistent with this rationale, the same reaction conducted in THF proceeds relatively slower (entry 10). Nevertheless, the PCL thus produced has a satisfactorily small PDI, indicating that the interfering ThF coordination is reversible and does not much induce undesirable side reactions.

In contrast, PCL produced from catalytic [3b]Al(OCH2Ph) has a relatively larger PDI (entry 11), reminiscent of that acquired from [3b]AlMe as compared with [3a]AlMe (entries 4 vs. 2). Complexes [3a]AlMe and [3a]Al(OCH2Ph) thus outperform [3b]AlMe and [3b]AlMe(THF) in this catalysis. Interestingly, [3a]Al(OCH2Ph) polymerizes ε-CL in a living fashion. The PCLs thus produced (entries 9 and 12–14) have Mn’s linearly proportional to the consumed monomer-to-catalyst ratios (Figure 5) while maintaining consistently small PDIs.

### Table 2 summarizes ROP results with respect to rac-LA.

In the presence of one equiv of benzyl alcohol, [3a]AlMe and [3b]AlMe complete polymerization of 100 equiv of rac-LA in toluene at 70°C in 6 h, producing PLAs quantitatively (entries 1–2). The former complex is again a superior catalyst precursor to the latter in view of the smaller PDI derived. These reactions are faster than those by catalytic [2a]AlMe(THF) and [2b]AlMe(THF) (entries 3–4) (Chang et al., 2016). Interestingly, [3a]Al(OCH2Ph) is also competent in living ROP of rac-LA (entries 5–8), affording PLAs having Mn’s directly proportional to the consumed monomer-to-catalyst ratios (Figure 6) while keeping their PDIs consistently small. In contrast, PLA produced by catalytic [3b]Al(OCH2Ph) has a relatively larger PDI (entry 9). A reaction run in THF is again slow but does not change PDI much (entry 10). Catalysis run at room temperature results in slow reaction and low conversion (entry 11). In the presence of one equiv of poly(ethylene glycol) methyl ether (Mn 2000, denoted MePEG2000 in Table 2), [3a]AlMe polymerizes rac-LA to give PEG-b-PLA copolymers with satisfactorily small PDIs (entries 12–13).

Kinetics of rac-LA polymerization by catalytic [3a]Al(OCH2Ph) was studied. Monitoring the reaction progress by 1H NMR spectroscopy reveals linear semilogarithmic plots for rac-LA consumptions vs. time (Figure 7), indicating a pseudo-first order dependence of the polymerization rates on the concentrations of rac-LA, i.e., \(-d[rac-LA]/dt = k_{obs}[rac-LA]\)³, where \(k_{obs} = k_p[catalyst]\)³ and \(k_p = propagation\ rate\ constant\). A plot of the observed rate constants vs. concentrations of [3a]Al(OCH2Ph) shows a linear dependence of the former on the latter (Figure 8), thus giving \(x = 1\). The overall rate law of this catalysis is therefore expressed as \(-d[rac-LA]/dt = \)

### Table 1 | ROP of ε-CL by catalytic [3a-b]AlMe and [3a-b]Al(OCH2Ph)².

| Entry | Cat             | [cat]₀/[I]₀/[ε-CL]₀ | Time (h) | conv (%)³ | Mn [calcd, kg/mol]⁴ | Mn [exp, kg/mol]⁵,⁶ | PDI⁷ |
|-------|-----------------|----------------------|----------|-----------|---------------------|---------------------|------|
| 1     | [3a]AlMe        | 1/1/100              | 1        | 72        | 8.3                 | 3.4                 | 1.14 |
| 2     | [3a]AlMe        | 1/1/100              | 2        | >99       | 11.5                | 5.2                 | 1.15 |
| 3     | [3b]AlMe        | 1/1/100              | 1        | 60        | 7.0                 | 4.3                 | 1.15 |
| 4     | [3b]AlMe        | 1/1/100              | 2        | >99       | 11.5                | 10.1                | 1.49 |
| 5     | [2a]AlMe(THF)   | 1/1/100              | 1        | 45        | 5.2                 | 3.4                 | 1.08 |
| 6     | [2b]AlMe(THF)   | 1/1/100              | 1        | 32        | 3.8                 | 3.1                 | 1.14 |
| 7     | [1a]AlMe        | 1/1/100              | 1        | 35        | 4.1                 | 3.6                 | 1.36 |
| 8     | [1a]AlMe        | 1/1/100              | 3        | >99       | 11.5                | 10.6                | 1.38 |
| 9     | [3a]Al(OCH2Ph)  | 1/0/100              | 2        | >99       | 11.5                | 5.4                 | 1.11 |
| 10²   | [3a]Al(OCH2Ph)  | 1/0/100              | 2        | 82        | 9.5                 | 4.8                 | 1.15 |
| 11    | [3b]Al(OCH2Ph)  | 1/0/100              | 2        | >99       | 11.5                | 10.6                | 1.29 |
| 12    | [3a]Al(OCH2Ph)  | 1/0/200              | 3        | >99       | 22.9                | 10.8                | 1.07 |
| 13    | [3a]Al(OCH2Ph)  | 1/0/300              | 4        | >99       | 34.4                | 14.9                | 1.07 |
| 14    | [3a]Al(OCH2Ph)  | 1/0/400              | 4        | >99       | 45.8                | 22.1                | 1.07 |

²Unless otherwise noted, all reactions were conducted in toluene (2.24 mL total) at 70°C with benzyl alcohol being the initiator; [cat]₀ = 8.3 mM.
³Determined by 1H NMR analysis.
⁴Calculated from (fw of ε-CL × [ε-CL]/[cat]₀) x conversion) + fw of initiator, assuming one propagating chain per aluminum atom.
⁵Measured by GPC in THF, calibrated with polystyrene standards.
⁶Multiplied by a corrected factor of 0.56 (Save et al., 2002).
⁷Data selected from Chang et al. (2016).
⁸Reaction run in THF.
k_p[catalyst][rac-LA], where $k_p = 1.47 (9) \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ at 70°C.

To kinetically quantify the P-substituent effect, we turn our attention to the relative ROP rates of rac-LA by catalytic [3a]AlMe, [3b]AlMe, [2a]AlMe(THF), and [2b]AlMe(THF) in the presence of one equiv of benzyl alcohol. Figure 9 depicts their semilogarithmic plots of rac-LA conversions with time. As a result, the reactivity of these catalyst precursors follows the order of [3a]AlMe > [3b]AlMe > [2a]AlMe(THF) > [2b]AlMe(THF). In this catalysis, [3a]AlMe is more reactive than [3b]AlMe by 1.8 times and [2a]AlMe(THF) is more reactive than [2b]AlMe(THF) by 2.0 times. More importantly, [3a]AlMe is more reactive than [2a]AlMe(THF) by 23.6 times and [3b]AlMe is more reactive than [2b]AlMe(THF) by 26.1 times. Collectively, tert-butyl is a superior P-substituent to phenyl and P=O is a superior biphenolate bridge to P in view of offering higher reactivity in this ROP catalysis.

**CONCLUSIONS**

We have prepared the first examples of biphenolate phosphinoxide complexes of aluminum and characterized their solution and solid state structures by NMR spectroscopy.

### TABLE 2 | ROP of rac-LA by catalytic [3a-b]AlMe and [3a-b]Al(OCH$_2$Ph)\(^3\).

| Entry | Cat            | [cat]/[I]/[rac-LA]$_0$ | Time (h) | Conv (%)$^b$ | Mn (calcd, kg/mol)$^c$ | Mn (exp, kg/mol)$^{d,e}$ | PDI$^d$ |
|-------|----------------|------------------------|----------|-------------|-------------------------|---------------------------|--------|
| 1     | [3a]AlMe       | 1/1/100                | 6        | >99         | 14.5                    | 12.0                       | 1.09   |
| 2     | [3b]AlMe       | 1/1/100                | 6        | >99         | 14.5                    | 10.5                       | 1.34   |
| 3$^f$ | [2a]AlMe(THF)  | 1/1/100                | 7        | 40          | 5.9                     | 3.0                        | 1.08   |
| 4$^f$ | [2b]AlMe(THF)  | 1/1/100                | 7        | 34          | 5.0                     | 2.3                        | 1.10   |
| 5     | [3a]Al(OCH$_2$Ph) | 1/0/100                | 6        | >99         | 14.5                    | 12.8                       | 1.10   |
| 6     | [3a]Al(OCH$_2$Ph) | 1/0/200                | 6        | >99         | 28.9                    | 29.4                       | 1.16   |
| 7     | [3a]Al(OCH$_2$Ph) | 1/0/300                | 6        | >99         | 43.3                    | 39.0                       | 1.16   |
| 8     | [3a]Al(OCH$_2$Ph) | 1/0/400                | 6        | >99         | 57.8                    | 56.5                       | 1.19   |
| 9     | [3b]Al(OCH$_2$Ph) | 1/0/100                | 6        | >99         | 14.5                    | 13.2                       | 1.23   |
| 10$^g$| [3a]Al(OCH$_2$Ph) | 1/0/100                | 6        | 67          | 9.8                     | 8.8                        | 1.16   |
| 11$^h$| [3a]Al(OCH$_2$Ph) | 1/0/100                | 6        | 12          | 1.8                     | NA$^i$                     | NA$^i$ |
| 12$^j$| [3a]AlMe       | 1/1/100                | 48       | 98          | 16.1                    | 14.3$^k$                   | 1.13   |
| 13$^j$| [3a]AlMe       | 1/1/200                | 48       | 92          | 28.5                    | 21.1$^k$                   | 1.14   |

$^a$Unless otherwise noted, all reactions were conducted in toluene (2.24 mL total) at 70°C with benzyl alcohol being the initiator. [cat]$_0$ = 8.3 mM.

$^b$Determined by $^1$H NMR analysis.

$^c$Calculated from ([fw of LA x [LA]/([cat]$_0$/[I]$_0$)) x conversion] + fw of initiator, assuming one propagating chain per aluminum atom.

$^d$Measured by GPC in THF, calibrated with polystyrene standards.

$^e$Multiplied by a corrected factor of 0.58 (Save et al., 2002).

$^f$Data selected from Chang et al. (2016).

$^g$Reaction run in THF.

$^h$Reaction run at room temperature.

$^i$Not applicable due to the formation of low Mn oligomers.

$^j$Reaction run with MePEG2000 as the initiator.

$^k$Corrected by applying a factor of 0.58 to the PLA block.
and X-ray crystallography, respectively. The coordination chemistry of these complexes is compared with those of their amine 1 (Liang et al., 2013b) and phosphine 2 (Chang et al., 2016) counterparts, so are their catalytic activities with respect to ROP of ε-CL and rac-LA. In addition to the inherent discrepancies of neutral donors in 1, 2, and 3, the 6-membered chelating rings rendered by the rigid 3 are advantageous to enhance substantially the reactivity of aluminum complexes in comparison with those derived from 1 and 2 as demonstrated by their relative ROP rates. Of particular note is also the competence of 3a complexes in living ROP of ε-CL and rac-LA.

EXPERIMENTAL SECTION

General Procedures

Unless otherwise specified, all experiments were performed under nitrogen using standard Schlenk or glovebox techniques. Compounds H$_2$[rBuP(2-O-3,5-tBu$_2$C$_6$H$_4$)$_2$] (H$_2$[2a]) (Hsu and Liang, 2010) and H$_2$[PhP(O)(2-O-3,5-tBu$_2$C$_6$H$_5$)$_2$] (H$_2$[3b]) (Siebert et al., 2000) were prepared according to literature procedures. ε-CL was dried over CaH$_2$ (1 wt%) at 80°C for 0.5 h and distilled under reduced pressure. rac-LA was purified by recrystallization (four times) from mixtures of toluene and ethyl acetate. All other chemicals were obtained from commercial vendors and used as received. All solvents were reagent grade or better and purified by standard methods. All NMR spectra were recorded at room temperature in specified solvents unless otherwise noted. Chemical shifts (δ) are listed as parts per million downfield from tetramethylsilane and coupling constants (J) are listed in hertz. Routine coupling constants are not listed. $^1$H NMR spectra are referenced by recrystallization using the residual solvent peak at δ 7.16 for C$_6$D$_6$ or δ 2.09 for toluene-d$_8$ (the most upfield signal). $^{13}$C NMR spectra are referenced using the internal solvent peak at δ 128.39 for C$_6$D$_6$. The assignment of the carbon atoms for all new compounds is based on the DEPT $^{13}$C NMR spectroscopy. $^{31}$P NMR spectra are referenced externally using 85% H$_3$PO$_4$ at δ 0. The NOE data were obtained with a $^1$H NMR NOEDIF experiment. GPC analyses were carried out at 45°C with HPLC grade THF supplied at a constant flow rate of 1.0 mL/min. Molecular weights (Mn and Mw) were determined by interpolation from calibration plots established with polystyrene standards. Mass spectra were recorded on a Finnigan MAT 95XL Mass Spectrometer. Elemental analysis was performed on a Heraeus CHN-O Rapid analyzer.

X-Ray Crystallography

Crystallographic data for H$_2$[3a], [3a]AlMe•AlMe$_3$, and [(3a)Al(μ$_2$-OCH$_2$Ph)$_2$]$_2$ are available in Supplementary Material. Data were collected on a diffractometer with graphite monochromated Mo-K$_\alpha$ radiation (λ = 0.7107 Å). Structures were solved by direct methods and
refined by full matrix least squares procedures against F² using SHELXL-97 (Sheldrick, 1998). All full-weight non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions. CCDC 1540209, 1540209, 1540210 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Synthesis of H₂[tBuP(0)(2-O-3,5-tBuC₆H₄)₂] (H₂[3a])**

To a THF solution (10 mL) of H₂[2a] (500 mg, 1.0 mmol) was added H₂O₂ (0.23 mL, 30% in aqueous solution, 2.0 mmol, 2 equiv) under ambient conditions. The solution was stirred at room temperature for 3 h and evaporated to dryness under reduced pressure. The solid thus obtained was washed with acetonitrile (4 mL) to afford the product as an off-white solid; yield 450 mg (87%). Colorless crystals suitable for X-ray diffraction analysis were grown from a concentrated THF solution at −35°C. ¹H NMR (CD₂Cl₂, 300 MHz) δ 12.19 (s, 2, ArOH), 7.62 (s, 2, ArH), 7.55 (d, 2, J_HH = 12, ArH), 1.52 (s, 18, ArCMe₃), 1.27 (s, 18, ArCMe₃). ¹³C[¹H] NMR (CD₂Cl₂, 121.5 MHz) δ 65.16. ¹³C[¹H] NMR (CD₂Cl₂, 75 MHz) δ 162.1 (s, C), 140.2 (d, J_CP = 11.3, C), 139.1 (d, J_CP = 6.8, C), 129.2 (s, ArH), 125.2 (d, J_CP = 9.8, ArH), 109.1 (d, J_CP = 89.3, C), 36.9 (d, J_CP = 67.5, PCME₃), 35.8 (s, ArCMe₃), 34.5 (s, ArCMe₃), 31.8 (s, ArCMe₃), 30.0 (s, ArCMe₃), 24.5 (s, PCME₃). Anal. Calc’d for C₃₂H₅₂O₃P: C, 74.66; H, 9.99. Found: C, 74.65; H, 9.94. MS (EI): calculated for C₃₂H₅₂O₃P m/z 514.4, found m/z 514.5.

**Synthesis of [3a]AlMe**

A THF solution (6 mL) of AlMe₃ (0.20 mL, 2 M in toluene, 0.4 mmol) was chilled to 0°C. To this was added a pre-chilled THF solution (6 mL) of H₂[3a] (206.2 mg, 0.4 mmol) at 0°C. The reaction solution was stirred at room temperature for 1 h and evaporated to dryness under reduced pressure. The solid thus obtained was washed with pentane (2 mL) to afford the product as an off-white solid; yield 215.2 mg (97%). ¹H NMR (CD₂Cl₂, 300 MHz) δ 7.58 (d, 2, J_HH = 3.0, Ar), 7.41 (dd, 2, J_HH = 15.0 and J_HH = 3.0, Ar), 1.54 (s, 18, ArCMe₃), 1.36 (d, 9, J_HH = 15, PCME₃), 1.19 (s, 18, ArCMe₃), 0.01 (s, 3, AlMe₃). ³¹P[¹H] NMR (CD₂Cl₂, 121.5 MHz) δ 61.37. ³¹C[¹H] NMR (CD₂Cl₂, 75 MHz) δ 163.9 (s, C), 141.6 (d, J_CP = 6.8, C), 139.1 (d, J_CP = 12.8, C), 129.4 (s, CH), 122.5 (d, J_CP = 12.8, CH), 114.1 (d, J_CP = 90.0, C), 35.9 (s, ArCMe₃), 35.2 (d, J_CP = 68.3, PCME₃), 34.3 (s, ArCMe₃), 31.6 (s, ArCMe₃), 29.7 (s, ArCMe₃), 26.1 (s, PCME₃), −16.4 (s, AlMe₃). Anal. Calc’d for C₃₃H₅₂AlO₃P: C, 71.44; H, 9.45. Found: C, 71.37; H, 9.38. MS (EI): calculated for C₃₃H₅₂AlO₃P m/z 554.4, found m/z 554.5.

**Synthesis of [3b]AlMe**

The procedures were all identical to those of [3a]AlMe except using H₂[3b] in the place of H₂[3a], affording the product as an off-white solid; yield 95%. ¹H NMR (CD₂Cl₂, 300 MHz) δ 7.70 (m, 2, Ar), 7.64 (d, 2, J_HH = 1.2, Ar), 7.14 (d, 2, J_HH = 1.2, Ar), 7.02 (m, 1, Ar), 6.92 (m, 2, Ar), 1.62 (s, 18, ArCMe₃), 1.13 (s, 18, ArCMe₃), 0.05 (s, 3, AlMe₃). ³¹P[¹H] NMR (CD₂Cl₂, 121.5 MHz) δ 55.06. ³¹C[¹H] NMR (CD₂Cl₂, 75 MHz) δ 164.4 (s, C), 141.4 (s, C), 139.4 (d, J_CP = 7.5, C), 134.1 (d, J_CP = 68.3, CH), 129.8 (s, CH), 129.0 (d, J_CP = 68.3, CH), 128.4 (s, CH), 125.1 (d, J_CP = 6.8, CH), 112.8 (d, J_CP = 62.3, C), 35.9 (s, CMe₃), 34.2 (s, CMe₃), 31.5 (s, CMe₃), 29.7 (s, CMe₃), −16.5 (s, AlMe₃). Anal. Calc’d for C₃₅H₆₈AlO₃P: C, 73.13; H, 8.42. Found: C, 72.75; H, 8.26.

**Synthesis of [3a]Al(µ₂-OCH₂Ph₂)₂**

A THF solution of [3a]AlMe was prepared in situ as describe above from the reaction of H₂[3a] (206.2 mg, 0.4 mmol) and AlMe₃ (0.20 mL, 2 M in toluene, 0.4 mmol). To this was added
PhCH₂OH (43.2 mg, 0.4 mmol). The reaction solution was stirred at room temperature overnight and evaporated to dryness under reduced pressure. The solid thus obtained was washed with pentane (4 mL × 2) to afford the product as an off-white solid; yield 168.4 mg (65%).¹H NMR (CD₂Cl₂, 300 MHz) δ 7.76 (d, 4, JHH = 7.5, Ar), 7.57 (d, 4, JHH = 21.1, Ar), 7.38 (dd, 4, JHP = 13.5 and JHH = 21.1, Ar), 7.21 (t, 4, JHH = 7.5, Ar), 7.01 (t, 2, JHH = 7.2, Ar), 5.72 (s, 4, OCH₂Ph), 1.54 (s, 36, ArCMe₃), 1.18 (s, 36, ArCMe₃), 1.12 (d, 18, JHP = 14.7, PCMe₃).³¹P{¹H} NMR (CD₂Cl₂, 121.5 MHz) δ 56.74.¹³C{¹H} NMR (CD₂Cl₂, 75 MHz) δ 164.9 (s, C), 143.0 (s, ipso-OCH₂Ph), 141.4 (d, JCP = 6.8, C), 137.9 (d, JCP = 12.9, C), 128.8 (s, CH), 128.3 (s, CH), 125.8 (s, para-OCH₂Ph), 125.6 (s, CH), 122.4 (d, JCP = 12.6, CH), 114.01 (d, JCP = 91.5, C), 114.01 (d, JCP = 71.2, PCMe₃), 34.2 (s, ArCMe₃), 31.6 (s, ArCMe₃), 30.1 (s, ArCMe₃), 25.8 (s, PCMe₃). Anal. Calcd for (C₉₅H₅₆AlO₄P)₂: C, 72.40; H, 8.73. Found: C, 72.06; H, 8.47.

**Synthesis of [{3b}Al(µ₂-OCH₂Ph)]₂**

The procedures were all identical to those of [{3a}Al(µ₂-OCH₂Ph)]₂ except using H₂[3b] in the place of H₂[3a], affording the product as an off-white solid; yield 68%.¹H NMR (toluene-d₈, 300 MHz) δ 7.60 (m, 8, Ar), 7.25 (m, 4, Ar), 6.90–7.09 (m, 16, Ar), 5.65 (s, 4, OCH₂Ph), 1.55 (s, 36, ArCMe₃), 1.13 (s, 36, ArCMe₃).³¹P{¹H} NMR (toluene-d₈, 121.5 MHz) δ 51.75.¹³C{¹H} NMR (CD₂Cl₂, 75 MHz) δ 165.5 (s, C), 143.0 (s, ipso-OCH₂Ph), 141.5 (d, JCP = 7.7, C), 138.2 (d, JCP = 13.4, C), 133.9 (d, JCP = 10.4, CH), 132.9 (s, CH), 129.2 (s, CH), 128.4 (s, CH), 127.6 (s, CH), 126.0 (s, CH), 125.2 (d, JCP = 14.3, CH), 125.0 (d, JCP = 12.2, CH), 112.9 (d, JCP = 104.1, C), 67.5 (s, OCH₂Ph), 35.9 (s, ArCMe₃), 34.1 (s, ArCMe₃), 31.5 (s, ArCMe₃), 30.2 (s, ArCMe₃). Anal. Calcd for (C₄₁H₅₂AlO₄P)₂: C, 73.85; H, 7.86. Found: C, 73.51; H, 7.65.

**Catalytic ROP of e-CL or rac-LA (Tables 1, 2)**

A toluene solution (1 mL) containing an alcohol initiator (PhCH₂OH or MePEG2000) where appropriate and monomer (e-CL or rac-LA having prescribed [monomer]₀/[catalyst]₀ ratios) was heated in an oil bath at 70°C. To this was added a toluene solution (1.24 mL) of catalyst [{3a-b}AlMe₃] (0.0187 mmol) or [{3a-b}Al(µ₂-OCH₂Ph)]₂ (0.00935 mmol). The reaction solution was stirred at 70°C for a period of prescribed time and quenched with a methanol solution of HCl. The solid thus precipitated was washed with hexane, isolated, and dried under reduced pressure until constant weights.

**Kinetic Studies on ROP of rac-LA**

The procedures were similar to those described above except that the reactions were conducted in toluene-d₈. The monomer conversion was monitored over time by ¹H NMR spectrometry.

**AUTHOR CONTRIBUTIONS**

All authors made substantial contributions to this work. X-RZ and Y-NC conducted experiments, analyzed results, and tabulated data. K-WH participated in the development and discussion of this work. L-CL conceived the project, directed the investigations, and composed the manuscript.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2018.00607/full#supplementary-material

X-ray crystallographic data for H₂[3a], [{3a}AlMe₃], [{3a-b}AlMe₃], and [{3a-b}Al(µ₂-OCH₂Ph)]₂.

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