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# Phosphasalen group IV metal complexes: Synthesis, Characterisation and Ring Opening Polymerization of Lactide

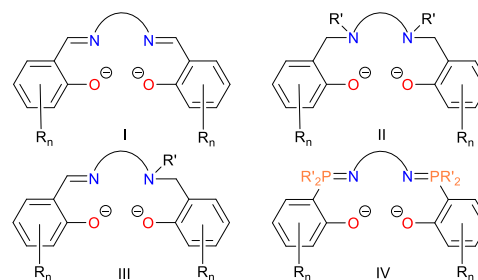
Adrien T. Normand,<sup>a</sup> Raluca Malacea-Kabbara,<sup>a</sup> Rosita Lapenta,<sup>c</sup> Aymeric Dajnak,<sup>a</sup> Philippe Richard,<sup>a</sup> H  l  ne Cattey,<sup>a</sup> Ana  lle Bolley,<sup>c</sup> Alfonso Grassi,<sup>d</sup> Stefano Milione,<sup>d</sup> Audrey Auffrant,<sup>\*b</sup> Samuel Dagorne<sup>\*c</sup> and Pierre Le Gendre<sup>\*a</sup>

We report the synthesis of a series of Zr and Ti complexes bearing phosphasalen which differs from salen by the incorporation of two P atoms in the ligand backbone. The reaction of phosphasalen proligands (**1a-1c**)H<sub>2</sub> with Zr(CH<sub>2</sub>Ph)<sub>4</sub> led to different products depending on the nature of the N,N-linker in the ligand. In case of ethylene-linked phosphasalen, octahedral Zr complex **2a** formed as a single stereoisomer in *trans* geometry. With the phenylene linker, it was shown by dynamic NMR spectroscopy that complex **2b** exists as a mixture of *trans* and *cis*- $\beta$  isomers in solution, both enantiomers ( $\Delta$  and  $\Lambda$ ) of the *cis*- $\beta$  isomer being in fast equilibrium with respect to the NMR time-scale. The use of a propylene-linked phosphasalen proligand **1cH<sub>2</sub>** led to a mixture of complexes among which a binuclear Zr complex **2c** bridged only by one phosphasalen ligand could be isolated and characterized. Addition of 2 equiv of <sup>t</sup>PrOH to **2a** and **2b** afforded diisopropoxy Zr complexes **3a** and **3b** as a mixture of *trans* and *cis*- $\beta$  isomers, the latter undergoing fast  $\Delta/\Lambda$  isomerization in solution. Addition of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> to **2a** and **2b** gave cationic monobenzyl Zr complexes **4a** and **4b** which have been further converted into cationic alkoxy Zr complexes **5a-b** and **6a-b** by alcoholysis with <sup>t</sup>PrOH and (*S*)-methyl-lactate, respectively. The reaction of the phosphasalen proligands with Ti(NMe<sub>2</sub>)<sub>4</sub> proceeded diastereoselectively giving rise to Ti complexes **7a-c** in octahedral geometry with *cis*- $\beta$  wrapping of the ligand. The complexes have been tested for the ROP of *rac*-lactide. The neutral phosphasalen Ti and Zr complexes showed only poor activity probably due to the encumbered and electron donating nature of the phosphasalen ligand. In contrast, the cationic Zr alkoxides **5a**, **6a** and **6b** are effective initiators for the controlled and hetero-selective ROP of *rac*-lactide.

## Introduction

Poly(lactic acid) (PLA) is considered today as the most promising biosourced and biodegradable alternative to petrochemically based plastics.<sup>1</sup> Depending on its microstructure, PLA features highly different mechanical and thermal properties and can find applications ranging from soft materials to engineering plastic materials.<sup>2</sup> The Ring Opening Polymerization (ROP) of lactide constitutes the most attractive route to produce such polymers in a controlled manner. Intensive research has been carried out in this field and highly active initiators able to give high molecular weight PLA polymers with low polydispersity and controlled tacticity have been described.<sup>3</sup> Group 4 complexes have shown great potential as ROP initiators and some

combinations with salen (I), salan (II) and salalen (III) ligands have been found to be particularly efficient (Figure 1).<sup>4</sup> For example, dialkoxy titanium complexes with salen ligands lead to atactic PLA with narrow PDIs and high molecular weights.<sup>5</sup> Switching to more flexible salan and salalen ligand leads to chelate zirconium and hafnium complexes able to produce high molecular weight heterotactically or isotactically enriched PLA from *rac*-lactide.<sup>6</sup> In 2011, one of us described for the first time phosphasalen ligands (IV), a variant of salen which consists in a bis(iminophosphorane) moiety flanked by two phenoxy groups.<sup>7</sup> Phosphasalen ligands resemble salen but their wrapping pattern and electron donating ability differ notably. In the former, the tetrahedral phosphorus atoms impart both increased flexibility and steric bulk to the ligand. Additionally,



<sup>a</sup> Institut de Chimie Mol  culaire de l'Universit   de Bourgogne (ICMUB), Universit   de Bourgogne Franche-Comt   (UMR-CNRS 6302), 9, av. A. Savary, 21078 Dijon, France.

<sup>b</sup> Laboratoire de Chimie Mol  culaire, CNRS UMR 9168,   cole Polytechnique, Institut Polytechnique de Paris, 91128 Palaiseau, France.

<sup>c</sup> Institut de Chimie de Strasbourg (UMR-CNRS 7177), Universit   de Strasbourg.

<sup>d</sup> Dipartimento di Chimica e Biologia, Universita degli Studi di Salerno, via Giovanni Paolo II, 132-84084 Fisciano (SA), Italy

Electronic Supplementary Information (ESI) available: CIF files for compounds **1aH<sub>2</sub>**, **1bH<sub>2</sub>**, **1cH<sub>2</sub>**, **2a**, **2c'**, **2c''**, **3a**, **3b**, **6c**, **7c**; NMR spectra of new compounds and ROP studies.

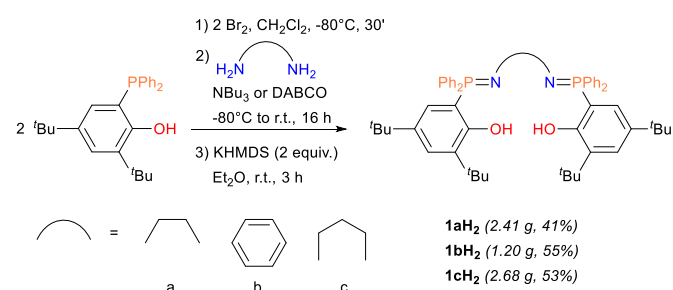
**Figure 1** Salen (I), salan (II), salalen (III) and phosphasalens (IV) ligands

the stronger basicity of iminophosphoranes compared to imines, along with their lack of  $\pi$ -accepting properties, make phosphasalens better net donors than salen. These ligands, associated with rare earth metals (Sc, Y, La, Lu), were shown to be powerful initiators for the polymerization of *rac*-lactide with excellent rates and high stereoselectivities.<sup>8</sup> In light of these results, we set out to combine phosphasalens ligands with group IV metal complexes to develop new lactide ROP catalysts. To the best of our knowledge, such combination has yet to be reported. Herein, we describe the synthesis and characterization of a series of phosphasalens Ti and Zr complexes along with a preliminary assessment of their performance as lactide ROP initiators.

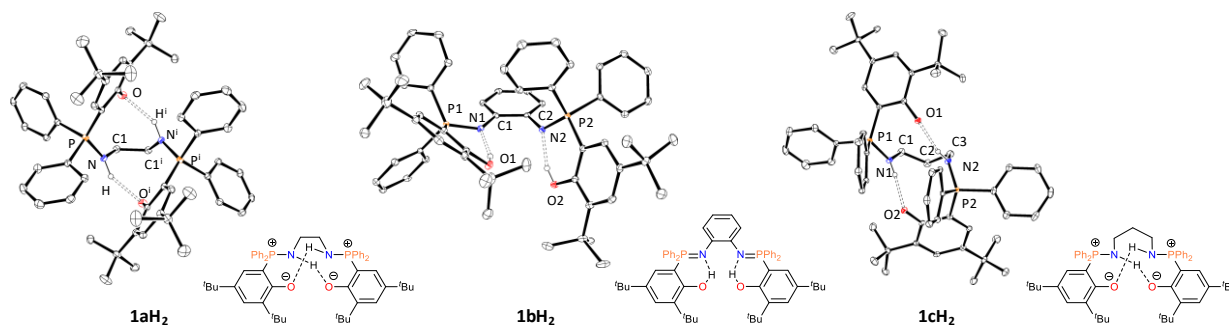
## Results and discussion

### Synthesis and characterization of the phosphasalens proligands

Phosphasalens proligands (**1a-1c**)H<sub>2</sub> were synthesized by adapting a previously reported procedure based on the Kirsanov reaction between 4,6-di(*tert*-butyl)-2-(diphenylphosphino)phenol with bromine and the appropriate diamine, using either tributylamine or DABCO as HBr trapping agent (Scheme 1).<sup>8b,8c</sup> Further deprotonation with two equivalents of potassium bis(trimethylsilyl)amide led to the proligands (**1a-1c**)H<sub>2</sub> in 41–55% yields. The range of diamines were chosen to study the impact of the bridging unit on the structure of the resultant metal complex and on the polymerization performances. Ortho-*tert*-butyl-substituted ligands were selected for their propensity to form discrete mononuclear species. The phosphasalens proligands (**1a-1c**)H<sub>2</sub>



**Scheme 1** Synthesis of phosphasalens proligands (**1a-1c**)H<sub>2</sub>

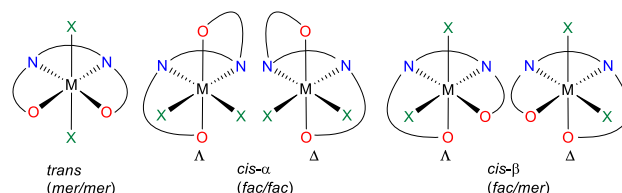


**Figure 2** ORTEP view of phosphasalens proligands (**1a-1c**)H<sub>2</sub>. For the sake of clarity, H atoms (except for relevant ones) as well as disorder and solvent molecules (if any) are not shown. †: 1-X, +Y, 3/2-Z.

were characterized by <sup>31</sup>P{<sup>1</sup>H}, <sup>1</sup>H, <sup>13</sup>C NMR, EA and X-Ray diffraction analysis. In the solid state, **1b**H<sub>2</sub> shows intramolecular hydrogen bonding between iminophosphorane moieties and nearby hydroxyl groups (Figure 2). Both phenol rings are tilted by 43° and 71° with respect to the mean plane defined by the four atoms N1, C1, C2 and N2 with the phenol oxygens O1 and O2 dipping below this plane. P-N bond lengths in **1b**H<sub>2</sub> are 1.579(2) Å and 1.586(2) Å in the range of those reported for iminophosphoranes.<sup>7b,9</sup> Proligands **1a**H<sub>2</sub> and **1c**H<sub>2</sub> feature different dipolar form and spatial arrangement compared to **1b**H<sub>2</sub>. Both phenolic protons are transferred to iminophosphoranes resulting in zwitterionic forms. This is consistent with the more basic character of the iminophosphorane functions in **1a**H<sub>2</sub> and **1c**H<sub>2</sub> due to the alkylene spacer. Intramolecular electrostatic and hydrogen bonding interactions between the two opposite phenoxyaminophosphonium in a complementary pairing constrain the ligands to adopt a helical twist in a C<sub>2</sub>-symmetric fashion<sup>5</sup>. As expected, P-N bond lengths in **1a**H<sub>2</sub> and **1c**H<sub>2</sub> are longer than that in **1b**H<sub>2</sub> due to protonation (1.637(2) Å for **1a**H<sub>2</sub> and 1.624(2), 1.623(2) Å for **1c**H<sub>2</sub>).<sup>10</sup> The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **1b**H<sub>2</sub> shows a signal at 18.1 ppm in the range observed for other iminophosphoranes,<sup>7a</sup> while **1a**H<sub>2</sub> and **1c**H<sub>2</sub> give downfield shifted signals at  $\delta$  = 42.7 and 39.4 ppm, respectively.

### Synthesis and characterization of the phosphasalens Zr complexes

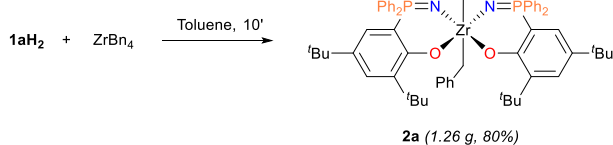
Based on previous studies of group IV metal complexes with salan/salalen ligands, we first targeted Zr complexes that generally lead to more active ROP initiators. If phosphasalens behaves as tetradentate ligand, three modes of coordination around the octahedral metal centre can be expected: *trans*, *cis- $\alpha$*  or *cis- $\beta$*  (Figure 3). In the last two cases, complexes are chiral and can exist as two enantiomers ( $\Delta$  and  $\Lambda$ ).



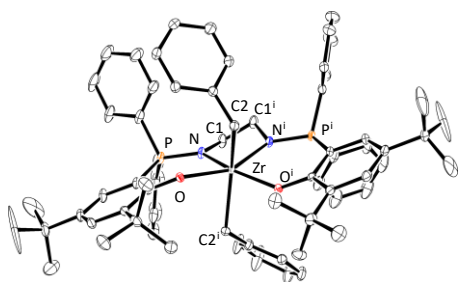
**Figure 3** Possible coordination modes of tetradentate O,N,N,O ligands around an octahedral metal centre

The reaction of the proligands (**1a-1c**)H<sub>2</sub> with Zr(CH<sub>2</sub>Ph)<sub>4</sub> led to different outcomes (Schemes 2-4). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of complex **2a** in C<sub>6</sub>D<sub>6</sub> at 298 K shows a singlet at δ = 36.5 ppm upfield shifted with respect to the signal of **1a**. The presence of only two singlets for the <sup>t</sup>Bu groups, one singlet for the two residual benzylic groups and one multiplet for the ethylene spacer in the <sup>1</sup>H NMR spectrum of **2a** suggests a C<sub>2v</sub>-symmetric *trans* complex in solution. X-ray diffraction analysis conducted on a single crystal of **2a** corroborated this hypothesis. The Zr atom is located on a true crystallographic C<sub>2</sub>-symmetry axis and, as shown in Figure 4, exhibits a pseudo-octahedral coordination scheme. Comparison with (<sup>t</sup>BuSalfen)Zr(CH<sub>2</sub>Ph)<sub>2</sub> reported by Arnold in the same *trans* geometry shows shorter Zr-N bond distances (by ca 0.15 Å) and longer Zr-C distances (by ca 0.03 Å) in the phosphasalen complex.<sup>11</sup> P-N bonds lengths are slightly shortened (by ca 0.018(3) Å) compared to those in **1a**H<sub>2</sub>.

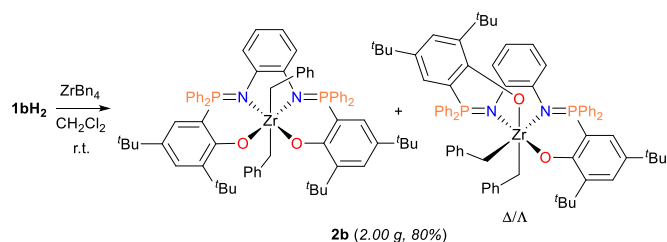
The reaction of the proligand **1b**H<sub>2</sub> with Zr(CH<sub>2</sub>Ph)<sub>4</sub> gave complex **2b** as a mixture of *trans* and *cis*-β isomers which was characterized by VT and low temperature NMR experiments (Scheme 3). At 200 K, the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **2b** recorded at 243 MHz in d<sub>8</sub>-THF shows one peak at δ = 29.5 ppm, which can be tentatively assigned to the *trans* isomer and a set of two peaks at δ = 28.3 and 30.8 ppm consistent with a C<sub>1</sub>-symmetric *cis*-β complex (Figure 5). Upon heating up to 330 K, the <sup>31</sup>P signal of the *trans* isomer does not change significantly whereas those of *cis*-β isomer broaden slowly, collapse at 300 K and then decoalesce to give one broad peak centred at δ = 28.3 ppm (Δν<sub>1/2</sub> = 131.9 Hz).



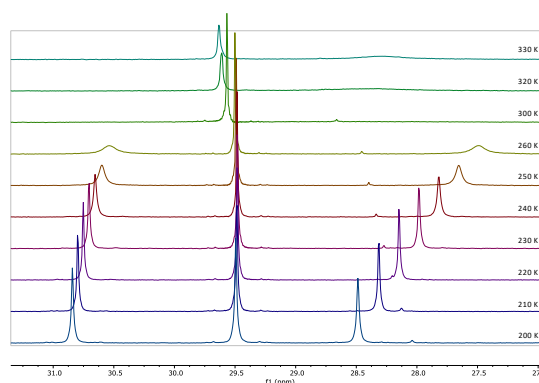
Scheme 2



**Figure 4** ORTEP view of complex **2a** (hydrogen atoms are omitted for clarity). Selected distances (Å) and angles (deg): C2–Zr 2.350(2), N–P 1.6194(18), N–Zr 2.2033(17), O–Zr 2.0582(14), C2–Zr–C2 143.92(12), N–Zr–N 74.74(9), O–Zr–O<sup>i</sup> 122.96(8). <sup>i</sup>1–X, +Y, 3/2–Z.



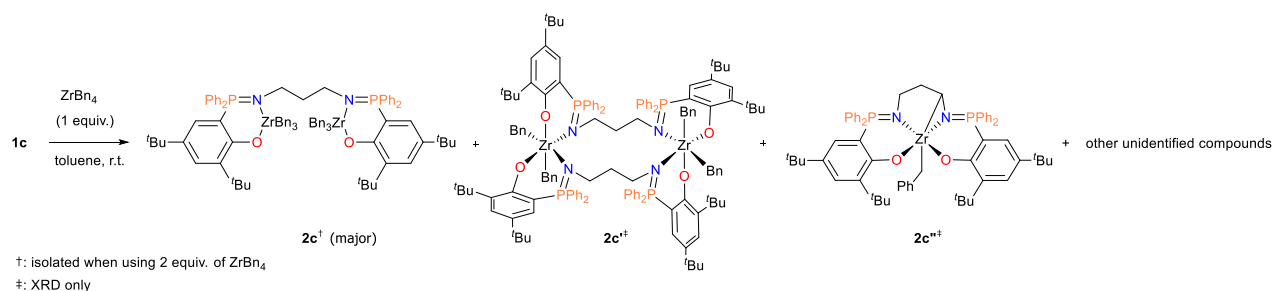
Scheme 3 (only one *cis*-β enantiomer shown for clarity)



**Figure 5** Variable-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **2b** (243 MHz, d<sub>8</sub>-THF)

Heating the sample also induces the partial isomerization of *trans*-**2b** to *cis*-β-**2b** (ratio *trans*:*cis*-β = 1:1.4 at 200 K and 1:2.4 at 330 K). In the <sup>1</sup>H NMR spectra of complex **2b** recorded from 200 K up to 330 K, the benzyl methylenic protons of the *trans* isomer appear as one singlet at chemical shifts ranging from 1.74 to 1.83 ppm consistent with a C<sub>2v</sub>-symmetric complex. The same protons in the *cis*-β isomer produce four multiplets centred at δ = 1.67, 1.79, 2.09 and 2.37 ppm at 210 K and one broad singlet centred at δ = 2.06 ppm at 300 K. The dynamic NMR behaviour of the *cis*-β isomer of **2b** can be explained by an isomerization between Δ and Λ enantiomers. In order to get accurate thermodynamic constants, analogous VT NMR experiments were conducted in d<sub>8</sub>-toluene solution of **2b** within a broader temperature range (200 K to 350 K). An Eyring plot of ln(k/T) against 1/T gives an enthalpy of activation ΔH<sup>‡</sup> = 45.9 (±4.3) kJ.mol<sup>-1</sup> and an entropy of activation ΔS<sup>‡</sup> = -34 (±16) J.mol<sup>-1</sup>,<sup>55</sup> comparable to other *cis*-β Zr complexes which undergo the same inversion of configuration at the metal centre (Fig. S33, SI).<sup>12</sup>

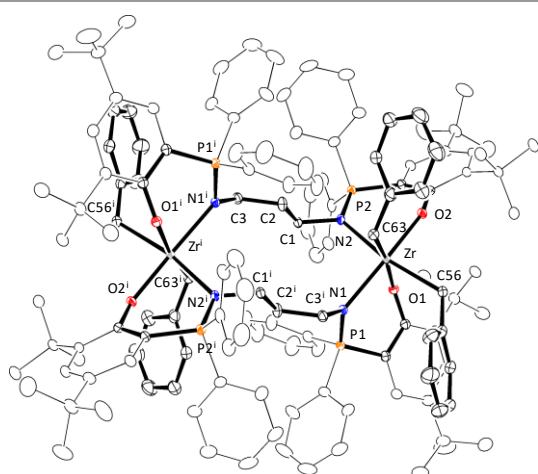
In the case of the proligand **1c**H<sub>2</sub>, the reaction with one equivalent of tetrabenzylzirconium led to a mixture of products among which two binuclear complexes **2c** (major) and **2c'** as well as one mononuclear complex **2c''** (Scheme 4). Complex **2c**, which features two tris(benzyl)zirconium fragments bridged by one phosphasalen ligand, was independently prepared from



**1c**H<sub>2</sub> and two equivalents of Zr(CH<sub>2</sub>Ph)<sub>4</sub> and isolated in 59% yield.<sup>13</sup> Two characteristic <sup>t</sup>Bu signals at δ = 1.51 and 1.22 ppm integrating for 18 protons each and one benzylic methylene signal at δ = 1.83 ppm integrating for 12 protons can be observed in the <sup>1</sup>H NMR spectrum of **2c**. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum shows a signal at δ = 30.8 ppm. Complexes **2c'** and **2c''** could be identified by X-ray diffraction analysis of single crystals. In complex **2c'**, a second phosphasalen ligand bridges the two Zr centres giving a centrosymmetric binuclear complex with both Zr atoms in a pseudo-octahedral geometry where the coordinating atoms of the same nature (C,C), (N,N) and (O,O) are located *cis* to one another (Figure 6). Complex **2c''** is a mononuclear complex with only one benzyl group present and the phosphasalen ligand coordinated in an unusual pentadentate fashion by the four ONNO atoms and by one C atom of the propylene linker (Figure 7). Complex **2c'''** is best

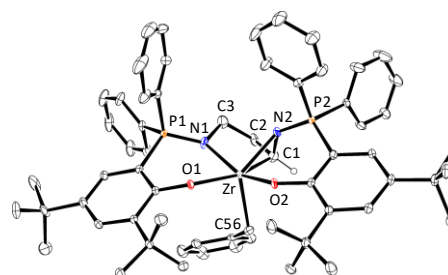
binuclear complexes formation and/or side reactions at the propylene backbone.

Alkoxide derivatives were then targeted for use as lactide ROP initiators. Complexes **3a** and **3b** could be readily prepared by adding two equivalents of <sup>t</sup>PrOH to dichloromethane solutions of **2a** and **2b**, respectively (Scheme 5). The NMR spectroscopic characterization of **3a** and **3b** revealed that both complexes are fluxional in solution and form as mixtures of *trans* and *cis*-β isomers. In the <sup>1</sup>H NMR spectrum of **3a** (CD<sub>2</sub>Cl<sub>2</sub>, 250 K), isopropoxy groups resonances consist of a heptet at δ = 3.70 ppm for the *trans* isomer and a set of two heptets at δ = 4.60 and 3.23 ppm for the *cis*-β isomer with integrations corresponding to a *trans*:*cis*-β ratio of 1:4. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **3a** recorded under the same conditions displays a

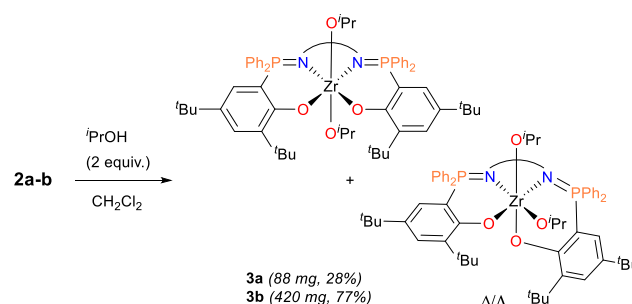


**Figure 6** ORTEP view of complex **2c'** (hydrogen atoms are omitted for clarity). Selected distances (Å) and angles (deg): N1–P1 1.630(2), N1–Zr 2.289(2), N2–P2 1.614(2), N2–Zr 2.295(2), O1–Zr 2.0840(19), O2–Zr 2.0370(18), N1–Zr–N2 94.87(8), O2–Zr–O1 95.76(7), C63–Zr–C56 87.45(10). <sup>1</sup>-X, 1-Y, 1-Z.

described as a pseudo-square pyramidal complex with the remaining benzyl ligand in apical position and one of the basal positions occupied by two atoms (N2 and C1) which form a small acute N2–Zr–C1 angle of 38.27°(11). The formation of **2c''** probably involves an entropically favored (toluene is liberated) σ-bond metathesis reaction between the C–H bond α to N and the Zr–C bond of the benzyl moiety.<sup>14</sup> Thus, the greater flexibility of ligand **2c** brought by the extra carbon spacer favours



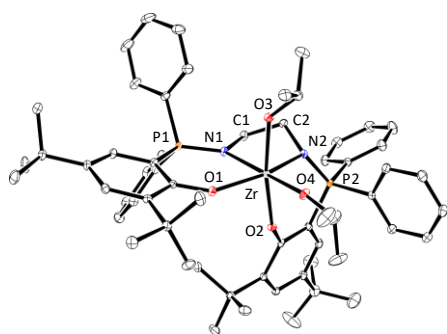
**Figure 7** ORTEP view of complex **2c''** (hydrogen atoms are omitted for clarity except on C1). Selected distances (Å) and angles (deg): Zr–O1 2.0717(19), Zr–O2 2.064(2), Zr–N1 2.248(3), Zr–N2 2.193(2), Zr–C1 2.207(4), Zr–C56 2.282(3), P1–N1 1.593(2), P2–N2 1.583(2), O1–Zr–O2 97.13(8), N1–Zr–N2 81.50(9), C1–Zr–C56 85.90(12).



signal at δ = 32.7 ppm for the *trans* isomer and a set of two signals at δ = 31.6 and 29.6 ppm for the *cis*-β isomer. Similar characteristic signals can be found in the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR



spectra of **3b** in  $d_8$ -THF at 250 K with a different *trans*:*cis*- $\beta$  ratio of 1:1. Variable temperature experiments were conducted on **3a** and **3b** in  $d_8$ -toluene and line broadening analysis revealed activation parameters for the  $\Delta$ - $\Lambda$  isomerisation of  $\Delta H^\ddagger = 63.7$  ( $\pm 4.1$ ) kJ.mol<sup>-1</sup> and  $\Delta S^\ddagger = 6$  ( $\pm 13$ ) J.mol<sup>-1</sup> for **3a** and  $\Delta H^\ddagger = 48.5$  ( $\pm 4.6$ ) kJ.mol<sup>-1</sup> and  $\Delta S^\ddagger = -48$  ( $\pm 16$ ) J.mol<sup>-1</sup> for **3b** (Fig. S52 and Fig. S65, SI).<sup>55</sup> The slightly positive entropy of activation for **3a**, as opposed to the negative values for complexes **2b** and **3b**, might be indicative of a dissociation/recoordination mechanism for the ethylene-linked complex **3a**, whereas **2b** and **3b**, with a more rigid phenylene linker, would isomerize via a Bailar twist process.<sup>15</sup> It is worth noting that a partial and reversible *cis*- $\beta$ -*trans* isomerization was also observed in complex **3a** upon heating. Suitable crystals for X-Ray diffraction analysis of **3a** and **3b** were obtained by vapour diffusion of pentane into saturated CH<sub>2</sub>Cl<sub>2</sub> solutions of the complexes. The ORTEP view of **3a** shows the zirconium atom in a pseudo-octahedral environment with the phosphasalen ligand adopting a *cis*- $\beta$  coordination mode (Figure 8). As for the proligand, the phosphasalen ligand is able to undergo geometrical deformation, the phosphorus atom authorizing the *fac*-wrapping mode around the metal. Comparison with the salan and salalen-Zr complexes reported by Jones in the same *cis*- $\beta$  configuration shows that the coordination sphere is a little bit more congested with phosphasalen with shorter Zr-N bond distances (by ca 0.1 Å) and

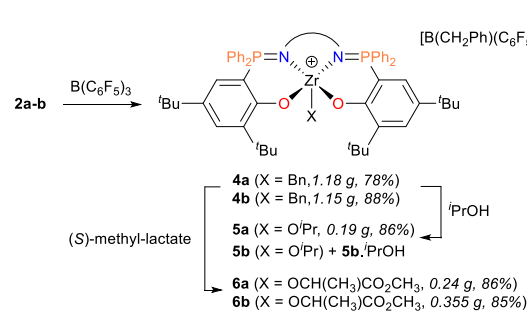


**Figure 8** ORTEP view of complex **3a** (For the sake of clarity, H atoms as well as disorder and solvent molecules are not shown). Selected distances (Å) and angles (deg): N1–P1 1.601(2), N1–Zr 2.321(2), N2–P2 1.609(2), N2–Zr 2.286(2), O1–Zr 2.0424(17), O2–Zr 2.1236(17), O3–Zr 2.0095(17), O4–Zr 1.9586(17), O1–Zr–O2 92.67(7), N1–Zr–N2 73.89(7), O3–Zr–O4 92.43(7).

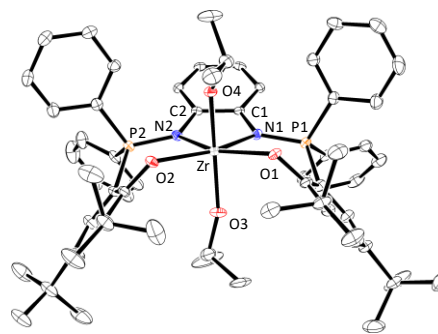
longer Zr–O'Pr distances (by ca 0.05 Å).<sup>6d,6f</sup> The solid state structure of **3b** shows the complex in a distorted octahedral *trans* configuration with *cis* angles in the range 69.77(16)–125.61(15) Å (Figure 9). The phenylene linker is bent upward by 26.1(6)° and the two aryloxy rings tilted downward (by 51.8(2)° and 49.4(2)°) with respect to the mean coordination plane defined by O1, N1, N2 and O2. As a consequence, one of the two isopropoxy groups is sandwiched between the two aryloxy rings and short intramolecular CH/ $\pi$  interactions can be found. The Zr–O and Zr–N bond lengths are slightly longer by a value ranging from 0.051(4) to 0.073(5) Å than those in complex **2a**, also in *trans* configuration. P–N bonds are slightly elongated (0.022(5) Å to 0.035(5) Å) compared to those in **1bH<sub>2</sub>**.

Considering that the Zr atom in these phosphasalen complexes is coordinatively saturated, which may limit the reactivity, we envisaged alternative cationic complexes with an open

coordination site. We synthesized the cationic benzyl complexes **4a** and **4b** by addition of tris(pentafluorophenyl)borane to the dibenzyl complexes **2a** and **2b** (scheme 6). NMR and EA analysis confirmed the formation of the cations as a single product. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **4a** shows one signal at  $\delta = 38.2$  ppm downfield shifted with respect to its neutral counterpart. The <sup>1</sup>H NMR spectrum displays two <sup>t</sup>Bu peaks at  $\delta = 1.10$  and 1.57 ppm, and two signals integrating each for two protons for the benzyl groups on zirconium and boron ( $\delta = 2.02$  and 2.78 ppm, respectively). The ethylene spacer protons appear as a poorly resolved multiplet which simplifies to a signal corresponding to an AA'BB' system upon <sup>31</sup>P decoupling of the spectrum. All these



**Scheme 6**



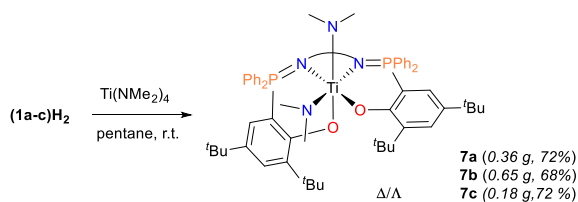
**Figure 9** ORTEP view of complex **3b** (For the sake of clarity, H atoms as well as disorder and solvent molecules are not shown). Selected distances (Å) and angles (deg): N1–P1 1.608(5), N1–Zr 2.276(5), N2–P2 1.614(5), N2–Zr 2.269(4), O1–Zr 2.125(4), O2–Zr 2.109(4), O3–Zr 1.956(4), O4–Zr 1.979(4), N1–Zr–N2 69.77(16), O1–Zr–O2 125.61(15), O3–Zr–O4 164.94(18).

observations are consistent with a  $C_s$ -symmetry in solution for **4a**. Complex **4b** showed similar NMR patterns. Cationic alkoxyde complexes **5a–5b** and **6a–6b** were next synthesized *via* an alcoholysis route using either one equivalent of isopropanol or one equivalent of (*S*)-methyl-lactate. NMR characterization revealed that **5a**, **6a** and **6b** have formed as a single product whereas **5b** was contaminated by 15% of an impurity, which was identified as an isopropanol adduct **5b**·iPrOH (Fig. S94–S96, SI). The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of **5a** displays one signal at  $\delta = 37.0$  ppm reasonably downfield shifted with respect to those of **3a**. The <sup>1</sup>H NMR spectrum is comparable to that of **4a** with the signals corresponding to the isopropoxy group replacing those of the benzyl group. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of **6a** and **6b** are similar showing only two sharp singlets ( $\nu_{1/2} \approx 3$  Hz) of equal intensity at  $\delta = 35.7/35.5$  ppm and 33.1/31.6 ppm, respectively. The complexes **6a** and **6b** exhibit only two CH<sub>3</sub> resonances for

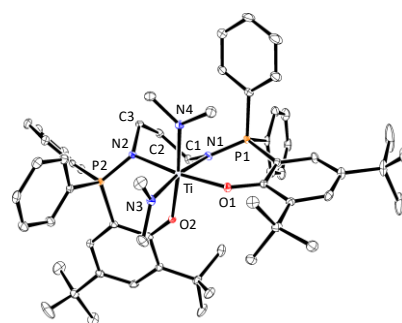
the methyl and methoxy groups of the lactate confirming the presence of only one species in solution. With regards to the geometry of the complexes, if the lactate were in  $\kappa^2$ -coordination mode, phosphasalen ligands would be necessary in *cis*- $\alpha$  or *cis*- $\beta$  wrapping. This would imply that complexes **6a** and **6b** are formed as a single diastereoisomer (out of six possible!). Considering that *cis*- $\beta$  wrapping creates highly asymmetric complexes, it should be reflected in NMR observables, which is not the case. For example, the  $^{13}\text{C}$  NMR spectrum of **6a** shows for the ethylene spacer a set of signals with reasonable shape symmetry composed of two doublets of doublets at  $\delta = 52.1$  and  $51.9$  ppm, respectively, with similar  $^{13}\text{C}$ - $^{31}\text{P}$  coupling constant values ( $^3J_{\text{CP}} = 12.8/11.8$  Hz,  $^2J_{\text{CP}} = 3.9/4.0$  Hz). On the other hand, the ethylene spacer in **3a** (*cis*- $\beta$  isomer) gives signals with different multiplicity and more distinct chemical shifts  $\{\delta$  (ppm) =  $52.9$  (d,  $^2J_{\text{PC}} = 3.3$  Hz),  $50.1$  (dd,  $^3J_{\text{PC}} = 18.2$  Hz,  $^2J_{\text{PC}} = 4.7$  Hz)}. Additionally, the  $^1\text{H}$  NMR spectrum of **6a** shows two multiplets at  $\delta = 3.48$  and  $3.09$  ppm for the ethylene bridge whereas four well-distinct signals are observed in the case of **3a** ( $\delta = 3.90, 2.80, 2.68, 2.55$  ppm). On the other hand, a *cis*- $\alpha$  wrapping mode would lead to a pseudo  $C_2$ -symmetric complex but would require considerable distortion of the phosphasalen skeleton, which is also unlikely, especially for **6b**. It therefore rather suggests that **6a** and **6b** are five coordinated complexes with methyl-lactate in a  $\kappa^1$ -coordination mode. Conversely, a downfield shift in  $^{13}\text{C}$  NMR of the carbonyl carbon of the lactate ligand in complexes **6a** ( $\delta = 192.9$  ppm) and **6b** ( $\delta = 192.8$  ppm) with respect to methyl lactate ( $\delta = 176.1$  ppm) is indicative of a coordination of the carbonyl to the Zr centre.<sup>16</sup> This apparent inconsistency could be explained i) either by a hemilabile behavior of the lactate ligand in solution, giving rise to a fast equilibrium between a five- and six- coordinate metal centre as previously described for salen methyl lactate Al complexes;<sup>17</sup> or ii) by an alternative coordination mode (*i.e.* not derived from *cis*- $\alpha$ , *cis*- $\beta$  or *trans* geometries) displaying a pseudo  $C_2$  symmetry.

#### Synthesis and characterization of the phosphasalen Ti complexes

The ability of phosphasalen ligand to form Zr(IV) complexes being demonstrated we next turned our attention toward Ti. To



Scheme 7



**Figure 10** ORTEP view of complex **7c** (hydrogen atoms are omitted for clarity). Selected distances (Å) and angles (deg): Ti–N1 2.247(2), Ti–N2 2.126(2), Ti–O1 1.9414(17), Ti–O2 2.0260(16), Ti–N3 1.951(2), Ti–N4 1.980(2), O1–Ti–O2 93.83(7), N1–Ti–N2 83.38(7), N3–Ti–N4 94.91(9).

avoid the delicate and tedious synthesis of  $Ti(CH_2Ph)_4$ , we used instead  $Ti(NMe_2)_4$  also *a priori* suitable for undergoing protonolysis reaction with the phosphasalen proligands **(1a-1c)H<sub>2</sub>**. The targeted bis(dimethylamido) phosphasalen Ti complexes **7a-c** were obtained as a single product in 68-72% yields (Scheme 7). Complexes **7a-c** are not fluxional in solution on the NMR-time scale. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of complexes **7a-c** recorded at 300 K show a set of two sharp peaks ( $\Delta\nu_{1/2} < 6$  Hz) at  $\delta = 32.0/26.1, 27.0/17.9$  and  $34.4/30.3$  ppm, respectively. The  $^1\text{H}$  NMR spectra of **7a-c** display four signals for the  $^t\text{Bu}$  groups and two signals for the  $\text{NMe}_2$  ligands in the aliphatic region. It therefore appears that all three phosphasalen ligands wrap the metal in a *cis*- $\beta$  fashion and that they are locked in solution. Single crystal diffraction analysis confirmed that complex **7c** adopts a *cis*- $\beta$  geometry (Figure 10). Complex **7c** displays a pseudo-octahedral geometry with *cis* arrangement of the  $\text{NMe}_2$  ligands ( $N3\text{-Ti-N4} = 94.91^\circ(9)$ ). The Ti–N1 bond *trans* to the  $\text{NMe}_2$  ligand is longer than Ti–N2 bond *trans* to the aryloxy ligand (by  $0.121(3)$  Å) and, to a lesser extent, the P1–N1 bond is shorter than the P2–N2 bond (by  $0.017(3)$  Å).

#### ROP of Lactide

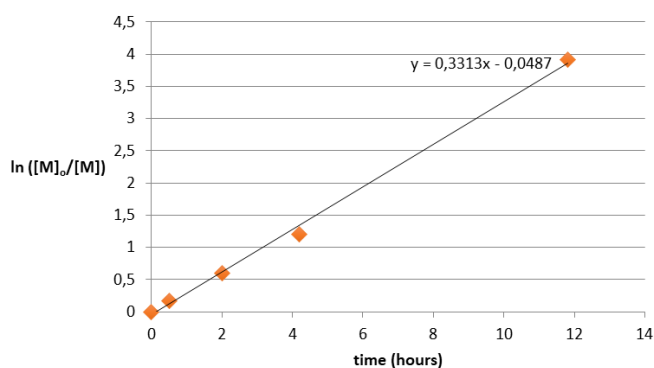
The phosphasalen Ti and Zr complexes **2a-7a** and **2b-4b** were tested as ROP initiators of *rac*-lactide. The results are compiled in Table 1. Both neutral Zr(IV) dibenzyl complexes **2a** and **2b** showed poor activity ( $90^\circ\text{C}$ , toluene), though the ethylene-bridged complex **2a** led to PLA with higher molecular weight and better conversion after a shorter reaction time (entries 1-2). Likewise, the Ti diamido complex **6a** also exhibited poor activity (entry 5). Performing lactide ROP using **2a-2b** in the presence of an alcohol source ( $^t\text{PrOH}$ , 1 equiv) for *in situ* generation of a  $\text{M-O}^i\text{Pr}$  species led to ill-defined and broadly disperse materials. Both neutral diisopropoxy Zr complexes **3a** and **3b** promote ROP of lactide in toluene at  $90^\circ\text{C}$  to give oligomers with low conversions, as deduced from GPC and NMR data (entries 3-4). Comparison with literature values shows that the neutral phosphasalen Zr complexes display much lower ROP performances, whether regarding activity and ROP control, compared to the best systems described by Jones and Kol based on salalen ligands and the titanium-salen complexes reported by Gibson and Long.<sup>5a,6</sup> This is likely due steric and electronic factors: *i*) the severe steric bulk of phosphasalen ligand certainly prevents effective lactide coordination/activation and thus

subsequent ring-opening; *ii*) the strong electron-donating properties of the phosphasalen ligand may drastically quench the Lewis acidity of the metal center. With this in mind, we set out using coordinatively unsaturated cationic Zr(IV) benzyl/alkoxide complexes **4a-b**, **5a** and **6a-b** as lactide ROP initiators. The use of discrete cationic metal complexes for promoting ROP of cyclic esters to enhance the electrophilicity of the metal and its reactivity is a well-established approach but remains little explored with group 4 metal complexes.<sup>18</sup> Initial ROP tests using Zr–Bn<sup>+</sup> cations **4a** and **4b** as initiators showed that the ethylene-bridged cation **4a** efficiently polymerize lactide in toluene solution (86% conv. within 6 h, toluene, 90 °C), yet to afford ill-defined PLA material (GPC data with a bimodal distribution). The phenylene-bridged complex **4b** is a less active ROP catalyst than **4a** (entries 6-7, Table 1), indicating that the flexibility of the metal-chelate is beneficial to ROP activity.<sup>19</sup> However, under bulk polymerization reactions (130 °C, neat lactide; entries 9-10, table 1), the more thermally robust phenylene-bridged **4b** allowed the production of well-defined PLA according to GPC data.

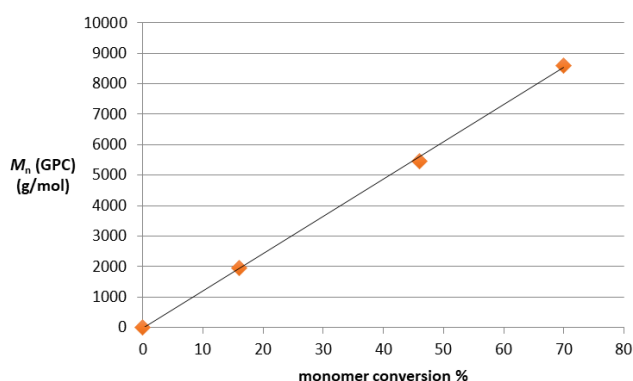
**Table 1** ROP of lactide mediated by phosphasalen Ti and Zr complexes<sup>a</sup>

Entry	Cat.	t (h)	Conv. (%) <sup>b</sup>	$M_{n, exp}^c$ (g mol <sup>-1</sup> )	$M_{n, theo}^d$ (g mol <sup>-1</sup> )	$\mathcal{D}^e$
1	<b>2a</b>	6	34	2835	4900	1.34
2	<b>2b</b>	24	10	425	1441	1.03
3	<b>3a</b>	24	22	430	3171	1.11
4	<b>3b</b>	24	15	505	2162	1.11
5	<b>7a</b>	24	35	578	5045	1.35
6	<b>4a</b>	6	86	13370 <sup>f</sup>	12395	--
7	<b>4b</b>	24	60	5150 <sup>f</sup>	8648	--
8 <sup>g</sup>	<b>2a</b>	4	76	700	10960	--
9 <sup>g</sup>	<b>4a</b>	1	78	27460 <sup>f</sup>	11250	--
10 <sup>g</sup>	<b>4b</b>	4	92	16060	13260	1.42
11 <sup>i</sup>	<b>5a</b>	14	98	12000	14130	1.10
12 <sup>h</sup>	<b>5a</b>	15	93	9840	13404	1.20
13 <sup>i</sup>	<b>6a</b>	14	99	11000	14250	1.07
14 <sup>h</sup>	<b>6b</b>	15	32	5820	4610	1.09

<sup>a</sup> Polymerization conditions:  $[rac-LA]_0 = 1$  M, 100 equiv of *rac*-LA, 1 equiv of metal catalyst, toluene, 90 °C. <sup>b</sup> Monomer conversion. <sup>c</sup> Measured by GPC in THF (30 °C) using PS standards and corrected by applying the appropriate correcting factor (0.58). <sup>d</sup> Calculated using  $M_{n, theo} = [rac-LA]_0/[catalyst]_0 \times M_{LA} \times conversion$ . <sup>e</sup> Measured by GPC in THF (30 °C). <sup>f</sup> bimodal distribution. <sup>g</sup> Bulk polymerisation conditions (100 equiv of *rac*-LA, 130 °C). <sup>h</sup> Reaction performed at 70 °C. <sup>i</sup> Reaction duration not optimized.



**Figure 11.** Plot of  $\ln([M]_0/[M])$  versus time for the ROP of *rac*-lactide mediated by initiator **5a** ( $M = \text{monomer}$ ). Conditions:  $[M]_0 = 1$  M,  $[M]_0/[5a]_0 = 100$ , toluene, 90 °C.



**Figure 12.** Plot of  $M_n$  (GPC) of PLA versus monomer conversion for the ROP of *rac*-lactide mediated by initiator **5a**. Conditions:  $[M]_0 = 1$  M,  $[M]_0/[5a]_0 = 100$ , toluene, 90 °C.

The ROP tests with cations **4a** and **4b** (toluene, 90 °C) in the presence of *i*PrOH (1 equiv), for *in situ* generation of **5a** and **5b**, only led to the formation of oligomers. Satisfyingly, well-defined cationic Zr–O<sup>*i*</sup>Pr and Zr–lactate complexes **5a** and **6a-b** turned out to be more active and well-behaved lactide ROP catalysts (entries 11-14, Table 1). Thus, in toluene (70 or 90 °C), the Zr–O<sup>*i*</sup>Pr<sup>+</sup> cation **5a** mediated the ROP of *rac*-lactide (100 equiv) to quantitatively afford chain-length controlled and narrow disperse PLA, as deduced from GPC and <sup>1</sup>H NMR data. Kinetic data and PLA characterization agree with a well-behaved ROP process proceeding through a coordination-insertion mechanism. These data include: *i*) an observed pseudo-first order in monomer (Figure 11), *ii*) a linear correlation between the PLA  $M_n$  values and monomer conversion as the ROP proceeds (Figure 12) and *iii*) MALDI-TOF MS data for PLA in line with GPC-estimated values, consistent with the presence an O<sup>*i*</sup>Pr group at the ester end and marginal transesterifications during the ROP (Fig. S145-S147, SI). Thus, due to a more electrophilic metal and a less sterically hindered metal centre, the ROP activity of cation **5a** is far superior to those of its neutral di-alkoxide counterpart **3a**. It gets close to the performances of the best salen, salalen and salan group IV metal complexes but does not compare with other phosphasalen pentacoordinate yttrium and indium catalysts.<sup>6,8</sup> In regards to the stereoselectivity of the ROP of *rac*-LA, it should be noted that cation **5a** produced PLA moderately heterotactic ( $P_r = 0.63$  for the ROP test conducted at 90 °C). With a similar activity to that of **5a**, the ethylene-bridged Zr–(*S*)-Me-lactate cation **6a** also efficiently catalyzed the controlled ROP of *rac*-LA with the production of narrow disperse and heterotactic-enriched PLA ( $P_r = 0.71$ ), as deduced from GPC and NMR analysis (Fig. S149-S150, SI). The phenylene-bridged **6b** is much less active than **5a/6a** in lactide ROP (entry 14 vs 12-13, Table 1), further reflecting the importance of a flexible ligand backbone for optimal ROP performances in these systems. The MALDI-TOF MS data of isolated PLA (from lactide ROP with **6b**) confirmed the presence of a Me-lactate moiety at the ester end of PLA and little transesterification reactions during the ROP process (Fig.



S153, SI). This results implies a metal-controlled coordination-insertion mechanism, distinct from the cationic zirconocene-catalyzed ROP of lactones that operates via an activated chain end mechanism (and through which the reactive site is moving away from the metal ion).<sup>18</sup>

## Conclusions

Given the analogy between phosphasalen and salen, salalen or salan ligands and the efficacy of the latter with group IV metal ions in ROP of lactide, we set out to study the coordination chemistry of phosphasalen ligands toward Ti and Zr metal ions and to assess their performance in ROP catalysis. Phosphasalen have been found to be particularly suitable ligands for Ti and Zr ions giving rise to a variety of complexes. X-Ray diffraction studies coupled with NMR studies showed that phosphasalen can wrap the early metal ions in *trans* or *cis*- $\beta$  geometry. These results highlight the superior ability of phosphasalen to withstand geometrical deformation compared to salen and to create out-of-plane coordination of the metal. Most importantly, a series of discrete mononuclear cationic phosphasalen Zr complexes has been isolated and characterized. Advantage was thus taken from the strong electron donating properties of phosphasalen ligand for stabilizing cationic coordinatively unsaturated Zr species. With respect to lactide polymerization activity, the neutral phosphasalen Ti and Zr complexes were found poorly active in lactide ROP catalysis, which can be attributed to the encumbered and electron donating nature of the phosphasalen ligand. On the other hand, a much superior ROP activity was achieved with cationic Zr alkoxy complexes affording heterotactic-enriched PLA with controlled molecular weight and narrow polydispersities. To the best of our knowledge, this is the first example of a stereocontrolled ROP of lactide with a cationic group IV metal complex. The ROP process was shown to proceed through a coordination-insertion mechanism, which authorizes further development of the phosphasalen platform for the identification of robust and stereoselective cationic group IV metal catalysts for the ROP of cyclic esters.

## Experimental section

### Reagents and conditions

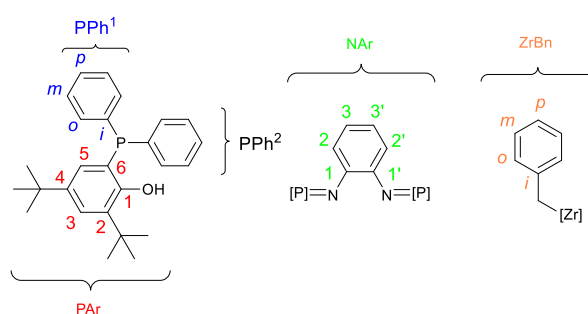
All reactions were carried out under Ar using conventional Schlenk techniques or in an Ar glovebox. Toluene, CH<sub>2</sub>Cl<sub>2</sub>, Et<sub>2</sub>O, pentane and THF were dried using an MBraun MB SPS-800 solvent purification system. Bromobenzene was distilled over CaH<sub>2</sub> and stored over activated 3 Å molecular sieves in the glovebox. Deuterated solvents were dried by passage through a short column of activated neutral alumina (Brockman grade II) and stored over activated 3 Å molecular sieves in the glovebox, either at room temperature (C<sub>6</sub>D<sub>6</sub>, C<sub>6</sub>D<sub>5</sub>Br...) or at -18 °C (d<sub>8</sub>-THF, CD<sub>2</sub>Cl<sub>2</sub>...). Alumina and molecular sieves were activated by heating for at least 6 hours above 230 °C under vacuum. Diatomaceous earth (dicalite) was dried in an oven at 110 °C. Compound Zr(CH<sub>2</sub>Ph)<sub>4</sub> was prepared according to literature

procedures.<sup>20</sup> All other reagents were commercially available and used as received.

### Analyses

The identity and purity of the compounds were established using elemental analysis, high-resolution mass spectrometry (ESI-MS), X-ray diffraction analysis, cyclic voltammetry, NMR, EPR and UV-vis spectroscopies. Some elemental analyses were performed by Mr. Stephen Boyer (London Metropolitan University). All other analyses were performed using analytical equipment of the Plateforme d'Analyse de l'Institut de Chimie Moléculaire de l'Université de Bourgogne (Ms Marie-José Penouilh-Suzette: ESI-MS; Mr Marcel Soustelle: elemental analyses). NMR spectra (<sup>1</sup>H, <sup>11</sup>B, <sup>13</sup>C, <sup>19</sup>F, <sup>31</sup>P) were recorded on Bruker AV500 and AV600 spectrometers. NMR spectroscopy chemical shifts are quoted in parts per million ( $\delta$ ) relative to TMS (for <sup>1</sup>H and <sup>13</sup>C), BF<sub>3</sub>·Et<sub>2</sub>O (for <sup>11</sup>B and <sup>19</sup>F) or H<sub>3</sub>PO<sub>4</sub> (for <sup>31</sup>P). For <sup>1</sup>H and <sup>13</sup>C spectra, values were determined by using solvent residual signals (e.g. CDHCl<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub>) as internal standards.<sup>21</sup> The <sup>31</sup>P, <sup>19</sup>F and <sup>11</sup>B NMR spectra were referenced according to IUPAC recommendations (Absolute referencing).

Ring nomenclature: the positions of carbon and hydrogen atoms in the aromatic rings were labelled according to the following Figure. Where applicable, the phenyl rings of the diphenylphosphino moiety are differentiated in chiral compounds (PPh<sup>1</sup>, PPh<sup>2</sup>).



The number-average, weight-average molar masses ( $M_n$  and  $M_w$ , respectively) and molar mass distribution ( $M_w/M_n$ ) of PLA samples were determined by gel permeation chromatography (GPC) at 30 °C with Shimadzu LC20AD ultra-fast liquid chromatography equipped with a Shimadzu RID10A refractometer detector. Tetrahydrofuran (THF) was used as the eluent and the flow rate was set up at 1.0 mL/min. A Varian PLGel pre-column and a Varian PLGel 5  $\mu$ m were used. Calibrations were performed using polystyrene standards (400-100000 g/mol) and raw values of  $M_n$  values ( $M_{n,GPC}$ ) were thus obtained. Mass spectra were acquired on a time-of-flight mass spectrometer (MALDI-TOF-TOF-Autoflex II TOF-TOF, Bruker Daltonics, Bremen, Germany) equipped with a nitrogen laser ( $\lambda = 337$  nm) at the « Service de Spectrométrie de Masse de l'Institut de Chimie de Strasbourg » and run in a positive mode. An external multi-point calibration was carried out before each measurement using the singly charged peaks of a standard peptide mixture (0.4  $\mu$ m in water acidified with FlewAnalysis 3.0 software).  $\alpha$ -cyano-4-hydroxy-cinnamic acid (CHCA) was obtained from Sigma (St Louis, MO, USA) and 1,8, 9-anthracenetriol (dithranol) from Alfa Aesar (Karlsruhe,

Germany). Matrix solutions were freshly prepared: CHCA was dissolved to saturation in H<sub>2</sub>O, CH<sub>3</sub>CN, HCOOH (50/50.1%) solution and dithranol to saturation in THF. Typically, a 1/1 mixture of the sample solution in CH<sub>2</sub>Cl<sub>2</sub> was mixed with the matrix solution and 0.5 μL of the resulting mixture was deposited on the stainless plate.

#### X-ray diffraction analyses

Crystals of all compound were selected and mounted on a mylar loop with oil on a 'Bruker APEX-II CCD' or a 'Bruker D8 venture Photon 100' diffractometer. Crystal were kept at 115 K or 100 K during data collection. Using Olex2,<sup>22</sup> the structures were solved with the ShelXT<sup>23</sup> structure solution program using Direct Methods and refined with the XL<sup>24</sup> refinement package using Least Squares minimization. More details about crystals, data collections and refinements can be found in the Supporting Information and in the Crystallographic Information Files in which are included .res and .hkl files.

#### Synthesis of compounds

For the syntheses of the proligands (**1a-c**)H<sub>2</sub> not included here, see the Supporting Information.

#### Synthesis of complex 2a

Ligand **1aH<sub>2</sub>** (1.155 g, 1.38 mmol) and tetrabenzylzirconium (0.630 g, 1.38 mmol) were dissolved in toluene (15 mL) and stirred for 10 min. The volatiles were removed under vacuum, and the residue was suspended in hexane (10 mL). The resulting solid was filtered and washed with hexane (4 x 2 mL) to give **2a** as a yellow powder (1.263 g, 80%). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 36.5 (v<sub>1/2</sub> ≈ 4 Hz). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 7.82 (d, 2H, <sup>4</sup>J<sub>HH</sub> = 2.10 Hz, H<sub>3</sub> of PAr), 7.30-7.22 (m, 8H, o of PPh<sub>2</sub>), 7.12-7.07 (m, 12H, overlapping m and p of PPh<sub>2</sub>), 6.74 (m, 4H, m of ZrBn), 6.65 (dd, <sup>3</sup>J<sub>PH</sub> = 16.0 Hz, <sup>4</sup>J<sub>HH</sub> = 2.1 Hz, 2H, H<sub>5</sub> of PAr), 6.56 (m, 2H, p of ZrBn), 6.13 (m, 4H, o of ZrBn), 3.15 (m, 4H, NCH<sub>2</sub>), 2.36 (s, 4H, CH<sub>2</sub> of ZrBn), 1.96 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 1.13 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K): δ = 166.5 (d, <sup>2</sup>J<sub>PC</sub> = 2.2 Hz, C1 of PAr), 155.9 (s, i of ZrBn), 138.9 (d, <sup>3</sup>J<sub>CP</sub> = 7.2 Hz, C2 of PAr), 138.4 (d, <sup>3</sup>J<sub>CP</sub> = 15.4 Hz, C4 of PAr), 133.8 (d, <sup>2</sup>J<sub>CP</sub> = 9.9 Hz, o of PPh<sub>2</sub>), 132.3 (s, p of PPh<sub>2</sub>), 129.8 (s, C3 of PAr), 129.1 (d, <sup>3</sup>J<sub>CP</sub> = 12.1 Hz, m of PPh<sub>2</sub>), 129.0 (d, <sup>1</sup>J<sub>CP</sub> = 115.9 Hz, i of PPh<sub>2</sub>), 127.7 (d, <sup>2</sup>J<sub>CP</sub> = 14.9 Hz, C5 of PAr), 127.5 (s, m of ZrBn), 125.5 (s, o of ZrBn), 116.7 (s, p of ZrBn), 108.2 (d, <sup>1</sup>J<sub>CP</sub> = 130.0 Hz, C6 of PAr), 59.8 (s, CH<sub>2</sub> of ZrBn), 51.9 (dd, <sup>3</sup>J<sub>CP</sub> = 17.6 Hz, <sup>2</sup>J<sub>CP</sub> = 3.8 Hz, NCH<sub>2</sub>), 36.2 (s, C of <sup>t</sup>Bu<sup>2</sup>), 34.3 (s, C of <sup>t</sup>Bu<sup>4</sup>), 31.6 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 30.9 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>). Elemental Analysis: calculated for C<sub>68</sub>H<sub>78</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Zr: C, 73.68; H, 7.09; N, 2.53. Found: C, 73.17; H, 7.34; N, 2.20.

#### Synthesis of complex 2b

Ligand **1bH<sub>2</sub>** (1.770 g, 2.00 mmol) and tetrabenzylzirconium (0.912 g, 2.00 mmol) were dissolved in dichloromethane (50 mL) then stirred at room temperature for 3h30, during which a yellow precipitate appeared. The suspension was filtered, and the solid was washed with dichloromethane (3x5 mL) and dried under vacuum to give complex **2b** containing 1.2 eq of CH<sub>2</sub>Cl<sub>2</sub>

(1.999 g, 80 %). The mixture of isomers was characterized by multinuclear NMR in d<sub>8</sub>-THF at 210 K on a 500 MHz, spectrometer. Under these conditions, the *cis*-β<sup>A</sup> / *cis*-β<sup>A</sup> isomerisation was frozen. Some signals in the aromatic regions of <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra could not be assigned, in which case they are labelled as CH-Ar or CH-Ar. <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, d<sub>8</sub>-THF, 210 K): δ = 30.5 (s, v<sub>1/2</sub> ≈ 3 Hz, P(β)), 29.2 (s, v<sub>1/2</sub> ≈ 4 Hz, P(T)), 28.0 (s, v<sub>1/2</sub> ≈ 5 Hz, P(β)). <sup>1</sup>H NMR (600 MHz, d<sub>8</sub>-THF 210 K): δ = 7.83 (m, 1H, CH-Ar), 7.75-7.63 (m, CH-Ar), 7.63-7.51 (m, CH-Ar overlapping with H<sub>3</sub> of PAr(T)), 7.51-7.43 (m, 1H + 8H, H<sub>3</sub> of PAr(β) overlapping with o of PAr(T)), 7.31 (s, 1H, H<sub>3</sub> of PAr(β)), 7.23 (m, CH-Ar), 7.08 (d, 1H, <sup>3</sup>J<sub>PH</sub> = 15.6 Hz, H<sub>5</sub> of PAr(β)), 6.75 (m, 2H, m of ZrBn(β)), 6.72-6.65 (m, CH-Ar overlapping with H<sub>5</sub> of PAr(β)), 6.65 (d, 1H, <sup>3</sup>J<sub>PH</sub> = 15.0 Hz, H<sub>5</sub> of PAr(β) overlapping with CH-Ar), 6.56-6.38 (m, CH-Ar overlapping with m of ZrBn(T), m of ZrBn(β), H<sub>2</sub> of NAr(T) and p of ZrBn(β)), 6.52 (m, 4H, m of ZrBn(T)), 6.46 (m, 2H, m of ZrBn(β)), 6.40 (m, 1H, p of ZrBn(β)), 6.35 (d, <sup>3</sup>J<sub>PH</sub> = 15.7 Hz, H<sub>5</sub> of PAr(T)), 6.31 (m, 2H, p of ZrBn(T)), 6.22 (t, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, H<sub>3</sub> of NAr(β) overlapping with p of ZrBn(β)), 6.18 (m, 1H, p of ZrBn(β) overlapping with two H<sub>3</sub> of NAr(β), H<sub>2</sub> of NAr(β) and H<sub>3</sub> of NAr(T)), 6.18-6.10 (m, 2+1 H, H<sub>3</sub> of NAr(β), H<sub>2</sub> of NAr(β) and H<sub>3</sub> of NAr(T) overlapping with p of ZrBn(β)), 6.01 (m, 4H, o of ZrBn(T)), 5.77 (d, <sup>3</sup>J<sub>HH</sub> = 8.0 Hz, 1H, H<sub>2</sub> of NAr(β)), 2.37 (d, <sup>2</sup>J<sub>HH</sub> = 10.1 Hz, 1H, CH<sub>2</sub> of ZrBn(β)), 2.09 (d, <sup>2</sup>J<sub>HH</sub> = 8.3 Hz, 1H, CH<sub>2</sub> of ZrBn(β)), 1.79 (d, <sup>2</sup>J<sub>HH</sub> = 10.1 Hz, 1H, CH<sub>2</sub> of ZrBn(β)), 1.74 (s, 4H, CH<sub>2</sub> of ZrBn(T)), 1.67 (d, <sup>2</sup>J<sub>HH</sub> = 8.3 Hz, 1H, CH<sub>2</sub> of ZrBn(β)), 1.42 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(β)), 1.27 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(T)), 1.18 (two s, 18H, two overlapping CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>(β)), 1.13 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>(T)), 0.52 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(β)). <sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz, d<sub>8</sub>-THF, 210 K): δ = 166.7 (s, C1 of PAr(T)), 165.6 (s, C1 of PAr(β)), 163.0 (s, C1 of PAr(β)), 154.7 (s, i of ZrBn(T)), 154.5 (s, i of ZrBn(β)), 153.2 (s, i of ZrBn(β)), 145.1 (dd, <sup>3</sup>J<sub>PC</sub> = 13.0 Hz, <sup>2</sup>J<sub>PC</sub> = 2.1 Hz, C1 of NAr(β)), 144.9 (dd, <sup>3</sup>J<sub>PC</sub> = 14.3 Hz, <sup>2</sup>J<sub>PC</sub> = 2.8 Hz, C1 of NAr(β)), 142.3 (dd, <sup>3</sup>J<sub>PC</sub> = 17.7 Hz, <sup>2</sup>J<sub>PC</sub> = 2.7 Hz, C1 of NAr(T)), 139.9 (d, <sup>3</sup>J<sub>PC</sub> = 15.1 Hz, C4 of PAr(β) overlapping with C2 of PAr(β)), 139.8 (d, <sup>3</sup>J<sub>PC</sub> = 7.2 Hz, C2 of PAr(β) overlapping with C4 of PAr(β)), 138.7 (d, <sup>3</sup>J<sub>PC</sub> = 6.1 Hz, C2 of PAr(β) overlapping with C4 of PAr(β)), 138.7 (d, <sup>3</sup>J<sub>PC</sub> = 13.1 Hz, C4 of PAr(β) overlapping with C2 of PAr(β)), 138.2 (d, <sup>3</sup>J<sub>PC</sub> = 15.4 Hz, C4 of PAr(T)), 138.0 (d, <sup>3</sup>J<sub>PC</sub> = 6.7 Hz, C2 of PAr(T)), 135.5 (d, <sup>2</sup>J<sub>PC</sub> = 10.4 Hz, o of PPh<sub>2</sub>(β)), 135.0 (d, <sup>2</sup>J<sub>PC</sub> = 8.8 Hz, o of PPh<sub>2</sub>(β)), 134.5 (m, p of PPh<sub>2</sub>(β)), 134.5 (s, CH-Ar), 134.0 (d, <sup>2</sup>J<sub>PC</sub> = 9.9 Hz, o of PPh<sub>2</sub>(T) overlapping with CH-Ar), 133.9 (s, CH-Ar overlapping with o of PPh<sub>2</sub>(T) and CH-Ar), 133.8 (s, CH-Ar overlapping with CH-Ar), 133.5 (s, CH-Ar), 132.9 (d, <sup>2</sup>J<sub>PC</sub> = 10.0 Hz, o of PPh<sub>2</sub>(β)), 132.2 (s, CH-Ar), 131.7 (d, <sup>1</sup>J<sub>PC</sub> = 89.6 Hz, i of PPh<sub>2</sub>(β)), 130.6 (s, C3 of PAr(T)), 130.4 (s, CH-Ar overlapping with CH-Ar), 130.3 (s, CH-Ar overlapping with CH-Ar and i of PPh<sub>2</sub>(β)), 130.3-129.7 (m, several overlapping CH-Ar overlapping i of PPh<sub>2</sub>(β)), 129.9 (d, <sup>1</sup>J<sub>PC</sub> = 90.4 Hz, i of PPh<sub>2</sub>(β)), 129.2 (s, C3 of PAr(β)), 129.1-128.8 (m, overlapping CH-Ar), 128.4 (d, <sup>2</sup>J<sub>PC</sub> = 15.4 Hz, C5 of PAr(β) overlapping with i of PPh<sub>2</sub>(β)), 128.2 (d, <sup>1</sup>J<sub>PC</sub> = 89.8 Hz, i of PPh<sub>2</sub>(β) overlapping with C5 of PAr(β) and C5 of PAr(T)), 127.9 (d, <sup>2</sup>J<sub>PC</sub> = 12.9 Hz, C5 of PAr(T) overlapping with two i of PPh<sub>2</sub>(β)), 127.8 (d, <sup>1</sup>J<sub>PC</sub> = 72.4 Hz, i of PPh<sub>2</sub>(β) overlapping with C5 of PAr(T) and m of ZrBn(T)), 127.3 (s, m of ZrBn(T) overlapping with i of

PPh<sub>2</sub>(β) and *i* of PPh<sub>2</sub>(T)), 127.0 (s, *m* of ZrBn(β) overlapping with *i* of PPh<sub>2</sub>(T)), 126.9 (s, *m* of ZrBn(β) overlapping with *i* of PPh<sub>2</sub>(T)), 126.9 (d, <sup>1</sup>J<sub>PC</sub> = 92.6 Hz, *i* of PPh<sub>2</sub>(T) overlapping with two *m* of ZrBn(β)), 126.5 (s, *o* of ZrBn(β)), 125.8 (m, *o* of ZrBn(T) overlapping with *o* of ZrBn(β)), 124.4 (d, <sup>3</sup>J<sub>PC</sub> = 6.0 Hz, C2 of NAr(β)), 122.2 (d, <sup>3</sup>J<sub>PC</sub> = 3.3 Hz, C2 of NAr(β)), 121.1 (s, C3 of NAr(β)), 120.7 (d, <sup>3</sup>J<sub>PC</sub> = 10.2 Hz, C2 of NAr(T)), 120.6 (s, C3 of NAr(β)), 119.9 (s, C3 of NAr(T)), 118.1 (two overlapping s, *ρ* of ZrBn(β)), 117.5 (s, *ρ* of ZrBn(T)), 115.3 (d, <sup>1</sup>J<sub>PC</sub> = 120.4 Hz, C6 of PAr(T)), 112.9 (d, <sup>1</sup>J<sub>PC</sub> = 118.0 Hz, C6 of PAr(β)), 111.7 (d, <sup>1</sup>J<sub>PC</sub> = 110.7 Hz, C6 of PAr(β)), 68.2 (s, CH<sub>2</sub> of ZrBn(β)), 64.0 (s, CH<sub>2</sub> of ZrBn(T)), 62.6 (s, CH<sub>2</sub> of ZrBn(β)), 36.1 (s, C of <sup>t</sup>Bu<sup>2</sup>(β)), 35.9 (s, C of <sup>t</sup>Bu<sup>2</sup>(T)), 35.3 (s, C of <sup>t</sup>Bu<sup>2</sup>(β)), 34.8 (s, C of <sup>t</sup>Bu<sup>4</sup>(β)), 34.7 (s, C of <sup>t</sup>Bu<sup>4</sup>(β)), 34.6 (s, C of <sup>t</sup>Bu<sup>4</sup>(T)), 31.5 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>(T)), 31.4 (two overlapping s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>(β)), 30.6 (two overlapping s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(T) and CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(β)), 28.7 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(β)). **Elemental Analysis:** calculated for C<sub>72</sub>H<sub>78</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Zr: C, 74.77; H, 6.80; N, 2.42. Found: C, 69.03; H, 7.15; N, 2.59. A satisfactory elemental analysis could not be obtained (C was always too low).

### Synthesis of complex 2c

Ligand **1cH<sub>2</sub>** (172mg, 0.2 mmol) was suspended in Et<sub>2</sub>O (10ml) and tetrabenzylzirconium (0.182 g, 0.4 mmol) were added then stirred at room temperature for 4h, during which a yellow precipitate appeared. The suspension was filtered, and the solid was washed with Et<sub>2</sub>O (2x5 mL) and dried under vacuum to give complex **2c** containing 1 eq of Et<sub>2</sub>O (195 mg, 59%). **<sup>31</sup>P{<sup>1</sup>H} NMR (243MHz, CDCl<sub>3</sub>, 300 K):** δ = 30.8 (v<sub>1/2</sub> = 7 Hz). **<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 300 K):** δ = 7.71 (s, 2H, H3 of PAr), 7.35-7.29 (m, 4H, PPh<sub>2</sub>), 7.25-7.17 (m, 16H, PPh<sub>2</sub>), 6.95 (brt, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 12H, *m* of ZrBn), 6.76 (brd, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 12H, *o* of ZrBn), 6.72 (bd, <sup>3</sup>J<sub>PH</sub> = 13.1 Hz, 2H, H5 of PAr), 6.58 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 6H, *ρ* of ZrBn), 2.25 (dt, <sup>3</sup>J<sub>PH</sub> = 25.5, <sup>3</sup>J<sub>HH</sub> = 8.1, 4H, NCH<sub>2</sub>), 1.83 (s, 12H, CH<sub>2</sub> of ZrBn) 1.51 (s, 18H, <sup>t</sup>Bu<sup>2</sup>), 1.35 (bs, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 1.22 (s, 18H, <sup>t</sup>Bu<sup>4</sup>). **<sup>13</sup>C{<sup>1</sup>H} NMR (150.9 MHz, CDCl<sub>3</sub>, 300 K):** δ = 165.4 (s, C1 of PAr), 148.4 (s, Ci of ZrBn), 140.3 (d, <sup>3</sup>J<sub>CP</sub> = 12.2 Hz, C4 of PAr), 139.5 (d, <sup>3</sup>J<sub>CP</sub> = 5.9 Hz, C2 of PAr), 133.7 (s, *ρ* of PPh<sub>2</sub>), 133.4 (d, J<sub>CP</sub> = 9.8 Hz, *o*/*m* of PPh<sub>2</sub>), 130.7 (s, C3 of PAr), 129.6 (d, J<sub>CP</sub> = 12.1 Hz, *m*/*o* of PPh<sub>2</sub>), 129.0 (d, <sup>2</sup>J<sub>CP</sub> = 10.8 Hz, C5 of PAr), 128.3 (s, *m* of ZrBn), 126.6 (s, *o* of ZrBn), 125.2 (d, <sup>1</sup>J<sub>CP</sub> = 103.1 Hz, Ci of PPh<sub>2</sub>), 120.6 (s, *ρ* of ZrBn), 109.4 (d, <sup>1</sup>J<sub>CP</sub> = 100.1 Hz, C6 of PAr), 72.3 (s, CH<sub>2</sub> of ZrBn), 40.8 (d, <sup>3</sup>J<sub>CP</sub> = 4.3 Hz, NCH<sub>2</sub>), 35.4 (s, C of <sup>t</sup>Bu<sup>2</sup>), 34.4 (s, C of <sup>t</sup>Bu<sup>4</sup>), 33.7 (s, NCH<sub>2</sub>-CH<sub>2</sub>), 31.5 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 30.5 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>). **Elemental Analysis:** calculated for C<sub>97</sub>H<sub>108</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Zr<sub>2</sub>: C, 73.82; H, 6.90; N, 1.77. Found: C, 71.09; H, 7.19; N, 1.89. A satisfactory elemental analysis could not be obtained (C was always too low).

### Synthesis of complex 3a

Complex **2a** (340 mg, 0.3 mmol) and <sup>i</sup>PrOH (180 mg, 3.0 mmol) were mixed in 6 mL of CH<sub>2</sub>Cl<sub>2</sub>. The reaction mixture was stirred for 20 min, during which it turned gradually colourless. The volatiles were removed under vacuum, and the solid residue was triturated with pentane, then dried under vacuum, yielding **3a** as a white solid (88 mg, 28 %). The low yield is due to the solubility of **3a** in pentane. Alternatively, **3a** may be synthesized *via* the reaction of ligand **1aH<sub>2</sub>** with [Zr(NMe<sub>2</sub>)<sub>4</sub>] followed by alcoholysis with <sup>i</sup>PrOH. **<sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 250 K):**

δ = 32.7 (s, v<sub>1/2</sub> ≈ 5 Hz, P(T)), 31.6 (s, v<sub>1/2</sub> ≈ 5 Hz, P(β)), 29.6 (s, v<sub>1/2</sub> ≈ 5 Hz, P(β)). **<sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 250 K):** δ = 7.98 (m, 2H, *o* of PPh<sub>2</sub>(β)), 7.88 (m, 2H, *o* of PPh<sub>2</sub>(β)), 7.66-7.58 (m, CH-Ar), 7.58-7.32 (m, CH-Ar), 7.22 (m, 2H, *o* of PPh<sub>2</sub>(β)), 6.78 (dd, <sup>3</sup>J<sub>PH</sub> = 16.0 Hz, 1H, <sup>4</sup>J<sub>HH</sub> = 2.2 Hz, H5 of PAr(β)), 6.69 (dd, <sup>3</sup>J<sub>PH</sub> = 13.3 Hz, <sup>4</sup>J<sub>HH</sub> = 2.2 Hz, 1H, H5 of PAr(β)), 6.46 (dd, <sup>3</sup>J<sub>PH</sub> = 15.6 Hz, 1H, <sup>4</sup>J<sub>HH</sub> = 2.2 Hz, H5 of PAr(T)), 4.60 (hept, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, CH of <sup>i</sup>Pr(β)), 3.90 (m, 1H, CH<sub>2</sub>N(β)), 3.70 (hept, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 1H, CH of <sup>i</sup>Pr(T)), 3.23 (hept, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 1H, CH of <sup>i</sup>Pr(β)), 3.13 (m, 4H, CH<sub>2</sub>N(T)), 2.80 (m, 1H, CH<sub>2</sub>N(β)), 2.68 (m, 1H, CH<sub>2</sub>N(β)), 2.55 (m, 1H, CH<sub>2</sub>N(β)), 1.47 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(β)), 1.45 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(T)), 1.22 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 3H, CH<sub>3</sub> of <sup>i</sup>Pr(β)), 1.17 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(β) overlapping with CH<sub>3</sub> of <sup>i</sup>Pr(β)), 1.16 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 3H, CH<sub>3</sub> of <sup>i</sup>Pr(β) overlapping with CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(β)), 1.13 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>(β)), 1.08 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>(β)), 1.04 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>(T)), 0.64 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 3H, CH<sub>3</sub> of <sup>i</sup>Pr(β)), 0.54 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 3H, CH<sub>3</sub> of <sup>i</sup>Pr(β)), 0.51 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 12H, CH<sub>3</sub> of <sup>i</sup>Pr(T)). **<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 250 K):** δ = 168.3 (d, <sup>2</sup>J<sub>PC</sub> = 4.1 Hz, C1 of PAr(β)), 167.3 (d, <sup>2</sup>J<sub>PC</sub> = 1.9 Hz, C1 of PAr(T)), 164.5 (d, <sup>2</sup>J<sub>PC</sub> = 2.2 Hz, C1 of PAr(β)), 139.3 (d, <sup>3</sup>J<sub>PC</sub> = 6.9 Hz, C2 of PAr(β)), 139.0 (d, <sup>3</sup>J<sub>PC</sub> = 7.6 Hz, C2 of PAr(β)), 137.9 (d, <sup>3</sup>J<sub>PC</sub> = 7.6 Hz, C2 of PAr(T)), 137.0 (d, <sup>3</sup>J<sub>PC</sub> = 14.3 Hz, C4 of PAr(β)), 136.1 (d, <sup>3</sup>J<sub>PC</sub> = 14.9 Hz, C4 of PAr(T)), 134.0 (d, <sup>3</sup>J<sub>PC</sub> = 13.7 Hz, C4 of PAr(β) overlapping with *o* of PPh<sub>2</sub>(β)), 133.9 (d, <sup>2</sup>J<sub>PC</sub> = 9.0 Hz, *o* of PPh<sub>2</sub>(β) overlapping with C4 of PAr(β)), 133.6 (d, <sup>2</sup>J<sub>PC</sub> = 9.2 Hz, *o* of PPh<sub>2</sub>(β) overlapping with *o* of PPh<sub>2</sub>(β)), 133.5 (d, <sup>2</sup>J<sub>PC</sub> = 10.2 Hz, *o* of PPh<sub>2</sub>(β) overlapping with *o* of PPh<sub>2</sub>(β)), 133.4 (d, <sup>2</sup>J<sub>PC</sub> = 9.5 Hz, *o* of PPh<sub>2</sub>(T)), 133.1 (d, <sup>2</sup>J<sub>PC</sub> = 9.2 Hz, *o* of PPh<sub>2</sub>(β)), 132.1 (d, <sup>4</sup>J<sub>PC</sub> = 2.4 Hz, *ρ* of PPh<sub>2</sub>(β)), 132.0 (d, <sup>4</sup>J<sub>PC</sub> = 1.7 Hz, *ρ* of PPh<sub>2</sub>(β)), 131.8 (d, <sup>4</sup>J<sub>PC</sub> = 1.7 Hz, *ρ* of PPh<sub>2</sub>(T) overlapping with *i* of PAr(β)), 131.6 (d, <sup>1</sup>J<sub>PC</sub> = 89.5 Hz, *i* of PAr(β) overlapping with *ρ* of PPh<sub>2</sub>(T) and *ρ* of PPh<sub>2</sub>(β)), 131.5 (d, <sup>4</sup>J<sub>PC</sub> = 2.2 Hz, two *ρ* of PPh<sub>2</sub>(β) overlapping with *i* of PAr(β)), 130.3 (d, <sup>1</sup>J<sub>PC</sub> = 113.5 Hz, *i* of PAr(β) overlapping with *i* of PAr(β)), 130.0 (d, <sup>1</sup>J<sub>PC</sub> = 88.1 Hz, *i* of PAr(β) overlapping with *i* of PAr(β)), 129.2 (d, <sup>1</sup>J<sub>PC</sub> = 90.9 Hz, *i* of PAr(T)), 128.6-128.3 (m, overlapping CH-Ar), 128.3 (s, CH-Ar), 128.0 (s, C3 of PAr(β)), 127.6 (d, <sup>2</sup>J<sub>PC</sub> = 11.3 Hz, C5 of PAr(β)), 127.3 (d, <sup>2</sup>J<sub>PC</sub> = 12.8 Hz, C5 of PAr(β) overlapping with *i* of PAr(β)), 127.1 (d, <sup>1</sup>J<sub>PC</sub> = 87.9 Hz, *i* of PAr(β)), 126.4 (d, <sup>2</sup>J<sub>PC</sub> = 14.2 Hz, C5 of PAr(T)), 112.1 (d, <sup>1</sup>J<sub>PC</sub> = 122.0 Hz, C6 of PAr(T)), 109.8 (d, <sup>1</sup>J<sub>PC</sub> = 102.1 Hz, C6 of PAr(β)), 108.7 (d, <sup>1</sup>J<sub>PC</sub> = 117.4 Hz, C6 of PAr(β)), 69.4 (s, CH of <sup>i</sup>Pr(β)), 69.2 (s, CH of <sup>i</sup>Pr(β)), 67.6 (s, CH of <sup>i</sup>Pr(T)), 52.9 (d, <sup>2</sup>J<sub>PC</sub> = 3.3 Hz, CH<sub>2</sub>N(β)), 51.6 (dd, <sup>3</sup>J<sub>PC</sub> = 17.5 Hz, <sup>2</sup>J<sub>PC</sub> = 3.9 Hz, CH<sub>2</sub>N(T)), 50.1 (dd, <sup>3</sup>J<sub>PC</sub> = 18.2 Hz, <sup>2</sup>J<sub>PC</sub> = 4.7 Hz, CH<sub>2</sub>N(β)), 35.7 (d, <sup>4</sup>J<sub>PC</sub> = 1.4 Hz, C of <sup>t</sup>Bu<sup>2</sup>(β)), 35.5 (m, C of <sup>t</sup>Bu<sup>2</sup>(T)), 35.3 (d, <sup>4</sup>J<sub>PC</sub> = 1.5 Hz, C of <sup>t</sup>Bu<sup>2</sup>(β)), 34.0 (s, C of <sup>t</sup>Bu<sup>4</sup>(β)), 33.9 (s, C of <sup>t</sup>Bu<sup>4</sup>(β) overlapping with C of <sup>t</sup>Bu<sup>4</sup>(T)), 31.3 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>(β)), 31.2 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>(T)), 31.1 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>(β)), 29.7 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(β) overlapping with CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(T)), 29.4 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>(β)), 27.5 (s, CH<sub>3</sub> of <sup>i</sup>Pr(β)), 27.5 (s, CH<sub>3</sub> of <sup>i</sup>Pr(β)), 26.9 (s, CH<sub>3</sub> of <sup>i</sup>Pr(T)), 26.7 (s, CH<sub>3</sub> of <sup>i</sup>Pr(β)), 26.7 (s, CH<sub>3</sub> of <sup>i</sup>Pr(β)). **Elemental Analysis:** calculated for C<sub>60</sub>H<sub>78</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Zr: C, 69.00; H, 7.53; N, 2.68. Found: C, 67.32; H, 7.31; N, 2.62.

### Synthesis of complex 3b

Complex **2b** (0.588 g, 0.5 mmol) was suspended in dichloromethane (15 mL) then isopropanol (0.30 g, 5 mmol) was added and the solution was stirred for 3 hrs. The volatiles were removed under vacuum. The residue was suspended in pentane (5 mL), filtered and washed with pentane (3x5 mL), yielding **3b** as a white powder (0.418 g, 77%). **<sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, d<sub>8</sub>-THF, 250 K):**  $\delta$  = 26.8 (s,  $\nu_{1/2} \approx 3$  Hz, P( $\beta$ )), 24.3 (s,  $\nu_{1/2} \approx 3$  Hz, P(T)), 21.5 (s,  $\nu_{1/2} \approx 4$  Hz, P( $\beta$ )). **<sup>1</sup>H NMR (600 MHz, d<sub>8</sub>-THF, 250 K):**  $\delta$  = 8.01 (m, 2H, *o* of PPh<sub>2</sub>( $\beta$ )), 7.86-7.71 (m, CH-Ar overlapping with *o* of PPh<sub>2</sub>( $\beta$ )), 7.82 (m, 2H, *o* of PPh<sub>2</sub>(T) overlapping with CH-Ar), 7.71-7.55 (m, CH-Ar), 7.61 (m, 2H, *p* of PPh<sub>2</sub>(T)), 7.52-7.43 (m, CH-Ar overlapping with *p* of PPh<sub>2</sub>( $\beta$ )), 7.46 (m, 2H, *p* of PPh<sub>2</sub>( $\beta$ ) overlapping with CH-Ar), 7.40 (m, CH-Ar), 7.35 (d,  $^4J_{\text{HH}} = 1.8$  Hz, 1H, H3 of PAR( $\beta$ ) overlapping with CH-Ar), 7.33-7.24 (m, CH-Ar overlapping with two H3 of PAR( $\beta$ ) and H3 of PAR(T)), 7.32 (d,  $^4J_{\text{HH}} = 2.1$  Hz, 1H, H3 of PAR(T) overlapping with CH-Ar), 7.30 (m, H3 of PAR( $\beta$ ) overlapping with CH-Ar), 7.03 (m, 2H, *o* of PPh<sub>2</sub>( $\beta$ )), 6.61 (dd,  $^3J_{\text{PH}} = 16.2$  Hz, 1H,  $^4J_{\text{HH}} = 1.9$  Hz, H5 of PAR( $\beta$ )), 6.53 (dd,  $^3J_{\text{PH}} = 15.5$  Hz,  $^4J_{\text{HH}} = 2.2$  Hz, 1H, H5 of PAR( $\beta$ )), 6.42 (dd,  $^3J_{\text{PH}} = 15.9$  Hz, 1H,  $^4J_{\text{HH}} = 2.1$  Hz, H5 of PAR(T)), 7.61-6.03 (m, H2 / H3 of NAr( $\beta$  / T)), 6.03-5.97 (m, H2 / H3 of NAr( $\beta$  / T)), 4.19 (hept,  $^3J_{\text{HH}} = 6.0$  Hz, CH of <sup>*i*</sup>Pr( $\beta$ )), 3.78 (hept,  $^3J_{\text{HH}} = 6.0$  Hz, 1H, CH of <sup>*i*</sup>Pr(T)), 3.40 (hept,  $^3J_{\text{HH}} = 6.0$  Hz, 1H, CH of <sup>*i*</sup>Pr( $\beta$ )), 1.36 (s, 9H, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>2</sup>( $\beta$ )), 1.30 (s, 18H, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>2</sup>(T)), 1.12 (s, 9H, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>4</sup>( $\beta$ )), 1.07 (s, 9H, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>4</sup>( $\beta$ ) overlapping with CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>4</sup>(T)), 1.06 (s, 18H, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>4</sup>(T) overlapping with CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>4</sup>( $\beta$ )), 1.02 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 3H, CH<sub>3</sub> of <sup>*i*</sup>Pr( $\beta$ ) overlapping with CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>2</sup>( $\beta$ )), 1.00 (s, 9H, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>2</sup>( $\beta$ ) overlapping with CH<sub>3</sub> of <sup>*i*</sup>Pr( $\beta$ )), 0.86 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 3H, CH<sub>3</sub> of <sup>*i*</sup>Pr( $\beta$ )), 0.79 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 3H, CH<sub>3</sub> of <sup>*i*</sup>Pr( $\beta$ )), 0.65 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 12H, CH<sub>3</sub> of <sup>*i*</sup>Pr(T)), 0.49 (d,  $^3J_{\text{HH}} = 6.0$  Hz, 3H, CH<sub>3</sub> of <sup>*i*</sup>Pr( $\beta$ )). **<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, d<sub>8</sub>-THF, 250 K):**  $\delta$  = 169.1 (d,  $^2J_{\text{PC}} = 2.9$  Hz, C1 of PAR( $\beta$ )), 168.8 (d,  $^2J_{\text{PC}} = 1.9$  Hz, C1 of PAR(T)), 165.1 (d,  $^2J_{\text{PC}} = 1.2$  Hz, C1 of PAR( $\beta$ )), 146.8 (dd,  $^3J_{\text{PC}} = 10.2$  Hz,  $^2J_{\text{PC}} = 2.2$  Hz, C1 of NAr( $\beta$ )), 143.7 (dd,  $^3J_{\text{PC}} = 18.5$  Hz,  $^2J_{\text{PC}} = 2.4$  Hz, C1 of NAr(T)), 143.2 (dd,  $^3J_{\text{PC}} = 18.7$  Hz,  $^2J_{\text{PC}} = 5.2$  Hz, C1 of NAr( $\beta$ )), 139.9 (d,  $^3J_{\text{PC}} = 7.6$  Hz, C2 of PAR( $\beta$ )), 138.6 (d,  $^3J_{\text{PC}} = 7.6$  Hz, C2 of PAR( $\beta$ )), 137.9 (d,  $^3J_{\text{PC}} = 15.1$  Hz, C2 of PAR(T)), 137.7 (d,  $^3J_{\text{PC}} = 15.2$  Hz, C4 of PAR( $\beta$ )), 136.5 (d,  $^3J_{\text{PC}} = 15.5$  Hz, C4 of PAR(T)), 135.0 (d,  $^3J_{\text{PC}} = 14.4$  Hz, C4 of PAR( $\beta$ )), 134.7 (d,  $^2J_{\text{PC}} = 9.0$  Hz, *o* of PPh<sub>2</sub>( $\beta$ )), 134.4 (d,  $^2J_{\text{PC}} = 10.2$  Hz, *o* of PPh<sub>2</sub>( $\beta$ ) overlapping with *o* of PPh<sub>2</sub>( $\beta$ )), 134.3 (d,  $^2J_{\text{PC}} = 10.1$  Hz, *o* of PPh<sub>2</sub>( $\beta$ ) overlapping with *o* of PPh<sub>2</sub>( $\beta$ )), 134.2 (d,  $^2J_{\text{PC}} = 9.5$  Hz, *o* of PPh<sub>2</sub>(T)), 133.9 (d,  $^2J_{\text{PC}} = 9.4$  Hz, *o* of PPh<sub>2</sub>( $\beta$ )), 133.0 (m, *p* of PPh<sub>2</sub>( $\beta$ )), 132.7 (m, *p* of PPh<sub>2</sub>(T)), 132.5 (m, two overlapping *p* of PPh<sub>2</sub>( $\beta$ ) overlapping with *i* of PAR( $\beta$ )), 131.6 (d,  $^1J_{\text{PC}} = 89.5$  Hz, *i* of PAR( $\beta$ ) overlapping with *p* of PPh<sub>2</sub>(T) and *p* of PPh<sub>2</sub>( $\beta$ )), 132.1 (m, *p* of PPh<sub>2</sub>( $\beta$ )), 131.2 (d,  $^1J_{\text{PC}} = 107.6$  Hz, *i* of PAR( $\beta$ )), 130.2 (d,  $^1J_{\text{PC}} = 89.1$  Hz, *i* of PAR( $\beta$ )), 129.5-129.1 (m, overlapping CH-Ar overlapping with *i* of PAR( $\beta$ )), 129.1 (d,  $^1J_{\text{PC}} = 88.2$  Hz, *i* of PAR( $\beta$ ) overlapping with CH-Ar), 128.8-128.6 (m, CH-Ar overlapping with *i* of PAR( $\beta$ )), 128.2 (d,  $^1J_{\text{PC}} = 89.2$  Hz, *i* of PAR( $\beta$ ) overlapping with C5 of PAR( $\beta$ ) and *i* of PAR(T)), 128.1 (d,  $^2J_{\text{PC}} = 13.9$  Hz, C5 of PAR( $\beta$ ) overlapping with *i* of PAR( $\beta$ ) and *i* of PAR(T)), 127.8 (d,  $^1J_{\text{PC}} = 92.0$  Hz, *i* of PAR(T) overlapping with C5 of PAR( $\beta$ ) and *i* of PAR( $\beta$ )), 126.9 (d,  $^2J_{\text{PC}} = 14.8$  Hz, C5 of PAR(T)), 126.5 (d,  $^2J_{\text{PC}} = 14.4$  Hz, C5 of PAR( $\beta$ )), 124.5 (d,  $^3J_{\text{PC}} = 5.1$  Hz, C2 of NAr( $\beta$ )), 121.2 (s, C3 of NAr( $\beta$ )),

120.1-119.9 (m, overlapping C2 of NAr( $\beta$ ) and NAr(T)), 118.7 (s, C3 of NAr(T)), 118.2 (s, C3 of NAr( $\beta$ )), 117.2 (d,  $^1J_{\text{PC}} = 123.6$  Hz, C6 of PAR(T)), 115.4 (d,  $^1J_{\text{PC}} = 124.0$  Hz, C6 of PAR( $\beta$ )), 109.4 (d,  $^1J_{\text{PC}} = 110.6$  Hz, C6 of PAR( $\beta$ )), 70.2 (s, CH of <sup>*i*</sup>Pr( $\beta$ )), 69.9 (s, CH of <sup>*i*</sup>Pr( $\beta$ )), 68.9 (s, CH of <sup>*i*</sup>Pr(T)), 36.0 (d,  $^4J_{\text{PC}} = 1.1$  Hz, C of <sup>*t*</sup>Bu<sup>2</sup>( $\beta$ )), 35.7 (d,  $^4J_{\text{PC}} = 1.7$  Hz, C of <sup>*t*</sup>Bu<sup>2</sup>(T)), 35.5 (d,  $^4J_{\text{PC}} = 1.5$  Hz, C of <sup>*t*</sup>Bu<sup>2</sup>( $\beta$ )), 34.5 (s, C of <sup>*t*</sup>Bu<sup>4</sup>( $\beta$ )), 34.4 (s, C of <sup>*t*</sup>Bu<sup>4</sup>(T)), 34.3 (s, C of <sup>*t*</sup>Bu<sup>4</sup>( $\beta$ )), 31.6 (m, two CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>4</sup>( $\beta$ ) overlapping with CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>4</sup>(T)), 30.4 (s, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>4</sup>(T)), 30.2 (s, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>2</sup>( $\beta$ )), 30.0 (s, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>2</sup>( $\beta$ )), 27.5 (s, CH<sub>3</sub> of <sup>*i*</sup>Pr( $\beta$ ) overlapping with CH<sub>3</sub> of <sup>*i*</sup>Pr(T)), 27.4 (s, CH<sub>3</sub> of <sup>*i*</sup>Pr( $\beta$ )), 27.3 (s, CH<sub>3</sub> of <sup>*i*</sup>Pr( $\beta$ )), 27.1 (s, CH<sub>3</sub> of <sup>*i*</sup>Pr( $\beta$ )). **Elemental Analysis:** calculated for C<sub>64</sub>H<sub>78</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Zr: C, 70.36; H, 7.20; N, 2.56. Found: C, 69.03; H, 7.15; N, 2.59.

#### Synthesis of complex 4a

Complex **2a** (1.00 g, 0.87 mmol) and tris(pentafluorophenyl)borane (0.447 g, 0.87 mmol) were dissolved in dichloromethane (20 mL) and stirred for 10 min. The volatiles were removed under vacuum to obtain a foamy solid, which was triturated in pentane (5 mL) to give a light-brown oil. The supernatant solution was removed and the oil was washed with pentane (5x5 mL), and then dried under vacuum to give **6a** as a beige powder containing 66 mol% of pentane (1.181 g, 78%). The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR characterization was performed on a batch prepared by direct evaporation of a dichloromethane solution, hence the presence of 19 mol% of dichloromethane. **<sup>31</sup>P{<sup>1</sup>H} NMR (122 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):**  $\delta$  = 38.2 ( $\nu_{1/2} \approx 5$  Hz). **<sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):**  $\delta$  = 7.73 (m, 2H, *p* of PPh<sub>2</sub> overlapping with H3 of PAR), 7.71 (d,  $^4J_{\text{HH}} = 2.4$  Hz, 2H, H3 of PAR overlapping with *p* of PPh<sub>2</sub>), 7.69 (m, 2H, *p* of PPh<sub>2</sub>), 7.59 (m, 4H, *m* of PPh<sub>2</sub>), 7.53 (m, 4H, *m* of PPh<sub>2</sub>), 7.38 (m, 4H, *o* of PPh<sub>2</sub>), 7.26 (m, 4H, *o* of PPh<sub>2</sub>), 6.85 (m, 2H, *m* of BBn overlapping with *m* of ZrBn), 6.83 (m, 2H, *m* of ZrBn overlapping with *m* of BBn), 6.79 (m, 1H, *p* of ZrBn overlapping with *p* of BBn), 6.76 (m, 1H, *p* of BBn overlapping with *p* of ZrBn), 6.72 (m, 2H, *o* of BBn), 6.58 (dd,  $^3J_{\text{PH}} = 15.9$  Hz,  $^4J_{\text{HH}} = 2.4$  Hz, 2H, H5 of PAR), 6.23 (m, 2H, *o* of ZrBn), 3.43 (m, 2H, CH<sub>2</sub>N), 3.34 (m, 2H, CH<sub>2</sub>N), 2.79 (bs, 2H, CH<sub>2</sub> of BBn), 2.03 (s, 2H, CH<sub>2</sub> of ZrBn), 1.58 (s, 18H, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>2</sup>), 1.11 (s, 18H, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>4</sup>). **<sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):**  $\delta$  = 161.4 (s, C1 of PAR), 149.2 (s, *i* of BBn), 148.6 (dm,  $^1J_{\text{CF}} = 236$  Hz, CF of C<sub>6</sub>F<sub>5</sub>), 145.0 (s, *i* of ZrBn), 144.0 (d,  $^3J_{\text{CP}} = 15.0$  Hz, C4 of PAR), 139.1 (d,  $^3J_{\text{CP}} = 7.0$  Hz, C2 of PAR), 138.0 (dm,  $^1J_{\text{CF}} = 241$  Hz, CF of C<sub>6</sub>F<sub>5</sub>), 136.7 (dm,  $^1J_{\text{CF}} = 255$  Hz, CF of C<sub>6</sub>F<sub>5</sub>), 134.4 (d,  $^4J_{\text{CP}} = 2.4$  Hz, *p* of PPh<sub>2</sub>), 134.3 (d,  $^4J_{\text{CP}} = 2.5$  Hz, *p* of PPh<sub>2</sub>), 133.4 (d,  $^2J_{\text{CP}} = 10.4$  Hz, *o* of PPh<sub>2</sub>), 133.2 (d,  $^2J_{\text{CP}} = 10.3$  Hz, *o* of PPh<sub>2</sub>), 131.4 (m, C3 of PAR), 130.1 (d,  $^3J_{\text{CP}} = 2.7$  Hz, *m* of PPh<sub>2</sub>), 130.0 (d,  $^3J_{\text{CP}} = 2.4$  Hz, *m* of PPh<sub>2</sub>), 129.1 (s, *m* of ZrBn), 128.9 (s, *o* of BBn), 128.2 (d,  $^2J_{\text{CP}} = 13.8$  Hz, C5 of PAR), 127.1 (s, *m* of BBn), 126.2 (m, *o* of ZrBn), 125.6 (m, two overlapping *i* of PPh<sub>2</sub>), 122.6 (s, *p* of BBn), 122.4 (s, *p* of ZrBn), 111.9 (d,  $^1J_{\text{CP}} = 115.8$  Hz, C6 of PAR), 67.6 (s, CH<sub>2</sub> of ZrBn), 52.1 (dd,  $^3J_{\text{CP}} = 15.4$  Hz,  $^2J_{\text{CP}} = 4.1$  Hz, CH<sub>2</sub>N), 36.2 (s, C of <sup>*t*</sup>Bu<sup>2</sup>), 34.8 (s, C of <sup>*t*</sup>Bu<sup>4</sup>), 31.9 (n.o., CH<sub>2</sub> of BBn, visible in HSQC spectrum), 31.3 (s, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>4</sup>), 30.3 (s, CH<sub>3</sub> of <sup>*t*</sup>Bu<sup>2</sup>). **<sup>19</sup>F{<sup>1</sup>H} NMR (282 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):**  $\delta$  = -131.4 (m, *o* of C<sub>6</sub>F<sub>5</sub>), -164.8 (t,  $J_{\text{FF}} = 20.6$  Hz, *p* of C<sub>6</sub>F<sub>5</sub>), -167.7 (m, *m* of C<sub>6</sub>F<sub>5</sub>). **<sup>11</sup>B{<sup>1</sup>H} NMR (96 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K):**  $\delta$  = -12.7. **Elemental Analysis:** calculated for

C<sub>86</sub>H<sub>78</sub>BF<sub>15</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Zr(C<sub>5</sub>H<sub>12</sub>)<sub>0.66</sub>: C, 64.30; H, 5.19; N, 1.68. Found: C, 63.60; H, 4.94; N, 1.75.

#### Synthesis of complex 4b

Complex **2b** (1.000 g, 0.75 mmol) and tris(pentafluorophenyl)borane (0.386 g, 0.75 mmol) were dissolved in toluene (20 mL) and stirred for 1h. The volatiles were removed under vacuum to give a foamy solid. The solid was suspended in pentane (10 mL), resulting in the formation of a brown oil, and the supernatant was removed. The oil was washed with pentane (4x5 mL) then dried under vacuum to give **6b** as a pale yellow powder containing 66 mol % of toluene (1.148 g, 88%). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ = 34.5 (v<sub>1/2</sub> ≈ 3 Hz). <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ = 7.83 (m, 2H, *p* of PPh<sub>2</sub>), 7.70 (d, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 2H, *H3* of PAR overlapping with *m* of PPh<sub>2</sub>), 7.69 (m, 4H, *m* of PPh<sub>2</sub> overlapping with *H3* of PAR), 7.64-7.57 (m, 4H, *o* of PPh<sub>2</sub> overlapping with *p* of PPh<sub>2</sub>), 7.56 (m, 2H, *p* of PPh<sub>2</sub>), 7.37-7.30 (m, 4H, *o* of PPh<sub>2</sub>), 7.27 (m, 4H, *m* of PPh<sub>2</sub>), 6.87 (m, 2H, *m* of BBn), 6.81-6.66 (m, 8H, *p* of BBn overlapping with *o* of BBn, *H5* of PAR, *m* of ZrBn and *p* of ZrBn), 6.60 (m, 2H, *o* of ZrBn), 6.37 (m, 2H, *H3* of NAr), 6.07 (m, 2H, *H2* of NAr), 2.84 (bs, 2H, CH<sub>2</sub> of BBn), 2.15 (s, 2H, CH<sub>2</sub> of ZrBn), 1.36 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 1.19 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ = 161.4 (d, <sup>3</sup>J<sub>PC</sub> = 1.0 Hz, C1 of PAR), 149.1 (s, *i* of BBn overlapping with CF of C<sub>6</sub>F<sub>5</sub>), 148.6 (dm, <sup>1</sup>J<sub>CF</sub> = 241 Hz, CF of C<sub>6</sub>F<sub>5</sub> overlapping with *i* of BBn), 144.1 (d, <sup>3</sup>J<sub>CP</sub> = 14.5 Hz, C4 of PAR), 140.0 (dd, <sup>3</sup>J<sub>CP</sub> = 13.6 Hz, <sup>2</sup>J<sub>CP</sub> = 3.7 Hz, C1 of NAr), 139.2 (d, <sup>3</sup>J<sub>CP</sub> = 6.4 Hz, C2 of PAR), 138.0 (dm, <sup>1</sup>J<sub>CF</sub> = 243 Hz, CF of C<sub>6</sub>F<sub>5</sub> overlapping with *i* of ZrBn and CF of C<sub>6</sub>F<sub>5</sub>), 137.0 (s, *i* of ZrBn overlapping with two CF of C<sub>6</sub>F<sub>5</sub>), 136.7 (dm, <sup>1</sup>J<sub>CF</sub> = 246 Hz, CF of C<sub>6</sub>F<sub>5</sub> overlapping with CF of C<sub>6</sub>F<sub>5</sub> and *i* of ZrBn), 135.1 (d, <sup>4</sup>J<sub>CP</sub> = 2.7 Hz, *p* of PPh<sub>2</sub>), 134.4 (d, <sup>4</sup>J<sub>CP</sub> = 2.8 Hz, *p* of PPh<sub>2</sub>), 134.1 (d, <sup>2</sup>J<sub>CP</sub> = 10.7 Hz, *o* of PPh<sub>2</sub>), 133.1 (d, <sup>2</sup>J<sub>CP</sub> = 10.2 Hz, *o* of PPh<sub>2</sub>), 131.8 (d, <sup>4</sup>J<sub>CP</sub> = 1.8 Hz, C3 of PAR), 130.2 (d, <sup>3</sup>J<sub>CP</sub> = 13.1 Hz, *m* of PPh<sub>2</sub>), 130.0 (d, <sup>3</sup>J<sub>CP</sub> = 12.7 Hz, *m* of PPh<sub>2</sub>), 129.6 (s, *m* of ZrBn), 129.0 (s, *o* of BBn), 128.8 (n.o., *i* of C<sub>6</sub>F<sub>5</sub> visible in HMBC spectrum), 128.5 (d, <sup>2</sup>J<sub>PC</sub> = 15.0 Hz, C5 of PAR overlapping with toluene signal and *o* of ZrBn), 128.4 (s, *o* of ZrBn overlapping with C5 of PAR), 127.1 (s, *m* of BBn), 126.2 (d, <sup>1</sup>J<sub>CP</sub> = 96.5 Hz, *i* of PPh<sub>2</sub> overlapping with *i* of PPh<sub>2</sub>), 125.4 (d, <sup>1</sup>J<sub>CP</sub> = 89.1 Hz, *i* of PPh<sub>2</sub> overlapping with *i* of PPh<sub>2</sub>), 125.0 (s, *p* of ZrBn), 122.6 (s, *p* of BBn), 122.5 (d, <sup>3</sup>J<sub>CP</sub> = 5.6 Hz, C2 of NAr), 122.4 (s, C3 of NAr), 113.3 (d, <sup>1</sup>J<sub>CP</sub> = 114.7 Hz C6 of PAR), 67.3 (s, CH<sub>2</sub> of ZrBn), 35.9 (s, C of <sup>t</sup>Bu<sup>2</sup>), 34.9 (s, C of <sup>t</sup>Bu<sup>4</sup>), 31.8 (n.o., CH<sub>2</sub> of BBn visible in HSQC spectrum), 31.3 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 30.4 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>). <sup>19</sup>F{<sup>1</sup>H} NMR (470 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ = -131.3 (m, *o* of C<sub>6</sub>F<sub>5</sub>), -165.0 (t, <sup>1</sup>J<sub>CF</sub> = 20.5 Hz, *p* of C<sub>6</sub>F<sub>5</sub>), -167.8 (m, *m* of C<sub>6</sub>F<sub>5</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ = -12.7. Elemental Analysis: calculated for C<sub>90</sub>H<sub>78</sub>BF<sub>15</sub>N<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Zr(C<sub>5</sub>H<sub>8</sub>)<sub>0.66</sub>: C, 65.40; H, 4.90; N, 1.63. Found: C, 65.06; H, 5.11; N, 1.63.

#### Synthesis of complex 5a

Complex **4a** (0.339 g, 0.2 mmol) was dissolved in 6 mL of CH<sub>2</sub>Cl<sub>2</sub> and a 0.2 M solution of <sup>i</sup>PrOH in CH<sub>2</sub>Cl<sub>2</sub> (500 μL) was added over 1 min. The solution became progressively paler and some precipitate appeared. The suspension was filtered over diatomaceous earth in a pipette fitted with a borosilicate fiber filter. The clear solution was evaporated to dryness, and the

residue was triturated in 5 mL of pentane. The supernatant solution was discarded and the residue was dried under vacuum, yielding complex **5a** as a white powder containing 50 mol% of pentane (0.195 g, 86 %). <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ = 37.0 (v<sub>1/2</sub> ≈ 9 Hz). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ = 7.72 (m, 2H, two overlapping *p* of PPh<sub>2</sub>), 7.69 (m, 2H, *p* of PPh<sub>2</sub> overlapping with *p* of PPh<sub>2</sub>), 7.64-7.51 (m, 12H, *H3* of PAR overlapping with *m* of PPh<sub>2</sub>, *o* of PPh<sub>2</sub> and *m* of PPh<sub>2</sub>), 7.45 (m, 4H, *o* of PPh<sub>2</sub>), 6.86 (m, 2H, *m* of BBn), 6.77 (m, 1H, *p* of BBn overlapping with *o* of BBn), 6.73 (m, 2H, *p* of BBn overlapping with *o* of BBn), 6.63 (dd, <sup>3</sup>J<sub>PH</sub> = 15.3 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 2H, *H5* of PAR), 3.95 (m, 1H, CH of <sup>i</sup>Pr), 3.50 (m, 2H, CH<sub>2</sub>N), 3.33 (m, 2H, CH<sub>2</sub>N), 2.80 (bs, 2H, CH<sub>2</sub> of BBn), 1.51 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 1.09 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 0.73 (d, 6H, <sup>3</sup>J<sub>HH</sub> = 5.8 Hz, CH<sub>3</sub> of <sup>i</sup>Pr). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ = 162.0 (s, C1 of PAR), 149.1 (s, *i* of BBn), 148.6 (dm, <sup>1</sup>J<sub>CF</sub> = 238 Hz, CF of C<sub>6</sub>F<sub>5</sub>), 142.8 (d, <sup>3</sup>J<sub>CP</sub> = 14.0 Hz, C4 of PAR), 139.1 (d, <sup>3</sup>J<sub>CP</sub> = 7.0 Hz, C2 of PAR), 137.9 (dm, <sup>1</sup>J<sub>CF</sub> = 243 Hz, CF of C<sub>6</sub>F<sub>5</sub>), 136.8 (dm, <sup>1</sup>J<sub>CF</sub> = 245 Hz, CF of C<sub>6</sub>F<sub>5</sub>), 134.1 (m, *p* of PPh<sub>2</sub>), 133.3 (d, <sup>2</sup>J<sub>CP</sub> = 10.0 Hz, *o* of PPh<sub>2</sub>), 133.2 (d, <sup>2</sup>J<sub>CP</sub> = 10.2 Hz, *o* of PPh<sub>2</sub>), 131.0 (s, C3 of PAR), 130.0 (m, *m* of PPh<sub>2</sub>), 129.0 (s, *o* of BBn), 128.8 (n.o., *i* of C<sub>6</sub>F<sub>5</sub> visible in HMBC), 127.7 (d, <sup>2</sup>J<sub>CP</sub> = 13.6 Hz, C5 of PAR), 127.1 (s, *m* of BBn overlapping with *i* of PPh<sub>2</sub>), 126.8 (d, <sup>1</sup>J<sub>CP</sub> = 93.4 Hz, *i* of PPh<sub>2</sub> overlapping with *i* of PPh<sub>2</sub> and *m* of BBn), 126.0 (d, <sup>1</sup>J<sub>CP</sub> = 93.8 Hz, *i* of PPh<sub>2</sub> overlapping with *i* of PPh<sub>2</sub>), 122.6 (s, *p* of BBn), 111.6 (d, <sup>1</sup>J<sub>CP</sub> = 115.0 Hz, *i* of PAR), 76.1 (bs, CH of <sup>i</sup>Pr), 52.0 (dd, <sup>3</sup>J<sub>CP</sub> = 16.2 Hz, <sup>2</sup>J<sub>CP</sub> = 4.1 Hz, NCH<sub>2</sub>), 36.1 (s, C of <sup>t</sup>Bu<sup>2</sup>), 34.7 (s, C of <sup>t</sup>Bu<sup>4</sup>), 32.0 (n.o., CH<sub>2</sub> of BBn visible in HSQC), 31.2 (s, C of <sup>t</sup>Bu<sup>4</sup>), 30.2 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 26.2 (bs, CH<sub>3</sub> of <sup>i</sup>Pr). <sup>19</sup>F{<sup>1</sup>H} NMR (565 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ = -131.4 (m, *o* of C<sub>6</sub>F<sub>5</sub>), -165.1 (t, <sup>1</sup>J<sub>FF</sub> = 20.5 Hz, *p* of C<sub>6</sub>F<sub>5</sub>), -167.9 (t, <sup>1</sup>J<sub>FF</sub> = 19.9 Hz, *m* of C<sub>6</sub>F<sub>5</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (192 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 300 K): δ = -12.8. Elemental Analysis: calculated for C<sub>82</sub>H<sub>78</sub>BF<sub>15</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Zr(C<sub>5</sub>H<sub>12</sub>)<sub>0.5</sub>: C, 62.55; H, 5.22; N, 1.72. Found: C, 61.93; H, 4.96; N, 1.32. HRMS (ESI-pos): calculated for C<sub>57</sub>H<sub>71</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Zr<sup>+</sup> [M-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>CH<sub>2</sub>Ph]<sup>+</sup>: 983.39815. Found: 983.38712 (-11.2 ppm). Calculated for C<sub>55</sub>H<sub>67</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Zr<sup>+</sup> [M-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>CH<sub>2</sub>Ph-O<sup>i</sup>Pr+MeO]<sup>+</sup>: 955.36685. Found: 955.36372 (-3.3 ppm).

#### Synthesis of complex 6a

Complex **4a** (0.339 g, 0.2 mmol) was dissolved in 6 mL of CH<sub>2</sub>Cl<sub>2</sub> and (-)-L-methyl lactate (21 mg, 0.2 mmol) was added to the solution. The reaction mixture was stirred for 20 min, then it was evaporated to dryness, and the residue was triturated in 5 mL of pentane. The supernatant solution was discarded and the residue was dried under vacuum, yielding complex **6a** as a white powder containing 90 mol% of pentane and 10 mol% of toluene (0.240 g, 86 %). <sup>31</sup>P{<sup>1</sup>H} NMR (243 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 37.7 (v<sub>1/2</sub> ≈ 3 Hz), 37.5 (v<sub>1/2</sub> ≈ 3 Hz). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K): δ = 7.73-7.66 (m, 2H, *p* of PPh<sub>2</sub> overlapping with *p* of PPh<sub>2</sub>), 7.65-7.55 (m, 12H, *p* of PPh<sub>2</sub> overlapping with *H3* of PAR and *o* and *m* of PPh<sub>2</sub>), 7.46-7.36 (m, 8H, *m* of PPh<sub>2</sub> overlapping with *o* of PPh<sub>2</sub>), 6.86 (m, 2H, *m* of BBn), 6.81-6.71 (m, 5H, *p* of BBn overlapping with *o* of BBn and *H5* of PAR), 4.84 (q, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 1H, CH of lactate), 3.68 (s, 3H, OCH<sub>3</sub> of lactate), 3.48 (m, 2H, CH<sub>2</sub>N), 3.09 (m, 2H, CH<sub>2</sub>N), 2.81 (bs, 2H, CH<sub>2</sub> of BBn), 1.36 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 1.34 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 1.30 (d, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, 3H, CH<sub>3</sub> of lactate), 1.15 (s, 18H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (151



**MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):**  $\delta$  = 192.9 (s, C=O of lactate), 162.6 (d,  $^2J_{PC}$  = 1.6 Hz, C1 of PAr), 162.5 (d,  $^2J_{PC}$  = 1.8 Hz, C1 of PAr), 149.1 (s, *i* of BBn overlapping with CF of C<sub>6</sub>F<sub>5</sub>), 148.6 (dm,  $^1J_{CF}$  = 237 Hz, CF of C<sub>6</sub>F<sub>5</sub>), 142.1 (d,  $^3J_{CP}$  = 12.7 Hz, C4 of PAr overlapping with C4 of PAr), 142.1 (d,  $^3J_{CP}$  = 12.7 Hz, C4 of PAr overlapping with C4 of PAr), 139.3 (d,  $^3J_{CP}$  = 6.7 Hz, C2 of PAr overlapping with C2 of PAr), 139.2 (d,  $^3J_{CP}$  = 6.7 Hz, C2 of PAr overlapping with C2 of PAr), 137.9 (dm,  $^1J_{CF}$  = 243 Hz, CF of C<sub>6</sub>F<sub>5</sub> overlapping with CF of C<sub>6</sub>F<sub>5</sub>), 136.7 (dm,  $^1J_{CF}$  = 246 Hz, CF of C<sub>6</sub>F<sub>5</sub> overlapping with CF of C<sub>6</sub>F<sub>5</sub>), 134.0 (d,  $^4J_{PC}$  = 2.8 Hz, *p* of PPh<sub>2</sub>), 133.9 (d,  $^4J_{PC}$  = 2.8 Hz, *p* of PPh<sub>2</sub>), 133.7 (d,  $^4J_{PC}$  = 2.7 Hz, *p* of PPh<sub>2</sub>), 133.6 (m, *p* of PPh<sub>2</sub> overlapping with *o* of PPh<sub>2</sub>), 133.6 (d,  $^2J_{CP}$  = 9.9 Hz, *o* of PPh<sub>2</sub> overlapping with *p* of PPh<sub>2</sub>), 133.5 (d,  $^2J_{CP}$  = 10.2 Hz, *o* of PPh<sub>2</sub>), 133.1 (d,  $^2J_{CP}$  = 2.2 Hz, *o* of PPh<sub>2</sub>), 133.0 (d,  $^2J_{CP}$  = 2.1 Hz, *o* of PPh<sub>2</sub>), 130.6 (d,  $^4J_{CP}$  = 1.9 Hz, C3 of PAr), 130.6 (d,  $^4J_{CP}$  = 1.9 Hz, C3 of PAr), 129.8 (d,  $^3J_{CP}$  = 3.0 Hz, *m* of PPh<sub>2</sub> overlapping with *m* of PPh<sub>2</sub>), 129.8 (d,  $^3J_{CP}$  = 2.2 Hz, *m* of PPh<sub>2</sub> overlapping with two *m* of PPh<sub>2</sub>), 129.7 (d,  $^3J_{CP}$  = 3.2 Hz, *m* of PPh<sub>2</sub> overlapping with two *m* of PPh<sub>2</sub>), 129.7 (d,  $^3J_{CP}$  = 1.9 Hz, *m* of PPh<sub>2</sub> overlapping with *m* of PPh<sub>2</sub>), 129.1 (s, *o* of BBn), 128.8 (n.o., *i* of C<sub>6</sub>F<sub>5</sub> visible in HMBC), 127.6-124.9 (m, four overlapping *i* of PPh<sub>2</sub> overlapping with two C5 of PAr and *m* of BBn), 127.2 (d,  $^2J_{CP}$  = 13.0 Hz, C5 of PAr overlapping with *i* of PPh<sub>2</sub>), 127.1 (d,  $^2J_{CP}$  = 13.2 Hz, C5 of PAr overlapping with *i* of PPh<sub>2</sub> and *m* of BBn), 127.1 (s, *m* of BBn overlapping with C5 of PAr and *i* of PPh<sub>2</sub>), 122.6 (s, *p* of BBn), 112.2 (d,  $^1J_{CP}$  = 50.0 Hz, C6 of PAr), 111.5 (d,  $^1J_{CP}$  = 50.0 Hz, C6 of PAr), 77.2 (s, CH of lactate), 56.6 (s, OCH<sub>3</sub> of lactate), 52.1 (dd,  $^3J_{CP}$  = 12.8 Hz,  $^2J_{CP}$  = 3.9 Hz, NCH<sub>2</sub>), 51.9 (dd,  $^3J_{CP}$  = 11.8 Hz,  $^2J_{CP}$  = 4.0 Hz, NCH<sub>2</sub>), 35.7 (d,  $^4J_{PC}$  = 1.7 Hz, C of <sup>t</sup>Bu<sup>2</sup>), 35.7 (d,  $^4J_{PC}$  = 1.7 Hz, C of <sup>t</sup>Bu<sup>2</sup>), 34.7 (s, C of <sup>t</sup>Bu<sup>4</sup>), 32.1 (bs, CH<sub>2</sub> of BBn), 31.4 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup> overlapping with CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 31.3 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup> overlapping with CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 29.9 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 29.8 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 21.4 (s, CH<sub>3</sub> of lactate). **<sup>19</sup>F{<sup>1</sup>H} NMR (565 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):**  $\delta$  = -131.4 (m, *o* of C<sub>6</sub>F<sub>5</sub>), -165.1 (m, *p* of C<sub>6</sub>F<sub>5</sub>), -167.8 (m, *m* of C<sub>6</sub>F<sub>5</sub>). **<sup>11</sup>B{<sup>1</sup>H} NMR (192 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):**  $\delta$  = -12.7. **Elemental Analysis:** calculated for C<sub>83</sub>H<sub>78</sub>BF<sub>15</sub>N<sub>2</sub>O<sub>5</sub>P<sub>2</sub>Zr(C<sub>5</sub>H<sub>12</sub>)<sub>0.9</sub>(C<sub>7</sub>H<sub>8</sub>)<sub>0.1</sub>: C, 62.07; H, 5.29; N, 1.64. Found: C, 61.14; H, 5.43; N, 1.48. **HRMS (ESI-pos):** calculated for C<sub>58</sub>H<sub>71</sub>N<sub>2</sub>O<sub>5</sub>P<sub>2</sub>Zr<sup>+</sup> [M-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>CH<sub>2</sub>Ph]<sup>+</sup>: 1027.38798. Found: 1027.38350 (-4.4 ppm). Calculated for C<sub>55</sub>H<sub>67</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Zr<sup>+</sup> [M-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>CH<sub>2</sub>Ph-lactate+MeO]<sup>+</sup>: 955.36685. Found: 955.36399 (-3.0 ppm).

#### Synthesis of complex 6b

Complex **4b** (0.435 g, 0.25 mmol) and (-)-L-methyl lactate (26 mg, 0.25 mmol) were dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub> and the reaction mixture was stirred at room temperature for 30 min. The volatiles were removed under vacuum to give a foamy solid, which was triturated in pentane (5 mL) to give a light-brown oil. The supernatant solution was removed and the oil was washed with pentane (5x3 mL), then dried under vacuum to give **6b** as a white powder containing 100 mol% of pentane (0.355 g, 85%). **<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):**  $\delta$  = 33.1 ( $\nu_{1/2}$   $\approx$  3 Hz), 31.6 ( $\nu_{1/2}$   $\approx$  3 Hz). **<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):**  $\delta$  = 7.81-7.72 (m, 2H, *p* of PPh<sub>2</sub>), 7.67-7.54 (m, 12H, *o/m* of PPh<sub>2</sub> overlapping with *p* of PAr and *H3* of NAR), 7.53-7.40 (m, 6H, *o* of PPh<sub>2</sub> overlapping with *p* of PPh<sub>2</sub>), 7.32 (m, 2H, *m* of PPh<sub>2</sub>),

7.19 (m, 2H, *m* of PPh<sub>2</sub>), 6.89 (m, 1H, *H5* of PAr overlapping with *m* of BBn), 6.87 (m, 2H, *m* of BBn overlapping with *H5* of PAr), 6.81 (m, 1H, *H5* of PAr overlapping with *o* of BBn), 6.78 (m, 1H, *p* of BBn overlapping with *H5* of PAr and *p* of BBn), 6.76 (m, 2H, *o* of BBn overlapping with *p* of BBn), 6.42 (m, 1H, *H3* of NAR overlapping with *H3* of NAR), 6.39 (m, 1H, *H3* of NAR overlapping with *H3* of NAR), 6.20 (m, 1H, *H2* of NAR), 6.16 (m, 1H, *H2* of NAR), 4.61 (q, 1H,  $^3J_{HH}$  = 7.0 Hz, CH of lactate), 3.58 (s, 3H, OCH<sub>3</sub> of lactate), 2.82 (bs, 2H, CH<sub>2</sub> of BBn), 1.25-1.178 (m, 39H, <sup>t</sup>Bu overlapping with CH<sub>3</sub> of lactate). **<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):** 192.8 (s, C=O of lactate), 162.6 (m, C1 of PAr), 162.4 (d,  $^2J_{PC}$  = 1.1 Hz, C1 of PAr), 149.2 (s, *i* of BBn overlapping with CF of C<sub>6</sub>F<sub>5</sub>), 148.6 (dm,  $^1J_{CF}$  = 238 Hz, CF of C<sub>6</sub>F<sub>5</sub>), 142.6 (d,  $^3J_{CP}$  = 14.5 Hz, C4 of PAr overlapping with C4 of PAr), 142.5 (d,  $^3J_{CP}$  = 15.1 Hz, C4 of PAr overlapping with C4 of PAr), 141.6 (dd,  $^3J_{CP}$  = 12.9 Hz,  $^2J_{CP}$  = 3.6 Hz, C1 of NAR), 141.1 (dd,  $^3J_{CP}$  = 14.1 Hz,  $^3J_{CP}$  = 3.7 Hz, C1 of NAR), 139.4 (d,  $^3J_{CP}$  = 1.9 Hz, C2 of PAr overlapping with C2 of PAr), 139.4 (d,  $^3J_{CP}$  = 1.7 Hz, C2 of PAr overlapping with C2 of PAr), 138.0 (dm,  $^1J_{CF}$  = 242 Hz, CF of C<sub>6</sub>F<sub>5</sub> overlapping with CF of C<sub>6</sub>F<sub>5</sub>), 136.7 (dm,  $^1J_{CF}$  = 248 Hz, CF of C<sub>6</sub>F<sub>5</sub> overlapping with CF of C<sub>6</sub>F<sub>5</sub>), 134.7 (d,  $^4J_{CP}$  = 2.5 Hz, *p* of PPh<sub>2</sub>), 134.5 (d,  $^4J_{CP}$  = 2.6 Hz, *p* of PPh<sub>2</sub> overlapping with *o* of PPh<sub>2</sub>), 134.4 (d,  $^2J_{CP}$  = 10.9 Hz, *o* of PPh<sub>2</sub> overlapping with *p* of PPh<sub>2</sub>), 134.1 (d,  $^4J_{CP}$  = 2.8 Hz, *p* of PPh<sub>2</sub> overlapping with *o* of PPh<sub>2</sub>), 134.1 (d,  $^2J_{CP}$  = 11.3 Hz, *o* of PPh<sub>2</sub> overlapping with two *p* of PPh<sub>2</sub>), 133.9 (d,  $^4J_{CP}$  = 2.7 Hz, *p* of PPh<sub>2</sub> overlapping with *o* of PPh<sub>2</sub>), 133.5 (d,  $^2J_{CP}$  = 10.2 Hz, *o* of PPh<sub>2</sub>), 133.2 (d,  $^2J_{CP}$  = 10.3 Hz, *o* of PPh<sub>2</sub>), 131.2-131.0 (m, C3 of PAr), 130.0 (d,  $^3J_{PC}$  = 2.8 Hz, *m* of PPh<sub>2</sub> overlapping with two *m* of PPh<sub>2</sub>), 129.9 (d,  $^3J_{PC}$  = 12.6 Hz, *m* of PPh<sub>2</sub> overlapping with three *m* of PPh<sub>2</sub>), 129.9 (d,  $^3J_{PC}$  = 2.8 Hz, *m* of PPh<sub>2</sub> overlapping with three *m* of PPh<sub>2</sub>), 129.7 (d,  $^3J_{PC}$  = 12.6 Hz, *m* of PPh<sub>2</sub> overlapping with two *m* of PPh<sub>2</sub>), 129.1 (s, *o* of BBn), 128.3-125.4 (m, four overlapping *i* of PPh<sub>2</sub> overlapping with two C5 of PAr and *m* of BBn), 128.0 (d,  $^2J_{CP}$  = 12.9 Hz, C5 of PAr overlapping with *i* of PPh<sub>2</sub>), 127.7 (d,  $^2J_{CP}$  = 13.2 Hz, C5 of PAr overlapping with *i* of PPh<sub>2</sub>), 127.1 (s, *m* of BBn overlapping with *i* of PPh<sub>2</sub>), 122.7 (s, *p* of BBn), 122.5 (s, C3 of NAR), 122.3 (d,  $^3J_{CP}$  = 5.3 Hz, C2 of NAR), 122.1 (s, C3 of NAR), 121.9 (d,  $^3J_{CP}$  = 5.6 Hz, C2 of NAR), 112.1-111.1 (m, two overlapping C6 of PAr), 77.7 (s, CH of lactate), 56.6 (s, OCH<sub>3</sub> of lactate), 35.6 (m, two overlapping C of <sup>t</sup>Bu<sup>2</sup>), 34.8 (s, C of <sup>t</sup>Bu<sup>4</sup> overlapping with C of <sup>t</sup>Bu<sup>4</sup>), 34.8 (s, C of <sup>t</sup>Bu<sup>4</sup> overlapping with C of <sup>t</sup>Bu<sup>4</sup>), 31.9 (n.o., CH<sub>2</sub> of BBn, visible in HSQC spectrum), 31.4 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 29.7 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup> overlapping with CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 29.6 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup> overlapping with CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 21.4 (s, CH<sub>3</sub> of lactate). **<sup>19</sup>F{<sup>1</sup>H} NMR (470 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):**  $\delta$  = -131.3 (m, *o* of C<sub>6</sub>F<sub>5</sub>), -165.0 (m, *p* of C<sub>6</sub>F<sub>5</sub>), -167.8 (m, *m* of C<sub>6</sub>F<sub>5</sub>). **<sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K):**  $\delta$  = -12.7. **Elemental Analysis:** calculated for C<sub>87</sub>H<sub>78</sub>BF<sub>15</sub>N<sub>2</sub>O<sub>5</sub>P<sub>2</sub>Zr(C<sub>5</sub>H<sub>12</sub>): C, 63.05; H, 5.18; N, 1.64. Found: C, 62.24; H, 5.27; N, 1.60. **HRMS (ESI-pos):** calculated for C<sub>62</sub>H<sub>71</sub>N<sub>2</sub>O<sub>5</sub>P<sub>2</sub>Zr<sup>+</sup> [M-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>CH<sub>2</sub>Ph]<sup>+</sup>: 1075.38790. Found: 1075.38799 (+0.0 ppm). Calculated for C<sub>58</sub>H<sub>65</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Zr<sup>+</sup> [M-B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>CH<sub>2</sub>Ph-lactate+OH]<sup>+</sup>: 989.35175. Found: 989.35238 (-0.6 ppm).

#### Synthesis of complex 7a

Proligand **1aH<sub>2</sub>** (419 mg, 0.50 mmol) was suspended in pentane and Ti(NMe<sub>2</sub>)<sub>4</sub> (112 mg, 0.50 mmol) was added dropwise. The mixture was stirred for 45 min during which a red-orange precipitate appeared. The solid was filtered, rinsed with 2 mL of pentane and dried under vacuum, affording complex **7a** (362 mg, 72 %) containing 50 mol% of pentane. **<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, d<sub>8</sub>-THF, 300 K):** δ = 32.0 (v<sub>1/2</sub> ≈ 3 Hz), 26.1 (v<sub>1/2</sub> ≈ 2 Hz). **<sup>1</sup>H NMR (500 MHz, d<sub>8</sub>-THF, 300 K):** δ = 8.01 (m, 2H, o of PPh<sub>2</sub>), 7.58-7.31 (m, 18H, CH-Ar), 7.19 (m, 2H, m of PPh<sub>2</sub>), 6.86 (dd, <sup>3</sup>J<sub>PH</sub> = 12.9 Hz, <sup>4</sup>J<sub>HH</sub> = 2.7 Hz, 1H, H5 of PAR), 6.81 (dd, <sup>3</sup>J<sub>PH</sub> = 16.3 Hz, <sup>4</sup>J<sub>HH</sub> = 2.5 Hz, 1H, H5 of PAR), 3.13 (s, 6H, NMe<sub>2</sub> overlapping with CH<sub>2</sub>N), 3.12-2.97 (m, 1H, CH<sub>2</sub>N overlapping with NMe<sub>2</sub>), 2.91 (m, 1H, CH<sub>2</sub>N), 2.74-2.63 (m, 2H, two overlapping CH<sub>2</sub>N), 2.60 (s, 6H, NMe<sub>2</sub>), 1.49 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 1.23 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 1.10 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 1.02 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>). **<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, d<sub>8</sub>-THF, 300 K):** δ = 170.2 (d, <sup>2</sup>J<sub>PC</sub> = 4.3 Hz, C1 of PAR), 169.9 (d, <sup>2</sup>J<sub>PC</sub> = 2.4 Hz, C1 of PAR), 140.6 (d, <sup>3</sup>J<sub>CP</sub> = 6.9 Hz, C2 of PAR), 140.0 (d, <sup>3</sup>J<sub>CP</sub> = 8.4 Hz, C2 of PAR), 137.1 (d, <sup>3</sup>J<sub>CP</sub> = 14.6 Hz, C4 of PAR), 134.8 (m, two overlapping o of PPh<sub>2</sub>), 134.1 (d, <sup>3</sup>J<sub>CP</sub> = 12.9 Hz, C4 of PAR overlapping with i of PPh<sub>2</sub>), 134.1 (d, <sup>1</sup>J<sub>PC</sub> = 88.2 Hz, i of PPh<sub>2</sub> overlapping with C4 of PAR and two o of PPh<sub>2</sub>), 133.8 (d, <sup>2</sup>J<sub>CP</sub> = 8.0 Hz, o of PPh<sub>2</sub> overlapping with i of PPh<sub>2</sub> and o of PPh<sub>2</sub>), 133.7 (d, <sup>2</sup>J<sub>CP</sub> = 7.0 Hz, o of PPh<sub>2</sub> overlapping with i of PPh<sub>2</sub> and o of PPh<sub>2</sub>), 132.7 (d, <sup>1</sup>J<sub>PC</sub> = 116.5 Hz, i of PPh<sub>2</sub> overlapping with p of PPh<sub>2</sub>), 132.3 (d, <sup>4</sup>J<sub>PC</sub> = 2.3 Hz, p of PPh<sub>2</sub> overlapping with i of PPh<sub>2</sub>), 132.1 (d, <sup>4</sup>J<sub>PC</sub> = 2.9 Hz, p of PPh<sub>2</sub>), 131.7 (d, <sup>4</sup>J<sub>PC</sub> = 2.6 Hz, p of PPh<sub>2</sub>), 131.5 (d, <sup>4</sup>J<sub>PC</sub> = 2.6 Hz, p of PPh<sub>2</sub>), 130.5 (d, <sup>1</sup>J<sub>CP</sub> = 85.6 Hz, i of PPh<sub>2</sub>), 129.6 (d, <sup>1</sup>J<sub>CP</sub> = 86.0 Hz, i of PPh<sub>2</sub>), 129.0-128.7 (m, overlapping CH-Ar), 128.7-128.4 (m, overlapping CH-Ar), 127.9 (m, C3 of PAR), 127.5 (d, <sup>2</sup>J<sub>CP</sub> = 12.7 Hz, C5 of PAR), 109.0 (d, <sup>1</sup>J<sub>CP</sub> = 88.0 Hz, C6 of PAR), 108.2 (d, <sup>1</sup>J<sub>CP</sub> = 108.1 Hz, C6 of PAR), 52.5-52.2 (m, two overlapping CH<sub>2</sub>N), 51.3 (s, NMe<sub>2</sub>), 49.0 (s, NMe<sub>2</sub>), 36.2 (d, <sup>4</sup>J<sub>PC</sub> = 1.8 Hz, C of <sup>t</sup>Bu<sup>2</sup>), 35.9 (d, <sup>4</sup>J<sub>PC</sub> = 1.8 Hz, C of <sup>t</sup>Bu<sup>2</sup>), 34.5 (m, two overlapping C of <sup>t</sup>Bu<sup>4</sup>), 31.8 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 31.6 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 30.5 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 30.3 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>). **Elemental Analysis:** calculated for C<sub>58</sub>H<sub>76</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Ti(C<sub>5</sub>H<sub>12</sub>)<sub>0.5</sub>: C, 72.15; H, 8.21; N, 5.56. Found: C, 71.55; H, 7.86; N, 5.56. Calculated for C<sub>58</sub>H<sub>76</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Ti: C, 71.74; H, 7.89; N, 5.77. The sample was sent for analysis in a sealed ampule under partial vacuum, therefore it is likely that some pentane desorbed between sample preparation and analysis.

#### Synthesis of complex **7b**

Proligand **1bH<sub>2</sub>** (830 mg, 0.938 mmol) was suspended in pentane and Ti(NMe<sub>2</sub>)<sub>4</sub> (210 mg, 0.938 mmol) was added dropwise. The mixture was stirred for 10 min, affording a red-orange solution. After removal of the volatiles, the residue was taken up in pentane, filtered over diatomaceous earth and evaporated to dryness. Complex **7b** (650 mg, 68 %) was obtained as a crusty orange-red solid containing 66 mol% of pentane. **<sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):** δ = 27.0 (v<sub>1/2</sub> ≈ 3 Hz), 17.9 (v<sub>1/2</sub> ≈ 3 Hz). **<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):** δ = 8.28 (m, 2H, o of PPh<sub>2</sub>), 7.95 (m, 2H, o of PPh<sub>2</sub>), 7.72 (d, <sup>3</sup>J<sub>PH</sub> = 2.4 Hz, 1H, H3 of PAR overlapping with o of PAR), 7.68 (m, 2H, o of PPh<sub>2</sub> overlapping with H3 of PAR), 7.62 (d, <sup>3</sup>J<sub>PH</sub> = 2.6 Hz, 1H, H3 of PAR), 7.28 (m, 2H, m of PPh<sub>2</sub>), 7.19 (m, 1H, p of PPh<sub>2</sub>), 7.13 (m, 2H, o of PPh<sub>2</sub> overlapping with solvent signal), 7.06 (m, 1H, p of PPh<sub>2</sub>), 7.02 (m, 1H, p of PPh<sub>2</sub>), 6.97-6.90 (m, 4H, two m of PPh<sub>2</sub>

overlapping with p of PPh<sub>2</sub>), 6.89 (m, 1H, p of PPh<sub>2</sub> overlapping with m of PPh<sub>2</sub>), 6.82 (dd, <sup>3</sup>J<sub>PH</sub> = 16.5 Hz, <sup>4</sup>J<sub>HH</sub> = 2.4 Hz, 1H, H5 of PAR), 6.75 (dd, <sup>3</sup>J<sub>PH</sub> = 14.7 Hz, <sup>4</sup>J<sub>HH</sub> = 2.4 Hz, 1H, H5 of PAR overlapping with m of PPh<sub>2</sub>), 6.71 (m, 2H, m of PPh<sub>2</sub>), 6.46 (m, 1H, H2 of NAr), 6.41 (m, 1H, H3 of NAr), 6.26 (m, 1H, H3 of NAr), 6.19 (m, 1H, H2 of NAr), 3.44 (s, 6H, NMe<sub>2</sub>), 2.91 (s, 6H, NMe<sub>2</sub>), 1.76 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 1.34 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 1.24 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 1.17 (s, 9H, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>). **<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):** δ = 169.3 (d, <sup>2</sup>J<sub>PC</sub> = 3.3 Hz, C1 of PAR), 167.1 (d, <sup>2</sup>J<sub>PC</sub> = 1.3 Hz, C1 of PAR), 147.4 (dd, <sup>3</sup>J<sub>PC</sub> = 10.9 Hz, <sup>2</sup>J<sub>PC</sub> = 2.8 Hz, C1 of NAr), 144.1 (dd, <sup>3</sup>J<sub>PC</sub> = 19.7 Hz, <sup>2</sup>J<sub>PC</sub> = 2.9 Hz, C1 of NAr), 140.7 (d, <sup>3</sup>J<sub>CP</sub> = 7.7 Hz, C2 of PAR), 139.6 (d, <sup>3</sup>J<sub>CP</sub> = 8.2 Hz, C2 of PAR), 137.1 (d, <sup>3</sup>J<sub>CP</sub> = 15.5 Hz, C4 of PAR), 134.9 (d, <sup>2</sup>J<sub>CP</sub> = 8.9 Hz, o of PPh<sub>2</sub>), 134.3 (d, <sup>3</sup>J<sub>CP</sub> = 15.7 Hz, C4 of PAR overlapping with i of PPh<sub>2</sub>), 134.0 (d, <sup>1</sup>J<sub>PC</sub> = 89.4 Hz, i of PPh<sub>2</sub> overlapping with C4 of PAR and two o of PPh<sub>2</sub>), 134.0 (d, <sup>2</sup>J<sub>CP</sub> = 9.9 Hz, o of PPh<sub>2</sub> overlapping with i of PPh<sub>2</sub>), 133.7 (d, <sup>2</sup>J<sub>CP</sub> = 9.2 Hz, o of PPh<sub>2</sub> overlapping with i of PPh<sub>2</sub>), 132.8 (d, <sup>1</sup>J<sub>PC</sub> = 84.8 Hz, i of PPh<sub>2</sub> overlapping with o of PPh<sub>2</sub>), 132.6 (d, <sup>2</sup>J<sub>CP</sub> = 10.9 Hz, o of PPh<sub>2</sub> overlapping with i of PPh<sub>2</sub>), 131.8 (d, <sup>4</sup>J<sub>PC</sub> = 2.8 Hz, p of PPh<sub>2</sub> overlapping with i of PPh<sub>2</sub>), 131.7 (d, <sup>1</sup>J<sub>PC</sub> = 113.8 Hz, i of PPh<sub>2</sub> overlapping with four p of PPh<sub>2</sub>), 131.6 (d, <sup>4</sup>J<sub>PC</sub> = 2.6 Hz, p of PPh<sub>2</sub> overlapping with i of PPh<sub>2</sub>), 131.5 (m, two p of PPh<sub>2</sub> overlapping with i of PPh<sub>2</sub>), 130.1 (d, <sup>1</sup>J<sub>PC</sub> = 85.5 Hz, i of PPh<sub>2</sub>), 129.4 (d, <sup>2</sup>J<sub>CP</sub> = 13.0 Hz, C5 of PAR), 128.8 (d, <sup>3</sup>J<sub>PC</sub> = 7.7 Hz, m of PPh<sub>2</sub> overlapping with m of PPh<sub>2</sub> and C3 of PAR), 128.7 (d, <sup>3</sup>J<sub>PC</sub> = 5.8 Hz, m of PPh<sub>2</sub> overlapping with m of PPh<sub>2</sub> and C3 of PAR), 128.7 (d, <sup>4</sup>J<sub>PC</sub> = 2.5 Hz, C3 of PAR overlapping with two m of PPh<sub>2</sub>), 128.6 (d, <sup>4</sup>J<sub>PC</sub> = 1.8 Hz, C3 of PAR), 128.4 (d, <sup>3</sup>J<sub>PC</sub> = 11.9 Hz, m of PPh<sub>2</sub>), 128.1 (d, <sup>3</sup>J<sub>PC</sub> = 11.2 Hz, m of PPh<sub>2</sub>), 127.7 (d, <sup>2</sup>J<sub>CP</sub> = 14.2 Hz, C5 of PAR), 124.6 (m, C2 of NAr), 120.8 (d, <sup>4</sup>J<sub>PC</sub> = 1.4 Hz, C3 of NAr), 118.9 (d, <sup>3</sup>J<sub>PC</sub> = 9.1 Hz, C2 of NAr), 117.5 (d, <sup>4</sup>J<sub>PC</sub> = 1.5 Hz, C3 of NAr), 113.4 (d, <sup>1</sup>J<sub>CP</sub> = 127.2 Hz, C6 of PAR), 107.9 (d, <sup>1</sup>J<sub>CP</sub> = 108.2 Hz, C6 of PAR), 51.5 (bs, NMe<sub>2</sub>), 49.1 (s, NMe<sub>2</sub>), 36.1 (d, <sup>4</sup>J<sub>PC</sub> = 1.7 Hz, C of <sup>t</sup>Bu<sup>2</sup>), 35.6 (d, <sup>4</sup>J<sub>PC</sub> = 1.8 Hz, C of <sup>t</sup>Bu<sup>2</sup>), 34.3 (d, <sup>4</sup>J<sub>PC</sub> = 0.9 Hz, C of <sup>t</sup>Bu<sup>4</sup>), 34.0 (d, <sup>4</sup>J<sub>PC</sub> = 0.7 Hz, C of <sup>t</sup>Bu<sup>4</sup>), 31.8 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 31.7 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>4</sup>), 30.8 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>), 30.5 (s, CH<sub>3</sub> of <sup>t</sup>Bu<sup>2</sup>). **Elemental Analysis:** calculated for C<sub>62</sub>H<sub>76</sub>N<sub>4</sub>O<sub>2</sub>P<sub>2</sub>Ti(C<sub>5</sub>H<sub>12</sub>)<sub>0.66</sub>: C, 73.52; H, 7.93; N, 5.25. Found: C, 72.59; H, 7.70, 5.38.

#### Synthesis of complex **7c**

To a solution of **1cH<sub>2</sub>** (220 mg, 0.26 mmol) in 2ml pentane was added Ti(NMe<sub>2</sub>)<sub>4</sub> (58 mg, 0.26 mmol) under argon. After one night stirring at RT the orange precipitate was filtered and washed with pentane (2\*2ml) to give of **7c** as an orange solid (180 mg, 72% yield). **<sup>31</sup>P {<sup>1</sup>H} NMR (243MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):** δ = 34.4 (v<sub>1/2</sub> = 3.9 Hz), 30.3 (v<sub>1/2</sub> = 5.5 Hz). **<sup>1</sup>H NMR (600.2 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):** δ = 8.16 (dd, <sup>3</sup>J<sub>PH</sub> = 12.53 Hz, <sup>3</sup>J<sub>HH</sub> = 7.67 Hz, 2H, o of PPh<sub>2</sub>), 7.82-7.77 (m, 2H, o of PPh<sub>2</sub>), 7.76 (d, <sup>4</sup>J<sub>HH</sub> = 2.31 Hz, 1H, H3 of PAR), 7.74 (d, <sup>4</sup>J<sub>HH</sub> = 2.31 Hz, 1H, H3 of PAR), 7.59 (dd, <sup>3</sup>J<sub>PH</sub> = 8.88 Hz, <sup>3</sup>J<sub>HH</sub> = 7.34 Hz, 2H, o of PPh<sub>2</sub>), 7.49 (dd, <sup>3</sup>J<sub>PH</sub> = 8.94 Hz, <sup>3</sup>J<sub>HH</sub> = 7.32 Hz, 2H, o of PPh<sub>2</sub>), 7.22 (t, <sup>3</sup>J<sub>HH</sub> = 7.22 Hz, 2H, m of PPh<sub>2</sub>), 7.14-7.07 (m, 4H, 2m and 2p of PPh<sub>2</sub>), 7.06-6.95 (m, 6H, 2m and 2p of PPh<sub>2</sub> and 2H5 of PAR), 6.91 (t, <sup>3</sup>J<sub>HH</sub> = 7.60 Hz, 2H, m of PPh<sub>2</sub>), 4.18-4.04 (m, 1H, NCH<sub>2</sub>), 3.63-3.51 (m, 1H, NCH<sub>2</sub>), 3.34 (s, 6H, NMe<sub>2</sub>), 3.06-2.90 (m, 1H, NCH<sub>2</sub>), 2.91 (s, 6H, NMe<sub>2</sub>), 2.77-2.67 (m, 1H, NCH<sub>2</sub>), 1.81 (s, 9H, <sup>t</sup>Bu<sup>2</sup>), 1.63 (s, 9H, <sup>t</sup>Bu<sup>2</sup>), 1.28-1.21 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>), 1.23 (s, 9H, <sup>t</sup>Bu<sup>4</sup>), 1.20 (s, 9H, <sup>t</sup>Bu<sup>4</sup>). **<sup>13</sup>C NMR**

(150.9 MHz, C<sub>6</sub>D<sub>6</sub>, 300 K):  $\delta$  = 169.7 (s, C1 of PAR), 166.4 (s, C1 of PAR), 140.4 (d,  $^3J_{CP}$  = 7.5 Hz, C2 of PAR), 140.0 (d,  $^3J_{CP}$  = 8.2 Hz, C2 of PAR), 136.0 (d,  $^3J_{CP}$  = 15.1 Hz, C4 of PAR), 135.5 (d,  $^1J_{CP}$  = 91.8 Hz, Ci of PPh<sub>2</sub>), 134.4 (d,  $^2J_{CP}$  = 3.2 Hz, o of PPh<sub>2</sub>), 134.3 (d,  $^2J_{CP}$  = 2.9 Hz, o of PPh<sub>2</sub>), 133.4 (d,  $^3J_{CP}$  = 13.6 Hz, C4 of PAR), 133.3 (d,  $^1J_{CP}$  = 102.1 Hz, Ci of PPh<sub>2</sub>), 133.0 (d,  $^2J_{CP}$  = 9.7 Hz, o of PPh<sub>2</sub>), 132.0 (d,  $^2J_{CP}$  = 10.2 Hz, o of PPh<sub>2</sub>), 131.2 (d,  $^1J_{CP}$  = 89.4 Hz, Ci of PPh<sub>2</sub>), 131.1 (p of PPh<sub>2</sub>), 130.9 (p of PPh<sub>2</sub>), 130.7 (p of PPh<sub>2</sub>), 130.6 (d,  $^1J_{CP}$  = 87.2 Hz, Ci of PPh<sub>2</sub>), 130.5 (p of PPh<sub>2</sub>), 128.9 (d,  $^2J_{CP}$  = 10.9 Hz, C5 of PAR), 128.6-126.9 (overlapping 2C3 and C5 of PAR with m of PPh<sub>2</sub>), 111.4 (d,  $^1J_{CP}$  = 118.4 Hz, Ci of PAR), 115.8 (d,  $^1J_{CP}$  = 108.5 Hz, Ci of PAR), 51.1 (s, NMe<sub>2</sub>), 50.1 (s, NMe<sub>2</sub>), 46.5 (d,  $^2J_{CP}$  = 3.3 Hz, NCH<sub>2</sub>), 44.6 (d,  $^2J_{CP}$  = 4.4 Hz, NCH<sub>2</sub>), 35.8 (s, C of tBu<sup>2</sup>), 35.7 (s, C of tBu<sup>2</sup>), 33.9 (s, C of tBu<sup>4</sup>), 33.8 (s, C of tBu<sup>4</sup>), 33.2 (s, NCH<sub>2</sub>-CH<sub>2</sub>), 31.5 (s, CH<sub>3</sub>, tBu), 31.4 (s, CH<sub>3</sub>, tBu), 30.6 (s, CH<sub>3</sub>, tBu), 30.4 (s, CH<sub>3</sub>, tBu). **HRMS (ESI-pos)**: calculated for C<sub>56</sub>H<sub>69</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub>Ti<sup>+</sup> [M-2(NMe<sub>2</sub>)+OMe]<sup>+</sup>: 927.42574. Found: 927.42835 (+2.8 ppm).

#### Typical procedure for *rac*-lactide polymerization

In a glovebox, the catalyst (2.5·10<sup>-6</sup> mol, 1 equiv) and *rac*-lactide (100 equiv) were charged in a vial equipped with a Teflon<sup>TM</sup>-tight screw cap and toluene (for a 1M in *rac*-lactide) was added. Addition of <sup>i</sup>PrOH (1 equiv) is also done for selected runs. The resulting mixture was heated at the appropriate temperature under vigorous stirring for the desired time. The vial was then removed from the glovebox and the reaction mixture was quenched with pentane provoking the precipitation of the polymer, which was washed several times with pentane, dried *in vacuo* until constant weight. The sample was subsequently analyzed by <sup>1</sup>H NMR, GPC and by MALDI-TOF spectrometry.

#### Conflicts of interest

There are no conflicts to declare.

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#### Notes and references

§ Crystallographic C2 axis for **1aH<sub>2</sub>** while approximate C2 axis for **1cH<sub>2</sub>**

§§ Expanded uncertainties at the 95% confidence interval are estimated from the residual variance of the fit.

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