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Heteroscorpionate Rare-Earth Metal Zwitterionic Complexes: Syntheses, Characterization, and Heteroselective Catalysis on the Ring-Opening Polymerization of *rac*-Lactide

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Dedicated to Professor Christian Bruneau on the occasion of his 60th birthday

Abstract: Novel neutral phosphine-modified heteroscorpionate ligand $(3,5\text{-}Me_2Pz)_2CHPPh_2$ (**1**) and its derivatives oxophosphine (**2**) and iminophosphine (**3**) heteroscorpionates were synthesized for the first time. These neutral heteroscorpionate ligands displayed unique chemistry towards rare-earth metal tris(alkyl)s $[Ln(CH_2SiMe_3)_3(thf)_2]$ (Ln = Y, Lu, Sc). The reaction between compound **1** and $[Ln(CH_2SiMe_3)_3(thf)_2]$ afforded heteroscorpionate rare-earth metal trialkyl adduct complexes **4a–c**. Compounds **2** and **3** were treated with $[Ln(CH_2SiMe_3)_3(thf)_2]$ to give the unprecedented zwitterionic heteroscorpionate rare-earth metal dialkyls **5** and **6**, respectively. In the process, the heteroscorpionates transferred to the carbanions by means of methine C−H bond cleavage that was attributed to the presence of the electron-withdrawing groups. In addition the ligand and central metal showed a concerted effect on both the catalytic activity and specific selectivity of complexes **4–6** for the ring-opening polymerization (ROP) of *rac*-lactide (*rac*-LA). All the adduct complexes **4** were nonselective and gave atactic polylactide (PLA), probably due to the dissociation of ligand **1** from the active metal center during the polymerization. Strikingly, zwitterionic complexes **5** catalyzed rapid ROP of *rac*-LA to produce PLAs with heterotacticity up to 0.87. However, the zwitterionic complexes **6** were less active and less selective than **5**, which might be on account of the stronger coordination of the tetradentate ligand. Complexes **5** represent rare examples of the selective ROP of *rac*-LA mediated by rare-earth metal complexes supported by non-bisphenolate ligands.

Keywords: C−H activation · heteroscorpionates · polymerization · rare earths · zwitterions

Introduction

Well-defined rare-earth metal complexes have seen an upsurge in research interest because of their marvelous catalysis in polymerization reactions, especially ethylene homopolymerization and copolymerizations with α-olefins,[1] highly regio- or stereoselective polymerizations of conjugated dienes,[2] and polar monomers.[3] Note that landmark works are always attributed to the innovation of complexes that bear novel spectator ligands, to which the cyclopentadienyl (Cp) auxiliaries contribute a great deal.[4] In the meantime, non-Cp ligands such as amidinates, guanidinates, β-diketiminates, salicylaldiminates, and pincer-type compounds have attracted increasing attention over the past decade.[5–9] Heteroscorpionates derived from bis(pyrazolyl)methane are tripodal and amenable to structural modification by varying the substituents of the pyrazole rings and/or the functional group (Scheme 1).[10] Most research works concentrate on introducing protic functional groups to construct anionic heteroscorpionates that are six-electron donating and formally isolobal as cyclopentadienyls (Cp^-).[11] However, the neutral-group-substituted heteroscorpionate ligands are more promising because the apical hydrogen atom can be abstracted to form ambidentate carbanionic species that feature the characteristics of both Cp and non-Cp ligands. The carbanion species can coordinate to the central metal with apical carbanion in κ^1 mode or through the heteroatoms of the pyrazole and X group in κ^3 mode to form zwitterionic metal complexes that have been reported to possess special properties and unique catalysis.[12] Unfortunately, C−H acti-

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X = functional group
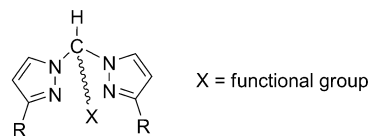
Scheme 1. Architecture of the heteroscorpionate ligand.

vation of the methine group is difficult. Thus the neutral heteroscorpionates and their coordination chemistry are explored less often. Only recently has Otero's group reported a carboxamide-functionalized anionic heteroscorpionate, the methide proton of which was abstracted when treated with neodymium tris(amide)s to afford a dimeric neodymium monoamido complex.[13]

Polylactides (PLAs) are very important synthetic biodegradable and biocompatible polymers derived from renewable resources,[14] which have found a range of applications such as packaging materials, delivery matrices for controlled release of drugs, and tissue engineering.[15] They are also promising substitutes for the widely used polyolefins from petrochemical feedstocks on account of their excellent physical and mechanical properties, which are intrinsically determined by the microstructures.[16] Therefore it is very important to find efficient catalysts for synthesizing PLAs with controllable structural parameters in terms of molecular weight, molecular-weight distribution, and especially the stereoregularity. However, stereocontrol in polymerization is very difficult; it requires the concerted influence of the metal center and the chelating ligands. Most efforts have been dedicated to metal catalysts based on main-group and d-block metals[14,17–21] such as aluminum, zinc, and so on, because these small-radius metal ions allow one to easily tune the spatial environment around the active metal centers by varying the coordinating ancillary that is believed to be responsible for the stereoselectivity. Be that as it may, few ligands such as bisphenolate or β-diiminate match these metal ions in achieving high stereoselectivity. Moreover, these catalysts usually suffer low activity even at high catalyst loadings and elevated temperatures. By contrast, discrete rare-earth metal complexes are highly active catalysts for the ring-opening polymerization (ROP) of rac-lactide (rac-LA) at room temperature, but are usually nonselective, which can be partly ascribed to the difficulty of finding "bulky" ligands with respect to the large rare-earth metal ions. Hitherto, stereoselective rare-earth metal complexes have been limited to those attached to sterically hindered cagelike bisphenolate auxiliaries.[22,23] Hence, the search for novel coordinating ligands for rare-earth metal complexes to achieve rapid selective polymerization is an attractive but very tough prospect.

Herein we report the preparation of novel phosphine-modified neutral heteroscorpionates. The ligands undergo apical methide C–H bond cleavage and transfer to carbanions when treated with strong basic rare-earth metal tris(alkyl)s, thus leading to the formation of unprecedented zwitterionic heteroscorpionate rare-earth metal dialkyl complexes. In addition, the zwitterionic complexes are highly active initiators for the ROP of rac-LA and, strikingly, produce heterotactic PLAs with a heterotacticity value (P_r) of 0.87. This represents a rare example of stereoselective metal-based initiators supported by ligands other than bisphenols.

Results and Discussion

Bis(3,5-dimethylpyrazolyl)methane was lithiated with an equimolar amount of *n*BuLi at −80 °C in THF.[24] The in situ generated lithium salt reacted with diphenylphosphine chloride to give the targeted [bis(3,5-dimethylpyrazolyl)methyl]diphenylphosphine compound (**1**) as white solids. When exposed to oxygen atmosphere or treated with organoazide compound, **1** transferred cleanly to the corresponding oxophosphine or iminophosphine derivatives **2** and **3** (Scheme 2).
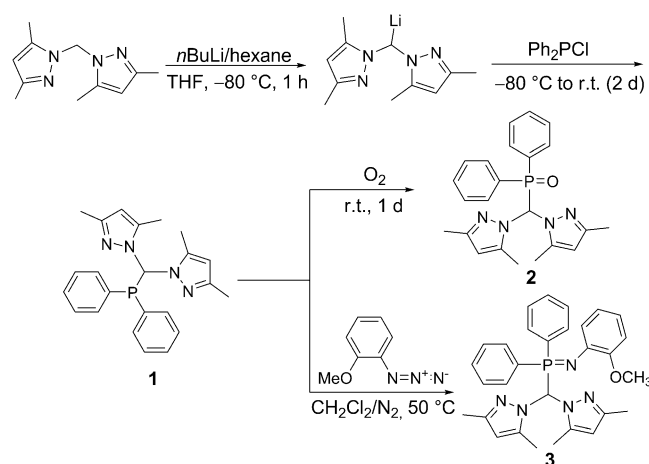
Scheme 2. Syntheses of heteroscorpionate ligands **1–3**.

The reaction between compound **1** and trialkyl rare-earth metal complexes [Ln(CH₂SiMe₃)₃(thf)₂] (Ln = Y, Lu, Sc) at low temperature afforded complexes **4a–c** (Scheme 3). The NMR spectra of these complexes have similar topology, which indicates that they are structural homologues. Take complex **4a**, for instance: the yttrium–methylene groups give a resonance at $\delta = 0.13$ ppm, whereas the apical methide proton of ligand shifts highfield from $\delta = 6.77$ to 6.0 ppm, thus indicating the chelation of yttrium by **1**. The 3:1 integral ratio of the above two moieties indicates that **4a** is an adduct of neutral heteroscorpionate and the yttrium tris(alkyl)s. It is interesting to observe that three trimethylsilyl groups give resonances at $\delta = 0.54$ and 0.40 ppm in an integral ratio of 2:1, thus suggesting their nonequivalent locations. X-ray diffraction analysis resolved the molecular structure of **4a** as shown in Figure 1. The heteroscorpionate ligand **1** facially chelates to the yttrium ion through the phosphorus atom and the two nitrogen atoms of the pyrazole rings in a κ³ mode. Three alkyl groups bond to the yttrium ion in *cis* positions. These ligands generate a six-coordinate distorted octahedral geometry around the central yttrium ion with P1 and C24 atoms occupying the apices and the N1, N3, C28, and C32 atoms forming the horizontal plane.

Treatment of the heteroscorpionate ligand **2** that bears an electron-withdrawing group with rare-earth metal tris(alkyl)s afforded the corresponding dialkyl derivatives **5** by
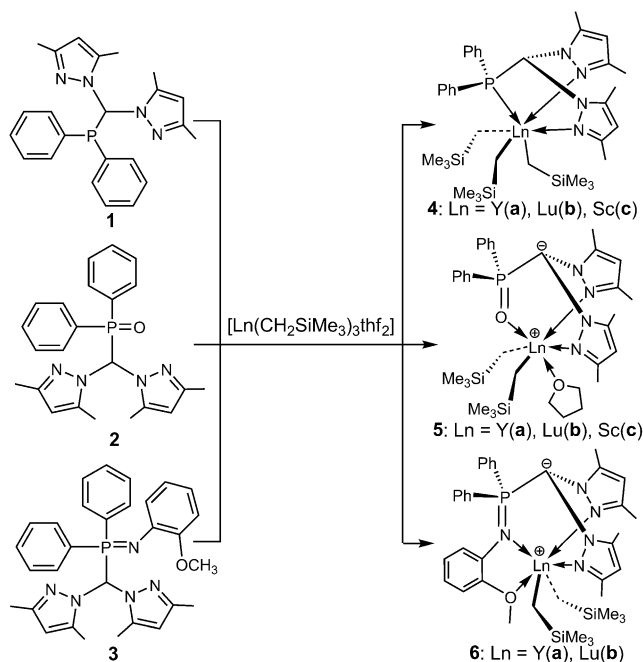
Scheme 3. Syntheses of heteroscorpionate rare-earth metal complexes **4**–**6**.

Figure 2. Molecular structure of complex **5a**. Hydrogen atoms have been omitted for clarity.
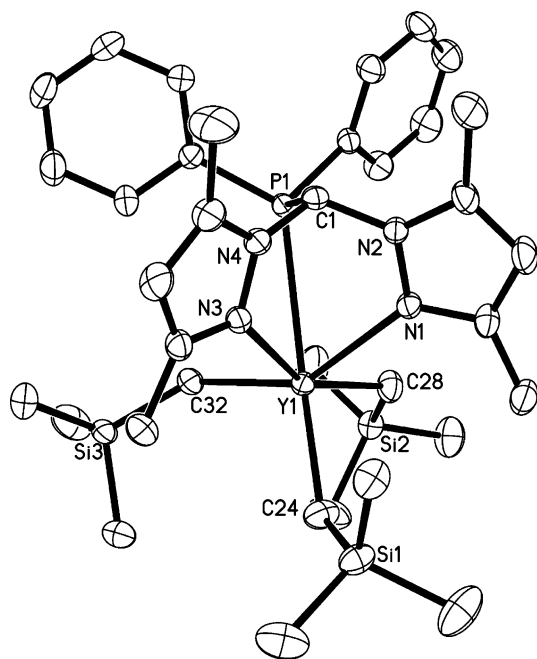

Figure 1. Molecular structure of complex **4a**. Hydrogen atoms have been omitted for clarity.

means of the C−H bond cleavage of the methide groups (Scheme 3). This was proven first by the ^{1}H NMR spectroscopic analysis that revealed the disappearance of the methanide protons in the ligands. The overall molecular structures of **5a**–**c** were defined by X-ray diffraction analysis, strikingly, as zwitterionic complexes (Figure 2, **5a**; for **5b**
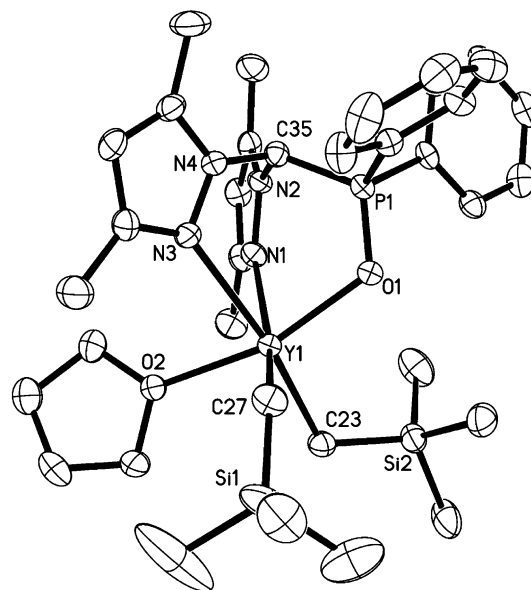
and **5c** see the Supporting Information). Transition-metal-based zwitterionic complexes have been explored widely that exhibited novel structures, electronic, magnetic, and nonlinear optical properties or unique catalysis.[12] To date, the only rare-earth-metal-based zwitterion was mentioned in a previous work as a formula [Sc{C(3,5-Me$_2$Pz)$_3$}Cl$_2$(thf)] without characterization.[25] Thus complexes **5a**–**c** represented the first well-defined rare-earth metal zwitterions. In **5a**, the heteroscorpionate carbanion does not directly bond to the yttrium ion but caps on it in a κ^3 fashion through the O1, N1, and N3 atoms. The two alkyl groups bond to yttrium against the carbanionic fragment. There is a thf solvent in the molecule. These ligands generate a distorted octahedral geometry around the yttrium ion with two oxygen atoms occupying the apices and the N1, N3, C23, and C27 atoms forming a basal plane. Moreover Y1, O1, and C35 define a mirror plane that bisects the molecule. The bond lengths of Y−C (2.430(5) and 2.414(5) Å) and Y−N (2.551(4) and 2.571(4) Å) are comparable to those of complex **4a**. The bond lengths of P=O and P−C are 1.5392(19) and 1.730(3) Å, respectively, which falls in the normal range for the bond lengths formed by these atoms.[26] The distance from C35 to the plane established by P1, N2, and N4 is 0.431 Å. Three angles of P1-C35-N2, P1-C35-N4, and N2-C35-N4 are 111.8(3), 115.4(3), and 111.7(4)°, respectively, slightly larger than 109.5°. These data suggest that C35 is sp^3 hybridized rather than sp^2. Furthermore, the distance of 3.451 Å from Y1 to C35 is apparently longer than that (2.903(7) Å) reported by Otero,[14] which indicates no bond linkage between them (covalent radii of yttrium and carbon are 1.9 and 0.68 Å). Thus, complex **5a** is a zwitterion with one negative charge that resides on C35 and a positive charge on Y1.

Similarly, reaction between heteroscorpionate **3** and [Ln-(CH$_2$SiMe$_3$)$_3$(thf)$_2$] (Ln = Y, Lu) resulted in zwitterionic heteroscorpionate dialkyl metal complexes **6a** and **6b**, which were structurally characterized by NMR spectra and single-crystal X-ray diffraction (Scheme 3 and Figure 3). Unlike
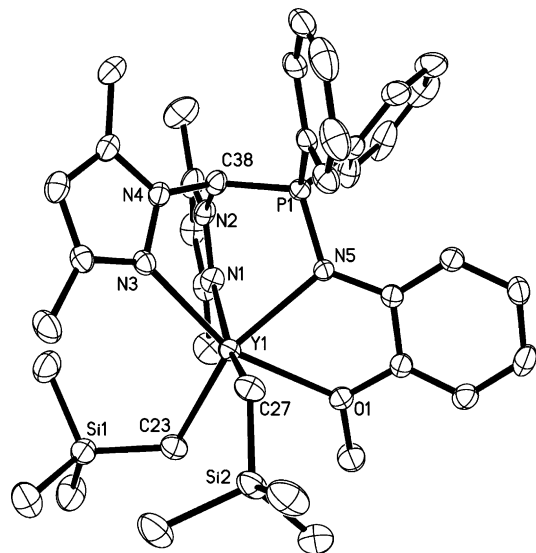

Figure 3. Molecular structure of complex **6a**. Hydrogen atoms have been omitted for clarity.

complexes **5**, complexes **6** were solvent-free on account of the coordination of the pendant methoxy group to the central metal ions (δ_{Y-OCH_3} = 4.21 ppm in complex **6a** and δ_{OCH_3} = 4.04 ppm in compound **3**). The carbanion ligand chelates to the yttrium ion through N1, N3, N5, and O1 in a κ^4 fashion (Figure 3).

These results suggest that the introduction of electron-withdrawing groups facilitates the C−H activation of the methine protons of the neutral phosphine heteroscorpionates, thus leading to the unprecedented zwitterionic heteroscorpionate rare-earth metal complexes, which also significantly influences the catalysis of the corresponding complexes (vide infra).

The ROPs of *rac*-LA catalyzed by heteroscorpionate metal complexes have been reported, which show good control of the molecular weight and the molecular-weight distribution.[13,27] However, many of them suffered low activity even at elevated temperatures. We

then investigated the catalysis of our heteroscorpionate metal complexes **4–6** for the ROP of *rac*-lactide. The representative data are listed in Table 1 and show that the polymerization was severely dependent on the ligand and the central metal. Compounds **4a** and **4b** completely transferred 300 equiv *rac*-LA to PLAs with moderate heterotacticity and medium molecular-weight distribution within 1 h at room temperature (runs 1 and 2). However, their scandium counterpart **4c** was absolutely inert even at prolonged reaction time (run 3). To explain these results, a blank polymerization by using the precursor [Sc(CH$_2$SiMe$_3$)$_3$(thf)$_2$] was carried out under the same conditions; it did not produce any PLA either. Similarly, the heterotacticities of PLAs obtained by using [Y(CH$_2$SiMe$_3$)$_3$(thf)$_2$] and [Lu(CH$_2$SiMe$_3$)$_3$(thf)$_2$] were close to those of PLAs obtained by **4a** and **4b** systems. Thus we suggested that in the polymerization process the neutral heteroscorpionate ligand probably dissociates from the metal center. From the viewpoint of hard/soft acid–base theory, phosphorus is a soft base, whereas rare-earth metal ion is a hard acid. Therefore the bonding between them is not sufficiently stable. Thus complexes **4a–c** are hemilabile. To our delight, complexes **5a–c** were robust, because the heteroscorpionate ligand chelates to metal ions through hard bases, and in addition, that coordination is reinforced by the electrostatic forces between them. These ensure the carbanion heteroscorpionate remained attached to the metal center during polymerization. As a result, complexes **5a** and **5b** not only initiated rapid ROP of *rac*-LA under the same conditions but also displayed remarkable heterotactic selectivity (P_r values were 0.81 for **5a** and 0.87 for **5b**, runs 4 and 5) relative to the previously reported heteroscorpionate metal complexes. This clearly demonstrated that the coordi-

Table 1. ROP of *rac*-LA by heteroscorpionate rare-earth metal complexes.[a]

rac-Lactide   Heterotactic Polylactide

Run	Cat	[LA]/[cat] (molar ratio)	Conversion [%]	M_n calcd[b] (10^4)	M_n[c] (10^4)	M_w/M_n[c]	P_r[d]
1	**4a**	300	100	1.4	4.1	1.5	0.67
2	**4b**	300	100	1.4	4.5	1.6	0.69
3[e]	**4c**	300	0				
4	**5a**	300	100	2.2	3.2	1.8	0.81
5	**5b**	300	100	2.2	4.6	1.8	0.87
6	**5c**	300	73	1.8	1.7	1.1	0.77
7	**5b**	400	100	2.9	5.7	1.7	0.86
8	**5b**	500	100	3.6	6.7	1.8	0.87
9	**5b**	700	100	5.0	8.4	1.7	0.86
10	**5b**	1000	100	7.2	11.2	1.8	0.85
11	**6a**	300	10	–	–	–	–
12	**6b**	300	7	–	–	–	–
13[f]	**6a**	300	95	2.1	2.6	1.3	0.68
14[f]	**6b**	300	85	1.8	2.7	1.3	0.7

[a] Conditions: 10 μmol catalyst, THF (5 mL), T = 20 °C, t = 1 h. [b] M_n calculated for initiation by each alkyl group. [c] Determined by GPC against polystyrene standard, M_n using a correcting factor for polylactides (0.58). [d] Determined by homonuclear decoupled ^{1}H NMR spectroscopy. [e] t = 20 h. [f] t = 5 h.

nating ancillary ligand played a significant role in stereoregularity control. Complex **5b** was potent even at higher monomer loadings. The molecular weight of the resulting PLA increased from 5.7×10^4 to 11.2×10^4 with the *rac*-LA-to-Lu ratio varying from 400 to 1000, and both the molecular-weight distribution (PDI = 1.7–1.8) and heterotacticity remained in narrow ranges ($P_r = 0.85$–0.87) (runs 5 and 7–10). Comparatively, scandium complex **5c** was less active and less heteroselective ($P_r = 0.77$) but provided PLA with narrow molecular-weight distribution ($M_w/M_n = 1.1$, run 6). The low activity of **5c** was consistent with previous reports on the ROP of lactide mediated by scandium-based complexes.[22b] To our surprise, zwitterionic dialkyl complexes **6a** and **6b** were less active than **5a** and **5b**. Under the same conditions, only traces of PLAs were isolated unless the polymerization time was prolonged to more than 20 h. The resulting PLAs had narrower molecular-weight distribution ($M_w/M_n = 1.3$) but lower heterotacticity ($P_r = 0.7$) than those obtained from **5a** and **5b** systems (runs 11–14). This could be explained by the much stronger coordination of methoxy group to the metal center in **6a** and **6b** than that of the solvated thf molecule in **5a** and **5b**. It is known that the thf coordination to the metal center is flexible and reversible, which is crucial for the alternating coordination of D-LA and L-LA monomers to the metal center, thus leading to heterotactic PLAs.[22c, 23b] The different heterotacticity of PLAs produced by **5** and **6** unambiguously supported that the coordination–insertion mechanism operated in the polymerization initiated by the metal–alkyl moiety, not anionic polymerization aroused by the carbanion. That means the heteroscorpionate carbanion kept binding to the metal ion during the polymerization as the Y—CH$_2$SiMe$_3$ active species nucleophilically attacked the carbonyl carbon of the coordinated LA molecule and cleavage of acyl-oxygen bond ensued. MALDI-TOF MS analysis of the oligomeric PLA obtained with **5b** revealed that the molecule chains are indeed capped by —CH$_2$SiMe$_3$ groups (see the Supporting Information).

Conclusion

We have demonstrated the preparation of new neutral phosphine heteroscorpionate and its oxophosphine and iminophosphine derivatives. The neutral phosphine heteroscorpionate reacted with rare-earth metal tris(alkyl)s to form adduct complexes that were highly active but nonselective for the ROP of *rac*-LA on account of the dissociation of the ligand from the metal center. However, the reaction between the rare-earth-metal tris(alkyl)s and oxophosphine (or iminophosphine) compound afforded the unprecedented zwitterionic heteroscorpionate rare-earth-metal dialkyl complexes. This was attributed to the presence of electron-withdrawing groups in the ligand that weaken the C—H bond. The zwitterionic complexes displayed high heteroselectivity for the ROP of *rac*-LA, which was governed by the bulky cagelike geometry of the heteroscorpionate ligand. This rep-

resents a rare example of stereoselective rare-earth-metal initiators supported by ligands other than bisphenols, which sheds new light on the design of specifically selective catalysts for the ROP of *rac*-LA and also facilitates further investigation of the mechanism.

Experimental Section

General procedures: All reactions were carried out in a glovebox filled with dry nitrogen. Hexane and toluene were purified using an SPS Braun system. THF was dried by distillation over sodium potassium alloy with benzophenone as indicator under a nitrogen atmosphere and was stored over freshly cut sodium in a glovebox. Rare-earth-metal tris(alkyl)s were synthesized according to a previous report.[1] Bis(3,5-dimethylpyrazolyl)-methane was synthesized according to the literature from 3,5-dimethylpyrazole and dichloromethane catalyzed by nBu$_4$NBr.[2] The molecular weight and molecular-weight distribution of the polymers were measured using a TOSOH HLC 8220 GPC instrument at 40°C with THF as eluent against polystyrene standards. Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox by the use of NMR spectroscopy tubes and then sealed by paraffin film. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AV400 or Bruker AV300 spectrometer. MALDI-TOF-MS analyses were performed by at the National Analytical Research Centre of the Changchun Institute of Applied Chemistry (CIAC).

X-ray crystallographic studies: Crystals for X-ray analysis were obtained as described in the following preparations. The crystals were manipulated in a glovebox. Data collection was performed at −86.5°C using a Bruker SMART APEX diffractometer with a CCD area detector and graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The determination of crystal class and unit-cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program.

ROP of *rac*-LA: A typical procedure for polymerization of *rac*-LA was performed in a 10 mL round flask in a glovebox. A solution of complex **4a** (7.4 mg, 10 μmol, [LA]/[Y] = 300:1) in THF (2 mL) was added to a stirred solution of D,L-LA (0.432 g, 3 mmol) in THF (3 mL). The polymerization took place immediately at room temperature. The system became viscous in a few minutes. It was stirred for 1 h and then was quenched by adding an excess amount of ethanol. The polymers were filtered, washed with ethanol, and then dried at 40°C for 24 h in vacuo to give polymer product (0.432 g, 100%). The molecular weight and the molecular-weight distribution of the resulting polymer were determined by GPC. The tacticity of the PLA was calculated according to the methine region homonuclear decoupling ^{1}H NMR spectrum.

Synthesis of 1: A solution of bis(3,5-dimethylpyrazolyl)methane (3.06 g, 15 mmol) in THF in an ampule was cooled down to −78°C, followed by slow addition of nBuLi in hexane (8.7 mL, 1.73 mol L^{-1}) with a syringe over 20 min under vigorous agitation, which immediately resulted in a white suspension. The mixture was stirred for another 1 h at this temperature. Then Ph$_2$PCl (2.7 mL, 15 mmol) was added dropwise over 10 min, which generated an orange solution. The reaction mixture warmed to room temperature and stirred for an additional 24 h to give a white suspension. Removal of the THF led to brown solids, followed by suspension in CH$_2$Cl$_2$ and suction filtration to generate orange solution. Brown solids were obtained after the removal of CH$_2$Cl$_2$ under reduced pressure at room temperature. Then they were suspended in a mixed CH$_2$Cl$_2$/hexane, followed by suction filtration to get the light-yellow pure product **1**. Another portion of product was obtained by concentrating the mother liquor (overall yield: 58%). ^{1}H NMR (300 MHz, CDCl$_3$): 7.29–7.16 (m, 10H; Ph−H), 6.77 (s, 1H; C−H), 5.68 (s, 2H; Pz−H), 2.21 (s, 6H; CH$_3$), 2.12 ppm (s, 6H; CH$_3$); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 148.32$ (s, 2C; $C^{3,3'}$ or $C^{5,5'}$), 140.47 (s, 2C; $C^{3,3'}$ or $C^{5,5'}$), 135.64, 135.42, 133.58, 133.32, 132.23, 131.99, 131.87, 129.35, 128.55, 128.47 (Ph), 107.11 (s, 1C, 2C;

$C^{4,4'}$), 73.0 (d, J(P,C) = 7.5 Hz, 1 C), 13.76 (s, 2 C; CH_3), 11.68 (s, 1 C; CH_3), 11.61 ppm (s, 1 C; CH_3); MS: m/z: 411.2 [M+Na]$^+$; elemental analysis calcd (%) for $C_{23}H_{25}N_4P$: C 71.12, H 6.49, N 14.42; found: C 71.02, H 6.35, N 14.31.

Synthesis of 2: Exposure of dichloromethane solution of compound **1** to oxygen at room temperature for 2 d gave rise to compound **2** (yield: 96 %). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.71 (s, 1 H; Ph–H), 7.68 (s, 1 H; Ph–H), 7.67 (s, 1 H; Ph–H), 7.65 (s, 1 H; Ph–H), 7.46 (t, J(H,H) = 7.5 Hz, 2 H; Ph–H), 7.40–7.34 (td, ^3J(H,H) = 7.5 Hz, ^4J(H,H) = 3.0 Hz, 4 H; Ph–H), 6.95 (d, J(H,P) = 8.4 Hz, 1 H; C–H), 5.74 (s, 2 H; Pz–H), 2.18 (s, 6 H; Pz–CH_3), 2.04 ppm (s, 6 H; Pz–CH_3); ^{13}C NMR: (75 MHz, CDCl$_3$): δ = 148.6 (s, 2 C; $C^{3,3'}$ or $C^{5,5'}$) , 142.0, 141.9 (s, 2 C; $C^{3,3'}$ or $C^{5,5'}$), 132.4, 132.3, 132.1, 132.0, 131.9, 130.6, 128.7, 128.5 (Ph), 107.7 (s, 2 C; $C^{4,4'}$), 73.5 (d, J-(P,C) = 82.5 Hz, 1 C), 13.8 (s, 2 C; CH_3), 11.6 ppm (s, 2 C; CH_3); ^{31}P NMR (161.9 MHz, CDCl$_3$): δ = 26.77 ppm (s, 1 P); MS: m/z: 405.2 [M+H]$^+$; elemental analysis calcd (%) for $C_{23}H_{25}N_4OP$: C 68.30, H 6.23, N 13.85; found: C 68.18, H 6.13, N 13.71.

Synthesis of compound 3: 2-Azidoanisole (9.5 mmol) in dichloromethane (10 mL) was added dropwise to a stirred solution of **1** (9.5 mmol) in dichloromethane (20 mL) in a glovebox. The resulting reddish-brown solution was stirred for 1 d followed by heating at 50 °C for another day under N$_2$ atmosphere. The reaction mixture was concentrated under reduced pressure to approximately 10 mL. Then it was added dropwise to stirred ethyl acetate (50 mL) to generate a brown suspension. After filtration, a gray solid was obtained, which was washed by a small amount of ethyl acetate, followed by drying under reduced pressure at room temperature (yield: 74 %). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.61–7.40 (m, 10 H; Ph–H), 6.77 (td, J(H,H) = 7.5 Hz, 1 H; Ar–H), 6.65 (td, 1 H, ^3J-(H,H) = 7.5 Hz, ^4J(H,H) = 1.5 Hz; Ar–H), 6.48 (td, ^3J(H,H) = 7.5 Hz, ^4J-(H,H) = 1.5 Hz, 1 H; Ar–H), 6.41 (d, J(H,H) = 7.5 Hz, 1 H; Ar–H), 6.28 (s, 1 H, CH), 5.67 (s, 2 H; Pz–H), 4.04 (s, 3 H; ArOCH_3), 2.47 (s, 6 H; Pz–CH_3), 1.91 ppm (s, 6 H; Pz–CH_3); ^{13}C NMR (100 MHz, CDCl$_3$) δ = 152.4, 152.2, 151.5, 139.3, 137.9, 132.9, 131.9, 131.8, 128.9, 128.8, 125.4, 124.6, 122.2, 122.1, 120.6, 118.6, 109.7, 106.2, 65.6, 64.5, 55.3, 13.7, 10.6 ppm; MS: m/z: 510.2 [M+H]$^+$; elemental analysis calcd (%) for $C_{30}H_{32}N_5OP$: C 70.71, H 6.33, N 13.74; found: C 70.58, H 6.22, N 13.65.

Synthesis of 4a: Trialkyl yttrium complex [Y(CH$_2$SiMe$_3$)$_3$(thf)$_2$] (0.2 g, 0.4 mmol) was dissolved in dry hexane and cooled to -30 °C. A toluene suspension of compound **1** at -30 °C was added into the stirred trialkyl yttrium solution. After overnight reaction at this temperature, the reaction mixture was concentrated to a small portion. Colorless crystals precipitated at the bottom of the bottle from a saturated toluene/hexane solution. The solids were dried in vacuo at room temperature to give complex **4a** in 62 % yield. ^{1}H NMR (C$_6$D$_6$, 25 °C, 300 MHz): δ = 7.13–7.13 (m, 4 H; Ph–H), 6.92 (m, 6 H; Ph–H), 6.0 (d, 1 H; C–H), 5.17 (s, 2 H; Pz–H), 2.54 (s, 6 H; CH_3), 1.32 (s, 6 H; CH_3), 0.54 (s, 18 H; Si–(CH_3)$_3$), 0.4 (s, 9 H; Si–(CH_3)$_3$), 0.13 ppm (s, 6 H; Y–CH_2); ^{13}C NMR (C$_6$D$_6$, 25 °C, 100 MHz): δ = 154.1 (s; $C^{3,3'}$ or $C^{5,5'}$), 140.6 (s; $C^{3,3'}$ or $C^{5,5'}$), 134.3, 134.1, 131.7, 129.6, 129.5 (Ph), 108.3 (s; $C^{4,4'}$), 68.3 (s; P–C), 38.1 (d, J(Y,C) = 100 Hz; Y–C), 36.1 (d, J(Y,C) = 100 Hz; Y–C), 15.8 (s; CH_3), 10.9 (s; CH_3), 5.7 (s; Si(CH_3)$_3$), 5.4 ppm (s; Si(CH_3)$_3$); ^{31}P NMR (C$_6$D$_6$, 25 °C, 161.9 MHz): δ = 1.05 ppm; elemental analysis calcd (%) for $C_{35}H_{58}N_4PSi_3Y$: C 56.88, H 7.91, N 7.58; found: C 56.78, H 7.79, N 7.48. Single crystals suitable for X-ray analysis were obtained from saturated toluene/hexane solution at -30 °C.

Complex 5a: Yield: 57 %; ^{1}H NMR (C$_6$D$_6$, 25 °C, 300 MHz): δ = 8.07 (s, 4 H; Ph–H), 7.06–6.97 (m, 6 H; Ph–H), 5.40 (s, 2 H; Pz–H), 3.61 (s, 4 H; THF), 2.16 (s, 6 H; Pz–CH_3), 2.10 (s, 6 H; Pz–CH_3), 1.23 (s, 4 H; THF), 0.61 (s, 18 H; Si–(CH_3)$_3$), -0.11 ppm (s, 4 H; Y–CH_2); ^{13}C NMR (C$_6$D$_6$, 25 °C, 100 MHz): δ = 148.8, 145.2, 145.1 ($C^{3,3'}$ and $C^{5,5'}$), 132.7, 132.6, 131.5 (Ph), 105.0 ($C^{4,4'}$), 70.6 (THF), 67.3 (*ipso-C*–P), 31.4(Y–CH_2), 31.0 (Y–CH_2), 25.2 (THF), 14.5 (3-CH_3–Pz), 12.2 (5-CH_3–Pz), 5.0 ppm (Si-(CH_3)$_3$); ^{31}P NMR (C$_6$D$_6$, 25 °C, 161.9 MHz): δ = 34.24 ppm; elemental analysis calcd (%) for $C_{35}H_{54}N_4O_2PSi_2Y$ (%): C 56.89, H 7.37, N 7.58; found: C 56.78, H 7.29, N 7.50. Single crystals suitable for X-ray analysis were obtained from saturated toluene/hexane solution at -30 °C.

Complex 6a: Yield: 47 %; ^{1}H NMR (400 MHz, CDCl$_3$, 25 °C): δ = 7.49 (br, 4 H; Ph–H), 6.92 (br, 6 H; Ph–H), 6.60 (d, J = 6 Hz, 1 H; Ph–H), 6.51

(t, J = 6 Hz, 1 H; Ph–H), 6.41 (t, J = 6 Hz, 1 H; Ph–H), 6.14, (d, J = 6 Hz, 1 H; Ph–H) 5.35 (s, 2 H; Pz–H), 4.21 (s, 3 H; OCH_3), 2.45 (s, 6 H; Pz–CH_3), 1.76 (s, 6 H; Pz–CH_3), 0.39 (s, 18 H; Si(CH_3)$_3$), 0.07 (d, J = 3 Hz, 1 H; Y–CH_2), 0.03 (d, J = 3 Hz, 1 H; Y–CH_2), -0.07 (d, J = 3 Hz, 1 H; Y–CH_2), -0.10 ppm (d, J = 3 Hz, 1 H; Y–CH_2); ^{13}C NMR (75 MHz, C$_6$D$_6$) δ = 152.7 (d, J = 16.5 Hz, 1 C; $C^{3,3'}$ or $C^{5,5'}$) 149.7 (s, 2 C; $C^{3,3'}$ or $C^{5,5'}$), 146.0 (d, J = 6.75 Hz, 2 C; Ph), 139.8 (d, J = 9 Hz, 1 C; Ph), 132.9 (d, J = 9 Hz, 4 C; Ph), 131.7 (d, J = 2.25 Hz, 2 C; Ph), 127.0 (s, 1 C; Ph), 123.4 (s, 1 C; Ar), 121.4 (d, J = 10.5 Hz, 1 C; Ar), 118.5 (s, 1 C; Ar), 111.3 (s, 1 C; Ar), 105.5 (s, 2 C; $C^{4,4'}$), 68.0 (s, 1 C; *ipso-C*), 59.16 (s, 1 C; OCH_3), 34.1 (s, 1 C; Y–CH_2), 33.6 (s, 1 C; Y–CH_2), 15.1 (s, 2 C; 3-CH_3–Pz), 11.9 (s, 2 C; 5-CH_3–Pz), 5.0 ppm (s, 6 C; Si(CH_3)$_3$); ^{31}P NMR (C$_6$D$_6$, 25 °C, 161.9 MHz): δ = 13.63 ppm; elemental analysis calcd (%) for $C_{38}H_{53}N_5OPSi_2Y$: C 59.13, H 6.92, N 9.07; found: C 59.07, H 6.83, N 8.96. Single crystals suitable for X-ray structural analysis were grown from mixed hexane/THF solution at -30 °C.

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