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Group 4 metal complexes with new chiral pincer NHC-ligands: synthesis, structure and catalytic activity†

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Chiral group 4 NHC–metal complexes were prepared in good yields by amine elimination from $M(NR_2)_4$ (M = Ti, Zr, Hf; R = Me, Et) and chiral pincer NHC-ligands, **L4** (**L4a** and **L4b**), **L5** and **L6**, which are derived from (*S*,*S*)-diphenyl-1,2-ethanediamine. Treatment of $M(NR_2)_4$ with 1 equiv. of **L4** in THF gives, after recrystallization from a benzene solution, the chiral titanium amides (**L4**)Ti(NMe_2)(Br)(THF) (**7**) and (**L4**)Ti(NMe_2)(Cl)(THF) (**11**), zirconium amides (**L4**)Zr(NMe_2)(Br)(THF) (**8**), (**L4**)Zr(NEt_2)(Br)(THF) (**10**), (**L4**)Zr(NMe_2)(Cl)(THF) (**12**) and (**L4**)Zr(NEt_2)(Cl)(THF) (**14**), and hafnium amides (**L4**)Hf(NMe_2)(Br)(THF) (**9**) and (**L4**)Hf(NMe_2)(Cl)(THF) (**13**), respectively. Similarly, the reactions of **L5** or **L6** with 1 equiv. of $M(NR_2)_4$ yield the titanium amide (**L6**)Ti(NMe_2)(Cl)(THF) (**16**), the zirconium amides (**L5**)Zr(NMe_2)(Cl)(THF) (**15**), (**L6**)Zr(NMe_2)(Cl)(THF) (**17**) and (**L6**)Zr(NEt_2)(Cl)(THF) (**19**), and the hafnium amide (**L6**)Hf(NMe_2)(Cl)(THF) (**18**), respectively. Complexes **7–19** were characterized by various spectroscopic techniques and elemental analyses. The molecular structures of **10** and **14–19** were also established by X-ray diffraction analyses, which represent the first example of the structurally characterized group 4 chiral NHC–metal complex. Furthermore, **7–19** are active catalysts for the polymerization of *rac*-lactide in the presence of isopropanol, leading to the heterotactic-rich polylactides.

Introduction

Biodegradable polymers derived from renewable resources such as polylactides have received much attention over the past decade because of their attractive physical and mechanical properties.[1] In addition, the chain stereochemistry determines the polymer properties and the rate of degradation.[2] For example, whereas the enantiopure polylactide melts at 180 °C, a much higher melting temperature (230 °C) is found for stereocomplex polymers formed by an equivalent mixture of poly(L-lactide) and poly(D-lactide).[3] Therefore, the polymerization of *rac*-lactide with stereoselective catalysts remains a challenge and an opportunity for chemists. To date, numerous reviews have covered catalyst systems for the ring-opening polymerization (ROP) of cyclic esters based on metals such as magnesium, zinc, calcium, aluminum, lanthanides, tin, group 4 metals, germanium, indium and iron,[1d,4] but among these, the chiral group 4 catalysts are especially promising.[5] Unfortunately, compared to other metals, structurally well-characterized chiral group 4 complexes that initiate the controlled ring-opening polymerization of lactides are still scarce.[5]

In recent years, transition-metal complexes with chiral N-heterocyclic carbene (NHC) ligands have become increasingly popular because of their stability to air and moisture and their strong σ-donating, but poor π-accepting abilities.[6] An additional driving force is the longstanding interest in catalysts for enantioselective reactions such as olefin metathesis,[7] conjugate addition of enones,[8] allylic alkylations,[9] olefin hydrogenations[10] and hydrosilylations.[11] Encouraged by the attractive features of chiral NHC-ligands in general, we are now focusing on the preparation of group 4 metal complexes coordinated by chiral multi-dentate NHC-ligands, and to our knowledge no chiral group 4 metal NHC-catalyst has yet been structurally authenticated.[6,12] More recently, we have designed and prepared a new series of tridentate chiral pincer NHC-ligands **L4–L6** from (*S*,*S*)-diphenyl-1,2-ethanediamine, and found them to be useful ligands for group 4 metals, which are potential catalysts for the polymerization of lactides. Herein, we report on the synthesis of these chiral NHC-ligands, their use in group 4 chemistry, and the application of the resulting

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complexes as catalysts in the polymerization of *rac*-lactide (*rac*-LA).

Experimental

General methods

Group 4 complexes and catalytic reactions were performed under an atmosphere of dry dinitrogen with rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or a glovebox. All organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Racemic lactide (*rac*-LA) was recrystallized twice from dry toluene and then sublimed under vacuum prior to use. All chemicals were purchased from Aldrich Chemical Co. and Beijing Chemical Co. and used as received unless otherwise noted. Infrared spectra were obtained from KBr pellets on an Avatar 360 Fourier transform spectrometer. Molecular weights of the polymer were estimated by gel permeation chromatography (GPC) using a PL-GPC 50 apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 500 spectrometer at 500 and 125 MHz, respectively. All chemical shifts are reported in δ units with reference to the residual protons of the deuterated solvents for proton and carbon chemical shifts. Melting points were measured on X-6 melting point apparatus and were uncorrected. Elemental analyses were performed on a Vario EL elemental analyzer.

Syntheses

Preparation of 1. Salicylaldehyde (1.22 g, 10.0 mmol) was mixed with (*S*,*S*)-diphenyl-1,2-ethanediamine (1.06 g, 5.0 mmol) in absolute ethanol (30 mL) and stirred for 4 h at room temperature. $NaBH_4$ (2.00 g, 52.6 mmol) was added in small portions at 0 °C, and the solution was then warmed to 50 °C and kept at this temperature for 2 h. The solvent was removed, the residue was treated with H_2O (20 mL), extracted with ethyl acetate (20 mL × 3) and washed with brine (20 mL). The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue was further purified by flash column chromatography (hexane–ethyl acetate = 10 : 1) to give **1** as a colorless oil. Yield: 2.01 g (95%) (Found: C, 79.12; H, 6.60; N, 6.64. $C_{28}H_{28}N_2O_2$ requires: C, 79.22; H, 6.65; N, 6.60%). ^{1}H NMR (C_6D_6): δ 7.14–7.07 (m, 4H, aryl), 6.91 (m, 6H, aryl), 6.68 (m, 2H, aryl), 6.58 (m, 2H, aryl), 6.52 (m, 4H, aryl), 3.57 (s, 2H, C*H*), 3.51 (d, J = 13.8 Hz, 2H, CH_2), 3.19 (d, J = 13.8 Hz, 2H, CH_2); N*H* and O*H* protons were not observed. ^{13}C NMR (C_6D_6): δ 158.9, 138.3, 129.4, 129.0, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 66.7, 50.1. IR (KBr, cm^{-1}): $\bar{\nu}$ 3427 (s), 2853 (w), 1616 (s), 1588 (s), 1489 (s), 1454 (s), 1251 (s), 755 (s).

Preparation of 2. This compound was prepared as colorless oil from the reaction of 3-*tert*-butylsalicylaldehyde (1.78 g, 10.0 mmol) with (*S*,*S*)-diphenyl-1,2-ethanediamine (1.06 g, 5.0 mmol) in absolute ethanol (30 mL) at room temperature, followed by reduction with $NaBH_4$ (2.00 g, 52.6 mmol) in ethanol, and purification by flash column chromatography (hexane–ethyl acetate = 10 : 1) by a similar procedure as outlined in the synthesis of **1**. Yield: 2.47 g (92%) (Found: C, 80.53; H, 8.30; N, 5.30. $C_{36}H_{44}N_2O_2$ requires: C, 80.56; H, 8.26; N, 5.22%). ^{1}H NMR (C_6D_6): δ 10.84 (s, 2H, O*H*), 7.21–7.09 (m, 12H, aryl), 6.62 (m, 4H, aryl), 4.06 (s, 2H, C*H*), 3.78 (d, J = 13.4 Hz, 2H, CH_2), 3.59 (d, J = 13.4 Hz, 2H, CH_2), 3.33 (s, 2H, N*H*), 1.38 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 156.1, 137.1, 135.7, 127.1, 126.8, 126.7, 126.6, 126.4, 125.7, 125.2, 121.7, 117.6, 65.6, 49.4, 33.7, 28.6. IR (KBr, cm^{-1}): $\bar{\nu}$ 3427 (s), 2957 (s), 1590 (m), 1437 (s), 1389 (m), 1235 (s), 1087 (s), 749 (s).

Preparation of 3. This compound was prepared as colorless oil from the reaction of 3,5-di-*tert*-butyl-salicylaldehyde (2.34 g, 10.0 mmol) with (*S*,*S*)-diphenyl-1,2-ethanediamine (1.06 g, 5.0 mmol) in absolute ethanol (30 mL) at room temperature, followed by reduction with $NaBH_4$ (2.00 g, 52.6 mmol) in ethanol, and purification by flash column chromatography (hexane–ethyl acetate = 10 : 1) by a similar procedure as outlined in the synthesis of **1**. Yield: 2.92 g (90%) (Found: C, 81.40; H, 9.40; N, 4.30. $C_{44}H_{60}N_2O_2$ requires: C, 81.43; H, 9.32; N, 4.32%). ^{1}H NMR (C_6D_6): δ 7.08–7.01 (m, 10H, aryl), 6.97 (d, J = 2.1 Hz, 2H, aryl), 6.55 (d, J = 2.1 Hz, 2H, aryl), 3.84 (d, J = 5.2 Hz, 2H, CH_2), 3.72 (s, 2H, C*H*), 3.42 (d, J = 5.2 Hz, 2H, CH_2), 1.25 (s, 18H, C(CH_3)$_3$), 1.08 (s, 18H, C(CH_3)$_3$); N*H* and O*H* protons were not observed. ^{13}C NMR (C_6D_6): δ 154.0, 149.4, 142.3, 142.2, 139.8, 137.5, 135.3, 127.3, 127.1, 127.0, 126.9, 126.8, 66.1, 50.3, 34.4, 33.3, 30.9, 29.1. IR (KBr, cm^{-1}): $\bar{\nu}$ 3428 (s), 2960 (s), 1604 (m), 1480 (s), 1233 (s), 875 (s).

Preparation of L4a. Compound **1** (2.00 g, 4.71 mmol), NH_4Br (0.69 g, 7.07 mmol) and triethyl orthoformate (15 mL) were heated at 120 °C for one day. After the reaction mixture was cooled to room temperature, diethyl ether (40 mL) was added to precipitate a colorless solid, which was filtered and washed with diethyl ether to give **L4a** as a colorless solid. Yield: 2.23 g (92%) (Found: C, 67.54; H, 5.30; N, 5.42. $C_{29}H_{27}N_2BrO_2$ requires: C, 67.58; H, 5.28; N, 5.43%). M.p.: 273–275 °C. ^{1}H NMR (DMSO-d_6): δ 10.17 (s, 2H, O*H*), 9.13 (s, 1H, NC*H*N), 7.40 (m, 6H, aryl), 7.17 (m, 6H, aryl), 6.95 (m, 4H, aryl), 6.75 (m, 2H, aryl), 4.83 (d, J = 14.3 Hz, 2H, CH_2), 4.70 (s, 2H, C*H*), 4.10 (d, J = 14.3 Hz, 2H, CH_2). ^{13}C NMR (DMSO-d_6): δ 158.3, 156.0, 135.8, 130.8, 130.3, 129.5, 129.4, 127.0, 119.1, 118.7, 115.6, 71.5, 45.9. IR (KBr, cm^{-1}): $\bar{\nu}$ 3435 (m), 3175 (s), 2927 (m), 1648 (s), 1599 (s), 1461 (s), 1373 (s), 1277 (s), 1106 (s), 757 (s).

Preparation of L4b. This compound was prepared as a colorless solid from the reaction of **1** (2.00 g, 4.71 mmol), NH_4Cl (0.38 g, 7.07 mmol) and triethyl orthoformate (15 mL) at 120 °C, followed by washing with diethyl ether by a similar procedure as described for the synthesis of **L4a**. Yield: 2.11 g (95%) (Found: C, 73.90; H, 5.78; N, 5.93. $C_{29}H_{27}N_2ClO_2$ requires: C, 73.95; H, 5.78; N, 5.95%). M.p.: 260–262 °C. ^{1}H NMR (DMSO-d_6): δ 10.48 (s, 2H, O*H*), 9.20 (s, 1H, NC*H*N), 7.38 (m, 6H, aryl), 7.17 (m, 6H, aryl), 7.07 (m, 2H, aryl), 6.93 (m, 2H, aryl), 6.72 (m, 2H, aryl), 4.85 (d, J = 14.3 Hz, 2H, CH_2), 4.68 (s, 2H, C*H*), 4.09 (d, J = 14.3 Hz, 2H, CH_2). ^{13}C NMR (DMSO-d_6): δ 158.3, 156.2, 135.9, 130.7, 130.1, 129.5, 129.4, 127.1, 119.0, 118.7, 115.8, 71.5, 46.0. IR (KBr, cm^{-1}): $\bar{\nu}$ 3424 (m),

3093 (s), 2954 (m), 1648 (s), 1600 (s), 1461 (s), 1374 (s), 1277 (s), 1197 (s), 1108 (s), 757 (s).

Preparation of L5. This compound was prepared as a colorless solid from the reaction of **2** (2.00 g, 3.73 mmol), NH_4Cl (0.30 g, 5.60 mmol) and triethyl orthoformate (15 mL) at 120 °C, followed by washing with diethyl ether by a similar procedure as described for the synthesis of **L4a**. Yield: 1.83 g (84%) (Found: C, 76.21; H, 7.43; N, 4.82. $C_{37}H_{43}N_2ClO_2$ requires: C, 76.20; H, 7.43; N, 4.80%). M.p.: 240–242 °C. ^{1}H NMR (DMSO-d_6): δ 9.25 (s, 1H, NC*H*N), 9.10 (s, 2H, O*H*), 7.41–7.32 (m, 6H, aryl), 7.21 (m, 2H, aryl), 7.10 (m, 4H, aryl), 6.70 (m, 4H, aryl), 5.33 (d, J = 14.6 Hz, 2H, CH_2), 4.54 (s, 2H, C*H*), 4.17 (d, J = 14.6 Hz, 2H, CH_2), 1.40 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): δ 166.0, 157.0, 154.3, 139.5, 136.0, 129.5, 129.3, 129.0, 127.4, 127.0, 121.9, 120.3, 71.2, 47.0, 34.5, 29.7. IR (KBr, cm^{-1}): $\bar{\nu}$ 3412 (m), 3090 (s), 2956 (s), 1638 (s), 1589 (m), 1438 (s), 1378 (s), 1208 (s), 1093 (s), 752 (s). Colorless crystals of **2**(**L5**)·C_6H_6 suitable for X-ray structural analysis were grown from a benzene solution.

Preparation of L6. This compound was prepared as a colorless solid from the reaction of **3** (2.00 g, 3.08 mmol), NH_4Cl (0.25 g, 4.62 mmol) and triethyl orthoformate (15 mL) at 120 °C, followed by washing with diethyl ether by a similar procedure as in the synthesis of **L4a**. Yield: 1.84 g (86%) (Found: C, 77.69; H, 8.53; N, 4.05. $C_{45}H_{59}N_2ClO_2$ requires: C, 77.72; H, 8.55; N, 4.03%). M.p.: 235–237 °C. ^{1}H NMR (DMSO-d_6): δ 9.22 (s, 1H, NC*H*N), 8.84 (s, 2H, O*H*), 7.34 (m, 2H, aryl), 7.31 (m, 4H, aryl), 7.18 (d, J = 2.0 Hz, 2H, aryl), 7.04 (m, 4H, aryl), 6.61 (d, J = 2.0 Hz, 2H, aryl), 5.32 (d, J = 14.5 Hz, 2H, CH_2), 4.44 (s, 2H, C*H*), 4.17 (d, J = 14.6 Hz, 2H, CH_2), 1.38 (s, 18H, C(CH_3)$_3$), 1.14 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (DMSO-d_6): δ 157.0, 151.8, 141.8, 138.5, 135.9, 129.5, 129.2, 127.2, 125.9, 123.9, 120.8, 71.1, 47.4, 34.7, 33.7, 31.2, 29.7. IR (KBr, cm^{-1}): $\bar{\nu}$ 3422 (w), 3085 (w), 2957 (s), 1637 (s), 1482 (s), 1362 (m), 1201 (s), 699 (s).

Preparation of (L4)Ti(NMe$_2$)(Br)(THF) (7). While stirring a THF solution (5 mL) of Ti(NMe$_2$)$_4$ (0.11 g, 0.50 mmol) was slowly added to a THF (15 mL) suspension of **L4a** (0.26 g, 0.50 mmol) at room temperature. After this mixture was stirred overnight at room temperature, the solution was filtered and the solvent was removed under reduced pressure. The resulting red solid was recrystallized from a benzene solution to give **7** as red microcrystals. Yield: 0.25 g (74%) (Found: C, 61.96; H, 5.62; N, 6.25. $C_{35}H_{38}N_3BrO_3Ti$ requires: C, 62.14; H, 5.66; N, 6.21%). M.p.: 145–147 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.19 (m, 2H, aryl), 6.93 (m, 2H, aryl), 6.85 (m, 4H, aryl), 6.70 (m, 4H, aryl), 6.55 (m, 6H, aryl), 4.56 (br s, 1H, C*H*), 4.38 (m, 3H, C*H* and CH_2), 3.74 (s, 6H, NCH_3), 3.67 (m, 4H, THF), 3.49 (br s, 2H, CH_2), 1.41 (m, 4H, THF). ^{13}C NMR (C_6D_6): δ 208.4, 164.3, 163.8, 136.6, 129.4, 128.9, 128.6, 128.2, 127.8, 118.8, 118.1, 117.8, 75.1, 68.0, 53.1, 48.1, 25.0. IR (KBr, cm^{-1}): $\bar{\nu}$ 2962 (m), 1593 (s), 1482 (s), 1450 (s), 1260 (s), 1108 (s), 1034 (s), 886 (s), 799 (s).

Preparation of (L4)Zr(NMe$_2$)(Br)(THF) (8). This compound was prepared as pale yellow microcrystals from the reaction of **L4a** (0.26 g, 0.50 mmol) with Zr(NMe$_2$)$_4$ (0.14 g, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.24 g (68%) (Found: C, 58.27; H, 5.42; N, 5.80. $C_{35}H_{38}N_3BrO_3Zr$ requires: C, 58.40; H, 5.32; N, 5.84%). M.p.: 177–179 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.20 (m, 2H, aryl), 6.90 (m, 8H, aryl), 6.68 (m, 8H, aryl), 4.54 (br s, 2H, CH_2), 3.80 (m, 6H, CH_2 and THF), 3.38 (m, 8H, CH and NCH_3), 1.36 (m, 4H, THF). ^{13}C NMR (C_6D_6): δ 209.0, 162.1, 138.1, 137.8, 137.2, 129.3, 129.2, 128.3, 125.7, 119.5, 119.2, 118.8, 117.9, 75.4, 69.4, 47.0, 45.5, 24.8. IR (KBr, cm^{-1}): $\bar{\nu}$ 2963 (m), 1595 (w), 1384 (m), 1260 (s), 1091 (s), 1018 (s), 798 (s).

Preparation of (L4)Hf(NMe$_2$)(Br)(THF) (9). This compound was prepared as colorless microcrystals from the reaction of **L4a** (0.26 g, 0.50 mmol) with Hf(NMe$_2$)$_4$ (0.18 g, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.29 g (72%) (Found: C, 52.15; H, 4.67; N, 5.26. $C_{35}H_{38}N_3BrO_3Hf$ requires: C, 52.09; H, 4.75; N, 5.21%). M.p.: 230–232 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.24 (m, 2H, aryl), 6.90 (m, 8H, aryl), 6.70 (m, 8H, aryl), 4.53 (br s, 2H, CH_2), 3.78 (m, 6H, C*H* and THF), 3.54 (s, 6H, NCH_3), 3.30 (br s, 2H, CH_2), 1.36 (m, 4H, THF). ^{13}C NMR (C_6D_6): δ 213.6, 163.1, 138.7, 137.8, 130.1, 129.6, 128.8, 128.4, 127.6, 126.1, 120.5, 120.1, 118.0, 76.0, 69.5, 47.3, 45.2, 25.4. IR (KBr, cm^{-1}): $\bar{\nu}$ 2962 (s), 1595 (m), 1451 (m), 1384 (s), 1260 (s), 1090 (s), 1019 (s), 798 (s).

Preparation of (L4)Zr(NEt$_2$)(Br)(THF) (10). This compound was prepared as pale yellow crystals from the reaction of **L4a** (0.26 g, 0.50 mmol) with Zr(NEt$_2$)$_4$ (0.19 mg, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.27 g (73%) (Found: C, 59.50; H, 5.57; N, 5.64. $C_{37}H_{42}N_3BrO_3Zr$ requires: C, 59.42; H, 5.66; N, 5.62%). M.p.: 120–122 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.18 (m, 4H, aryl), 6.94 (m, 6H, aryl), 6.81 (m, 2H, aryl), 6.66 (m, 6H, aryl), 5.33 (br s, 1H, C*H*), 4.56 (br s, 3H, C*H* and CH_2), 4.26 (br s, 2H, CH_2), 3.95 (m, 2H, THF), 3.83 (m, 2H, THF), 3.62 (br s, 2H, CH_2), 3.35 (br s, 2H, CH_2), 1.36 (m, 4H, THF), 1.25 (m, 6H, N(CH$_2$CH_3)$_2$). ^{13}C NMR (C_6D_6): δ 209.2, 162.1, 137.6, 137.4, 129.6, 129.3, 129.2, 128.7, 128.3, 125.6, 119.1, 118.2, 117.9, 75.6, 70.0, 47.3, 46.2, 24.7, 14.9. IR (KBr, cm^{-1}): $\bar{\nu}$ 2962 (s), 1595 (s), 1480 (s), 1453 (s), 1260 (s), 1090 (s), 1019 (s), 797 (s).

Preparation of (L4)Ti(NMe$_2$)(Cl)(THF) (11). This compound was prepared as red microcrystals from the reaction of **L4b** (0.24 g, 0.50 mmol) with Ti(NMe$_2$)$_4$ (0.11 g, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.22 g (70%) (Found: C, 66.58; H, 6.05; N, 6.60. $C_{35}H_{38}N_3ClO_3Ti$ requires: C, 66.51; H, 6.06; N, 6.65%). M.p.: 154–156 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.20 (m, 2H, aryl), 6.95 (m, 4H, aryl), 6.86 (m, 6H, aryl), 6.67 (m, 6H, aryl), 4.49 (d, J = 10.1 Hz, 2H, CH_2), 4.43 (d, J = 10.1 Hz, 2H, CH_2), 3.86 (br s, 6H, C*H* and THF), 3.62 (s, 6H, NCH_3), 1.41 (m, 4H, THF). ^{13}C NMR (C_6D_6): δ 209.4, 166.1, 137.5, 129.4, 128.9, 128.2, 127.8, 126.0, 120.2, 119.5, 118.5, 118.3, 117.6, 75.4, 67.4, 52.9, 47.8, 25.0. IR (KBr, cm^{-1}): $\bar{\nu}$ 2962 (m), 1593 (m), 1480 (m), 1452 (m), 1260 (s), 1090 (s), 1018 (s), 798 (s).

Preparation of (L4)Zr(NMe$_2$)(Cl)(THF) (12). This compound was prepared as pale yellow crystals from the reaction of **L4b** (0.24 g, 0.50 mmol) with Zr(NMe$_2$)$_4$ (0.14 g, 0.50 mmol) in THF

(20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.22 g (66%) (Found: C, 62.22; H, 5.66; N, 6.22. $C_{35}H_{38}N_3ClO_3Zr$ requires: C, 62.24; H, 5.67; N, 6.22%). M.p.: 163–165 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.24 (m, 2H, aryl), 6.95 (m, 8H, aryl), 6.70 (m, 8H, aryl), 4.53 (m, 2H, CH_2), 3.83 (s, 2H, CH), 3.63 (br s, 6H, CH_2 and THF), 3.44 (br s, 3H, NCH_3), 3.32 (br s, 3H, NCH_3), 1.39 (m, 4H, THF). ^{13}C NMR (C_6D_6): δ 210.1, 162.6, 138.5, 137.9, 137.3, 130.0, 129.6, 128.6, 128.3, 125.4, 119.3, 118.5, 118.0, 75.7, 68.1, 46.4, 45.5, 25.5. IR (KBr, cm^{-1}): $\bar{\nu}$ 2963 (m), 1593 (w), 1481 (m), 1384 (m), 1260 (s), 1091 (s), 1018 (s), 798 (s).

Preparation of (L4)Hf(NMe$_2$)(Cl)(THF) (13). This compound was prepared as colorless microcrystals from the reaction of **L4b** (0.24 g, 0.50 mmol) with Hf(NMe$_2$)$_4$ (0.18 g, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.27 g (70%) (Found: C, 55.11; H, 5.02; N, 5.56. $C_{35}H_{38}N_3ClHfO_3$ requires: C, 55.12; H, 5.02; N, 5.51%). M.p.: 214–216 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.23 (m, 2H, aryl), 6.95 (m, 8H, aryl), 6.65 (m, 8H, aryl), 4.54 (m, 2H, CH_2), 3.86 (s, 2H, CH), 3.73–3.24 (m, 12H, CH_2 and THF and NCH_3), 1.39 (m, 4H, THF). ^{13}C NMR (C_6D_6): δ 214.5, 164.3, 138.5, 137.4, 129.9, 129.6, 129.1, 128.5, 127.7, 125.4, 120.1, 119.2, 117.5, 76.1, 67.7, 47.8, 47.0, 25.5. IR (KBr, cm^{-1}): $\bar{\nu}$ 2962 (m), 1594 (w), 1450 (m), 1384 (m), 1260 (s), 1091 (s), 1019 (s), 798 (s).

Preparation of (L4)Zr(NEt$_2$)(Cl)(THF) (14). This compound was prepared as pale yellow crystals from the reaction of **L4b** (0.24 g, 0.50 mmol) with Zr(NEt$_2$)$_4$ (0.19 g, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.26 g (73%) (Found: C, 63.21; H, 6.06; N, 5.96. $C_{37}H_{42}N_3ClO_3Zr$ requires: C, 63.18; H, 6.02; N, 5.97%). M.p.: 200–202 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.18 (m, 2H, aryl), 6.92 (m, 8H, aryl), 6.81 (m, 4H, aryl), 6.73 (m, 4H, aryl), 5.38 (br s, 1H, CH), 4.57 (br s, 4H, CH_2), 4.27 (br s, 1H, CH), 3.81 (m, 2H, THF), 3.73 (m, 2H, THF), 3.58 (br s, 2H, CH_2), 3.36 (br s, 2H, CH_2), 1.37 (m, 4H, THF), 1.26 (m, 6H, N(CH$_2$CH_3)$_2$). ^{13}C NMR (C_6D_6): δ 209.3, 161.5, 136.8, 128.9, 128.5, 128.0, 127.5, 126.5, 125.0, 118.6, 117.4, 117.1, 74.8, 68.3, 46.6, 45.4, 24.1, 14.4. IR (KBr, cm^{-1}): $\bar{\nu}$ 2962 (m), 1594 (w), 1481 (m), 1384 (m), 1260 (s), 1089 (s), 1017 (s), 797 (s).

Preparation of (L5)Zr(NMe$_2$)(Cl)(THF) (15). This compound was prepared as pale yellow crystals from the reaction of **L5** (0.29 g, 0.50 mmol) with Zr(NMe$_2$)$_4$ (0.14 g, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.28 g (70%) (Found: C, 65.55; H, 6.89; N, 5.34. $C_{43}H_{54}N_3ClO_3Zr$ requires: C, 65.58; H, 6.91; N, 5.34%). M.p.: 156–158 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.44 (m, 2H, aryl), 6.93 (m, 8H, aryl), 6.69 (m, 6H, aryl), 4.75 (d, J = 14.1 Hz, 2H, CH_2), 4.55 (s, 2H, CH), 3.64 (m, 4H, THF), 3.39 (d, J = 14.1 Hz, 2H, CH_2), 3.29 (s, 6H, N(CH_3)$_2$), 1.76 (s, 9H, C(CH_3)$_3$), 1.39 (s, 9H, C(CH_3)$_3$), 1.37 (m, 4H, THF). ^{13}C NMR (C_6D_6): δ 212.9, 162.7, 139.1, 138.6, 137.8, 137.3, 129.4, 129.2, 128.6, 127.8, 126.4, 125.6, 117.9, 78.4, 69.7, 50.1, 45.2, 35.7, 30.5, 25.6. IR (KBr, cm^{-1}): $\bar{\nu}$ 2961 (s), 1585 (s), 1416 (s), 1384 (m), 1257 (s), 1092 (s), 1020 (s), 870 (s), 810 (s).

Preparation of (L6)Ti(NMe$_2$)(Cl)(THF) (16). This compound was prepared as red crystals from the reaction of **L6** (0.35 g, 0.50 mmol) with Ti(NMe$_2$)$_4$ (0.11 g, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.28 g (65%) (Found: C, 71.54; H, 8.23; N, 4.93. $C_{51}H_{70}N_3ClO_3Ti$ requires: C, 71.52; H, 8.24; N, 4.91%). M.p.: 143–145 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.63 (d, J = 10.1 Hz, 2H, aryl), 6.97 (m, 4H, aryl), 6.86 (m, 6H, aryl), 6.40 (m, 2H, aryl), 4.58 (m, 3H, CH and CH_2), 4.16 (br s, 1H, CH), 3.57 (m, 4H, THF), 3.53 (s, 6H, NCH_3), 3.21 (br s, 2H, CH_2), 1.98 (s, 9H, C(CH_3)$_3$), 1.92 (s, 9H, C(CH_3)$_3$), 1.38 (m, 4H, THF), 1.25 (s, 18H, C(CH_3)$_3$). ^{13}C NMR (C_6D_6), δ 201.8, 157.3, 152.3, 140.9, 139.1, 136.5, 135.5, 128.2, 127.2, 126.8, 125.7, 124.3, 120.1, 70.4, 66.4, 48.5, 40.4, 34.3, 32.8, 30.2, 29.1, 25.8. IR (KBr, cm^{-1}): $\bar{\nu}$ 2962 (s), 1602 (w), 1443 (m), 1384 (m), 1260 (s), 1091 (s), 1018 (s), 799 (s).

Preparation of (L6)Zr(NMe$_2$)(Cl)(THF) (17). This compound was prepared as pale yellow crystals from the reaction of **L6** (0.35 g, 0.50 mmol) with Zr(NMe$_2$)$_4$ (0.14 g, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.28 g (63%) (Found: C, 68.04; H, 7.85; N, 4.66. $C_{51}H_{70}N_3ClO_3Zr$ requires C, 68.08; H, 7.84; N, 4.67%). M.p.: 158–160 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.57 (m, 4H, aryl), 7.09 (m, 4H, aryl), 7.02 (m, 2H, aryl), 6.92 (m, 4H, aryl), 4.40 (br s, 2H, CH_2), 3.63 (br s, 8H, CH, CH_2 and THF), 3.20 (s, 6H, NCH_3), 1.91 (s, 9H, C(CH_3)$_3$), 1.89 (s, 9H, C(CH_3)$_3$), 1.22 (s, 13H, C(CH_3)$_3$ and THF), 1.20 (s, 9H, C(CH_3)$_3$). ^{13}C NMR (C_6D_6): δ 206.2, 160.2, 139.3, 137.9, 137.6, 129.0, 128.9, 128.8, 128.7, 125.5, 125.4, 125.0, 124.1, 78.8, 68.1, 45.3, 39.1, 34.0, 33.9, 30.5, 30.4, 25.5. IR (KBr, cm^{-1}): $\bar{\nu}$ 2962 (s), 1384 (s), 1260 (s), 1092 (s), 1020 (s), 799 (s).

Preparation of (L6)Hf(NMe$_2$)(Cl)(THF) (18)·2THF (18·2THF). This compound was prepared as colorless crystals from the reaction of **L6** (0.35 g, 0.50 mmol) with Hf(NMe$_2$)$_4$ (0.18 g, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.40 g (71%) (Found: C, 62.63; H, 7.67; N, 3.73. $C_{59}H_{86}N_3ClHfO_5$ requires: C, 62.64; H, 7.66; N, 3.71%). M.p.: 110–112 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.59 (s, 2H, aryl), 7.09 (m, 4H, aryl), 7.02 (m, 4H, aryl), 6.93 (d, J = 6.8 Hz, 2H, aryl), 6.11 (m, 2H, aryl), 5.15 (d, J = 13.0 Hz, 1H, CH), 4.64 (d, J = 11.1 Hz, 1H, CH), 4.40 (m, 2H, CH_2), 3.72 (m, 12H, THF), 3.29 (s, 6H, NCH_3), 3.15 (m, 2H, CH_2), 1.93 (s, 9H, C(CH_3)$_3$), 1.88 (s, 9H, C(CH_3)$_3$), 1.22 (s, 18H, C(CH_3)$_3$), 1.21 (m, 12H, THF). ^{13}C NMR (C_6D_6): δ 216.9, 160.7, 139.0, 138.7, 138.4, 138.2, 129.0, 128.9, 126.2, 125.6, 125.3, 124.8, 124.1, 78.9, 69.9, 50.5, 44.7, 35.8, 33.9, 31.7, 30.3, 25.4. IR (KBr, cm^{-1}): $\bar{\nu}$ 2962 (s), 1602 (w), 1442 (m), 1384 (m), 1260 (s), 1091 (s), 1018 (s), 799 (s).

Preparation of (L6)Zr(NEt$_2$)(Cl)(THF) (19)·3C$_6$H$_6$ (19·3C$_6$H$_6$). This compound was prepared as pale yellow crystals from the reaction of **L6** (0.35 g, 0.50 mmol) with Zr(NEt$_2$)$_4$ (0.19 g, 0.50 mmol) in THF (20 mL) and recrystallization from a benzene solution by a similar procedure to the synthesis of **7**. Yield: 0.42 g (73%) (Found: C, 73.40; H, 7.97; N, 3.64. $C_{71}H_{92}N_3ClO_3Zr$ requires: C, 73.38; H, 7.98; N, 3.62%). M.p.: 102–104 °C (dec.). ^{1}H NMR (C_6D_6): δ 7.57 (m, 2H, aryl),

7.12 (m, 24H, aryl), 7.08 (m, 2H, aryl), 6.90 (m, 2H, aryl), 6.12 (m, 2H, aryl), 5.48 (br s, 1H, C*H*), 4.76 (br s, 1H, C*H*), 4.46 (br s, 2H, CH_2), 4.29 (br s, 2H, CH_2), 3.75 (m, 4H, THF), 3.28 (m, 4H, CH_2), 1.94 (s, 9H, $C(CH_3)_3$), 1.88(s, 9H, $C(CH_3)_3$), 1.21 (s, 18H, $C(CH_3)_3$), 1.14 (m, 10H, $N(CH_2CH_3)_2$ and THF). ^{13}C NMR (C_6D_6): δ 214.5, 160.2, 139.3, 138.4, 138.0, 137.9, 129.0, 128.0, 127.8, 127.5, 125.5, 125.1, 124.2, 79.0, 69.4, 51.0, 44.2, 35.8, 33.9, 31.7, 30.5, 25.4, 14.0. IR (KBr, cm^{-1}): $\bar{\nu}$ 2962 (s), 1603 (w), 1438 (m), 1384 (s), 1260 (s), 1092 (s), 1019 (s), 798 (s).

General procedure for polymerization of a *rac*-lactide

In a glovebox, *rac*-lactide (*rac*-LA) (0.360 g, 2.5 mmol), 2-propanol (0.01 mmol, in 0.5 mL of toluene or THF), complex (typically 0.01 mmol, in 0.5 mL of toluene or THF), and toluene or THF (4.0 mL) were added sequentially into a Schlenk flask with stirring. The flask containing the reaction mixture was subsequently placed in an oil bath and stirred for 0.5 h at 70 °C. The polymerization was quenched by the addition of cold acidified methanol. The precipitated polylactide was collected, washed with cold methanol several times, and dried in vacuum at 50 °C overnight.

X-ray crystallography

Single-crystal X-ray diffraction measurements were carried out on a Bruker SMART CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[13] All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 program package.[14] All the hydrogen atoms were geometrically fixed using the riding model. Disordered solvents in the voids of **15**, **16** and **17** were modeled or removed using the SQUEEZE program.[15] The crystal data and experimental data for **L5**, **10** and **14–19** are summarized in Tables 1 and 2. Selected bond lengths and angles are listed in Table 3.

Results and discussion

Synthesis and characterization of pro-ligands

Condensation of (*S*,*S*)-diphenyl-1,2-ethanediamine with 1 equiv. of salicylaldehyde, 3-*tert*-butylsalicylaldehyde or 3,5-di-*tert*-butylsalicylaldehyde in absolute ethanol at ambient temperature, followed by reduction with an excess of $NaBH_4$ in ethanol forms the chiral diamines **1–3** (Schemes 1–3). Subsequent cyclization of **1–3** with triethyl orthoformate in the presence of NH_4Br or NH_4Cl at 120 °C gives the imidazolium salts **L4** (**L4a** and **L4b**), **L5** and **L6**, respectively, in good yields (Schemes 1–3). All compounds are air-stable and have been characterized by various spectroscopic techniques and elemental analyses. The ^{1}H and ^{13}C NMR spectra are consistent with their C_2-symmetric structure. In addition, besides aromatic stretches the IR spectra of **L4–L6** also feature the characteristic O–H (at *ca.* 3420 cm^{-1}) and strong C=N stretches (at *ca.* 1640 cm^{-1}). The C_2 symmetric structure of **L5** was also confirmed by X-ray diffraction analysis (Fig. 1).

Synthesis and characterization of complexes

Amine elimination between $M(NMe_2)_4$ and protic reagents is a very efficient way for the synthesis of group 4 metal amide complexes.[16] Hence, a similar reaction is expected for the acidic protons in the ligands **L4** (**L4a** and **L4b**), **L5** and **L6** and metal amides. In fact, treatment of $M(NR_2)_4$ (M = Ti, Zr, Hf; R = Me, Et) with 1 equiv. of **L4** in THF gives, after recrystallization from a benzene solution, the chiral titanium amides (**L4**)Ti(NMe_2)(Br)-(THF) (**7**) and (**L4**)Ti(NMe_2)(Cl)(THF) (**11**), zirconium amides (**L4**)

Table 1 Crystal data and experimental parameters for compounds **L5**, **10** and **14–15**

Compound	**2**(**L5**)·C_6H_6	**10**	**14**	**15**
Formula	$C_{80}H_{92}N_2Cl_2O_4$	$C_{37}H_{42}N_3BrO_3Zr$	$C_{37}H_{42}N_3ClO_3Zr$	$C_{43}H_{54}N_3ClO_3Zr$
Formula weight	1244.48	747.87	703.41	787.56
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$C222_1$
a (Å)	10.306(1)	11.088(1)	11.160(1)	18.048(1)
b (Å)	31.646(4)	14.680(1)	14.834(2)	24.570(1)
c (Å)	11.070(1)	21.126(1)	20.608(2)	46.164(2)
β (°)	99.48(1)	90	90	90
V (Å^3)	3561.2(7)	3438.4(4)	3411.5(7)	20 471.3(13)
Z	2	4	4	16
D_{calc} (g cm^{-3})	1.161	1.445	1.370	1.022
μ(Mo/Kα)$_{calc}$ (mm^{-1})	0.143	1.521	0.440	0.300
Size (mm)	0.49 × 0.30 × 0.22	0.42 × 0.36 × 0.30	0.27 × 0.12 × 0.08	0.22 × 0.13 × 0.11
F(000)	1332	1536	1464	6624
2θ range (°)	4.00 to 50.50	3.86 to 55.24	4.16 to 55.10	3.76 to 50.50
No. of reflns collected	17 778	20 249	20 265	18 556
No. of obsd reflns	9062	7178	7149	15 790
Abs corr (T_{max}, T_{min})	0.97, 0.93	0.66, 0.57	0.97, 0.89	0.97, 0.94
R	0.055	0.029	0.032	0.051
R_w	0.135	0.060	0.063	0.121
wR_2 (all data)	0.146	0.061	0.065	0.125
Gof	1.01	1.00	1.02	1.04
CCDC	975119	975120	975123	975124

Table 2 Crystal data and experimental parameters for compounds **16–19**

Compound	**16**	**17**	**18**·2THF	**19**·3C_6H_6
Formula	$C_{51}H_{70}N_3ClO_3Ti$	$C_{51}H_{70}N_3ClO_3Zr$	$C_{59}H_{86}N_3ClHfO_5$	$C_{71}H_{92}N_3ClO_3Zr$
Formula weight	856.45	899.77	1131.25	1162.15
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	12.392(1)	12.729(2)	12.781(1)	15.211(1)
b (Å)	15.178(2)	15.022(2)	14.952(1)	18.900(1)
c (Å)	29.978(3)	30.104(4)	30.090(2)	22.591(2)
V (Å^3)	5638.4(10)	5756.1(12)	5750.3(5)	6494.5(8)
Z	4	4	4	4
D_{calc} (g cm^{-3})	1.009	1.038	1.307	1.189
μ(Mo/Kα)$_{calc}$ (mm^{-1})	0.236	0.273	1.908	0.257
Size (mm)	0.45 × 0.22 × 0.18	0.60 × 0.18 × 0.13	0.45 × 0.40 × 0.26	0.45 × 0.42 × 0.39
F(000)	1840	1912	2360	2480
2θ range (°)	3.82 to 50.50	3.84 to 50.50	3.84 to 50.50	3.88 to 50.50
No. of reflns collected	10 187	10 419	28 673	31 878
No. of obsd reflns	9028	9645	9927	10 522
Abs corr (T_{max}, T_{min})	0.96, 0.90	0.97, 0.85	0.64, 0.48	0.91, 0.89
R	0.040	0.031	0.022	0.041
R_w	0.097	0.076	0.048	0.102
wR_2 (all data)	0.101	0.077	0.048	0.108
Gof	1.04	1.04	1.01	1.04
CCDC	975125	975126	975127	975128

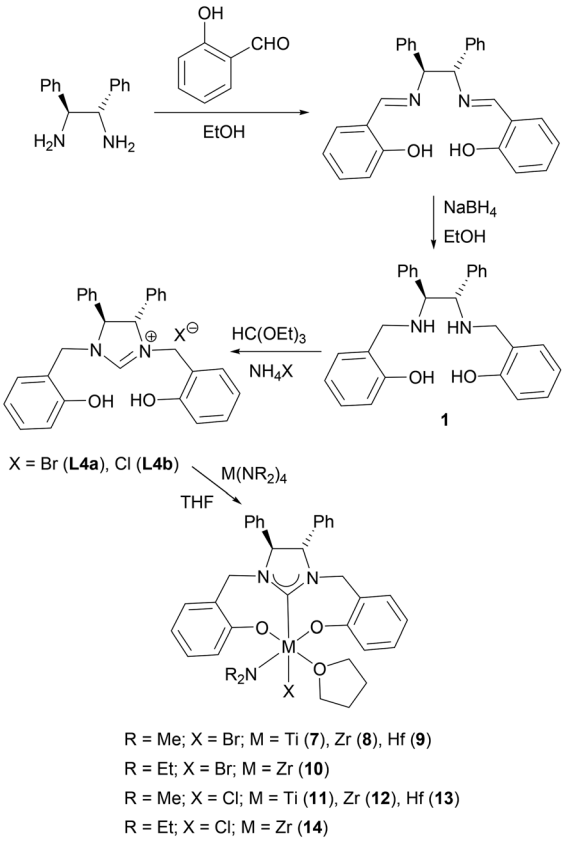
Table 3 Selected bond distances (Å) and bond angles (°) for compounds **10** and **14–19**

Compound	M–O (av.)	M–O(THF)	M–X	M–C	M–N	Sum angle of N(3)
10 (Zr)	2.136(2)	2.401(2)	Br: 2.661(1)	2.416(2)	2.046(2)	359.3(2)
14 (Zr)	2.139(2)	2.406(2)	Cl: 2.498(1)	2.419(2)	2.046(2)	359.5(2)
15 (Zr)	2.115(3)	2.332(3)	Cl: 2.499(1)	2.397(4)	2.046(4)	359.7(4)
16 (Ti)	1.993(2)	2.208(2)	Cl: 2.410(1)	2.252(2)	1.901(2)	359.9(2)
17 (Zr)	2.110(2)	2.313(2)	Cl: 2.501(1)	2.401(2)	2.044(2)	359.6(2)
18 (Hf)	2.098(2)	2.290(2)	Cl: 2.478(1)	2.370(3)	2.041(3)	359.7(3)
19 (Zr)	2.122(2)	2.344(2)	Cl: 2.515(1)	2.410(4)	2.052(3)	360.0(3)

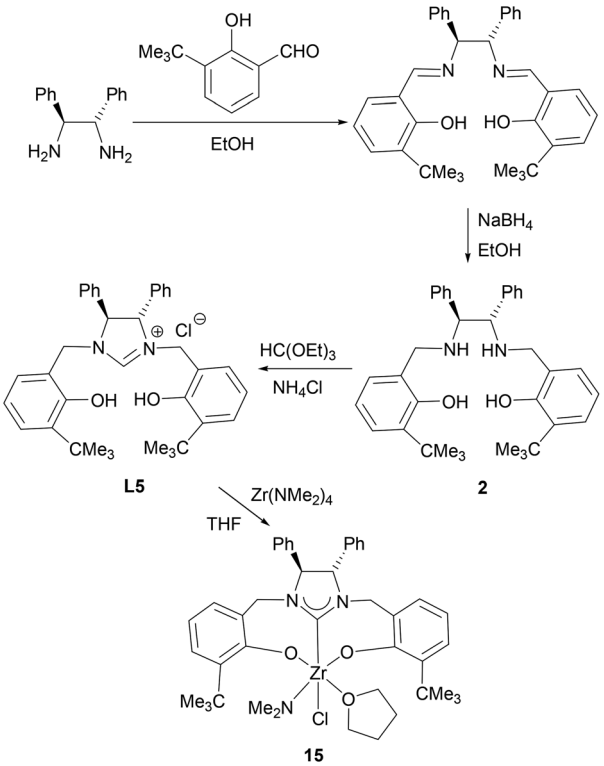
Zr(NMe$_2$)(Br)(THF) (**8**), (**L4**)Zr(NEt$_2$)(Br)(THF) (**10**), (**L4**)Zr(NMe$_2$)-(Cl)(THF) (**12**) and (**L4**)Zr(NEt$_2$)(Cl)(THF) (**14**), and hafnium amides (**L4**)Hf(NMe$_2$)(Br)(THF) (**9**) and (**L4**)Hf(NMe$_2$)(Cl)(THF) (**13**), respectively, in good yields (Scheme 1). Similarly, the reactions of **L5** or **L6** with 1 equiv. of M(NR$_2$)$_4$ (M = Ti, Zr, Hf; R = Me, Et) also afford the chiral titanium amide (**L6**)Ti(NMe$_2$)-(Cl)(THF) (**16**), zirconium amides (**L5**)Zr(NMe$_2$)(Cl)(THF) (**15**), (**L6**)Zr(NMe$_2$)(Cl)(THF) (**17**) and (**L6**)Zr(NEt$_2$)(Cl)(THF) (**19**), and the hafnium amide (**L6**)Hf(NMe$_2$)(Cl)(THF) (**18**), respectively, in good yields (Schemes 2 and 3).

Complexes **7–19** are stable in a dry nitrogen atmosphere, while they are very sensitive to moisture. They are soluble in organic solvents such as THF, DME, pyridine, toluene, and benzene, and only sparingly soluble in aliphatic solvents such as *n*-hexane. They have been characterized by various spectroscopic techniques and elemental analyses. The 1 : 1 : 1 ratio between the NR$_2$ (R = Me, Et) group, the coordinate THF and the ligand **L4**, **L5** or **L6** is established by ^{1}H NMR spectroscopy. Furthermore, the characteristic O–H and C=N stretches at *ca.* 3420 and 1640 cm^{-1} in **L4–L6** disappear upon treatment with M(NR$_2$)$_4$, supporting the formation of complexes **7–19**. The solid-state structures of **10** and **14–19** have further been confirmed by X-ray diffraction analyses.

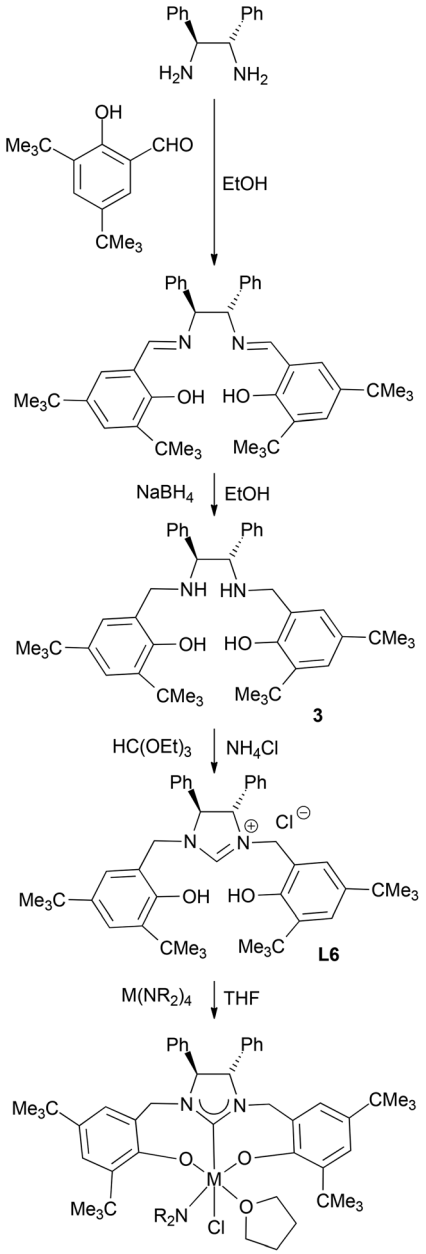
Complexes **16** and **17** are isostructural. The M^{4+} ion features a distorted-octahedral ligand environment in (**L4**)Zr(NEt$_2$)(Br)-(THF) (**10**), (**L4**)Zr(NEt$_2$)(Cl)(THF) (**14**), (**L5**)Zr(NMe$_2$)(Cl)(THF) (**15**), (**L6**)Ti(NMe$_2$)(Cl)(THF) (**16**), (**L6**)Zr(NMe$_2$)(Cl)(THF) (**17**), (**L6**)Hf(NMe$_2$)(Cl)(THF) (**18**) and (**L6**)Zr(NEt$_2$)(Cl)(THF) (**19**) (Fig. 2–8). Complexes **10** and **14–19** represent, to our knowledge, the first example of the structurally characterized group 4 chiral NHC–metal complex. The average M–O distances are 1.993(2) Å for Ti, 2.110(2) Å to 2.139(2) Å for Zr, and 2.098(2) Å for Hf. The Zr–Br distance is 2.661(1) Å (for **10**), and the M–Cl distance is 2.410(1) Å for Ti, 2.498(1) Å to 2.515(1) Å for Zr, and 2.478(1) Å for Hf. The M–C(carbene) distances of 2.252 (2) Å for Ti, 2.397(4) Å to 2.419(2) Å for Zr, and 2.370(3) Å for Hf are in the typical range for a M–C σ-bond. These structural data can be compared with those found in [η^3-*O*,*C*,*O*-{(3,5-(Me$_3$C)$_2$-C$_6$H$_2$O)$_2$N$_2$C$_3$H$_4$}]M(O^{i}Pr)(Cl)(THF) (M = Ti, Zr)[17a,b] and [η^3-*O*,*C*,*O*-{(3,5-(Me$_3$C)$_2$-C$_6$H$_2$O)$_2$N$_2$C$_3$H$_4$}]-MCl$_2$(THF) (M = Ti, Zr).[17c,d] Furthermore, the M–NR$_2$ (R = Me, Et) distances are short with 1.901(2) Å for Ti, 2.044(2) Å to 2.052(3) Å for Zr, and 2.041(3) Å for Hf. This in combination with the planar geometry around the nitrogen atom N(3) suggests that the sp^2-hybridized N-atom engages in N(p_π)→M(d_π) interactions.[16]



Scheme 1 Synthesis of complexes **7–14**.



Scheme 2 Synthesis of complex **15**.



Scheme 3 Synthesis of complexes **16–19**.

Polymerization of *rac*-lactide

Efficient ring opening polymerization (ROP) of *rac*-lactide (*rac*-LA) is achieved by the chiral group 4 NHC–metal complexes **7–19** under the conditions listed in Table 4. With the zirconium and hafnium complexes **8–10** and **12–14** complete conversion of 250 equiv. of lactide is achieved within 0.5 h at 70 °C in toluene at [*rac*-LA] = 0.5 mol L^{-1} (Table 4, entries 2, 7, 8 and 10–12). A more detailed analysis was undertaken for **8** that acts as a single-site initiator for the controlled polymerization of *rac*- LA. The formed polylactides have experimental M_n values ($M_{n,exp}$) that are very close to the calculated $M_{n,calcd}$

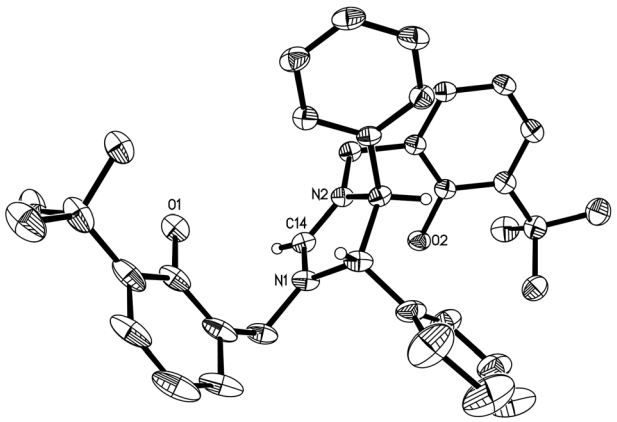


Fig. 1 Molecular structure of the cation in **L5** (thermal ellipsoids drawn at the 35% probability level).

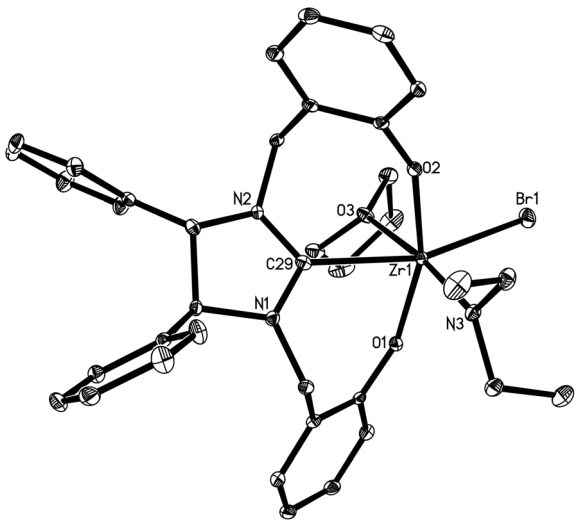


Fig. 2 Molecular structure of **10** (thermal ellipsoids drawn at the 35% probability level).

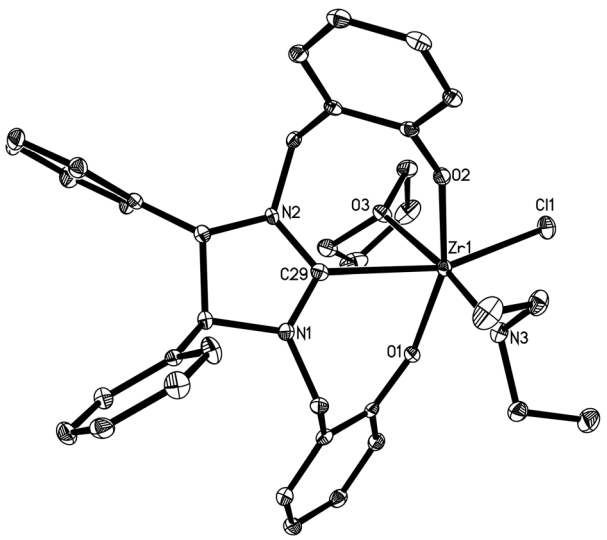


Fig. 3 Molecular structure of **14** (thermal ellipsoids drawn at the 35% probability level).

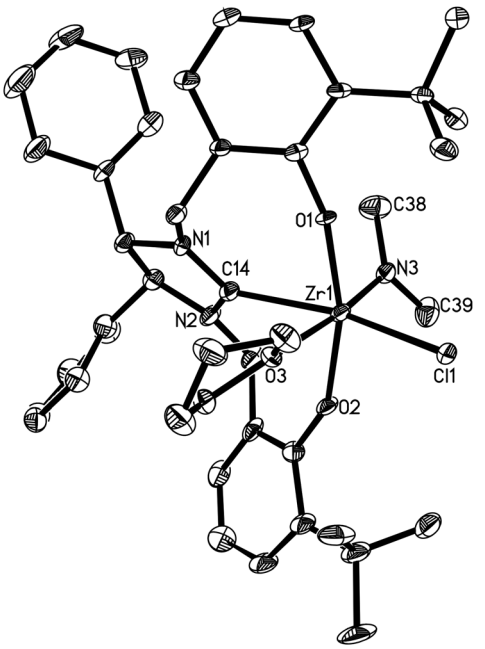


Fig. 4 Molecular structure of **15** (thermal ellipsoids drawn at the 35% probability level).

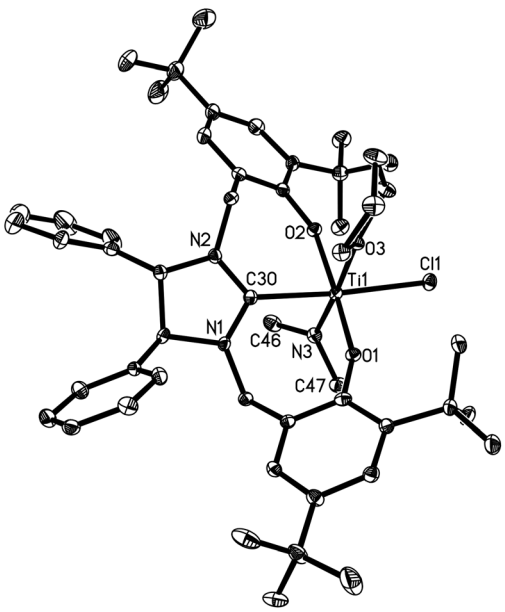


Fig. 5 Molecular structure of **16** (thermal ellipsoids drawn at the 35% probability level).

values and that the molar mass distributions are very narrow (M_w/M_n = 1.18–1.21; Table 4, entries 2–6). In addition, for complex **8** a first order kinetic dependence on the concentration of *rac*-LA and no induction period were observed (Fig. 9). The $M_{n,exp}$ values increase linearly with the monomer conversion, whereas the M_w/M_n values remain in the narrow range of 1.17–1.22 (Fig. 10). However, when the more bulky ligands **L5** and **L6** are used, the polymerization with the

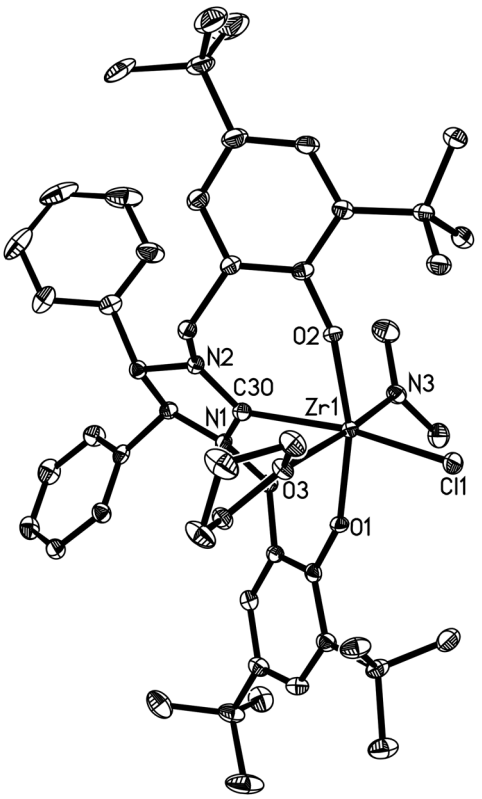


Fig. 6 Molecular structure of **17** (thermal ellipsoids drawn at the 35% probability level).

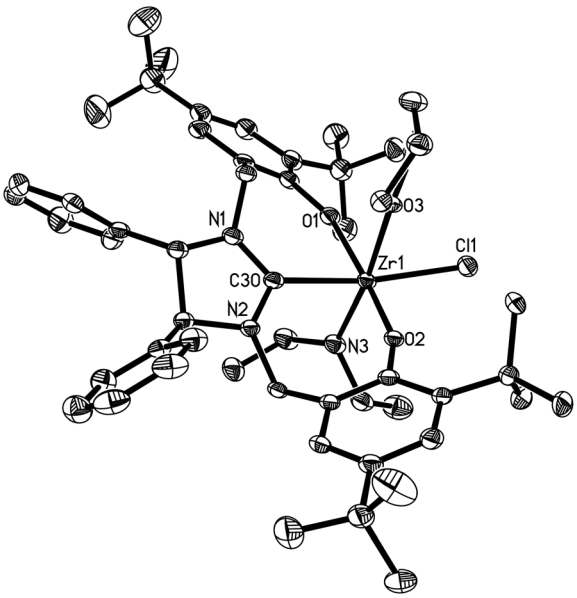


Fig. 8 Molecular structure of **19** (thermal ellipsoids drawn at the 35% probability level).

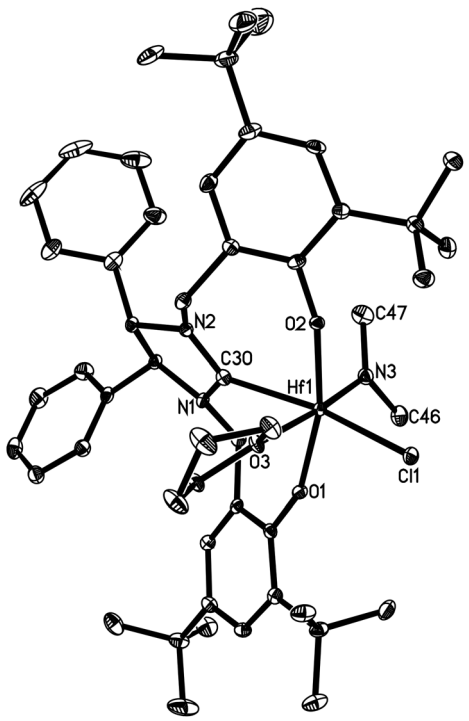


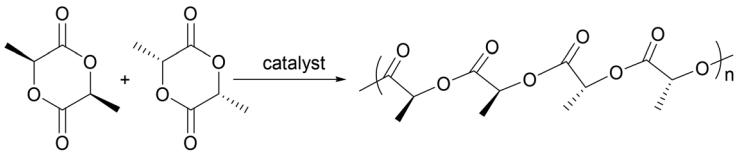
Fig. 7 Molecular structure of **18** (thermal ellipsoids drawn at the 35% probability level).

zirconium and hafnium complexes **15** and **17–19** is slightly slower (Table 4, entries 13, and 15–17), presumably because of the increased steric hindrance at the metal centers. Although the zirconium and hafnium complexes are effective catalysts for the polymerization of *rac*-LA, the titanium complexes **7**, **11** and **16** exhibit only poor catalytic activity (Table 4, entries 1, 9 and 14), consistent with the smaller ionic radius of Ti^{4+}. These differences also prevail in THF solution (Table 4, entries 18–30), but the polymerization with these group 4 initiators/catalysts proceeds much more slowly in THF (Table 4, entries 18–30), most likely a consequence of competitive monomer–solvent coordination to the metal ion. A similar competition was observed for the organoyttrium and organoaluminum catalysts.[16a,18] In the absence of isopropanol, no polymerization occurs in toluene or THF solution even when heated at 70 °C for 72 h. The polymer microstructure, as determined by homo-decoupled ^{1}H NMR experiments,[19] shows that the polylactides are heterotactic-rich polylactides under conditions examined. The catalytic activities of **7–19** resemble that of [η^3-*O*,*C*,*O*-{(3,5-$(Me_3C)_2$-$C_6H_2O)_2N_2C_3H_4$}]M(O^iPr)(Cl)-(THF) (M = Ti, Zr),[17a,b] while the microstructures of the resulting polylactides are similar to those initiated by [(*R*)-(2-O-C_6H_4)-CH=NCH(Me)(C_6H_5)]$_2$Zr(O^iPr)$_2$.[5c]

Conclusions

Chiral group 4 NHC–metal complexes were prepared and structurally characterized. These complexes represent the first example of the structurally characterized group 4 chiral NHC–metal complex, and they can initiate the ring-opening polymerization of *rac*-lactide in the presence of isopropanol, leading to the heterotactic-rich polylactides. Nevertheless, the reactivity is

Table 4 Polymerization of *rac*-lactide catalyzed by chiral group 4 NHC-complexes **7–19**[a]



rac-Lactide Heterotactic Polylactide

Entry	Precat.	Solvent	Conv. (%)	$M_{n,exp}$ [b] (kg mol^{-1})	$M_{n,calcd}$ [c] (kg mol^{-1})	M_w/M_n [b]	P_r [d]
1	**7** (Ti)	Toluene	65	22.9	23.4	1.18	0.70
2	**8** (Zr)	Toluene	100	35.4	36.0	1.21	0.74
3[e]	**8** (Zr)	Toluene	100	14.9	14.4	1.20	0.73
4[f]	**8** (Zr)	Toluene	100	21.3	21.6	1.18	0.73
5[g]	**8** (Zr)	Toluene	100	29.2	28.8	1.19	0.74
6[h]	**8** (Zr)	Toluene	92	40.4	39.7	1.21	0.73
7	**9** (Hf)	Toluene	100	36.2	36.0	1.21	0.72
8	**10** (Zr)	Toluene	100	35.4	36.0	1.23	0.67
9	**11** (Ti)	Toluene	70	24.6	25.2	1.20	0.72
10	**12** (Zr)	Toluene	100	36.8	36.0	1.23	0.70
11	**13** (Hf)	Toluene	100	35.3	36.0	1.21	0.66
12	**14** (Zr)	Toluene	100	35.7	36.0	1.25	0.70
13	**15** (Zr)	Toluene	95	34.6	34.2	1.22	0.69
14	**16** (Ti)	Toluene	30	11.2	10.8	1.16	0.69
15	**17** (Zr)	Toluene	94	32.7	33.8	1.24	0.68
16	**18** (Hf)	Toluene	92	32.6	33.1	1.27	0.67
17	**19** (Zr)	Toluene	90	32.8	32.4	1.22	0.71
18	**7** (Ti)	THF	35	12.4	12.6	1.20	0.70
19	**8** (Zr)	THF	62	22.6	22.3	1.26	0.72
20	**9** (Hf)	THF	64	23.2	23.0	1.31	0.70
21	**10** (Zr)	THF	58	19.9	20.9	1.36	0.68
22	**11** (Ti)	THF	38	13.5	13.7	1.21	0.71
23	**12** (Zr)	THF	59	21.6	21.2	1.32	0.72
24	**13** (Hf)	THF	62	21.8	22.3	1.35	0.70
25	**14** (Zr)	THF	60	22.3	21.6	1.36	0.67
26	**15** (Zr)	THF	48	18.5	17.3	1.32	0.70
27	**16** (Ti)	THF	16	5.9	5.8	1.19	0.68
28	**17** (Zr)	THF	50	17.2	18.0	1.34	0.69
29	**18** (Hf)	THF	45	15.8	16.2	1.30	0.71
30	**19** (Zr)	THF	48	16.4	17.3	1.35	0.70

[a] Conditions: 70 °C, precat./isopropanol/LA (mol/mol/mol) = 1/1/250; precatalyst (0.01 mmol); polymerization time, 0.5 h; solvent, 5 mL; [LA] = 0.5 mol L^{-1}. [b] Measured by GPC (using polystyrene standards in THF). [c] Calculated by ([LA]/[precat.]) × 144 × X (X = conv.). [d] P_r is the probability of forming an *r*-dyad by insertion and is determined from the methine region of the homonuclear decoupled ^{1}H NMR spectrum in $CDCl_3$ at 25 °C.[19] [e] Precat./isopropanol/LA (mol/mol/mol) = 1/1/100. [f] Precat./isopropanol/LA (mol/mol/mol) = 1/1/150. [g] Precat./isopropanol/LA (mol/mol/mol) = 1/1/200. [h] Precat./isopropanol/LA (mol/mol/mol) = 1/1/300.

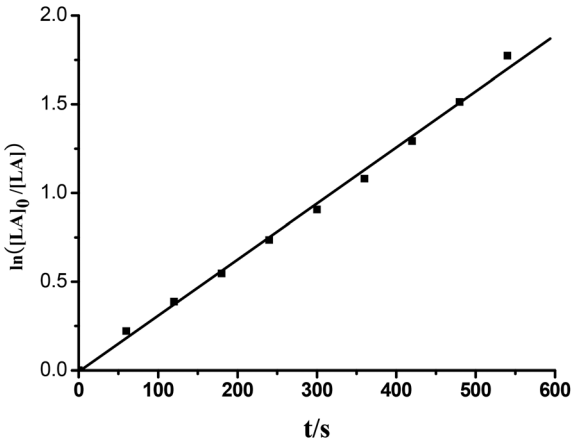


Fig. 9 Ln([LA]$_0$/[LA]) *vs*. time plot for the ROP of *rac*-LA initiated by complex **8**. Conditions: precat./isopropanol/LA (mol/mol/mol) = 1/1/150, [LA] = 0.5 mol L^{-1}, solvent = toluene, T = 70 °C. k_{obs} = 3.14 × 10^{-3} s^{-1}.

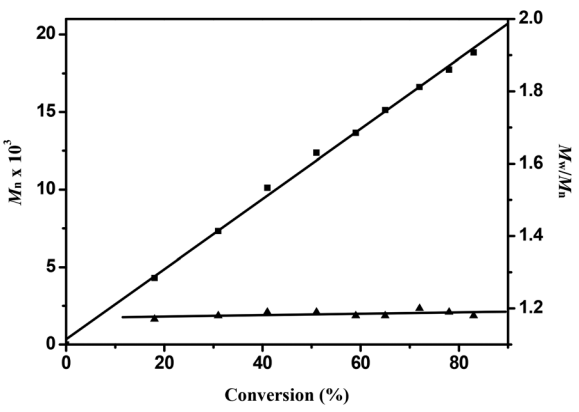


Fig. 10 M_n and M_w/M_n *vs*. conversion plots for the ROP of *rac*-LA initiated by complex **8**. Conditons: precat./isopropanol/LA (mol/mol/mol) = 1/1/150, [LA] = 0.5 mol L^{-1}, solvent = toluene, T = 70 °C.

strongly influenced by the size of the metal ion and the solvents. For example, fast polymerization is observed in toluene, whereas the conversion is slow in THF because of competitive monomer–solvent coordination to the metal ions. The zirconium and hafnium complexes are efficient precatalysts for polymerization of *rac*-LA, while the titanium complexes exhibit only poor catalytic activity because of the smaller ionic radius of Ti^{4+}. Further studies will focus on the application of these complexes towards other asymmetric reactions and the exploration of new group 4 metal complexes based on chiral ligands.

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