

Group 4 Salicyloxazolines are Potent Polymerisation Catalysts

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SUPPORTING INFORMATION

Contents

Details of preparative procedures

Reactions of L^6ZrCl_2 with MAO/ Me_3Al

Tables of crystallographic and refinement data for L^2ZrCl_2 and L^4ZrCl_2 .

2-Methyl-6-(3,3-dimethyloxazoliny)phenol, HL²

2-Hydroxy-3-methylbenzoic acid (15.2 g, 0.1 mol) and 1,1'-carbonyldiimidazole (17.6 g, 0.11 mol) in dry tetrahydrofuran (200 mL) were heated at reflux for 1 h, before the addition of 2-amino-2-methyl-propan-1-ol (13.4 g, 0.15 mol) and heating at reflux for a further 18 h. The yellow/ orange oily intermediate (6.9 g, 30.9 mmol) was purified by column chromatography (eluent diethyl ether/ light petroleum 1:4), dissolved into dry dichloromethane at 0 °C and treated dropwise with thionyl chloride (7.35 g, 61.8 mmol, 4.5 mL). The solution was allowed to warm slowly to room temperature and was then stirred for 18 h. The resulting HCl salt was filtered off, treated with saturated aqueous sodium hydrogen carbonate until basic, and extracted with diethyl ether (3 x 200 mL). The yellow solution was dried over $MgSO_4$, and concentrated to give the title compound as a pale yellow/ peach oil (5.17 g, 25.2 mmol, 25.2 %).

¹H NMR (300 MHz, 298 K, C_6D_6) δ 12.8 (br, 1 H, OH), 7.54 (dd, 1 H, J = 7.8, 1.6 Hz, Ar-H), 7.26 (dd, 1 H, J = 7.3, 1.6 Hz, Ar-H), 6.81 (t, 1 H, J = 7.6 Hz, Ar-H), 4.12 (s, 2 H, CH_2), 2.34 (s, 3 H, Ar- CH_3), 1.42(s, 6 H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, 298 K, C_6D_6) δ 163.8 (O-C=N), 158.1 (Ar-C), 133.9 (Ar-CH), 125.6 (Ar-C), 125.3 (Ar-CH), 117.9 (Ar-CH), 110.0 (Ar-C), 78.2 ($\text{C}(\text{CH}_3)_2$), 28.4 ($\text{C}(\text{CH}_3)_2$), 15.8 (Ar- CH_3).

EA. Found (calcd. for $\text{C}_{12}\text{H}_{15}\text{NO}_2$): C: 69.84 (70.22), H: 7.15 (7.37), N: 6.61 (6.82).

MS: $\text{M}^+ = 178$.

2-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)-4,6-diisopropylphenol, HL³

To 3,5-di-isopropylsalicylic acid (2.45 g, 11 mmol) in a Schlenk vessel was added PPh_3 (11.5 g, 44 mmol), and the atmosphere in the vessel replaced with argon. Acetonitrile (~25 ml), and then triethylamine (6 ml, 43 mmol) were added, with stirring. 2-amino-2-methyl-1-propanol (0.98 g, 11 mmol) was injected in a small volume of acetonitrile. CCl_4 (10.6 ml, 110 mmol) was added dropwise over 4 hours. The mixture was stirred for 48 hours, after which time the solution was filtered under suction. The residue was washed with Et_2O (*ca.* 30 ml) which caused a further precipitation in the filtrate. This precipitate was removed by filtration. The solvents were removed in *vacuo*, and the product extracted with hexane (3 x 100 ml). The combined extracts were dried *in vacuo*, and the pale yellow powder was purified by flash chromatography on a silica column, eluted with hexane-ethyl acetate (50:1), affording HL³ as a pale yellow crystalline solid (1.01 g, 33%) after removal of solvent.

^1H NMR (CDCl_3): δ ppm 12.25 (s, 1H, OH), 7.27 (d, $^4J_{\text{HH}} = 2$ Hz, 1H, ArH), 7.09 (d, $^4J_{\text{HH}} = 2$ Hz, 1H, ArH), 4.00 (s, 2H, CH_2), 3.30 (sept., $^3J_{\text{HH}} = 7$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 2.77 (sept., $^3J_{\text{HH}} = 7$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 1.30 (s, 6H, CH_3), 1.18 (d, 6H, $^3J_{\text{HH}} = 7$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.15 (d, 6H, $^3J_{\text{HH}} = 7$ Hz, $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ ppm 164.1 (N=C-O); 155.5, 138.5, 135.7 (Ar), 128.5, 122.3 (Ar C-H), 109.9 (Ar), 78.3 ($\text{C}(\text{CH}_3)_2$), 67.0 (CH_2), 33.6 ($\text{CH}(\text{CH}_3)_2$), 28.6 (CH_3), 27.1 ($\text{CH}(\text{CH}_3)_2$), 24.2, 22.5 ($\text{CH}(\text{CH}_3)_2$).

EA: found (calc) C: 74.01 (74.14), H: 9.15 (9.15), N: 5.03 (5.09)

MS (EI): m/z 275 (M^+), 260 ($[\text{M} - \text{CH}_3]^+$), 188 ($[\text{M} - 4\text{CH}_3, \text{H}]^+$). IR (ATR): cm^{-1} : 2962, 2137, 1674, 1635 (C=N), 1597, 1455, 1365, 1249, 1193, 1168, 1092, 978, 944, 888, 799, 785, 745.

2-tert-Butyl-6-(3, 3-dimethyloxazoliny)phenol, HL⁴

A solution of 3-tert-butyl-2-hydroxybenzotrile (2.00 g, 11.4 mmol) 2-amino-2-methylpropan-1-ol (1.27 g, 14.3 mmol) was heated at reflux over zinc chloride (5 mol %) that had previously been melted *in vacuo*. The volatiles were removed *in vacuo* and the resulting oily solid was dissolved in dichloromethane, washed with saturated aqueous NaHCO₃ solution, and dried over MgSO₄. The solution was concentrated and the desired product was obtained at -20 °C as yellow crystals (1.07 g, 4.3 mmol, 40 %).

¹H NMR (300 MHz, 298 K, CDCl₃) δ 12.85 (br, 1 H, OH), 7.55 (dd, 1 H, Ar-H, J = 7.8, 1.3 Hz), 7.40 (dd, 1 H, Ar-H, J = 7.7, 1.4 Hz), 6.81 (t, 1 H, Ar-H, J = 7.8 Hz), 4.10 (s, 2 H, CH₂), 1.46 (s, 9 H, ^tBu), 1.42 (s, 6 H, Me).

¹³C{¹H} NMR (75.6 MHz, 298 K, CDCl₃) □ 182.3 (O-C=N), 164.7 (Ar-C), 159.0 (Ar-C), 137.0 (Ar-C), 130.2 (Ar-CH), 125.9 (Ar-CH), 117.7 (Ar-CH), 78.2 (oxazoline-CH₂), 67.1 (C(CH₃)₂), 34.8 (C(CH₃)₃), 29.4 (C(CH₃)₃).

EA found (calcd. for C₁₅H₂₁NO₂): C: 72.65 (72.84), H 8.32 (8.56), N: 5.50(5.66)

MS M⁺ = 206.

2,4-di-tert-butyl-6-(4,5-dihydrooxazol-2-yl)phenol, HL⁵

From 3,5-di-tert-butyl salicylic acid (2.49 g, 10 mmol) using a similar method to HL². Purification by flash chromatography on a silica column [hexane-ethyl acetate (50:1)] afforded a pale yellow powder (1.3 g, 47%).

¹H NMR (CDCl₃): δ ppm 12.47 (s, 1H, OH), 7.44 (d, ⁴J_{HH} = 2.5 Hz, 1H, ArH), 7.33 (d, ⁴J_{HH} = 2.5 Hz, 1H, ArH), 4.30 (t, ³J_{HH} = 9 Hz, 2H, CH₂), 3.99 (t, ³J_{HH} = 9 Hz, 2H, ArH), 1.34 (s, 9H, C(CH₃)₃), 1.21 (s, 9H, C(CH₃)₃).

¹³C{¹H} NMR (CDCl₃): δ ppm 167.1 (N=C-O), 156.8, 140.0, 136.4 (Ar), 127.9, 122.2 (Ar C-H), 109.9 (Ar), 66.5, 53.4 (CH₂), 35.2, 34.3 (C(CH₃)₃), 31.5, 29.5 (C(CH₃)₃).

EA: found (calc) C: 74.20 (74.14), H: 9.35 (9.15), N: 4.98 (5.09)

MS (EI): m/z 275 (M⁺). IR (ATR): cm⁻¹: 2956, 1636 (C=N), 1596, 1438, 1370, 1251, 1216, 1187, 1099, 1013, 960, 890, 799, 780, 722

2,4-di-tert-butyl-6-(4,4-dimethyl-4,5-dihydrooxazol-2-yl)phenol, HL⁶

From 3,5-di-tert-butyl salicylic acid (2.5 g, 10 mmol) using a similar method to HL². Purification by flash chromatography on a silica column [hexane-ethyl acetate (50:1)] afforded a pale yellow powder (1.4 g, 46%).

¹H NMR (CDCl₃): δ ppm 12.60 (s, 1H, OH), 7.54 (d, ⁴J_{HH} = 2 Hz, 1H, ArH), 7.44 (d, ⁴J_{HH} = 2 Hz, 1H, ArH), 4.09 (s, 2H, CH₂), 1.46 (s, 9H, C(CH₃)₃), 1.40 (s, 6H, CH₃) 1.32 (s, 9H, C(CH₃)₃).

¹³C{¹H} NMR (CDCl₃): δ ppm 164.3 (N=C-O), 156.8, 140.0, 136.3 (Ar), 127.8, 122.0 (Ar C-H), 109.9 (Ar), 78.1 (CH₂), 67.0 (C(CH₃)₂), 35.1, 34.2 (C(CH₃)₃), 31.5, 29.5 (C(CH₃)₃), 28.6 (CH₃).

EA: found (calc) C: 75.14 (75.21), H: 9.63 (9.63), N: 4.62 (4.51).

MS (EI): m/z 303 (M⁺), 288 ([M-CH₃]⁺).

IR (ATR): cm⁻¹: 2963, 2137, 1634 (C=N), 1595, 1438, 1366, 1251, 1183, 1098, 978, 891, 805, 781, 721.

bis(2-Methyl-6-(oxazoliny)phenolato)titanium dichloride, L¹₂TiCl₂.

HL¹ (2.00 g, 11.3 mmol) was added to a suspension of sodium hydride (0.30 g, 12.4 mmol) in tetrahydrofuran and then stirred for 4 h. The peach coloured solution was cooled to -78 °C and TiCl₄(THF)₂ (1.51 g, 4.5 mmol) was added. The solution was allowed to reach room temperature and then stirred for a further 18 h. The volatiles were removed *in vacuo* and the resulting dark orange foam was extracted with dichloromethane. The red solution was concentrated and placed in the freezer at -20°C. The title compound was obtained as red microcrystals (1.2 g, 2.8 mmol, 64 %) at -20°C.

^1H NMR (300 MHz, 298 K, CD_2Cl_2) δ 7.60 (d, 1 H, $J = 7.7$ Hz, Ar- H), 7.37 (d, 1 H, $J = 7.2$, Ar- H), 6.92 (t, 1 H, $J = 7.6$ Hz, Ar- H), 4.44 (br, 1 H, CH_2), 4.26 (br, 2 H, CH_2), 3.75 (br, 1 H, CH_2), 2.39 (s, 3 H, Ar- CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, 298 K, CD_2Cl_2) \square 137.0 (Ar-CH), 127.1 (Ar-CH), 121.5 (Ar-CH), 69.0 (CH_2), 16.3 (CH_3).

EA found (Calc. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4\text{TiCl}_2$): C: 50.79 (50.98), H: 4.22 (4.28), N: 5.79 (5.95), Cl: 15.19 (15.05).

bis(2-methyl-6-(3, 3-dimethyloxazoliny)phenolato)titanium dichloride, $\text{L}^2_2\text{TiCl}_2$.

From HL^2 (1.00 g, 4.9 mmol) using a similar method as for $\text{L}^1_2\text{TiCl}_2$ giving red microcrystals (0.8 g, 1.5 mmol, 63 %).

^1H NMR (300 MHz, 298 K, CD_2Cl_2) δ 7.71 (dd, 1 H, Ar- H , $J = 8.1, 1.5$ Hz), 7.49 (dd, 1 H, Ar- H , $J = 7.4, 1.5$ Hz), 6.95 (t, 1 H, Ar- H , $J = 7.8$ Hz), 4.31 (d, 1 H, CH_2 , $J = 8.4$ Hz), 4.04 (d, 1 H, CH_2 , $J = 8.4$ Hz), 2.42 (s, 3 H, $\text{C}(\text{CH}_3)_2$), 1.76 (s, 3 H, Ar- CH_3), 1.07 (s, 3 H, $\text{C}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, 298 K, CD_2Cl_2) \square 167.1 (O- $\text{C}=\text{N}$), 163.6 (Ar-C), 137.0 (Ar-CH), 127.7 (Ar-CH), 126.8 (Ar-C), 121.3 (Ar-CH), 116.4 (Ar-C), 80.6 (CH_2), 71.1 ($\text{C}(\text{CH}_3)_2$), 29.2 ($\text{C}(\text{CH}_3)_2$), 27.1 (Ar- CH_3), 16.5 ($\text{C}(\text{CH}_3)_2$).

bis(2-methyl-6-(3, 3-dimethyloxazoliny)phenolato) zirconium dichloride, $\text{L}^2_2\text{ZrCl}_2$.

From HL^2 (1.00 g, 4.9 mmol) using a similar method as for $\text{L}^1_2\text{TiCl}_2$. The pale yellow dichloromethane extract was concentrated, layered with light petroleum and cooled to -20 °C to give colourless crystals (0.64 g, 1.14 mmol, 47 %).

^1H NMR (300 MHz, 298 K, CD_2Cl_2) δ 7.73 (m, 1 H, Ar- H), 7.51 (dd, 1 H, $J = 6.6, 0.8$ Hz, Ar- H), 6.95 (m, 1 H, Ar- H), 4.67, 4.25 ($2 \times$ m, 1 H, CH_2), 2.42 (s, 3 H, $\text{C}(\text{CH}_3)_2$), 1.76 (s, 3 H, Ar- CH_3), 1.05 (s, 3H, oxazoline-Me).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, 298 K, CD_2Cl_2) δ 140.5 (O-C=N), 140.5 (Ar-C), 137.2 (Ar-CH), 136.2 (Ar-C), 128.4 (Ar-C), 128.1 (Ar-CH), 120.3 (Ar-CH), 80.1 (oxazoline- CH_2), 69.7 (oxazoline-CMe₂), 28.7 (Ar-CH₃), 27.0 (oxazoline-(CH₃)₂).

EA Found (calc for $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_4\text{ZrCl}_2(1/2 \text{CH}_2\text{Cl}_2)$): C, 47.97 (48.00); H, 5.20 (4.77); N, 4.28 (4.57)

bis(2-tert-Butyl-6-(3,3-dimethyloxazoliny)phenolato)titanium dichloride, (L^4TiCl_2).

From HL⁴ (2.00 g, 8.1 mmol) using a similar method as for $\text{L}^1_2\text{TiCl}_2$. The dichloromethane extract was concentrated and cooled to -20 °C to give shiny red crystals (1.78 g, 2.9 mmol, 73 %).

^1H NMR (300 MHz, 298 K, CD_2Cl_2) δ 7.78 (dd, 1 H, J = 7.9, 1.7 Hz, Ar-H), 7.65 (dd, 1 H, J = 7.8, 1.7 Hz, Ar-H), 6.99 (t, 1 H, J = 7.8 Hz, Ar-H), 4.28, 3.94 (2 × d, 1 H, J = 8.5 Hz, CH₂), 1.59 (s, 12 H, overlapping oxazoline CH₃, C(CH₃)₃), 1.16 (s, 3 H, oxazoline CH₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, 298 K, CD_2Cl_2) δ 167.5 (O-C=N), 164.2, 139.3 (Ar-C), 133.6, 121.4 (Ar-CH), 118.1 (Ar-C), 79.7 (C(CH₂)₂), 71.8 (C(CH₃)₂), 35.4 (C(CH₃)₃), 30.4 (C(CH₃)₃), 28.6, 25.7 (oxazoline-CH₃).

EA found (Calc. for $\text{C}_{30}\text{H}_{40}\text{N}_2\text{O}_4\text{TiCl}_2(1/2 \text{CH}_2\text{Cl}_2)$): C: 57.53 (57.43), H: 6.51 (6.45), N: 4.48 (4.43), Cl: 13.10 (14.01).

bis(2-tert-Butyl-6-(3,3-dimethyloxazoliny)phenolato)zirconium dichloride, ($\text{L}^4_2\text{ZrCl}_2$).

From HL⁴ (2.00 g, 8.1 mmol) using a similar method as for $\text{L}^1_2\text{TiCl}_2$. The dichloromethane extract was concentrated and cooled to -20 °C to give pale yellow crystals (1.9 g, 2.8 mmol, 68 %).

^1H NMR (300 MHz, 298 K, CD_2Cl_2) δ 7.80 (dd, 1 H, J = 8.0, 1.7 Hz, Ar-H), 7.62 (dd, 1 H, J = 7.7, 1.7 Hz, Ar-H), 6.93 (t, 1 H, J = 7.9 Hz, Ar-H), 4.26, 4.00 (2 × d, 1 H, J = 8.5 Hz, CH₂), 1.56 (s, 12 H, overlapping C(CH₃)₃, oxazoline CH₃), 1.17 (s, 3 H, oxazoline CH₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, 298 K, CD_2Cl_2) δ 169.4 (O-C=N), 161.9 (Ar-C), 140.3 (Ar-C), 133.7 (Ar-CH), 128.7 (Ar-CH), 120.1 (Ar-CH), 116.1 (Ar-C), 79.3 (oxazoline-CH₂), 70.2 (oxazoline-C(CH₃)₂), 35.3 (C(CH₃)₃), 30.1 (C(CH₃)₃), 29.0 (oxazoline-CH₃)₂, 26.4 (oxazoline-C(CH₃)₂).

EA found (Calc. for $C_{30}H_{40}N_2O_4ZrCl_2(2/5CH_2Cl_2)$): C, 53.07 (53.01), H: 5.72 (5.97), N: 3.96 (4.07); Cl: 13.37 (14.41)

bis(2,6-di-tert-Butyl-6-(3,3-dihydrooxazoliny)phenolato)titanium dichloride, $L^5_2TiCl_2$.

To a stirred solution of $TiCl_4$ (0.46 ml of 10% v/v solution in dichloromethane, 0.42 mmol) at $-78\text{ }^\circ\text{C}$ was added HL^5 (0.240 g, 0.42 mmol) in dichloromethane. The vessel was allowed to warm to room temperature, and stirring was continued for 16 h. The solution was filtered *via* cannula, and the volatiles were then removed *in vacuo*. The solid was sublimated at $275\text{ }^\circ\text{C}$, yielding 0.179 g as a red powder (63 %).

1H NMR¹ 500 MHz (d_8 -toluene, 253 K): δ ppm [7.87, 7.85, 7.74, 7.60 (4 x d, $^4J_{HH} = 2\text{ Hz}$, 1H, *ArH*), 7.85, 7.80 (2 x d, $^4J_{HH} = 2\text{ Hz}$, 1H, *ArH*), 2.8–4.7 (overlapping multiplets from both isomers, 4H from each, CH_2-CH_2), 1.85, 1.31 (2 x s, 9H, *t*Bu), [1.40, 1.31, 1.27, 1.23 (4 x s, 9H, *t*Bu)].

$^{13}C\{^1H\}$ NMR 125 MHz (d_8 -toluene): δ ppm 166.3 (N=C), 162.4, 142.9, 139.1, (*Ar*) 130.7, 123.7 (*Ar C-H*), 115.4 (*Ar*), 79.2 (O- CH_2-CH_2 -N), 54.6 (O- CH_2-CH_2 -N), 35.8, 34.7 ($C(CH_3)_3$), 31.5, 30.17 ($C(CH_3)_3$).

EA: found (calc) C: 59.64 (61.18), H: 7.01 (7.25), N: 3.98 (4.20).

MS (EI^+): m/z 666 (M^+), 631 ($[M-Cl]^+$), 596 ($[M-2Cl]^+$)

bis(2,6-di-tert-Butyl-6-(3,3-dihydrooxazoliny)phenolato)zirconium dichloride, $L^5_2ZrCl_2$.

To HL^5 (0.204 g, 0.711 mmol) in a Schlenk vessel under argon was added NaH (35 mg, 1.5 mmol), and then THF (20 ml) with stirring. The mixture was stirred for 20 h. Stirring was ceased, allowing excess NaH to settle out. The solution was filtered *via* cannula into another Schlenk vessel containing $[ZrCl_4]$ (83 mg, 0.36 mmol) with stirring. The mixture turned from pale to slightly darker yellow. Stirring was continued for 20 h, and then ceased to allow NaCl precipitate to settle, before

¹ Resonances arising from the minor *cis-cis-cis* isomer (*ca.* 25%) are enclosed in square brackets in the 1H spectrum. The 1H signals from the oxazole CH_2-CH_2 protons or both isomers overlap considerably, precluding detailed assignment of this region of the spectrum. Assignment of minor isomer peaks in ^{13}C was not feasible. Integrals are consistent within each species.

filtering the solution *via* cannula. The solvent was removed *in vacuo*, yielding a crude product which was purified by sublimation at 275-300 °C, yielding 99.9 mg (20%).

^1H NMR (CD_2Cl_2): δ ppm 7.68 (d, $^4J_{\text{HH}} = 2.5$ Hz, 1H, ArH), 7.63 (d, $^4J_{\text{HH}} = 2.5$ Hz, 1H, ArH), 4.48 (br. m, 2H, CH_2), 3.7-4.2 (br, 2H, CH_2), 1.50 (s, 9H, ^tBu), 1.29 (s, 9H, ^tBu).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ ppm 169.5 (oxazole N=C-O), 159.9, 142.5, 139.0 (Ar) 131.3, 124.3 (Ar C-H), 113.7 (Ar) 68.2 (CH_2), 35.6, 34.8 ($\text{C}(\text{CH}_3)_3$), 31.5 29.8 ($\text{C}(\text{CH}_3)_3$).

EA: found (calc) C: 57.28 (57.44), H: 6.71 (6.81), N: 4.02 (3.61).

MS (EI^+): m/z 708 (M^+), 694 ($[\text{M}-\text{CH}_3]^+$).

bis(2,6-di-tert-Butyl-6-(3,3-dimethyloxazolinyl)phenolato)titanium dichloride, $\text{L}^6_2\text{TiCl}_2$.

From HL^6 (0.330 g, 1.09 mmol) using a similar method to $\text{L}^5_2\text{ZrCl}_2$. The product was sublimated at 290 °C, yielding 0.285 g of red crystalline solid (70%).

^1H NMR (CD_2Cl_2): δ ppm 7.80 (d, $^4J_{\text{HH}} = 2$ Hz, 1H, ArH), 7.75 (d, $^4J_{\text{HH}} = 2$ Hz, 1H, ArH), 4.31 (d, $^2J_{\text{HH}} = 8$ Hz, 1H, oxazole CH_2), 3.98 (d, $^2J_{\text{HH}} = 2$ Hz, 1H, oxazole CH_2), 1.64 (s, 3H, CH_3), 1.63 (s, 9H, ^tBu), 1.39 (s, 9H, ^tBu), 1.20 (s, 3H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ ppm 167.8 (N=C), 162.3, 143.8, 138.5 (Ar) 131.4, 124.6 (Ar C-H), 117.4 (Ar), 79.7 (O-C-C(CH_3) $_2$), 71.8 (C-C(CH_3) $_2$ -N), 35.7, 34.9 ($\text{C}(\text{CH}_3)_3$), 31.5, 30.5 ($\text{C}(\text{CH}_3)_3$), 28.8, 25.9 ($\text{C}(\text{CH}_3)_2$).

EA: found (calc) C: 62.84 (63.07), H: 7.78 (7.80), N: 3.87 (3.76).

MS (EI^+): m/z 722 (M^+), 687 ($[\text{M}-\text{Cl}]^+$), 652 ($[\text{M}-2\text{Cl}]^+$), 420 ($[\text{M}-\text{L}^{11}]^+$), 302 ($[\text{L}^{11}]^+$).

bis(2,6-di-tert-Butyl-6-(3,3-dimethyloxazolinyl)phenolato)zirconium dichloride, $\text{L}^6_2\text{ZrCl}_2$.

From HL^6 (0.318 g, 1.05 mmol) using a similar method to $\text{L}^5_2\text{ZrCl}_2$. The crude product was recrystallised from dichloromethane/pentane, yielding 0.180 g of pale yellow crystalline solid (44%).

^1H NMR (CD_2Cl_2): δ ppm 7.80 (d, $^4J_{\text{HH}} = 2.5$ Hz, 1H, ArH), 7.71 (d, $^4J_{\text{HH}} = 2.5$ Hz, 1H, ArH), 4.30 (d, $^2J_{\text{HH}} = 8.5$ Hz, 1H, CH_2), 4.03 (d, $^2J_{\text{HH}} = 8.5$ Hz, 1H, CH_2), 1.60 (s, 3H, CH_3), 1.59 (s, 9H, ^tBu), 1.37 (s, 9H, ^tBu), 1.22 (s, 3H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ ppm 169.5 (N=C), 159.7, 142.1, 139.2, (Ar) 131.4, 124.5 (Ar C-H), 117.4 (Ar), 79.2 (O-C-C(CH_3) $_2$), 69.9 (C-C(CH_3) $_2$ -N), 35.4, 34.6 (C(CH_3) $_3$), 31.3, 30.0 (C(CH_3) $_3$), 28.9, 26.3 (C(CH_3) $_2$).

EA: found (calc) C: 59.55 (59.51), H: 7.28 (7.36), N: 3.74 (3.65). MS (EI^+): m/z 766 (M^+), 751 ($[\text{M}-\text{CH}_3]^+$), 730 ($[\text{M}-\text{Cl}]^+$).

bis(2,6-di-isopropyl-6-(3,3-dimethyloxazoliny)phenolato)titanium dichloride, $\text{L}^3_2\text{TiCl}_2$.

From HL^3 (0.233 g, 0.85 mmol) using a similar method to $\text{L}^5_2\text{ZrCl}_2$. The crude product was sublimated at 275 °C, yielding 0.098 g of red crystalline solid (35%).

^1H NMR (CD_5Br): δ ppm 7.75 (d, $^4J_{\text{HH}} = 2$ Hz, 1H, ArH), 7.46 (d, $^4J_{\text{HH}} = 2$ Hz, 1H, ArH), 3.89 (sept., $^3J_{\text{HH}} = 7$ Hz, 1H CH(CH_3) $_2$), 3.83 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, O-CH $_2$) 3.61 (d, $^3J_{\text{HH}} = 8$ Hz, 1H, O-CH $_2$) 2.81 (sept., $^3J_{\text{HH}} = 7$ Hz, 1H CH(CH_3) $_2$), 1.76 (s, 1H, CH $_3$) 1.53 (d, $^3J_{\text{HH}} = 7$ Hz, 3H, CH(CH_3) $_2$) 1.38 (d, $^3J_{\text{HH}} = 7$ Hz, 3H, CH(CH_3) $_2$) 1.20 (d, $^3J_{\text{HH}} = 7$ Hz, 3H, CH(CH_3) $_2$) 1.19 (d, $^3J_{\text{HH}} = 7$ Hz, 3H, CH(CH_3) $_2$) 0.94 (s, 1H, CH $_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (CD_5Br): , 137.0, 133.1, 120.2, 111.8, 75.5, 66.4, 29.6, 24.9, 20.2, 20.0, 19.8, 18.0, 23.8, 22.5.

EA: found (calc) C: 60.95 (61.18) H: 7.14 (7.25), N: 4.16 (4.20).

MS (EI^+): m/z 666 (M^+), 631 ($[\text{M}-\text{Cl}]^+$).

bis(2,6-di-isopropyl-6-(3,3-dimethyloxazoliny)phenolato)zirconium dichloride, $\text{L}^3_2\text{ZrCl}_2$.

From HL^3 (0.441 g, 1.6 mmol) using a similar method to $\text{L}^5_2\text{ZrCl}_2$. The crude product was sublimated at 275 °C, yielding 0.066 g of yellow solid (6%).

^1H NMR 2 (d_5 -pyridine): δ ppm 7.83 (d, $^4J_{\text{HH}} = 2$ Hz, 1H, ArH), 7.63 (d, $^4J_{\text{HH}} = 2$ Hz, 1H, ArH), 3.6-4.3 (m, 6H, overlapping signals from O-CH $_2$, CH(CH_3) $_2$), 2.8-3.0 (m, 2H, overlapping signals from

2 Two isomers present in a ratio *ca.* 4:1 with many overlapping peaks. Detailed assignment not feasible. Not sufficiently soluble for ^{13}C NMR spectroscopy.

$CH(CH_3)_2$ from both isomers). 1.92 (s, 3H, CH_3), 1.35-1.50 (m, 12H, overlapping CH_3 signals) 1.15-1.30 (m, 18H, overlapping CH_3 signals).

EA: found (calc) C: 56.58 (57.44) H: 6.74 (6.81), N: 3.90 (3.94). MS (EI^+): m/z 708 (M^+), 694 ($M-CH_3$)⁺, 673 ($[M-Cl]^+$).

bis(2,6-di-tert-Butyl-6-(3,3-dimethyloxazoliny)phenolato)zirconium dibenzyl, $L^5Zr(CH_2Ph)_2$

To HL⁵ (0.175 g, 0.61 mmol), in a Schlenk vessel under argon was added $Zr(CH_2Ph)_2$ (0.139 g, 0.5 eq), and the mixture made up with pentane, at -78 °C with stirring and the exclusion of light. The mixture was allowed to warm to r.t, and stirred for 3h. The product was recrystallised from pentane, yielding 0.110 g of pale yellow powder (44%).

¹H NMR 400 MHz (C_6D_6): δ ppm 8.07 (d, ⁴ $J_{HH} = 2$ Hz, 1H, ArH), 7.86 (br. s, 1H, ArH), 6.9-7.2 (m, 4H, overlapping benzyl C_6H_5 signals), 6.75 (m, 1H, C_6H_5), 3-4 (br. m, 4H, CH_2-CH_2), 2.92 (br. s, 2H, CH_2Ph), 1.87 (br. s, 9H, $C(CH_3)_3$), 1.43 (s, 9H, $C(CH_3)_3$)

EA: found (calc) C: 65.78 (70.11), H: 7.46 (7.60), N: 3.64 (3.41)

MS (EI^+): m/z 820 (M^+), 729 ($[M-(CH_2Ph)]^+$)

bis(2,6-di-tert-Butyl-6-(3,3-dimethyloxazoliny)phenolato)zirconium dibenzyl, $L^6Zr(CH_2Ph)_2$

To HL⁶ (0.320 g, 1.06 mmol), in a Schlenk vessel under argon was added $Zr(CH_2Ph)_2$ (240 mg, 0.5 eq), and the mixture made up with toluene, with stirring and the exclusion of light. The mixture was stirred for 30 min, then the solvent removed in vacuo. The product was recrystallised from pentane, yielding 0.250 g of deep yellow powder (27%).

¹H NMR 400 MHz (d_8 -toluene): δ ppm 8.03, 7.80 (2 x d, ⁴ $J_{HH} = 3$ Hz, 1H, ArH), 6.89 (m, 4H, overlapping benzyl C_6H_5 signals), 6.60-6.66 (m, 1H, C_6H_5), 3.30, 3.20 (2 x d, ² $J_{HH} = 8$ Hz, 1H, O- CH_2), 2.92, 2.80 (2 x d, 1H, ² $J_{HH} = 11$ Hz, CH_2Ph), 1.78, 1.32 (2 x s, 9H, $C(CH_3)_3$), 0.98, 0.73 (2 x s, 3H, N- $C(CH_3)_2$)

$^{13}\text{C}\{^1\text{H}\}$ NMR 100 MHz (d_8 -toluene): δ ppm 168.3 (N=C), 161.0, 150.2, 141.1, 139.3 (Ar), 130.7, 127.8, 126.5, 124.8, 120.1 (Ar C-H), 116.5 (Ar), 78.0 (O-C-C(CH₃)₂), 72.0 (CH₂Ph), 69.2 (C-C(CH₃)₂-N), 35.9, 34.7 (C(CH₃)₃), 31.8, 31.7 (C(CH₃)₃), 27.7, 26.5 (C(CH₃)₂)

EA: found (calc) C: 69.50 (71.11), H: 8.00 (8.03), N: 3.08 (3.19)

MS (EI⁺): m/z 878(M⁺), 785 ([M-(CH₂Ph)]⁺)

bis(2,6-di-isopropyl-6-(3,3-dimethyloxazoliny)phenolato)zirconium dibenzyl, L³Zr(CH₂Ph)₂

To HL³ (0.183 g, 0.66 mmol), in a Schlenk vessel under argon was added Zr(CH₂Ph)₂ (0.152 g, 0.5 eq), and the mixture made up with toluene, with stirring and the exclusion of light. The mixture was stirred for 30 min, then the solvent removed in vacuo. The product was recrystallised from pentane, yielding 0.140 g of deep yellow powder (26%).

^1H NMR 400 MHz (C₆D₆): δ ppm 7.85, 7.46 (2 x d, $^4J_{\text{HH}} = 2$ Hz, 1H, ArH), 7.00-7.10 (m, 4H, overlapping benzyl C₆H₅ signals), 6.70-6.86 (m, 1H, C₆H₅), 4.03 (sept., $^3J_{\text{HH}} = 7$ Hz, 1H, CH(CH₃)₂), 3.38, 3.30 (2 x d, $^2J_{\text{HH}} = 8$ Hz, 1H, O-CH₂), 2.82 (sept., $^3J_{\text{HH}} = 7$ Hz, 1H, CH(CH₃)₂) 2.74, 2.69 (2 x d, 1H, $^2J_{\text{HH}} = 11$ Hz, CH₂Ph), 1.54, 1.46 (2 x d, $^3J_{\text{HH}} = 7$ Hz, 3H, CH(CH₃)₂), 1.28 (s, 3H, N-C(CH₃)₂), 1.27, 1.25 (2 x d, $^3J_{\text{HH}} = 7$ Hz, 3H, CH(CH₃)₂), 0.70 (s, 3H, N-C(CH₃)₂)

$^{13}\text{C}\{^1\text{H}\}$ NMR 100 MHz (C₆D₆): δ ppm 167.5 (N=C), 159.1, 149.6, 139.4, 138.9 (Ar), 130.1, 126.3, 124.6, 120.1 (Ar C-H), 114.8 (Ar), 78.3 (O-C-C(CH₃)₂), 70.4 (CH₂Ph), 68.8 (C-C(CH₃)₂-N), 34.0, 26.7 (CH(CH₃)₂), 27.8, 27.7, 24.4, 24.4 (CH(CH₃)₂), 23.9, 23.5 (C(CH₃)₂)

EA: found (calc) C: 69.21 (70.11), H: 7.48 (7.60), N: 3.52 (3.41)

MS (EI⁺): m/z 729 ([M-(CH₂Ph)]⁺)

Reactions of L^6ZrCl_2 with MAO/ $AlMe_3$

L^6ZrCl_2 reacts with MAO-2 ($Al/Zr = 45$, $[Zr] = 0.004$ M) to give multiple unidentified species with broadened lines. After storing this sample for 2d at RT, L^6ZrCl_2 is completely converted to $L^6AlMe_2 \cdot MAO$. The latter was assigned by comparison of its 1H NMR spectrum with that for L^6AlMe_2 formed in the system $L^6ZrCl_2/AlMe_3/MAO$ ($Zr:Al:Al_{MAO} = 1:85:3.5$); MAO was added as a catalyst of ligand exchange process. NMR shifts of L^6AlMe_2 slightly differ from those of $L^6AlMe_2 \cdot MAO$. See Figure 1 overleaf.

1H NMR spectrum of L^6ZrCl_2 (toluene- d_8 , 20 °C, δ): 8.02 (d, 1H, $J=2.6$ Hz, aryl), 7.81 (d, 1H, $J=2.6$ Hz, aryl), 3.46 (d, 1H, $J= 8.3$ Hz, CHH), 3.29 (d, 1H, $J= 8.3$ Hz, CHH), 1.82 (s, 18H, tBu), 1.46 (s, 6H, $C(CH_3)CH_3$), 1.28 (s, 18H, tBu), 0.90 (s, 6H, $C(CH_3)CH_3$).

L^6AlMe_2 (toluene- d_8 , 20 °C, δ): 7.72 (d, 1H, $J=2.7$ Hz, aryl), 7.68 (d, 1H, $J=2.6$ Hz, aryl), 3.26 (s, 2H, CH_2), 1.57 (s, 9H, tBu), 1.30 (s, 9H, tBu), 0.92 (s, 6H, $C(CH_3)_2$).

L^6AlMe_2 (toluene- d_8 , -5 °C, δ): 7.78 (d, 1H, $J=2.7$ Hz, aryl), 7.70 (d, 1H, $J=2.6$ Hz, aryl), 3.12 (s, 2H, CH_2), 1.61 (s, 9H, tBu), 1.32 (s, 9H, tBu), 0.85 (s, 6H, $C(CH_3)_2$), -0.26 (s, 6H, $Al(CH_3)_2$).

$L^6AlMe_2 \cdot MAO$ (toluene- d_8 , 20 °C, δ): 7.77 (unresolved, 1H, aryl), 7.71 (unresolved, 1H, aryl), 3.27 (s, 2H, CH_2), 1.61 (s, 9H, tBu), 1.35 (s, 9H, tBu), 0.95 (s, 6H, $C(CH_3)_2$).

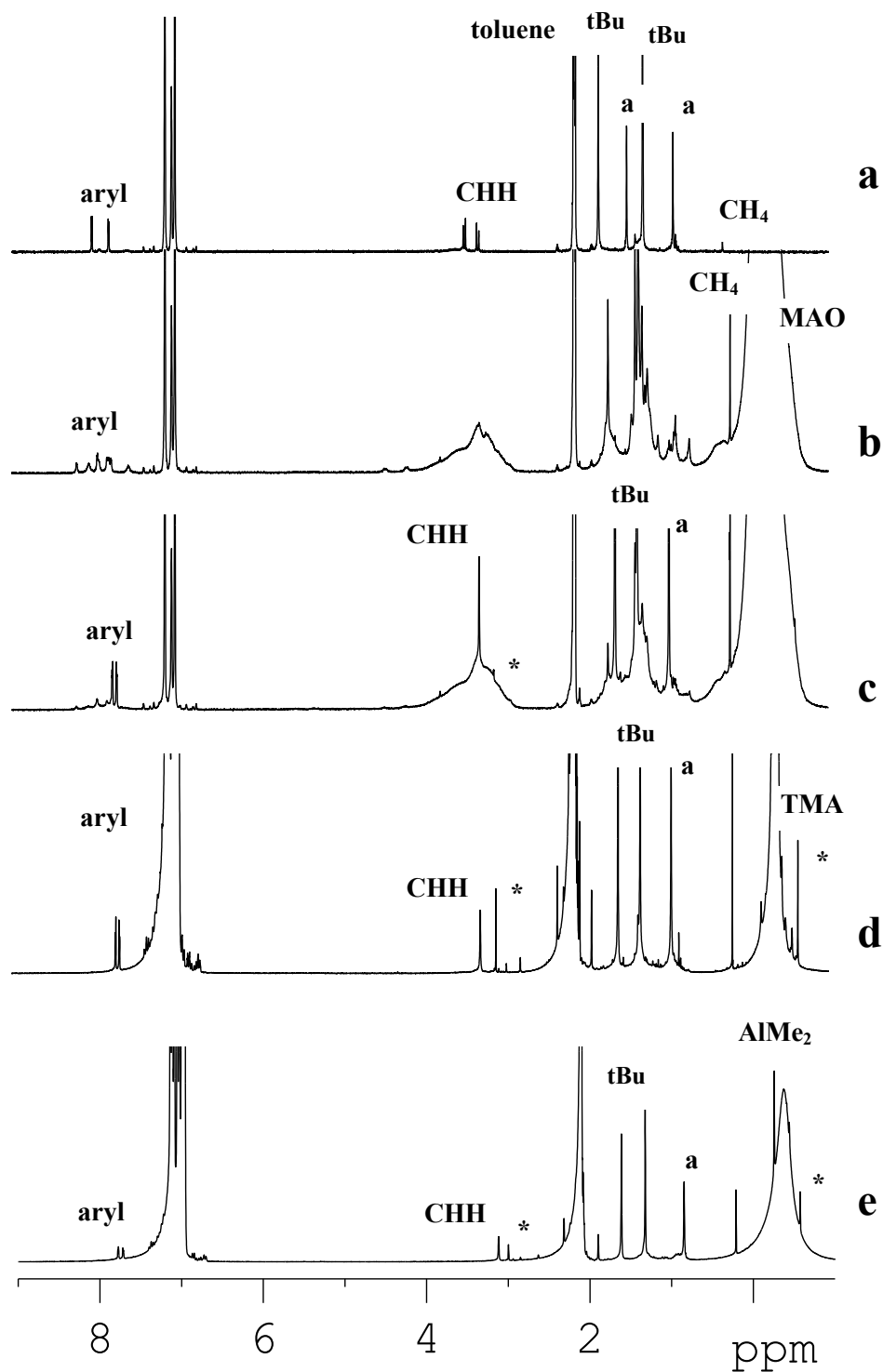


Figure 1. ^1H NMR spectra (toluene- d_8 , 20 °C unless otherwise noted) of complex $\text{Zr}(\text{Sal}')_2\text{Cl}_2$ (a); the system $\text{Zr}(\text{Sal}')_2\text{Cl}_2/\text{MAO-2}$, $\text{Al}/\text{Zr}=45$, $[\text{Zr}] = 0.004 \text{ M}$ (b); the same system in 2 days (c); $\text{Zr}(\text{Sal}')_2\text{Cl}_2/\text{AlMe}_3/\text{MAO}$, $\text{Zr}:\text{Al}:\text{Al}_{\text{MAO}}=1:85:3.5$ in 1 day (d); the same at -5 °C (e). 'a' stand for $\text{C}(\text{CH}_3)_2$ peaks. Asterisks mark impurities in MAO or TMA.

Table 1. Crystal data and structure refinement of [L₂ZrCl₂].

Identification code	04src0192	
Empirical formula	C ₂₄ H ₂₈ Cl ₂ N ₂ O ₄ Zr	
Formula weight	570.60	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	
Unit cell dimensions	$a = 11.4174(18) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 13.9809(9) \text{ \AA}$	$\beta = 90^\circ$
	$c = 15.0376(17) \text{ \AA}$	$\gamma = 90^\circ$
Volume	2400.4(5) Å ³	
Z	4	
Density (calculated)	1.579 Mg / m ³	
Absorption coefficient	0.715 mm ⁻¹	
$F(000)$	1168	
Crystal	Plate; Colourless	
Crystal size	0.40 × 0.20 × 0.04 mm ³	
θ range for data collection	3.08 – 27.48°	
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 16, -19 ≤ l ≤ 19	
Reflections collected	26703	
Independent reflections	5479 [$R_{int} = 0.0502$]	
Completeness to $\theta = 27.48^\circ$	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9720 and 0.7631	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5479 / 0 / 305	
Goodness-of-fit on F^2	1.032	
Final R indices [$F^2 > 2\sigma(F^2)$]	$RI = 0.0286$, $wR2 = 0.0618$	
R indices (all data)	$RI = 0.0368$, $wR2 = 0.0648$	
Absolute structure parameter	-0.04(3)	
Extinction coefficient	0.0023(3)	

Largest diff. peak and hole

0.463 and $-0.440 \text{ e \AA}^{-3}$

Diffraction: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *asymmetric unit* sphere). **Cell determination:** DirAx (Duisenberg, A.J.M.(1992). *J. Appl. Cryst.* 25, 92-96.) **Data collection:** Collect (Collect: Data collection software, R. Hooft, Nonius B.V., 1998). **Data reduction and cell refinement:** *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. 276: *Macromolecular Crystallography*, part A, pp. 307-326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction:** *SORTAV* (R. H. Blessing, *Acta Cryst.* A51 (1995) 33-37; R. H. Blessing, *J. Appl. Cryst.* 30 (1997) 421-426). **Structure solution:** *SHELXS97* (G. M. Sheldrick, *Acta Cryst.* (1990) A46 467-473). **Structure refinement:** *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** *Cameron* - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

Special details:

All hydrogen atoms were fixed.

Table 2. Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] and site occupancy factors.

U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U_{eq}	<i>S.o.f.</i>
C11	437(1)	1603(1)	8532(1)	23(1)	1
C12	736(1)	1626(1)	6197(1)	25(1)	1
Zr1	2014(1)	1521(1)	7483(1)	14(1)	1
C1	3863(2)	530(2)	6143(2)	16(1)	1
C2	4987(2)	1545(2)	5397(2)	33(1)	1
C3	4245(2)	2101(2)	6057(2)	21(1)	1
C4	3450(3)	2787(2)	5576(2)	33(1)	1
C5	4995(3)	2605(2)	6733(2)	39(1)	1
C6	3451(2)	-431(2)	6331(2)	16(1)	1
C7	2613(2)	-597(2)	6980(2)	16(1)	1
C8	2216(2)	-1525(2)	7151(2)	20(1)	1
C9	2651(2)	-2254(2)	6639(2)	23(1)	1
C10	3463(2)	-2097(2)	5983(2)	23(1)	1
C11	3873(2)	-1195(2)	5827(2)	21(1)	1
C12	1308(3)	-1689(2)	7840(2)	30(1)	1
N1	3550(2)	1331(2)	6492(1)	16(1)	1
O1	4669(2)	572(1)	5509(1)	24(1)	1
O2	2174(1)	131(1)	7432(1)	17(1)	1
C21	3417(2)	2314(2)	9157(2)	17(1)	1
C22	4289(2)	1212(2)	9992(2)	21(1)	1
C23	3918(2)	758(2)	9117(2)	17(1)	1
C24	3161(2)	-108(2)	9293(2)	23(1)	1
C25	4958(2)	506(2)	8544(2)	23(1)	1
C26	2968(2)	3269(2)	9017(2)	17(1)	1
C27	2494(2)	3538(2)	8206(2)	19(1)	1
C28	2121(2)	4474(2)	8068(2)	22(1)	1
C29	2174(2)	5103(2)	8762(2)	25(1)	1
C30	2619(2)	4840(2)	9578(2)	26(1)	1

C31	3034(2)	3930(2)	9704(2)	21(1)	1
C32	1669(3)	4763(2)	7179(2)	30(1)	1
N21	3253(2)	1557(2)	8688(1)	14(1)	1
O21	4070(2)	2217(1)	9881(1)	20(1)	1
O22	2391(1)	2903(1)	7552(1)	20(1)	1

Table 3. Bond lengths [Å] and angles [°].

C11–Zr1	2.3964(6)	C9–H9	0.9500
C12–Zr1	2.4275(6)	C10–C11	1.366(4)
Zr1–O2	1.9532(14)	C10–H10	0.9500
Zr1–O22	1.9831(15)	C11–H11	0.9500
Zr1–N21	2.2997(18)	C12–H12A	0.9800
Zr1–N1	2.317(2)	C12–H12B	0.9800
C1–N1	1.287(3)	C12–H12C	0.9800
C1–O1	1.325(3)	C21–N21	1.285(3)
C1–C6	1.451(4)	C21–O21	1.327(3)
C2–O1	1.419(3)	C21–C26	1.445(4)
C2–C3	1.519(4)	C22–O21	1.437(3)
C2–H2A	0.9900	C22–C23	1.521(3)
C2–H2B	0.9900	C22–H22A	0.9900
C3–N1	1.488(3)	C22–H22B	0.9900
C3–C5	1.505(4)	C23–N21	1.498(3)
C3–C4	1.506(4)	C23–C25	1.509(3)
C4–H4A	0.9800	C23–C24	1.510(4)
C4–H4B	0.9800	C24–H24A	0.9800
C4–H4C	0.9800	C24–H24B	0.9800
C5–H5A	0.9800	C24–H24C	0.9800
C5–H5B	0.9800	C25–H25A	0.9800
C5–H5C	0.9800	C25–H25B	0.9800
C6–C7	1.386(3)	C25–H25C	0.9800
C6–C11	1.395(3)	C26–C27	1.387(3)
C7–O2	1.323(3)	C26–C31	1.387(3)
C7–C8	1.398(4)	C27–O22	1.328(3)
C8–C9	1.371(4)	C27–C28	1.392(4)
C8–C12	1.484(4)	C28–C29	1.366(4)
C9–C10	1.372(4)	C28–C32	1.490(4)

C29-C30	1.377(4)	C31-H31	0.9500
C29-H29	0.9500	C32-H32A	0.9800
C30-C31	1.372(4)	C32-H32B	0.9800
C30-H30	0.9500	C32-H32C	0.9800
O2-Zr1-O22	162.08(7)	N1-C3-C4	110.5(2)
O2-Zr1-N21	89.73(7)	C5-C3-C4	111.6(3)
O22-Zr1-N21	78.66(8)	N1-C3-C2	102.4(2)
O2-Zr1-N1	77.88(7)	C5-C3-C2	111.3(2)
O22-Zr1-N1	88.93(7)	C4-C3-C2	110.4(2)
N21-Zr1-N1	92.54(7)	C3-C4-H4A	109.5
O2-Zr1-Cl1	98.26(5)	C3-C4-H4B	109.5
O22-Zr1-Cl1	94.69(5)	H4A-C4-H4B	109.5
N21-Zr1-Cl1	86.69(5)	C3-C4-H4C	109.5
N1-Zr1-Cl1	176.07(6)	H4A-C4-H4C	109.5
O2-Zr1-Cl2	94.90(5)	H4B-C4-H4C	109.5
O22-Zr1-Cl2	96.50(6)	C3-C5-H5A	109.5
N21-Zr1-Cl2	175.16(6)	C3-C5-H5B	109.5
N1-Zr1-Cl2	87.07(5)	H5A-C5-H5B	109.5
Cl1-Zr1-Cl2	94.02(3)	C3-C5-H5C	109.5
N1-C1-O1	116.6(2)	H5A-C5-H5C	109.5
N1-C1-C6	129.4(2)	H5B-C5-H5C	109.5
O1-C1-C6	114.0(2)	C7-C6-C11	119.5(2)
O1-C2-C3	105.6(2)	C7-C6-C1	121.1(2)
O1-C2-H2A	110.6	C11-C6-C1	119.4(2)
C3-C2-H2A	110.6	O2-C7-C6	119.6(2)
O1-C2-H2B	110.6	O2-C7-C8	119.8(2)
C3-C2-H2B	110.6	C6-C7-C8	120.6(2)
H2A-C2-H2B	108.7	C9-C8-C7	118.0(2)
N1-C3-C5	110.2(2)	C9-C8-C12	122.0(2)

C7-C8-C12	119.9(2)	N21-C23-C24	112.5(2)
C8-C9-C10	122.0(2)	C25-C23-C24	111.3(2)
C8-C9-H9	119.0	N21-C23-C22	101.65(19)
C10-C9-H9	119.0	C25-C23-C22	111.9(2)
C11-C10-C9	120.2(2)	C24-C23-C22	110.0(2)
C11-C10-H10	119.9	C23-C24-H24A	109.5
C9-C10-H10	119.9	C23-C24-H24B	109.5
C10-C11-C6	119.7(2)	H24A-C24-H24B	109.5
C10-C11-H11	120.1	C23-C24-H24C	109.5
C6-C11-H11	120.1	H24A-C24-H24C	109.5
C8-C12-H12A	109.5	H24B-C24-H24C	109.5
C8-C12-H12B	109.5	C23-C25-H25A	109.5
H12A-C12-H12B	109.5	C23-C25-H25B	109.5
C8-C12-H12C	109.5	H25A-C25-H25B	109.5
H12A-C12-H12C	109.5	C23-C25-H25C	109.5
H12B-C12-H12C	109.5	H25A-C25-H25C	109.5
C1-N1-C3	107.6(2)	H25B-C25-H25C	109.5
C1-N1-Zr1	124.92(16)	C27-C26-C31	119.8(2)
C3-N1-Zr1	127.08(15)	C27-C26-C21	121.0(2)
C1-O1-C2	107.80(19)	C31-C26-C21	119.2(2)
C7-O2-Zr1	145.17(15)	O22-C27-C26	120.3(2)
N21-C21-O21	116.5(2)	O22-C27-C28	119.4(2)
N21-C21-C26	129.1(2)	C26-C27-C28	120.3(2)
O21-C21-C26	114.4(2)	C29-C28-C27	118.6(2)
O21-C22-C23	105.00(19)	C29-C28-C32	121.8(2)
O21-C22-H22A	110.7	C27-C28-C32	119.6(2)
C23-C22-H22A	110.7	C28-C29-C30	121.6(2)
O21-C22-H22B	110.7	C28-C29-H29	119.2
C23-C22-H22B	110.7	C30-C29-H29	119.2
H22A-C22-H22B	108.8	C31-C30-C29	119.9(2)
N21-C23-C25	109.08(19)	C31-C30-H30	120.1

C29-C30-H30	120.1
C30-C31-C26	119.7(2)
C30-C31-H31	120.1
C26-C31-H31	120.1
C28-C32-H32A	109.5
C28-C32-H32B	109.5
H32A-C32-H32B	109.5
C28-C32-H32C	109.5
H32A-C32-H32C	109.5
H32B-C32-H32C	109.5
C21-N21-C23	107.79(18)
C21-N21-Zr1	122.65(16)
C23-N21-Zr1	129.40(16)
C21-O21-C22	107.10(19)
C27-O22-Zr1	135.14(16)

Table 4. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$]. The anisotropic displacementfactor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C11	18(1)	34(1)	18(1)	-4(1)	3(1)	1(1)
C12	22(1)	35(1)	17(1)	-5(1)	-5(1)	7(1)
Zr1	15(1)	15(1)	13(1)	-1(1)	0(1)	1(1)
C1	13(1)	24(1)	12(1)	1(1)	0(1)	3(1)
C2	33(2)	23(2)	44(2)	9(1)	19(1)	0(1)
C3	21(1)	17(1)	24(1)	5(1)	5(1)	-4(1)
C4	35(2)	33(2)	32(2)	20(1)	11(1)	10(1)
C5	37(2)	48(2)	32(2)	6(1)	-1(1)	-22(2)
C6	14(1)	19(1)	15(1)	-3(1)	-2(1)	1(1)
C7	15(1)	18(1)	14(1)	-1(1)	-2(1)	1(1)
C8	20(1)	19(1)	20(1)	2(1)	-2(1)	2(1)
C9	23(1)	17(1)	29(1)	-3(1)	-8(1)	-2(1)
C10	20(1)	23(2)	26(1)	-9(1)	-3(1)	6(1)
C11	17(1)	23(1)	22(1)	-2(1)	0(1)	3(1)
C12	37(2)	24(2)	30(1)	0(1)	8(1)	-8(1)
N1	15(1)	17(1)	17(1)	2(1)	1(1)	0(1)
O1	25(1)	21(1)	25(1)	1(1)	12(1)	0(1)
O2	20(1)	14(1)	17(1)	-3(1)	4(1)	0(1)
C21	12(1)	22(1)	16(1)	2(1)	1(1)	-1(1)
C22	24(1)	19(1)	18(1)	3(1)	-4(1)	2(1)
C23	19(1)	19(1)	14(1)	1(1)	-1(1)	2(1)
C24	29(2)	20(1)	20(1)	4(1)	-2(1)	1(1)
C25	22(1)	27(2)	21(1)	-1(1)	-1(1)	8(1)
C26	15(1)	18(1)	20(1)	-2(1)	3(1)	-2(1)
C27	16(1)	18(1)	23(1)	-2(1)	3(1)	0(1)
C28	18(1)	18(1)	29(1)	2(1)	2(1)	0(1)
C29	24(2)	13(1)	39(2)	1(1)	2(1)	1(1)

C30	27(2)	18(2)	32(1)	-9(1)	2(1)	0(1)
C31	19(1)	23(1)	20(1)	-3(1)	2(1)	-3(1)
C32	36(2)	19(1)	35(2)	7(1)	-7(1)	1(1)
N21	14(1)	14(1)	13(1)	2(1)	0(1)	2(1)
O21	20(1)	20(1)	18(1)	0(1)	-4(1)	1(1)
O22	28(1)	15(1)	17(1)	-1(1)	-2(1)	3(1)

Table 5. Hydrogen coordinates [$\times 10^4$] and isotropic displacement parameters [$\text{\AA}^2 \times 10^3$].

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	<i>S.o.f.</i>
H2A	4824	1758	4781	40	1
H2B	5831	1637	5522	40	1
H4A	2952	2432	5160	50	1
H4B	3924	3252	5246	50	1
H4C	2957	3124	6008	50	1
H5A	4492	2920	7174	58	1
H5B	5480	3086	6434	58	1
H5C	5501	2139	7032	58	1
H9	2383	-2888	6742	27	1
H10	3741	-2617	5635	28	1
H11	4443	-1087	5378	25	1
H12A	1522	-1347	8385	45	1
H12B	1250	-2375	7966	45	1
H12C	551	-1454	7624	45	1
H22A	3823	951	10492	25	1
H22B	5129	1092	10110	25	1
H24A	2389	100	9502	35	1
H24B	3531	-508	9748	35	1
H24C	3072	-476	8743	35	1
H25A	4684	255	7972	35	1
H25B	5434	20	8844	35	1
H25C	5433	1080	8442	35	1
H29	1896	5738	8681	30	1
H30	2638	5289	10052	31	1
H31	3365	3752	10260	25	1
H32A	1165	5327	7243	45	1
H32B	1216	4236	6921	45	1
H32C	2329	4917	6787	45	1

Table 1. Crystal data and structure refinement for [L⁴ZrCl₂].

Identification code	04src0532 (rb225)	
Empirical formula	C ₃₀ H ₄₀ Cl ₂ N ₂ O ₄ Zr	
Formula weight	654.76	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	$a = 15.947(3) \text{ \AA}$	$\alpha = 90^\circ$
	$b = 8.3503(17) \text{ \AA}$	$\beta = 90.41(3)^\circ$
	$c = 22.819(5) \text{ \AA}$	$\gamma = 90^\circ$
Volume	3038.6(11) Å ³	
Z	4	
Density (calculated)	1.431 Mg / m ³	
Absorption coefficient	0.575 mm ⁻¹	
$F(000)$	1360	
Crystal	Plate; colourless	
Crystal size	0.14 × 0.12 × 0.05 mm ³	
θ range for data collection	3.11 – 27.50°	
Index ranges	-20 ≤ h ≤ 20, -10 ≤ k ≤ 10, -29 ≤ l ≤ 29	
Reflections collected	15884	
Independent reflections	3478 [$R_{int} = 0.0383$]	
Completeness to $\theta = 27.50^\circ$	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9718 and 0.9239	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3478 / 0 / 183	
Goodness-of-fit on F^2	1.041	
Final R indices [$F^2 > 2\sigma(F^2)$]	$RI = 0.0303$, $wR2 = 0.0698$	
R indices (all data)	$RI = 0.0400$, $wR2 = 0.0739$	

Extinction coefficient	0.0016(2)
Largest diff. peak and hole	0.317 and $-0.434 \text{ e } \text{\AA}^{-3}$

Diffractometer: *Nonius KappaCCD* area detector (ϕ scans and ω scans to fill *asymmetric unit* sphere). **Cell determination:** DirAx (Duisenberg, A.J.M.(1992). *J. Appl. Cryst.* 25, 92-96.) **Data collection:** Collect (Collect: Data collection software, R. Hoof, Nonius B.V., 1998). **Data reduction and cell refinement:** *Denzo* (Z. Otwinowski & W. Minor, *Methods in Enzymology* (1997) Vol. 276: *Macromolecular Crystallography*, part A, pp. 307–326; C. W. Carter, Jr. & R. M. Sweet, Eds., Academic Press). **Absorption correction:** *SORTAV* (R. H. Blessing, *Acta Cryst.* A51 (1995) 33–37; R. H. Blessing, *J. Appl. Cryst.* 30 (1997) 421–426). **Structure solution:** *SHELXS97* (G. M. Sheldrick, *Acta Cryst.* (1990) A46 467–473). **Structure refinement:** *SHELXL97* (G. M. Sheldrick (1997), University of Göttingen, Germany). **Graphics:** Cameron - A Molecular Graphics Package. (D. M. Watkin, L. Pearce and C. K. Prout, Chemical Crystallography Laboratory, University of Oxford, 1993).

Special details:

Table 2. Atomic coordinates [$\times 10^4$], equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] and site occupancy factors. U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U_{eq}	$S.o.f.$
C1	5988(1)	130(2)	6315(1)	19(1)	1
C2	6126(1)	912(2)	5773(1)	22(1)	1
C3	5626(1)	2404(2)	5591(1)	24(1)	1
C4	4676(1)	2096(3)	5591(1)	31(1)	1
C5	5854(2)	2940(3)	4968(1)	37(1)	1
C6	5843(1)	3776(3)	6014(1)	32(1)	1
C7	6777(1)	310(3)	5434(1)	27(1)	1
C8	7281(1)	-958(3)	5607(1)	29(1)	1
C9	7160(1)	-1677(3)	6141(1)	26(1)	1
C10	6510(1)	-1124(2)	6504(1)	20(1)	1
C11	3552(1)	-1779(2)	7905(1)	19(1)	1
C12	3061(1)	-3366(2)	7182(1)	26(1)	1
C13	3729(1)	-2229(2)	6932(1)	21(1)	1
C14	4458(1)	-3168(2)	6678(1)	25(1)	1
C15	3340(1)	-1101(3)	6481(1)	30(1)	1
N1	3998(1)	-1281(2)	7463(1)	19(1)	1
O1	5364(1)	583(2)	6666(1)	20(1)	1
O2	3045(1)	-3022(2)	7803(1)	25(1)	1
Cl1	3936(1)	2676(1)	7230(1)	29(1)	1
Zr1	5000	733(1)	7500	16(1)	1

Table 3. Bond lengths [Å] and angles [°].

C1–O1	1.337(2)	C10–C11 ⁱ	1.460(3)
C1–C10	1.404(3)	C11–N1	1.306(2)
C1–C2	1.419(3)	C11–O2	1.335(2)
C2–C7	1.393(3)	C11–C10 ⁱ	1.460(3)
C2–C3	1.534(3)	C12–O2	1.448(2)
C3–C4	1.536(3)	C12–C13	1.539(3)
C3–C6	1.536(3)	C12–H12A	0.9900
C3–C5	1.538(3)	C12–H12B	0.9900
C4–H4A	0.9800	C13–N1	1.505(2)
C4–H4B	0.9800	C13–C14	1.520(3)
C4–H4C	0.9800	C13–C15	1.525(3)
C5–H5A	0.9800	C14–H14A	0.9800
C5–H5B	0.9800	C14–H14B	0.9800
C5–H5C	0.9800	C14–H14C	0.9800
C6–H6A	0.9800	C15–H15A	0.9800
C6–H6B	0.9800	C15–H15B	0.9800
C6–H6C	0.9800	C15–H15C	0.9800
C7–C8	1.386(3)	N1–Zr1	2.3217(16)
C7–H7	0.9500	O1–Zr1	1.9965(13)
C8–C9	1.373(3)	C11–Zr1	2.4239(6)
C8–H8	0.9500	Zr1–O1 ⁱ	1.9965(13)
C9–C10	1.409(3)	Zr1–N1 ⁱ	2.3216(16)
C9–H9	0.9500	Zr1–C11 ⁱ	2.4239(6)
O1–C1–C10	118.04(16)	C7–C2–C3	122.09(17)
O1–C1–C2	120.91(17)	C1–C2–C3	121.71(16)
C10–C1–C2	121.05(16)	C2–C3–C4	111.98(17)
C7–C2–C1	116.07(18)	C2–C3–C6	108.82(16)

C4-C3-C6	110.06(17)	C10-C9-H9	120.4
C2-C3-C5	111.13(16)	C1-C10-C9	120.12(17)
C4-C3-C5	106.73(17)	C1-C10-C11 ⁱ	121.28(16)
C6-C3-C5	108.02(18)	C9-C10-C11 ⁱ	118.36(17)
C3-C4-H4A	109.5	N1-C11-O2	116.42(16)
C3-C4-H4B	109.5	N1-C11-C10 ⁱ	129.46(17)
H4A-C4-H4B	109.5	O2-C11-C10 ⁱ	114.04(15)
C3-C4-H4C	109.5	O2-C12-C13	104.85(15)
H4A-C4-H4C	109.5	O2-C12-H12A	110.8
H4B-C4-H4C	109.5	C13-C12-H12A	110.8
C3-C5-H5A	109.5	O2-C12-H12B	110.8
C3-C5-H5B	109.5	C13-C12-H12B	110.8
H5A-C5-H5B	109.5	H12A-C12-H12B	108.9
C3-C5-H5C	109.5	N1-C13-C14	111.41(15)
H5A-C5-H5C	109.5	N1-C13-C15	109.29(15)
H5B-C5-H5C	109.5	C14-C13-C15	111.66(17)
C3-C6-H6A	109.5	N1-C13-C12	102.77(14)
C3-C6-H6B	109.5	C14-C13-C12	110.82(16)
H6A-C6-H6B	109.5	C15-C13-C12	110.55(17)
C3-C6-H6C	109.5	C13-C14-H14A	109.5
H6A-C6-H6C	109.5	C13-C14-H14B	109.5
H6B-C6-H6C	109.5	H14A-C14-H14B	109.5
C8-C7-C2	123.39(18)	C13-C14-H14C	109.5
C8-C7-H7	118.3	H14A-C14-H14C	109.5
C2-C7-H7	118.3	H14B-C14-H14C	109.5
C9-C8-C7	120.18(18)	C13-C15-H15A	109.5
C9-C8-H8	119.9	C13-C15-H15B	109.5
C7-C8-H8	119.9	H15A-C15-H15B	109.5
C8-C9-C10	119.12(19)	C13-C15-H15C	109.5
C8-C9-H9	120.4	H15A-C15-H15C	109.5

H15B-C15-H15C	109.5
C11-N1-C13	107.51(15)
C11-N1-Zr1	125.47(13)
C13-N1-Zr1	127.01(11)
C1-O1-Zr1	144.21(12)
C11-O2-C12	108.07(14)
O1-Zr1-O1 ⁱ	172.81(7)
O1-Zr1-N1	97.13(6)
O1 ⁱ -Zr1-N1	77.59(6)
O1-Zr1-N1 ⁱ	77.59(5)
O1 ⁱ -Zr1-N1 ⁱ	97.13(6)
N1-Zr1-N1 ⁱ	87.15(8)
O1-Zr1-Cl1 ⁱ	94.40(4)
O1 ⁱ -Zr1-Cl1 ⁱ	90.41(4)
N1-Zr1-Cl1 ⁱ	167.11(4)
N1 ⁱ -Zr1-Cl1 ⁱ	89.72(4)
O1-Zr1-Cl1	90.41(4)
O1 ⁱ -Zr1-Cl1	94.40(4)
N1-Zr1-Cl1	89.72(4)
N1 ⁱ -Zr1-Cl1	167.11(4)
Cl1 ⁱ -Zr1-Cl1	95.97(3)

Symmetry transformations used to generate equivalent atoms:

(i) $-x+1, y, -z+3/2$

Table 4. Anisotropic displacement parameters [$\text{\AA}^2 \times 10^3$]. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C1	14(1)	21(1)	21(1)	-3(1)	0(1)	-1(1)
C2	18(1)	25(1)	22(1)	-1(1)	-1(1)	-1(1)
C3	22(1)	26(1)	24(1)	4(1)	2(1)	2(1)
C4	23(1)	36(1)	33(1)	8(1)	-3(1)	3(1)
C5	41(1)	38(1)	31(1)	12(1)	8(1)	10(1)
C6	30(1)	26(1)	39(1)	1(1)	2(1)	3(1)
C7	24(1)	34(1)	23(1)	0(1)	4(1)	2(1)
C8	24(1)	37(1)	27(1)	-4(1)	7(1)	7(1)
C9	20(1)	28(1)	29(1)	-3(1)	1(1)	6(1)
C10	16(1)	21(1)	24(1)	-2(1)	-1(1)	1(1)
C11	13(1)	15(1)	29(1)	1(1)	-2(1)	0(1)
C12	24(1)	25(1)	29(1)	-9(1)	5(1)	-6(1)
C13	18(1)	21(1)	25(1)	-4(1)	1(1)	-1(1)
C14	20(1)	27(1)	28(1)	-7(1)	3(1)	-2(1)
C15	28(1)	32(1)	30(1)	-3(1)	-7(1)	2(1)
N1	14(1)	16(1)	25(1)	-2(1)	1(1)	1(1)
O1	16(1)	21(1)	23(1)	1(1)	3(1)	3(1)
O2	22(1)	24(1)	29(1)	-2(1)	2(1)	-9(1)
Cl1	20(1)	25(1)	41(1)	7(1)	5(1)	7(1)
Zr1	12(1)	15(1)	21(1)	0	3(1)	0
