

## Experimental Details

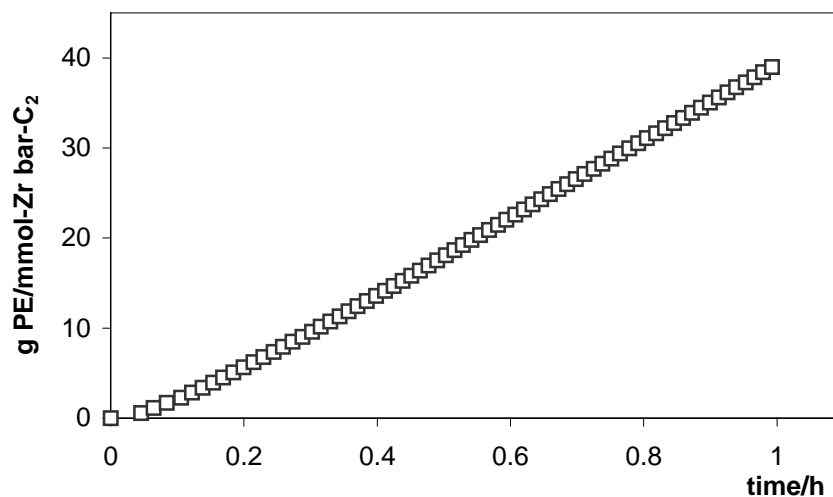
### Problems and solutions for alkene polymerisation catalysts incorporating Schiff-bases; migratory insertion and radical mechanisms of catalyst deactivation<sup>†</sup>

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Uptake of ethene with catalyst  $[\text{ZrL}^2\text{Cl}_2]$ . Temperature, 323 K; ethene pressure, 1.2 bar; solvent, toluene (500 ml); catalyst,  $[\text{ZrL}^2(\text{Cl})_2]$  (10 mg, 0.0139 mmol); cocatalyst,  $[\text{MAO}]$  (Al:Zr molar ratio, 1000:1)

### <sup>1</sup>H NMR spectra showing products of both decomposition mechanisms

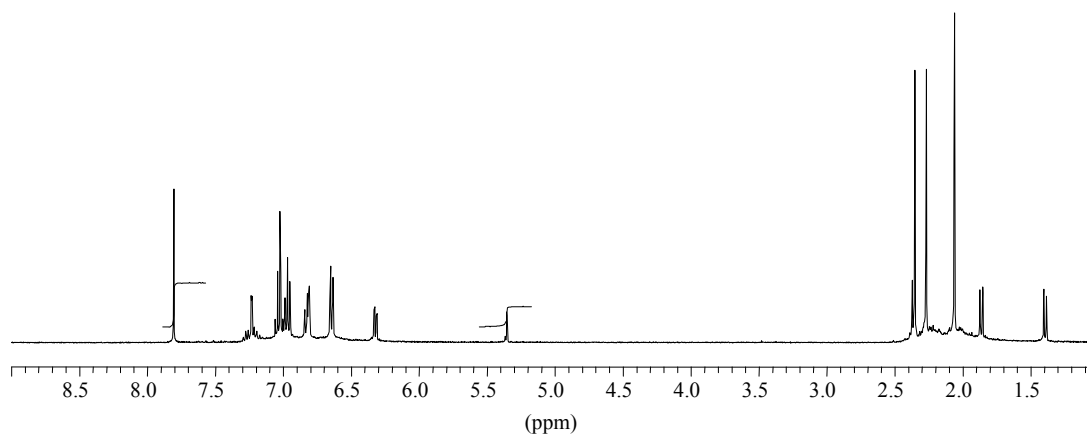


Figure A. <sup>1</sup>H NMR spectrum of  $[\text{ZrL}^3\text{Bn}_2]$  at 298 K (before noticeable decomposition)

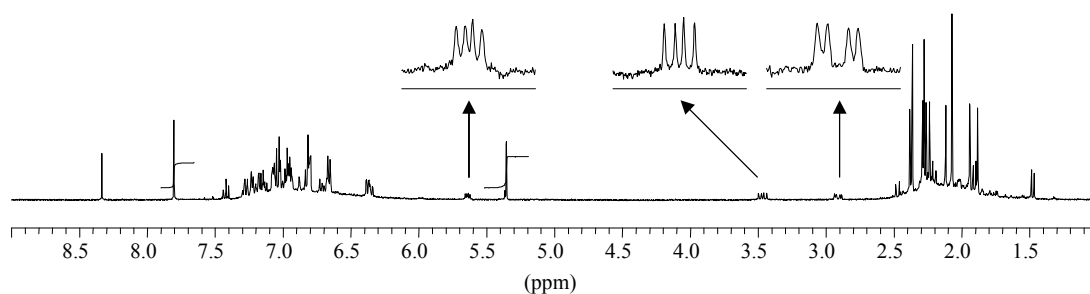


Figure B.  $^1\text{H}$  NMR spectrum of  $[\text{ZrL}^3\text{Bn}_2]$  at 298 K after 340 min. showing decomposition of complex *via* intramolecular 1,2-migratory insertion. New singlet at *ca.* 8.3 ppm is assigned to remaining imine proton. Multiplets at *ca.* 5.6, 3.5 and 2.9 ppm are assigned to the former imine proton and “migrated” benzyl  $\text{CH}_2$  protons respectively. See also P. R. Woodman, I. J. Munslow, P. B. Hitchcock and P. Scott, *J. Chem. Soc., Dalton Trans.*, 1999, 4069.

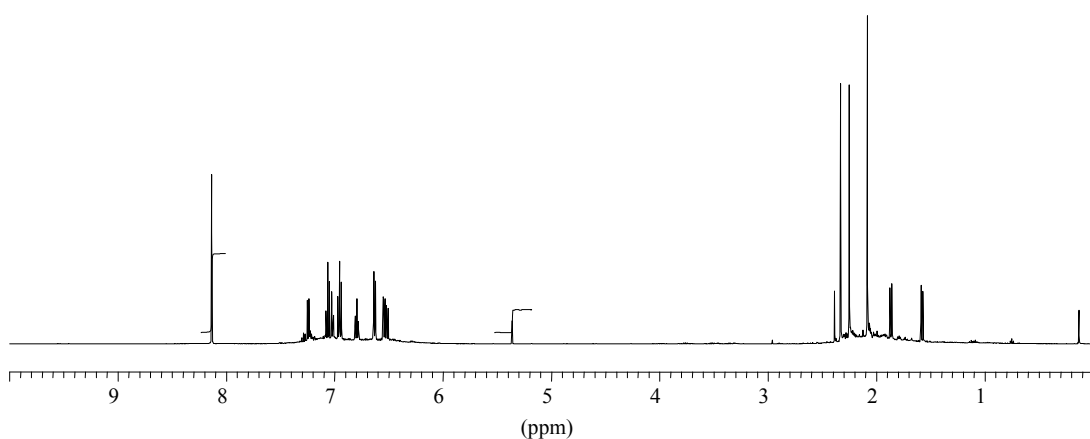


Figure C.  $^1\text{H}$  NMR spectrum of  $[\text{ZrL}^4\text{Bn}_2]$  at 298 K (before noticeable decomposition)

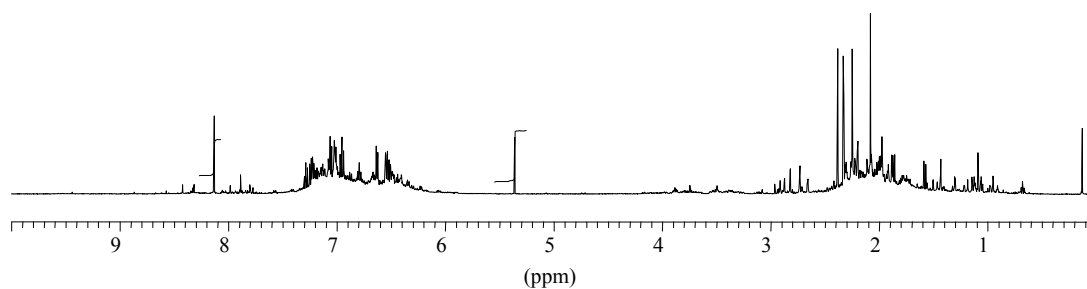


Figure D. <sup>1</sup>H NMR spectrum of [ZrL<sup>4</sup>Bn<sub>2</sub>] at 298 K after 180 min (expanded below)

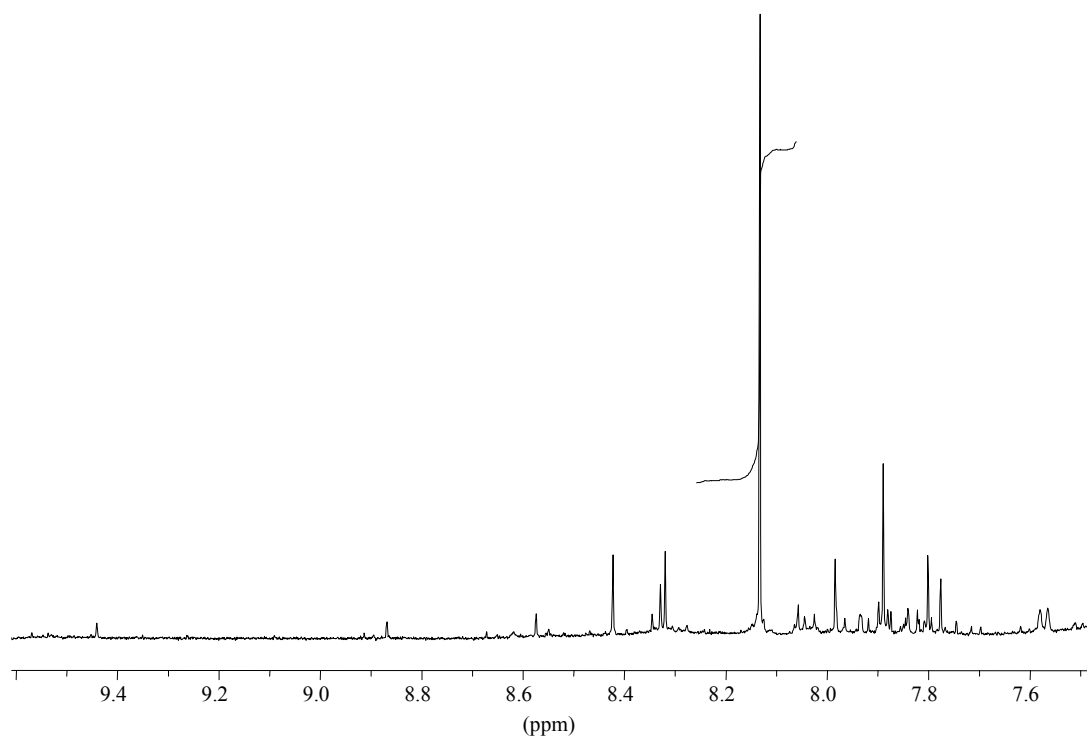


Figure E. Imine region of <sup>1</sup>H NMR spectrum of [ZrL<sup>4</sup>Bn<sub>2</sub>] at 298 K after 180 min. Large number of imine peaks indicates formation of several decomposition products. Note that the starting material peak is well separated and readily integrated for kinetic analysis.

### Kinetic data analysis

All measurements were made by integration of the imine peak from  $^1\text{H}$  NMR spectra *versus* the internal standard of residual protio solvent resonance of  $\text{CD}_2\text{Cl}_2$ .

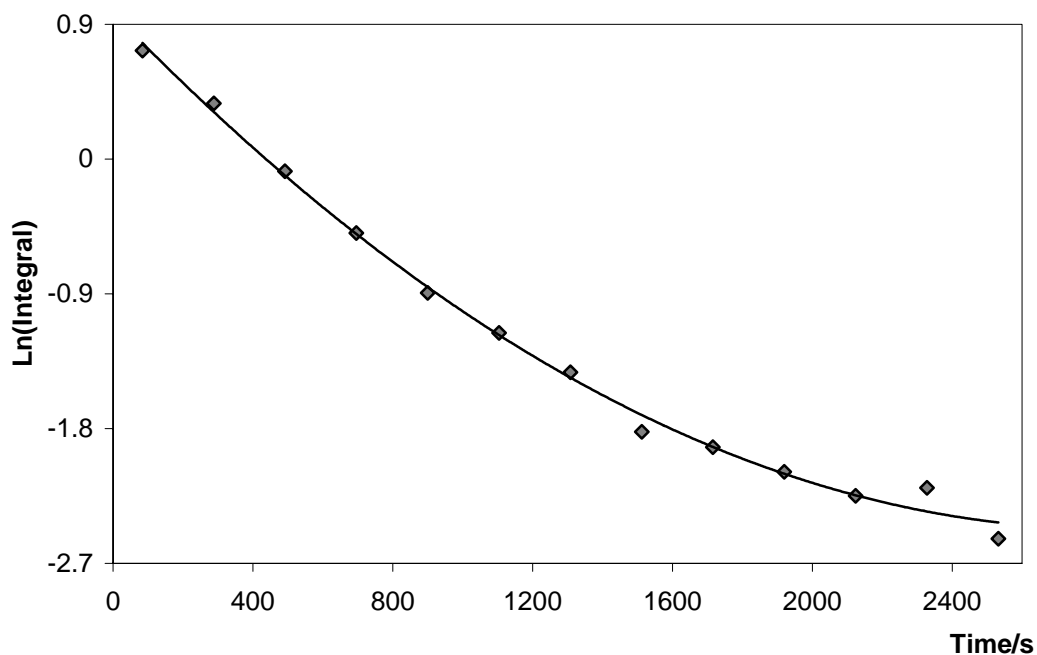


Figure F. 1<sup>st</sup> order plot for decomposition of  $[\text{ZrL}^4\text{Bn}_2]$  at 323 K. Non-linearity of graph highlights deviation from 1<sup>st</sup> order kinetics

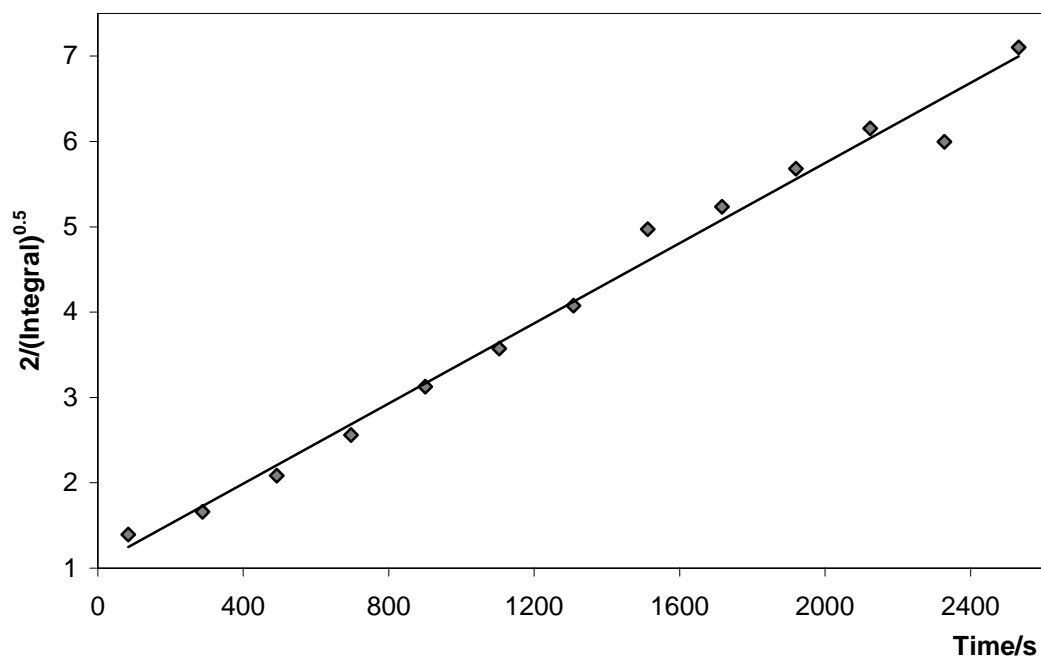


Figure G. 1.5 order plot for decomposition of  $[\text{ZrL}^4\text{Bn}_2]$  at 323 K

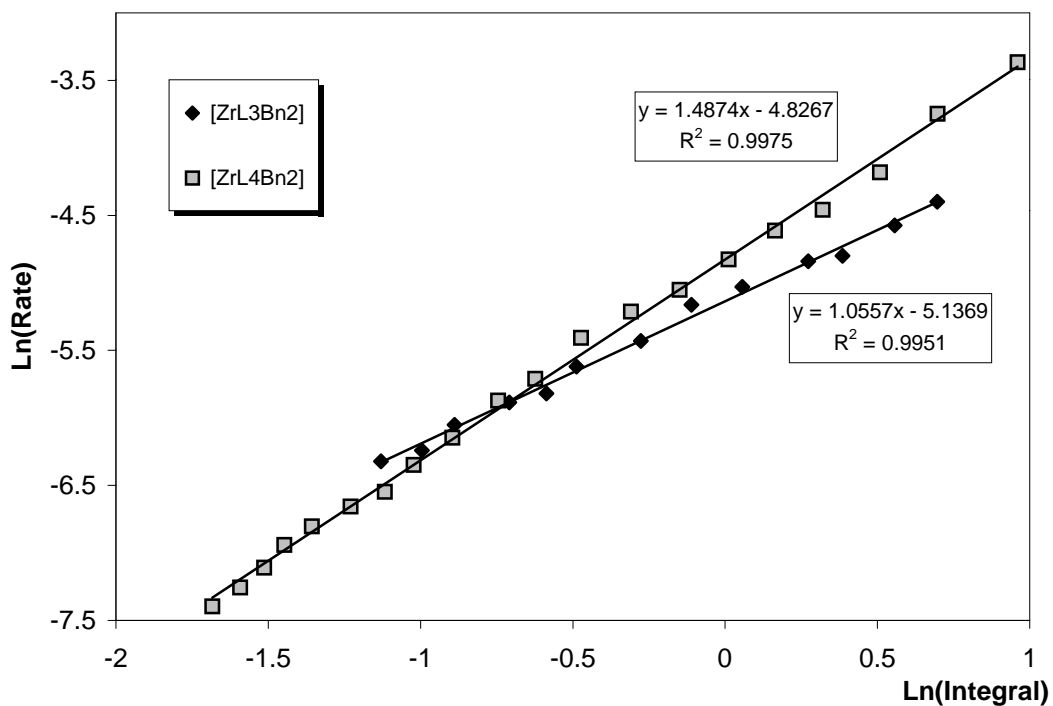


Figure H. Van't Hoff plots for  $[\text{ZrL}^3\text{Bn}_2]$  and  $[\text{ZrL}^4\text{Bn}_2]$  at 303 K giving slopes of *ca.* 1 and 1.5 as expected.

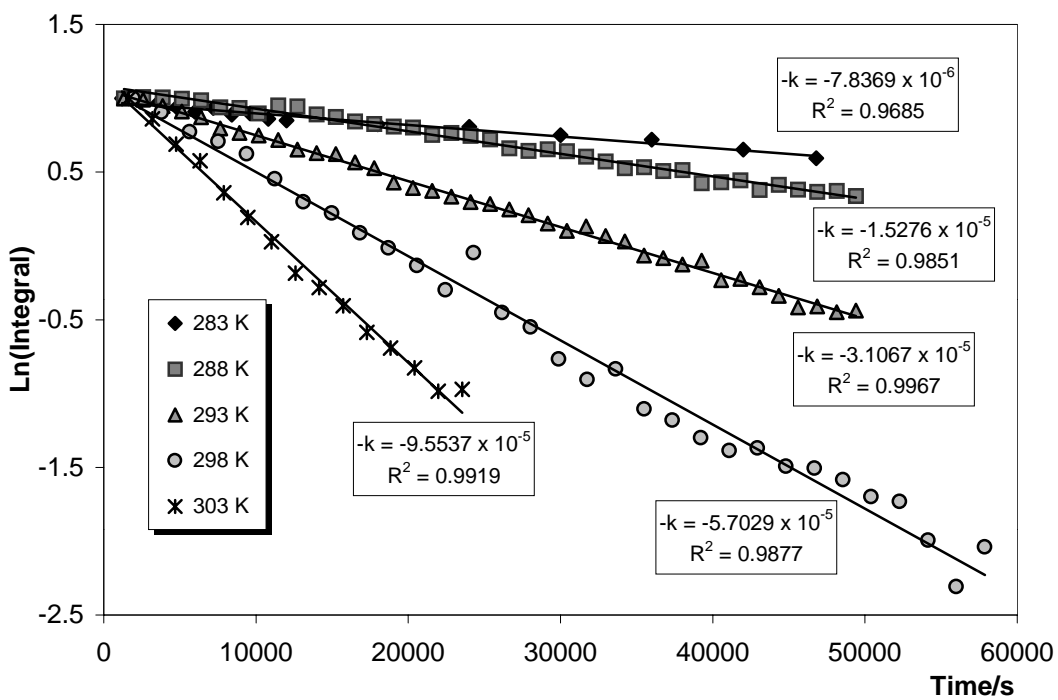


Figure I. Normalised 1<sup>st</sup> order kinetic plots for decomposition of  $[\text{ZrL}^3\text{Bn}_2]$  between 283 and 303 K.

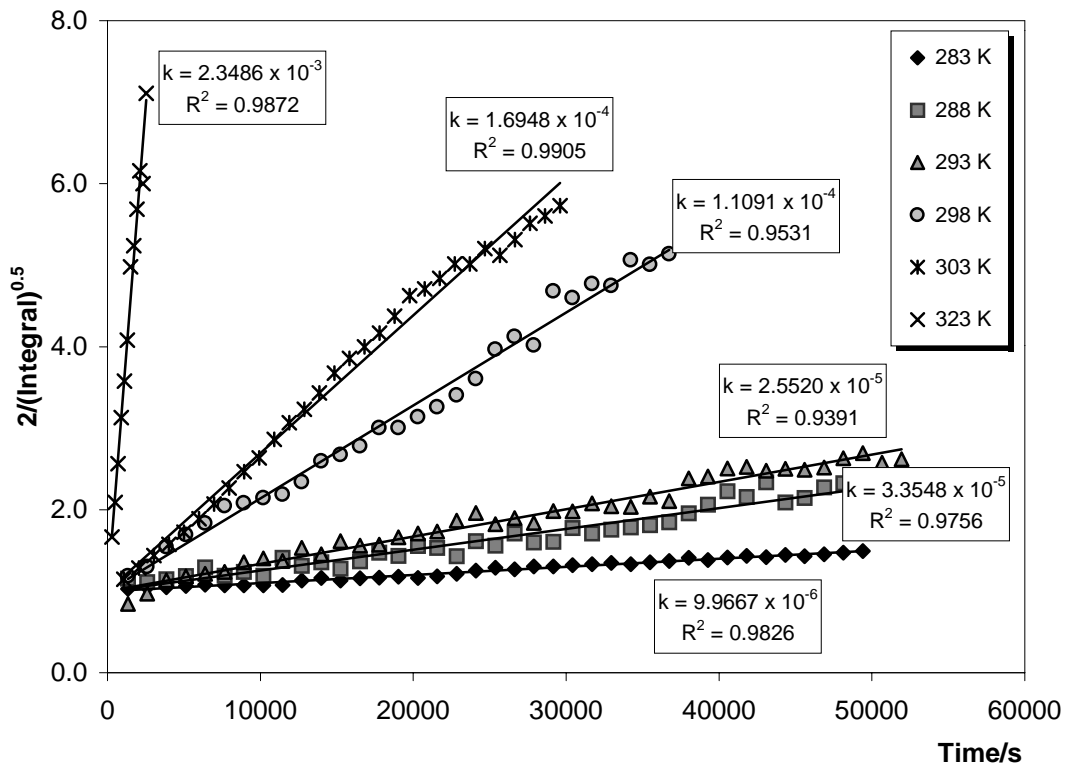


Figure J. Normalised 1.5 order kinetic plots for decomposition of  $[\text{ZrL}^4\text{Bn}_2]$  between 283 and 323 K.

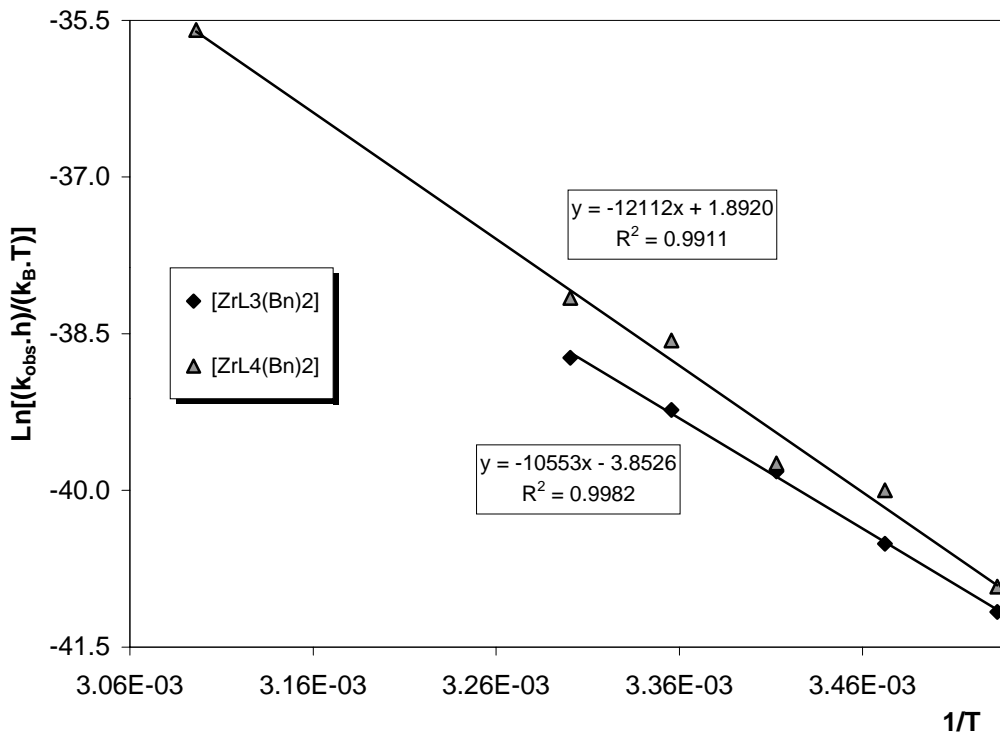


Figure K. Eyring plots for decomposition of  $[\text{ZrL}^3\text{Bn}_2]$  and  $[\text{ZrL}^4\text{Bn}_2]$

### Possible mechanism consistent with 1.5 order kinetics

An initiation step involving homolytic fission of the Zr–Bn bond leads to formation of two radicals:

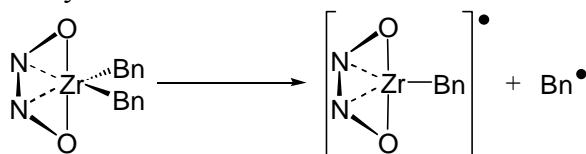


Figure L.

Each of these radicals is free to propagate; we will follow a possible pathway for the free benzyl radical. This can attack the ligand of another complex (either at the imine, a benzylic position or elsewhere) to form a new radical species:

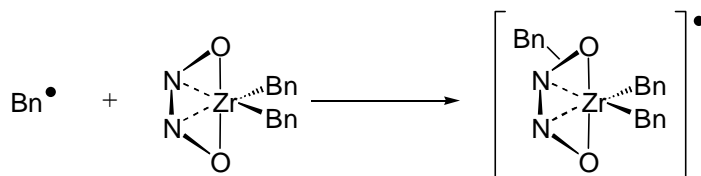


Figure M.

The new radical complex,  $[Zr(BnL)Bn_2]^\bullet$  can then decompose forming a non-radical complex and a benzyl radical ( $Bn^\bullet$ ):

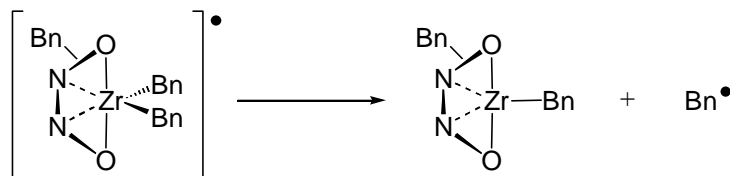
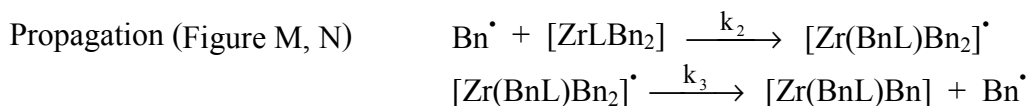


Figure N.

This leads to a radical propagation which terminates when two radicals combine.

Kinetic equations can then be constructed for the initiation, propagation and termination steps of the reaction:



Under steady state conditions, an equation for the formation of benzyl radicals can be written:

$$k_1 \cdot [ZrL(Bn)_2] - k_2 \cdot [Bn^\bullet] \cdot [ZrL(Bn)_2] + k_3 \cdot [Zr(BnL)(Bn)_2]^\bullet - k_4 \cdot [Bn^\bullet]^2 = 0$$

An equation for formation of complex radicals under steady state conditions can also be written:

$$k_2 \cdot [Bn^\bullet] \cdot [ZrL(Bn)_2] - k_3 \cdot [Zr(BnL)(Bn)_2]^\bullet = 0$$

Addition of these linear equations gives:

$$k_1 \cdot [ZrL(Bn)_2] - k_4 \cdot [Bn^\bullet]^2 = 0$$

$$k_4 \cdot [Bn^\bullet]^2 = k_1 \cdot [ZrL(Bn)_2]$$

$$[Bn^\bullet]^2 = \left( \frac{k_1}{k_4} \right) \cdot [ZrL(Bn)_2]$$

$$[\text{Bn}\cdot] = \left(\frac{k_1}{k_4}\right)^{0.5} \cdot [\text{ZrL}(\text{Bn})_2]^{0.5} \quad \text{eq.1}$$

The rate of reaction is measured as the rate of change in concentration of reactants or products. In this case the rate is determined by radical propagation, thus the rate can be defined as:

$$\text{Rate} = k_2 \cdot \frac{\delta[\text{Zr}(\text{BnL})(\text{Bn})_2]^\bullet}{\delta t} = k_2 \cdot [\text{Bn}\cdot] \cdot [\text{ZrL}(\text{Bn})_2]$$

Substituting  $[\text{Bn}\cdot]$  with eq.1 gives:

$$\text{Rate} = k_2 \cdot \left(\frac{k_1}{k_4}\right)^{0.5} \cdot [\text{ZrL}(\text{Bn})_2]^{0.5} \cdot [\text{ZrL}(\text{Bn})_2]$$

$$\text{Rate} = k_2 \cdot \left(\frac{k_1}{k_4}\right)^{0.5} \cdot [\text{ZrL}(\text{Bn})_2]^{1.5}$$

As  $k_1$ ,  $k_2$  and  $k_4$  are all constants:

$$\text{Rate} = k_{\text{obs}} \cdot [\text{ZrL}(\text{Bn})_2]^{1.5}$$

### Calculation of errors\*

TSS is the Total Sum of Squares, and is the sum of squared deviations from the mean.

$$\text{TSS}_x = \sum (X_i - \bar{X})^2$$

Where  $\bar{X}$  = mean of X

RSS is the sum of squared residuals (errors) and reflects overall accuracy of predictions.

$$\text{RSS} = \sum e_i^2 = \sum (Y_i - \hat{Y}_i)^2$$

Where  $\hat{Y}_i$  = predicted value of Y from the derived linear equation  $Y = C + M \cdot X$

$s_e$  is the residual standard deviation, and is an indication of goodness of fit of the line. It is the standard deviation of error in Y.

$$s_e = \sqrt{\frac{\text{RSS}}{n - K}}$$

K = number of estimated parameters (i.e. 2 for linear equation).

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\* Lawrence C. Hamilton, *Regression With Graphics – A second course in applied statistics*, 1992, 1<sup>st</sup> edn., Brooks/Cole, CA, Chapter 2, 29 – 64; Leland Blank, *Statistical Procedures for Engineering, Management, and Science*, 1980, 1<sup>st</sup> edn., McGraw-Hill, NY, Chapter 27, 487 – 515.



Standard error in the slope,  $SE_m$ :

$$SE_m = \frac{s_e}{\sqrt{TSS_x}}$$

Standard error in the intercept,  $SE_c$ :

$$SE_c = s_e \sqrt{\frac{1}{n} + \frac{\bar{X}^2}{TSS_x}}$$

## Experimental

### General Procedures and Techniques

Unless otherwise stated, all organic preparations were carried out under normal atmospheric conditions. Inorganic and organometallic manipulations were performed under an atmosphere of dry argon, using conventional Schlenk line techniques and an MBraun glove box. All solvents for inorganic and organometallic preparations were pre-dried over sodium wire, distilled over an appropriate drying agent (sodium for toluene; potassium for THF and benzene; sodium-potassium alloy for diethyl ether, petroleum ether and pentane; calcium hydride for dichloromethane, pyridine and acetonitrile) and degassed before use. All glassware, cannulae and Celite were stored in an oven at  $>373$  K. Deuterated solvents were degassed by the freeze-thaw degas method and dried over the appropriate agent (potassium for toluene and benzene; calcium hydride for dichloromethane, pyridine and acetonitrile) before trap-to-trap distillation and storage in the glove box. Inorganic and organometallic NMR samples were prepared in the glovebox in tubes sealed with Young's concentric stopcocks.

NMR spectra were recorded on Bruker AC-250, DPX-300, DPX-400, DRX-500 or AC-400 spectrometers and the spectra referenced internally using residual protio solvent resonances relative to tetramethylsilane ( $\delta = 0.0$  ppm). Proton and carbon NMR assignments were confirmed by  $^1\text{H}$ - $^1\text{H}$  (COSY) or  $^1\text{H}$ - $^{13}\text{C}$  (HMQC) experiments. All NMR kinetic data was obtained from spectra recorded on Bruker AC-400 and DRX-500 spectrometers. Infra-red spectra were carried out on sodium chloride plates in an airtight holder, and obtained as thin film (dichloromethane as solvent) or nujol mulls on a Perkin Elmer FT-IR spectrometer. EI mass spectra were obtained on a VG Autospec mass spectrometer and elemental analyses were performed by Warwick Analytical Services. Unless otherwise stated, all purchased chemical reagents were used as received.

## Synthesis of salicylaldehydes

### General procedure for preparation of salicylaldehydes

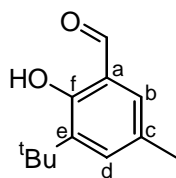
The reaction was performed under argon. Acetonitrile and triethylamine were dried over  $\text{CaH}_2$ , paraformaldehyde dried over  $\text{P}_2\text{O}_5$  and anhydrous  $\text{MgCl}_2$  (98 %) purchased from Aldrich was dried over  $\text{P}_2\text{O}_5$  at  $120^\circ\text{C}$ . A 1 l side arm round bottom flask with stirrer bar was placed under an argon atmosphere and charged with the appropriate phenol (100 mmol) and dry acetonitrile (500 ml). To this was added dry triethylamine (52.2 ml, 375 mmol), anhydrous  $\text{MgCl}_2$  (14.28 g, 150 mmol) and the solution was stirred for 15 min. Dry paraformaldehyde (20.25 g, 675 mmol) was added and a wide bore condenser fitted to the round bottom flask. The solution was heated at reflux temperature under argon for *ca.* 2 h. The solution was allowed to cool to room temperature and then added to 5 %  $\text{HCl}_{(\text{aq})}$  (800 ml) followed by stirring for 30 min. This was extracted with diethyl ether (7 x 100 ml portions) and the ether fractions collected together and washed with saturated  $\text{NaCl}_{(\text{aq})}$  (3 x 100 ml portions). The ether layer was dried over anhydrous  $\text{MgSO}_4$  followed by filtration. Volatiles were removed under reduced pressure to yield the corresponding salicylaldehydes.

### Synthesis of 3-*tert*-butyl-5-methyl-2-hydroxybenzaldehyde

Using the general procedure, 2-*tert*-butyl-4-methylphenol (16.43 g) was used as the reagent and the mixture heated at reflux temperature for 2 h, during which time the solution turned orange/yellow. A yellow solid was obtained and was found to contain 3-*tert*-butyl-5-methyl-2-hydroxybenzaldehyde (67 % purity by  $^1\text{H}$  NMR). The solid was dissolved in pentane, concentrated down and kept at  $-30^\circ\text{C}$  to yield pale green crystals which were isolated by vacuum filtration. These were found to be the pure aldehyde and further crops were obtained by concentration of the supernatant.

Yield = 9.70 g, 50 %.

Anal. found (Calculated for  $\text{C}_{12}\text{H}_{16}\text{O}_2$ ) % C 75.08 (74.97), 8.46 (8.39).



$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 11.61 (s, 1H, ArOH), 9.81 (s, 1H, HC=O), 7.33 (d, 1H, ArH<sub>d</sub>,  $^4J_{\text{HH}} = 2$  Hz), 7.17 (d, 1H, ArH<sub>b</sub>,  $^4J_{\text{HH}} = 2$  Hz), 2.32 (s, 3H, Me<sub>c</sub>), 1.41 (s, 9H, CMe<sub>3</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 196.9 (HC=O), 159.0 (C<sub>f</sub>), 137.8 (C<sub>e</sub>), 135.3 (C<sub>d</sub>), 131.3 (C<sub>b</sub>), 128.0 (C<sub>c</sub>), 120.2 (C<sub>a</sub>), 34.6 (CMe<sub>3</sub>), 29.1 (CMe<sub>3</sub>), 20.4 (Me<sub>c</sub>).

IR ( $\text{CH}_2\text{Cl}_2$  Thin film)  $\nu$   $\text{cm}^{-1}$  3357 (b, OH), 3002, 2964, 2868, 1649 (s, C=O), 1599, 1514, 1461, 1392, 1356, 1323, 1266 (m, C-O), 1232, 1197, 1161, 1020, 972, 932, 866, 793, 768, 747, 710.

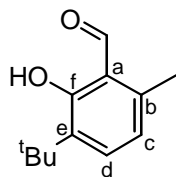
MS (EI)  $m/z$  192 [ $\text{M}$ ]<sup>+</sup>, 177 [ $\text{M}-\text{CH}_3$ ]<sup>+</sup>, 163 [ $\text{M}-\text{CHO}$ ]<sup>+</sup>.

### Synthesis of 3-tert-butyl-6-methyl-2-hydroxybenzaldehyde

Using the general procedure, 2-tert-butyl-5-methylphenol (16.43 g) was used as the reagent with heating at reflux temperature for 2 h, during which time the solution turned green/yellow. A yellow/orange gum was obtained (15.44 g) which was found to contain 3-tert-butyl-6-methyl-2-hydroxybenzaldehyde (66 % by  $^1\text{H}$  NMR). A sample of the solid (2.00 g) was purified by flash column chromatography (hexane: ether, 4:1), to yield a yellow/green oil. The gum was also purified by distillation at 110 °C, 2 mm Hg, to yield a yellow/green oil.

Yield = 8.21 g, 43 % (From distillation).

Anal. found (Calculated for  $\text{C}_{12}\text{H}_{16}\text{O}_2$ ) % C 75.11 (74.97), H 8.42 (8.39).



$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 12.72 (s, 1H, ArOH), 10.29 (s, 1H, HC=O), 7.37 (d, 1H, ArH<sub>d</sub>,  $^3J_{\text{HH}} = 8$  Hz), 6.64 (dd, 1H, ArH<sub>c</sub>,  $^3J_{\text{HH}} = 8$  Hz,  $^4J_{\text{HH}} = 1$  Hz), 2.55 (s, 3H, Me<sub>b</sub>), 1.40 (s, 9H, CMe<sub>3</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 195.7 (HC=O), 162.7 (C<sub>f</sub>), 139.6 (C<sub>b</sub>), 136.3 (C<sub>e</sub>), 134.4 (C<sub>d</sub>), 120.9 (C<sub>c</sub>), 118.2 (C<sub>a</sub>), 34.4 (CMe<sub>3</sub>), 29.1 (CMe<sub>3</sub>), 17.7 (Me<sub>b</sub>).

IR (Thin film)  $\nu$   $\text{cm}^{-1}$  3473 (b, OH), 3262, 2959, 2772, 2590, 1898, 1765, 1638 (s, C=O), 1578, 1485, 1452, 1427, 1401, 1380, 1362, 1332, 1306, 1285, 1266 (m, C-O), 1241, 1196, 1133, 1083, 1051, 1028, 969, 948, 930, 818, 794, 735, 643, 607, 595.

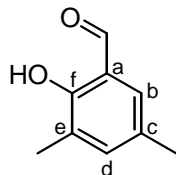
MS (EI)  $m/z$  192 [ $\text{M}$ ]<sup>+</sup>, 177 [ $\text{M}-\text{CH}_3$ ]<sup>+</sup>.

### Synthesis of 3,5-dimethyl-2-hydroxybenzaldehyde

Using the general procedure, 2,4-dimethylphenol (12.21 g) was used as the reagent, with heating the reaction mixture at reflux temperature for 2 h. During this period the solution turned yellow. A yellow oil was obtained (14.21 g) and was found to contain 3,5-dimethyl-2-hydroxybenzaldehyde (94 % by  $^1\text{H}$  NMR). Distillation under reduced pressure at 100°C yielded the product as a pale green oil.

Yield = 13.60 g, 90 %.

Anal. found (Calculated for  $\text{C}_9\text{H}_{10}\text{O}_2$ ) % C 71.89 (71.99), H 6.72 (6.71).



$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 11.07 (s, 1H, ArOH), 9.81 (s, 1H, HC=O), 7.20 (s, 1H, ArH<sub>d</sub>), 7.16 (s, 1H, ArH<sub>b</sub>), 2.29 (s, 3H, Me<sub>c</sub>), 2.23 (s, 3H, Me<sub>e</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 196.6 (HC=O), 157.8 (C<sub>f</sub>), 139.0 (C<sub>d</sub>), 130.8 (C<sub>b</sub>), 128.4 (C<sub>c</sub>), 126.4 (C<sub>e</sub>), 119.6 (C<sub>a</sub>), 20.1 (Me<sub>c</sub>), 14.8 (Me<sub>e</sub>).

IR ( $\text{CH}_2\text{Cl}_2$  Thin film)  $\nu$   $\text{cm}^{-1}$  3163 (b, OH), 3103, 2923, 2845, 2740, 1652 (s, C=O), 1621, 1470, 1415, 1380, 1323, 1263 (s, C-O), 1214, 1165, 1036, 969, 953, 863, 788, 745, 711.

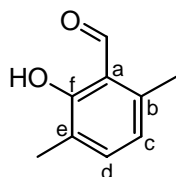
MS (EI)  $m/z$  150 [ $\text{M}$ ]<sup>+</sup>, 149 [ $\text{M}-\text{H}$ ]<sup>+</sup>, 135 [ $\text{M}-\text{CH}_3$ ]<sup>+</sup>, 121 [ $\text{M}-\text{CHO}$ ]<sup>+</sup>.

### Synthesis of 2,5-dimethyl-6-hydroxybenzaldehyde

Using the general procedure, 2,5-dimethylphenol (12.21 g) was used as the reagent and the reaction mixture was heated at reflux temperature for 2 h, during which time the solution turned green. A yellow solid was obtained (14.92 g), which was found to contain 2,5-dimethyl-6-hydroxybenzaldehyde (90 % by  $^1\text{H}$  NMR). A sample of the solid (2.00 g) was purified by flash column chromatography, using hexane: ether, 4:1 as the eluent. Similar fractions (TLC analysis) were collected together and volatiles removed under reduced pressure to leave a pale green crystalline solid (1.71 g).

Yield = 1.71 g, 84 % (Isolated yield).

Anal. found (Calculated for  $\text{C}_9\text{H}_{10}\text{O}_2$ ) % C 71.57 (71.99), H 6.73 (6.71).



$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 12.17 (s, 1H, ArOH), 10.29 (s, 1H, HC=O), 7.23 (d, 1H, ArH<sub>d</sub>,  $^3J_{\text{HH}} = 7$  Hz), 6.61 (d, 1H, ArH<sub>c</sub>,  $^3J_{\text{HH}} = 7$  Hz), 2.56 (s, 3H, Me<sub>b</sub>), 2.20 (s, 3H, Me<sub>e</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 195.4 (HC=O), 161.5 (C<sub>f</sub>), 139.3 (C<sub>b</sub>), 138.0 (C<sub>d</sub>), 124.9 (C<sub>e</sub>), 121.1 (C<sub>c</sub>), 117.8 (C<sub>a</sub>), 17.8 (Me<sub>b</sub>), 14.8 (Me<sub>e</sub>).

IR ( $\text{CH}_2\text{Cl}_2$  Thin film)  $\nu$   $\text{cm}^{-1}$  2955, 1645 (m, C=O), 1626, 1513, 1462, 1432, 1408, 1376, 1330, 1280 (m, C-O), 1252, 1236, 1058, 1030, 974, 822, 775, 740, 696.  $\nu$  (OH) not detected.

MS (EI)  $m/z$  150 [ $\text{M}$ ]<sup>+</sup>, 149 [ $\text{M}-\text{H}$ ]<sup>+</sup>, 135 [ $\text{M}-\text{CH}_3$ ]<sup>+</sup>.

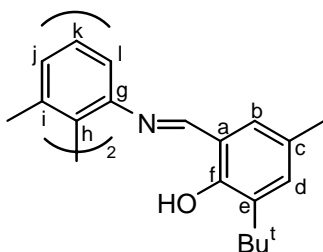
### Synthesis of ligands $\text{H}_2\text{L}^{1-4}$

#### Synthesis of $\text{H}_2\text{L}^1$

A 100 ml round bottom flask with stirrer bar was charged with 3-*tert*-butyl-5-methyl-2-hydroxybenzaldehyde (2.00 g, 10.40 mmol). To this was added 2,2'-diamino-6,6'-dimethylbiphenyl (1.08 g, 5.09 mmol). The reactants were dissolved in ethanol (50 ml), and refluxed for *ca.* 18 h, using a condenser fitted with a  $\text{CaCl}_2$  drying tube. The solution turned yellow and a yellow solid formed as a precipitate. The solid was isolated by vacuum filtration and washed with cold ethanol. All remaining volatiles were removed *in vacuo*.

Yield = 2.52 g, 88 %.

Anal. found (Calculated for  $\text{C}_{38}\text{H}_{44}\text{N}_2\text{O}_2$ ) % C 81.33 (81.39), H 7.97 (7.91), N 5.04 (5.00).



$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 12.84 (s, 2H, ArOH), 8.37 (s, 2H, N=CH), 7.32 (t, 2H, ArH<sub>k</sub>,  $^3J_{\text{HH}} = 8$  Hz), 7.21 (d, 2H, ArH<sub>j</sub>,  $^3J_{\text{HH}} = 8$  Hz), 7.07 (d, 2H, ArH<sub>d</sub>,  $^4J_{\text{HH}} = 2$  Hz), 7.02 (2H, ArH<sub>l</sub>,  $^3J_{\text{HH}} = 8$  Hz), 6.85 (d, 2H, ArH<sub>b</sub>,  $^4J_{\text{HH}} = 2$  Hz), 2.23 (s, 6H, Me<sub>c</sub>), 2.09 (s, 6H, Me<sub>i</sub>), 1.32 (s, 18H, CMe<sub>3</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 162.1 (N=CH), 158.2 (C<sub>f</sub>), 146.9 (C<sub>g</sub>), 137.0 (C<sub>i</sub>), 136.9 (C<sub>e</sub>), 133.2 (C<sub>h</sub>), 130.8 (C<sub>d</sub>), 130.0 (C<sub>b</sub>), 128.2 (C<sub>k</sub>), 128.1 (C<sub>j</sub>), 126.2 (C<sub>c</sub>), 118.5 (C<sub>a</sub>), 115.1 (C<sub>l</sub>), 34.6 (CMe<sub>3</sub>), 29.1 (CMe<sub>3</sub>), 20.5 (Me<sub>c</sub>), 19.7 (Me<sub>i</sub>).

IR ( $\text{CH}_2\text{Cl}_2$  Thin film)  $\nu$   $\text{cm}^{-1}$  3357 (b, OH), 2957, 2916, 2864, 2740, 1619 (s, N=C), 1568, 1462, 1438, 1390, 1384, 1359, 1318, 1266 (w, C-O), 1230, 1210, 1163, 1104, 1024, 980, 948, 927, 861, 813, 786, 772, 746, 688.

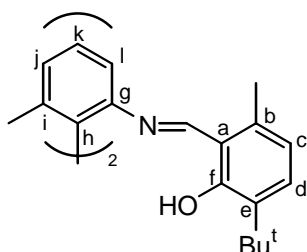
MS (EI)  $m/z$  560 [ $\text{M}$ ]<sup>+</sup>, 545 [ $\text{M}-\text{CH}_3$ ]<sup>+</sup>.

### Synthesis of H<sub>2</sub>L<sup>2</sup>

The ligand was synthesised analogously to H<sub>2</sub>L<sup>1</sup>, using 3-*tert*-butyl-6-methyl-2-hydroxybenzaldehyde (1.36 g, 7.08 mmol), 2,2'-diamino-6,6'-dimethylbiphenyl (0.74 g, 3.49 mmol) and ethanol (30 ml). A yellow solid was obtained.

Yield = 1.56 g, 80 %.

Anal. found (Calculated for C<sub>38</sub>H<sub>44</sub>N<sub>2</sub>O<sub>2</sub>) % C 81.38 (81.39), H 7.87 (7.91), N 4.99 (5.00).



$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 13.87 (s, 2H, ArOH), 8.71 (s, 2H, N=CH), 7.34 (t, 2H, ArH<sub>k</sub>,  $^3J_{\text{HH}} = 8$  Hz), 7.23 (d, 2H, ArH<sub>j</sub>,  $^3J_{\text{HH}} = 7$  Hz), 7.12 (d, 2H, ArH<sub>d</sub>,  $^3J_{\text{HH}} = 8$  Hz), 7.04 (d, 2H, ArH<sub>l</sub>,  $^3J_{\text{HH}} = 8$  Hz), 6.48 (dd, 2H, ArH<sub>c</sub>,  $^3J_{\text{HH}} = 8$  Hz,  $^4J_{\text{HH}} = 1$  Hz), 2.23 (s, 6H, Me<sub>b</sub>), 2.11 (s, 6H, Me<sub>i</sub>), 1.30 (s, 18H, CMe<sub>3</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 161.6 (C<sub>f</sub>), 159.9 (N=CH), 147.3 (C<sub>g</sub>), 137.2 (C<sub>b</sub>), 137.0 (C<sub>i</sub>), 135.5 (C<sub>e</sub>), 133.0 (C<sub>h</sub>), 129.9 (C<sub>d</sub>), 128.3 (C<sub>k</sub>), 128.2 (C<sub>j</sub>), 119.3 (C<sub>c</sub>), 116.7 (C<sub>a</sub>), 115.4 (C<sub>l</sub>), 34.4 (CMe<sub>3</sub>), 29.1 (CMe<sub>3</sub>), 19.8 (Me<sub>i</sub>), 18.4 (Me<sub>b</sub>).

IR ( $\text{CH}_2\text{Cl}_2$  Thin film)  $\nu$   $\text{cm}^{-1}$  3426 (b, OH), 2957, 2871, 2361, 2094, 1643 (m, N=C), 1601, 1568, 1484, 1436, 1361, 1288, 1266 (m, C-O), 1236, 1197, 1136, 1051, 1018, 976, 942, 813, 792, 770, 739.

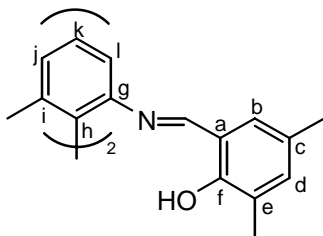
MS (EI)  $m/z$  560 [ $\text{M}$ ]<sup>+</sup>, 545 [ $\text{M}-\text{CH}_3$ ]<sup>+</sup>.

### Synthesis of H<sub>2</sub>L<sup>3</sup>

The ligand was synthesised analogously to H<sub>2</sub>L<sup>1</sup>, using 3,5-dimethyl-2-hydroxybenzaldehyde (4.31 g, 28.54 mmol), 2,2'-diamino-6,6'-dimethylbiphenyl (3.05 g, 14.39 mmol) and ethanol (40 ml). A bright orange solid was obtained.

Yield = 6.45 g, 95%.

Anal. found (Calculated for C<sub>32</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>) % C 80.69 (80.64), H 6.80 (6.77), N 6.00 (5.88).



$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 12.12 (s, 2H, ArOH), 8.32 (s, 2H, N=CH), 7.32 (t, 2H, ArH<sub>k</sub>,  $^3J_{\text{HH}} = 8$  Hz), 7.21 (d, 2H, ArH<sub>j</sub>,  $^3J_{\text{HH}} = 7$  Hz), 7.01 (d, 2H, ArH<sub>i</sub>,  $^3J_{\text{HH}} = 7$  Hz), 6.94 (s, 2H, ArH<sub>d</sub>), 6.82 (s, 2H, ArH<sub>b</sub>), 2.21 (s, 6H, Me<sub>c</sub>), 2.12 (s, 6H, Me<sub>e</sub>), 2.04 (s, 6H, Me<sub>i</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 162.3 (N=CH), 157.0 (C<sub>f</sub>), 147.4 (C<sub>g</sub>), 137.0 (C<sub>i</sub>), 134.8 (C<sub>d</sub>), 133.2 (C<sub>h</sub>), 129.7 (C<sub>b</sub>), 128.4 (C<sub>k</sub>), 128.2 (C<sub>j</sub>), 126.9 (C<sub>c</sub>), 125.7 (C<sub>e</sub>), 118.1 (C<sub>a</sub>), 115.5 (C<sub>l</sub>), 20.2 (Me<sub>c</sub>), 19.8 (Me<sub>i</sub>), 15.5 (Me<sub>e</sub>).

IR ( $\text{CH}_2\text{Cl}_2$  Thin film)  $\nu$   $\text{cm}^{-1}$  2919, 2361, 1622 (s, N=C), 1598, 1569, 1470, 1435, 1379, 1362, 1324, 1283, 1266 (s, C-O), 1242, 1220, 1167, 1108, 1049, 1019, 975, 943, 860, 806, 788, 751, 738, 700.

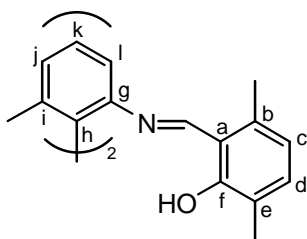
MS (EI)  $m/z$  476 [ $\text{M}$ ]<sup>+</sup>, 461 [ $\text{M}-\text{CH}_3$ ]<sup>+</sup>.

### Synthesis of H<sub>2</sub>L<sup>4</sup>

The ligand was synthesised analogously to H<sub>2</sub>L<sup>1</sup>, using 2,5-dimethyl-6-hydroxybenzaldehyde (2.00 g, 13.33 mmol), 2,2'-diamino-6,6'-dimethylbiphenyl (1.41 g, 6.65 mmol) and ethanol (40 ml). An orange solid was obtained.

Yield = 2.44 g, 77%.

Anal. found (Calculated for C<sub>32</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>) % C 80.69 (80.64), H 6.80 (6.77), N 6.00 (5.88).



$^1\text{H}$  NMR 300 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 13.24 (s, 2H, ArOH), 8.68 (s, 2H, N=CH), 7.33 (t, 2H, ArH<sub>k</sub>,  $^3J_{\text{HH}} = 8$  Hz), 7.22 (d, 2H, ArH<sub>j</sub>,  $^3J_{\text{HH}} = 7$  Hz), 6.99 (d, 2H, ArH<sub>i</sub>), 6.99 (d, 2H, ArH<sub>d</sub>), 6.47 (d, 2H, ArH<sub>c</sub>,  $^3J_{\text{HH}} = 8$  Hz), 2.26 (s, 6H, Me<sub>b</sub>), 2.09 (s, 6H, Me<sub>e</sub>), 2.07 (s, 6H, Me<sub>i</sub>).

$^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz ( $\text{CDCl}_3$ )  $\delta$  ppm 160.5 (N=CH), 160.4 (C<sub>f</sub>), 147.9 (C<sub>g</sub>), 137.0 (C<sub>i</sub>), 137.0 (C<sub>b</sub>), 133.9 (C<sub>d</sub>), 132.7 (C<sub>h</sub>), 128.5 (C<sub>k</sub>), 128.3 (C<sub>j</sub>), 124.1 (C<sub>e</sub>), 119.8 (C<sub>c</sub>), 116.3 (C<sub>a</sub>), 116.2 (C<sub>l</sub>), 19.9 (Me<sub>i</sub>), 18.6 (Me<sub>b</sub>), 15.4 (Me<sub>e</sub>).

IR ( $\text{CH}_2\text{Cl}_2$  Thin film)  $\nu$   $\text{cm}^{-1}$  3428 (b, OH), 2923, 1605 (s, N=C), 1569, 1454, 1379, 1359, 1283 (m, C-O), 1253, 1224, 1056, 1034, 985, 938, 804, 759.

MS (EI)  $m/z$  476 [ $\text{M}$ ]<sup>+</sup>.

### Preparation of sodium salts of ligands H<sub>2</sub>L<sup>1,2</sup>

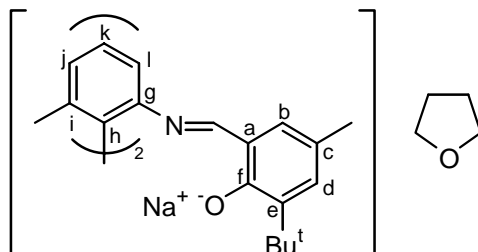
#### General method for preparation of Na<sub>2</sub>L<sup>n</sup>.THF<sub>x</sub>

A Schlenk tube with stirrer bar was charged with the appropriate ligand (0.8 – 1.5 g), and a twofold excess of NaH. THF (40 ml) was added and the solution stirred overnight. The stirring was ceased and unreacted NaH allowed to settle before filtering the solution through a cannula. THF was removed under reduced pressure to yield a solid. The product was analysed by  $^1\text{H}$  NMR and the THF content measured by integration.

## Synthesis of Na<sub>2</sub>L<sup>1</sup>.THF<sub>x</sub>

Following the general method, a Schlenk tube with stirrer bar was charged with H<sub>2</sub>L<sup>1</sup> (0.85 g, 1.52 mmol), NaH (0.15 g, 6.13 mmol) and THF (40 ml). During the course of the reaction a gas was evolved. A yellow solid was obtained and analysis by <sup>1</sup>H NMR showed the composition of the product to be Na<sub>2</sub>L<sup>1</sup>.THF<sub>2.35</sub>.

Yield = 0.99 g, 84 %.



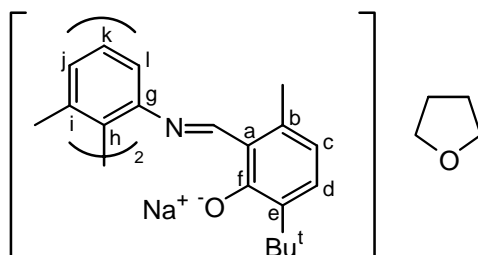
<sup>1</sup>H NMR 300 MHz (d<sub>5</sub>-pyridine) δ ppm 8.53 (s, 2H, N=CH), 7.17 (d, 2H, ArH<sub>d</sub>, <sup>4</sup>J<sub>HH</sub> = 3 Hz), 7.07 (d, 2H, ArH<sub>b</sub>, <sup>4</sup>J<sub>HH</sub> = 2 Hz), 6.91 (d, 2H, ArH<sub>j</sub>), 6.91 (t, 2H, ArH<sub>k</sub>), 6.55 (d, 2H, ArH<sub>i</sub>), 3.67 (m, THF), 2.20 (s, 6H, Me<sub>c</sub>), 1.96 (Me<sub>i</sub>), 1.63 (m, THF), 1.56 (CMe<sub>3</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR 75 MHz (d<sub>5</sub>-pyridine) δ ppm 172.7 (C<sub>f</sub>), 166.1 (N=CH), 152.9 (C<sub>g</sub>), 141.5 (C<sub>e</sub>), 137.7 (C<sub>i</sub>), 133.3 (C<sub>b</sub>), 132.0 (C<sub>h</sub>), 131.2 (C<sub>d</sub>), 127.9 (C<sub>k</sub>), 125.6 (C<sub>j</sub>), 122.9 (C<sub>c</sub>), 119.0 (C<sub>l</sub>), 116.0 (C<sub>a</sub>), 67.8 (THF), 35.4 (CMe<sub>3</sub>), 30.1 (CMe<sub>3</sub>), 25.8 (THF), 20.9 (Me<sub>c</sub>), 20.4 (Me<sub>i</sub>).

## Synthesis of Na<sub>2</sub>L<sup>2</sup>.THF<sub>x</sub>

Following the general method, a Schlenk tube with stirrer bar was charged with H<sub>2</sub>L<sup>2</sup> (0.84 g, 1.50 mmol), NaH (0.14 g, 6.00 mmol) and THF (40 ml). During the course of the reaction the solution turned green/yellow and a gas was evolved. A yellow solid was obtained and analysis by <sup>1</sup>H NMR showed the composition of the product to be Na<sub>2</sub>L<sup>2</sup>.THF<sub>1.23</sub>.

Yield = 0.92 g, 89 %.



<sup>1</sup>H NMR 300 MHz (d<sub>5</sub>-pyridine) δ ppm 8.66 (s, 2H, N=CH), 7.16 (d, 2H, ArH<sub>d</sub>, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.03 (d, 2H, ArH<sub>j</sub>, <sup>3</sup>J<sub>HH</sub> = 7 Hz), 6.93 (t, 2H, ArH<sub>k</sub>, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 6.63 (d, 2H, ArH<sub>l</sub>, <sup>3</sup>J<sub>HH</sub> = 7 Hz), 6.21 (d, 2H, ArH<sub>c</sub>, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 3.67 (m, THF), 2.28 (s, 6H, Me<sub>b</sub>), 2.13 (s, 6H, Me<sub>i</sub>), 1.63 (m, THF), 1.53 (s, 18H, CMe<sub>3</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR 75 MHz (d<sub>5</sub>-pyridine) δ ppm 174.8 (C<sub>f</sub>), 163.8 (N=CH), 152.6 (C<sub>g</sub>), 140.2 (C<sub>e</sub>), 139.2 (C<sub>b</sub>), 138.4 (C<sub>i</sub>), 131.3 (C<sub>h</sub>), 129.1 (C<sub>d</sub>), 127.9 (C<sub>k</sub>), 125.5 (C<sub>j</sub>), 122.0 (C<sub>a</sub>), 119.8 (C<sub>l</sub>), 111.8 (C<sub>c</sub>), 67.8 (THF), 35.3 (CMe<sub>3</sub>), 30.2 (CMe<sub>3</sub>), 25.8 (THF), 20.7 (Me<sub>i</sub>), 20.4 (Me<sub>b</sub>).

## Synthesis of zirconium chloride complexes of ligands H<sub>2</sub>L<sup>1,2</sup>

### General synthesis of [Zr<sup>n</sup>(Cl)<sub>2</sub>]

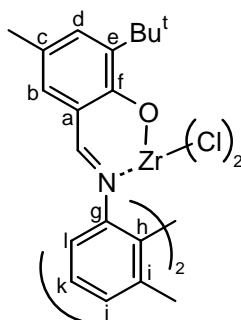
A Schlenk tube with stirrer bar was charged with the appropriate disodium salt of the ligand (0.5 g – 1.2 g) and a slight excess of [ZrCl<sub>4</sub>(THF)<sub>2</sub>]. The Schlenk tube was cooled to –78 °C and THF (40 ml) was

added. The solution was allowed to warm to room temperature and stirred for 20 h, during which time a precipitate formed. Stirring was ceased and the precipitate allowed to settle before filtering the solution through a cannula. The solvent was then removed under reduced pressure to give an orange/yellow solid. The solid was then dissolved in dichloromethane and filtered, followed by removal of the solvent under reduced pressure. The solid obtained was then sublimated at 250 °C – 350 °C, 10<sup>-6</sup> mm Hg, to yield the product.

### Synthesis of [ZrL<sup>1</sup>(Cl)<sub>2</sub>]

Following the general method, a Schlenk tube with stirrer bar was charged with Na<sub>2</sub>L<sup>1</sup>.THF<sub>2.35</sub> (1.13 g, 1.46 mmol), [ZrCl<sub>4</sub>(THF)<sub>2</sub>] (564 mg, 1.50 mmol) and THF (40 ml). During the course of the reaction the solution turned from yellow to orange. After sublimation at 350 °C, 10<sup>-6</sup> mm Hg, a yellow solid was obtained. The product was also crystallised from THF.

Yield = 420 mg, 40 % (From sublimation).



<sup>1</sup>H NMR 300 MHz (CD<sub>2</sub>Cl<sub>2</sub>) δ ppm 8.10 (s, 2H, N=CH), 7.40 (d, 2H ArH<sub>d</sub>, <sup>4</sup>J<sub>HH</sub> = 2 Hz), 7.22 (t, 2H, ArH<sub>k</sub>, <sup>3</sup>J<sub>HH</sub> = 8 Hz), 7.15 (d, 2H, ArH<sub>j</sub>, <sup>3</sup>J<sub>HH</sub> = 7 Hz), 7.02 (d, 2H, ArH<sub>b</sub>, <sup>4</sup>J<sub>HH</sub> = 2 Hz), 7.01 (d, 2H, ArH<sub>l</sub>), 2.30 (s, 6H, Me<sub>c</sub>), 2.06 (s, 6H, Me<sub>i</sub>), 1.45 (s, 18H, CMe<sub>3</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR 75 MHz (CD<sub>2</sub>Cl<sub>2</sub>) δ ppm 170.3 (N=CH), 158.7 (C<sub>f</sub>), 149.1 (C<sub>g</sub>), 139.0 (C<sub>e</sub>), 137.9 (C<sub>i</sub>), 136.1 (C<sub>d</sub>), 132.5 (C<sub>b</sub>), 131.1 (C<sub>h</sub>), 129.2 (C<sub>c</sub>), 129.1 (C<sub>j</sub>), 128.6 (C<sub>k</sub>), 123.1 (C<sub>a</sub>), 121.6 (C<sub>l</sub>), 34.9 (CMe<sub>3</sub>), 29.3 (CMe<sub>3</sub>), 20.5 (Me<sub>c</sub>), 19.8 (Me<sub>i</sub>).

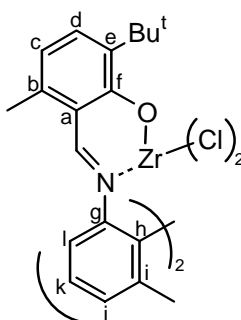
IR (Nujol) ν cm<sup>-1</sup> 1610 (N=C), 1590, 1548, 1431, 1410, 1340, 1295, 1269 (m, C-O), 1245, 1210, 1174, 1097, 1036, 1010, 979, 930, 902, 842, 794, 777, 764, 740, 549.

MS (EI) *m/z* 720 [M]<sup>+</sup>, 685 [M-Cl]<sup>+</sup>, 651 [M-(Cl)<sub>2</sub>]<sup>+</sup>.

### Synthesis of [ZrL<sup>2</sup>Cl<sub>2</sub>]

Following the general method, a Schlenk tube with stirrer bar was charged with Na<sub>2</sub>L<sup>2</sup>.THF<sub>1.23</sub> (900 mg, 1.30 mmol), [ZrCl<sub>4</sub>(THF)<sub>2</sub>] (500 mg, 1.33 mmol) and THF (40 ml). During the course of the reaction the solution turned from green/yellow to orange. After sublimation at 350 °C, 10<sup>-6</sup> mm Hg, a yellow solid was obtained.

Yield = 704 mg, 77 %.





$^1\text{H}$  NMR 300 MHz ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  ppm 8.38 (s, 2H,  $\text{N}=\text{CH}$ ), 7.46 (d, 2H,  $\text{ArH}_d$ ,  $^3J_{\text{HH}} = 8$  Hz), 7.23 (t, 2H,  $\text{ArH}_k$ ,  $^3J_{\text{HH}} = 8$  Hz), 7.17 (d, 2H,  $\text{ArH}_j$ ,  $^3J_{\text{HH}} = 7$  Hz), 7.11 (d, 2H,  $\text{ArH}_i$ ,  $^3J_{\text{HH}} = 8$  Hz), 6.72 (d, 2H,  $\text{ArH}_c$ ,  $^3J_{\text{HH}} = 8$  Hz), 2.35 (s, 6H,  $\text{Me}_b$ ), 2.11 (s, 6H,  $\text{Me}_i$ ), 1.47 (s, 18H,  $\text{CMe}_3$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  ppm 167.7 ( $\text{N}=\text{CH}$ ), 161.0 ( $\text{C}_f$ ), 149.4 ( $\text{C}_g$ ), 140.0 ( $\text{C}_b$ ), 137.7 ( $\text{C}_i$ ), 137.3 ( $\text{C}_e$ ), 134.3 ( $\text{C}_d$ ), 131.3 ( $\text{C}_h$ ), 129.0 ( $\text{C}_j$ ), 128.5 ( $\text{C}_k$ ), 122.1 ( $\text{C}_a$ ), 122.0 ( $\text{C}_c$ ), 121.7 ( $\text{C}_l$ ), 34.8 ( $\text{CMe}_3$ ), 29.4 ( $\text{CMe}_3$ ), 19.9 ( $\text{Me}_i$ ), 19.3 ( $\text{Me}_b$ ).

IR (Nujol)  $\nu$   $\text{cm}^{-1}$  1877, 1598 ( $\text{N}=\text{C}$ ), 1580, 1552, 1402, 1384, 1300, 1268 (m,  $\text{C}-\text{O}$ ), 1227, 1197, 1138, 1097, 1060, 1030, 978, 937, 904, 833, 816, 803, 780, 763, 743, 648, 618, 564.

MS (EI)  $m/z$  720  $[\text{M}]^+$ , 685  $[\text{M}-\text{Cl}]^+$ , 651  $[\text{M}-(\text{Cl})_2]^+$ .

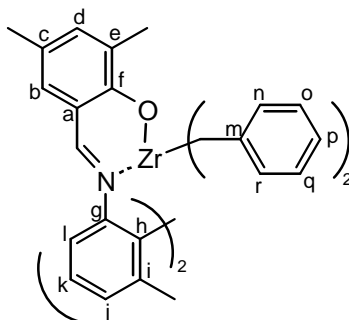
## Synthesis of zirconium benzyl complexes of ligands $\text{H}_2\text{L}^{3,4}$

### Synthesis of $[\text{ZrL}^3(\text{CH}_2\text{Ph})_2]$

A Schlenk tube with stirrer bar was charged with  $\text{H}_2\text{L}^3$  (246 mg, 0.52 mmol) and  $[\text{Zr}(\text{CH}_2\text{Ph})_4]$  (252 mg, 0.55 mmol). The Schlenk tube was placed in an acetone/dry ice bath at  $-78$  °C and acetonitrile (20 ml) added. This was transferred to an ice bath at  $0$  °C and allowed to stir for 10 min. An orange precipitate formed and was filtered at  $0$  °C, followed by washing with cold acetonitrile. The orange solid was dried *in vacuo*.

Yield = 251mg, 65%.

Anal. found (Calculated for  $\text{C}_{46}\text{H}_{44}\text{N}_2\text{O}_2\text{Zr}$ ) % C 72.09 (73.86), H 5.83 (5.93), N 4.42 (3.74).



$^1\text{H}$  NMR 400 MHz ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  ppm 7.77 (s, 2H,  $\text{N}=\text{CH}$ ), 7.20 (s, 2H,  $\text{ArH}_d$ ), 7.01 (t, 2H,  $\text{ArH}_k$ ,  $^3J_{\text{HH}} = 8$  Hz), 6.98 (d, 2H,  $\text{ArH}_j$ ), 6.93 (t, 4H,  $\text{ArH}_{o,q}$ ,  $^3J_{\text{HH}} = 8$  Hz), 6.78 (t, 2H,  $\text{ArH}_p$ ), 6.77 (s, 2H,  $\text{ArH}_b$ ), 6.63 (d, 4H,  $\text{ArH}_{n,r}$ ,  $^3J_{\text{HH}} = 7$  Hz), 6.34 (dd, 2H,  $\text{ArH}_l$ ,  $^3J_{\text{HH}} = 7$  Hz,  $^4J_{\text{HH}} = 1$  Hz), 2.33 (s, 6H,  $\text{Me}_e$ ), 2.24 (s, 6H,  $\text{Me}_c$ ), 2.04 (s, 6H,  $\text{Me}_i$ ), 1.87 (d, 2H,  $\text{CH}_2\text{Ph}$ ,  $^2J_{\text{HH}} = 8$  Hz), 1.44 (d, 2H,  $\text{CH}_2\text{Ph}$ ,  $^2J_{\text{HH}} = 8$  Hz).

$^{13}\text{C}\{^1\text{H}\}$  NMR 75 MHz ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  ppm 168.8 ( $\text{N}=\text{CH}$ ), 160.0 ( $\text{C}_f$ ), 150.0 ( $\text{C}_g$ ), 144.2 ( $\text{C}_m$ ), 138.2 ( $\text{C}_d$ ), 137.0 ( $\text{C}_i$ ), 132.1 ( $\text{C}_b$ ), 131.2 ( $\text{C}_h$ ), 128.7 ( $\text{C}_{n,r}$ ), 128.5 ( $\text{C}_{o,q}$ ), 128.2 ( $\text{C}_k$ ), 128.1 ( $\text{C}_j$ ), 127.2 ( $\text{C}_c$ ), 127.2 ( $\text{C}_e$ ), 121.2 ( $\text{C}_a$ ), 121.2 ( $\text{C}_p$ ), 119.9 ( $\text{C}_l$ ), 60.8 ( $\text{CH}_2\text{Ph}$ ), 20.4 ( $\text{Me}_c$ ), 19.9 ( $\text{Me}_i$ ), 17.2 ( $\text{Me}_e$ ).

IR (Nujol)  $\nu$   $\text{cm}^{-1}$  2729, 2360, 1615 (s,  $\text{N}=\text{C}$ ), 1591, 1557, 1295, 1264 (s,  $\text{C}-\text{O}$ ), 1218, 1173, 1098, 1054, 1028, 973, 965, 942, 899, 848, 825, 802, 759, 749, 737, 698.

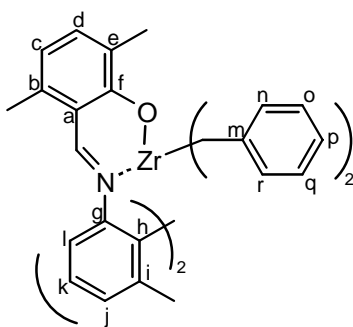
MS (EI)  $m/z$  656  $[\text{M}-\text{CH}_2\text{Ph}]^+$ , 565  $[\text{M}-(\text{CH}_2\text{Ph})_2]^+$ , 550  $[\text{M}-\{(\text{CH}_2\text{Ph})_2 \text{ and } \text{CH}_3\}]^+$ .

### Synthesis of $[\text{ZrL}^4(\text{CH}_2\text{Ph})_2]$

A Schlenk tube with stirrer bar was charged with  $\text{H}_2\text{L}^4$  (247 mg, 0.52 mmol) and  $[\text{Zr}(\text{CH}_2\text{Ph})_2]$  (250 mg, 0.55 mmol). The Schlenk tube was placed in a dry ice/acetone bath at  $-78$  °C and dichloromethane (30 ml) was added. This was stirred for 30 min and then filtered at  $-78$  °C, followed by removal of solvent under reduced pressure. The orange solid obtained was then washed with acetonitrile, filtered and dried *in vacuo*.

Yield = 266 mg, 68 %.

Anal. found (Calculated for  $\text{C}_{46}\text{H}_{44}\text{N}_2\text{O}_2\text{Zr}$ ) % C 69.22 (73.86), H 5.60 (5.93), N 3.85 (3.74).



$^1\text{H}$  NMR 400 MHz ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  ppm 8.14 (s, 2H,  $\text{N}=\text{CH}$ ), 7.24 (d, 2H,  $\text{ArH}_d$ ,  $^3J_{\text{HH}} = 8$  Hz), 7.06 (t, 2H,  $\text{ArH}_k$ ,  $^3J_{\text{HH}} = 8$  Hz), 7.02 (d, 2H,  $\text{ArH}_j$ ,  $^3J_{\text{HH}} = 7$  Hz), 6.96 (t, 4H,  $\text{ArH}_{o,q}$ ,  $^3J_{\text{HH}} = 8$  Hz), 6.79 (t, 2H,  $\text{ArH}_p$ ,  $^3J_{\text{HH}} = 7$  Hz), 6.64 (d, 4H,  $\text{ArH}_{n,r}$ ,  $^3J_{\text{HH}} = 7$  Hz), 6.55 (d, 2H,  $\text{ArH}_c$ ,  $^3J_{\text{HH}} = 7$  Hz), 6.53 (d, 2H,  $\text{ArH}_l$ ,  $^3J_{\text{HH}} = 7$  Hz), 2.34 (s, 6H,  $\text{Me}_e$ ), 2.25 (s, 6H,  $\text{Me}_b$ ), 2.09 (s, 6H,  $\text{Me}_i$ ), 1.89 (d, 2H,  $\text{CH}_2\text{Ph}$ ,  $^2J_{\text{HH}} = 8$  Hz), 1.61 (d, 2H,  $\text{CH}_2\text{Ph}$ ,  $^2J_{\text{HH}} = 8$  Hz).

$^{13}\text{C}\{^1\text{H}\}$  NMR 100 MHz ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  ppm 165.7 ( $\text{N}=\text{CH}$ ), 161.9 ( $\text{C}_f$ ), 150.4 ( $\text{C}_g$ ), 144.1 ( $\text{C}_m$ ), 138.8 ( $\text{C}_b$ ), 136.7 ( $\text{C}_i$ ), 136.0 ( $\text{C}_d$ ), 131.3 ( $\text{C}_h$ ), 128.4 ( $\text{C}_{o,q}$ ), 128.2 ( $\text{C}_{n,r}$ ), 127.9 ( $\text{C}_j$ ), 127.7 ( $\text{C}_k$ ), 126.0 ( $\text{C}_e$ ), 120.9 ( $\text{C}_p$ ), 120.0 ( $\text{C}_l$ ), 120.0 ( $\text{C}_a$ ), 120.0 ( $\text{C}_c$ ), 60.3 ( $\text{CH}_2\text{Ph}$ ), 19.8 ( $\text{Me}_i$ ), 19.2 ( $\text{Me}_b$ ), 16.9 ( $\text{Me}_e$ ).

IR (Nujol)  $\nu$   $\text{cm}^{-1}$  2727, 2284, 1600 (m  $\text{N}=\text{C}$ ), 1562, 1297 (m,  $\text{C}-\text{O}$ ), 1249, 1219, 1140, 1062, 1027, 993, 968, 940, 915, 876, 815, 748, 720, 697, 646.

MS (CI)  $m/z$  747  $[\text{M}-\text{H}]^+$ , 733  $[\text{M}-\text{CH}_3]^+$ , 718  $[\text{M}-(\text{CH}_3)_2]^+$ , 657  $[\text{M}-\text{CH}_2\text{Ph}]^+$ .