Electronic Supplementary Information for Dalton Transactions

Awakening a Dormant Catalyst: Salicylaldimine Systems for Ethene/*tert*-Butylstyrene Copolymerization

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Supplementary Information

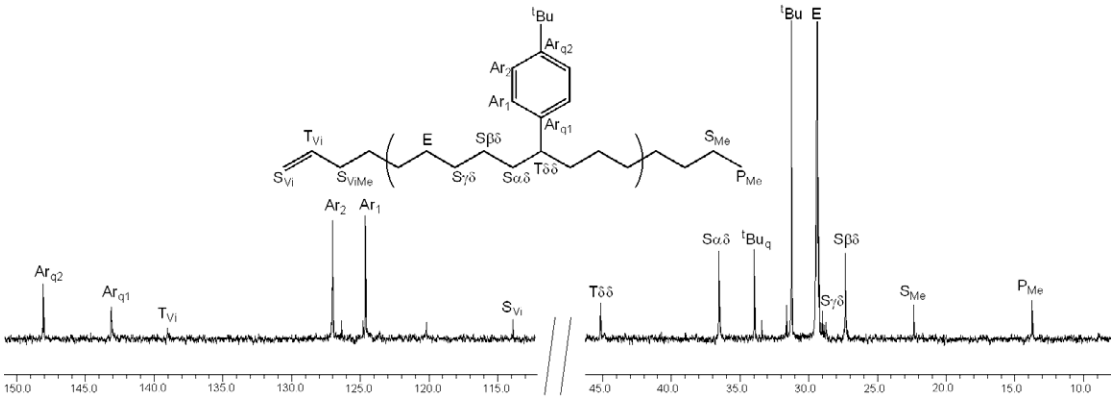
General Procedure for Polymerizations

Toluene was refluxed over sodium metal for 3 d then distilled. *tert*-Butylstyrene (Aldrich) was dried over 4Å molecular sieves. Styrene (Aldrich) was vacuum distilled from CaH_2. Methylaluminoxane (10 % (w/v) in toluene) was purchased from Witco.

Polymerizations were carried out in a jacketed 500 ml vessel equipped with a Pt thermocouple and burette system for the monitoring of gas delivery at a fixed pressure. Toluene, co-monomer and MAO (1000 eq.) were charged into a measuring ampoule, and transferred by cannula into the jacketed vessel. The argon atmosphere was replaced by ethene at 1.2 Bar. The vessel was heated by a thermostatic recirculator unit. The catalyst was dissolved in toluene no more than five minutes prior to use, and injected into the jacketed vessel to begin the polymerization. Reactions were terminated by addition of methanol (5 ml) and the polymer was precipitated by pouring into 5 % $HCl_{(aq)}$. The sample was filtered on a glass sinter and dried in a vacuum oven at 70 ºC for 16 h. Polymer analysis:

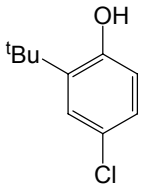
- ^{13}C NMR (Bruker DPX at 400 MHz) in 1,1,2,2-tetrachloroethane (10,000 scans, 4 s relaxation time, 90 ºC) ensuring that the sample was fully dissolved
- High temperature GPC (run at RAPRA), utilizing a Polymer Labs GPC220 with a PLgel guard column and two 30 cm Mixed Bed B columns in 1,2,4-trichlorobenzene at 160 ºC. The RI detector used monitors the deflection of a light beam caused by the refractive index difference between the contents of the sample cell and that of the reference cell. Hence, if the sample has a lower refractive index than the standard, the output voltage is negative. It is known that for the particular detector used, PS gives a negative output voltage and PE gives a positive output. The copolymer at 10% styrenic gives a positive response. See http://www.chromatography-online.org/HPLC/Refractive-Index/rs34.html.
- Thermal analyses were carried out on a Perkin-Elmer PC7 series system. Sample masses in each case were *ca*. 3 mg and the samples were purged with dinitrogen.

^{13}C spectrum of a typical ethene-co-TBS polymer



^{13}C NMR spectrum of polymer from run 9, with assignments.[1-4]

Synthesis of 2-*tert*-butyl-4-chlorophenol[5]



Diphenylsulfide (0.09 ml, 0.10 g, 0.54 mmol) and $AlCl_3$ (0.10 g, 0.75 mmol) were dissolved in 2-*tert*-butylphenol (15.35 ml, 15.02 g, 0.10 mol) in a three neck round bottom flask, under nitrogen flow. The flask outlet was fitted with a sat. $NaOH_{(aq)}$ scrubber. The solution was cooled in an ice bath, and sulfuryl chloride (7.97 ml, 13.4 g, 0.10 mol) was added dropwise. The solution became yellow, then red, and was stirred at ambient temperature overnight. The solution was concentrated and purified by vacuum distillation using a 12 cm Vigreux column. Fraction results summarised below.

Fraction	Stillhead temp. ºC	Heating block temp. ºC	r.f (hexane / diethyl ether 20:1)	Assignment by ^{1}H NMR
1	40-46	60-110	0.41	*ortho*
2	50-80	120-170	0.12/0.41	mixture
3	80-90	180-190	0.12	*para*

All products were clear oils. Fraction 2 was further purified by column chromatography (hexane/diethyl ether 20:1). Overall yield of *ortho* isomer = 7.49 g, 40 %; *para* isomer = 9.40 g, 51 %.

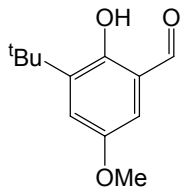
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (1H, d, ^{4}J = 2Hz, H^3), 7.05 (1H, dd, ^{4}J = 2Hz, ^{3}J = 8Hz, H^2), 6.63 (1H, d, ^{3}J = 8Hz, H^1), 5.14 (1H, s, OH), 1.42 (9H, s, ^{t}Bu).

Synthesis of salicylaldehydes[6]

These reactions were carried out under argon. Acetonitrile and triethylamine were distilled over CaH_2 prior to use. Paraformaldehyde was dried over P_2O_5, and $MgCl_2$ was dried in a vacuum oven at 80 ºC overnight.

A 500 ml side arm round bottom Schlenk vessel with stirrer bar was placed under argon, and charged with the phenol (typically 100 mmol), acetonitrile (350 ml), triethylamine (3.75 eq) $MgCl_2$ (1.5 eq) and the solution stirred for 15 min. After this time, paraformaldehyde (6.75 eq) was added and the Schlenk vessel fitted with a reflux condenser. The solution was heated to reflux for ca. 3.5 h, and typically became a vivid yellow during the first 30 min. The solution was allowed to cool to room temperature, poured into 800 ml of 5 % $HCl_{(aq)}$, and stirred for 30 min. The diethyl ether fractions (4 x 200 ml) were combined and washed with saturated $NaCl_{(aq)}$ then dried over Na_2SO_4, filtered, and evaporated in vacuo to yielding samples containing the corresponding salicylaldehydes.

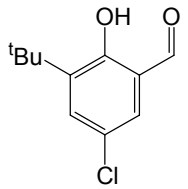
2-hydroxy-3-*tert*-butyl-5-methoxy-benzaldehyde[7-9]



Following the general procedure with 3-*tert*-butyl-4-hydroxy-anisole (18.02 g, 100 mmol) gave a yellow oil without further purification. (18.88 g, 90 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.42 (1H, s, OH), 9.76 (1H, s, CHO), 7.10 (1H, d, ^{4}J = 3 Hz, Ar), 6.74 (1H, d, ^{4}J = 3 Hz, Ar), 3.73 (3H, s, OCH_3), 1.33 (9H, s, ^{t}Bu).
^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0 (CHO), 155.6, 151.4, 139.5 (Ar q), 123.2 (Ar), 119.1 (Ar q), 111.0 (Ar), 55.1 (OCH_3), 34.3 (^{t}Bu q), 28.4 (^{t}Bu).
Anal. Calc. C: 69.21, H: 7.74; found C: 69.65, H: 8.18.
MS (EI) m/z: 193.0 $[M\text{-}CH_3]^+$

2-hydroxy-3-*tert*-butyl-5-chloro-benzaldehyde[7]



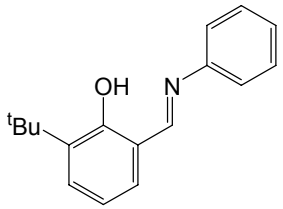
Following the general procedure with 2-*tert*-butyl-4-chloro-phenol (9.4 g, 50 mmol) gave an orange solution during reflux, and a yellow oil on work up. This solidified upon standing, and was recrystallised from heptane. (9.1 g, 85 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.75 (1H, s, OH), 9.85 (1H, s, CHO), 7.49 (1H, d, ^{4}J = 2 Hz, Ar), 7.41 (1H, d, ^{4}J = 2 Hz, Ar), 1.44 (9H, s, ^{t}Bu).
^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1 (CHO), 159.8, 140.8 (Ar q), 134.3 (Ar), 130.43 (Ar), 124.1, 121.0 (Ar q), 35.1 (^{t}Bu q), 28.9 (^{t}Bu).
Anal. Calc. C: 62.12, H: 6.16, Cl: 16.67; found C: 62.20, H: 6.18, Cl: 16.46.
MS (EI) m/z: 212.9 $[M]^{-}$

Synthesis of salicylaldimine proligands[10]

A 100 ml round bottom flask with stirrer bar was charged with the appropriate salicylaldehyde and a stoichiometric amount of aniline. The reactants were dissolved in methanol (50 ml) and a reflux condenser with nitrogen bubbler was fitted to the flask. The solution was heated to reflux for ca. 12 h, then allowed to cool to room temperature. Solids were seen to crystallise over the next 12 h period, were collected by vacuum filtration and washed with cold methanol.

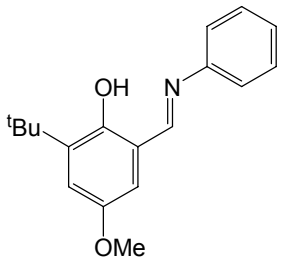
Synthesis of HL^1 proligand[10]



Following the general procedure with 2-hydroxy-3-*tert*-butyl-benzaldehyde (1.50 g, 8.41 mmol) gave an orange solid (1.7 g, 80 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ 13.81 (1H, s, OH), 8.55 (1H, s, C=N), 7.34 (3H, m, Ar), 7.20 (4H, m, Ar), 6.80 (1H, t, Ar), 1.39 (9H, s, ^{t}Bu).
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4 (C=N), 160.57, 148.5, 137.6 (Ar q) 130.7, 130.4, 129.4, 126.7, 121.2, 119.1, 118.3 (Ar), 34.9 (^{t}Bu q), 29.3 (^{t}Bu).
Anal. Calc. C: 80.60, H: 7.56, N: 5.53; found C: 80.15, H: 7.64, N: 5.03.
MS (EI) m/z: 254.1 $[M]^+$.

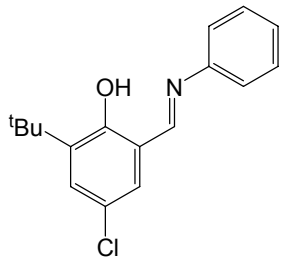
Synthesis of HL^2 proligand [8, 9]



Following the general procedure with 2-hydroxy-3-*tert*-butyl-5-methoxy-benzaldehyde (3.0 g, 14.40 mmol) gave an orange flaky solid (3.64 g, 89 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ 13.55 (1H, s, OH), 8.63 (1H, s, C=N), 7.45 (2H, t, ^{3}J = 7 Hz, Ar), 7.31 (3H, d & t overlapping, Ar), 7.08 (1H, d, ^{4}J = 3 Hz, Ar), 6.76 (1H, d, ^{4}J = 3 Hz, Ar), 3.84 (3H, s, OCH_3), 1.50 (9H, s, ^{t}Bu).
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1 (C=N), 155.2, 151.5, 148.5, 139.3 (Ar q), 129.4, 126.7, 121.2, 119.4 (Ar), 118.3 (Ar q), 111.9 (Ar), 55.81 (OCH_3), 35.1 (^{t}Bu q), 29.3 (^{t}Bu).
Anal. Calc. C: 76.30, H: 7.47, N: 4.94; found C: 75.89, H: 7.51, N: 4.71.
MS (EI) m/z: 284.1 $[M]^{+}$

Synthesis of HL^3 proligand



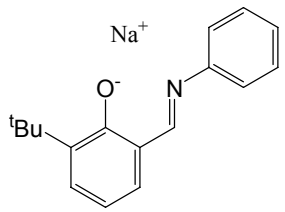
Following the general procedure with 2-hydroxy-3-*tert*-butyl-5-chloro-benzaldehyde (2.0 g, 9.40 mmol) gave orange needles (1.83 g, 67 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ 13.98 (1H, s, OH), 8.59 (1H, s, C=N), 7.47 (2H, t, Ar), 7.33 (4H, m, Ar), 7.27 (1H, d, Ar), 1.48 (9H, s, ^{t}Bu).
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.0 (C=N), 159.1, 147.9, 139.9 (Ar q), 130.4, 129.5, 129.2, 127.1 (Ar), 123.0 (Ar q), 121.2 (Ar), 119.7 (Ar q), 35.2 (^{t}Bu q), 29.1 (^{t}Bu).
Anal. Calc. C: 70.95, H: 6.30, N: 4.87, Cl: 12.32; found C: 70.93, H: 6.32, N: 4.90, Cl: 12.21.
MS (EI) m/z: 288.1 $[M]^{+}$

Synthesis of sodium salts of salicylaldimine proligands.

To a Schlenk vessel under argon was charged the proligand and a two-fold excess of NaH. The vessel was cooled to -78 ºC, and THF (ca. 40 ml) added via cannula. The solution was allowed to warm to room temperature, and stirred for 18 h under reduced pressure, with initial purging to remove H_2 gas. The solution was removed via filter cannula leaving and concentrated to a solid. ^{1}H NMR was used to estimate the THF content of the product.

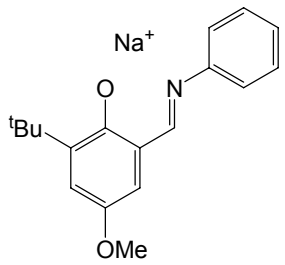
Synthesis of $NaL^1.THF_x$



Following the general procedure with HL^1 (1.0 g, 3.90 mmol) gave a yellow solid shown by ^{1}H NMR to be $NaL^1.THF_{0.38}$ (0.99 g, 84 %).

^{1}H NMR (400 MHz, Pyr): δ 8.69 (1H, s, C=N), 7.17 (3H, m, Ar), 7.04 (4H, m, Ar), 6.40 (1H, t, Ar), 3.62 (4H, m, THF), 1.65 (9H, s, ^{t}Bu), 1.58 (4H, m, THF).

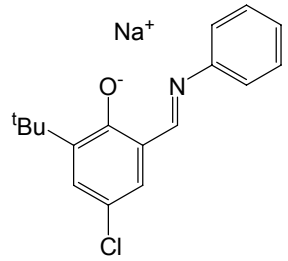
Synthesis of $NaL^2.THF_x$



Following the general procedure with HL^2 (1.0 g, 3.50 mmol) gave a yellow solid shown by ^{1}H NMR to be $NaL^1.THF_{0.46}$ (1.01 g, 85 %).

^{1}H NMR (400 MHz, Pyr): δ 8.96 (1H, s, C=N), 7.37 (1H, d, Ar), 7.32 (1H, d, Ar), 7.16 (3H, m, Ar), 7.07 (2H, d, Ar), 6.99 (1H, t, Ar), 3.74 (3H, s, OCH_3), 3.62 (4H, m, THF), 1.65 (9H, s, ^{t}Bu), 1.58 (4H, m, THF).

Synthesis of $NaL^3.THF_x$



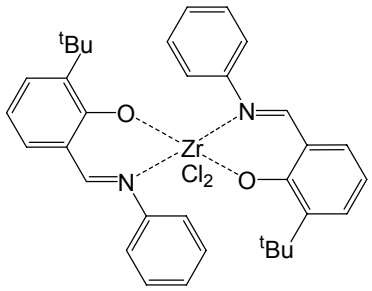
Following the general procedure with HL^3 (1.0 g, 3.50 mmol) gave a yellow solid shown by ^{1}H NMR to be $NaL^1.THF_{0.73}$ (1.1 g, 86 %).

^{1}H NMR (400 MHz, Pyr): δ 8.08 (1H, s, C=N), 7.16 (2H, t, Ar), 7.03 (2H, m, Ar), 6.92 (1H, d, Ar), 6.79 (2H, d, Ar), 3.40 (4H, m, THF), 1.63 (4H, m, THF), 1.22 (9H, s, ^{t}Bu).

Synthesis of zirconium dichloride complexes

$ZrCl_4.THF_2$ and two equivalents of the appropriate sodium salt proligand were charged into a Schlenk vessel under argon, and cooled to -78 ºC. THF (40 ml) was added via cannula, and the reaction allowed to warm to room temperature and stirred for ca. 16 h. The THF was removed, and co-evaporated with DCM. The residue was dissolved in DCM and filtered to remove NaCl. The solution was concentrated *in vacuo* and purified by sublimation at 250 ºC, 10^{-6} mmHg to give the desired complex. 1H NMRs were obtained at -60 ºC to resolve minor isomers.

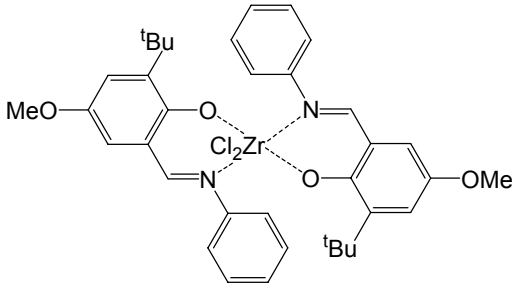
Synthesis of $ZrCl_2L^1_2$ precatalyst[8, 9, 11, 12]



Following the general procedure using $NaL^1.THF_{0.38}$ (0.50 g, 1.60 mmol) and $ZrCl_4.THF_2$ (0.31 g, 0.83 mmol) gave a yellow solid (270 mg, 49 %).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.19 (2H, s, C=N), 7.46 (2H, dd, Ar), 7.18 (2H, dd, Ar), 7.10 (10H, m, Ar), 6.86 (2H, t, Ar), 1.33 (18H, s, ^{t}Bu).
^{13}C NMR (100 MHz, Pyr): δ 170.9 (C=N), 159.7, 151.1, 139.7 (Ar q), 134.9, 134.0, 129.2, 127.2 (Ar), 123.7 (Ar q), 123.4, 120.3 (Ar), 35.1 (^{t}Bu q), 29.6 (^{t}Bu).
Anal. Calc. for $C_{34}H_{36}Cl_2N_2O_2Zr$: C: 61.24; H: 5.44; N: 4.20. found: C: 61.33; H: 5.51; N: 4.26.
MS (Maldi) m/z: 631.8 $[M\text{-}Cl]^+$

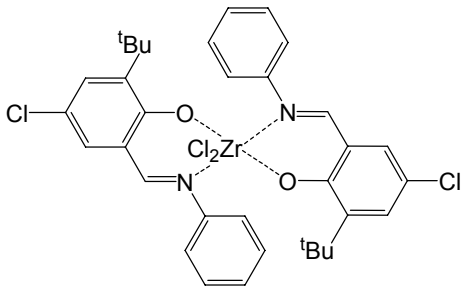
Synthesis of $ZrCl_2L^2_2$ precatalyst[8, 9]



Following the general procedure using $NaL^2.THF_{0.46}$ (0.50 g, 1.47 mmol) and $ZrCl_4.THF_2$ (0.28 g, 0.73 mmol) gave a yellow solid (190 mg, 35 %). Crystals were grown in toluene at -15 ºC for CHN.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.15 (2H, s, C=N), 7.13 (4H, m, Ar), 7.08 (6H, m, Ar), 7.03 (10H, m, Ar), 6.56 (2H, t, Ar), 3.73 (6H, s, OCH_3), 1.30 (18H, s, ^{t}Bu).
^{13}C NMR (100 MHz, Pyr): δ 170.6 (C=N) 154.9, 152.9, 151.2, 141.3 (Ar q), 129.2, 127.2, 124.2, 123.3 (Ar), 123.1 (Ar q), 114.0 (Ar), 56.1 (OCH_3), 35.3 (^{t}Bu q), 29.5 (^{t}Bu).
Anal. Calc. for $C_{36}H_{40}Cl_2N_2O_4Zr$ + $0.8_{toluene}$: C: 62.41, H: 5.84, N: 3.50; found C: 62.65, H: 5.89, N: 3.01.
MS (Maldi) m/z: 726.1 $[M]^+$

Synthesis of $ZrCl_2L^3_2$



Following the general procedure using $NaL^3.THF_{0.73}$ (0.47 g, 1.31 mmol) and $ZrCl_4.THF_2$ (0.24 g, 0.65 mmol) gave a yellow solid (120 mg, 25 %).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.46 (2H, s, C=N), 7.38 (5H, m, Ar), 7.23 (6H, m, Ar), 7.11 (3H, m, Ar), 1.43 (18H, s, ^{t}Bu).

^{13}C NMR (100 MHz, Pyr): δ 169.8 (C=N), 150.5, 142.1, 134.8, 132.0, 129.4, 127.6 (Ar), 124.3 (Ar q), 123.2 (Ar), 29.42 (^{t}Bu).

Anal. Calc. for $C_{34}H_{34}Cl_4N_2O_2Zr$ C: 55.51, H: 4.66, N: 3.81; found C: 55.23, H: 4.84, N: 3.68.

MS (Maldi) m/z: 700.02 $[M\text{-}Cl]^+$.

References

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