Supporting Information

From Alternating to Selective Distributions in Chromium-catalysed Ethylene Oligomerisation with Asymmetric BIMA Ligands

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Synthesis of Ligands and Complexes

General considerations.

Air and moisture sensitive syntheses were carried out using standard Schlenk techniques under an atmosphere of purified nitrogen. Air and moisture sensitive compounds were stored in a nitrogen filled glove-box at room temperature. Heptane, pentane and toluene were dried by passing through a cylinder filled with commercially available Q-5 reactant and Al₂O₃ under a pressure of nitrogen. Dichloromethane and acetonitrile were dried by heating at reflux temperature over calcium hydride. Diethyl ether and tetrahydrofuran were dried in a similar manner by heating at reflux temperature over sodium benzophenone ketyl. All solvents were degassed prior to use. All NMR solvents, CD₂Cl₂, CDCl₃ and C₆D₆ were dried and stored over molecular sieves (4Å). The syntheses of complex [Cr(I)Cl₃] has been described previously.¹

¹H and ¹³C NMR data were recorded on 400 MHz or 500 MHz Bruker spectrometers and were referenced internally to the residual ¹H and ¹³C NMR signal of the deuterated solvents. IR spectra were recorded on a Perkin-Elmer 1760X FT-IR spectrometer using KBr discs. Mass Spectra were recorded on a Micromass Autospec Q Spectrometer using electrospray ionisation (ESI). Elemental Analyses were carried out by the London Metropolitan University. Crystallographic data were collected by Dr. A. White at Imperial College London. Ethylene oligomerisation products were
analysed via Gas Chromatography using an Agilent 6890 series GC equipped with a SGE BPX-5 capillary column (5% diphenyl 95% dimethylpolysilphenylene-siloxane, 60 m × 0.32 mm). Quantification of individual products was accomplished by comparing the area of the peaks to the integrated area of an added standard, either n-nonane or 2,2,4,4,6,8,8-heptamethyl nonane.

The following precursors were synthesised according to published procedures or modifications thereof: 2-(chloromethyl)-1-methyl-benzimidazole,\(^2\) 2-(chloromethyl)-5,6-dimethyl-benzimidazole,\(^3\) and 2-(1-chloroethyl)-benzimidazole.\(^4\) Ethylene (CP grade) was purified by passing it through an Oxy-trap and gas drier (Alltech Associates).

**Synthesis of ligand precursors**

**2-(Chloromethyl)-1-phenylbenzimidazole**

\[
\text{N=CCl} + \text{EtOH} + \text{HCl (g)} \rightarrow \text{toluene} \quad \rightarrow \quad \text{EtO} \quad \text{NH} \quad \text{Cl} \\
\text{Ph} \quad \text{HCl} \quad \text{NH} \quad \text{Cl} \quad \text{DCM} \quad \text{Ph} \\
\text{NH} \quad \text{Cl} \quad \text{EtO} \quad \text{Cl} \quad \text{70 \%}
\]

\(N\)-phenylbenzene-1,2-diamine (4.86 g, 26.38 mmol) and ethyl 2-chloroethanimidoate dihydrochloride (4.17 g, 26.38 mmol) were stirred together in dry dichloromethane (30 mL) at room temperature for 12 hours. The resulting solid was filtered and washed with water (150 mL) to give a white solid. Yield = 4.40 g (70%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) : \(\delta\) 7.85 (1H, d, \(^3\)J\(\text{HH}\) = 8.0 Hz, ArH), 7.64 - 7.55 (3H, m, ArH), 7.50 - 7.48 (2H, m, ArH), 7.36 - 7.27 (3H, m, ArH), 7.19 (1H, d, \(^3\)J\(\text{HH}\) = 8.6 Hz) and 4.70 (2H, s, CH\(_2\)).

\(^13\)C NMR (101 MHz, CDCl\(_3\)) : \(\delta\) 149.2, 142.4, 136.6, 135.1, 130.1, 129.4, 127.2, 124.2, 123.2, 120.3, 110.7 and 36.5.
IR (KBr, cm\(^{-1}\)): \(\tilde{\nu}\) 3445 (w), 3053 (w), 1610 (w), 1594 (m), 1495 (s), 1455 (s), 1423 (m), 1405 (m), 1335 (m), 1287 (w), 1265 (s), 1243 (w), 1191 (w), 1144 (m), 1073 (w), 1036 (w), 1016 (m), 979 (w), 950 (w), 921 (w), 899 (m), 869 (m), 759 (m), 744 (s), 720 (w), 698 (s), 641 (m), 617 (w), 573 (m) and 469 (w).

MS (ESI): \(m/z\) 243 ([M+H]\(^+\), 100 %).


5,6-Dichloro-2-(chloromethyl)-1H-benzimidazole

\[
\begin{align*}
\text{N} & \quad \text{Cl} \\
\text{Cl} & \quad \text{H} \\
\text{\(\text{C}_{14}\)H\(_{11}\)ClN\(_2\)} & \quad \text{\(\text{C}_{14}\)H\(_{11}\)ClN\(_2\)}
\end{align*}
\]

Prepared according to the procedure for 2-(chloromethyl)-1-phenylbenzimidazole, using 4,5–dichlorobenzene–1,2–diamine (7.00 g, 39.54 mmol) and ethyl 2–chloroethanimidoate dihydrochloride (6.87 g, 43.49 mmol) in dichloromethane (40 mL). Yield = 6.50 g (70 %).

\(^1\)H NMR (400 MHz, \(d_6\)-DMSO): \(\delta\) 13.13 (1H, s, NH), 7.75 (2H, s, ArH) and 4.94 (2H, s, CH\(_2\)).

\(^{13}\)C NMR (101 MHz, \(d_6\)-DMSO) : \(\delta\) 153.0, 125.3, 117.2 and 38.3.

IR (KBr, cm\(^{-1}\)): \(\tilde{\nu}\) 3431 (w), 3015 (m), 1622 (w), 1576 (w), 1538 (w), 1444 (s), 1403 (s), 1335 (w), 1295 (m), 1261 (m), 1243 (w), 1223 (m), 1206 (w), 1146 (w), 1100 (m), 1021 (m), 1001 (w), 967 (w), 902 (w), 882 (w), 865 (m), 739 (w), 717 (m), 660 (w), 662 (m) and 541 (w).

MS (ESI): \(m/z\) 235 ([M+H]\(^+\), 98 %).

Elem. Anal. Caled for C\(_8\)H\(_5\)Cl\(_3\)N\(_2\): C, 40.80; H, 2.14; N, 11.90. Found: C, 40.49; H, 2.03; N, 12.15.

2-(Chloromethyl)-1H-naphtho[2,3-d]-imidazole

\[
\begin{align*}
\text{N} & \quad \text{Cl} \\
\text{\(\text{C}_{8}\)H\(_5\)Cl\(_3\)N\(_2\)} & \quad \text{\(\text{C}_{8}\)H\(_5\)Cl\(_3\)N\(_2\)}
\end{align*}
\]

Prepared according to the procedure for 2-(chloromethyl)-1-phenylbenzimidazole using naphthalene-2,3-diamine (5.20 g, 32.87 mmol) and ethyl 2-chloroethanimidoate
dihydrochloride (5.71 g, 36.20 mmol) in dichloromethane (40 mL) for 16 hours. Yield = 7.00 g (98%).

\[ \text{\(^1\)H NMR (400 MHz, } d_6\text{-DMSO)}: \delta 12.97 (1H, s, NH), 8.11 (2H, s, ArH), 8.02 – 7.99 (2H, m, ArH), 7.39 – 7.36 (2H, m, ArH) and 5.03 (2H, s, CH\textsubscript{2}). \]

\[ \text{\(^{13}\)C NMR (101 MHz, } d_6\text{-DMSO)}: \delta 154.7, 139.7, 130.4, 128.3, 124.0, 111.9, \text{ and } 38.7. \]

IR (KBr, cm\(^{-1}\)): \( \tilde{\nu} \) 3444 (m), 3123 (m), 3045 (s), 2805 (m), 1504 (w), 1472 (m), 1455 (w), 1435 (s), 1423 (m), 1405 (s), 1348 (w), 1267 (s), 1226 (w), 1158 (m), 1015 (w), 998 (w), 952 (w), 874 (w), 851 (s), 752 (m), 718 (w), 633 (m), 607 (w) and 476 (m).

MS (ESI): \( m/z \) 217 ([M+H]+, 100 %).

\[ 2-(\text{Chloromethyl})-1\text{H}-\text{perimidine} \]

\[
\begin{array}{c}
\text{NH} \\
\text{Cl}
\end{array}
\]

Prepared according to the procedure for 2-(chloromethyl)-1-phenylbenzimidazole using 1,8-diamino-naphthalene (3.20 g, 20.23 mmol) and ethyl 2-chloroethanimidoate dihydrochloride (3.52 g, 22.25 mmol) in dry dichloromethane (50 mL) at room temperature for 12 hours. Yield = 3.40 g (78 %).

\[ \text{\(^1\)H NMR (400 MHz, } d_6\text{-DMSO)}: \delta 10.90 (1H, s, NH), 7.13 (2H, t, \text{ }^3J_{HH} = 8.0 \text{ Hz, ArH}), 7.05 (2H, d, \text{ }^3J_{HH} = 8.3 \text{ Hz, ArH}), 6.50 (2H, d, \text{ }^3J_{HH} = 7.2 \text{ Hz, ArH}) \text{ and } 4.23 (2H, s, -CH\textsubscript{2}). \]

\[ \text{\(^{13}\)C NMR (101 MHz, } d_6\text{-DMSO)}: \delta 153.6, 135.5, 128.9, 122.0, 119.5 \text{ and } 43.9. \]

IR (KBr, cm\(^{-1}\)): \( \tilde{\nu} \) 3194 (m), 2937 (m), 1644 (m), 1634 (s), 1610 (s), 1600 (s), 1539 (m), 1505 (w), 1479 (m), 1446 (m), 1413 (m), 1372 (s), 1343 (m), 1286 (m), 1253 (w), 1228 (w), 1164 (m), 1051 (m), 1030 (w), 994 (w), 824 (s), 768 (s), 658 (m) and 559 (w).

MS (ESI): \( m/z \) 217 ([M+H]+, 100 %).

Elem. Anal. Calcd for C\textsubscript{12}H\textsubscript{9}ClN\textsubscript{2}: C, 66.52; H, 4.19; N, 12.93. Found: C, 66.60; H, 4.27; N, 13.03.
2-(Chloromethyl)-4,7-diphenyl-1\(^H\)-benzimidazole

Prepared according to the procedure for 2-(chloromethyl)-1-phenylbenzimidazole using 1,1':4',1"-terphenyl-2',3'-diamine (0.30 g, 1.15 mmol) and ethyl 2-chloroethanamidoate dihydrochloride (0.20 g, 1.27 mmol) in dry dichloromethane (30 mL). Yield = 0.26 g (71 %).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) : \(\delta\) 7.83 (4H, d, \(^3\)J\(_{HH}\) = 7.3 Hz, Ar\(H\)), 7.54 (4H, t, \(^3\)J\(_{HH}\) = 7.5 Hz, Ar\(H\)), 7.49 (2H, s, Ar\(H\)), 7.43 (2H, t, \(^3\)J\(_{HH}\) = 7.4 Hz, Ar\(H\)) and 4.88 (2H, s, -CH\(_2\)-).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) : \(\delta\) 149.2, 138.1, 129.0, 128.5, 127.8, 123.2 and 38.5.

IR (KBr, cm\(^{-1}\)) : \(\nu\) 3138 (s), 3100 (s), 1682 (w), 1600 (w), 1485 (w), 1447 (s), 1407 (s), 1365 (m), 1317 (w), 1292 (w), 1263 (m), 1235 (w), 1152 (w), 1112 (w), 1072 (w), 1028 (m), 947 (w), 935 (w), 912 (w), 825 (m), 793 (w), 750 (s), 714 (w), 695 (s), 668 (m), 641 (w), 624 (w), 610 (w), 572 (w), 552 (w), 495 (w) and 476 (w).

MS (ESI): m/z 319 ([M+H]\(^+\), 100 %).

Elem. Anal. Calcd for C\(_{20}\)H\(_{15}\)ClN\(_2\) : C, 75.35; H, 4.74; N, 8.79. Found: C, 66.38; H, 4.50; N, 8.86.

Synthesis of ligands

1-(1\(^H\)-Benzimidazol-2-yl)-N-methyl-N-[(1-methyl-1\(^H\)-benzimidazol-2-yl)methyl]methanamine, 2
Triethylamine (2.17 g, 21.44 mmol) was added to a mixture of 2-\((N\)-methylaminomethyl\)benzimidazole dihydrochloride (1.67 g, 7.15 mmol) and 2-(chloromethyl)-1-methyl-1\(^H\)-benzimidazole (1.29 g, 7.15 mmol) in acetonitrile (40 mL) and stirred for 16 hours. After this time the precipitate was filtered and washed with acetonitrile (10 mL), and then stirred in water (50 mL) to remove triethylamine hydrochloride. Filtration and subsequent drying in vacuo gave a white solid. Yield = 1.04 g (48 %).

\(^1\)H NMR (400 MHz, \(d_6\)-DMSO) : \(\delta\) 12.34 (1H, s, NH), 7.65 – 7.45 (4H, m, ArH), 7.28 – 7.12 (4H, m, ArH), 3.93 (2H, s, -CH\(_2\)-), 3.88 (2H, s, -CH\(_2\)-), 3.84 (3H, s, NCH\(_3\)) and 2.25 (3H, s, NCH\(_3\)).

\(^{13}\)C NMR (101 MHz, \(d_6\)-DMSO) : \(\delta\) 152.3, 152.1, 142.4, 136.6, 122.5, 121.8, 119.3, 110.4, 55.2, 53.9, 42.6 and 30.4.

IR (KBr, cm\(^{-1}\)) : \(\tilde{\nu}\) 3445 (w), 3052 (w), 2986 (w), 2948 (m), 2849 (w), 2817 (w), 2788 (m), 1645 (w), 1615 (w), 1539 (w), 1515 (m), 1478 (s), 1455 (s), 1440 (w), 1399 (m), 1351 (m), 1334 (m), 1330 (w), 1292 (w), 1271 (m), 1236 (w), 1217 (w), 1195 (w), 1157 (w), 1120 (m), 1030 (m), 1011 (m), 995 (m), 981 (w), 860 (m), 769 (m), 760 (s), 659 (w) and 484 (w).
MS (ESI): m/z 306 ([M+H]^+, 100 %).
Elem. Anal. Calcd for C_{18}H_{19}N_{5}: C, 70.80; H, 6.27; N, 22.93. Found: C, 70.76; H, 6.38; N, 23.02.

1-(1H-Benzimidazol-2-yl)-N-methyl-N-[(1-phenyl-1H-benzimidazol-2-yl)methyl]methanamine, 3

![Structural formula of 3](image)

Prepared according to the procedure for 2 using triethylamine (3.75 g, 37.06 mmol), 2-[(N-methylaminomethyl)benzimidazole dihydrochloride (2.89 g, 12.35 mmol) and 2-(chloromethyl)-1-phenylbenzimidazole (3.00 g, 12.35 mmol) in acetonitrile (50 mL) to give a white solid. Yield = 1.00 g (22 %).

^1H NMR (400 MHz, CDCl₃) : δ 7.91 (1H, d, ^3J_{HH} = 7.9 Hz, ArH), 7.72 – 7.59 (4H, m, ArH), 7.56 – 7.49 (2H, m, ArH), 7.38 (1H, t, ^3J_{HH} = 8.2 Hz, ArH), 7.34 – 7.25 (4H, m, ArH), 3.95 (2H, s, -CH₂-), 3.82 (2H, s, -CH₂-) and 2.39 (3H, s, NCH₃).

^13C NMR (101 MHz, CDCl₃) : δ 151.3, 141.8, 136.3, 135.8, 130.0, 129.1, 127.0, 123.6, 123.1, 122.2, 119.6, 110.6, 53.8, 52.5 and 43.1.

IR (KBr, cm⁻¹): ν 3050 (m), 2943 (m), 2904 (m), 2842 (m), 2784 (m), 1621 (w), 1598 (m), 1538 (w), 1512 (w), 1499 (s), 1458 (s), 1443 (m), 1433 (m), 1420 (m), 1407 (m), 1352 (w), 1333 (w), 1308 (w), 1268 (m), 1220 (w), 1190 (w), 1118 (m), 1031 (w), 977 (w), 861 (w), 840 (w), 769 (m), 750 (s), 705 (m), 661 (w), 620 (w), 585 (w) and 486 (w).

MS (ESI): m/z 368 ([M+H]^+, 100 %).
Elem. Anal. Calcd for C_{23}H_{21}N_{5}: C, 75.18; H, 5.76; N, 19.06. Found: C, 75.20; H, 5.67; N, 19.07.

1-(1H-Benzimidazol-2-yl)-N-(1,3-benzothiazol-2-ylmethyl)-N-methylmethanamine, 4

![Structural formula of 4](image)
Prepared according to the procedure for 2 using triethyl amine (1.62 g, 16.01 mmol), 2-(chloromethyl)-1,3-benzothiazole (0.98 g, 5.34 mmol) and 2-(N-methylaminomethyl)benzimidazole dihydrochloride (1.25 g, 5.34 mmol) in acetonitrile (25 mL). Yield = 0.87 g (53 %).

$^1$H NMR (400 MHz, $d_6$-DMSO) : $\delta$ 12.37 (1H, s, NH), 8.08 – 8.06 (1H, m, ArH), 7.96 – 7.94 (1H, m, ArH), 7.54 – 7.40 (4H, m, ArH), 7.17 – 7.15 (2H, m, ArH), 4.16 (2H, s, -CH$_2$-), 3.98 (2H, s, -CH$_2$-) and 2.40 (2H, s, NCH$_3$).

$^{13}$C NMR (101 MHz, $d_6$-DMSO) : $\delta$ 172.6, 153.4, 151.8, 135.5, 126.4, 125.4, 122.9, 122.7, 122.0, 58.9, 55.0 and 42.9.

IR (KBr, cm$^{-1}$): 3065 (m), 2820 (m), 2788 (m), 1621 (w), 1589 (w), 1558 (w), 1523 (m), 1480 (w), 1456 (s), 1426 (s), 1411 (s), 1350 (s), 1314 (m), 1304 (m), 1271 (m), 1252 (m), 1238 (w), 1225 (w), 1212 (m), 1169 (w), 1159 (w), 1145 (w), 1127 (m), 1119 (s), 1064 (w), 1036 (s), 1017 (m), 996 (w), 986 (w), 967 (w), 924 (w), 861 (m), 837 (m), 763 (s), 745 (s), 731 (s), 709 (m), 700 (m), 667 (m), 619 (w), 516 (w) and 486 (m).

MS (ESI): m/z 309 ([M+H]$^+$, 100 %).

Elem. Anal. Calcd for C$_{17}$H$_{16}$N$_4$S: C, 66.21; H, 5.23; N, 18.17; S, 10.40. Found: C, 66.16; H, 5.19; N, 18.24; S, 10.35.

1-(1$^H$-Benzimidazol-2-yl)-N-[(5,6-dimethyl-1$^H$-benzimidazol-2-yl)methyl]-N-methylmethanamine, 5

Prepared according to the procedure for 2 using triethylamine (6.50 g, 64.24 mmol), 2-(N-methylaminomethyl)benzimidazole dihydrochloride (5.01 g, 21.41 mmol), 2-(chloromethyl)-5,6-dimethyl-1$^H$-benzimidazole (4.17 g, 21.41 mmol) in acetonitrile (50 mL). Yield = 1.00 g (22 %).

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 11.45 (2H, s, NH), 9.58 – 9.55 (2H, m, ArH), 7.31 (2H, s, ArH), 7.26 – 7.24 (2H, m ArH), 3.92 (2H, s, CH$_2$), 3.91 (2H, s, CH$_2$), 2.35 (3H, s, CH$_3$) and 2.34 (6H, s, NCH$_3$).
$^{13}$C NMR (101 MHz, CDCl$_3$) : $\delta$ 151.6, 150.6, 131.8, 122.6, 115.2, 53.4, 43.0 and 20.3

IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3401 (s), 3053 (s), 2944 (s), 1621 (w), 1538 (s), 1330 (m), 1308 (m), 1271 (m), 1122 (w), 1042 (w), 1022 (w), 999 (w), 855 (m), 768 (w), 743 (s) and 668 (w).

MS (ESI): m/z 320 ([M+H]$^+$, 100 %).


1-(1H-Benzimidazol-2-yl)-N-[(5,6-dichloro-1H-benzimidazol-2-yl)methyl]-N-methylmethanamine, 6

\[\text{Cl} \quad \text{Cl} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{Cl} \quad \text{Cl} \]

Prepared according to the procedure for 2 using triethyl amine (3.87 g, 38.24 mmol), 5,6-dichloro-2-(chloromethyl)-1H-benzimidazole (3.00 g, 12.75 mmol) and 2-(N-methylaminomethyl)benzimidazole dihydrochloride (2.99 g, 12.75 mmol) in acetonitrile (50 mL). Yield = 0.75 g (20 %).

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 11.36 (2H, br. s, NH), 7.62 (2H, s, ArH), 7.57 – 7.55 (2H, m, ArH), 7.29 – 7.27 (2H, m, ArH), 3.96 (2H, s, -CH$_2$-) 3.92 (2H, s, -CH$_2$-) and 2.40 (3H, s, NCH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) : $\delta$ 154.1, 151.8, 138.0, 137.7, 126.3, 122.9, 116.2, 115.0, 54.4, 54.3 and 43.1.

IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3094 (s), 1622 (w), 1538 (w), 1446 (s), 1401 (m), 1324 (m), 1272 (m), 1221 (w), 1121 (w), 1096 (m), 1043 (w), 1018 (w), 959 (w), 863 (m), 768 (w), 743 (s), 647 (w) and 541 (w).

MS (ESI): m/z 360 ([M+H]$^+$, 100 %).

Elem. Anal. Calcd for C$_{17}$H$_{15}$Cl$_2$N$_5$: C, 56.68; H, 4.20 N, 19.44. Found: C, 56.56; H, 4.08; N, 19.38.
1-(1H-Benzimidazol-2-yl)-N-[(4,7-diphenyl-1H-benzimidazol-2-yl)methyl]-N-methylmethanamine, 7

Prepared according to the procedure for 2 using triethyl amine (1.20 g, 11.86 mmol), 2-(chloromethyl)-4,7-diphenyl-1H-benzimidazole (1.26 g, 3.95 mmol) and 2-(N-methylaminomethyl)benzimidazole dihydrochloride (0.93 g, 3.95 mmol) in acetonitrile (50 mL). Yield = 0.80 g (44%).

$^1$H NMR (400 MHz, CDCl$_3$) : $\delta$ 7.88 – 7.77 (4H, m, ArH), 7.55 – 7.41 (10H, m, ArH), 7.27 – 7.25 (2H, m, ArH), 3.87 (2H, s, -CH$_2$), 3.85 (2H, s, -CH$_2$) and 2.48 (3H, s, NCH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) : $\delta$ 151.4, 150.2, 141.7, 138.4, 137.8, 128.9, 128.6, 127.9, 127.7, 123.7, 122.8, 122.4, 52.6, 52.3 and 43.2.

IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3440 (m), 3056 (s), 2940 (s), 1600 (w), 1527 (m), 1483 (m), 1435 (s), 1386 (w), 1365 (w), 1348 (w), 1331 (w), 1274 (m), 1217 (w), 1179 (w), 1157 (w), 1105 (m), 1075 (w), 1030 (w), 1018 (w), 925 (w), 820 (w), 797 (w), 755 (s), 733 (s), 717 (w), 699 (s), 571 (w), 532 (w) and 476 (w).

MS (ESI): m/z 444 ([M+H]$^+$, 100 %).

Elem. Anal. Calcd for C$_{29}$H$_{25}$N$_5$: C, 78.53; H, 5.68; N, 15.79. Found: C, 78.58; H, 5.61 N, 15.73.

1-(1H-Benzimidazol-2-yl)-N-methyl-N-(1H-naphtho[2,3-d]imidazol-2-ylmethyl)methanamine, 8
Prepared according to the procedure for 2 using triethylamine (4.20 g, 41.51 mmol), 2-(N-methylaminomethyl)benzimidazole dihydrochloride (3.24 g, 13.84 mmol) and 2-(chloromethyl)-1H-naphtho[2,3-d]imidazole (3.00 g, 13.84 mmol) in acetonitrile (50 mL). Yield = 1.00 g (22 %).

1H NMR (400 MHz, CDCl$_3$) : δ 12.46 (2H, s, NH$_2$), 8.16 – 7.99 (4H, m, ArH), 7.57 (2H, s, ArH), 7.38 – 7.36 (2H, m, ArH), 7.19 – 7.17 (2H, m, ArH), 4.03 (2H, s, CH$_2$), 3.99 (2H, s, CH$_2$) and 2.34 (2H, s, NCH$_3$).

13C NMR (101 MHz, CDCl$_3$) : δ 157.7, 152.7, 130.2, 128.3, 123.8, 122.3, 55.5, 55.4 and 42.7

IR (KBr, cm$^{-1}$): ν 3391 (s), 3050 (s), 1621 (w), 1539 (w), 1505 (w), 1470 (m), 1455 (m), 1434 (s), 1417 (m), 1334 (m), 1308 (w), 1270 (s), 1224 (w), 1159 (w), 1121 (w), 1043 (w), 1014 (w), 859 (s), 767 (w), 743 (s), 668 (w), 611 (w), and 474 (w).

MS (ESI): m/z 342 ([M+H]$^+$, 100 %).

Elem. Anal. Calcd for C$_{21}$H$_{19}$N$_5$: C, 73.88; H, 5.61; N, 20.51. Found: C, 73.80; H, 5.55; N, 20.43.

**N-Methyl-N-(1H-perimidin-2-ylmethyl)-1H-benzimidazol-2-amine, 9**

Prepared according to the procedure for 2 using 2-(chloromethyl)-1H-perimidine (2.34 g, 10.80 mmol), triethyl amine (3.28 g, 32.41 mmol), and 2-(N-methylaminomethyl)benzimidazole dihydrochloride (2.52 g, 10.8 mmol) in acetonitrile (50 mL). Yield = 0.75 g (20 %).

1H NMR (400 MHz, CDCl$_3$) : δ 7.59 – 7.57 (2H, m, ArH), 7.26 – 7.23 (2H, m, ArH), 7.13 – 7.06 (4H, m, ArH), 6.55 – 6.53 (2H, m, ArH), 3.96 (2H, s, -CH$_2$-), 3.33 (2H, s, -CH$_2$-) and 2.43 (3H, s, NCH$_3$).
1³C NMR (101 MHz, CDCl₃):  δ 155.3, 151.2, 135.7, 128.1, 122.6, 119.8, 59.6, 54.8 and 43.0.
IR (KBr, cm⁻¹):  ν 3048 (m), 1634 (s), 1600 (s), 1593 (s), 1575 (w), 1532 (w), 1520 (w), 1475 (w), 1456 (m), 1447 (m), 1418 (m), 1372 (m), 1335 (m), 1271 (m), 1163 (w), 1124 (w), 1054 (m), 994 (w), 824 (m), 768 (s), 748 (s), 667 (w).
MS (ESI): m/z 342 ([M+H]+, 100 %).

1-(1H-Benzimidazol-2-yl)-N-(1H-benzimidazol-2-ylmethyl)-N-methylethanamine, 10

Prepared according to the procedure for 2 using triethyl amine (1.68 g, 16.60 mmol), 2-(1-chloroethyl)-1H-benzimidazole (1.00 g, 5.53 mmol) and 2-(N-methylaminomethyl)-benzimidazole dihydrochloride (1.30 g, 5.53 mmol) in acetonitrile (20 mL). Recrystallised from dichloromethane. Yield = 0.75 g (27 %).

¹H NMR (400 MHz, CDCl₃) : δ 12.33 (2H, br. s, NH₂), 7.58 – 7.53 (4H, m, ArH), 7.19 – 7.13 (4H, m, ArH), 4.25 (1H, q, ³JHH = 6.8 Hz, -CH(CH₃)-), 3.90 (2H, dd, ²JHH = 14.6 Hz, ²JHH = 54.6 Hz), 2.18 (3H, s, NCH₃) and 1.53 (3H, d, ³JHH = 6.8 Hz, CCH₃).
¹³C NMR (101 MHz, CDCl₃) : δ 156.1, 153.6, 121.9, 57.5, 52.7, 38.3 and 13.8.
IR (KBr, cm⁻¹): ν 3047 (s), 2978 (s), 1620 (w), 1589 (w), 1520 (w), 1455 (s), 1400 (s), 1372 (w), 1333 (m), 1307 (m), 1294 (m), 1270 (s), 1224 (m), 1157 (w), 1121 (w), 1092 (m), 1043 (w), 1020 (m), 1008 (w), 1000 (w), 972 (w), 936 (w), 899 (w), 768 (w), 748 (s), 668 (w), 616 (w) and 482 (w).
MS (ESI): m/z 306 ([M+H]+, 100 %).
Elem. Anal. Calcd for C_{18}H_{19}N_{5}: C, 70.80; H, 6.27; N, 22.93. Found: C, 70.63; H, 6.33; N, 22.88.

**2-(1H-Benzimidazol-2-yl)-N-(1H-benzimidazol-2-ylmethyl)-pyrrolidine, 11**

![Diagram of 11]

Triethylamine (2.15 g, 21.22 mmol), 2-(benzimidazolyl)pyrrolidine dihydrochloride (1.84 g, 7.07 mmol) and 2(2'-chloromethyl)benzimidazole (1.18 g, 7.07 mmol) were stirred under reflux in acetonitrile (40 mL) for 16 hours. The white precipitate formed was filtered off. The filtrate was rotary evaporated and the product formed was washed with water to remove any triethylamine hydrochloride that may be present. Then the product was dried in a vacuum oven over-night. The product was obtained as a brown amorphous solid; 0.770 g (35%); δ_{H} (CDCl_{3}, 400 MHz): 7.49-7.42 (m, 4H, Ar-H), 7.22-7.15 (m, 4H, Ar-H), 4.17 (d, 1H, J_{HH} 14.5 Hz, CH_{2}), 4.05 (t, 1H, J_{HH} 7.3 Hz, CH), 3.84 (d, 1H, J_{HH} 14.5 Hz, CH_{2}), 3.20 (t, 1H, J_{HH} 9.7 Hz, CH), 2.46 (m, 1H, CH), 2.25 (m, 1H, CH), 2.10 (m, 1H, CH), 1.88 (m, 1H, CH), 1.76 (m, 1H, CH); δ_{C} (CDCl_{3}, 101 MHz) 156.9, 152.9, 138.3, 122.6, 114.9, 62.9, 54.1, 52.1, 32.4, 23.5.

**2-(1H-benzimidazol-2-yl)-N-(1H-benzimidazol-2-ylmethyl)-N-methylethanamine (12)**

![Diagram of 12]

Triethylamine (2.17 g, 21.44 mmol), 2-(N-methylaminomethyl)benzimidazole dihydrochloride (1.67 g, 7.15 mmol) and 2(2'-chloroethyl)benzimidazole (1.29 g, 7.15 mmol) were stirred in acetonitrile (40 mL) for 16 hours. The white precipitate formed was filtered off. The filtrate was rotary evaporated and the product formed was washed with water to remove any triethylamine hydrochloride that may be present. Then the product was dried in a vacuum oven over-night. The product was obtained as a brown amorphous solid. Yield: 0.77 g (35%); δ_{H} (CDCl_{3}, 400 MHz) 7.70-7.60 (m, 4H, Ar-H), 7.33-7.25 (m, 4H, Ar-H), 3.97 (s, 2H, -CH_{2}-), 3.17 (t, 2H, J_{HH} 8.0 Hz, -CH_{2}-), 2.99 (t,
2H, $^3J_{HH} 8.0$ Hz, -CH$_2$-), 2.46 (s, 3H, NCH$_3$); $\delta$$_C$ (CDCl$_3$, 101 MHz) 153.6, 153.3, 138.5, 138.1, 122.5, 122.4, 114.9, 114.7, 55.7, 53.6, 42.7 & 26.9; $\nu$$_{max}$/cm$^{-1}$ (KBr) 3406.7 (w, N-H stretch), 3056.9 & 2847.1 (s, aromatic and aliphatic C-H stretch), 1654.9 & 1542.1 (m, C=N stretch), 1456.8 & 1438.1 (s, aromatic C=C stretch and aliphatic C-H bending), 1271.6 (s, C-N stretch), 741.9 (s, aromatic C-H bending); MS (ESI): m/z 306 ([M+H]$^+$, 100 %); Calc. for C$_{18}$H$_{19}$N$_5$: C, 70.78; H, 6.27; N, 22.94. Found: C, 70.86; H, 6.47; N, 23.01 %.
Synthesis of complexes

1-(1H-Benzimidazol-2-yl)-N-methyl-N-[(1-methyl-1H-benzimidazol-2-yl)methyl]methanamine chromium(III) chloride, [Cr(2)Cl₃]

The ligand 2 (0.95 g, 3.11 mmol) and chromium(III) chloride tetrahydrofuran complex (1.17 g, 3.11 mmol) were stirred together in THF (40 mL) for approximately 16 hours. After this time the green insoluble solid was isolated via filtration, washed with THF (20 mL) and dried in vacuo. Yield = 1.37 g (94 %).

IR (KBr, cm⁻¹): 3226 (m), 2930 (m), 1620 (m), 1593 (m), 1505 (m), 1478 (m), 1455 (s), 1417 (m), 1387 (w), 1361 (w), 1275 (m), 1243 (w), 1150 (w), 1086 (w), 1052 (w), 1002 (m), 979 (w), 939 (w), 920 (w), 902 (w), 882 (m), 746 (s), 700 (w), 558 (w) and 535 (w).

MS (LSMIS): m/z 427 ([M-Cl]⁺, 35 %), and 392 ([M-2Cl]⁺, 20 %).


μₑffective = 3.6 BM.

1-(1H-Benzimidazol-2-yl)-N-methyl-N-[(1-phenyl-1H-benzimidazol-2-yl)methyl]methanamine chromium(III) chloride, [Cr(3)Cl₃]

Synthesised according to the procedure for [Cr(2)Cl₃] using ligand 3 (0.88 g, 2.39 mmol) and chromium(III) chloride tetrahydrofuran complex (0.90 g, 2.39 mmol) in THF (40 mL). Yield = 1.20 g (95 %).

IR (KBr, cm⁻¹): 3458 (m), 3189 (m), 3077 (m), 2936 (m), 1620 (w), 1594 (m), 1549 (w), 1504 (s), 1477 (m), 1470 (m), 1454 (s), 1417 (w), 1387 (w), 1361 (w), 1332 (m), 1276 (m), 1240 (w), 1148 (w), 1086 (w), 1050 (w), 1023 (w), 1002 (m), 934 (w), 920 (w), 903 (w), 876 (m), 749 (s), 696 (m), 622 (w), 563 (w), 546 (w), 518 (w) and 492 (w).
MS (LSMIS): m/z 489 ([M-Cl]^+, 12 %) and 454 ([M-2Cl]^+, 5 %).

Elem. Anal. Calcd for C_{23}H_{21}Cl_{3}CrN_{5}: C, 52.54; H, 4.03; N, 13.32.  Found: C, 52.44; H, 3.92; N, 13.25.

$$\mu_{\text{eff}} = 3.7 \text{ BM.}$$

1-(1\text{H}-Benzimidazol-2-yl)-N-(1,3-benzothiazol-2-ylmethyl)-N-methylmethanamine chromium(III) chloride, [Cr(4)Cl$_3$]

![Chemical structure](image)

Synthesised according to the procedure for [Cr(2)Cl$_3$] using ligand 4 (0.52 g, 1.69 mmol) and chromium(III) chloride tetrahydrofuran complex (0.63 g, 1.69 mmol) in tetrahydrofuran (50 mL). Yield = 0.70 g (89 %).

IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3446 (s), 3224 (s), 1622 (m), 1593 (m), 1505 (w), 1495 (m), 1475 (s), 1456 (s), 1436 (s), 1418 (w), 1386 (w), 1335 (w), 1316 (w), 1274 (m), 1238 (w), 1171 (w), 1155 (w), 1052 (w), 1000 (m), 979 (w), 903 (w), 871 (m), 760 (s) and 728 (m).

MS (LSIMS): m/z 430 ([M-Cl]^+, 20 %), 395 ([M-2Cl]^+, 25 %).

Elem. Anal. Calcd for C$_{17}$H$_{16}$Cl$_3$CrN$_4$S: C, 43.74; H, 3.46; N, 12.00; S, 6.87.  Found: C, 43.64; H, 3.35; N, 11.87; S, 6.93.

$$\mu_{\text{eff}} = 3.3 \text{ BM.}$$

1-(1\text{H}-Benzimidazol-2-yl)-N-[(5,6-dimethyl-1\text{H}-benzimidazol-2-yl)methyl]-N-methylmethanamine chromium(III) chloride, [Cr(5)Cl$_3$]

![Chemical structure](image)

Synthesised according to the procedure for [Cr(2)Cl$_3$] using ligand 5 (0.70 g, 2.19 mmol) and chromium(III) chloride tetrahydrofuran complex (0.82 g, 2.19 mmol) in THF (50 mL). Yield = 0.93 g (88 %).

IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3230 (s), 3065 (s), 2975 (s), 1622 (m), 1593 (m), 1548 (w), 1476 (s), 1455 (s), 1365 (m), 1323 (m), 1276 (m), 1218 (w), 1148 (w), 1087 (w), 1051 (m),
1002 (m), 979 (w), 942 (w), 921 (w), 877 (m), 749 (m), 633 (w), 539 (w) and 492 (w).

MS (LSMIS): m/z 441 ([M-Cl]^+, 45 %) and 406 ([M-2Cl]^+, 20 %).

Elem. Anal. Calcd for C_{19}H_{23}Cl_3CrN_5: C, 47.77; H, 4.43; N, 14.66. Found: C, 47.68; H, 4.46; N, 14.54. \( \mu_{\text{eff}} = 3.6 \text{ BM.} \)

\( N-[(5,6\text{-Dichloro-1H-benzimidazol-2-yl})\text{-methyl}]\text{-N-methyl-1H-benzimidazol-2-amine chromium(III) chloride, [Cr(6)Cl}_3] \)

Synthesised according to the procedure for [Cr(2)Cl_3] using ligand 6 (0.45 g, 1.25 mmol) and chromium(III) chloride tetrahydrofuran complex (0.47 g, 1.25 mmol) in tetrahydrofuran (50 mL). Yield = 0.30 g (46 %).

IR (KBr, cm\(^{-1}\)): \( \tilde{\nu} \) 3211 (s), 1618 (w), 1577 (w), 1540 (w), 1477 (m), 1446 (s), 1364 (w), 1274 (w), 1100 (w), 1049 (m), 984 (w), 880 (m), 747 (m) and 668 (m).

MS (LSIMS): m/z 483 ([M-Cl]^+, 90 %), 446 ([M-2Cl]^+, 40 %) and 411 ([M-3Cl]^+, 10 %).

Elem. Anal. Calcd for C_{17}H_{15}Cl_5CrN_5: C, 39.37; H, 2.92; N, 13.50. Found: C, 39.48; H, 2.86; N, 13.53. \( \mu_{\text{eff}} = 4.1 \text{ BM.} \)

\( 1-(1\text{H-Benzimidazol-2-yl})\text{-N-methyl-N-(1H-naphtho[2,3-d]imidazol-2-ylmethyl})methanamine chromium(III) chloride, [Cr(7)Cl}_3] \)

Synthesised according to the procedure for [Cr(2)Cl_3] using ligand 7 (0.28 g, 0.82 mmol) and chromium(III) chloride tetrahydrofuran complex (0.31 g, 0.82 mmol) in THF (40 mL). Yield = 0.28 g (68 %).
IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3224 (s), 3073 (s), 2930 (s), 1620 (m), 1592 (m), 1550 (m), 1497 (s), 1476 (s), 1454 (s), 1405 (m), 1339 (m), 1274 (s), 1229 (w), 1163 (w), 1146 (w), 1115 (w), 1087 (w), 1049 (m), 1000 (m), 979 (w), 941 (w), 918 (m), 877 (s), 745 (s), 613 (m), 571 (w) and 473 (m).

MS (LSIMS): m/z 463 ([M-Cl]$^+$, 83 %), and 428 ([M-2Cl]$^+$, 40 %).

Elem. Anal. Calcd for C$_{21}$H$_{19}$Cl$_3$CrN$_5$: C, 50.47; H, 3.83; N, 14.01. Found: C, 50.53; H, 3.95; N, 13.94.

$\mu_{\text{eff}}$ = 4.37 BM.

Green single crystals suitable for X-ray diffraction were grown by a vapour diffusion of diethyl ether into a DMF solution of the complex.

*Crystal data for* [Cr(7)Cl$_3$]: C$_{21}$H$_{19}$Cl$_3$CrN$_5$·2(C$_3$H$_7$NO), $M = 645.95$, orthorhombic, $Pbca$ (no. 61), $a = 18.2412(2)$, $b = 14.5616(2)$, $c = 23.1101(4)$ Å, $V = 6138.53(15)$ Å$^3$, $Z = 8$, $D_c = 1.398$ g cm$^{-3}$, $\mu$ (Mo-Kα) = 0.671 mm$^{-1}$, $T = 173$ K, dark green prisms, Oxford Diffraction Xcalibur 3 diffractometer; 9890 independent measured reflections ($R_{\text{int}} = 0.0189$), $F^2$ refinement,$^5$ $R_1$ (obs) = 0.0371, $wR_2$ (all) = 0.1042, 7669 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{\text{max}} = 65^\circ$], 373 parameters. CCDC 1473101.

1-(1H-Benzimidazol-2-yl)-N-[(4,7-diphenyl-1H-benzimidazol-2-yl)methyl]-N-methylmethanamine chromium(III) chloride, [Cr(8)Cl$_3$]

![Structure of the complex](image)

Synthesised according to the procedure for [Cr(2)Cl$_3$] using ligand 8 (0.13 g, 0.29 mmol) and chromium(III) chloride tetrahydrofuran complex (0.11 g, 0.29 mmol) in tetrahydrofuran (10 mL). Yield = 0.10 g (57 %).

IR (KBr, cm$^{-1}$): $\tilde{\nu}$ 3222 (s), 3060 (m), 2972 (m), 1622 (w), 1601 (w), 1538 (w), 1495 (m), 1479 (s), 1451 (s), 1418 (m), 1386 (w), 1367 (m), 1275 (m), 1228 (w), 1150 (w), 1096 (w), 1051 (m), 1030 (w), 988 (w), 937 (w), 917 (w), 876 (m), 830 (w), 788 (w), 753 (s), 717 (w), 697 (s), 624 (w), 609 (w), 577 (m) and 523 (w).

MS (LSIMS): m/z 565 ([M-Cl]$^+$, 40 %).
Elem. Anal. Calcd for C_{29}H_{25}Cl_{3}CrN_{5}: C, 57.87; H, 4.19; N, 11.64. Found: C, 57.97; H, 4.27; N, 11.67.

\( \mu_{\text{eff}} = 4.12 \text{ BM} \).

**N-Methyl-N-(1H-perimidin-2-ylmethyl)-1H-benzimidazol-2-amine chromium(III) chloride, [Cr(9)Cl₃]**

![Chemical structure](image)

Synthesised according to the procedure for [Cr(2)Cl₃] using ligand 9 (0.59 g, 1.73 mmol) and chromium(III) chloride tetrahydrofuran complex (0.65 g, 1.73 mmol) in tetrahydrofuran (20 mL) for 16 hours. Yield = 0.75 g (87 %).

IR (KBr, cm⁻¹): \( \tilde{\nu} \) 3226 (m), 1645 (m), 1600 (s), 1580 (m), 1558 (w), 1489 (m), 1455 (m), 1418 (m), 1373 (m), 1332 (w), 1278 (w), 1055 (m), 1000 (w), 881 (w), 847 (w), 822 (m), 767 (m) and 668 (w).

MS (LSIMS): m/z 463 ([M-Cl]⁺, 50 %), and 428 ([M-2Cl]⁺, 100 %).


\( \mu_{\text{eff}} = 3.5 \text{ BM} \).

**1-(1H-Benzimidazol-2-yl)-N-(1H-benzimidazol-2-ylmethyl)-N-methylethanamine chromium(III) chloride, [Cr(10)Cl₃]**

![Chemical structure](image)

Synthesised according to the procedure for [Cr(2)Cl₃] using ligand 10 (0.24 g, 0.78 mmol) and chromium(III) chloride tetrahydrofuran complex (0.30 g, 0.78 mmol) in THF (20 mL). Yield = 0.30 g (83 %).
IR (KBr, cm⁻¹): ν 3196 (s), 1615 (w), 1455 (s), 1435 (m), 1418 (w), 1386 (w), 1318 (w), 1271 (m), 1049 (w), 1006 (w) and 749 (s).

MS (LSMIS): m/z 427 ([M-Cl]⁺, 15 %), 392 ([M-2Cl]⁺, 25 %).

Elem. Anal. Calcd for C₁₈H₁₉Cl₃CrN₅: C, 46.62; H, 4.13; N, 15.10. Found: C, 46.68; H, 4.06; N, 15.06.

μₑffective = 3.2 BM.

2-(1H-Benzimidazol-2-yl)-N-(1H-benzimidazol-2-ylmethyl)-pyrrolidine chromium(III) chloride, [Cr(11)Cl₃]

Synthesised according to the procedure for [Cr(2)Cl₃] using ligand 11 (0.17 g, 0.54 mmol) and chromium(III) chloride tetrahydrofuran complex (0.20 g, 0.54 mmol) in THF (20 mL). Yield = 0.22 g (86 %).

IR (KBr, cm⁻¹): 3193 (v.s), 2968 (v.s), 1623 (m), 1595 (m), 1496 (m), 1456 (v.s), 1390 (w), 1327 (m), 1276 (m), 1226 (w), 1050 (m), 1005 (m), 932 (w), 879 (w), 748 (v.s).

Mass spectroscopy [ESI, DMSO, m/z (%)]: 517 ([M]-Cl+DMSO, 98%), 482 ([M]-2Cl+DMSO, 75%), 318 (L, 17%), 242 (50), 232 (100), 179 (65).

Elem. Anal. Calcd for C₁₉H₁₉Cl₃CrN₅: C, 47.97; H, 4.03; N, 14.72. Found: C, 46.03; H, 5.19; N, 15.05.

μₑffective = 3.2 BM.

Crystals suitable for X-ray diffraction were obtained from a concentrated solution in DMF.

Crystal data for [Cr(11)Cl₃]: C₁₉H₁₉Cl₃CrN₅·2(2C₃H₇NO), M = 621.93, monoclinic, P2₁/c (no. 14), a = 18.3091(3), b = 11.3311(2), c = 13.9361(2) Å, β = 100.1628(16)°, V = 2845.85(8) Å³, Z = 4, Dc = 1.452 g cm⁻³, μ(Cu-Kα) = 6.200 mm⁻¹, T = 173 K, green needles, Oxford Diffraction Xcalibur PX Ultra diffractometer; 5413 independent measured reflections (Rint = 0.0333), F² refinement, R₁(obs) = 0.0633, wR²(all) = 0.1294, 4230 independent observed absorption-corrected reflections [Fo > 4σ(Fo)], 2θmax = 145°, 396 parameters. CCDC 1473102.
2-(1H-benzimidazol-2-yl)-N-(1H-benzimidazol-2-ylmethyl)-N-methylethanamine chromium chloride [Cr(12)Cl3]

Ligand 12 (0.30 g, 0.98 mmols), chromium(III) chloride tetrahydrofuran complex (0.369 g, 0.98 mmols) and 20 mL of dry THF were stirred for 16 hours under a nitrogen atmosphere. The purple solution turned green and an insoluble solid formed which was filtered off, washed with 10 mL of dry THF and dried in vacuo. The complex was obtained as a grey/green amorphous solid; 0.27 g (59%); \( \nu_{\text{max}}/\text{cm}^{-1} \) (KBr) 3410.6 (w, N-H stretch), 3208.5 & 2917.0 (s, aromatic and aliphatic C-H stretch), 1617.8 & 1559.6 (m, C=N stretch), 1478.2 & 1456.8 (s, aromatic C=C stretch and aliphatic C-H bending), 1330.1 & 1250.3 (m, C-N stretch), 764.6 (s, aromatic C-H bending); MS (LSIMS): m/z 427 ([M-Cl]+, 58 %) & 392 ([M-2Cl]+, 38 %); Calc. for C18H19N5CrCl3: C, 46.60; H, 4.13; N, 15.11. Found: C, 46.69; H, 4.01; N, 15.03 %; \( \mu_{\text{eff}} = 4.1 \) BM.

1-(1H-Benzimidazol-2-yl)-N-methyl-N-[(1-methyl-1H-benzimidazol-2-yl)methyl]methanamine chromium(0) tricarbonyl, [Cr(2)(CO)3]

Tris(acetonitrile)tricarbonylchromium (0.19 g, 0.72 mmol) and 1-(1H-benzimidazol-2-yl)-N-methyl-N-[(1-methyl-1H-benzimidazol-2-yl)methyl]methanamine 2 (0.33 g, 0.72 mmol) were stirred together in THF (40 mL) for 16 hours. After this time the yellow precipitate was filtered, washed with pentane (2 x 20 mL) and dried in vacuo. Yield = 0.30 g (94 %).

\(^1\)H NMR (400 MHz, \( d^6\)-DMSO): \( \delta \) 12.80 (1H, s, NH), 8.11 – 8.09 (1H, m, ArH), 8.05 – 8.03 (1H, m, ArH), 7.49 – 7.47 (1H, m, ArH), 7.40 – 7.38 (1H, m, ArH), 7.80 – 7.14 (4H, m, ArH), 4.37 (1H, d, \(^3\)J\(_{HH} = 17.6\) Hz, \(-CH_2\)), 4.32 (1H, d, \(^3\)J\(_{HH} = 17.4\) Hz, \(-CH_2\)), 4.29 (1H, d, \(^3\)J\(_{HH} = 17.2\) Hz, \(-CH_2\)), 4.19 (2H, dd \(^3\)J\(_{HH} = 16.8\) Hz, \(-CH_2\)), 3.66 (3H, s, HCH\(_3\)) and 3.31 (3H, s, NCH\(_3\)).
\(^{13}\text{C}\) NMR (101 MHz, \(d^6\text{-DMSO})\): \(\delta\) 240.1, 233.0, 232.9, 154.5, 153.9, 141.8, 141.2, 135.5, 134.1, 122.6, 122.5, 122.3, 122.0, 118.1, 118.0, 111.7, 110.4, 60.4, 59.3, 54.9 and 30.5.

IR (KBr, cm\(^{-1}\)): \(\tilde{\nu}\) 3060 (w), 2979 (w), 2874 (w), 2010 (m), 1887 (s), 1844 (w), 1770 (s), 1746 (s), 1617 (w), 1496 (m), 1484 (m), 1456 (m), 1424 (w), 1416 (w), 1326 (w), 1282 (w), 1249 (w), 1131 (w), 1099 (w), 1052 (m), 1007 (w), 977 (w), 877 (w), 767 (m), 756 (m), 740 (m), 653 (w), 547 (w) and 526 (w).

**Ethylene oligomerisation procedure**

Due to the insoluble nature of the chromium complexes in the polymerisation solvent toluene, they were first pre-activated with the co-catalyst, methylaluminoxane (MAO). This solution was diluted with toluene to give a solution with a suitable catalyst concentration. A mechanically stirred pressure reaction vessel was filled with toluene (200 mL) followed by addition of MAO as a moisture scavenger. The pressure reaction vessel was submerged in a water bath set to the desired polymerisation temperature and the solvent saturated with ethylene at a pressure of 1 bar. The polymerisation was initiated by injection of an aliquot of the activated catalyst solution. Immediately after the injection the ethylene pressure was adjusted to the required pressure and kept constant over the reaction time. After one hour the reaction was terminated by turning off the ethylene supply and venting off excess unreacted monomer. A known amount of GC standard (2,2,4,4,6,8,8-heptamethylnonane) was added to the reaction mixture and then a small sample of the liquid phase was taken and passed through neutral alumina (\(\text{Al}_2\text{O}_3\) micro column) to remove any catalyst, and then analysed by GC. The remaining polymer product was precipitated by the addition of methanol (200 mL), followed by dilute HCl (20 mL).
NMR Spectroscopy

NMR spectra of selected examples

Figure S1. $^1$H NMR spectrum of ligand 2 in d$_6$-DMSO (*).

Figure S2. $^1$H NMR spectrum of ligand 5 in CDCl$_3$. 
Figure S3. $^1$H NMR spectrum of ligand 10 in d$_6$-DMSO (*).

Figure S4. $^1$H NMR spectrum of complex [Cr(2)(CO)$_3$] in d$_6$-DMSO (*).
Figure S5. Example of a GC Trace of the liquid fraction obtained with catalyst [Cr(1)Cl₃]/MAO. * = 2,2,4,4,6,8,8‒heptamethylnonane.
X-Ray Crystallography

The X-ray crystal structure of \([\text{Cr}(7)\text{Cl}_3]\)

The N–H hydrogen atoms on N12 and N18 in the structure of \([\text{Cr}(7)\text{Cl}_3]\) were located from \(\Delta F\) maps and refined freely subject to an N–H distance constraint of 0.90 Å.

The X-ray crystal structure of \([\text{Cr}(11)\text{Cl}_3]\)

The linkage between the two benzimidazole units in the structure of \([\text{Cr}(11)\text{Cl}_3]\) was found to be disordered. Two orientations were identified for C10, C11, C12 and C15 (corresponding to disorder across an approximate mirror plane through Cr, Cl2, N14 and C13; see Fig S8) of \(\text{ca. 67 and 33\% occupancy.}\) The geometries of both orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The O40-based included dimethylformamide solvent molecule was found to be disordered. Two orientations were identified of \(\text{ca. 53 and 47\% occupancy,}\) their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The N–H hydrogen atoms on N8 and N17 were located from \(\Delta F\) maps and refined freely subject to an N–H distance constraint of 0.90 Å.

Figures

![The crystal structure of \([\text{Cr}(7)\text{Cl}_3]\) (50\% probability ellipsoids).](image)

Fig. S6  The crystal structure of \([\text{Cr}(7)\text{Cl}_3]\) (50\% probability ellipsoids).
**Fig. S7** The crystal structure of [Cr(11)Cl₃] (50% probability ellipsoids).

**Fig. S8** The crystal structure of [Cr(11)Cl₃] showing the disorder of the linkage between the two benzimidazole units; the major (ca. 67%) occupancy orientation has been drawn with open bonds, whilst the minor (ca. 33%) occupancy orientation has been drawn with dark broken bonds.
## Oligomerisation Results

### Table S1. LAO distributions obtained with chromium catalysts [Cr(L)Cl₃]/MAO.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>mol%(n)</th>
<th>α</th>
<th>β</th>
<th>1-α-β</th>
<th>β/α</th>
<th>c₂/c₁</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(1)Cl₃]</td>
<td>17.95(0.89)⁺ + 20.22(−0.76)⁺</td>
<td>0.14</td>
<td>0.68</td>
<td>0.19</td>
<td>4.98</td>
<td>1.13</td>
<td>0.995</td>
</tr>
<tr>
<td>[Cr(1)Cl₃]⁻</td>
<td>25.16(0.90)⁺ + 23.06(−0.79)⁺</td>
<td>0.11</td>
<td>0.72</td>
<td>0.17</td>
<td>6.41</td>
<td>0.92</td>
<td>0.997</td>
</tr>
<tr>
<td>[Cr(2)Cl₃]</td>
<td>18.96(0.87)⁺ + 17.47(−0.72)⁺</td>
<td>0.15</td>
<td>0.63</td>
<td>0.23</td>
<td>4.21</td>
<td>0.92</td>
<td>0.977</td>
</tr>
<tr>
<td>[Cr(3)Cl₃]</td>
<td>19.82(0.88)⁺ + 16.84(−0.73)⁺</td>
<td>0.15</td>
<td>0.64</td>
<td>0.21</td>
<td>4.38</td>
<td>0.85</td>
<td>0.980</td>
</tr>
<tr>
<td>[Cr(4)Cl₃]</td>
<td>27.48(0.85)⁺ + 17.60(−0.73)⁺</td>
<td>0.12</td>
<td>0.61</td>
<td>0.27</td>
<td>5.09</td>
<td>0.64</td>
<td>0.999</td>
</tr>
<tr>
<td>[Cr(5)Cl₃]</td>
<td>20.74(0.88)⁺ + 16.64(−0.73)⁺</td>
<td>0.12</td>
<td>0.66</td>
<td>0.22</td>
<td>5.31</td>
<td>1.06</td>
<td>0.991</td>
</tr>
<tr>
<td>[Cr(6)Cl₃]</td>
<td>21.74(0.88)⁺ + 22.39(−0.75)⁺</td>
<td>0.12</td>
<td>0.66</td>
<td>0.22</td>
<td>5.31</td>
<td>1.08</td>
<td>0.989</td>
</tr>
<tr>
<td>[Cr(7)Cl₃]</td>
<td>24.62(0.85)⁺ + 16.71(−0.71)⁺</td>
<td>0.14</td>
<td>0.61</td>
<td>0.25</td>
<td>4.39</td>
<td>0.68</td>
<td>0.984</td>
</tr>
<tr>
<td>[Cr(8)Cl₃]</td>
<td>16.81(0.89)⁺ + 10.61(−0.75)⁺</td>
<td>0.14</td>
<td>0.67</td>
<td>0.18</td>
<td>4.72</td>
<td>0.63</td>
<td>0.998</td>
</tr>
<tr>
<td>[Cr(9)Cl₃]</td>
<td>30.05(0.83)⁺ + 14.33(−0.76)⁺</td>
<td>0.07</td>
<td>0.63</td>
<td>0.30</td>
<td>8.37</td>
<td>0.48</td>
<td>0.989</td>
</tr>
<tr>
<td>[Cr(10)Cl₃]</td>
<td>21.34(0.87)⁺ + 8.60(−0.81)⁺</td>
<td>0.06</td>
<td>0.70</td>
<td>0.23</td>
<td>11.3</td>
<td>0.40</td>
<td>0.995</td>
</tr>
<tr>
<td>[Cr(11)Cl₃]</td>
<td>10.80(0.94)⁺ + 9.65(−0.84)⁺</td>
<td>0.10</td>
<td>0.79</td>
<td>0.11</td>
<td>8.22</td>
<td>0.89</td>
<td>0.995</td>
</tr>
<tr>
<td>[Cr(11)Cl₃]</td>
<td>28.53(0.84)⁺ + 16.64(−0.80)⁺</td>
<td>0.04</td>
<td>0.68</td>
<td>0.28</td>
<td>15.8</td>
<td>0.58</td>
<td>0.985</td>
</tr>
<tr>
<td>[Cr(12)Cl₃]</td>
<td>21.48(0.88)⁺ + 14.70(−0.81)⁺</td>
<td>0.06</td>
<td>0.71</td>
<td>0.22</td>
<td>10.9</td>
<td>0.68</td>
<td>0.990</td>
</tr>
<tr>
<td>[Cr(12)Cl₃]</td>
<td>17.69(0.87)⁺ + 4.50(−0.83)⁺</td>
<td>0.05</td>
<td>0.72</td>
<td>0.23</td>
<td>14.6</td>
<td>0.25</td>
<td>0.994</td>
</tr>
</tbody>
</table>

a) 1-Hexene and 1-octene omitted from analysis. NOTE: For complexes [Cr(10)Cl₃] and [Cr(12)Cl₃], fitting of the entire oligomer distribution was not possible due to the large amounts of 1-hexene and 1-octene (see Figure 6).

### References

5. (a) SHELXTL, Bruker AXS, Madison, WI; (b) SHELX-97, G.M. Sheldrick, *Acta Cryst.*, 2008, A64, 112-122.