Supporting Information

Manuscript: **Thio-Pybox and Thio-Phebox Complexes of Chromium, Iron, Cobalt and Nickel and their Application in Ethylene and Butadiene Polymerisation Catalysis**

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X-Ray Crystallography

The X-ray crystal structure of L1

The structure of **L1** was found to have crystallographic C_2 symmetry about an axis that passes through N(1) and C(4). The compound crystallised in a chiral space group, and the absolute structure was determined by a combination of *R*-factor tests [$R_1^+ = 0.0389$, $R_1^- = 0.0396$] and by use of the Flack parameter [$x^+ = +0.07(7)$, $x^- = +0.93(7)$].

The X-ray crystal structure of [Cr(L2)Cl$_3$]

The included dichloromethane solvent molecule in the structure of [Cr(**L2**)Cl$_3$] was found to be disordered. Three orientations of *ca*. 55, 27 and 18% occupancy were identified, their geometries optimised, the thermal parameters of adjacent atoms restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically. The compound crystallised in a chiral space group, and the absolute structure was determined by a combination of *R*-factor tests [$R_1^+ = 0.0280$, $R_1^- = 0.0782$] and by use of the Flack parameter [$x^+ = +0.000(5)$].

The X-ray crystal structure of [Fe(L1)$_2$][FeCl$_4$]

The structure of [Fe(**L1**)$_2$][FeCl$_4$] was found to have crystallographic C_2 symmetry about an axis that bisects the N(7)–Fe(1)–N(7A) and N(17)–Fe(1)–N(17A) angles. The C(21)-based phenyl ring was found to be disordered. Two orientations of *ca*. 61 and 39% occupancy were identified, both were refined as idealised hexagons, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically. The included acetonitrile solvent molecule was found to be disordered across a C_2 axis, and this was modelled by using one 50% occupancy molecule (refined anisotropically), with the action of the C_2 axis generating the other orientation. The compound crystallised in a chiral space group, and the absolute structure was determined by a combination of *R*-factor tests [$R_1^+ = 0.0460$, $R_1^- = 0.0553$] and by use of the Flack parameter [$x^+ = +0.000(19)$].

The X-ray crystal structure of [Fe(**L2**)Br$_2$]

The structure of [Fe(**L2**)Br$_2$] was found to contain two crystallographically independent complexes ([Fe(**L2**)Br$_2$]-I and [Fe(**L2**)Br$_2$]-II), one in a general position (I, based on Fe) and one sited about a C_2 axis (II, based on Fe'); for the latter, the C_2 axis passes through Fe', N(1') and C(4'). The included tetrahydrofuran molecule was found to be disordered across a C_2 axis, and two orientations of *ca*. 33 and 17% occupancy were identified, with the action of the C_2 axis generating two further orientations. The geometries of the two unique orientations were optimised, the thermal parameters of adjacent atoms restrained to be similar, and all of the non-hydrogen atoms were refined isotropically. The compound crystallised in a chiral space group, and the absolute structure was determined by a combination of *R*-factor tests [$R_1^+ = 0.0293$, $R_1^- = 0.0572$] and by use of the Flack parameter [$x^+ = +0.000(5)$, $x^- = +1.012(5)$].

The X-ray crystal structure of [Co(**L2**)Cl$_2$]

The structure of [Co(**L2**)Cl$_2$] was found to contain two crystallographically independent complexes ([Co(**L2**)Cl$_2$]-I and [Co(**L2**)Cl$_2$]-II), one in a general position (based on Co) and one sited about a C_2 axis (based on Co'); for the latter, the C_2 axis passes through Co', N(1') and C(4'). The included dichloromethane solvent molecule was found to be disordered and two orientations of *ca*. 77 and 23% occupancy were identified, their geometries optimised, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically. The compound crystallised in a chiral space group, and the absolute structure was determined by a combination of *R*-factor tests [$R_1^+ = 0.0312$, $R_1^- = 0.1380$] and by use of the Flack parameter [$x^+ = +0.000(3)$].

The X-ray crystal structure of [Co(**L3**)Cl$_2$]

The structure of [Co(**L3**)Cl$_2$] was found to contain two crystallographically independent complexes, one in a general position (based on Co) and one sited about a C_2 axis (based on Co'); for the latter, the C_2 axis passes through Co', N(1') and C(4'). The compound crystallised in a chiral space group, and the absolute structure was determined by a combination of *R*-factor tests [$R_1^+ = 0.0216$, $R_1^- = 0.1300$] and by use of the Flack parameter [$x^+ = +0.0000(19)$].

The X-ray crystal structure of [Ni(**L8**)Br]

The structure of [Ni(**L8**)Br] was found to have crystallised in a chiral space group, and the absolute structure was determined by a combination of *R*-factor tests [$R_1^+ = 0.0310$, $R_1^- = 0.0647$] and by use of the Flack parameter [$x^+ = +0.000(6)$].

Figures

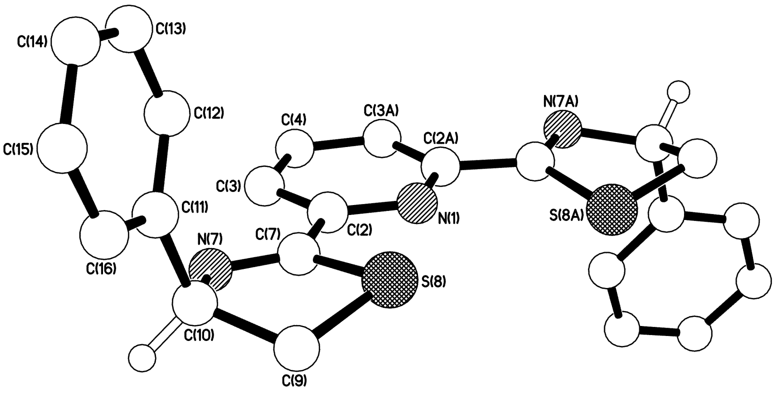

Fig. S1 The molecular structure of the C_2-symmetric molecule **L1**.

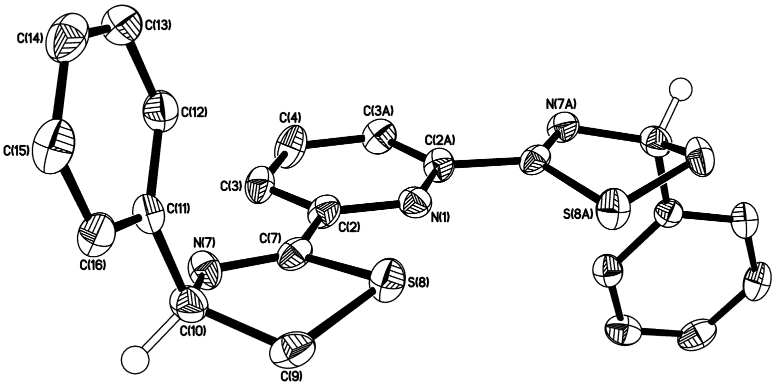

Fig. S2 The molecular structure of the C_2-symmetric molecule **L1** (50% probability ellipsoids).

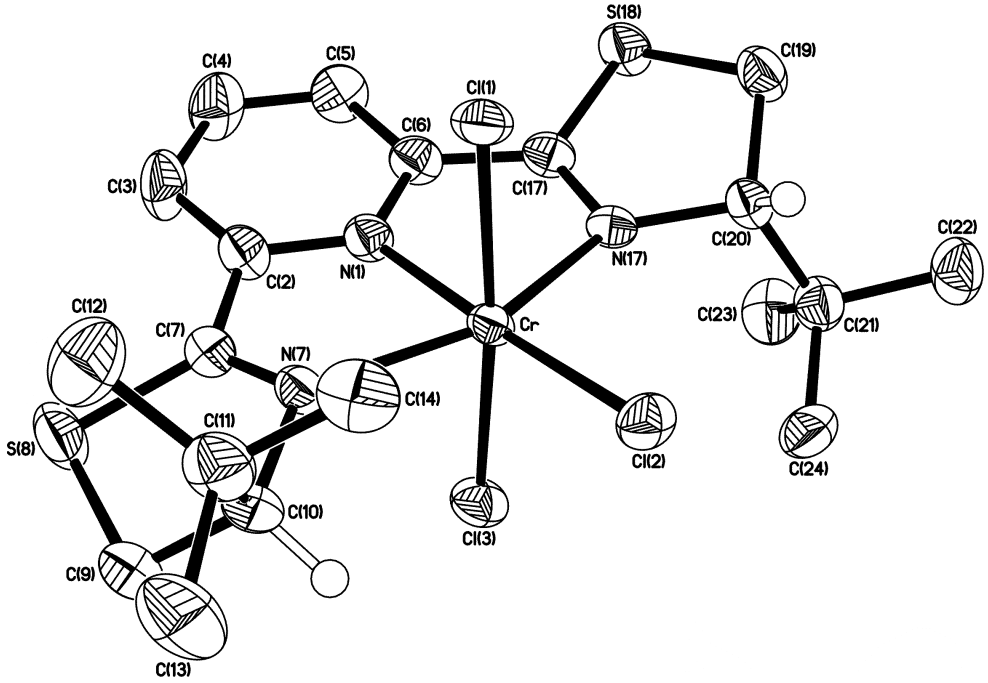

Fig. S3 The molecular structure of [Cr(**L2**)Cl_3] (50% probability ellipsoids).

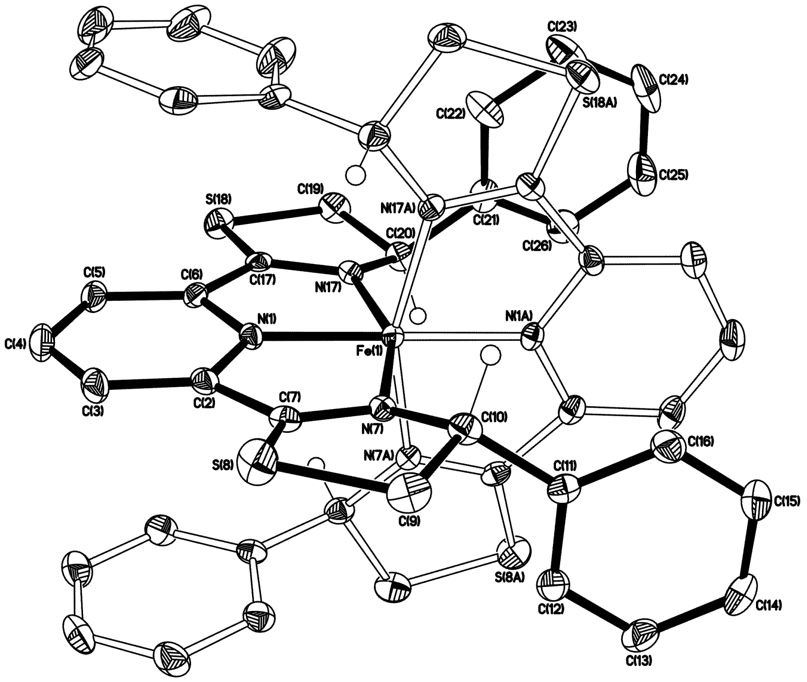

Fig. S4 The molecular structure of the C_2-symmetric $[Fe(\mathbf{L1})_2]^{2+}$ cation present in the crystals of $[Fe(\mathbf{L1})_2][FeCl_4]$ (30% probability ellipsoids).

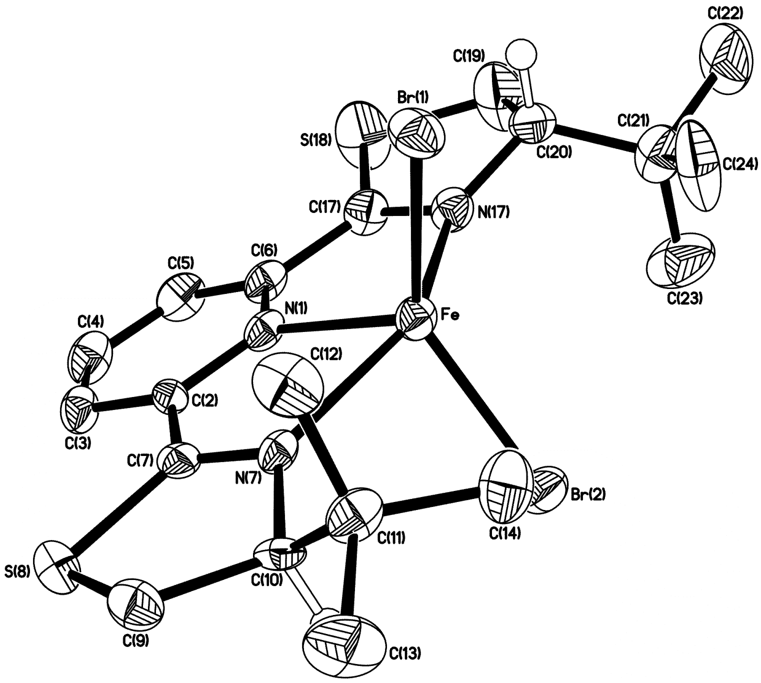

Fig. S5 The molecular structure of [Fe(**L2**)Br$_2$]-I, one of the two crystallographically independent complexes present in the crystals of [Fe(**L2**)Br$_2$] (50% probability ellipsoids).

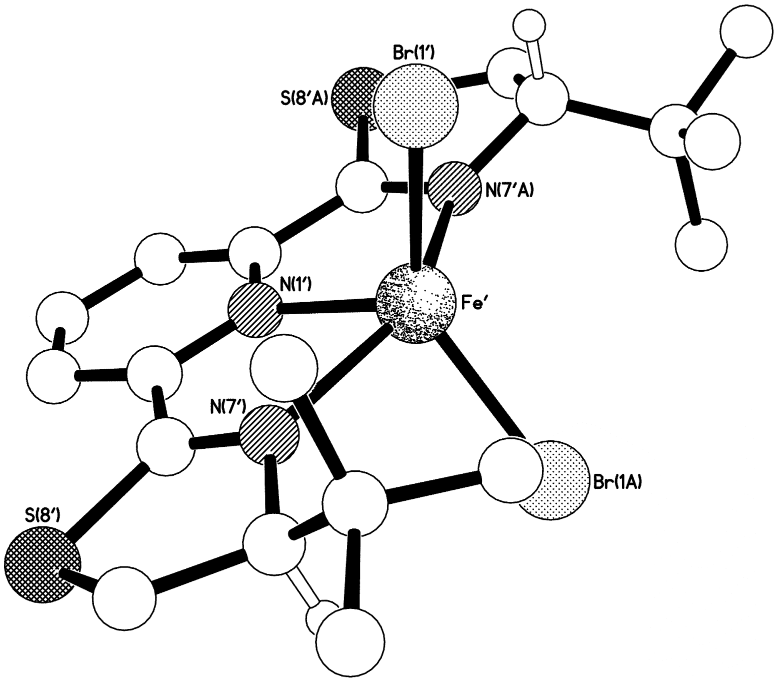

Fig. S6 The molecular structure of the C_2-symmetric complex [Fe(**L2**)Br$_2$]-II, one of the two crystallographically independent complexes present in the crystals of [Fe(**L2**)Br$_2$].

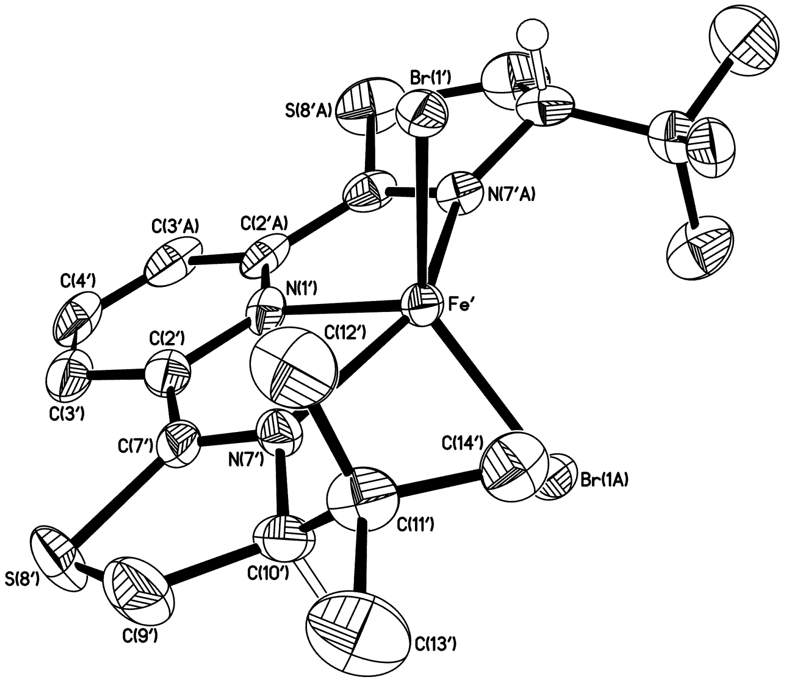

Fig. S7 The molecular structure of the C_2-symmetric complex [Fe(**L2**)Br_2]-II, one of the two crystallographically independent complexes present in the crystals of [Fe(**L2**)Br_2] (50% probability ellipsoids).

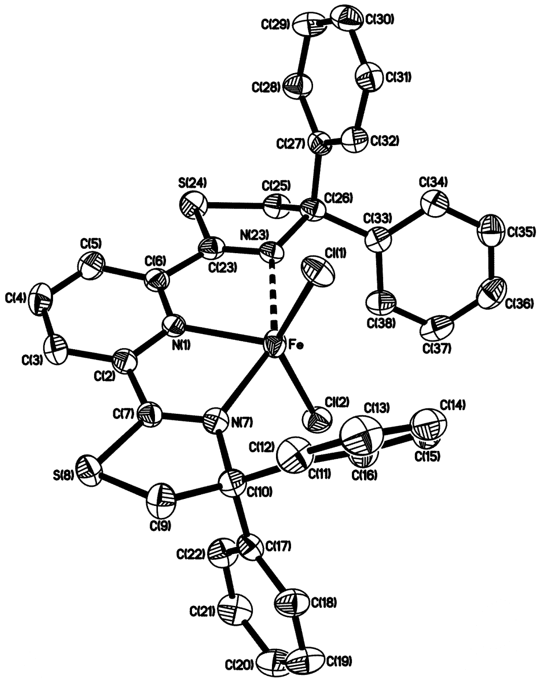

Fig. S8 The molecular structure of [Fe(**L4**)Cl_2] (50% probability ellipsoids).

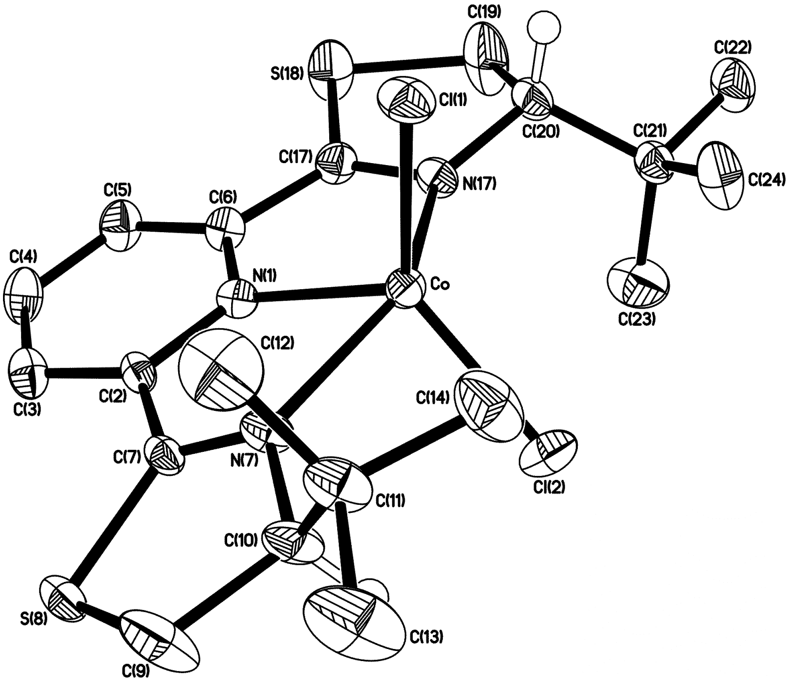

Fig. S9 The molecular structure of [Co(**L2**)Cl_2]-I, one of the two crystallographically independent complexes present in the crystals of [Co(**L2**)Cl_2] (50% probability ellipsoids).

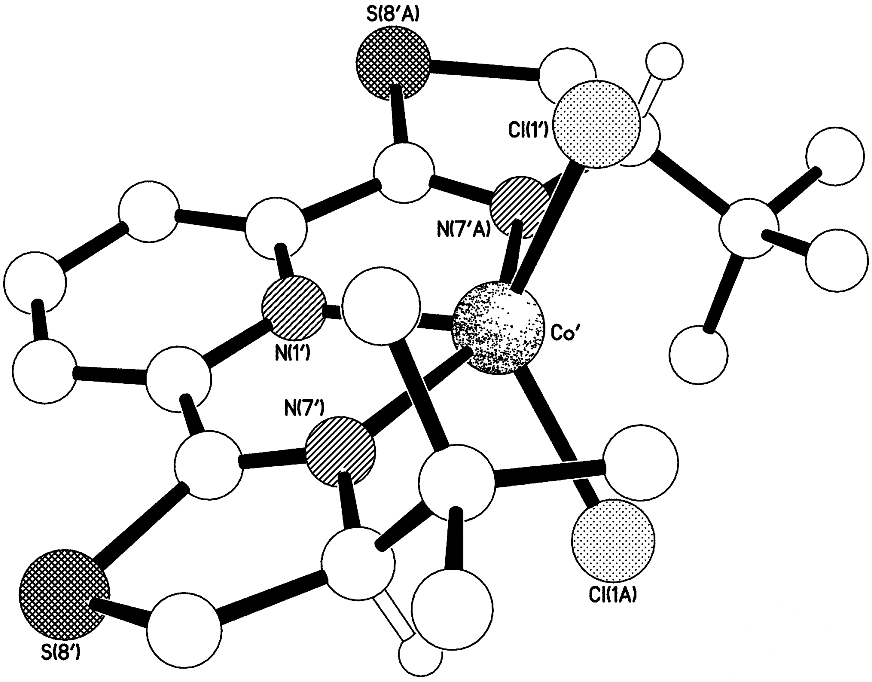

Fig. S10 The molecular structure of the C_2-symmetric complex [Co(**L2**)Cl_2]-II, one of the two crystallographically independent complexes present in the crystals of [Co(**L2**)Cl_2].

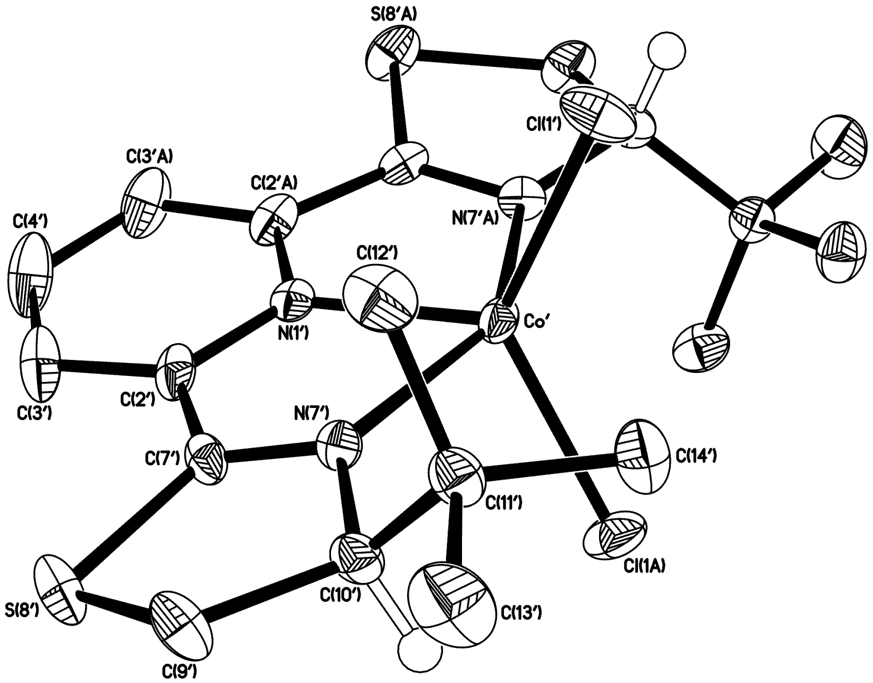

Fig. S11 The molecular structure of the C_2-symmetric complex [Co(**L2**)Cl_2]-II, one of the two crystallographically independent complexes present in the crystals of [Co(**L2**)Cl_2] (50% probability ellipsoids).

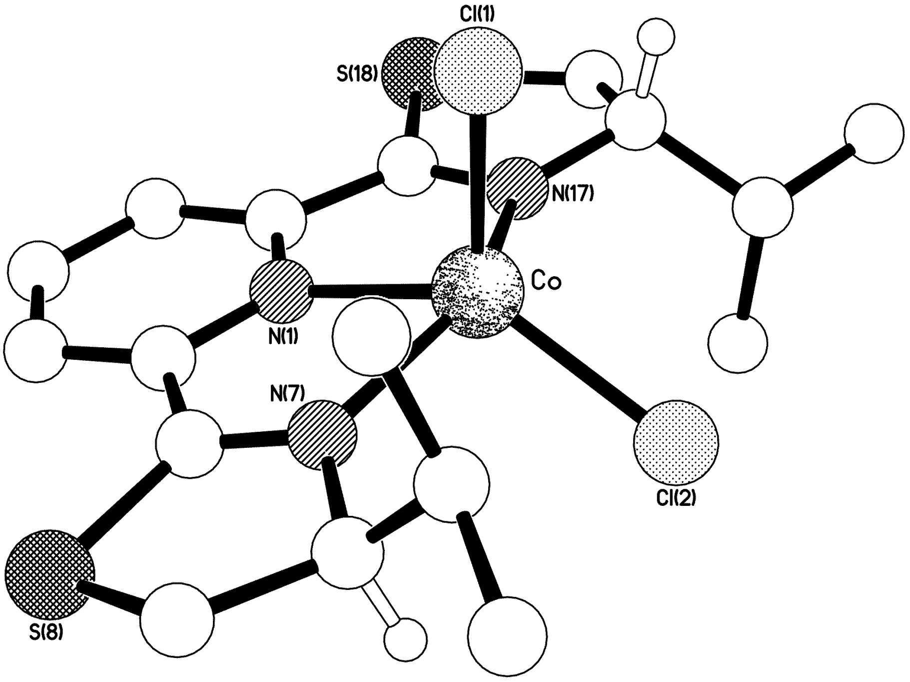

Fig. S12 The molecular structure of [Co(**L3**)Cl_2]-I, one of the two crystallographically independent complexes present in the crystals of [Co(**L3**)Cl_2].

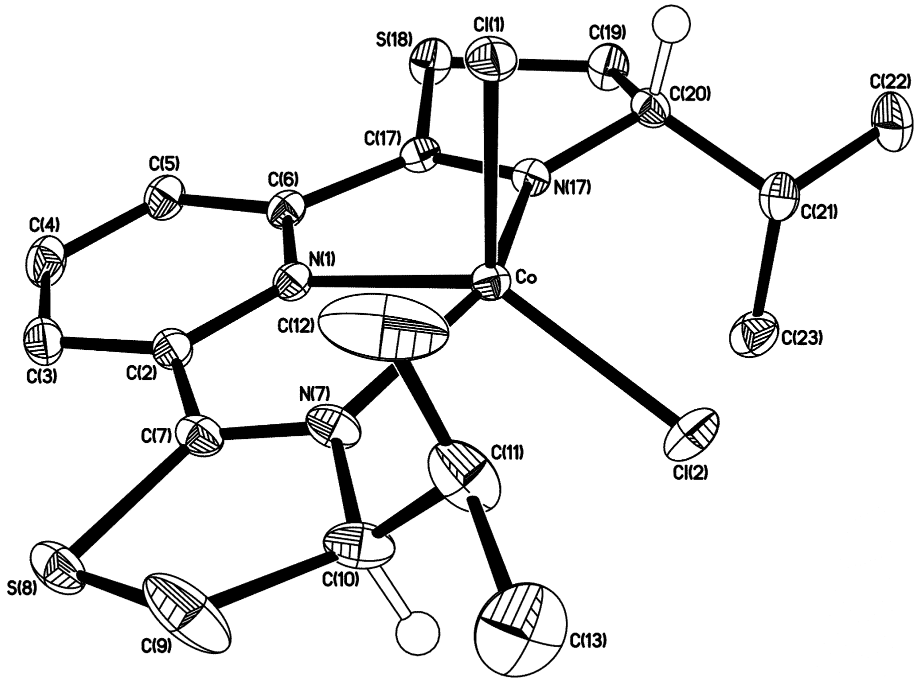

Fig. S13 The molecular structure of [Co(**L3**)Cl_2]-I, one of the two crystallographically independent complexes present in the crystals of [Co(**L3**)Cl_2] (30% probability ellipsoids).

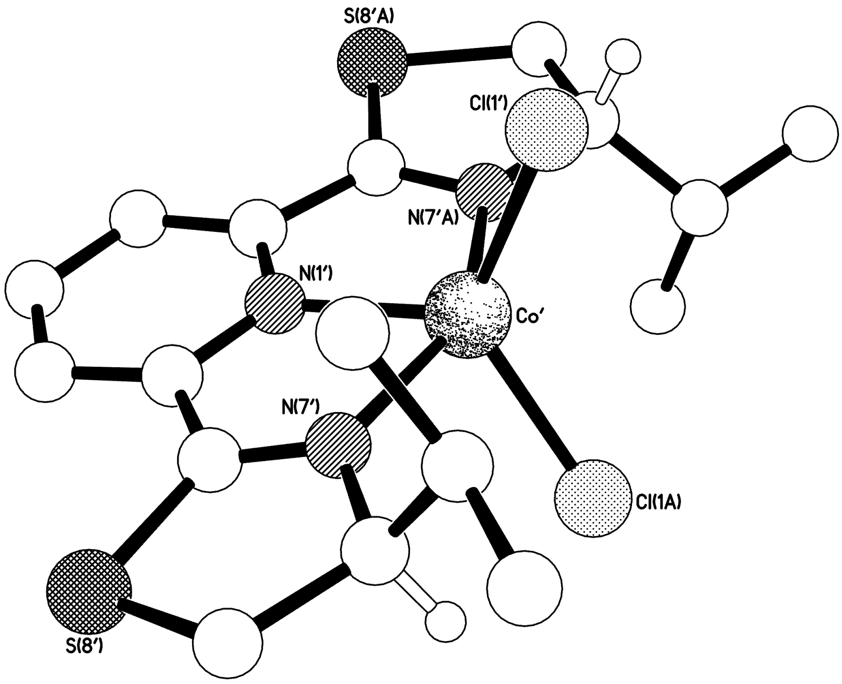

Fig. S14 The molecular structure of the C_2-symmetric complex [Co(**L3**)Cl_2]-II, one of the two crystallographically independent complexes present in the crystals of [Co(**L3**)Cl_2].

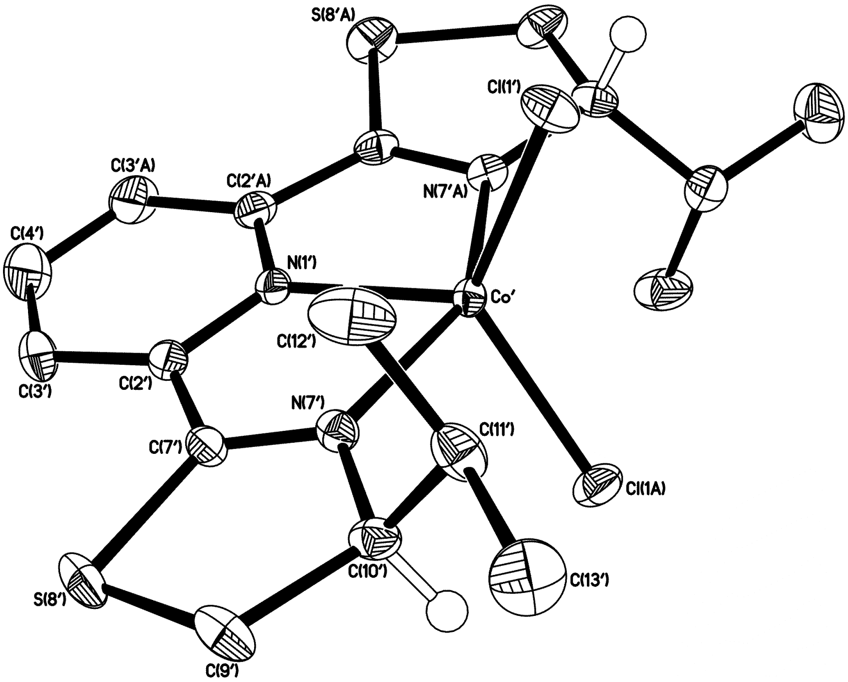

Fig. S15 The molecular structure of the C_2-symmetric complex [Co(**L3**)Cl_2]-II, one of the two crystallographically independent complexes present in the crystals of [Co(**L3**)Cl_2] (30% probability ellipsoids).

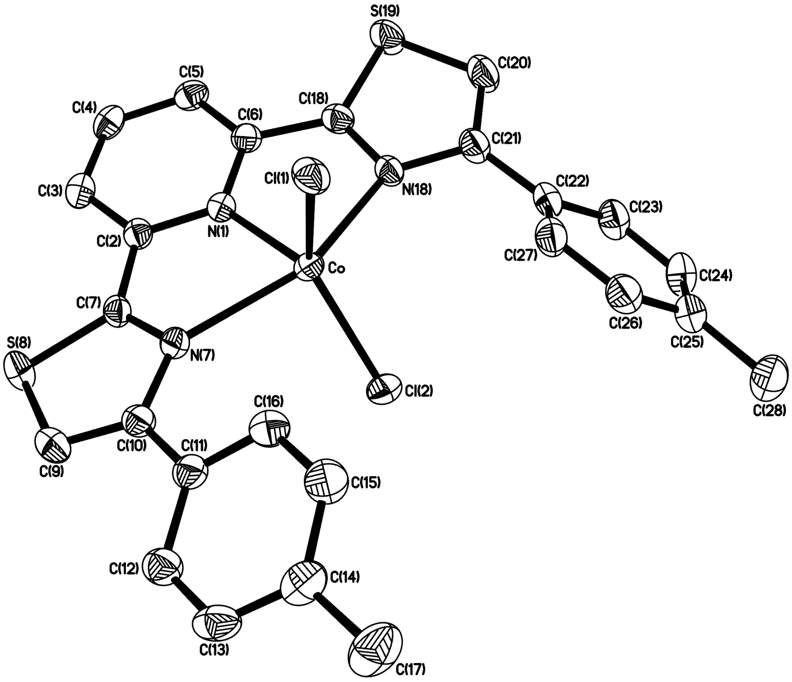

Fig. S16 The molecular structure of [Co(**L5**)Cl_2] (50% probability ellipsoids).

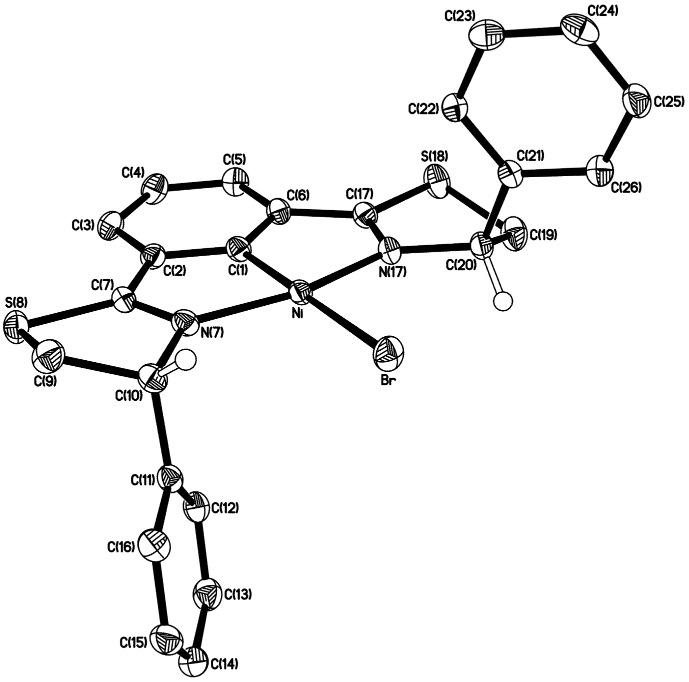

Fig. S17 The molecular structure of [Ni(**L8**)Br] (50% probability ellipsoids).

Oligomerisation results

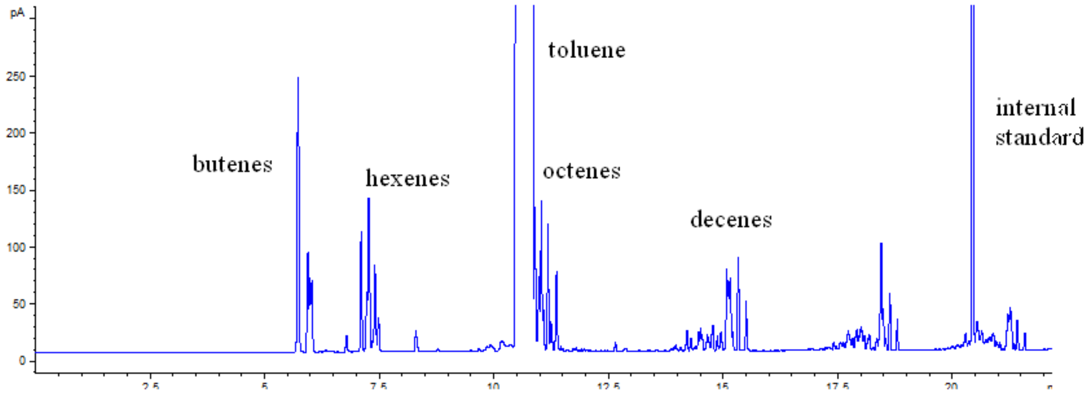

Figure S18. A GC trace of the liquid fraction obtained from the oligomerisation of ethylene by [Co(**L2**)Cl_2] with 500 eq. MAO. Internal standard: 2,2,4,4,6,8,8–heptamethylnonane.