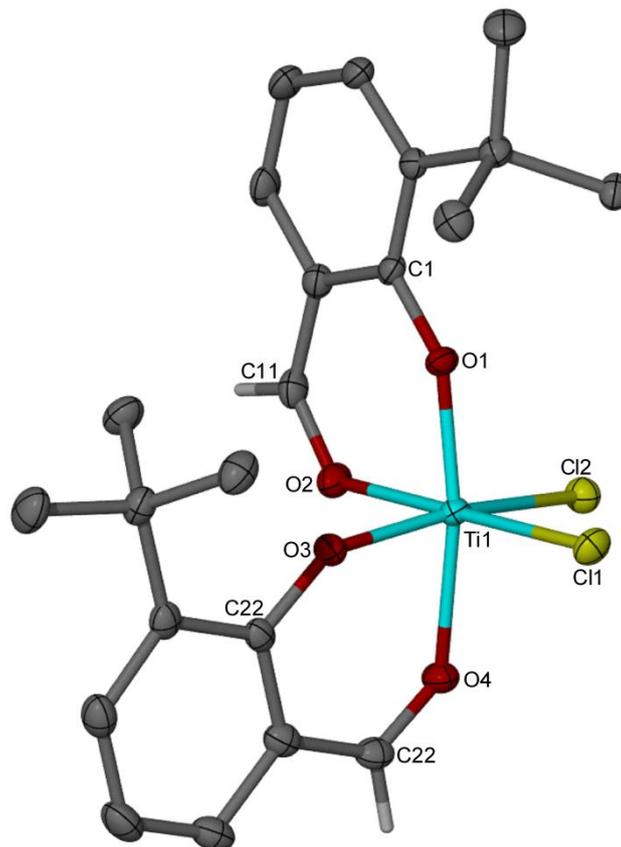


Supporting Information

# Ethylene polymerisation and oligomerisation with arene-substituted phenoxy-imine complexes of titanium: Investigation of multi-mechanism catalytic behaviour.

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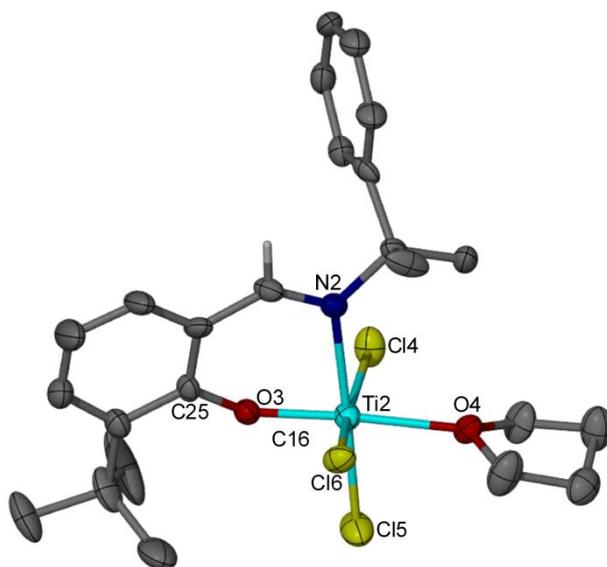
## X-Ray Structure of dichlorobis(3-*tert*-butyl-2-oxybenzoyl)titanium(IV) (S1)



**Fig. S1** Molecular structure of dichlorobis(3-*tert*-butyl-2-oxybenzoyl)titanium(IV) (**S1**). Thermal ellipsoids are shown at the 50% probability level. All methyl and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti1-O1,O3 1.8204(11), 1.8635(11), Ti1-O2,O4 2.1006(11)-2.0760(11), Ti1-Cl1,Cl2 2.2889(5), 2.3379(5), O-Ti1-O<sub>chelate ring</sub> 82.63(5)-83.87(5), X-Ti1-Y<sub>cis(acvclic),trans</sub> 83.32(4)-97.14(4), 163.62(4)-177.55(4), C<sub>phenoxyde</sub>-O-Ti1 140.67(10), 141.31(10), C<sub>aldehyde</sub>-O-Ti1 128.05(10), 130.36(11).

Hydrolysis product from an attempted recrystallisation of complex **13**. Structural geometry, bond lengths and bond angles are consistent with those for the previously reported analogous compound dichlorobis(3-*tert*-butyl-5-methyl-2-oxybenzoyl)titanium (IV).<sup>1</sup>

### X-Ray Structure of 13.



**Fig. S2** Molecular structure of **13**. Thermal ellipsoids are shown at the 50% probability level (one of two, similar molecules shown). Diffuse lattice solvent was removed in the refinement. All methyl and aromatic-ring hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti-O<sub>phenoxide.THF</sub> 1.786(5)-1.802(4), 2.195(4)-2.191(4), Ti-N 2.275(5)-2.277(5), Ti-Cl 2.2926(18)-2.3091(17), O-Ti-N<sub>chelate ring</sub> 83.85(19), 83.57(18), X-Ti-Y<sub>cis(acvclie).trans</sub> 81.67(13)-98.21(17), 164.59(8)-178.92(13), C-O-Ti<sub>chelate ring</sub> 140.0(4), 139.7(4).

#### C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>D<sub>4</sub> Co-oligomerisation – Mass Spectrum and Method of Calculation of Expected Isotopomer Distribution.

Comparison of the theoretical mass spectrum for 1-butene formed via a metallacycle mechanism and the experimental data is shown in figure S3. It is clear that no correlation between the two exists. The mass spectrum of 1-butene obtained by the co-oligomerisation of a 1:1 mixture of ethylene/perdeuterioethylene with **15**/MAO is shown in figure S4.

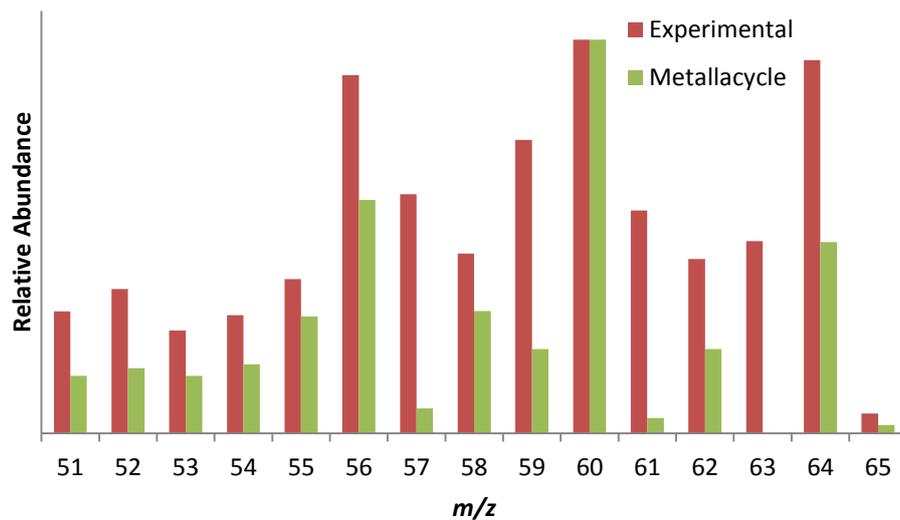
The statistical isotopomer distribution for 1-butene formed via a Cossee mechanism is shown in table S1. The actual theoretical mass spectrum, as reported in Figure 6 of the main article, is obtained by applying corrections for:

- The fragmentation pattern of 1-butene in the mass spectrometer.
- The natural abundance of <sup>13</sup>C (1.1 %).

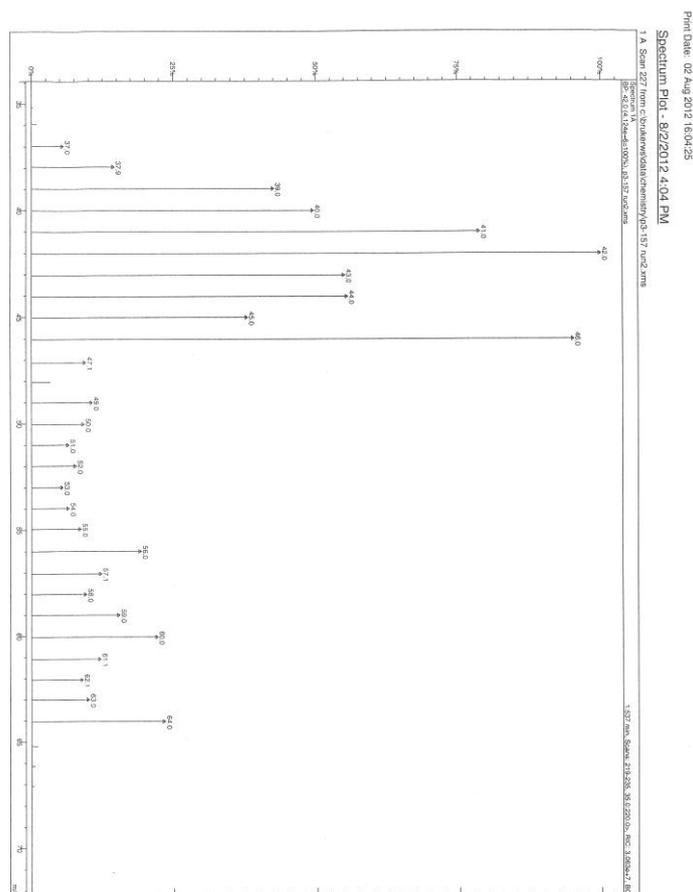
Full details of these calculations have been reported previously.<sup>2</sup>

**Table S1.** 1-butene isotopomer ratios predicted for metallacycle and Cossee mechanism.

Model	D <sub>0</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>	D <sub>5</sub>	D <sub>6</sub>	D <sub>7</sub>	D <sub>8</sub>
Metallacycle	1	0	0	0	2	0	0	0	1
Cossee	1	1	0	1	2	1	0	1	1



**Figure S3.** Experimental and theoretical mass spectrum of 1-butene formed from a 1:1 mixture of ethylene/perdeuteroethylene and **15**/MAO. Normalised to  $m/z$  60.

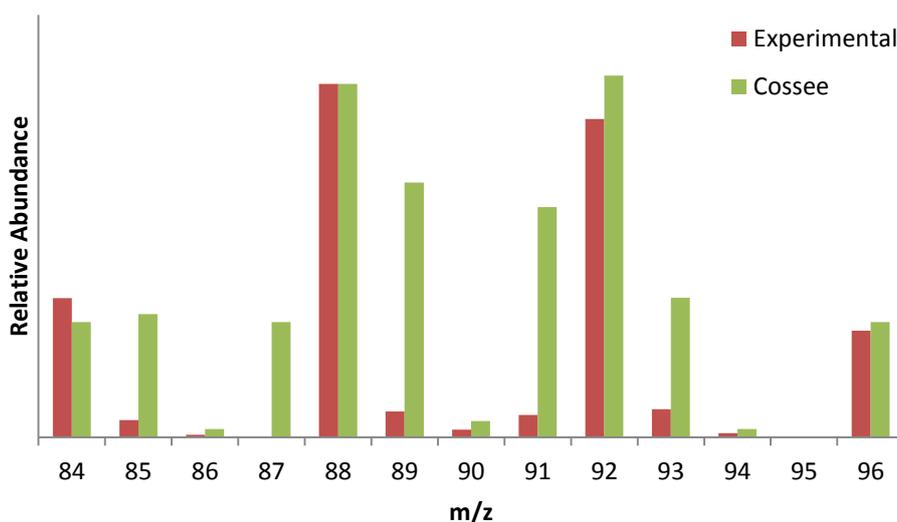


**Figure S4.** Mass spectrum of 1-butene produced from  $C_2H_4/C_2D_4$  with **15**/MAO.

Comparison of the theoretical mass spectrum for 1-hexene formed via a Cossee mechanism and the experimental data is shown in figure S5. It is clear that no correlation between the two exists. The mass spectrum of 1-hexene obtained by the co-oligomerisation of a 1:1 mixture of ethylene/perdeuteroethylene with **15**/MAO is shown in figure S6.

The statistical isotopomer distribution for 1-hexene formed via a metallacycle mechanism is shown in table S2. The actual theoretical mass spectrum, as reported in Figure 7 of the main article, is obtained by applying corrections for:<sup>3</sup>

- i. The natural abundance of deuterium in ethylene (0.016 %).
- ii. Hydrogen impurity in perdeuteroethylene (2 %).
- iii. The natural abundance of <sup>13</sup>C (1.1 %).



**Figure S5.** Experimental and theoretical mass spectrum of 1-hexene formed from a 1:1 mixture of ethylene/perdeuteroethylene and **15**/MAO. Normalised to  $m/z$  88.

**Table S2.** 1-hexene isotopomer ratios predicted for metallacycle and Cossee mechanism.

Model	D <sub>0</sub>	D <sub>1</sub>	D <sub>2</sub>	D <sub>3</sub>	D <sub>4</sub>	D <sub>5</sub>	D <sub>6</sub>	D <sub>7</sub>	D <sub>8</sub>	D <sub>9</sub>	D <sub>10</sub>	D <sub>11</sub>	D <sub>12</sub>
Metallacycle	1	0	0	0	3	0	0	0	3	0	0	0	1
Cossee	1	1	0	1	3	2	0	2	3	1	0	1	1

