# Supporting information

## Selective ethylene oligomerisation using supported tungsten mono-imido catalysts

Christopher M. R. Wright, Thomas Williams, Zoë R. Turner, Jean-Charles Buffet and Dermot O’Hare

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1. X-ray Crystallography

Table S1. Selected experimental crystallographic data.

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>W(N(C₆H₅))Cl₄(THF)</th>
<th>W(N(2,6-Me-C₆H₅))Cl₄(THF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>CCDC number</td>
<td>Chemical formula</td>
</tr>
<tr>
<td></td>
<td>1518771</td>
<td>C₁₀H₁₃Cl₄NOW</td>
</tr>
<tr>
<td></td>
<td>1518770</td>
<td>C₁₂H₁₅Cl₄NOW</td>
</tr>
<tr>
<td>Mr</td>
<td>488.86</td>
<td>516.92</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2₁/c</td>
<td>Triclinic, P1</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>α, β, γ (°)</td>
<td>90, 102.120(1), 90</td>
<td>7.9869(2), 8.7291(2), 12.9648(4)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>1448.82(5)</td>
<td>811.73(4)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>8.69</td>
<td>7.76</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.30 × 0.20 × 0.20</td>
<td>0.20 × 0.15 × 0.10</td>
</tr>
</tbody>
</table>

Data collection

<table>
<thead>
<tr>
<th>Diffractometer</th>
<th>Nonius KappaCCD diffraotometer</th>
<th>Nonius KappaCCD diffractometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption correction</td>
<td>Multi-scan SADABS</td>
<td>Multi-scan SADABS</td>
</tr>
<tr>
<td>Tmin, Tmax</td>
<td>0.67, 1</td>
<td>0.74, 1.00</td>
</tr>
<tr>
<td>No. of measured, independent and observed</td>
<td>6016, 3314, 2812</td>
<td>6820, 3709, 2978</td>
</tr>
<tr>
<td>(sin θ/λ)max (Å⁻¹)</td>
<td>0.650</td>
<td>0.649</td>
</tr>
</tbody>
</table>

Refinement

| R(F² > 2σ(F²)), wR(F²), S | 0.031, 0.074, 1.09 | 0.039, 0.087, 1.01 |
| No. of reflections | 3314 | 3709 |
| No. of parameters | 154 | 174 |
| No. of restraints | 0 | 0 |
| H-atom treatment | Constrained | Constrained |
| (Δ/σ)max | 0.001 | 0.001 |
| Δρmax, Δρmin (e Å⁻³) | 2.24, -1.45 | 1.95, -1.95 |
| Absolute structure | - | - |
| Absolute structure parameter | - | - |

<table>
<thead>
<tr>
<th>Crystal data</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td><strong>CCDC number</strong></td>
</tr>
<tr>
<td><strong>Chemical formula</strong></td>
</tr>
<tr>
<td><strong>Mr</strong></td>
</tr>
<tr>
<td><strong>Crystal system, space group</strong></td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
</tr>
<tr>
<td><strong>a, b, c (Å)</strong></td>
</tr>
<tr>
<td><strong>α, β, γ (°)</strong></td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
</tr>
<tr>
<td><strong>Z</strong></td>
</tr>
<tr>
<td><strong>μ (mm⁻¹)</strong></td>
</tr>
<tr>
<td><strong>Crystal size (mm)</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Data collection</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diffractometer</strong></td>
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<tr>
<td><strong>Absorption correction</strong></td>
</tr>
<tr>
<td><strong>Tmin, Tmax</strong></td>
</tr>
<tr>
<td><strong>No. of measured, independent and observed [I &gt; 2σ(I)] reflections</strong></td>
</tr>
<tr>
<td><strong>R(int)</strong></td>
</tr>
<tr>
<td><strong>(sin θ/λ)max (Å⁻¹)</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R(F² &gt; 2σ(F²)), wR(F²), S</strong></td>
</tr>
<tr>
<td><strong>No. of reflections</strong></td>
</tr>
<tr>
<td><strong>No. of parameters</strong></td>
</tr>
<tr>
<td><strong>No. of restraints</strong></td>
</tr>
<tr>
<td><strong>H-atom treatment</strong></td>
</tr>
<tr>
<td><strong>(Δ/σ)max</strong></td>
</tr>
<tr>
<td><strong>Δρmax, Δρmin (e Å⁻³)</strong></td>
</tr>
<tr>
<td><strong>Absolute structure</strong></td>
</tr>
<tr>
<td><strong>Absolute structure parameter</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crystal data</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>W(N(4-OMe-C₆H₄))Cl₄(THF) (1.5)</td>
</tr>
<tr>
<td><strong>CCDC number</strong></td>
</tr>
<tr>
<td>1518774</td>
</tr>
<tr>
<td><strong>Chemical formula</strong></td>
</tr>
<tr>
<td>C₁₁H₁₅Cl₄NO₂W</td>
</tr>
<tr>
<td><strong>Mr</strong></td>
</tr>
<tr>
<td>518.89</td>
</tr>
<tr>
<td><strong>Crystal system, space group</strong></td>
</tr>
<tr>
<td>Monoclinic, P2₁/c</td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
</tr>
<tr>
<td>150</td>
</tr>
<tr>
<td><strong>a, b, c (Å)</strong></td>
</tr>
<tr>
<td>13.2115(2), 8.0822(1), 15.7475(2)</td>
</tr>
<tr>
<td><strong>α, β, γ (°)</strong></td>
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<tr>
<td>90, 109.109(1), 90</td>
</tr>
<tr>
<td><strong>V (Å³)</strong></td>
</tr>
<tr>
<td>1588.83(4)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td><strong>μ (mm⁻¹)</strong></td>
</tr>
<tr>
<td>7.94</td>
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<tr>
<td><strong>Crystal size (mm)</strong></td>
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<tr>
<td>0.20 × 0.12 × 0.10</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Data collection</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diffractometer</strong></td>
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<tr>
<td>Nonius KappaCCD diffractometer</td>
</tr>
<tr>
<td><strong>Absorption correction</strong></td>
</tr>
<tr>
<td><strong>Tₘᵢₘₜ, Tₘₐₓ</strong></td>
</tr>
<tr>
<td>0.735, 1.000</td>
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<tr>
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<tr>
<td>7374, 3921, 3396</td>
</tr>
<tr>
<td><strong>Rᵢₙₜ</strong></td>
</tr>
<tr>
<td>0.027</td>
</tr>
<tr>
<td><strong>(sin θ/λ)ₘₐₓ (Å⁻¹)</strong></td>
</tr>
<tr>
<td>0.666</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R[F² &gt; 2σ(F²)], wR(F²), S</strong></td>
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<td>0.029, 0.075, 1.10</td>
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<tr>
<td><strong>No. of reflections</strong></td>
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<td>3921</td>
</tr>
<tr>
<td><strong>No. of parameters</strong></td>
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<tr>
<td>173</td>
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<td><strong>No. of restraints</strong></td>
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<td>0</td>
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<tr>
<td><strong>H-atom treatment</strong></td>
</tr>
<tr>
<td>Constrained</td>
</tr>
<tr>
<td><strong>(Δ/σ)ₘₐₓ</strong></td>
</tr>
<tr>
<td>0.001</td>
</tr>
<tr>
<td><strong>Δρₘₐₓ, Δρₘᵢₙ (e Å⁻³)</strong></td>
</tr>
<tr>
<td>1.74, -1.67</td>
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<tr>
<td><strong>Absolute structure</strong></td>
</tr>
<tr>
<td>-</td>
</tr>
<tr>
<td><strong>Absolute structure parameter</strong></td>
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<tr>
<td>-</td>
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<thead>
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<td><strong>CCDC number</strong></td>
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</tr>
<tr>
<td><strong>Mr</strong></td>
</tr>
<tr>
<td><strong>Crystal system, space group</strong></td>
</tr>
<tr>
<td><strong>Temperature (K)</strong></td>
</tr>
<tr>
<td><strong>a, b, c (Å)</strong></td>
</tr>
<tr>
<td><strong>α, β, γ (°)</strong></td>
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<tr>
<td><strong>V (Å³)</strong></td>
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<tr>
<td><strong>Z</strong></td>
</tr>
<tr>
<td><strong>μ (mm⁻¹)</strong></td>
</tr>
<tr>
<td><strong>Crystal size (mm)</strong></td>
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<thead>
<tr>
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<tr>
<td><strong>Diffractometer</strong></td>
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<tr>
<td><strong>Absorption correction</strong></td>
</tr>
<tr>
<td><strong>T_{min}, T_{max}</strong></td>
</tr>
<tr>
<td><strong>No. of measured, independent and observed [I &gt; 2σ(I)] reflections</strong></td>
</tr>
<tr>
<td><strong>R_{int}</strong></td>
</tr>
<tr>
<td><strong>(sin θ/λ)_{max} (Å⁻¹)</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>R[F² &gt; 2s(F²)], wR(F²), S</strong></td>
</tr>
<tr>
<td><strong>No. of reflections</strong></td>
</tr>
<tr>
<td><strong>No. of parameters</strong></td>
</tr>
<tr>
<td><strong>No. of restraints</strong></td>
</tr>
<tr>
<td><strong>H-atom treatment</strong></td>
</tr>
<tr>
<td><strong>(Δ/σ)_{max}</strong></td>
</tr>
<tr>
<td><strong>Δρ_{max}, Δρ_{min} (e Å⁻³)</strong></td>
</tr>
<tr>
<td><strong>Absolute structure</strong></td>
</tr>
<tr>
<td><strong>Absolute structure parameter</strong></td>
</tr>
</tbody>
</table>

## Crystal data

<table>
<thead>
<tr>
<th>Compound</th>
<th>CCDC number</th>
<th>Chemical formula</th>
<th>( W(\text{N}(2,6-\text{Me}-\text{C}_6\text{H}_3))\text{Me}_3\text{Cl} )</th>
<th>( W(\text{N}(3,5-\text{Me}-\text{C}_6\text{H}_3))\text{Me}_3\text{Cl} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1518776</td>
<td>( \text{C}<em>{11}\text{H}</em>{18}\text{ClN} )</td>
<td>( \text{C}<em>{11}\text{H}</em>{18}\text{ClN} )</td>
<td></td>
</tr>
<tr>
<td>Mr</td>
<td>383.56</td>
<td></td>
<td>383.56</td>
<td>383.56</td>
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<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, ( \text{P}_{2_1}/c )</td>
<td>Orthorhombic, ( \text{Pnma} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( a, b, c ) (Å)</td>
<td>10.4810(2), 10.8951(3), 12.1474(3)</td>
<td>21.1055(3), 7.2526(1), 17.4808(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \alpha, \beta, \gamma ) (°)</td>
<td>90, 110.473(1), 90</td>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( V ) (Å³)</td>
<td>1299.51(5)</td>
<td>2675.78(7)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Z )</td>
<td>4</td>
<td>8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \mu ) (mm⁻¹)</td>
<td>9.06</td>
<td>17.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.10 × 0.07 × 0.05</td>
<td>0.30 × 0.23 × 0.15</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Data collection

<table>
<thead>
<tr>
<th>Diffractometer</th>
<th>Nonius KappaCCD diffractometer</th>
<th>SuperNova, Dual, Cu at zero, Atlas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption correction</td>
<td>Multi-scan</td>
<td>Multi-scan from symmetry-related measurements using SORTAV (Blessing 1995)</td>
</tr>
<tr>
<td>( T_{\text{min}} ), ( T_{\text{max}} )</td>
<td>0.708, 1.000</td>
<td>0.106, 1.000</td>
</tr>
<tr>
<td>No. of measured, independent and observed (</td>
<td>I &gt; 2\sigma(I)</td>
<td>) reflections</td>
</tr>
<tr>
<td>( R_{\text{int}} )</td>
<td>0.027</td>
<td>0.054</td>
</tr>
<tr>
<td>(( \sin \theta/\lambda ))max (Å⁻¹)</td>
<td>0.650</td>
<td>0.625</td>
</tr>
</tbody>
</table>

## Refinement

| \( R(F^2 > 2\sigma(F^2)) \), \( wR(F^2) \), \( S \) | 0.032, 0.079, 1.06 | 0.043, 0.122, 1.10 |
| No. of reflections | 2964 | 2949 |
| No. of parameters | 132 | 158 |
| No. of restraints | 0 | 0 |
| H-atom treatment | Constrained | Constrained |
| \( \Delta\rho_{\text{max}}, \Delta\rho_{\text{min}} \) (e Å⁻³) | 2.28, −1.69 | 2.52, −1.75 |
| Absolute structure | - | - |
| Absolute structure parameter | - | - |

## Crystal Data

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal system, space group</th>
<th>Temperature (K)</th>
<th>a, b, c (Å)</th>
<th>α, β, γ (°)</th>
<th>V (Å³)</th>
<th>Z</th>
<th>μ (mm⁻¹)</th>
<th>Crystal size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W{N(4-OMe-C₆H₄)}Me₂Cl</td>
<td>Monoclinic, P2₁</td>
<td>150</td>
<td>6.0476(3), 7.3129(3), 14.2223(6)</td>
<td>90, 97.885(4), 90</td>
<td>623.04(5)</td>
<td>2</td>
<td>18.92</td>
<td>0.06 × 0.05 × 0.04</td>
</tr>
<tr>
<td>W{N(2,6-F-C₆H₃)}Me₂Cl</td>
<td>Triclinic, P1</td>
<td>150</td>
<td>7.3092(1), 7.5096(1), 11.8873(2)</td>
<td>90.124(1), 95.770(1), 118.542(1)</td>
<td>569.34(2)</td>
<td>2</td>
<td>10.37</td>
<td>0.15 × 0.12 × 0.10</td>
</tr>
</tbody>
</table>

### Data collection

<table>
<thead>
<tr>
<th>Diffractometer</th>
<th>SuperNova, Dual, Cu at zero, Atlas diffractometer</th>
<th>Nonius KappaCCD diffractometer</th>
</tr>
</thead>
</table>

| Tmin, Tmax | 0.736, 1.000 | 0.728, 1.000 |

| No. of measured, independent and observed [I > 2s(I)] reflections | 3247, 3247, 3164 | 4939, 2615, 2426 |

| Rint | - | 0.036 |
| (sin θ/λ)max (Å⁻¹) | 0.629 | 0.651 |

### Refinement

<table>
<thead>
<tr>
<th>R[F² &gt; 2s(F²)], wR(F²), S</th>
<th>0.039, 0.108, 1.10</th>
<th>0.031, 0.080, 1.04</th>
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</thead>
<tbody>
<tr>
<td>No. of reflections</td>
<td>3247</td>
<td>2615</td>
</tr>
<tr>
<td>No. of parameters</td>
<td>119</td>
<td>130</td>
</tr>
<tr>
<td>No. of restraints</td>
<td>5</td>
<td>0</td>
</tr>
<tr>
<td>H-atom treatment</td>
<td>Constrained</td>
<td>Constrained</td>
</tr>
<tr>
<td>(Δ/σ)max</td>
<td>0.001</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Δρ_max, Δρ_min (e Å⁻³)</td>
<td>1.39, -1.65</td>
<td>2.13, -3.00</td>
</tr>
</tbody>
</table>

| Absolute structure | Classical Flack method preferred over Parsons because s.u. lower. | - |

| Absolute structure parameter | 0.56(3) | - |

### Computer programs:

Table S2. Comparison of pKa values for the parent anilines,\textsuperscript{1,2} imido ligand volumes ($\text{Å}^3$)\textsuperscript{3} and steric parameters of the imido ligands ($\text{Å}$).

<table>
<thead>
<tr>
<th>Complex</th>
<th>$R$</th>
<th>pK\textsubscript{a}$\textsubscript{1,2}$</th>
<th>Ligand volume$\textsuperscript{3}$</th>
<th>Steric parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>4-Me-C\textsubscript{6}H\textsubscript{4} \textsuperscript{4}</td>
<td>31.7</td>
<td>155.78</td>
<td>4.287</td>
</tr>
<tr>
<td>C\textsuperscript{a}</td>
<td>4-I-C\textsubscript{6}H\textsubscript{4} \textsuperscript{5}</td>
<td>29.1\textsuperscript{b}</td>
<td>156.57</td>
<td>3.983</td>
</tr>
<tr>
<td>1.a</td>
<td>2,6-Pr-C\textsubscript{6}H\textsubscript{3} \textsuperscript{6}</td>
<td>-</td>
<td>273.60</td>
<td>8.481</td>
</tr>
<tr>
<td>1.1</td>
<td>C\textsubscript{6}H\textsubscript{5}</td>
<td>30.6</td>
<td>123.52</td>
<td>4.062</td>
</tr>
<tr>
<td>1.2</td>
<td>2,6-Me-C\textsubscript{6}H\textsubscript{3}</td>
<td>-</td>
<td>173.71</td>
<td>6.540</td>
</tr>
<tr>
<td>1.3</td>
<td>3,5-Me-C\textsubscript{6}H\textsubscript{3}</td>
<td>31.0\textsuperscript{d}</td>
<td>177.30</td>
<td>6.116</td>
</tr>
<tr>
<td>1.4</td>
<td>2,4,6-Me-C\textsubscript{6}H\textsubscript{3}</td>
<td>-</td>
<td>198.03</td>
<td>6.541</td>
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<tr>
<td>1.5</td>
<td>4-OMe-C\textsubscript{6}H\textsubscript{4}</td>
<td>32.5</td>
<td>161.97</td>
<td>4.070</td>
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<tr>
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<td>2,6-F-C\textsubscript{6}H\textsubscript{3}</td>
<td>24.8\textsuperscript{c}</td>
<td>128.85</td>
<td>4.679</td>
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<tr>
<td>1.7</td>
<td>3,5-CF\textsubscript{3}-C\textsubscript{6}H\textsubscript{3}</td>
<td>25.75</td>
<td>189.50</td>
<td>7.018</td>
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</table>

\textsuperscript{a} Coordinating solvent NCMe. \textsuperscript{b} 4-Br aniline. \textsuperscript{c} 2,6-Cl aniline. \textsuperscript{d} 3-Me aniline.

2. Solid Angle calculations and spacefilled models

Figure S1. Spacefilled molecular structure of W{N(2,6-Pr-C\textsubscript{6}H\textsubscript{3})Cl\textsubscript{4}}(THF) (1.a) showing the imido group from the front (left) and side on (right). (b) Solid-G\textsuperscript{3} calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

Figure S2. (a) Spacefilled molecular structure of W{N(2,6-Pr-C\textsubscript{6}H\textsubscript{3})}Me\textsubscript{3}Cl (2.a) showing the imido group from the front (left) and side on (right). (b) Solid-G\textsuperscript{3} calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).
Figure S3. (a) Spacefilled molecular structure of W(N(C₆H₅))Cl₄(THF) (1.1) showing the imido group from the front (left) and side on (right). (b) Solid-G³ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

Figure S4. (a) Spacefilled molecular structure of W(N(C₆H₅))Me₃Cl (2.1) showing the imido group from the front (left) and side on (right). (b) Solid-G³ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).

Figure S5. (a) Spacefilled molecular structure of W(N(2,6-Me-C₆H₃))Cl₄(THF) (1.2) showing the imido group from the front (left) and side on (right). (b) Solid-G³ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

Figure S6. (a) Spacefilled molecular structure of W(N(2,6-Me-C₆H₃))Me₃Cl (2.2) showing the imido group from the front (left) and side on (right). (b) Solid-G³ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).
Figure S7. (a) Spacefilled molecular structure of $W(N(3,5\text{-Me-}C_6H_3))\text{Cl}_4(\text{THF})$ (1.3) showing the imido group from the front (left) and side on (right). (b) Solid-G$^3$ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

Figure S8. (a) Spacefilled molecular structure of $W(N(3,5\text{-Me-}C_6H_3))\text{Me}_3\text{Cl}$ (2.3) showing the imido group from the front (left) and side on (right). (b) Solid-G$^3$ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).

Figure S9. (a) Spacefilled molecular structure of $W(N(2,4,6\text{-Me-}C_6H_2))\text{Cl}_4(\text{THF})$ (1.4) showing the imido group from the front (left) and side on (right). (b) Solid-G$^3$ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

Figure S10. (a) Spacefilled molecular structure of $W(N(4\text{-OMe-}C_6H_4))\text{Cl}_4(\text{THF})$ (1.5) showing the imido group from the front (left) and side on (right). (b) Solid-G$^3$ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).
Figure S11. (a) Spacefilled molecular structure of W[N(4-OMe-C₆H₄)]Me₃Cl (2.5) showing the imido group from the front (left) and side on (right). (b) Solid-G¹ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).

Figure S12. (a) Spacefilled molecular structure of W[N(2,6-F-C₆H₃)]Cl₄(THF) (1.6) showing the imido group from the front (left) and side on (right). (b) Solid-G¹ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).

Figure S13. (a) Spacefilled molecular structure of W[N(2,6-F-C₆H₃)]Me₃Cl (2.6) showing the imido group from the front (left) and side on (right). (b) Solid-G¹ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and methyl groups (blue) from the front of the imido group (left) and side on (right).

Figure S14. (a) Spacefilled molecular structure of W[N(3,5-CF₃-C₆H₃)]Cl₄(THF) (1.7) showing the imido group from the front (left) and side on (right). (b) Solid-G¹ calculations showing the steric protection afforded to the metal centre by the imido group (black), chlorides (green) and THF (red) from the front of the imido group (left) and side on (right).
3. Characterisation of the homogeneous catalysts

NMR spectroscopy

W(NR)Cl₄(THF) complexes

Figure S16. $^1$H NMR spectrum of 1.1 in $d_6$-benzene (7.16 ppm).

Figure S17. $^{13}$C($^1$H) NMR spectrum of 1.1 in $d_6$-benzene (128.06 ppm).
Figure S18. $^1$H NMR spectrum of 1.2 in $d_6$-benzene (7.16 ppm).

Figure S19. $^{13}$C\{${}^1$H\} NMR spectrum of 1.2 in $d_6$-benzene (128.06 ppm).
Figure S20. $^1$H NMR spectrum of 1.3 in $d_6$-benzene (7.16 ppm).

Figure S21. $^{13}$C($^1$H) NMR spectrum of 1.3 in $d_6$-benzene (128.06 ppm).
Figure S22. $^1$H NMR spectrum of 1.4 in $d_6$-benzene (7.16 ppm).

Figure S23. $^{13}$C($^1$H) NMR spectrum of 1.4 in $d_6$-benzene (128.06 ppm).
Figure S24. $^1$H NMR spectrum of 1.5 in $d_6$-benzene (7.16 ppm).

Figure S25. $^{13}$C{$^1$H} NMR spectrum of 1.5 in $d_6$-benzene (128.06 ppm).
Figure S26. $^1$H NMR spectrum of 1.6 in $d_6$-benzene (7.16 ppm).

Figure S27. $^{13}$C($^1$H) NMR spectrum of 1.6 in $d_6$-benzene (128.06 ppm).
Figure S28. $^{19}$F($^1$H) NMR spectra of 1.6 in $d_6$-benzene.

Figure S29. $^1$H NMR spectrum of 1.7 in $d_6$-benzene (7.16 ppm).
Figure S30. $^{13}$C($^1$H) NMR spectrum of 1.7 in $d_6$-benzene (128.06 ppm).

Figure S31. $^{19}$F($^1$H) NMR spectra of 1.7 in $d_6$-benzene.
W(NR)Me3Cl complexes

Figure S32. 1H NMR spectrum of 2.1 in d6-benzene (7.16 ppm).

Figure S33. 13C{1H} NMR spectrum of 2.1 in d6-benzene (128.06 ppm).
Figure S34. $^1$H NMR spectrum of 2.2 in $d_6$-benzene (7.16 ppm).

Figure S35. $^{13}$C($^1$H) NMR spectrum of 2.2 in $d_6$-benzene (128.06 ppm).
Figure S36. $^1$H NMR spectrum of 2.3 in $d_6$-benzene (7.16 ppm).

Figure S37. $^{13}$C($^1$H) NMR spectrum of 2.3 in $d_6$-benzene (128.06 ppm).
Figure S38. $^1$H NMR spectrum of 2.4 in $d_6$-benzene (7.16 ppm).

Figure S39. $^{13}$C{$^1$H} NMR spectrum of 2.4 in $d_6$-benzene (128.06 ppm).
Figure S40. $^1$H NMR spectrum of 2.5 in $d_6$-benzene (7.16 ppm).

Figure S41. $^{13}$C($^1$H) NMR spectrum of 2.5 in $d_6$-benzene (128.06 ppm).
**Figure S42.** $^1$H NMR spectrum of 2.6 in $d_6$-benzene (7.16 ppm).

**Figure S43.** $^{13}$C($^1$H) NMR spectrum of 2.6 in $d_6$-benzene (128.06 ppm).
Figure S44. $^{19}$F($^1$H) NMR spectra of 2.6 in $d_6$-benzene.

Figure S45. $^1$H NMR spectrum of 2.7 in $d_6$-benzene (7.16 ppm).
Figure S46. $^{13}\text{C}^{1\text{H}}$ NMR spectrum of 2.8 in $d_6$-benzene (128.06 ppm).
Fourier transform infrared (FTIR) spectroscopy

$\text{W(NR)Cl}_4(\text{THF})$ complexes

Figure S47. FTIR spectrum of 1.1.
Figure S48. FTIR spectrum of 1.2.

Figure S49. FTIR spectrum of 1.3.
Figure S50. FTIR spectrum of 1.4.

Figure S51. FTIR spectrum of 1.5.
Figure S52. FTIR spectrum of 1.6.

Figure S53. FTIR spectrum of 1.7.
W(NR)Me₃Cl complexes

Figure S54. FTIR spectrum of 2.1.

Figure S55. FTIR spectrum of 2.2.
Figure S56. FTIR spectrum of 2.5.

Figure S57. FTIR spectrum of 2.6.
4. Characterisation of the heterogeneous catalysts

Solid-state NMR spectroscopy

Figure S58. Solid-state $^{13}$C-$^{1}$H CP-MAS NMR spectra of sMAO-1.5.

Figure S59. Solid-state $^{27}$Al Hahn echo NMR spectra of sMAO-1.5.
Figure S60. Solid-state $^{13}$C-{$^1$H} CP-MAS NMR spectra of sMAO-1.6.

Figure S61. Solid-state $^{27}$Al Hahn echo NMR spectra of sMAO-1.6.
Figure S62. Solid-state $^{13}$C-$^1$H CPMAS NMR spectra of sMAO-2.6*. Resonances between 38 and 62 ppm attributed to $W^{13}\text{CH}_3$ groups of the supported complex.

Figure S63. Solid-state $^{27}$Al Hahn echo NMR spectra of sMAO-2.6*.
Figure S64. $^{13}$C-$^{1}H$ CPMAS (19F) decoupled SSNMR spectrum of 2.6.

Figure S65. Solid-state $^{13}$C-$^{1}H$ CP-MAS NMR spectra of sMAO-1.7.
Figure S66. Solid-state $^{27}$Al Hahn echo NMR spectra of sMAO-1.7.
Fourier transform infrared (FTIR) spectroscopy

sMAO-W(NR)Cl₄(THF) compounds

Figure S67. FTIR spectrum of sMAO.
Figure S68. FTIR spectrum of sMAO-1.1.

Figure S69. FTIR spectrum of sMAO-1.2.
Figure S70. FTIR spectrum of sMAO-1.3.

Figure S71. FTIR spectrum of sMAO-1.4.
Figure S72. FTIR spectrum of sMAO-1.5.

Figure S73. FTIR spectrum of sMAO-1.6.
Figure S74. FTIR spectrum of sMAO-1.7.

ICP-MS

Table S3. ICP-MS analysis and calculated Al/W ratios and percentage loading for sMAO-1.4, sMAO-1.5 and sMAO-1.7.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (mg)</th>
<th>$^{27}$Al (mol%)</th>
<th>$^{182}$W (mol%)</th>
<th>$^{184}$W (mol%)</th>
<th>$^{186}$W (mol%)</th>
<th>Mean Al/W</th>
<th>Complex loading (%)</th>
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<tbody>
<tr>
<td>sMAO-1.4</td>
<td>10.5</td>
<td>1.32800</td>
<td>286.66745</td>
<td>285.15483</td>
<td>269.35047</td>
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<td>56.8</td>
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<tr>
<td>sMAO-1.4</td>
<td>10.9</td>
<td>1.31104</td>
<td>314.49531</td>
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<td>287.95395</td>
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<td>258.44509</td>
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<td>255.20206</td>
<td>245.76385</td>
<td>238.04334</td>
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<td>sMAO-1.7</td>
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<td>217.26813</td>
<td>241.42522</td>
<td>216.83394</td>
<td>225.2</td>
<td>62.6</td>
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5. Heterogeneous oligomerisation studies

Statistical correlations

**Table S4.** Pearson correlations for all the W(NR)Cl₄(THF) complex parameters and the turnover frequency (TOF) of the sMAO supported catalysts.

<table>
<thead>
<tr>
<th></th>
<th>δ C&lt;sub&gt;ipso&lt;/sub&gt;</th>
<th>pKa</th>
<th>ECA</th>
<th>Solid-G</th>
<th>Ligand volume</th>
<th>W-N</th>
<th>W-N-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOF</td>
<td>0.517</td>
<td>−0.581</td>
<td>−0.105</td>
<td>−0.096</td>
<td>0.191</td>
<td>−0.158</td>
<td>−0.308</td>
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</tbody>
</table>

**Table S5.** Pearson correlations for the W(NR)Cl₄(THF) (R = C₆H₅, 2,6-Me-C₆H₃, 2,4,6-Me-C₆H₂, 2,6-i-Pr-C₆H₃ and 3,5-Me-C₆H₃) complexes parameters and the turnover frequency (TOF) of the sMAO supported catalysts.

<table>
<thead>
<tr>
<th></th>
<th>δ C&lt;sub&gt;ipso&lt;/sub&gt;</th>
<th>pKa</th>
<th>ECA</th>
<th>Solid-G</th>
<th>Ligand volume</th>
<th>W-N</th>
<th>W-N-C</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOF</td>
<td>0.806</td>
<td>−0.343</td>
<td>0.181</td>
<td>0.202</td>
<td>0.370</td>
<td>−0.332</td>
<td>−0.205</td>
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</table>

**Table S6.** Pearson correlations for the W(NR)Me₃Cl complexes parameters and the turnover frequency (TOF) of the sMAO-supported catalysts.

<table>
<thead>
<tr>
<th></th>
<th>W-N</th>
<th>W-Cl</th>
<th>W-N-C</th>
<th>δ C&lt;sub&gt;ipso&lt;/sub&gt;</th>
<th>δ W-Me</th>
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</thead>
<tbody>
<tr>
<td>TOF</td>
<td>0.310</td>
<td>−0.281</td>
<td>−0.242</td>
<td>0.059</td>
<td>0.55</td>
</tr>
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1-Hexene and 1-octene reactions

Figure S75. Reaction of sMAO-1.6 (W:Al = 1:150) with 1-hexene after 4 hours at 75 °C in $d_6$-benzene (7.16 ppm) containing Si(SiMe$_3$)$_4$ (0.27 ppm) showing almost complete isomerisation of the $\alpha$-olefin to cis- and trans-2-hexene.

Figure S76. Reaction of sMAO-1.6 (W:Al = 1:150) with 1-octene after 4 hours at 75 °C in $d_6$-benzene (7.16 ppm) containing Si(SiMe$_3$)$_4$ (0.27 ppm) showing almost complete isomerisation of the $\alpha$-olefin to cis- and trans-2-octene.
Temperature study

Figure S7. Reaction of sMAO-1.7 with ethylene (1 bar) at 75 °C in $d_6$-benzene.

Solvent properties

Table S7. Dielectric constants and donor numbers for solvents used in this study.\cite{7,8}

<table>
<thead>
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<th>Solvent</th>
<th>Dielectric Constant ($\varepsilon$)</th>
<th>Donor Number</th>
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</thead>
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<tr>
<td>Octane</td>
<td>Heptane = 1.9</td>
<td>Heptane = 0</td>
</tr>
<tr>
<td>Benzene</td>
<td>2.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.4</td>
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<td>DCM</td>
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<tr>
<td>Pyridine</td>
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<td>Chlorobenzene</td>
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<td>1,2-dichlorobenzene</td>
<td>9.9</td>
<td>3</td>
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<td>Mesitylene</td>
<td>$p$-Xylene = 2.3</td>
<td>10</td>
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Loading study

Figure S78. Effect of complex loading on the oligomerisation activity of sMAO-1.5. W:Al = 1:100, 1:150 and 1:200. 75 °C, $d_6$-benzene.

6. References