

## Chemical communications

## COMMUNICATION

## Tungsten imido catalysts for selective ethylene dimerisation

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**A tungsten imido complex  $W(NDipp)Me_3Cl$  (Dipp = 2,6-*i*-Pr-C<sub>6</sub>H<sub>3</sub>) is active for the selective dimerisation of ethylene to yield 1-butene under mild conditions. Immobilisation and activation of  $W(NDipp)Cl_4(THF)$  on layered double hydroxide, silica or polymethylaluminoxane yields active solid state catalysts for the selective dimerisation of ethylene. The polymethylaluminoxane-based catalyst displays a turnover frequency ( $4.0 \text{ mol}_{C_2H_4} \text{ mol}_W^{-1} \text{ h}^{-1}$ ) almost 7 times that of the homogeneous catalyst.**

Cheap feedstocks (methane, ethane) and energy derived from shale gas exploration has led to a \$135 billion investment in the US petrochemical industry.<sup>1</sup> Processes that upgrade short chain  $\alpha$ -olefins produced from such resources, especially with a high level of control, are therefore of great value. The last decade has seen the development of highly selective ethylene oligomerisation catalysts of which dimerisation and trimerisation are most prevalent.<sup>2</sup> Currently, the most selective and productive systems are chromium-based,<sup>3</sup> however, such high levels of selectivity are still difficult to achieve or predict. Perhaps the most famous industrial method is Axens's AlphaButol process based on a titanium catalyst which is high yielding (~93% conversion in 15 minutes at 2 MPa ethylene pressure) and highly selective for C<sub>4</sub> olefins (>99%).<sup>4</sup> Tungsten-based systems have also been shown to be efficient olefin dimerisation catalysts although to a much lesser extent.<sup>5–8</sup> The most prominent of these involve N-donor ligands and are formed either *in situ* from  $WCl_6$  and anilines or by activating tungsten imido complexes with aluminium alkyls; >99% selectivity towards dimer formation has been demonstrated.<sup>7</sup>

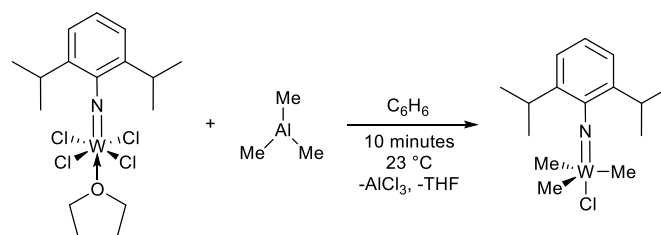
Making molecular catalytic systems heterogeneous has many industrial advantages such as ease of product separation and catalyst recycling.<sup>9</sup> Well-defined heterogeneous tungsten catalysts for alkene and alkane metathesis have been primarily

based on silica supports, using the concept of surface organometallic chemistry (SOMC)<sup>10</sup> to immobilise the complexes.<sup>11–14</sup> Basset and co-workers have reported that the highly reactive tungsten methyl bonds in  $WMe_6$  can be controlled when supported on partially dehydroxylated silica to produce a catalyst that is active for the metathesis of linear alkanes at elevated temperatures.<sup>15,16</sup>

Examples of supported oligomerisation catalysts in the literature are rare,<sup>17</sup> Wass and co-workers have described how a PNP pincer chromium complex formed from  $CrCl_3(THF)_3$  and  $\{C_6H_4(OMe)_2\}PN(Me)P\{C_6H_4(OMe)_2\}$ , which is active for ethylene trimerisation with >99% selectivity, could be successfully supported on MAO-modified silica with no apparent loss of activity or selectivity.<sup>18</sup>

Layered double hydroxides (LDHs),<sup>19–22</sup> represented by the formula  $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{q+}(X^{n-})_{q/n} \cdot yH_2O$ , have been shown to act as effective catalyst supports.<sup>23,24</sup> Recent work by O'Hare and co-workers has focused on supporting olefin polymerisation complexes on LDHs.<sup>25–27</sup>

Here we report a well-defined tungsten imido complex which is active for the selective dimerisation of ethylene to 1-butene, both in solution and when supported on layered double hydroxides, silica or polymethylaluminoxane.<sup>28</sup>

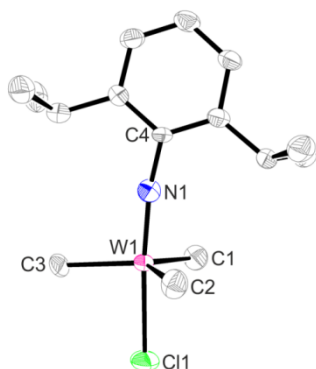


**Scheme 1.** Synthesis of  $W(NDipp)Me_3Cl$  from  $W(NDipp)Cl_4(THF)$  and trimethylaluminum.

The complex  $W(NDipp)Me_3Cl$  (Dipp = 2,6-*i*-Pr-C<sub>6</sub>H<sub>3</sub>) can be prepared from the reaction of  $W(NDipp)Cl_4(X)$  ( $X = THF$  or  $Et_2O$ )<sup>29</sup> and trimethylaluminum (TMA) (Scheme 1).<sup>30</sup> This reactivity is analogous to that reported by Dyer and

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co-workers to form the bis-imido complex  $W[N(\text{Dipp})\text{AlMe}_2(\mu\text{-Cl})](\text{NDipp})\text{Me}_2$ ,<sup>6</sup> however, in the case of  $W(\text{NDipp})\text{Me}_3\text{Cl}$  no aluminium coordination is observed. Excess TMA does not result in further methylation at ambient temperature, and complex formation also occurs when the starting material is reacted with an excess of methylaluminoxane (MAO) or dimethylaluminium chloride (DMAC).



**Fig. 1.** Molecular structure of  $W(\text{NDipp})\text{Me}_3\text{Cl}$ . Thermal ellipsoids are drawn at 50% probability. Hydrogen atoms omitted for clarity.

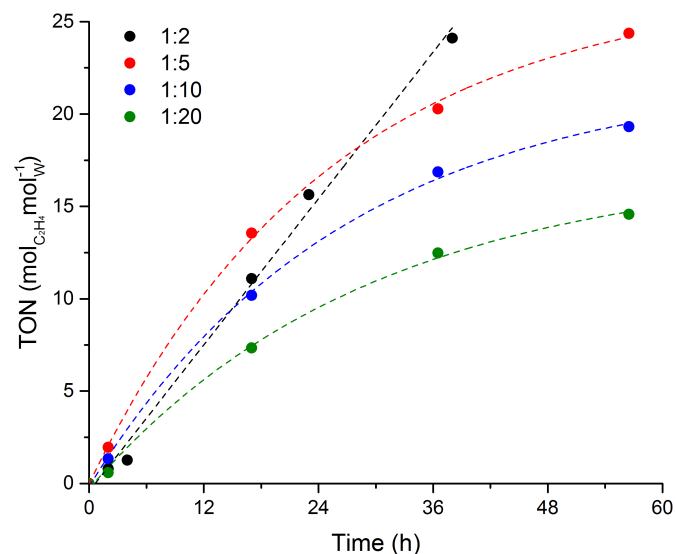
Analysis of the molecular structure of  $W(\text{NDipp})\text{Me}_3\text{Cl}$  (Fig. 1), shows that it adopts a trigonal bipyramidal arrangement with the methyl groups sitting in the equatorial plane. This orientation was also proposed by Pedersen *et al.* for the analogous complex  $W(\text{NPh})\text{Me}_3\text{Cl}$ , which was not structurally characterised.<sup>31</sup> The W1-N1-C4 angle in  $W(\text{NDipp})\text{Me}_3\text{Cl}$  shows a deviation away from linearity ( $171.0(5)^\circ$  vs  $178.4(3)^\circ$  in  $W(\text{NDipp})\text{Cl}_4(\text{THF})$ ) due to steric repulsion between the methyl and isopropyl substituents. This distortion is accompanied by an increase in the tungsten nitrogen bond length ( $1.750(8) \text{ \AA}$  vs  $1.721(4) \text{ \AA}$ ).  $^1\text{H}$  NMR spectroscopy displays a singlet resonance for the three methyl groups at 1.41 ppm with tungsten satellites ( $^2J_{\text{WH}} = 7.03 \text{ Hz}$ ). Density functional theory (DFT) calculations at the BP86<sup>32–34</sup> level of theory were carried out on  $W(\text{NDipp})\text{Me}_3\text{Cl}$  and the HOMO shows a  $\pi$ -bonding interaction between the W1  $d_{yz}$  and the imido N1  $p_y$  orbitals (Fig. S4).



**Scheme 2.** Dimerisation of ethylene to 1-butene catalysed by  $W(\text{NDipp})\text{Me}_3\text{Cl}$  and MAO.

A solution of  $W(\text{NDipp})\text{Me}_3\text{Cl}$  in benzene is active for the selective dimerisation of ethylene to 1-butene in the presence of MAO (Scheme 2). Reactions carried out at  $100^\circ\text{C}$  in  $\text{C}_6\text{D}_6$  with an internal standard show that lower W:MAO ratios result in greater activity and selectivity for 1-butene; isomerisation to 2-butenes is almost completely eliminated for the 1:2 ratio

(Fig. 2 and S6), with a total ethylene conversion of 88% and a 95% selectivity for 1-butene after 44.5 hours.



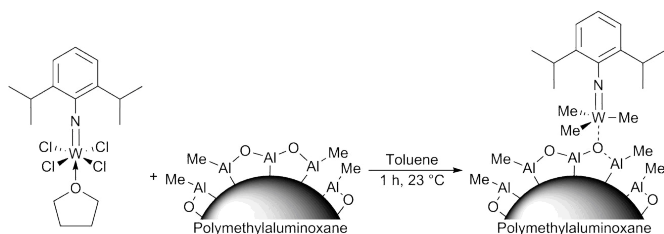
**Fig. 2.** Turnover number (TON) as a function of time for varying  $W(\text{NDipp})\text{Me}_3\text{Cl}$ :MAO ratios at  $100^\circ\text{C}$  in  $\text{C}_6\text{D}_6$ .  $[W(\text{NDipp})\text{Me}_3\text{Cl}]_0 = 4.55 \mu\text{mol}$ .

$^1\text{H}$  NMR spectroscopy shows that as the co-catalyst ratio is increased (from 1:2 to 1:40), the orange solution (1:2, 1:5 and 1:10) darkens to a brown colour (1:20) and then a dark brown (1:40) which corresponds to an intractable mixture of products which are unreactive towards ethylene (Fig. S12). A closer study of the product distribution for the 1:5 ratio (Fig. S9) shows that minor complex decomposition results in increased isomerisation to yield 2-butenes. In the presence of ethylene and 2-butenes the complex becomes active for the metathesis reaction to form propylene, a common transformation for complexes of this motif,<sup>35</sup> indicating that an alkylidene may form *in situ*.

Addition of other aluminium alkyls has a marked effect on the reactivity. In the presence of DMAC (W:DMAC = 1:2) resonances for the starting complex are unaffected yielding an active catalyst for dimerisation, however, addition of TMA (W:TMA = 1:2) and subsequent heating at  $100^\circ\text{C}$  results in a dark brown solution with multiple resonances exhibiting tungsten satellites in the  $^1\text{H}$  NMR spectrum, which is unreactive towards ethylene (Fig. S14). Reaction of  $W(\text{NDipp})\text{Me}_3\text{Cl}$  with MeLi results in a colour change from orange to yellow followed by rapid decomposition (no observable resonances in the  $^1\text{H}$  NMR spectrum) as described for  $W(\text{NPh})\text{Me}_3\text{Cl}$ .<sup>31</sup> In both cases we propose that an unstable tetramethyl species is formed which decomposes *via* a transient methylidene, explaining the observed metathesis chemistry from ethylene to propylene which is observed at higher temperatures.

It has been suggested that the high level of selectivity seen in tungsten systems may be a result of a metallocyclic mechanism, as seen in chromium systems.<sup>2</sup> Tobisch reported a DFT study on the role Lewis acids play in  $\alpha$ -olefin oligomerisation catalysed by mono(imido) tungsten complexes *via* a metallocyclic mechanism.<sup>36</sup> The complex  $W(\text{NPh})\text{R}_2\text{Cl}_2$  (R

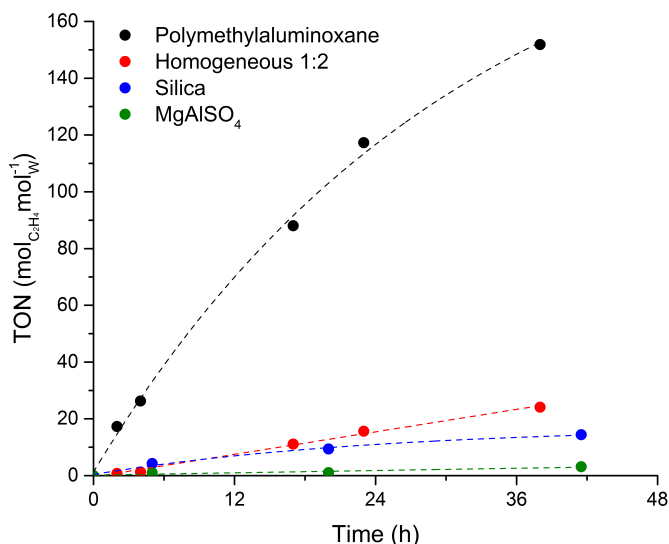
= olefin), proposed as the active species formed *in situ*, was used in the calculations and the Lewis acid ( $\text{AlMe}_2\text{Cl}$ ) was shown to decrease the activation energy irrespective of the coordination mode. Our results indicate that the *in situ* precatalyst may actually be a trimethyl complex  $\text{W}(\text{NPh})\text{Me}_3\text{Cl}$  which then coordinates ethylene (Scheme S4). Mixed  $\text{C}_2\text{H}_4/\text{C}_2\text{D}_4$  labelling studies on bis(imido) species and on an *in situ* tungsten initiator suggest a Cossee-type coordination-insertion mechanism may be involved, due to significant scrambling of the resulting oligomers.<sup>7,37</sup> The hydride species involved can lead to hydrogenation and isomerisation of the starting materials and products. Whilst we do see ethane and butane for all W:Al ratios, these along with isomerisation to 2-butenes of the product are significantly reduced with lower cocatalyst ratios.



**Scheme 3.** Schematic representation for the immobilisation of  $\text{W}(\text{NDipp})\text{Cl}_4(\text{THF})$  on polymethylaluminoxane to produce  $\text{W}(\text{NDipp})\text{Me}_3$  on the surface.

Utilising the SOMC concept,<sup>10</sup>  $\text{W}(\text{NDipp})\text{Cl}_4(\text{X})$  ( $\text{X} = \text{THF}, \text{Et}_2\text{O}$ ) can be supported on the surface hydroxyl groups of layered double hydroxides (LDHs) and silica, or on MAO-modified LDHs or polymethylaluminoxane (Scheme 3). Mixing of a green solution of complex in toluene (5% by weight) with a suspension of the solid support in toluene at ambient temperature for one hour resulted in a colourless solution and coloured support indicating immobilisation of the complex had occurred. Spectroscopic evidence indicates that methylation of the complex occurs *in situ* when grafted on an MAO-modified or polyaluminoxane support. A solution  $^1\text{H}$  NMR spectrum of the polymethylaluminoxane catalyst revealed a small quantity of leached complex with resonances corresponding to  $\text{W}(\text{NDipp})\text{Me}_3\text{Cl}$  (Fig. S45).

$^{13}\text{C}$  and  $^{27}\text{Al}$  solid state CPMAS NMR spectroscopic studies of the supported catalysts confirmed the presence of the diisopropylphenyl groups on the surface (Figs. S17–31). The  $^{27}\text{Al}$  NMR spectra of the LDH-supported species contain a small resonance for the surface aluminium species at  $\sim 77$  ppm, relative to the resonance at  $\sim 8$  ppm representing the bulk aluminium environment of the LDH.



**Fig. 3.** Comparison of the turnover numbers (TONs) of polymethylaluminoxane, silica and  $\text{Mg}_3\text{AlSO}_4$  supported  $\text{W}(\text{NDipp})\text{Cl}_4(\text{THF})$  with the homogeneous W:MAO = 1:2 reaction with 1 bar ethylene at 100 °C.

Oligomerisation studies in  $\text{C}_6\text{D}_6$  with MAO as a co-catalyst revealed that  $\text{W}(\text{NDipp})\text{Me}_3\text{Cl}$  supported on silica,  $\text{Mg}_3\text{AlSO}_4$  and  $\text{Mg}_3\text{AlCO}_3$  LDHs to be active heterogeneous catalysts for ethylene dimerisation, whereas the  $\text{Mg}_3\text{AlNO}_3$  only formed a small amount of polyethylene. It was also noted the turnover frequency (TOF) for the  $\text{Mg}_3\text{AlSO}_4$  was much greater than the  $\text{Mg}_3\text{AlCO}_3$ , in agreement with a previous study on supported ethylene polymerisation catalysts which showed this support to be more active.<sup>25</sup> However, these supported species displayed much lower activities than the homogeneous catalyst (silica  $\sim 70\%$ ,  $\text{Mg}_3\text{AlSO}_4 \sim 8\%$ ). The polymethylaluminoxane supported catalyst was by far the most active and selective displaying almost complete selectivity for 1-butene with a TOF almost 7 times that of the homogenous W:MAO = 1:2 ( $4.0 \text{ mol}_{\text{C}_2\text{H}_4} \text{mol}_{\text{W}}^{-1} \text{h}^{-1}$  vs  $0.6 \text{ mol}_{\text{C}_2\text{H}_4} \text{mol}_{\text{W}}^{-1} \text{h}^{-1}$ ) after 38 hours at 1 bar ethylene and 100 °C (Fig. 4). It was also shown that the catalyst was active for selective dimerisation in the gas phase when reacted in an NMR tube with ethylene at 100 °C (Fig. S47). This remarkable activity boost may be related to the presence of trimethylaluminium contained within the polymethylaluminoxane support, and its apparent porosity. Work is currently underway to elucidate the mechanism of the oligomerisation and the role of the polymethylaluminoxane support.

## Experimental

$\text{W}(\text{NDipp})\text{Cl}_4(\text{X})$  ( $\text{X} = \text{THF}$  or  $\text{Et}_2\text{O}$ ) and polymethylaluminoxane were synthesised according to literature procedures.<sup>28,29</sup> Layered Double Hydroxides (LDHs) of the type  $\text{Mg}_3\text{AlX}$  where  $\text{X} = \text{CO}_3, \text{NO}_3$  and  $\text{SO}_4$  were prepared by the aqueous miscible organic solvent treatment method,<sup>38–40</sup> and were thermally treated at 150 °C for 6 h under vacuum prior to use.

**$\text{W}(\text{NDipp})\text{Me}_3\text{Cl}$  (Dipp = 2,6- $^i\text{Pr}-\text{C}_6\text{H}_3$ )**  $\text{W}(\text{NAr})\text{Cl}_4(\text{Et}_2\text{O})$  (500 mg, 0.87 mmol) and trimethylaluminium (TMA) (62.7 mg, 0.87

mmol) were dissolved in benzene (~20 mL) and the TMA solution added dropwise to the W(NDipp)Cl<sub>4</sub>(Et<sub>2</sub>O) solution. The solvent was reduced *in vacuo* and the resulting brown solid was dissolved in hexane, filtered, reduced to minimum volume and cooled to -30 °C, resulting in orange crystals (300 mg) that were suitable for a single crystal X-ray diffraction study. Yield 79%. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ (ppm): 7.04 (d, 2H, ArH<sub>meta</sub>), 6.97 (dd, 1H, ArH<sub>para</sub>), 3.53 (sept, 2H, ArCH(CH<sub>3</sub>)<sub>2</sub>), 1.41 (s, 9H, W(CH<sub>3</sub>)<sub>3</sub>, <sup>2</sup>J<sub>WH</sub> = 7.027 Hz), 1.08 (d, 12H, ArCH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>) δ (ppm): 150.42 (Ar<sub>ipso</sub>N), 128.3 (Ar<sub>meta</sub>H), 128.13 (ArCH(CH<sub>3</sub>)<sub>2</sub>), 123.22 (Ar<sub>para</sub>H), 56.54 (W(CH<sub>3</sub>)<sub>3</sub>, <sup>1</sup>J<sub>WC</sub> = 156 Hz), 28.83 (ArCH(CH<sub>3</sub>)<sub>2</sub>), 24.28 (ArCH(CH<sub>3</sub>)<sub>2</sub>). Elemental analysis (CHN) (%): Expected C 40.98, H 5.96, N 3.19. Found C 40.92, H 5.88, N 3.18.

## Conclusions

Solutions of the complex W(NDipp)Me<sub>3</sub>Cl were found to be active for the dimerisation of ethylene in the presence of MAO. Lower cocatalyst ratios result in increased complex stability and hence much higher selectivity for 1-butene. This catalytic activity can be maintained when W(NDipp)Cl<sub>4</sub>(THF) is activated on inorganic solids such as a layered double hydroxide, silica or polymethylaluminumoxane. The polymethylaluminumoxane supported complex shows almost complete selectivity for 1-butene with a TOF 7 times greater than the homogeneous reaction.

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‡ Dr P. Dyer and co-workers, Department of Chemistry, University of Durham presented a poster on some aspect of solution phase ethylene dimerisation using W(NDipp)Me<sub>3</sub>Cl at UK Catalysis Conference, Loughborough, 2015.