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Selective dimerisation of 1-hexene mediated by aluminium alkyl chloride-activated tungsten imido complexes†

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Abstract: The selective dimerisation of 1-hexene to dodecenes was accomplished using catalysts generated from a tungsten *mono*- $[WCl_4(NR)(thf)]$ or *bis*- $[WCl_2(NR)_2(dme)]$ imido complex following activation with $EtAlCl_2$. These catalytic systems achieve 1-hexene dimerisation with productivities of up to 3760 (mol C_6)(mol W)$^{-1}$ and selectivities towards the dimer fraction of 88–99 wt%. Tungsten pro-catalysts bearing imido ligands with electron donating groups give high productivity and good selectivity towards the desired methyl-branched dimers. Contrastingly, complexes with electron withdrawing imido motifs are inactive for oligomerisation, instead mediating 1-hexene isomerisation. The efficacy of different aluminium-containing activators is described, with $EtAlCl_2$ giving the best catalytic performance at a low W:Al ratio of 8 – 20. Addition of catalyst modifiers (*e.g.* Oct_4NCl and Et_3N) is found to significantly improve the catalytic performance of the alkyl aluminium-activated olefin oligomerisation systems.

Keywords: dimerisation, 1-hexene, tungsten, imido, olefin

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1 Introduction

Transition metal-catalysed oligomerisation of light linear alpha olefins (LAOs), such as ethylene and propylene, is a crucial process for the petroleum industry[1-4] and consequently has received significant academic interest especially in the area of catalyst design.[5-9] The intensity of research in this field is a reflection of the wide ranging utility of the resulting oligomers, which find use as precursors for the synthesis of a broad range of everyday products such as synthetic lubricants, plasticiser and detergent alcohols, synthetic fatty acids, and as co-monomers.[10-13] In contrast, the dimerisation of heavier linear alpha olefins such as 1-pentene and 1-hexene has received much less attention despite the possible application of the resulting heavy olefinic products in the synthesis of lubricants and fuels.[14] This can be attributed principally to a combination of two factors: (i) the challenge of achieving good atom economy as a result of the propensity with which heavier alpha olefins isomerise towards poorly reactive internal olefins;[15-17] and (ii) the performance of well-established and readily accessible ethylene oligomerization catalytic systems decreases significantly with increasing formula weight of the LAO.[18]

The necessity for the development of heavy LAO oligomerisation systems became especially apparent after the emergence of technologies targeting the conversion of olefins into fuels (*e.g.* Mobil Olefins to Gasoline and Distillate process[19]) as a means of simplifying synthetic fuel production through processes such as Fisher Tropsch and methanol to olefins.[14] More recently, the importance of heavy LAO oligomerisation was further highlighted since it is a key step in the process of converting bio-derived butanol or ethanol to renewable jet fuels, which incorporate butene and 1-hexene oligomerisation steps, respectively.[20-22]

One of the earliest reports of the dimerisation of 1-hexene in 1966 described the use of a carbon-supported cobalt oxide catalyst, which gave modest conversions (≤36 % at 150 °C), but poor selectivity.[23] Subsequently, the dimerisation of 1-hexene has been reported using a number of different solid acid catalysts with various degrees of success. For example, catalysis mediated by phosphoric acid or zeolites have both been reported.[24, 25] However, in both cases elevated operating temperatures (80 - 300 °C) were necessary, coupled with conversions and selectivity being poor as a result of significant

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competing isomerisation, which gives rise to mixtures of mono-, di, and tri-branched C_{12} products. In contrast, it has been shown that 1-hexene dimerisation can be achieved using a number of different homogeneous catalysts with selectivities towards the dimer fraction of up to 98% operating under mild reaction conditions and productivities of up to ~3800 (mol C_6)(mol transition metal)$^{-1}$. Examples include systems based on Ni,[9, 26, 27] Co,[28, 29] Fe,[30] Ti,[9] and Zr,[9, 22, 31, 32] with the major dimerisation products being either linear dodecenes or methyl-branched dodecenes (*e.g*. 5-methyleneundecane).

Following the disclosure by The Goodyear Tire and Rubber company of the use of a soluble tungsten-based dimerisation catalyst generated *in situ* from $WCl_6/PhNH_2$ and an aluminium activator, tungsten-based systems have been found to show particular promise for the selective oligomerisation of heavy LAOs in the homogeneous catalysis arena.[9, 33-38] The catalytically active species of this Goodyear system was later demonstrated by Olivier *et al*. to involve tungsten imido species.[39] More recently, Sasol Technology UK described a related *in situ* system comprising $WCl_6/ArNH_2/Et_3N/EtAlCl_2$, which mediates dimerisation of both ethylene and heavier LAOs with improved activities and selectivities.[40, 41] In turn, this led to the development of well-defined tungsten *mono*- and *bis*-(imido) pro-catalysts, which in combination with $EtAlCl_2$ are able to ethylene dimerise efficiently. These systems are the most active, productive and selective tungsten-based catalysts for the dimerisation of ethylene to date, with performance paralleling that of Axens' commercial Ti-based AlphaButol process.[1, 2, 42-44] Given the high level of ethylene dimerisation activity established for these types of tungsten imido pro-catalysts it was of interest to explore their potential for the dimerisation of heavier olefins. In this work we now demonstrate that both tungsten *mono*- and *bis*-(imido) complexes in combination with $EtAlCl_2$ are also commercially competitive pro-catalysts for the dimerisation of 1-hexene with good productivities and selectivities towards the target dimer fraction.

2 Results and Discussion

The tungsten *bis*(imido) **1-3** and *mono*(imido) complexes **4-5** (Scheme 1) were synthesised according to previously published procedures from our group and others.[42, 43] Subsequently, complexes **1-5** were tested as pro-catalysts for the dimerisation of 1-hexene after activation with $EtAlCl_2$ (15 equivalents) at 60 °C. These test conditions are

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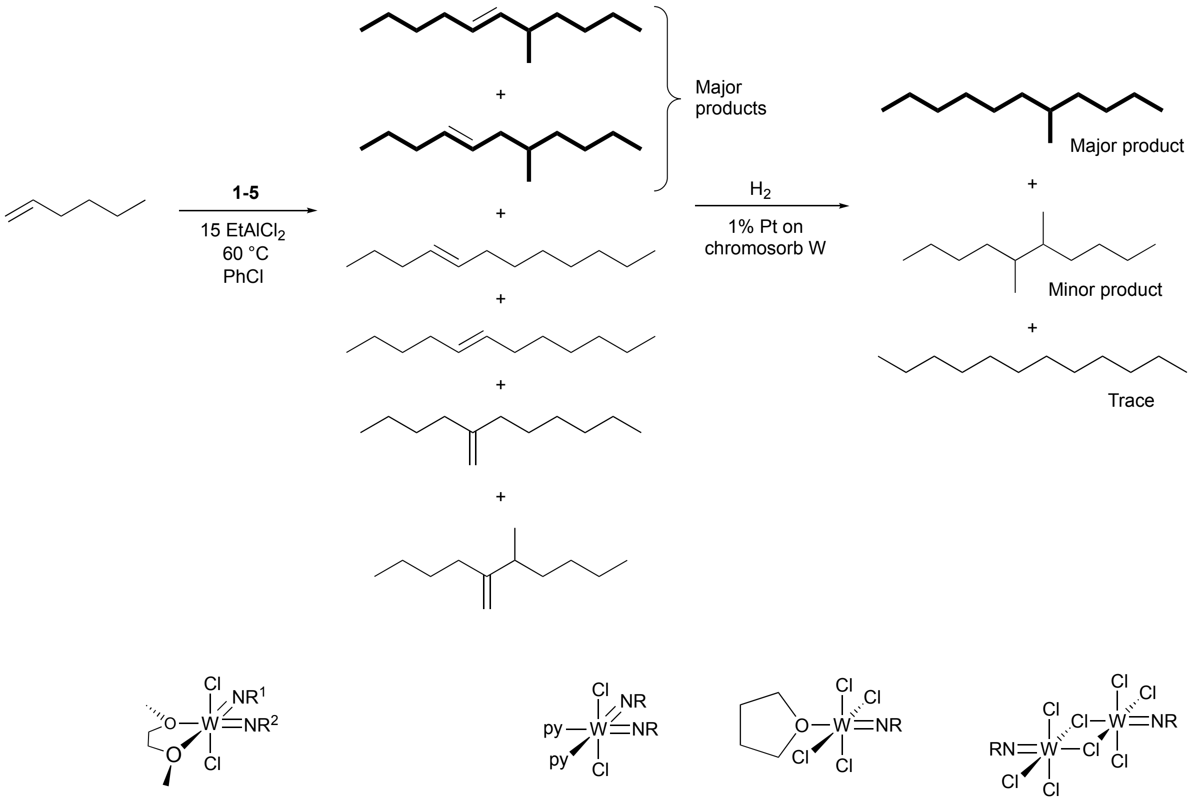
the same as those previously optimised for the dimerisation of 1-pentene using the *in situ* $WCl_6/ArNH_2/Et_3N$ system reported by Hanton *et al.*[40] Our previous work has demonstrated that the nature of the imido substituent in these types of ethylene dimerisation pro-catalysts has a significant impact on the performance of the resulting catalysts. Therefore, initial tests were undertaken to probe if this is also the case using 1-hexene as substrate.[42-44]



1a: R^1 = R^2 = Dipp (2,6-Diisopropylphenyl)
1b: R^1 = R^2 = Tpp (2,4,6-Triphenylphenyl)
1c: R^1 = R^2 = Tfp (2,4,6-Trifluorophenyl)
1d: R^1 = R^2 = Pfp (Perfluorophenyl)
1e: R^1 = R^2 = Mes^F (2,4,6-Trifluoromethylphenyl)
2a: R^1 = Dipp, R^2 = ^{t}Bu
2b: R^1 = Dipp, R^2 = Tpp
2c: R^1 = Dipp, R^2 = Tfp
2d: R^1 = Dipp, R^2 = Tcp (2,4,6-Trichlorophenyl)

3a: R = Dipp
3b: R = ^{t}Bu

4a: R = Dipp
4b: R = Ph
4c: R = 4-F-Ph
4d: R = Tfp
4e: R = Et

5a: R = Dipp
5b: R = Et
5c: R = Tfp

Scheme 1. Tungsten *mono*- and *bis*-(imido) complexes as pro-catalysts for the selective dimerisation of 1-hexene upon activation with $EtAlCl_2$ in PhCl at 60 °C.

2.1 Catalysis with tungsten *bis*(imido) complexes

Upon activation with $EtAlCl_2$, pro-catalysts **1-3** mediated dimerisation of 1-hexene with selectivities to the dimers fraction of between 88 and 99 wt% (Figure 1, Table 1), mirroring

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the previously reported ethylene dimerisation performance of these systems.[42-44] However, the effect of the imido substituent on 1-hexene dimerisation performance differs significantly from that observed previously with ethylene. For example, while it was found that electron withdrawing imido substituents such as Tfp and Pfp are beneficial in terms of activity and productivity for the dimerization of ethylene,[42] the opposite holds true with 1-hexene as the substrate: replacing the Dipp groups of **1a** (Entry 1, Table 1) with Tfp (Entry 2, Table 1) leads to a decrease in productivity from 2900 to 2280 (mol C_6)(mol W)$^{-1}$. Productivity was attenuated even further to 1810 (mol C_6)(mol W)$^{-1}$ using pro-catalyst **1d** bearing a Pfp group (Entry 4, Table 1). Pro-catalyst **1e** possessing a Mes^F imido substituent completes this downward trend, being barely active {>50 (mol C_6)(mol W)$^{-1}$}, albeit a behaviour that is paralleled for **1e** with ethylene as a substrate.[42] The same trend is also evident for the unsymmetrical *bis*(imido) pro-catalysts: **2c** is slightly less active than **1a** (Table 1, entries 1and 8), while replacing the chloro-substituted aryl group of **2d** for its fluoro counterpart **2c** led to a decrease in productivity of 880 (mol C_6)(mol W)$^{-1}$.

In terms of steric effects, the presence of bulky imido substituents on the pro-catalyst gives rise to less active 1-hexene dimerisation systems (Figure 1) as indicated by the decreased productivity of 1150 (mol C_6)(mol W)$^{-1}$ for **1b** (Table 1, Entry 2) (second lowest after **1e**). Again, this behaviour contrasts with that seen when using these systems for ethylene dimerisation, where increased steric bulk at the imido moiety gives more active catalysts. On the other hand, electron donating and sterically less demanding groups, such as ^{t}Bu, proved to be most effective for 1-hexene dimerisation: the asymmetric imido complex **2a** performed the best in terms of productivity compared to the other systems investigated. A comparison of the productivities of **3a** and **3b** further demonstrates the superior performance of the ^{t}Bu-substituted imido complexes for the dimerisation of 1-hexene. A productivity of 3760 (mol C_6)(mol W)$^{-1}$ and conversion to dimers and trimers of 80% is achieved using pro-catalyst **3b** (conversion to oligomers following the same trend to the productivities since these two values are proportional to each other).

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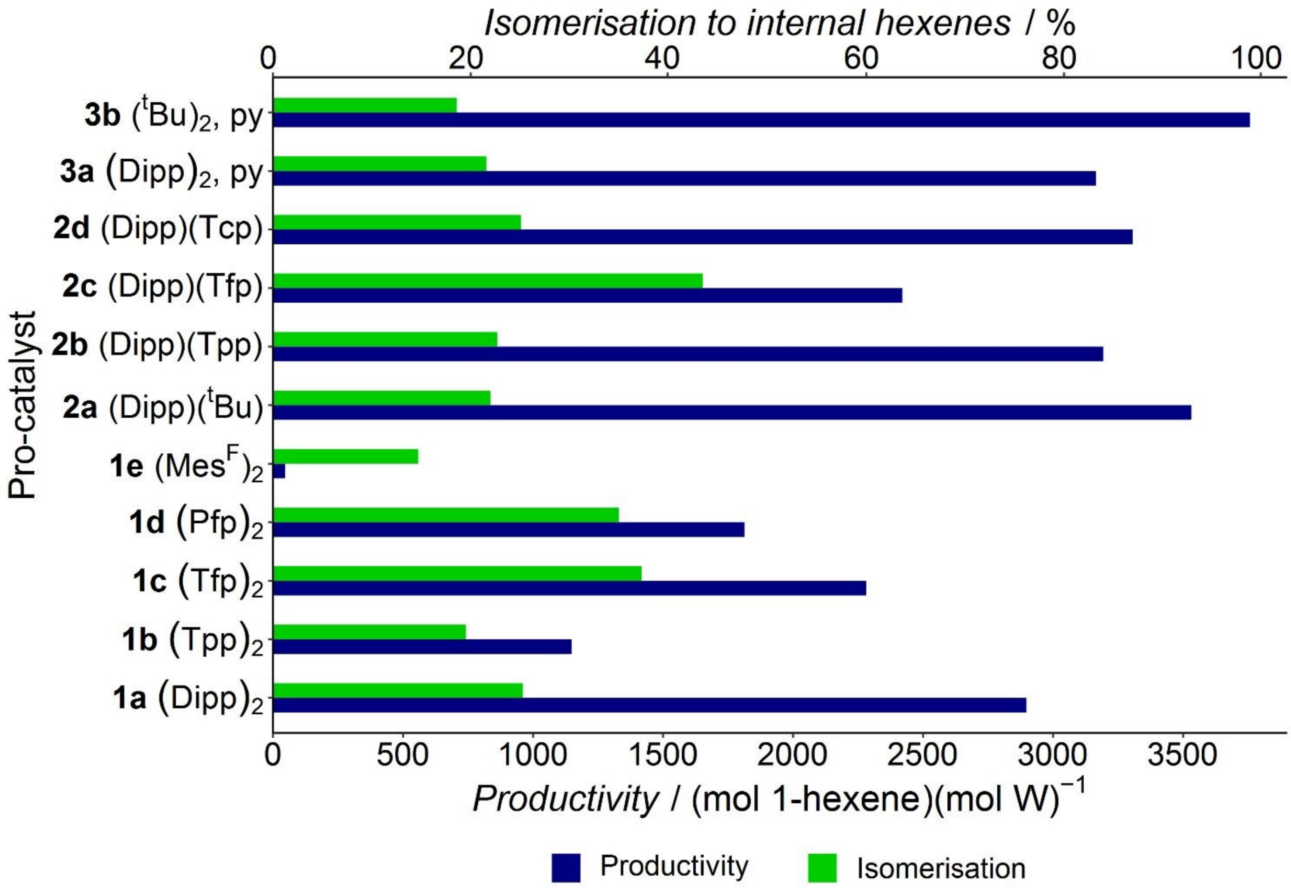

Figure 1. Productivity towards dimers and trimers and %isomerisation to internal hexenes for the dimerisation of 1-hexene mediated by various *bis*(imido) complexes (data taken from Table 1).

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Table 1 1-Hexene dimerisation catalysis with tungsten *bis*(imido) pro-catalysts, activated by $EtAlCl_2$ at 60 °C.[a]

Entry	Pro-catalyst	TON[b]	Conv., %[c]	Isom., %[d]	Conv. + Isom., %	Product selectivity		Dimers branching selectivity, %		
						C_{12}, wt%	C_{18}, wt%	Linear	Methyl branched	Dimethyl branched
1	$[WCl_2(NDipp)_2(dme)]$ (**1a**)	2900	63	25	88	96	4	<1	93	6
2	$[WCl_2(NTpp)_2(dme)]$ (**1b**)	1150	25	20	44	88	12	<1	92	8
3	$[WCl_2(NTfp)_2(dme)]$ (**1c**)	2280	52	37	89	99	1	<1	59	41
4	$[WCl_2(NPfp)_2(dme)]$ (**1d**)	1810	41	35	76	98	2	<1	57	43
5	$[WCl_2(NMes^F)_2(dme)]$ (**1e**)	<50	2	15	17	-	-	-	-	-
6	$[WCl_2(NDipp)(N^tBu)(dme)]$ (**2a**)	3530	74	22	97	97	3	<1	91	9
7	$[WCl_2(NDipp)(NTpp)(dme)]$ (**2b**)	3190	68	23	91	96	4	<1	94	6
8	$[WCl_2(NDipp)(NTfp)(dme)]$ (**2c**)	2420	50	44	94	96	4	<1	87	13
9	$[WCl_2(NDipp)(NTcp)(dme)]$ (**2d**)	3300	69	25	94	97	3	-	-	-
10	$[WCl_2(NDipp)_2(py)]$ (**3a**)	3170	67	22	89	96	4	<1	94	6
11	$[WCl_2(N^tBu)_2(py)]$ (**3b**)	3760	80	19	99	99	1	<1	88	12

[a] General conditions: 0.40 μmol tungsten and 6.0 μmol $EtAlCl_2$; PhCl (solvent) 282 μL; 60 °C; 1-hexene 250 μL (2.00 mmol); nonane standard (40.0 μL) added before activation; reaction time 300 min after which quenching followed by addition of d_6-acetone. [b] Reported in (mol C_6H_{12}) (mol W)$^{-1}$ and refers to the amount 1-hexene converted to oligomers as calculated from the sum of the masses of the dimers and trimers detected. [c] Defined as the %mass of hexenes converted to oligomers over the total mass of unreacted substrate, isomerised substrate, and products at the end of a run. [d] Defined as the fraction of 1-hexene that is isomerised to internal hexenes at the end of a run.

As stated above, many heavy LAO oligomerisation catalyst systems give rise to significant levels of unwanted substrate isomerisation to the more stable internal olefins, which are often resistant to dimerisation.[15-17] The tungsten *bis*(imido) pro-catalysts described herein are no exception, with between 19-44% of the 1-hexene substrate being isomerised depending on the pro-catalyst employed (Fig. 1, Table 1). This is significant since these catalysts demonstrate a complete lack of activity towards *trans*-3-hexene (Table 2, Entry 1). Note, pro-catalysts bearing electron withdrawing imido substituents are more effective in mediating isomerisation, with extents of isomerisation being in the range 35-44% (Table 1, entries 3,4,8 and Fig. 1), which is approximately 15% higher on average compared to pro-catalysts containing more electron donating imido substituents. While conversions to oligomers for the *bis*(imido) complexes reach a maximum of 80%, total conversions of 1-hexene to both oligomers and internal hexenes reach values of up to 99%. Doubling the W:1-hexene ratio to 1:10000 (Table 2, Entry 4) leads to a substantial decrease in the overall 1-hexene conversion from 88% to 68% with pro-catalyst **1a**.

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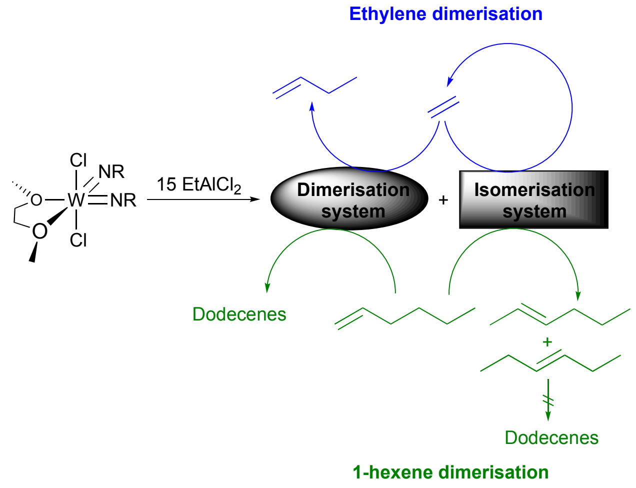
The trends in catalyst productivity for systems bearing increasingly electron withdrawing imido substituents appear contradictory for ethylene and 1-hexene as substrates, the former becoming more, and the latter, less productive. However, this difference in performance is accounted for in terms of the relative rates of isomerisation versus dimerisation. The presence of electron withdrawing imido ligands leads to formation of systems that are highly active for dimerisation, but also highly active olefin isomerisation catalysts. Thus, for ethylene such pro-catalysts mediate rapid dimerisation and hence high productivities. However, for 1-hexene the rate of dimerisation is also competitive with that of isomerisation, the latter leading to dimerisation-inactive internal hexenes and hence an apparent drop in productivity (Scheme 2).

Table 2. Catalytic dimerisation of various olefins over **1a** activated with $EtAlCl_2$ at 60 °C.[a]

Entry	Substrate	TON [b]	Conv. to products, % [c]	Isom., % [d]	Conv. + Isom., %
1	*trans*-3-hexene	0	0	-	-
2	2-Me-1-pentene	50	1	1	2
3	1-dodecene	1820	51	39	89
4	1-hexene [e]	3820	44	24	68

[a] General conditions: 0.40 μmol $[WCl_2(NDipp)_2(dme)]$ and 6.0 μmol $EtAlCl_2$; PhCl (solvent) 282 μL; 60 °C; 1-hexene 250 μL (2.00 mmol); nonane standard (40.0 μL) added before activation; reaction time 300 min after which quenching followed by addition of d_6-acetone. For entries 3 and 4 the selectivities to the dimers fraction were 94 and 95 wt% respectively. [b] Reported in (mol C_6H_{12}) (mol $W)^{-1}$ and refers to the amount 1-hexene converted to oligomers as calculated from the sum of the masses of the dimers and trimers detected. [c] Defined as the %mass of hexenes converted to oligomers over the total mass of unreacted substrate, isomerised substrate, and products at the end of a run. [d] Defined as the fraction of terminal alkene that is isomerised to internal alkenes at the end of a run. [e] 10000 equivalents to W.



Scheme 2 Simultaneous formation of olefin dimerisation and isomerisation catalytic systems after activation of tungsten imido complexes with $EtAlCl_2$ depicting the competing 1-hexene isomerisation process.

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Two possible mechanisms for 1-hexene isomerisation are envisioned. (i) 1-Hexene isomerisation occurs at tungsten *via* established sequential chain walking and β-hydride elimination processes,[45] with the relative rates of 1-hexene insertion and β-hydride elimination dictating the isomerisation to oligomerisation ratio. (ii) Alternatively, isomerisation is mediated by an aluminium-containing species, either the $EtAlCl_2$ co-catalyst or an aluminium complex formed during the pro-catalyst activation process. We have shown previously that activation of **1a** (or its molybdenum analogue $[MoCl_2(NDipp)_2(dme)]$) with methyl aluminium chlorides Me_2AlCl or $MeAlCl_2$ results in the formation of $[MMe_2(NDipp)_2]$ (M = Mo, W) and $[AlCl_2(dme)_2][MeAlCl_3]$ (**6**) or $[AlCl_2(dme)_2][AlCl_4]$,[46] respectively (Scheme 3 and section 8.1 of the ESI).[7, 47] Consequently, the reactivity of 1-hexene towards $[WMe_2(NDipp)_2]$ and aluminium complex **6** was explored to probe the viability of each of the two possible isomerisation pathways (i) and (ii).

Treating a chlorobenzene solution of 1-hexene with a catalytic quantity of aluminium salt **6** at 60 °C results in the rapid formation of internal hexenes with a conversion of ~71% achieved in 300 minutes. This was accompanied by a modest degree of 1-hexene dimerisation, TON ~70 (mol C_6H_{12}) (mol Al)$^{-1}$, a value in line with those reported previously for various aluminium-only containing olefin dimerisation systems.[9] In contrast, no reaction occurs on treating 1-hexene with a catalytic amount of $[WMe_2(NDipp)_2]$ in the absence of aluminium species. However, if 1-hexene is treated with $[WMe_2(NDipp)_2]$ in the presence of increasing amounts of $EtAlCl_2$ (Table S7, entries 2-4), on reaching a W:Al ratio of 1:15 catalytic dimerisation occurs with a productivity and selectivity comparable to that described in Entry 1, Table 1. While together these results cannot be used to identify the nature of the actual active isomerisation catalyst, they do clearly support the viability of competing 1-hexene dimerisation and isomerisation pathways.

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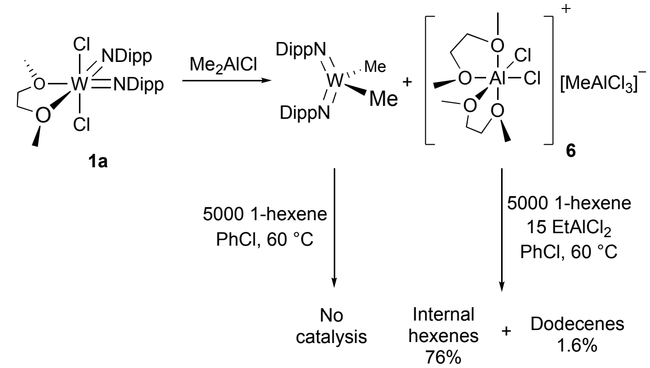

Scheme 3 Reaction of **1a** with Me_2AlCl to form previously reported $[WMe_2(NDipp)_2]$ and **6** with the latter catalysing the isomerization of 1-hexene under standard dimerization conditions.[47]

In terms of their selectivity towards dimers, all of the tungsten *bis*(imido) pro-catalysts **1**-**3** tested performed well achieving selectivities of between ~88 and 99 wt% (Figure 2). This high selectivity towards the dimers fraction is favoured as a result of the resulting dimer products either being either inert (internal *trans*-olefins; Table 2, Entry 1) or at best, poorly reactive (disubstituted terminal olefins, *e.g.* 2-butyl-1-octene; Table 2, Entry 2) under the oligomerisation test conditions employed, hence disfavouring reincorporation of dimers that would lead to unwanted oligomerisation reactions. Together, these observations are entirely consistent with previous reports that have highlighted the difficulty in achieving catalytic dimerisation of heavier olefins.[9, 18] This is further exemplified for these tungsten pro-catalysts since if 1-hexene is replaced by 1-dodecene as substrate, dimerisation productivity drops by a factor of 1.5 times under the same test conditions (Table 1, Entry 1 versus Table 2, Entry 3).

From a commercial standpoint, the branching selectivity associated with the products from catalytic dimerisation of heavy LAOs is important since increased branching reduces the cetane number of the resulting alkanes (obtained after hydrogenation of the olefinic products), which renders them less suitable for use as jet and diesel engine fuels.[22] From this perspective the tungsten *bis*(imido) complexes **1a,b**, **2a,b**, and **3a,b** all performed well with ~88 to 94% of the dimers fraction being 5-methylundecene (assigned using hydrogenative GC-FID analysis, Table 1). In contrast, complexes **1c,d** both performed poorly giving rise to over 40% di-branched products (Table 1, entries 3, 4), something that again, reflects how the nature of the imido substituent can have a significant impact

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on catalytic performance. The data presented in Figure show that electron withdrawing imido substituents give catalysts favouring formation of di-branched products, which in combination with their high substrate isomerisation ability and low productivity, lead to poor overall catalytic performance. In contrast, steric effects do not seem to influence significantly the branching selectivity within the dimers fraction since the diverse steric characteristics of pro-catalysts **1a**, **2a**, **1b**, and **2b** all performed in a comparable fashion within experimental error.

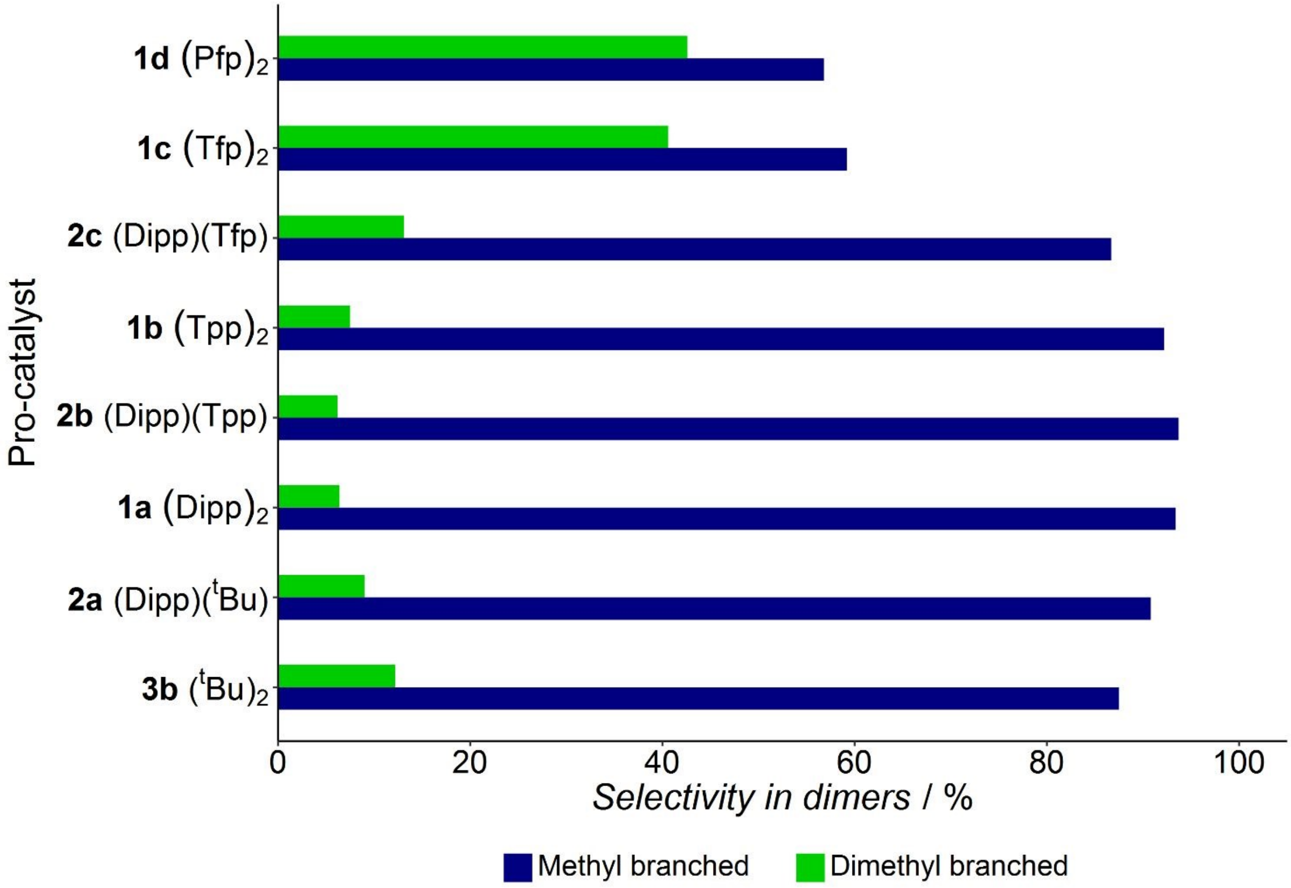

Figure 2. Effect of the imido ligand on the branching selectivity within the dimers fraction obtained from the catalytic dimerisation of 1-hexene using tungsten *bis*(imido) pro-catalysts.

The effect of the W:Al ratio on catalytic performance is extremely important from an industrial perspective with the use of lowest amounts of alkyl aluminium being desirable, not only due to improved cost efficiency, but also in terms of safety since alkyl aluminium reagents are extremely pyrophoric. Consequently, an investigation of the performance of pro-catalyst **1a** with varying amounts of activator followed (Figure 3). While the selectivity

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to the dimers fraction is independent of the amount of $EtAlCl_2$ used, the productivity increases dramatically on moving from 4 to 8 equivalents of $EtAlCl_2$ (Figure). Increasing the W:Al ratio above 1:8 has a small, but negative impact on productivity, something demonstrated previously for the dimerisation of ethylene using **1a**/$EtAlCl_2$.[42] However, there is a small, but marked increase in the extent of 1-hexene isomerisation at higher aluminium loadings. The extremely low W:Al ratio required to efficiently activate the tungsten imido pro-catalysts such as **1a** for the dimerisation of 1-hexene is clearly a benefit of this system (*vide supra*). In terms of the nature of the activator used, $EtAlCl_2$ outperformed all other potentially effective activators (see section 7 in the ESI for a detailed discussion).

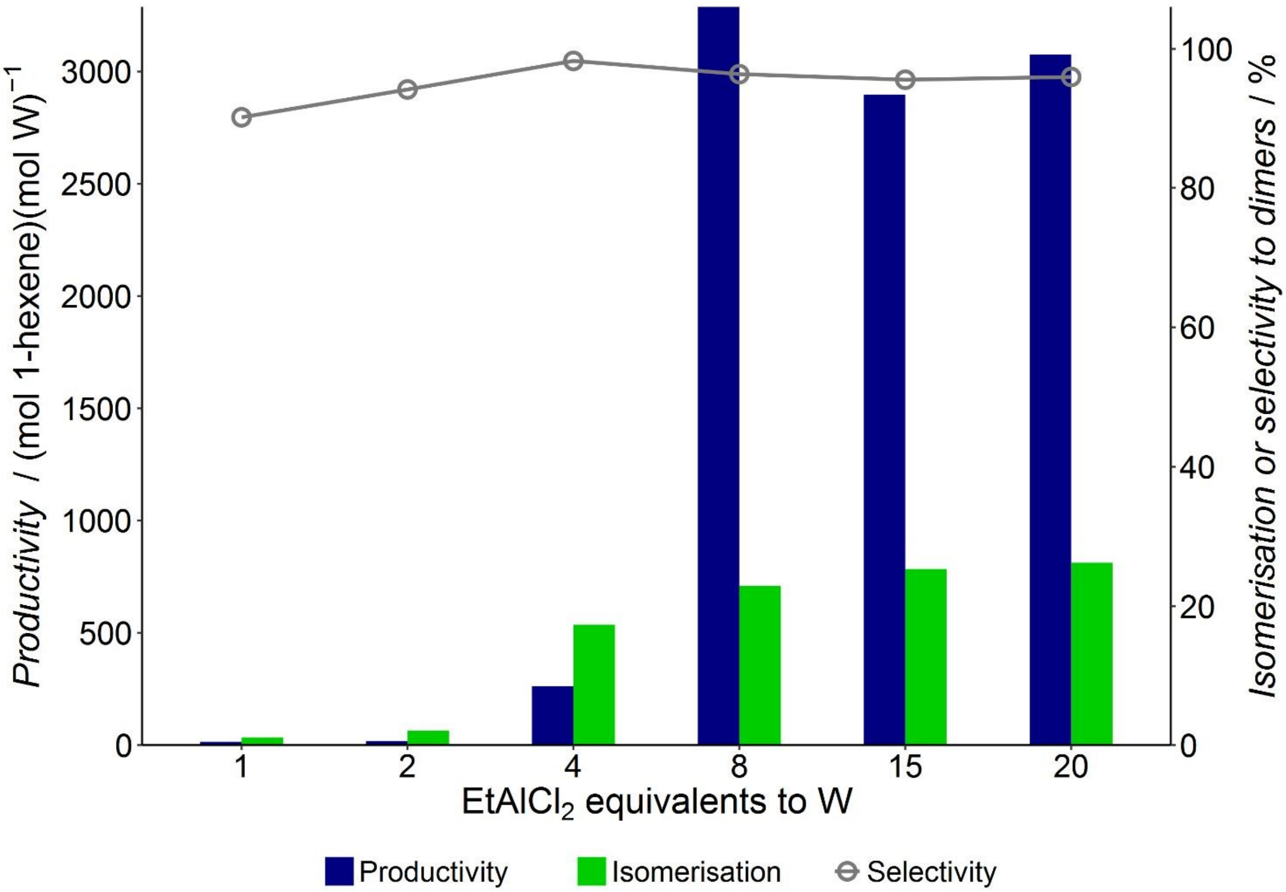

Figure 3. Productivity, % isomerisation, and selectivity towards dodecenes for the dimerization of 1-hexene mediated by $[WCl_2(NDipp)_2(dme)]$ (**1a**) versus number of equivalents of $EtAlCl_2$ per tungsten (data taken from Table S6).

Notably, the pre-formed tungsten *bis*(imido) 1-hexene dimerization pro-catalysts outperform the previously reported WCl_6/2 $ArNH_2$/4 Et_3N *in situ* system, with pro-catalyst

3b exhibiting a TON and conversion to dimers of 3760 (mol C_6H_{12}) (mol W)$^{-1}$ and 80 %, respectively, versus the 594 (mol C_6H_{12}) (mol W)$^{-1}$ and 67 % reported for the *in situ* system.[40] This trend exactly mirrors the results achieved for ethylene dimerisation using these two catalytic systems where again, the well-defined tungsten *bis*(imido) pro-catalysts show significantly superior catalytic performance compared to their *in situ* counterparts.[42]

2.2 1-Hexene dimerisation catalysis with tungsten *mono*(imido) complexes

We have previously reported that tungsten *mono*(imido) complexes are highly active ethylene dimerisation pro-catalysts in combination with $EtAlCl_2$ as activator.[43] Therefore, it was of interest to explore their 1-hexene dimerisation performance using the same conditions as employed for the *bis*(imido) pro-catalysts described above (Figure 4). However, as shown by the results presented in Table 3, the *mono*(imido) complex pro-catalysts dimerise 1-hexene with TONs of only up to ~2390 (mol C_6H_{12}) (mol W)$^{-1}$, somewhat lower productivities than those afforded by their *bis*(imido) counterparts (Table 1 vs Table 3); the selectivities towards the dimers fraction were comparable for both systems. Despite the total 1-hexene conversions for the *mono*(imido) pro-catalysts being in the range ~85 – 99%, a large proportion of the products arise from 1-hexene isomerisation consistent with the lower productivities of the *mono*- vs. *bis*-(imido) systems. Despite the differences in performance, the effect of the imido substituent on productivity and 1-hexene isomerization observed for the *mono*(imido) pro-catalysts is similar to that exhibited by their *bis*(imido) counterparts, namely the presence of electron withdrawing imido groups leads to less productive systems, which in turn gives rise to the formation of greater amounts of internal hexene isomers (Figure). The 1-hexene catalytic performance of the THF-free dimeric tungsten imido complexes **5a-c** is comparable to that of their THF-substituted analogues as expected since the aluminium activator effectively scavenges the Lewis base. However, for reasons that remain unclear, the trend between the imido electron withdrawing ability and productivity is lost for pro-catalysts **5a-c**, with **5a** being the most productive and **5b** the least productive.

In terms of selectivity to the dimers fraction (Figure 4), all of the tungsten imido complexes perform in a comparable fashion (Table 1 and Table 3) regardless of the

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number or type of imido ligands bound to the tungsten centre, or whether they are mono- or dimeric in nature (Table 3, Entries 6-8). This gross similarity in the selectivity to the dimers fraction through dimerisation of 1-hexene contrasts with the results obtained with the same pro-catalysts for ethylene where the selectivity varied upon changing the imido substituent. This observation again underlines the inference that the nature of the produced dimers, which inhibits re-insertion and hence formation of higher oligomers is the significant contributing factor to the observed selectivity (*vide supra*).

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Table 3. 1-Hexene dimerisation catalysis with tungsten *mono*(imido) pro-catalysts, activated by $EtAlCl_2$ at 60 °C.[a]

Entry	Pro-catalyst	TON[b]	Conv., %[c]	Isom., %[d]	Conv. + Isom., %	Product selectivity		Dimers branching selectivity, %		
						C_{12}, wt%	C_{18}, wt%	Linear	Methyl branched	Dimethyl branched
1	[WCl_4(NEt)(thf)] (**4a**)	2390	50	47	96	98	2	-	-	-
2	[WCl_4(NDipp)(thf)] (**4b**)	1880	41	49	90	92	7.6	<1	94	6
3	[WCl_4(NPh)(thf)] (**4c**)	1740	39	58	97	97	3	-	-	-
4	[WCl_4(N4-F-Ph)(thf)] (**4d**)	1160	27	69	96	96	4	-	-	-
5	[WCl_4(NTfp)(thf)] (**4e**)	1100	25	71	96	93	7	<1	72	28
6	[{WCl_3(μ-Cl)(NDipp)}$_2$] (**5a**)	2350	52	33	85	93	7	-	-	-
7	[{WCl_3(μ-Cl)(NEt)}$_2$] (**5b**)	150	34	63	97	99	2	-	-	-
8	[{WCl_3(μ-Cl)(NTfp)}$_2$] (**5c**)	1690	37	60	98	98	2	-	-	-

[a] General conditions: 0.40 μmol tungsten and 6.0 μmol $EtAlCl_2$; PhCl (solvent) 282 μL; 60 °C; 1-hexene 250 μL (2.00 mmol); nonane standard (40.0 μL) added before activation; reaction time 300 min after which quenching followed by addition of wet d_6-acetone. [b] Reported in (mol C_6H_{12}) (mol W)$^{-1}$ and refers to the amount 1-hexene converted to oligomers as calculated from the sum of the masses of the dimers and trimers detected. [c] Defined as the %mass of hexenes converted to oligomers over the total mass of unreacted substrate, isomerised substrate, and products at the end of a run. [d] Defined as the fraction of terminal alkene that is isomerised to internal alkenes at the end of a run.

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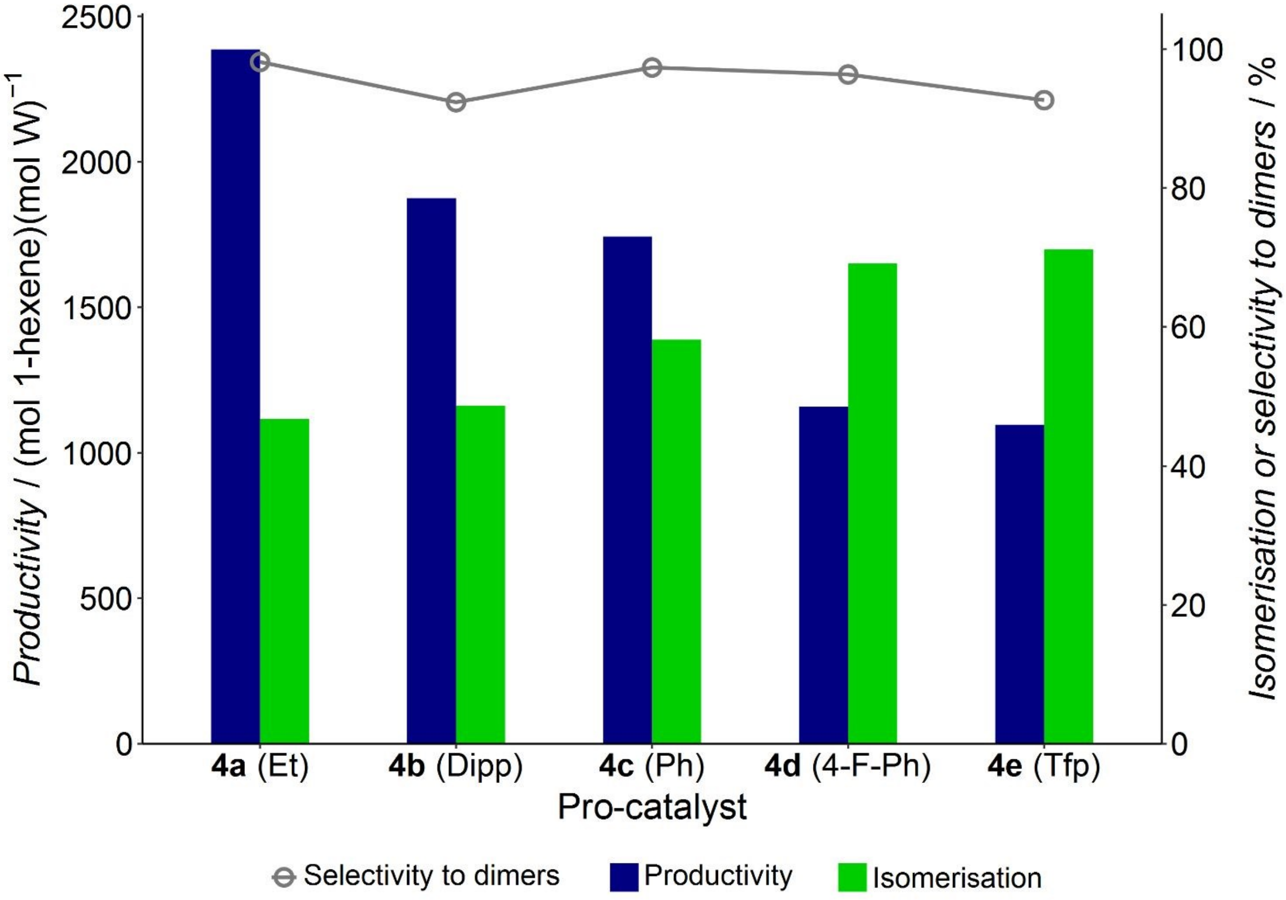

Figure 4. Productivity, % isomerisation, and selectivity towards dodecenes for the dimerisation of 1-hexene by various *mono*(imido) complexes (data from Table 3).

2.3 Effect of modifiers on catalysis

In the olefin dimerisation arena additives are often used to enhance catalytic performance in terms of productivity, activity, and/or selectivity.[1, 44, 48-51] Such additives, also known as modifiers, are added typically to the catalytic reaction mixture before activation and are usually simple, inexpensive compounds such as THF, Et_3N, Et_4NCl and PPh_3. In this context, we have recently reported that addition of Et_3N and Oct_4NCl significantly improves the catalytic activity and selectivity of tungsten *bis*(imido)-mediated ethylene dimerisation systems.[44] Accordingly, it was of interest to explore the use of such additives in the analogous catalytic LAO dimerisation; results are summarised in Table 4 and Figure . Surprisingly, in contrast to the considerable enhancement achieved for ethylene dimerisation,[44] the effect of these modifiers on 1-hexene dimerisation using *bis*(imido) tungsten complexes is either negligible (for 2,6-lutidine, Et_3NHCl, Et_3N, pyridine) or

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indeed, negative (DABCO, Oct_4NCl) in terms of productivity (Figure). Similar trends were also found for substrate isomerisation: in all experiments the conversion/isomerisation ratio is between 2.5 and 2.3, values similar to the ratios observed for the modifier-free test (Table 1, Entry 1) of 2.5. The only exception is for the reaction undertaken in the presence of 2,6-lutidine, which gives a slightly higher ratio of 3.0 suggesting that some substrate isomerisation suppression occurs when 2,6-lutidine is present in the reaction mixture. In terms of selectivity to the dimers fraction a very slight improvement is observed when modifiers are used in combination with **1a** from 96 wt% (Table 1, Entry 1) to 97 – 99 wt% (Table 4), something similar to the effect observed when ethylene was dimerised.[44]

Table 4. Effect of modifiers on the catalytic dimerisation of 1-hexene mediated by tungsten *bis*(imido) pro-catalysts activated with $EtAlCl_2$ at 60 °C.[a]

Entry	Pro-catalyst	Modifier[b]	TON [c]	Conv., % [d]	Isom., % [e]	Conv. + Isom., %	Product Selectivity	
							C_{12}, wt%	C_{18}, wt%
1	$[WCl_2(NDipp)_2(dme)]$ (**1a**)	Lutidine	2720	59	20	78	99	1
2	$[WCl_4(NDipp)(thf)]$ (**4b**)	Lutidine	2930	62	26	88	99	1
3	$[\{WCl(\mu\text{-}Cl)(NDipp)\}_2]$ (**5a**)	Lutidine	3200	68	25	93	99	1
4	$[WCl_2(NDipp)_2(dme)]$ (**1a**)	Et_3NHCl	2890	62	26	87	98	2
5	$[WCl_4(NDipp)(thf)]$ (**4b**)	Et_3NHCl	2760	57	36	93	97	3
6	$[\{WCl(\mu\text{-}Cl)(NDipp)\}_2]$ (**5a**)	Et_3NHCl	2980	62	33	95	98	2
7	$[WCl_2(NDipp)_2(dme)]$ (**1a**)	Et_3N	2680	55	22	78	97	3
8	$[WCl_4(NDipp)(thf)]$ (**4b**)	Et_3N	2910	62	28	90	98	2
9	$[\{WCl(\mu\text{-}Cl)(NDipp)\}_2]$ (**5a**)	Et_3N	2920	62	32	94	98	2
10	$[WCl_2(NDipp)_2(dme)]$ (**1a**)	pyridine	2760	59	24	83	98	2
11	$[WCl_4(NDipp)(thf)]$ (**4b**)	pyridine	2400	53	37	90	98	2
12	$[\{WCl(\mu\text{-}Cl)(NDipp)\}_2]$ (**5a**)	pyridine	3030	64	26	90	98	3
13	$[WCl_2(NDipp)_2(dme)]$ (**1a**)	dabco	1930	44	19	62	98	2
14	$[WCl_4(NDipp)(thf)]$ (**4b**)	dabco	2720	61	24	85	98	2
15	$[\{WCl(\mu\text{-}Cl)(NDipp)\}_2]$ (**5a**)	dabco	3090	71	21	92	100	0
16	$[WCl_2(NDipp)_2(dme)]$ (**1a**)	Oct_4NCl	1350	29	12	41	99	1
17	$[WCl_4(NDipp)(thf)]$ (**4b**)	Oct_4NCl	2790	59	31	90	99	1

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18	$[\{WCl(\mu\text{-}Cl)(NDipp)\}_2]$ (**5a**)	Oct_4NCl	3200	67	26	93	99	1

[a] General conditions: 0.40 μmol tungsten and 6.0 μmol $EtAlCl_2$; PhCl (solvent) 282 μL; 60 °C; 1-hexene 250 μL (2.00 mmol); nonane standard (40.0 μL) added before activation; reaction time 300 min after which quenching followed by addition of wet d_6-acetone. [b] 4 equivalents to tungsten were used. [c] Reported in (mol C_6H_{12}) (mol W)$^{-1}$ and refers to the amount of 1-hexene converted to oligomers as calculated from the sum of the masses of the dimers and trimers detected. [d] Defined as the %mass of hexenes converted to oligomers over the total mass of leftover substrate, isomerised substrate, and oligomers at the end of a run. [e] Defined as the fraction of terminal alkene substrate that is isomerised to internal alkenes at the end of a run.

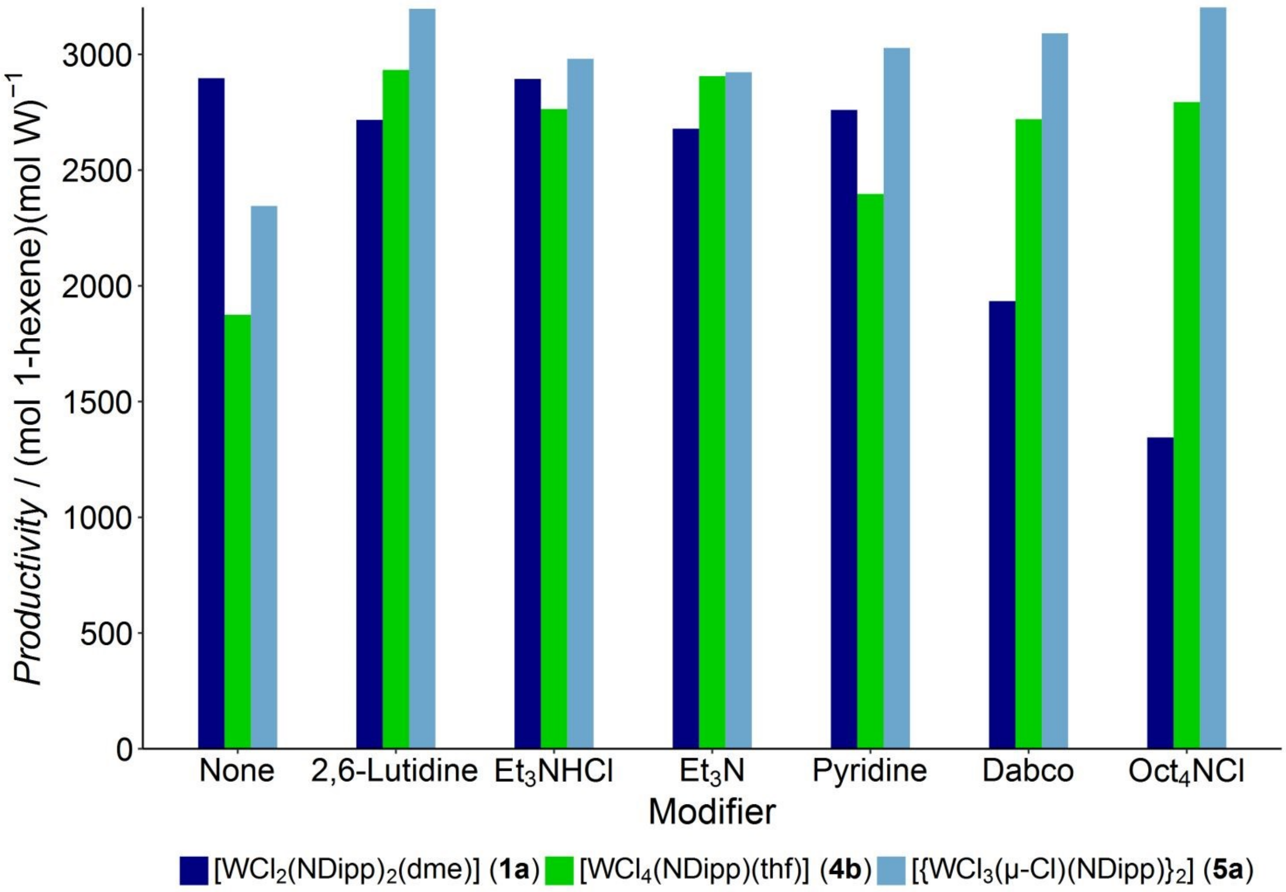

Figure 5. Effect of modifiers on productivity for the *mono*- and *bis*-(imido)-mediated catalytic dimerisation of 1-hexene at 60 °C.

In contrast to the effects observed for their *bis*(imido) counterparts, both monomeric and dimeric *mono*(imido) pro-catalysts significantly benefit from the presence of modifiers (Figure). An improvement in productivity of up to 56% and 37% are achieved for **4b** and **5a**, respectively, compared to that for the additive-free systems. In addition, the improvement in selectivity towards the dimers fraction observed for the *mono*(imido) pro-catalysts due to the addition of modifiers is more pronounced compared to the increase observed for the *bis*(imido) variants, increasing from 92 wt% and 93 wt% for **4b** and **5a**,

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respectively, to 97 – 100 wt% depending on the modifier used. However, the most notable effect of modifiers upon the tungsten *mono*(imido)-catalysed dimerisation of 1-hexene is the reduction in the amount of 1-hexene isomerised to internal hexenes. This effect is clearly observed by comparing the ratio of conversion:isomerisation between the modifier-free tests of 0.9 and 1.6 for **4b** and **5a**, respectively, to the ratios observed when modifiers are used of 1.4 – 2.6 for **4b** and 1.9 – 3.3 for **5a** depending on the modifier used. In all cases, DABCO is found to be the most effective inhibitor of LAO substrate isomerisation (Table 1, Table 3 and Table 4). However, from these preliminary results, it remains unclear whether the increase in the 1-hexene conversion:isomerisation ratio upon addition of modifiers is due to the suppression of the 1-hexene isomerisation side reaction or, instead, is due to an increase in the rate of the dimerisation reaction. Either way, it results in an overall increase in productivity slightly surpassing the productivity of the otherwise superior *bis*(imido) pro-catalysts.

3 Conclusions

In summary, both tungsten *mono*- and *bis*-(imido) complexes are active and selective pro-catalysts for the dimerisation of 1-hexene to methyl-branched dodecenes, products suitable for use as jet and diesel fuels following hydrogenation. This is especially the case for imido complexes bearing electron donating groups, which show higher productivities and branching selectivities towards the more desirable *mono*-methyl branched 1-hexene dimers compared to those achieved by systems possessing electron withdrawing imido substituents. Overall, *bis*(imido) pro-catalysts were found to be superior to their *mono*(imido) counterparts in terms of both activity and selectivity. Additionally, we have demonstrated that the presence of modifiers has no effect on catalysis mediated by *bis*(imido) systems, but that they greatly enhance both productivities and selectivities achieved using their *mono*(imido) pro-catalyst equivalents. Our studies demonstrate that industrially-relevant levels of catalytic performance for the dimerisation of 1-hexene may be achieved for these tungsten imido pro-catalysts with only low loadings of the activator $EtAlCl_2$ (optimal at 8 – 20 equivalents aluminium to tungsten). Overall, the performance of well-defined tungsten imido complex pro-catalysts for the dimerisation of 1-hexene compares well to that of previously-reported homogeneous systems that rely on transition metals such as Zr, Co, Ni, Ti, Fe, and Y making them a valuable addition to the heavy LAO dimerisation catalyst arsenal.

Supporting Information

† Electronic supplementary information (ESI) available: general experimental procedures, 1-hexene dimerisation catalysis protocols, GC-FID analysis of dimerisation reaction mixtures, definition of reported quantities, catalytic reproducibility determination, and reaction information. See DOI: 10.1039/abcdefg

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Author Contributions

The manuscript was written with contributions from all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

The authors declare no competing financial or interests.

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Graphical abstract:

Tungsten imido complexes, in combination with $EtAlCl_2$, were found to be efficient pro-catalysts for the selective dimerization of 1-hexene to methyl-branched dodecenes; products that can be used for the production of jet and diesel engine fuels. The developed dimerization systems benefit not only from the low cost of tungsten, but also from high TONs, use of low activator amounts and high selectivity within the dimers fraction with the main by-products being easily distilled internal hexenes.

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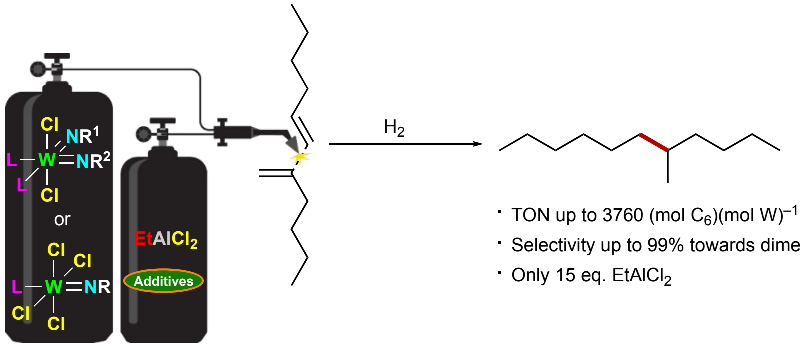

- TON up to 3760 (mol C_6)(mol W)$^{-1}$
- Selectivity up to 99% towards dimers
- Only 15 eq. $EtAlCl_2$