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Electronic Supplementary Information

Selective dimerization of 1-hexene mediated by aluminium alkyl chlorideactivated tungsten imido complexes

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1 General experimental procedures

All operations were conducted under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques, or in a Saffron Scientific nitrogen-filled glove box, unless otherwise stated. Nitrogen gas was passed through a drying column (silica/CaCO₃/P₂O₅). Bulk solvents were purified using an Innovative Technologies SPS facility, except chlorobenzene, which was dried by distillation from calcium hydride, and dme that was distilled under nitrogen from sodium/benzophenone. All solvents were degassed prior to use using standard methods.

CD₂Cl₂ and CD₃COCD₃ were purchased from Goss Scientific while C₆D₆ from Apollo Scientific. Each deuterated solvent was distilled from CaH₂, degassed and stored under nitrogen. EtAlCl₂, Et₃Al, MeAlCl₂, Me₃Al, Me₂AlCl, WCl₆, NaBH₄, (^{*n*}Oct)₄NBr, (^{*n*}Oct)₄NCl, Et₄NCl, Et₃NHCl, and ^{*n*}BuLi solution (2.5M in hexanes) were purchased from Sigma-Aldrich and used as received. 1-Hexene, 1-dodecene, *trans*-3-hexene, and 2-methyl-1-pentene were purchased from Sigma-Aldrich, distilled from CaH₂ and degassed prior to use. DABCO was purchased from Sigma-Aldrich and sublimed prior to use. Triethylamine was purchased from Sigma-Aldrich, dried over KOH, distilled and degassed prior to use. Nonane, pyridine, and 2,6-lutidine were purchased from Alfa-Aesar, dried over calcium hydride, distilled and degassed prior to use.

Solution phase NMR spectra were collected on a Varian Mercury 400 or 200, a Varian Inova 500, a Varian VNMRS-700 or 600 and a Bruker Advance 400 at ambient probe temperatures (290 K) unless otherwise stated. Chemical shifts were referenced to residual proton impurities in the deuterated solvent (¹H), ¹³C shift of the solvent (¹³C) or to external 85% H₃PO₄ aqueous solution (³¹P).¹

GC-FID analyses were conducted on a Perkin Elmer Clarus 400 GC or an Agilent Technologies 6890N GC instrument both equipped with a PONA column (50 m × 0.20 mm × 0.50 µm) and supplied with H₂ as a carrier gas. Hydrogenative GC-FID analysis was performed using an Agilent Technologies 6890N or a Perkin Elmer Clarus 400 GC System equipped an inlet liner packed with hydrogenating catalyst (Pt on Chromosorb W at 200 °C) and PONA column (50 m × 0.20 mm × 0.50 µm).²

2 Synthesis of pro-catalysts

All tungsten complexes used for catalysis were prepared as reported previously by our group^{3,4} while complex $[AlCl_2(dme)_2][MeAlCl_3]$ (6) was synthesized according to the following procedure: In a nitrogen filled glove box a vial was loaded with powdered Al_2Cl_6 (300 mg, 1.125 mmol), toluene (5 mL) and dme (496 µL, 4.50 mmol) followed by addition of MeAlCl₂ (254 mg, 2.25 mmol) under vigorous stirring to form a white slurry. Addition of hexane led to the precipitation of a white powder which was washed with hexane and dried under reduced pressure. The white powder was then dissolved in a minimal amount of THF and the solution layered with hexane. After 24 hours of

layering colorless crystals of **6a** formed in 71% yield (680 mg) some of which were suitable for an X-ray crystallographic analysis confirming the structure of the compound. ¹H NMR (400 MHz, THF-d₈): δ 3.43 (s, 8H), 3.27 (s, 12H), -0.60 (s, 3H). ¹³C{¹H} NMR (101 MHz, THF-d₈): δ 72.8, 59.0. ²⁷Al NMR (104 MHz, THF-d₈): δ 111.2 (br s, v_{1/2} =1053 Hz), 61.4 (br s, v_{1/2} = 587 Hz).

3 1-Hexene dimerisation catalysis protocol

1-Hexene dimerization experiments were conducted in NMR tubes (as conveniently-sized reaction vessels) in a nitrogen filled glove box. A selection of the catalysis runs was repeated on a larger scale in Schlenks using a home-made carousel reactor under a flow of nitrogen (Figure S1). Both catalysis procedures are outlined below.

3.1 Dimerisation of 1-hexene in NMR tubes

All of the operations were performed in a nitrogen-filled glove box and Eppendorf Reference® micropipettes were used for all solution additions. Pro-catalyst stock solutions (5.00 mM) were prepared in sample vials as follows: each complex (0.188 mmol) was dissolved in PhCI (3.00 mL). The desired pre-catalyst concentration was obtained by diluting an aliquot (400 µL) of the above solution with PhCI (4.60 mL). Stock solutions of the various activators and additives used for catalysis were prepared in a similar way and stored in a nitrogen filled glove box. Catalyst testing was undertaken in standard NMR tubes, which were oven dried (100 °C) and allowed to cool (1 hour) under vacuum. The NMR tubes were loaded with micro PTFE-coated stirrer bars, the appropriate amount of pro-catalyst stock solution (0.40 µmol in W), PhCl, and 1-hexene (5000 eq., 2.00 mmol). After addition of the substrate, each NMR tube was sealed and agitated. The resulting solutions were heated at 60 °C. Heating and stirring were achieved using an IKA stirrer-hotplate (temperature regulated to 60 °C using an IKA temperature probe) equipped with an aluminum heating block able to accommodate 25 NMR tubes. When thermal equilibrium was achieved the appropriate amount of activator stock solution was added. Care was taken to ensure that the initiation of the catalytic reaction was performed in exactly the same way for all samples in order to obtain reproducible results. The samples were left in the heating block for 5 hours, after which time they were taken out of the glove box and cooled to -78 °C in order to prevent the evaporation of any residual substrate. Subsequently, as-purchased d_6 -acetone (250 µL) and *n*-nonane (40.0 µL), were added under air to each tube. After being allowed to warm to room temperature, an aliquot (~0.25 mL) of each solution was collected and diluted with of PhCl (~0.5 mL). The resulting mixture was filtered and subjected to GC-FID and hydrogenative GC-FID analyses.

3.2 Dimerisation of 1-hexene in Schlenks

Pro-catalyst stock solutions (5.00 mM) were prepared in grease-free ampoules fitted with J. Youngs taps by dissolving the desired complex (0.200 mmol) in PhCl (40.0 mL). Two four-Schlenk arrangements were used (Figure S1). The Schlenks were oven-dried overnight (100 °C) and

subsequently allowed to cool (20 mins) under vacuum. Each of the 8 individual Schlenks was then loaded with a Teflon-coated magnetic stir bar, PhCl (8.50 mL) and the appropriate pre-catalyst stock solution (4.00 mL, 20.0 μ mol) followed by addition of *n*-nonane (1.000 mL, 5.60 mmol), and 1-hexene (12.4 mL, 100 mmol). Stirring was achieved using an IKA stirrer-hotplate set to 1000 rpm and an oil bath used for keeping the reaction to 60 °C in combination with an IKA temperature probe. After reaching thermal equilibrium, EtAlCl₂ activator (0.50 M stock solution in *n*-heptane, 0.60 mL, 300 μ mol) was added to the Schlenk. After 5 hours of reaction, a sample (0.5 mL) from the catalysis mixture was collected and quenched with a cold 50:50 toluene/HCl_{aq} (10% w/w) mixture (3 mL). The organic layer was then filtered and subject to GC-FID and hydrogenative GC-FID analyses.



Figure S1. Custom made carousel reactor used for 1-hexene dimerisation experiments.

4 GC-FID and ¹H NMR spectroscopic analysis of 1-hexene dimerisation products

The amount of unreacted 1-hexene, isomerised hexenes, dodecenes, and trimers present in the final catalysis mixtures were calculated from GC-FID analyses. Using the method of internal standards (nonane was used as the internal standard in the current study) equation 1 applies where: m_i , FW_i, A_i, and RF_i are the mass, formula weight, GC peak area, and response factor of the analyte respectively, while m_{st} , FW_{st}, A_{st}, and RF_{st} are the mass, formula weight, GC peak area, formula weight, GC peak area, and response factor of the internal standard.

 $\mathbf{m}_{i} = \frac{\mathbf{RF}_{st}}{\mathbf{RF}_{i}} \times \frac{\mathbf{A}_{i}}{\mathbf{A}_{st}} \times \frac{\mathbf{FW}_{i}}{\mathbf{FW}_{st}} \times \mathbf{m}_{st} \quad (eq. \ 1)$

According to previously published studies, FID detector response current changes from simple hydrocarbons are proportional to their molecular weight.⁵⁻⁷ Therefore, the response factor of the FID detector is approximately equal to the FW of the detected hydrocarbon⁶ and therefore equation 1 can be written as:

$$m_i = \frac{A_i}{A_{st}} \times m_{st}$$
 (eq. 2)

In order to validate the RF = FW approximation, 1-hexene was dimerised using $[WCl_2(NDipp)_2(dme)]$ (1) activated with 15 EtAlCl₂ and the produced dimers purified by fractional column distillation under vacuum in order to remove residual hexenes and traces of trimers. Subsequently, a calibration curve for the dodecene isomers formed during the dimerisation of 1-hexene as well as for the 1-hexene substrate were constructed by preparing and analysing eight standard solutions containing dodecene isomers, 1-hexene, and nonane internal standard in known amounts followed by subsequent GC-FID analysis (Figure S2, Table S1, Figure S3).



Figure S2. Example of a GC-FID chromatogram acquired from a standard sample used for constructing the calibration curves presented in Figure S3.

Sample	m _{C₆ (mg)}	m _{C₁₂ (mg)}	m _{st} (mg)	A _{C6}	А _{С₁₂}	A _{st}	m _{C₆} /m _{st}	m _{C12} /m _{st}	A_{C_6}/A_{st}	$\mathbf{A_{C_{12}}}/\mathbf{A_{st}}$
1	50.6	48.7	65.5	235191	249283	323171	0.772	0.744	0.7278	0.7714
2	169.2	79.9	60.3	774021	373096	278816	2.81	1.33	2.7761	1.3381
3	299.5	105.2	57.7	1060031	408318	216238	5.20	1.82	4.9021	1.8883
4	409.3	124.0	54.0	917215	301642	126830	7.58	2.30	7.2318	2.3783
5	527.1	562.6	65.2	1121758	1240686	142050	8.08	8.63	7.8970	8.7342
6	245.0	144.1	18.3	1338710	833337	106650	13.4	7.87	12.552	7.8138
7	92.6	89.1	34.1	1347082	1323356	492753	2.72	2.61	2.7338	2.6856
8	205.1	136.5	22.4	1359030	998519	151465	9.16	6.09	8.9726	6.5924

Table S1. Data used to construct the GC-FID calibration curves for 1-hexene and dodecenes.



Figure S3. GC-FID calibration curve for 1-hexene (■, red) and dodecenes (●, blue).

Curve	Slope (±2σ)	Intercept	Adjusted R ²	Residual sum of squares	Weight
A _{C6} /A _{st}	0.957 (±0.015)	0 (-)	0.9995	0.16862	No weighting
$A_{C_{12}}/A_{st}$	1.021 (±0.024)	0 (-)	0.9989	0.19675	No weighting

Since the slopes of the linear regressions presented in Figure S3 are close to 1.00 (Table S2), the approximation that FW=RF is applicable under the conditions used here, especially for the analysis of dodecenes.

After quantifying the amounts of dimers and trimers present at the end of each catalysis experiment from the gas chromatograms obtained, calculation of the branching selectivity can be achieved by repeating the GC run with an injection inlet liner loaded with a hydrogenation catalyst (Pt on Chromosorb W), which simplifies the resulted chromatogram (Figure S4).² The percentage of each branching pattern in the dimers fraction can then be calculated by dividing the area of each dodecane isomer chromatographic signal by the sum of the areas of all chromatographic signals corresponding to dodecanes after hydrogenation.



Figure S4. GC-FID chromatograms from a representative 1-hexene dimerisation reaction using $[WCl_2(NDipp)_2(dme)]$ (1) pre-catalyst and 15 equivalents of EtAlCl₂ activator before (top) and after (bottom) hydrogenation.

After calculating the masses of the 1-hexene, internal hexenes, dodecenes, and trimers in the final reaction mixtures the catalyst performance parameters can be calculated from the following formulae:

$$Productivity (TON) = \frac{mol \ C6 \ converted \ to \ products}{mol \ pre - catalyst} = \frac{(mass \ C12 + mass \ C18)/(FW \ C6)}{mol \ pre - catalyst} \quad (eq. 3)$$

 $Conversion \% = \frac{mass C12 + mass C18}{mass C6 + mass C12 + mass C18} \times 100 \quad (eq. 4)$

 $Isomerization \% = \frac{mass int. C6}{mass C6 + mass C12 + mass C18} \times 100 \quad (eq. 5)$

 $Cn wt\% \ product \ selectivity = \frac{mass \ Cn}{mass \ C12 + mass \ C18} \times 100 \quad (eq. 6)$

 $Branching \ selectivity \ \% = \frac{Hydrogenation \ GC \ FID \ C12 \ peak \ area}{Sum \ of \ Hydrogenation \ GC \ FID \ C12 \ peak \ areas} \times 100 \quad (eq. 7)$

All calculations were based on the total mass of reactants and products as calculated from the GC-FID data in the final reaction mixtures rather than from the amount of 1-hexene added initially to the reaction vessels at the start of each test. Therefore, a slight discrepancy is observed between TON and conversion since the latter contains the mass of C6 in the denominator. The reason for this is that a small amount of 1-hexene escapes from the reaction vessels during the addition of reagents and activation. The loss of substrate was confirmed by performing blank experiments, which are summarised in Table S3. It must be noted that the percentage of 1-hexene losses recorded when the reaction is performed in a Schlenk are twice as large compared to those observed when the reaction is performed in an NMR tube in a glovebox most likely due to the flow of nitrogen from the Schlenk line.

Entry	1-hexene loss in NMR tube reactions (mg)	1-hexene loss in Schlenk reactions (mg)
1	18.8	1775
2	20.7	1645
3	17.1	1645
Average	18.9	1688
St.Dev.	1.8	75.1
Relative St. Dev. %	9.5	4.4

Table S3. Amount of substrate lost due to evaporation during the 1-hexene catalytic dimerisation reactions in NMR tubes and in Schlenks [a].

[a] The reactions were performed under standard run conditions by replacing the pro-catalyst and activator stock solutions with pure solvent (PhCI); initial amount of 1-hexene added was 168.3 mg in the NMR tube and 8.345 g in the Schlenk tests.

The ¹H NMR spectra of a typical reaction mixture obtained post-catalysis, both before and after application of vacuum, are presented in Figure S5. The spectra are indicative of formation of internal dodecenes in line with the results presented by Nifant'ev and coworkers.⁸



Figure S5. ¹H NMR (400 MHz, d_6 -acetone) spectra of a typical 1-hexene dimerisation reaction using [WCl₂(NDipp)₂(dme)] (**1a**) pre-catalyst and 15 equivalents of EtAlCl₂ activator before (bottom) and after (top) application of vacuum with *p*-anisaldehyde used as internal standard.

5 Determination of catalytic reproducibility

The 1-hexene dimerisation experiment with [WCl₂(NDipp)₂(dme)] (1) and 15 EtAlCl₂ was repeated several times in NMR tubes (Table S4) and in Schlenks (Table S5). The standard deviations obtained for each catalysis parameter presented in Table S4 and Table S5 are henceforth taken as the uncertainty in the values obtained from every catalysis run presented in this study. According to the results presented in Table S4 and Table S5 much better reproducibility is obtained when catalysis is performed in NMR tubes rather than in Schlenks. The productivities obtained in Schlenks are comparable to those recorded in NMR tubes albeit somewhat lower possibly due to the greater amount of 1-hexene evaporating from the former (5% 1-hexene lost in NMR tube, 9% 1-hexene lost from Schlenks; see Table S3). Therefore, the majority of the catalysis tests described in this work were performed on a small scale in NMR tubes.

Table S4. Repeat catalysis with [WCl₂(NDipp)₂(dme)] (1) in NMR tubes and statistical analysis of the variability [a].

Entry	Pre-catalyst	TON [b]	Conv., % [c]	lsomer., %[d]	C ₁₂ in products, wt%	C ₁₈ in products, wt%	Linear in C ₁₂ , %	Methyl branched in C ₁₂ , %	Dimethyl branched in C ₁₂ , %
1	[WCl ₂ (NDipp) ₂ (dme)] (1)	2940	61	25	95	5	0.5	94	6

2	[WCl ₂ (NDipp) ₂ (dme)] (1)	2840	61	26	95	5	0.5	93	7
3	[WCl ₂ (NDipp) ₂ (dme)] (1)	2750	65	24	96	5	0.5	93	7
4	[WCl ₂ (NDipp) ₂ (dme)] (1)	3080	65	26	96	4			
Mean		2900	63	25	96	5	0.5	93	7
St. Dev.		140	2	1	1	1	0.1	1	1
%Relative St. Dev.		5	4	4	1	11	0.0	1	14

[a] General conditions: 0.40 µmol tungsten and 6.0 µmol EtAlCl₂; 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 d₆-acetone. [b] Reported in (mol C₆H₁₂) (mol W)⁻¹ and refers to the amount 1-hexene converted to oligomers. [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.

Table S5. Repeat catalysis with [WCl₂(NDipp)₂(dme)] (1) in Schlenks and statistical analysis of the variability [a].

Entry	Pre-catalyst	TON [b]	Conv., % [c]	lsomer., %[d]	C ₁₂ in products, wt%	C ₁₈ in products, wt%
1	[WCl ₂ (NDipp) ₂ (dme)] (1)	1850	47	24	95	5
2	[WCl ₂ (NDipp) ₂ (dme)] (1)	1700	52	27	100	0.0
3	[WCl ₂ (NDipp) ₂ (dme)] (1)	2840	66	19	96	4
Mean		2130	55	23	97	3
St. Dev.		620	10	4	3	3
%Relative St. Dev.		29	18	17	3	100

[a] General conditions: 0.40 µmol tungsten and 6.0 µmol EtAlCl₂; 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 d₆-acetone. [b] Reported in (mol C₆H₁₂) (mol W)⁻¹ and refers to the amount 1-hexene converted to oligomers. [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.

6 Miscelaneous catalysis experiments

Entry	EtAICI ₂ equivalents	TON [b]	Conv ., % [c]	lsomer., %[d]	C ₁₂ in products, wt%	C ₁₈ in products, wt%
1	1	15	0.5	1	90	10
2	2	20	0.5	2	94	6
3	4	260	6	17	98	2
4	8	3290	69	23	96	4
5	15	2900	63	25	96	4
6	20	3080	65	26	96	4

Table S6. Dimerisation of 1-hexene using [WCl₂(NDipp)₂(dme)] (1) with varying amounts of EtAlCl₂ activator [a].

[a] General conditions: 0.40 µmol tungsten and 6.0 µmol EtAlCl₂; 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. [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.

Table S7. Dimerisation of	1-hexene under various	catalysis conditions	a]
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Entry	Pre-catalyst	EtAICI ₂ equivalents to W	TON [b]	Conv. , % [c]	lsomer., %[d]	C ₁₂ in products, wt%	C ₁₈ in products, wt%
1	[AICl ₂ (dme) ₂][MeAICl ₂] (6)	15	70	2	71	83	17
2	[WMe ₂ (NDipp) ₂]	0	0	0	0		
3	[WMe ₂ (NDipp) ₂]	1	0	0	0		
4	[WMe ₂ (NDipp) ₂]	15	2460	54	20	96	4

[a] General conditions: 0.40 µmol tungsten and 6.0 µmol EtAlCl₂; 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 d₆-acetone. [b] Reported in (mol C₆H₁₂) (mol W)⁻¹ and refers to the amount 1-hexene converted to oligomers. [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.

7 Effect of the activator on 1-hexene dimerisation

Previously it has been shown that the nature of the activator used for 1-pentene dimerisation mediated by the *in situ* WCl₆/2 ArNH₂/4 Et₃N system has a tremendous impact on its catalytic performance,⁹ something mirrored for ethylene dimerisation using the well-defined mono- and bis-(imido) pro-catalysts.^{10, 11} Since in each of these cases EtAlCl₂ proved the best choice of activator, it was of interest to explore if this was also the case when 1-hexene was used as substrate. Consequently, a range of alkylating reagents were tested in conjunction with pro-catalysts **1a** and **4b**. As established previously for other olefinic substrates, EtAlCl₂ is again the optimal activator giving productivities 10-100 times greater than those achieved with other systems (Table S8). Methyl aluminium activators perform poorly giving productivities of less than ~220 (mol C₆H₁₂)(mol W)⁻¹ (Table S8, entries 1-2, 5-6), while systems activated by Et₃Al are barely active (Table S8, entries 3-4). These results echo the performance of these systems for ethylene and 1-pentene dimerisation,⁹, ^{10, 11} again exemplifying the importance of both the nature of the aluminium alkyl moiety (ethyl or methyl) and the chloride content.

Previous studies of both the *in situ* and well-defined tungsten-based olefin dimerisation catalyst systems have highlighted the difficulties in elucidating the precise nature of the active species, with hydride, metallacyclic oxidative coupling, and a combination of both mechanisms having been proposed.^{10, 11} Furthermore, both the nature of the aluminium alkyl moiety (ethyl or methyl) and the chloride content have been established as critical factors in determining the suitability of an activator for these systems. This mechanistic ambiguity is again evident with 1hexene as substrate. Although it might be expected that the ease of generation of a tungsten hydride intermediate from an ethyl-bearing activator *via* β -H elimination following Al-to-W transmetallation would favour catalysis, the performance of Et₃Al and Me₃Al are equally poor (Table S8, entries 1-4). Similarly, attempts to generate an active tungsten hydride species either directly through reaction of **1a** or **4b** with either Na[Al(H)₂(OCH₂CH₂OCH₃)₂] (RedAl) or KH, or indirectly *via* initial formation of a tungsten butyl species by reaction with "BuLi, in place of using an aluminium alkyl activator were all unsuccessful (Table S8, Entries 13-18). Additionally, no catalytic activity was found for the tests in which the pro-catalysts were pre-treated with Oct₄NCI prior to addition of trialkyl aluminium activator (Entries 7-12, Table S8). Together, this indicates that for successful activation to be achieved, it is necessary for the chloride to be bound to the aluminium activator. Lastly, a series of catalytic tests were undertaken that employed mono- and bis-(imido) tungsten methyl complexes,^{11,} ¹² rather than chloride pro-catalysts, both in the absence and presence of aluminium alkyl activator (Table S9). The results are consistent with our previous work^{10, 11, 12} and show that dimerisation only occurs in the presence of EtAICl₂ at a threshold level (W:Al 1:15). Indeed, in combination with 15 equivalents of EtAICl₂ the aforementioned tungsten imido methyl complexes were able to dimerize 1-hexene with productivities of up to 2460 (mol C_6H_{12})(mol W)⁻¹ (Table 5, Entry 5), performance that is comparable to that achieved using the corresponding chloride pro-catalysts with EtAlCl₂ as activator (W:AI 1:15).

Taking the above observations together, it can be deduced that an effective activator for the catalytic 1-hexene dimerisation mediated by mono- and bis-(imido) pro-catalysts requires the following characteristics: (i) an aluminium alkyl with available β -hydrogen atoms and (ii) possessing at least one chloride ligand. In line with our previous work^{10, 11, 12} and the computational studies reported by Tobisch,^{13, 14} the tests described herein highlight there being an essential synergistic interaction between the active tungsten species and the aluminium species generated during the transmetallation process rather than the aluminium being simply an alkylating agent.

Table S8. Effect of activator on the catalytic dimerisation of 1-hexene mediated by tungsten *bis*(imido) pro-catalysts at 60 °C.^{*a*}

Entra	Dre estalvat	Activator	TON	Conv.,		Conv. +	Product Selectivity	
Entry	PTO-Catalyst	ACTIVATOR		% ^e	% ^f	lsom., %	C ₁₂ , wt%	C ₁₈ , wt%
1	[WCl ₂ (NDipp) ₂ (dme)] (1a)	Me ₃ Al	10	<1	1	2	96	4
2	[WCl ₄ (NDipp)(thf)] (4b)	Me ₃ Al	30	<1	1	2	96	4

3	[WCl ₂ (NDipp) ₂ (dme)] (1a)	Et ₃ AI	10	<1	2	3	98	3
4	[WCl ₄ (NDipp)(thf)] (4b)	Et ₃ AI	20	<1	3	4	86	15
5	[WCl ₂ (NDipp) ₂ (dme)] (1a)	MeAICI ₂	130	3	46	49	87	13
6	[WCl ₄ (NDipp)(thf)] (4b)	MeAICI ₂	220	6	74	80	80	21
7	[WCl ₂ (NDipp) ₂ (dme)] (1a) ^b	Me ₃ Al	10	<1	1	1	74	26
8	[WCl ₄ (NDipp)(thf)] (4b) ^b	Me ₃ Al	20	<1	1	2	98	2
9	[WCl ₂ (NDipp) ₂ (dme)] (1a) ^b	Et ₃ AI	20	<1	2	3	22	79
10	[WCl ₄ (NDipp)(thf)] (4b) ^b	Et ₃ AI	20	<1	6	6	97	3
11	[WCl ₂ (NDipp) ₂ (dme)] (1a) ^b	MeAICI ₂	50	1	25	26	89	11
12	[WCl ₄ (NDipp)(thf)] (4b) ^b	MeAICI ₂	80	2	18	20	69	32
13	[WCl ₂ (NDipp) ₂ (dme)] (1a)	RedAl ^c	0	0	0	0		
14	[WCl ₄ (NDipp)(thf)] (4b)	RedAl ^c	0	0	0	0		
15	[WCl ₂ (NDipp) ₂ (dme)] (1a)	KH	0	0	0	0		
16	[WCl ₄ (NDipp)(thf)] (4b)	KH	0	0	0	0		
17	[WCl ₂ (NDipp) ₂ (dme)] (1a)	<i>n</i> BuLi	0	0	0	0		
18	[WCl₄(NDipp)(thf)] (4b)	<i>n</i> BuLi	0	0	0	0		

^{*a*} General conditions: 0.40 µmol tungsten and 6.0 µmol EtAlCl₂; 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 d₆-acetone. ^{*b*} 4 equivalents to tungsten of Oct₄NCl modifier used. ^{*c*} Na[Al(H)₂(OCH₂CH₂OCH₃)₂]. ^{*d*} Reported in (mol C₆H₁₂) (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. ^{*c*} 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. ^{*f*} Defined as the fraction of terminal alkene substrate that is isomerised to internal alkenes at the end of a run.

Table	S9.	1-Hexene	dimerisation	catalysis	with	alkylated	tungsten	mono-	and	<i>bis</i> -(imido)	pro-
cataly	sts at	t 60 °C.ª		-		-	-				-

Enter	Dre setskist	Activator	TON	Conv.,	lsom.,	Conv. +	Product Selectivity	
Entry	Pro-catalyst	(eq)	TON	% c	% d	lsom., %	C ₁₂ , wt%	C ₁₈ , wt%
1	[WMe ₂ (NDipp) ₂]	None	0	0	0	0		
2	[WMe ₂ (N{Dipp}AlMe ₂ {µ- Cl})(NDipp)]	None	0	0	0	0		
3	[(NDipp)Me ₃ W(µ-CI)(AICI ₃)]	None	0	0	0	0		
4	[WMe ₂ (NDipp) ₂]	$EtAICI_{2}(1)$	0	0	0	0		
5	[WMe ₂ (NDipp) ₂]	EtAICI ₂ (15)	2460	54	20	75	96	4
6	[WMe ₂ (N{Dipp}AlMe ₂ {µ- Cl})(NDipp)]	EtAICI ₂ (1)	50	1	3	4	97	3
7	[WMe ₂ (N{Dipp}AlMe ₂ {µ- Cl})(NDipp)]	EtAICI ₂ (15)	1800	40	17	56	97	3

^a General conditions: 0.40 µmol tungsten and 6.0 µmol EtAlCl₂; 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_{e} -acetone.^b 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. ^c 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. ^d Defined as the fraction of terminal alkene substrate that is isomerised to internal alkenes at the end of a run.

8 Reactions

8.1 Reaction of [WCl₂(NDipp)₂(dme)] (1a) with Me₂AlCl

A vial was loaded with a PTFE coated stirrer bar, $[WCl_2(NDipp)_2(dme)]$ (**1a**) (200 mg, 0.288 mmol), and CH₂Cl₂ (3 mL) in an N₂-filled glove box followed by addition of Me₂AlCl (26.7 µL, 0.288 mmol) under vigorous stirring. The resulting orange solution was stirred for five minutes during which time the color of the solution changed to dark red. Stirring was stopped and the solution was left to stand for 24 hours. This resulted in the formation of colorless crystals of [AlCl₂(dme)₂][AlCl₄] (37 mg, 76 % yield), as indicated from an X-ray crystallographic analysis, which were isolated by filtration.¹⁵ Meanwhile, the filtrate was dried resulting in the formation of a dark red residue which was extracted with pentane. The dark red pentane extracts were combined, condensed and stored at -30 °C. After 48 hours red crystals were formed the ¹H NMR and ¹³C NMR spectra of which were found to be identical to those reported by Wright *et al.*,¹⁶ confirming the formation of [WMe₂(NDipp)₂] (34 mg, 21 % yield).

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