Selective dimerisation of α-olefins using tungsten-based initiators†

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The selective dimerisation of the α-olefins 1-pentene through to 1-nonene is reported using an *in situ*-generated catalyst derived from tungsten hexachloride, aniline, triethylamine and alkylaluminium halide. The influence of reagent identity and reaction stoichiometry, along with activator, solvent and α-olefin substrate choice are probed. The catalyst is found to be highly selective towards dimerisation, minimising the formation of undesired heavier oligomers. Notably, the selectivity within the dimer fraction is found to favour the formation of products with methyl branches. The selectivity towards individual olefin isomers has been determined and the system is found to also produce trace levels of dienes and alkanes. A kinetic study of the system reveals a second order dependence on substrate. Comparison of the products observed, with those expected for metallacyclic and Cossee-type mechanisms, suggests that the latter is in operation, something confirmed by the results of a C_2H_4/C_2D_4 co-dimerisation experiment which showed full isotopic scrambling in the products. Thus a mechanistic proposal is made to account for the observed behaviour of the system, including the diene and alkane formation.

Introduction

The homogeneous, metal-catalysed dimerisation of olefins is a conversion of particular industrial interest.[1] Accordingly, many catalyst systems and several commercial processes, capable of effecting this reaction selectively are known.[2] Where the dimerisation of α-olefins is concerned, the selectivity towards dimerisation, but also towards specific branching in the skeleton of the product must be considered. In this regard, catalysts displaying enhanced selectivity towards linear,[3] mono-branched[4] and di-branched[5] products within the dimer fraction have been disclosed. Furthermore, the location of the unsaturation in the dimer product is dependent upon the catalyst system employed, and hence it is desirable to have control of this additional degree of variation to tailor products to specific applications.[3c]

The advantages of highly selective dimerisation processes are manifold, and include efficiency of feed usage *via* the avoidance of by-product formation, and the reduction of isomerisation processes.[1a] For example, group four cyclopentadienyl ligand-based catalysts when activated with aluminium co-catalysts produce methylidene (terminal) products from the dimerisation of α-olefins, but these systems suffer from significant formation of higher oligomers (up to 50%).[4,6] Meanwhile, recent reports of *bis*(imino)pyridyl ligand systems bound to iron, show these can be used as pre-catalysts in the dimerisation of α-olefins to give internal olefins with high skeletal selectivity (>99% linear), and much reduced formation of higher oligomers (15–20%).[3b]

The use of group six complexes with N-donor ligands in dimerisation catalysis has been reported on several previous occasions, in the form of a pre-catalyst formed *in situ*,[7] or from activation of tungsten imido complexes.[8] However, this class of dimerisation catalyst is relatively unexplored in comparison to many others, something that led us to re-examine systems of this type for the dimerisation of α-olefins. We recently reported an *in situ* catalyst system based upon tungsten hexachloride in combination with varying amounts of aniline and tertiary amine; which when activated with aluminium co-catalyst gives the highest selectivity to mono-methyl branched product reported to date for group six-based olefin dimerisation catalysts.[9] Furthermore, the catalyst is readily prepared from economically attractive precursors and the selectivity towards dimerisation (*vs.* higher oligomerisation) is often >99%, making this system highly desirable in terms of atom efficiency. Herein, we report full details of this initiator system and demonstrate that through modification of the many experimental parameters a degree of control can be exerted over the dimerisation of α-olefins.

Results and discussion

In situ catalysis

The catalyst system studied can be described by the general formula shown in Fig. 1. The catalyst is prepared by addition of a primary amine, preferably an aniline, and optionally a base, to a solution of tungsten hexachloride. The mixture is then left to stir for 15–30 min at the 'catalyst formation temperature' (T_F), before addition of olefin substrate, and finally, aluminium activator to initiate the dimerisation catalysis.

Previous reports of this class of catalyst system do not include the use of a base; the removal of HCl having been achieved *via*

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Table 1 Varying catalyst composition[a]

Entry	X Eq RNH_2	Y Eq Et_3N	T_F/T_C (°C)	Olefin (eq)	Act[b]	TON[c]	Conv. (%)	S[d] (%)	Branching selectivity					
									Linear	Me	Et	MeMe	MeEt	EtEt
1	0	0	60/60	1-C_6	0	0	0	—	—	—	—	—	—	—
2	1 (Ph)	0	60/60	1-C_6 [g]	51	205	41.0	nd	0	86.6	0	6.3	7.1	0
3	1.5 (Ph)	0	60/60	1-C_6 [g]	46	183	36.6	nd	0	85.5	0	6.8	7.7	0
4	2 (Ph)	0	60/60	1-C_6 [g]	60	240	48.0	nd	0	87.8	0	10.9	1.3	0
5	2.5 (Ph)	0	60/60	1-C_6 [g]	57	228	45.6	nd	0	86.1	0	9.4	4.5	0
6	3 (Ph)	0	60/60	1-C_6	117	468	46.8	nd	0	70.6	0	29.4	0	0
7	4 (Ph)	0	60/60	1-C_6 [g]	44	177	35.4	nd	0	71.1	0	28.9	0	0
8	6 (Ph)	0	60/60	1-C_6	146	584	58.4	nd	0	55.3	0	44.7	0	0
9	8 (Ph)	0	60/60	1-C_6	0	0	0	—	—	—	—	—	—	—
10	1 (Ph)	1	60/60	1-C_6 [g]	54[h]	325	65.1	nd	0	80.4	0.1	18.7	0.8	0
11	2 (Ph)	2	60/60	1-C_6 [g]	58[h]	349	69.8	nd	0	72.3	0.2	27.5	0	0
12	2 (Ph)	4	60/60	1-C_6	108	432	43.2	95.3	0	57.1	0	42.9	0	0
13	3 (Ph)	3	60/60	1-C_6 [g]	45	270	54.0	nd	0	63.1	0.1	36.8	0	0
14	1 (Ph)	0.5 (dabco)	60/60	1-C_6 [g]	46	275	55.0	nd	0	88.1	0.1	9.7	2.0	0
15	2 (Ph)	1 (dabco)	60/60	1-C_6 [g]	56	338	67.6	nd	0	79.2	0.3	20.5	0	0
16	3 (Ph)	1.5 (dabco)	60/60	1-C_6 [g]	56	336	67.2	nd	0	73.8	0.2	26.0	0	0
17	1 (Ph)	0	20/20	1-C_5	157	630	48.7	nd	0	57.8	0	42.0	0.2	0
18	2 (Ph)	0	20/20	1-C_5	218	870	87.0	nd	0.2	55.7	0	44.0	0.1	0
19	3 (Ph)	0	20/20	1-C_5	226	904	90.4	nd	0.2	58.4	1.9	36.6	2.2	0.7
20	4 (Ph)	0	20/20	1-C_5	211	845	84.5	nd	0.2	59.4	1.8	35.6	2.3	0.7
21	1 (Ph)	1	20/20	1-C_5	209	835	83.5	nd	0.2	57.1	0	42.7	0.1	0
22	1 (Ph)	3	20/20	1-C_5	202	808	80.8	nd	0.2	61.5	1.2	35.3	1.4	0.5
23	2 (Ph)	4	20/20	1-C_5	149	595	59.5	nd	0	56.1	0	43.9	0	0
24	2 (Ph)	4	100/100[e]	1-C_5	160	321	32.1	nd	0.5	50.9	0.5	48.1	0	0
25	1 (Ph)	0	132/20[f]	1-C_5	23	116	11.6	60.1	0	53.9	0	44.1	0	0
26	2 (4-F-Ph)	4	60/60	1-C_6	102	408	40.7	97.1	0	58.2	0	41.8	0	0
27	2 (4-Me-Ph)	4	60/60	1-C_6	24	95	9.5	80.0	0	57.5	0	42.5	0	0
28	2 (4-Cl-Ph)	4	60/60	1-C_6	14	55	5.5	62.6	0	61.1	0	38.9	0	0

[a] General conditions: 0.1 mmol WCl_6, X mmol $PhNH_2$, Y mmol Et_3N, 1.2 mmol $EtAlCl_2$ (EADC), PhCl (20 mL), catalyst formation period (30 mins @T_F°C), nonane standard (1 mL), catalysis temperature T_C°C, 1-olefin (0.1 mol), 240 mins. [b] (mol olefin)(mol W)$^{-1}$ hr^{-1}. [c] (mol olefin)(mol W)$^{-1}$ [d] Selectivity to the dimer fraction. [e] 120 mins. [f] According to method of US5,059,739, HCl removed *via* reflux under flow of N_2 for 60 mins, then cooled to 25 °C for catalysis, 300 mins. [g] 1-olefin (50 mmol). [h] 360 mins.

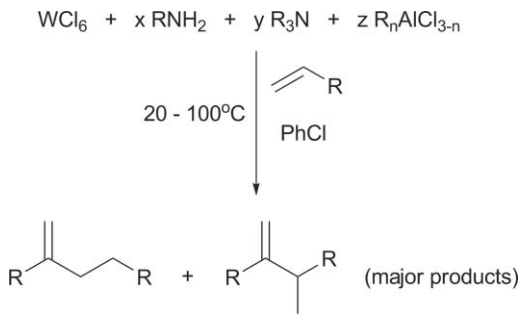

Fig. 1 The dimerisation of α-olefins using a tungsten-based catalyst prepared *in situ*.

using excess aluminium reagent[7a,c] or *via* sparging.[7b] However, there is an economic penalty with both these methods due to the cost of aluminium reagent or of sparging under reflux conditions, which is energetically expensive in chlorobenzene. To surmount these issues the incorporation of base into this catalyst system was explored, in varying ratios, and in combination with differing amounts of aniline (see Table 1). The use of a soluble, organic, low cost base was imperative, thus triethylamine and 1,4-diazabicyclo[2.2.2]octane (dabco) were examined. Table 1, entry 1, reveals that WCl_6 alone does not possess an inherent activity towards olefin dimerisation, no conversion being observed in this case. Thus the requirement for at least some aniline combined with the previous observation of HCl evolution, suggests that the active catalyst is constituted of a W-amido or -imido species, as has been suggested elsewhere.[8]

Initial examination of the base-free system at catalyst formation (T_F) and catalysis (T_C) temperatures of 60 °C (Table 1, entries 2–8), shows a general increase in activity and productivity as the amount of aniline is increased from 1 to 6 equivalents. However, it is strongly suspected that at least some of the aniline is behaving as a Lewis base and sequestering the HCl evolved, as in the case where 6 equivalents are employed, if all reacted with WCl_6, there would presumably be no vacant sites left at which catalysis could proceed. Indeed, when 8 equivalents of aniline are utilised this situation maybe realised, as no catalysis is observed (entry 9). However, an alternative explanation maybe that excess aniline coordinates to the active species, blocking catalysis. In terms of selectivity, it can be seen that a distinct swing in the degree of branching within the dimer fraction is observed when between 2.5 and 3 equivalents of aniline (entries 2–5 *vs.* 6–8) are employed, and a second shift on moving to 6 equivalents, suggesting significant changes to the structure of the active species occur at these points—possibly from amido to imido, or from mono- to *bis*-amido/imido tungsten species. Given the assumption that at least some of the aniline added is behaving not as a ligand precursor, but merely as a base scavenging HCl, the use of the tertiary amine bases triethylamine and dabco in conjunction with

Table 2 Effect of aluminium activator on α-olefin dimerisation[a]

Entry	Al activator (eq)	Act[b]	TON[c]	Conv (%)	S[d] (%)	Branching Selectivity		
						Lin	MB	DB
1	$AlCl_3$ (5)	—	—	0	—	—	—	—
2	$AlCl_3$ (15)	—	—	0.5	0	—	—	—
3	$AlCl_3$ (30)	—	—	0.6	0	—	—	—
4	EADC (5)	—	—	0.5	0	—	—	—
5	EADC (15)	21	427	42.7	98.4	1.1	58.3	40.5
6	EADC (30)	32	636	63.6	91.3	0.8	54.2	45.0
7	EASC (5)	6	110	11.0	99.3	0.5	62.9	36.6
8	EASC (10)	25	496	49.6	98.8	0.4	61.0	38.6
9	EASC (15)	14	272	27.2	98.3	0.4	60.3	39.3
10	EASC (30)	12	238	23.8	91.3	0.3	59.5	40.2
11	$AlEt_3$ (5)	—	—	0	—	—	—	—
12	$AlEt_3$ (10)	—	—	0	—	—	—	—
13	$AlEt_3$ (15)	—	—	0	—	—	—	—
14	$AlEt_3$ (30)	—	—	0	—	—	—	—
15	MAO (10)	—	—	0	—	—	—	—
16	MAO (25)	—	—	0.5	0	—	—	—
17	MAO (50)	—	—	0.7	0	—	—	—
18	MAO (100)	—	—	0.8	0	—	—	—
19	MAO (150)	—	—	0.7	0	—	—	—
20	$EtOAlEt_2$ (5)	—	—	0	—	—	—	—
21	$EtOAlEt_2$ (15)	—	—	0	—	—	—	—
22	$EtOAlEt_2$ (30)	—	—	0.5	0	—	—	—
23	$(Me\{Cl\}Al)_2O$ (5)	—	—	0.5	0	—	—	—
24	$(Me\{Cl\}Al)_2O$ (15)	4	73	7.3	94.5	2.8	63.4	33.9
25	$(Me\{Cl\}Al)_2O$ (30)	2	35	3.5	85.3	3.9	63.5	32.6
26	$(Et\{Cl\}Al)_2O$ (5)	—	—	0.5	0	—	—	—
27	$(Et\{Cl\}Al)_2O$ (15)	0.5	10	1	96.5	4.9	55.8	35.8
28	$(Et\{Cl\}Al)_2O$ (30)	7	138	13.8	96.5	1.6	56.6	38.3
29	$(iBu\{Cl\}Al)_2O$ (5)	—	—	0.5	0	—	—	—
30	$(iBu\{Cl\}Al)_2O$ (15)	2	38	3.8	0	—	—	—
31	$(iBu\{Cl\}Al)_2O$ (30)	4	81	8.1	89.3	0.6	57.3	31.4

[a] General conditions: 0.067 mmol WCl_6, 0.13 mmol $PhNH_2$, 0.27 mmol Et_3N, Al activator, PhCl (8 mL), catalyst formation period (30 mins @60 °C), nonane standard (1 mL), catalysis temperature 60 °C, 1-hexene (67 mmol), 20 h. [b] (mol 1-C_6)(mol W)$^{-1}$ hr^{-1}. [c] (mol 1-C_6)(mol W)$^{-1}$. [d] Selectivity to the dimer fraction.

aniline were examined. It can be seen that triethylamine gave a more productive and active catalyst as compared to that obtained using an analogous loading of tertiary amine *via* dabco (entries 10 and 14 *vs.* 11 and 15), although using dabco favoured the production of methyl-branched dimers. Comparing 2 equivalents of aniline with 1 equivalent each of aniline and triethylamine (entry 4 *vs.* entry 10) reveals an increase in activity, but a drop in selectivity to monomethyl-branched dimer. However, comparing entries 7 and 11 (4 equivalents of aniline *versus* 2 equivalents aniline and 2 equivalents of triethylamine) reveals an increase in activity and doubling of productivity, but a remarkably similar branching selectivity. Finally, comparing the system generated using 6 equivalents of aniline (entry 8) with that using 2 equivalents of aniline and 4 of triethylamine (entry 12), or 3 equivalents of both (entry 13), reveals a drop in activity, and a swing away from dimethyl-branched dimers to monomethyl-branched. Thus it is difficult to draw general conclusions regarding the effect of triethylamine. For entry 12, a mass balance was performed against an internal standard (nonane) and this revealed a selectivity to the dimer fraction (*versus* the formation of heavy products) of 95.3%, which is high compared to most catalysts available for the dimerisation of α-olefins. The heavy products observed were largely trimers and tetramers, with trace pentamers occasionally present. No polymer products were ever observed.

Previous literature reports have employed an elevated temperature during the catalyst formation period (T_F),[7] so to probe the necessity of this a set of tests were undertaken with a T_F of 20 °C (Table 1, entries 17–23). As can be seen, the observed activities and selectivities are relatively insensitive to the wide variance in aniline and triethylamine loading, suggesting that complete formation of the pre-catalyst species achieved at 60 °C does not occur at 20 °C. In order to probe the other extreme, a run was undertaken with T_F and T_C at 100 °C in an autoclave (Table 1, entry 24). This run gave the lowest selectivity to methyl-branched dimers observed and showed half the productivity of the equivalent run with T_F and T_C of 20 °C (entry 23). For the purposes of comparison with the literature, a run was conducted under the conditions employed by Hendrikson (entry 25);[7b] namely a T_F of 132 °C (chlorobenzene at reflux) for 30 min with N_2 sparging. As can be seen this gave a poorly active catalyst as compared with the protocols employed herein, and a lower selectivity to methyl-branched dimer. Significantly, the selectivity to the dimer fraction in this case, was found to be low at 60% (*cf*. entry 12, >95%).

The penultimate vector probed was the choice of aniline (Table 1, entries 26–28), as a previous report using W-imido complexes for propene dimerisation had clearly shown a rate enhancement when the aniline ring was substituted by electron withdrawing groups, and conversely a rate reduction for electron

Table 3 Effect of aluminium activator on α-olefin dimerisation[a]

		At 30 min				At 300 min				Branching selectivity					
Entry	Al activator (eq)	Act[b]	TON[c]	Conv (%)	S[d](%)	Act[b]	TON[c]	Conv (%)	S[d](%)	Linear	Me	Et	MeMe	MeEt	EtEt
1	EADC (12)	1025	513	57.3	>99.9	129	646	72.3	>99.9	0.2	57.3	0	42.5	0	0
2	EADC (12)	1019	510	57.8	>99.9	128	642	72.8	>99.9	0.2	57.4	0	42.4	0	0
3	EASC (6)	410	205	23.7	69.7[e]	60	298	34.4	99.6	0	63.0	0	37.0	0	0
4	EASC (12)	696	348	39.7	84.3[e]	101	503	57.3	99.6	0.2	60.5	0	39.3	0	0
5	DEAC (12)	59	29	1.9	31.8	33	163	5.1	96.8	0.5	69.2	0	30.3	0	0
6	MADC (12)	65	32	3.0	95.5	102	510	48.4	78.5	0.4	50.4	0	49.2	0	0
7	EADB (12)	153	76	8.6	0	18	92	10.4	0	—	—	—	—	—	—
8	EADB (20)	133	67	7.7	42.5	133	67	7.7	42.5	0.0	67.9	0	32.1	0	0

[a] General conditions: 0.1 mmol WCl_6, 0.2 mmol $PhNH_2$, 0.4 mmol Et_3N, Al activator, PhCl (10 mL), catalyst formation period (30 mins @45 °C), nonane standard (1 mL), catalysis temperature 45 °C, 1-hexene (~0.1 mol). [b] (mol 1-C_6)(mol W)$^{-1}$ hr^{-1}. [c] (mol 1-C_6)(mol W)$^{-1}$. [d] Selectivity to the dimer fraction. [e] See ref. 12.

donating groups.[8] It can be seen that introduction of a *p*-methyl group on the phenyl ring leads to a drop in rate of one order of magnitude, as expected from comparison with previous related work.[8] Surprisingly, however, the introduction of a *p*-fluorine substituent had no effect on catalysis in terms of selectivity (to the dimer fraction or within the dimer fraction) or activity, suggesting that a more electrophilic tungsten centre does not accelerate the rate determining step or influence the regiochemistry of coupling. Curiously, the *p*-chloro analogue performed worse than *p*-methyl, something that could be attributed to reaction with the aluminium activator *in situ* to yield a *p*-ethyl group, which then behaves in a very similar fashion to the *p*-methyl.[10] Finally, the use of $MoCl_5$ with aniline and triethylamine in place of WCl_6, was also examined; however, in these cases less than 2% conversion of the α-olefin substrate was observed.

From this initial screening the catalyst system employing WCl_6, $PhNH_2$ and Et_3N in a 1 : 2 : 4 ratio was chosen for further study on account of good activity at both 20 and 60 °C, and its selectivity towards only methyl- and dimethyl-branched products. The nature of the aluminium activator is well known to have a dramatic effect upon the activity and selectivity of many polymerisation and oligomerisation processes,[2-5,7-8,11] hence a number of alternatives were examined with this system (see Tables 2 and 3). Inspection of these results reveals a clear trend; the presence of both an alkyl and a halide group at the aluminium centre are crucial to catalysis, all of $EtAlCl_2$ (EADC), $Et_3Al_2Cl_3$ (EASC) and Et_2AlCl (DEAC) giving active systems, whilst $AlEt_3$, $AlCl_3$, $EtOAlEt_2$ and methylaluminoxane (MAO) all failed to promote dimerisation. Further substantiation of this conclusion comes from the use of $\{R(Cl)Al\}_2O$ (R = Me, Et, ^{i}Bu) based activators, which also gave catalysis, but were less active and productive than the simple alkyl aluminium halide species.

Table 3 shows some further results with the optimal activators (entries 1–5), along with variations chosen to further probe the constitutional requirements of the halide and alkyl substituents at aluminium (entries 6–8). Entries 1 and 2 illustrate the typical reproducibility of the catalysis reported herein; a variability in branching selectivity of ±0.1% is representative, whilst the variability in activity and turnover number (TON) is small enough to be within the experimental error for these particular two examples. It can be seen that under these conditions ($T_F = T_C =$ 45 °C) the selectivity to the dimer fraction with EADC is >99.9%, making this a very efficient catalyst in terms of substrate usage. The results shown in Table 2 reveal that when EADC was employed at low loadings (5 equivalents, entry 4), almost no activity was observed; whereas EASC gave an active catalyst across the range 5–30 equivalents (entries 7–10). Thus the use of EASC was examined at 6 and 12 equivalents under these conditions (Table 3). As can be seen, the higher loading gave the more active catalyst, but in both cases this was inferior to the EADC-based system, in terms of both activity/productivity and selectivity to the dimer fraction. It should be noted at this juncture that an examination of entries 3 and 4 in Table 3, reveals a significant increase in selectivity to the dimer fraction between 30 and 300 min. This is an artefact of the way in which the intermediate samples are taken and worked up during catalysis.[12] A comparison of entries 1, 4 and 5 reveals a clear trend of increasing performance as one moves through the series Et_2AlCl, $Et_3Al_2Cl_3$ and $EtAlCl_2$, suggesting that only a single alkyl group is necessary to alkylate the tungsten centre, whilst maximising the number of halide substituents enhances activity. An explanation for this may lie with the enhanced Lewis acidity of the aluminium species with more halide substituents. This elevated Lewis acidity may in turn be important as it will lead to enhanced interactions between the N-donor ligand and aluminium activator, such species having been observed experimentally,[13] and suggested computationally.[14]

The use of $MeAlCl_2$ (MADC) was examined to probe the necessity of β-hydrogens on the alkyl group in the aluminium activator. As can be seen from Table 3, entry 6 catalysis was successfully initiated by MADC, although the performance was significantly attenuated as compared to EADC. Nonetheless, this result suggests that a β-hydrogen elimination pathway from a tungsten alkyl generated *in situ* is not involved in the mechanistic trajectory followed during catalyst activation. Given the observation that the presence of a halide in the aluminium activator compound is essential, and the proclivity of such species to form halide bridges with themselves and active catalyst species,[15,16] the impact of the nature of the halide on activity was probed by investigating $EtAlBr_2$ (EADB, entries 7–8). The effect was dramatic; the resultant catalyst being far less active and much less selective to the dimer fraction, suggesting that the halide is indeed intimately involved in the active catalytic species, and supporting a similar proposition resulting from computational studies.[14]

Table 4 Effect of solvent choice upon α-olefin dimerisation[a]

Entry	Solvent	Act[b]	TON[c]	S [d](%)
1	Toluene	35.3	35.3	82.8
2	Xylenes	30.3	30.3	64.0
3	s-Butylbenzene	21.9	21.9	22.7
4	t-Butylbenzene	19.8	19.8	41.0
5	Cumene	25.6	25.6	73.7
6	Heptane	30.5	30.5	79.5

[a] General conditions: 0.1 mmol WCl_6, 0.2 mmol $PhNH_2$, 0.4 mmol Et_3N, EADC (1.2 mmol), solvent (10 mL), catalyst formation period (30 mins @ 60 °C), nonane standard (1 mL), catalysis temperature 60 °C, 1-hexene (0.1 mol), 60 mins. [b] (mol 1-C_6)(mol W)$^{-1}$ hr^{-1}. [c] (mol 1-C_6)(mol W)$^{-1}$. [d] Selectivity to the dimer fraction.

The catalysis described thus far was conducted in chlorobenzene, but the ability to use the most benign solvent possible for catalysis is always desirable, thus the effect of different reaction solvents was explored. Initial attempts to use pure hydrocarbon solvents were unsuccessful (Table 4), largely due to the lack of solubility of the catalyst system. Thus a set of strong donor solvents (THF, PhOMe and MeCN) was explored (see Table 5, entries 2, 3 and 4). Despite very good solubility of the catalyst in these media, only poor activity was observed, most probably due to competition between the substrate olefin and the solvent for binding at the metal centre. In order to probe this donor solvent inhibition further, a run was performed using chlorobenzene spiked with 0.5% by volume *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda); here again catalysis was effectively shutdown (entry 11). Catalysis in chlorinated alkane solvents did proceed, but did not show any improvement over chlorobenzene (entries 5–8). In DCM, only slightly attenuated activity and productivity as compared to chlorobenzene was observed. The selectivity to the dimer fraction remained unchanged, whilst the selectivity within the dimer fraction was perturbed towards dimethyl-branched dimers (entry 5). Reactions undertaken in chloroform showed a very high activity, but extremely low selectivity to the dimer fraction (entry 7). Chlorinated ethanes showed a good selectivity to the dimer fraction at 30 min, but after extended catalysis periods this dropped significantly, suggesting that catalyst decomposition had occurred (entries 6 and 8). Finally, the use of chlorinated additives was examined, such species having been utilised in the Phillips trimerisation system, where they are believed to interact with $Et_xAlCl_{(3-x)}$ type activators altering the nuclearity in solution.[16] Hexachlorobenzene had no effect within experimental error (entry 9), whilst hexachloroethane was detrimental, especially at longer reaction times, again confirming this trend for chlorinated ethanes (entries 10, and 6, 8).

The catalysis described thus far, has variously used 1-pentene, 1-hexene and 1-heptene substrates under slightly different reaction conditions, hence it was of interest to make a meaningful comparison under the same conditions, of the differences as the α-olefin chain length increases (C_5–C_9). The results of this are tabulated in Table 6, and shown graphically in Fig. 2–4. It is noted that the catalyst behaves fairly uniformly in terms of branching selectivity within the dimer fraction (Table 3, Fig. 2); there being a trend towards increased monomethyl-branched product formation as the olefin substrate mass increases, reaching a maximum at 1-heptene, after which it subsides. In terms of activity,

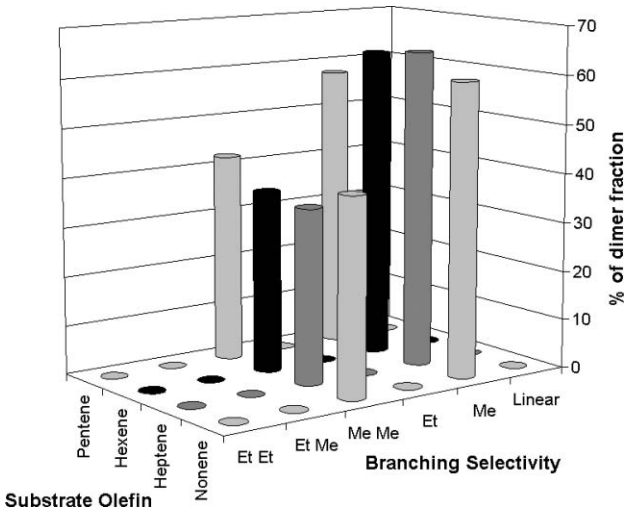

Fig. 2 Branching selectivity obtained with different olefin substrates (see Table 6 for experimental details).

an examination of the data at 30 min reveals the expected trend of decreasing activity as substrate molecular weight increases (Table 3 and Fig. 3). However, there are also some distinct anomalies; it is noted that 1-nonene is converted particularly slowly and that the selectivity to the dimer fraction is very poor (entry 4). This is rationalised as follows: 1-nonene is not substantially different from its dimerisation product in terms of inherent activity towards oligomerisation, and thus there is little differentiation by the catalyst between binding and oligomerising 1-nonene or its C_{18} dimer product, which is primarily an α,α′-disubstituted olefin. Perhaps a more significant anomaly is the lack of further 1-pentene conversion after 30 min. Despite a very fast initial rate of reaction with 1-pentene being observed, this is followed by complete catalyst deactivation, consistently and repeatedly. This is in part rationalised as being due to poor solubility of the catalyst in the chlorobenzene–1-pentene solvent mixture. To investigate this, a run was performed at a higher dilution and with much higher 1-pentene loading (under the conditions used for Table 6, entry 1, the catalyst was 4.6 mM, in a total volume of 21.6 mL of PhCl : 1-C_5 {1 : 0.73}, whereas in entry 5 the catalyst was 0.6 mM in a total volume of 618 mL of PhCl : 1-C_5 {1 : 2.085}), and under these conditions the catalyst does not deactivate after 30 min (entry 5). This unusual behaviour with 1-pentene remains without good explanation, as when the volume of chlorobenzene was dramatically increased, without also increasing the 1-pentene loading, catalyst deactivation was still seen after 30 min, indicating solubility alone was not the issue.

Two runs were also performed at increased loadings of 1-heptene whilst keeping the chlorobenzene solvent volume constant; these gave higher activities and productivities as expected (entries 6 and 7), although upon inspection entry 7 does not appear proportionately more active than entry 6. This observation is assigned to catalyst poisoning by trace impurities in the 1-heptene substrate, which at such high substrate loading begin to overwhelm the active species. Notably, with both entries 6 and 7, the selectivity to the dimer fraction and the branching selectivity remained unchanged compared to entry 3.

In terms of longevity of the active catalyst, the reactions described by Table 6 entries 2–7 were all allowed to run for a

Table 5 Impact of reaction of solvent upon α-olefin dimerisation[a]

		At 30 min				At 240 min				Branching selectivity					
Entry	Solvent	Act[b]	TON[c]	Conv (%)	S [d](%)	Act[b]	TON[c]	Conv (%)	S [d](%)	Linear	Me	Et	MeMe	MeEt	EtEt
1	PhCl	662	331	34.6	99.7	149	594	62.2	>99.9	>0.1	62.1	0	37.9	0	0
2	THF	0	0	0	—	0	0	0	—	—	—	—	—	—	—
3	PhOMe[e]	0	0	0	—	0	0	0	—	—	—	—	—	—	—
4	MeCN	0	0	0	—	33	142	15.5	0	—	—	—	—	—	—
5	DCM	562	281	30.1	>99.9	133	574	61.6	>99.9	>0.1	55.4	0	44.6	0	0
6	1,1,2,2-$C_2H_2Cl_4$	356	178	19.0	94.7	155	671	71.7	14.6	>0.1	69.6	0	30.4	0	0
7	$CHCl_3$	1923	961	96.6	5.3	244	975	97.9	5.0	—	—	—	—	—	—
8	1,2-$C_2H_4Cl_2$	838	419	43.9	>99.9	187	750	78.5	22.3	>0.1	62.4	0	37.6	0	0
9	PhCl + 2 g C_6Cl_6	553	277	28.5	99.1	149	597	61.5	>99.9	>0.1	62.2	0	37.8	0	0
10	PhCl + 2 g C_2Cl_6	328	164	17.0	90.0	193	772	80.1	12.4	>0.1	75.9	0	24.1	0	0
11	PhCl + 0.5% tmeda	41	20	2.1	78.8	No further conversion				>0.1	64.0	0	36.0	0	0

[a] General conditions: 0.2 mmol WCl_6, 0.4 mmol $PhNH_2$, 0.8 mmol Et_3N, EADC (2.4 mmol), solvent (20 mL), catalyst formation period (30 mins @40 °C), nonane standard (2 mL), catalysis temperature 40 °C, 1-heptene (0.2 mol), 240 mins. [b] (mol 1-C_7)(mol W)$^{-1}$ hr^{-1}. [c] (mol 1-C_7)(mol W)$^{-1}$. [d] Selectivity to the dimer fraction. [e] 1 mmol WCl_6, 2 mmol $PhNH_2$, 4 mmol Et_3N, EADC (12 mmol), PhOMe (200 mL), nonane standard (10 mL), 35 °C, 1-pentene (1 mol), 240 mins.

Table 6 The dimerisation of α-olefins with increasing molecular weight[a]

		At 30 min				At 360 min				Branching selectivity					
Entry	Olefin (eq)	Act[b]	TON[c]	Conv (%)	S [d](%)	Act[b]	TON[c]	Conv (%)	S [d](%)	Linear	Me	Et	MeMe	MeEt	EtEt
1	1-Pentene (834)	379	189	22.7	15.2[e]	No further conversion	>0.1	57.7	0	42.3	0	0			
2	1-Hexene (885)	183	92	10.4	77.4[e]	99	594	67.1	>99.9	>0.1	63.1	0	36.9	0	0
3	1-Heptene (920)	84	167	18.2	85.7[e]	94	563	61.8	>99.9	>0.1	64.4	0	35.6	0	0
4	1-Nonene (972)	14	28	2.9	20.6	5	28	2.8	30.5	>0.1	59.8	0	40.2	0	0
5	1-Pentene (3818)[f]	136	68	1.8	86.3[e]	112	673	17.6	99.8	>0.1	58.2	0	41.8	0	0
6	1-Heptene (2500)	433	217	8.7	86.4[e]	199	1193	47.7	>99.9	>0.1	64.3	0	35.7	0	0
7	1-Heptene (5000)	746	373	7.5	90.5[e]	213	1279	25.6	>99.9	>0.1	64.6	0	35.4	0	0

[a] General conditions: 0.1 mmol WCl_6, 0.2 mmol $PhNH_2$, 0.4 mmol Et_3N, EADC (1.2 mmol), PhCl (12.5 mL), catalyst formation period (30 mins @30 °C), nonane standard (1 mL), catalysis temperature 20 °C, α-olefin, 360 mins. [b] (mol olefin)(mol W)$^{-1}$ hr^{-1}. [c] (mol olefin)(mol W)$^{-1}$. [d] Selectivity to the dimer fraction. [e] See ref. 12 [f] 0.4 mmol WCl_6, 0.8 mmol $PhNH_2$, 1.6 mmol Et_3N, EADC (4.8 mmol), PhCl (200 mL), catalyst formation period (30 mins @30 °C), nonane standard (1 mL), catalysis temperature 20 °C, α-olefin, 360 mins.

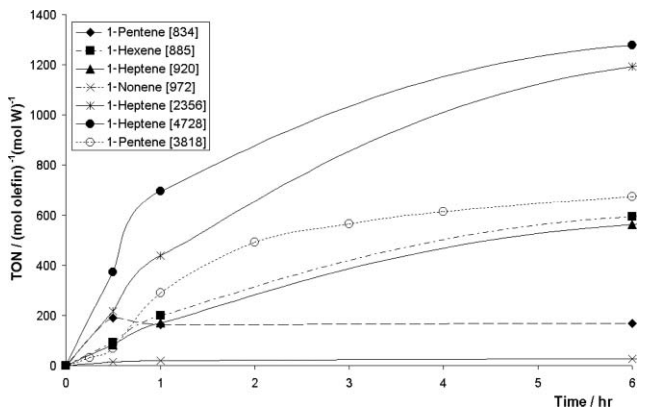

Fig. 3 TON's obtained with different olefin substrates (see Table 6 for experimental details).

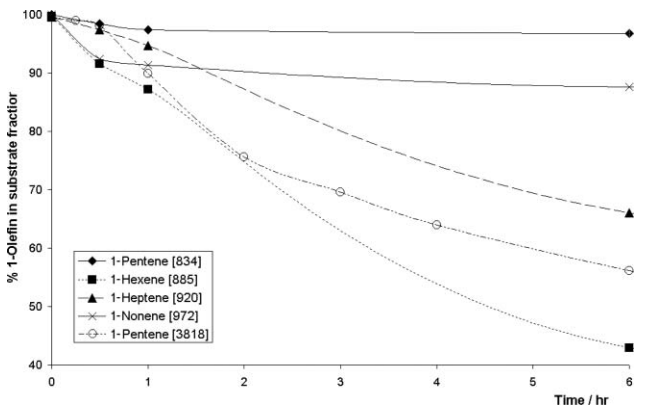

Fig. 4 The extent of isomerisation of the substrate olefin (see Table 6 for experimental details).

duration of 24 h. The catalyst remained active throughout this time, but little further conversion occurred after the initial 6 h. Considering the kinetics of dimerisation reactions, one would expect catalysis of this type to be higher order in substrate, and thus show a markedly reduced activity once high conversions are reached.[17] However, catalyst decomposition is potentially a further contributing factor to this type of behaviour and should be apparent when kinetic analyses are applied. However, one more vector must be considered, namely isomerisation of the α-olefin substrate to internal olefins. The catalyst shows isomerisation activity towards the α-olefin substrate to give a mixture of terminal and internal olefins, but appears capable of dimerising only α-olefins (*vide infra*). Hence, the effective concentration of α-olefin substrate will be diminished not just by dimerisation,

but by isomerisation processes as well. We thus undertook to determine the order of reaction in substrate, and attempt to deconvolute the effects of substrate isomerisation and catalyst deactivation, the results being depicted graphically in Fig. 5. The first reaction examined was the larger scale dimerisation of 1-pentene (Table 6, entry 5), because this reaction was sampled with increased frequency during catalysis. For plots of [1-C_5], ln([1-C_5]$_t$/[1-C_5]$_0$) and 1/[1-C_5] *versus* time, only the latter showed an approximately linear relationship, indicative of a second order dependence on the substrate. However, as can be seen from Fig. 5a, there was a distinct deviation from linearity, especially after 6 h. It should be noted that the substrate concentration values calculated for the plots in Fig. 5a were based upon the entire C_5 fraction, *i.e.* both unreacted and isomerised substrate. Thus, as the extent of isomerisation was quantified from the GC samples (see Fig. 4), the data was reprocessed based upon the concentration of 1-pentene specifically, as this is believed to be the only true substrate. Indeed, as can be seen from Fig. 5b, a linear plot was now obtained for 1/[1-C_5], which allowed derivation of a second order rate constant of 2.07×10^{-5} dm^{-3} mol^{-1} s^{-1}. It should be noted that a very small deviation from linearity remains, which is therefore indicative of trace catalyst decomposition.

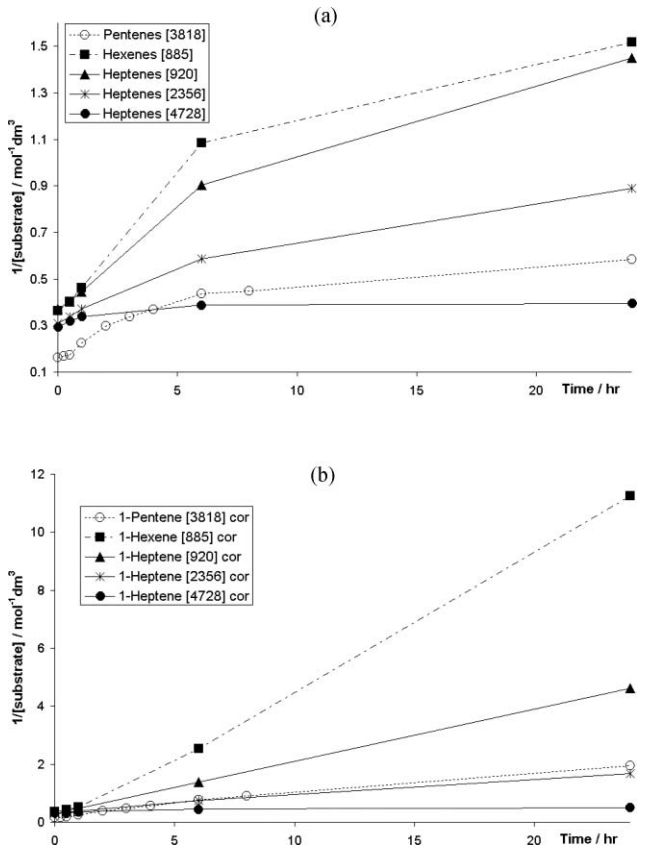

Fig. 5 (a) Plots of 1/[substrate] *versus* time for data from Table 6. (b) Plots of 1/[substrate] *versus* time for data from Table 6 after correction of [substrate] by removal of the contribution from internal olefins.

A similar analysis was performed on the data presented in Table 6, entries 2 and 3, in order to determine second order rate constants for the dimerisation of 1-hexene (1.28×10^{-4} dm^{-3} mol^{-1} s^{-1}) and 1-heptene (4.97×10^{-5} dm^{-3} mol^{-1} s^{-1}) under comparable reaction conditions. These values follow the trend expected, namely that as the substrate olefin increases in mass, its inherent reactivity towards oligomerisation decreases. As can be seen from Fig. 5a and 5b, once again the concentration of α-olefin rather than that of all isomers of the substrate is the crucial factor, and when this is accounted for, no signs of catalyst deactivation during catalysis are evident. Lastly, the reactions with elevated loadings of 1-heptene were examined (Table 6, entries 6 and 7), yielding second order rate constants of 1.56×10^{-5} dm^{-3} mol^{-1} s^{-1} and 2.10×10^{-5} dm^{-3} mol^{-1} s^{-1}, respectively. Fig. 5b shows that for 2356 equivalents of 1-heptene only a very slight deviation from linearity exists, whereas for 4728 equivalents of 1-heptene, a more marked deviation is present, strongly suggesting that at this substrate loading, catalyst poisoning is starting to become significant (*vide supra*).[18]

The finding that the $WCl_6 : PhNH_2 : Et_3N$ (1 : 2 : 4) catalyst system shows some activity towards isomerisation of the feed olefin (Fig. 4) is significant from a process perspective, as recycling of unreacted olefin feed is greatly facilitated if it remains un-isomerised. A further question is whether the catalyst is able to process olefin substrate once it has been isomerised to internal isomers. The branching selectivity with C_5–C_9 α-olefin substrates reveals no formation of branches longer than methyl which suggests that internal olefins are not converted. However, in order to probe this definitively, it was decided to investigate the behaviour of the catalyst system towards internal olefins. Thus, in six separate experiments, fresh batches of *in situ* prepared catalyst were exposed to *cis*-2-pentene, *trans*-2-pentene, *cis*-2-hexene, *trans*-2-hexene, *cis*-2-heptene and *trans*-2-heptene. In each case, no dimerisation activity or isomerisation of the double bond position was observed, although in the case of *cis*-2-pentene and *cis*-2-hexene, there was a small degree of isomerisation in the conformation of the double bond from *cis* to the more thermodynamically stable *trans* isomer (~ 15%).

Whilst isomerisation of the relatively light substrate olefins occurs, it was strongly suspected that the catalyst system had a very low propensity towards isomerisation of the product olefins. This inference is based upon the observation that the major products are the mono- and di-branched methylidene species (*vide infra*), which as terminal olefins are thermodynamically disfavoured. Thus, if isomerisation processes were facile for this catalyst, these products would not be isolated. However, to check this assertion, in two separate experiments fresh batches of *in situ* prepared catalyst were exposed to 4-methyl-4-nonene and 2-propyl-1-heptene. In both cases no isomerisation was observed, however with the 2-propyl-1-heptene (an α,α-substituted olefin) a small amount of dimerisation did occur (17.8% conversion after 4 h).

Product identification

From the catalysis performed we have clearly identified the selectivity towards dimerisation, and also identified the branching selectivity within the dimer fraction. The latter parameter was determined *via* hydrogenation of the product mixture using a hydrogenative GC method (see experimental section), although selected samples were also hydrogenated on a larger scale using Pd/C to confirm the veracity of the hydrogenative GC technique. The correlation between the results obtained by the two different methods was always in good agreement (< ±0.1%). A typical GC

trace of the product after hydrogenation can be seen in Fig. 6; the double peak for 4,5-dimethyloctane arises due to separation of the diastereoisomeric pairs present for this compound. As the EI mass spectra for different isomers of heavy alkanes can be very similar, identification *via* GC-MS alone can leave uncertainty, hence the alkanes were also identified *via* comparison with authentic standards, which were synthesised where necessary (4-methylnonane, 4,5-dimethyloctane).

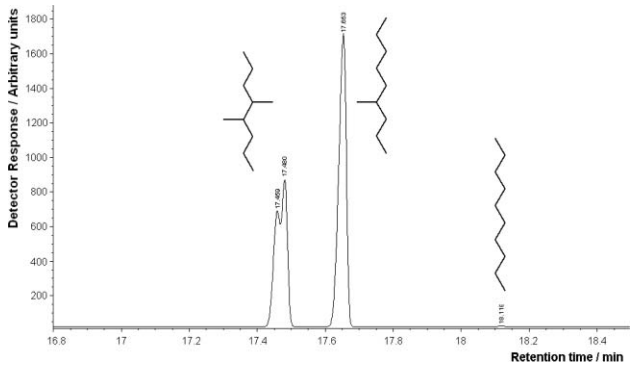

Fig. 6 The C_{10} region of a typical GC-trace from 1-pentene dimerisation using $WCl_6 : PhNH_2 : Et_3N$: EADC (1 : 2 : 4 : 12) after hydrogenation.

The further piece of analysis required is the selectivity towards specific olefin isomers within the variously branched skeletons. As with heavy alkanes, the rigorous identification of various heavy alkene isomers can be troublesome *via* routine GC-MS techniques due to the similarity of the compounds. This also hinders NMR analysis, which is additionally complicated by the complexity of the product mixture. Thus in order to probe the products of 1-pentene dimerisation, and knowing the carbon skeletons present, we undertook the synthesis of the relevant isomers of $C_{10}H_{20}$ that could not be obtained commercially. Specific focus was upon the 4-methylnonene skeleton, all nine isomers proving accessible *via* either Wittig synthesis or lithium-cuprate-based coupling (see ESI† for experimental details). A GC methodology was established that allowed the separation of all isomers, and hence, *via* comparison of GC traces of product mixtures and authentic samples it was possible to elucidate the identity of the majority of the olefin products. However, the second most abundant product did not show a GC retention time match with any 4-methylnonene standards and was known from hydrogenation to be a dimethyl-branched species. It was suspected to be a methylidene by comparison with the methyl-branched skeleton and its identity as 2-propyl-3-methyl-1-hexene, was established from a $^{13}C\{^1H\}$ NMR experiment of the product mixture, resonances at δ157.7 and 108.2 being characteristic, and observed in addition to those for 3-propyl-1-heptene (δ150.1 and 109.6). At this stage three trace products remained unassigned. GC-MS analysis of the mixture proved to be decisive in identifying these peaks, unambiguously confirming one to be a C_{10} alkane and the other two as C_{10} dienes. By correlation of the numerical data before and after hydrogenation, the C_{10} alkane was assigned as 4,5-dimethyloctane (Fig. 7). This was verified by a retention time match with an authentic sample and an EI mass spectra match in the GC-MS. Given the detection of the alkane corresponding to the dimethyl-branched C_{10} skeleton, we undertook to look

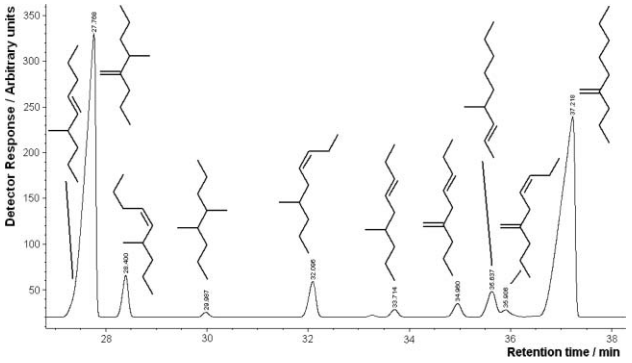

Fig. 7 The C_{10} region of a typical GC-trace from 1-pentene dimerisation using $WCl_6 : PhNH_2 : Et_3N$: EADC (1 : 2 : 4 : 12).

more carefully for the alkane corresponding to the monomethyl-branched skeleton (4-methylnonane), as the formation of one without the other seemed curious. Based on retention times, the GC methods available co-eluted 4-methylnonane with *trans*-2-propyl-1,4-heptadiene (*vide infra*), but from simple GC-MS analysis this peak was known to be the diene. However, extractive ion trace analysis (for *m*/*z*'s 138, 140 and 142 ±0.5) of the GC-MS results revealed that underlying this was a trace amount of alkane, but at such a small level as to be normally undetectable and below the limits of accurate quantification ($\gg$ 0.1%). When catalysis was performed on a larger scale with 1-pentene (Table 6, entry 5) we subjected the product mixture to an automated distillation procedure, which allowed significant fractionation of the products, some cuts being highly enriched in trace compounds. These fractions were subjected to an NMR study and this led to the identification of the previously unspecified diene products as *cis*- and *trans*-2-propyl-1,4-heptadiene, which constitute ~1% and ~2% of the dimer fraction respectively. It will be noted from Fig. 7 (data obtained using a GC instrument equipped with a PONA column), that the peaks for *trans*-6-methyl-4-nonene and 2-propyl-3-methyl-1-hexene overlap. The amounts of these two products could be determined *via* one of two methods; GC using a MDN-12 column allowed separation of these two peaks, whilst hydrogenative GC-analysis (see Fig. 6) allowed the overall branching profile to be determined, and thus the relative amounts of these two products to be deconvoluted. Generally, both these methods were applied to provide a double check, and in all cases were in good agreement (±0.1%).

One final piece of analysis concerned identification of the trace amounts of linear C_{10} species formed. This was performed on both normal strength samples and those enriched in linear C_{10} products after distillation. The analysis *via* both methods was in agreement, but the quantification is taken from the enriched sample analysis. All linear isomers of $C_{10}H_{20}$ with the exception of *cis*-4-decene were commercially available and hence *via* retention time matching, the formation of 1-decene, *cis*/*trans*-2-decene and *cis*/*trans*-3-decene could be eliminated. Five peaks were observed in the linear C_{10} region of the GC chromatogram, and GC-MS analysis revealed one of these to be decane (also confirmed by retention time match), two as linear C_{10} dienes and two as linear C_{10} olefins. As a percentage of the linear C_{10} fraction (which comprises only 0.1% of the total dimer fraction), the components were: *trans*-5-decene (20.1%), *cis*-4-decene (40.4%), diene (16.5%), diene (8.7%),

decane (14.3%). Due to the low concentrations of these species, it proved impossible to determine the precise constitution of the linear dienes. Of the two peaks confirmed by GC-MS to be linear C_{10} olefins, one gave a retention time match most indicative of *trans*-5-decene. However, this assignment is tentative as despite prolonged method development, it proved impossible to achieve baseline separation of *trans*-4-decene and *cis*/*trans*-5-decene, thus there may also be a component of these species in this peak as well. The other peak identified as a linear C_{10} olefin did not show a retention time match with any of the standards available and is thus assigned, *via* a process of elimination, as *cis*-4-decene.

As can be seen from Fig. 7 the catalyst has a clear preference towards the formation of methylidene products, whether mono- or dimethyl-branched, with the remainder featuring internal unsaturation on the chain. The notable absence of the thermodynamically most stable, tri- and tetra-substituted alkene isomers (4-methyl-3-nonene and 4-methyl-4-nonene) again illustrates the lack of isomerisation activity of this catalyst towards the product. When catalysis was performed with 1-hexene, 1-heptene or 1-nonene as substrates, an identical GC fingerprint was obtained for the dimer products, but was shifted to a higher retention time (due to increased carbon number), suggesting that the catalysis selectivity remains unchanged. The observation of alkane and diene products may at first seem surprising, but their formation during α-olefin dimerisation is not without precedent.[19] Comparison with the previous report (19% C_8 alkane, 28% C_8 diene), reveals that the levels of formation seen here are significantly lower (0.5% C_{10} alkane, C_{10} 3.0% diene), but that in both cases the amount of alkane observed is in deficit compared to the amount of diene. It would be expected however that the amounts of diene and alkane should correlate quite closely, unless the excess hydrogen is lost as H_2. In agreement with this,[20] inspection of the liquid fraction in this case reveals the presence of hydrogenated substrate at a level matching that expected,[21] suggesting that equimolar amounts of dienes and alkanes are formed. For example, absolute amounts present at the end of a run: a) pentane (0.277 mmol), 4,5-dimethyloctane (0.059 mmol), C_{10} diene (0.213 mmol), C_{10} diene (0.099 mmol), total alkane (0.336 mmol), total diene (0.312 mmol); b) pentane (0.593 mmol), 4,5-dimethyloctane (0.126 mmol), C_{10} diene (0.438 mmol), C_{10} diene (0.237 mmol), total alkane (0.719 mmol), total diene (0.675 mmol).

In order to probe if there was a temporal dependence of the selectivity to specific olefins, a 1-pentene dimerisation experiment was sampled over time; as can be seen from Fig. 8a and 8b, the catalyst selectivity remains constant.[22] Fig. 8c shows the accumulation of the products in mmols and confirms that catalysis continued to proceed throughout the sampling run, and that the constant selectivity was not due to a deactivated catalyst.

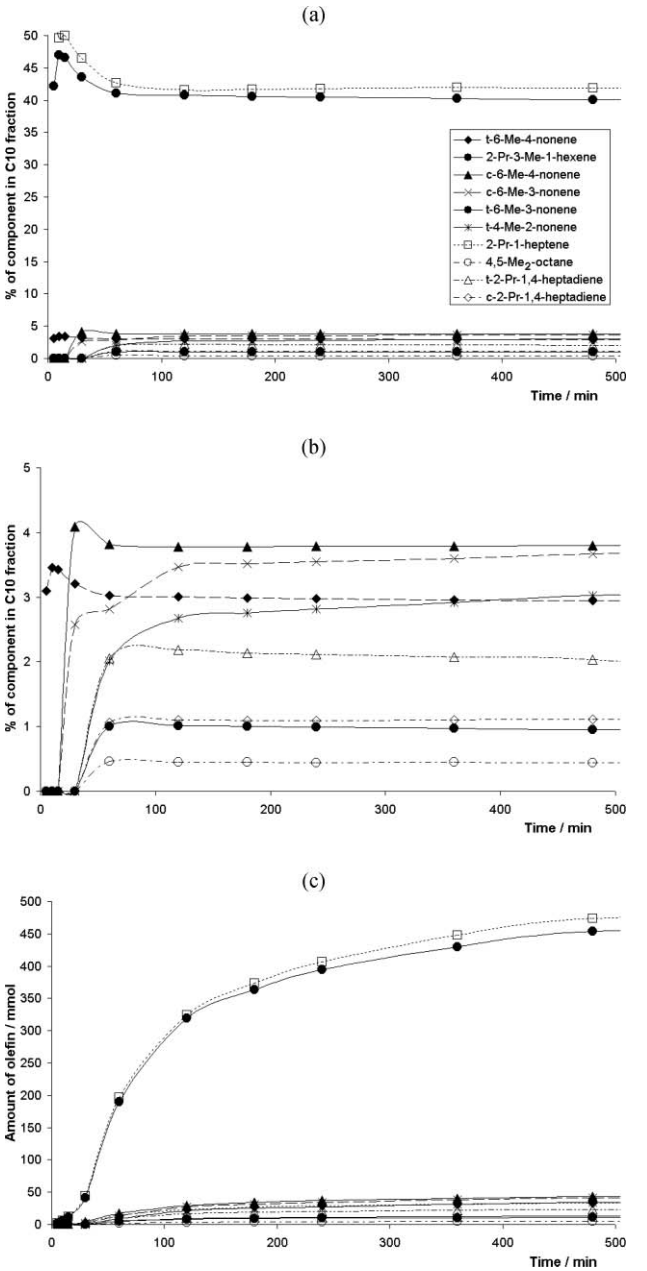

Fig. 8 (a) Product selectivity with time during a 1-pentene dimerisation using $WCl_6 : PhNH_2 : Et_3N$: EADC (1 : 2 : 4 : 12). (b) Expansion of ordinate to show the levels of minor products more clearly.[22] (c) Absolute amount of olefins formed with time.

Mechanistic considerations

Given the number of possible isomers of $C_{10}H_{20}$ (57 including *cis*/*trans* isomerisation) that could arise from the dimerisation of 1-pentene, the primary selectivity of this catalyst to just 8 isomers (plus trace alkanes and dienes) is quite remarkable. In part this is accounted for by the fact that the catalyst only dimerises terminal olefins and does not show any isomerisation activity towards the dimer products. This leads to mechanistic speculation, all of the products observed being accessible *via* metallacyclic[23] or Cossee-type[2b,24] mechanistic pathways. A metallacyclic pathway is often invoked for highly selective catalysts and not unreasonable for a group six metal given the precedents with chromium.[23] Indeed, Olivier *et al.* propose a metallacyclic pathway for dimerisation catalysis with tungsten-imido complexes,[8] although no experimental evidence is available in support. Reference is made to the isolation by Boncella *et al.* of an imido-tungstanacyclopentane complex, which whilst confirming the existence of metallacyclic species for tungsten, was the deactivation by-product from metathesis.[25] This, coupled with the ability to isolate and characterise this species suggests that it is kinetically inert, resisting breakdown of the metallacycle and hence perhaps not a

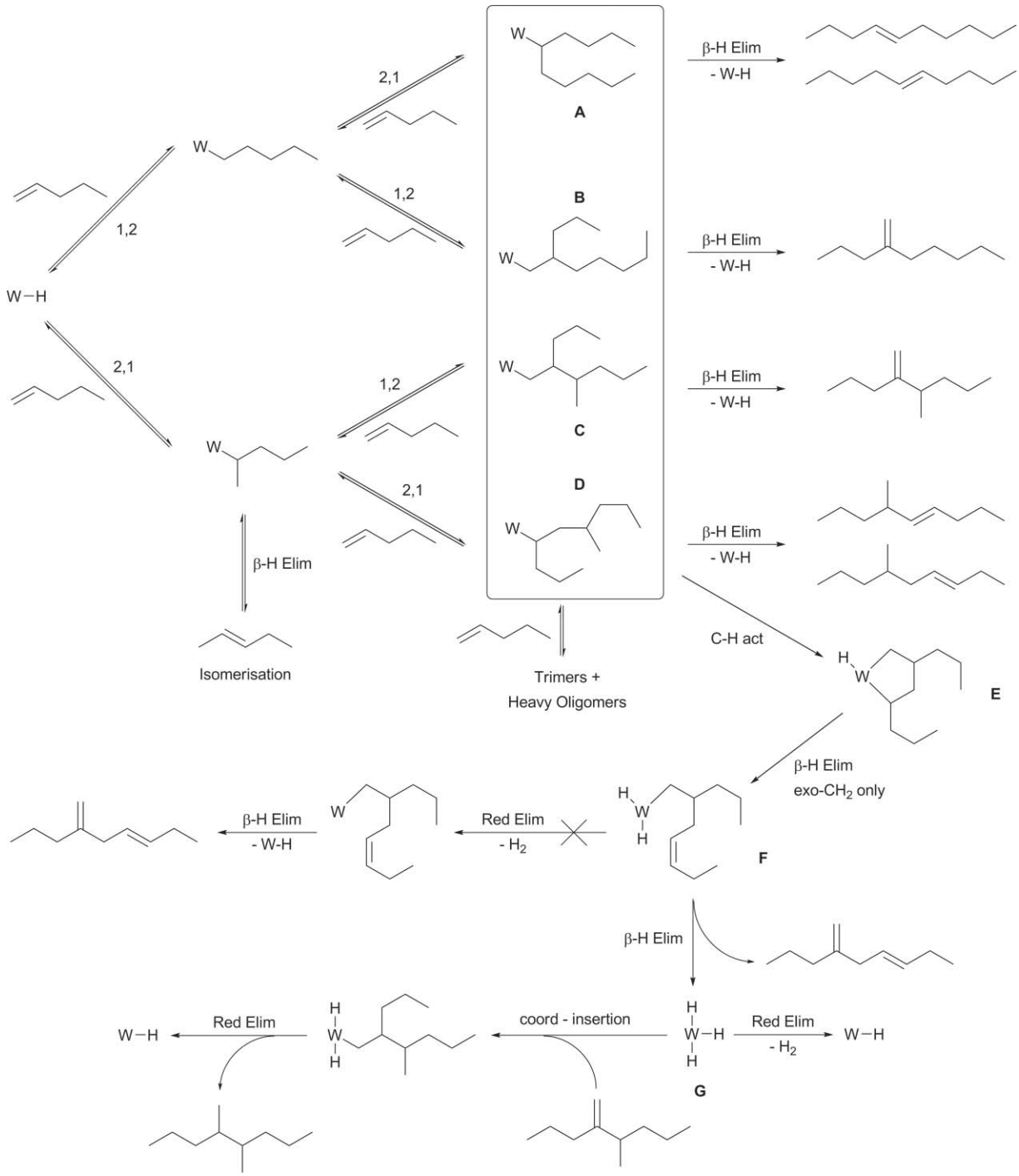

Fig. 9 Proposed mechanistic trajectories for the formation of the products observed.

catalytically important intermediate. Nonetheless, computational studies have suggested that a metallacyclic pathway may be energetically feasible for tungsten-imido based catalysts.[14] It was found that stepwise metallacycle breakdown *via* β-hydrogen elimination and subsequent reductive elimination was a lower energy pathway than the concerted hydride shift. This could be taken to suggest that β-hydrogen elimination and reductive elimination should also be feasible in the form of a Cossee-type pathway, but significantly a similar analysis of this mechanistic trajectory has not been reported.

Considering the experimental evidence obtained in this study, the observed isomerisation of the substrate olefin can be taken as indicative of a metal hydride species, which in itself suggests a Cossee-type mechanism.[2b,24] Given the lack of isomerisation of the products by the catalyst, a further potential clue to the mechanistic pathway lies in a consideration of the products expected from both metallacyclic and Cossee-type mechanisms. This reveals that the linear C_{10} olefins formed should be diagnostic; 3- and 4-decenes resulting from a metallacyclic pathway and 4- and 5-decenes from a chain-growth trajectory (see Fig. S3 in the ESI† and Fig. 9,

respectively). As discussed (*vide supra*), in practice no *cis* or *trans*-3-decene is observed, whilst analysis indicates the presence of *trans*-5-decene and *cis*-4-decene, along with possibly traces of *cis*-5-decene and *trans*-4-decene. It is thus suggested that catalysis with this *in situ* tungsten-based catalyst system proceeds *via* a Cossee-type mechanism, as depicted in Fig. 9.

In order to obtain a second verification of this result the *in situ* catalyst system was screened with a mixture of C_2H_4/C_2D_4 using the now well established isotopomer experiment for the discrimination of metallacyclic and Cossee-type mechanisms.[23] Analysis of the products from a dimerisation reaction using C_2H_4/C_2D_4 (3.5 : 1 ratio) revealed 1-butene as the primary product (73.7 mol%) with traces of internal butenes (2.5 mol%), methylpentenes (22.8 mol%) and linear internal hexenes (1.0 mol%).[26] Extractive ion trace GC-MS analysis reveals full isotopic scrambling of all the C_4 and C_6 products, which is indicative of the Cossee-type mechanism.[27] Thus, this experiment serves to confirm the mechanistic trajectory indicated by analysis of the 1-pentene dimerisation experiments, namely that a Cossee-type mechanism is in operation.

Considering this mechanism, and the observed levels of formation of the various products, it can be concluded that the first olefin insertion step is almost equally likely to proceed in a 1,2 or 2,1 fashion but that there is an element of regioselectivity in the subsequent insertion. Given the level of linear products *versus* 2-propyl-1-heptene (0.1% *versus* 41.9%), it is suggested that after an initial 1,2 insertion, a further 1,2 insertion is ~420 times more likely than a 2,1 insertion. Also, given the observation of 40.1% of 2-propyl-3-methyl-1-hexene and in total 14.5% of 6-methyl-3/4-nonene and 2-propyl-1,4-heptadiene, then following an initial 2,1 insertion, the subsequent insertion is ~2.8 times more likely to occur in a 1,2 rather than a 2,1 fashion. These statistics indicate that intermediates **B** and **C**, dominate over **A** and **D**, suggesting that the second insertion preferentially occurs to place steric bulk away from the tungsten centre.

The formation of dienes and alkanes also requires explanation, especially given the specificity with which this occurs. Herein, we invoke a C–H activation mechanism akin to that proposed by Small,[19] however there are differences due to the selectivity in this case, *versus* the less selective formation of dienes in the previous work. Most specifically, whilst Small invokes an intermolecular C–H activation, in this case an intramolecular mechanism seems most likely. In this case an intermolecular mechanism similar to that proposed by Small, would lead to the conjugated diene 2-propyl-1,3-heptadiene, not the 2-propyl-1,4-heptadiene observed. The latter product could be formed by invoking an isomerisation of the W-alkenyl, but such an isomerisation would likely be energetically unfavourable (see ESI† for further discussion). Indeed, if intermediate **D** (Fig. 9) were to intramolecularly cyclometallate the methyl group on the pendant alkyl chain to give intermediate **E**, the formation of 2-propyl-1,4-heptadiene only, and not 2-propyl-1,3-heptadiene, is readily explained. β-hydrogen elimination from metallacyclopentane species is well documented to be energetically disfavoured,[28] and thus it is not surprising that the product resulting from elimination involving the endocyclic methylene protons (2-propyl-1,3-heptadiene) is not observed. However, the exocyclic methylene protons are expected to be significantly more available towards metal-mediated elimination and would indeed give the observed 2-propyl-1,4-heptadiene. After, this initial β-hydrogen elimination step, the resulting alkenyl chain undergoes a further β-hydrogen elimination step to yield the diene.

Based on the products observed, there is a specificity of cyclometallation towards intermediate **D** only. This can be argued on the basis that the methyl group is predisposed towards such C–H activation, and hence no cyclometallation of intermediates **A** and **B** occurs. However, such an argument suggests that intermediate **C** should also cyclometallate, as it also features a methyl group on the γ-carbon of the pendant alkyl. The failure to observe any dienes of the dimethyl-branched skeleton is thus perhaps surprising, but can be explained in several ways. If cyclometallation of intermediate **C** has a slightly higher activation energy as compared to **D**, then diene formation may still occur, but the levels of diene formation could be pushed below the limit of detection by GC. Alternatively, if β-hydrogen elimination from intermediate **C** is significantly faster than from **D**, then cyclometallation of **C** may simply be kinetically disfavoured.

At this stage a consideration of alkane formation is timely, and given the good correlation between diene and alkane formation levels, the loss of the diene-derived-hydrogen as dihydrogen is considered unlikely. This necessarily invokes a tungsten trihydride species (Fig. 9, intermediate **G**), which is not unfeasible, tungsten polyhydride species being well known,[29] with tungsten-imido polyhydride complexes specifically being reported.[30] Given the suspicion of imido functionality in the active catalyst species, the formation of W–H species could be transient, with onwards reaction to give a tungsten-amido species. This amido species could then perform the hydrogenation, in the process regenerating the imido moiety. Such a species could then readily hydrogenate an olefin moiety *via* a normal coordination, insertion, reductive elimination pathway. Indeed the observation of trace levels of 4,5-dimethyloctane and decane fits with this hypothesis, but the very low level of 4-methylnonane remains without good explanation. However, the observation that the substrate olefin is the most hydrogenated species is to be expected, being the least sterically hindered olefin present and in the highest concentration for the majority of the experiment.

Conclusions

The ability to control selectivity whilst using an *in situ* $WCl_6/PhNH_2/Et_3N$-based catalyst system *via* a choice of stoichiometry has been demonstrated, allowing the exclusive formation of methyl and dimethyl-branched dimer products. Through optimum choice of aluminium activator and solvent, a selectivity to the dimer fraction of >99% has been demonstrated. The presence of the chloride in the aluminium species has been found to be crucial for successful initiation, suggesting the formation of aluminium-tungsten chloride-bridged species, as has been substantiated by us and co-workers elsewhere.[13] A kinetic study has revealed a second order dependence on substrate. The selectivity of the catalyst with different α-olefins has been shown to remain remarkably constant, giving methylidene species as the major products in both the methyl- and dimethyl-branched skeletons. Extensive product analysis has led to identification of all trace products from dimerisation catalysis and reveals the additional formation of dienes and alkanes in equimolar amounts. Following the identification of trace linear C_{10} species, it is proposed that this *in situ* catalyst operates *via* a Cossee-type mechanism.

A C_2H_4/C_2D_4 co-dimerisation experiment showed full isotopic scrambling of the products, and thus supports this mechanistic proposal. The highly selective diene formation is readily explained by this mechanism, as is the concomitant alkane formation.

Experimental

General procedures

All operations were conducted under dry nitrogen using standard Schlenk and cannula techniques, or in a nitrogen-filled glove box. Solvents were procured from Aldrich, purified using a Solvent Purification System, and de-oxygenated prior to use. All liquid reagents were dried and deoxygenated prior to use.[31] 1-Pentene, 1-hexene, 1-heptene and 1-nonene were stored over activated molecular sieves (4 Å), TMEDA was distilled from Na, aniline, triethylamine and 4-fluoroaniline from CaH_2.[31] All other chemicals were purchased from Aldrich or Akzo Nobel and used without further purification unless stated otherwise. 4-Nonanone was procured from Kodak Eastman. GC standards were purchased from ChemSampCo (linear decenes, 3-ethyl-4-methylheptane, 3-ethyloctane and 3,4-diethylhexane).

NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Chemical shifts are reported in δ (ppm) being referenced to residual protio impurities in the deuterated solvent (^1H) or ^{13}C shift of the solvent. All ^{13}C $\{^1H\}$ NMR spectra were obtained as DEPT135 acquisitions to assist in assignment. GC-FID analysis was performed on an Agilent Technologies 6890 N GC system equipped with PONA (50 m × 0.20 mm × 0.50 μm) and MDN-12 (60 m × 0.25 mm × 0.25 μm) columns. GC-MS analysis was performed on an Agilent Technologies 6890 N GC system equipped with PONA (50 m × 0.20 mm × 0.50 μm) and MDN12 (60 m × 0.25 mm × 0.25 μm) columns, coupled to an Agilent Technologies 5973 N MSD Mass Spectrometric instrument equipped with EI source. Hydrogenative GC-FID analysis was performed using an Agilent Technologies 6890 N GC System equipped with an inlet liner packed with hydrogenating catalyst (Pt on Chromosorb W at 200 °C) and a PONA column (50 m × 0.20 mm × 0.50 μm).[32] Elemental analyses were performed by the Science Technical Support Unit of London Metropolitan University. Fractional distillations were conducted using an automated, custom built Fisher Technology Spaltröhr HMS 500 AC rig.

Catalysis protocol

Catalysis was conducted in a Radleys 6-well (250 mL) carousel reactor retrofitted in-house to allow rigorous exclusion of oxygen and moisture when attached to a Schlenk line. Each well was magnetically stirred, fitted with a cooled reflux tube and had a side-arm to allow sampling *via* septa. The vessels were heated to 90 °C under vacuum for 1 h, before cooling to the desired catalyst formation temperature and back-filling with N_2. Dry solvent and nonane (internal standard) were added, followed by WCl_6, RNH_2 and Et_3N as stock solutions. The vessel was then stirred at the catalyst formation temperature for the desired period. If necessary the vessel temperature was then adjusted to the catalysis temperature. The olefin substrate was added and a sample taken for GC-FID analysis (t_0) to allow accurate determination of the ratio between internal standard and olefin initially. The aluminium activator was then added to initiate catalysis. When samples were taken during catalysis, they were subjected to a micro-scale acidified aqueous work-up and analysed by GC-FID as soon as possible. At the end of catalysis MeOH (1 mL) was added to each well, followed by 10% HCl_{aq} and after initial stirring, the mixture allowed to separate and a sample of the organic layer taken for GC-FID analysis. After GC-FID analysis using both PONA and MDN columns, the samples were subjected to hydrogenative GC-FID analysis to assist in the assignment of products.

Given that loss of substrate olefin by evaporation appears as heavy oligomers when a mass balance is applied, 'blank' experiments were conducted to assess the loss of substrate by evaporation during reaction. This loss was found to be very low and consistent (< 0.5% per hour during a 6 h period) and was corrected for in the mass balance.

The reaction conducted at 100 °C (Table 1, entry 24) was performed as normal, but in a 50 mL s^{-1} autoclave with mechanical stirring; no samples were taken *in operando*. Larger scale dimerisation reactions were conducted as normal but in 3-neck round-bottom flasks, equipped with thermometer, magnetic stirrer and reflux condenser connected to a Schlenk line. The whole assembly was maintained at constant temperature *via* a water bath.

The C_2H_4/C_2D_4 dimerisation was performed in a 250 mL autoclave equipped with mechanical stirring and a fluid-filled jacket for temperature control. The C_2H_4/C_2D_4 was prepared by condensing C_2D_4 into a 200 mL bomb, allowing it to warm to RT and noting the pressure (5.5 bar). The C_2H_4 was then added to the bomb, to give a total pressure of 25 bar (C_2H_4/C_2D_4 ratio 3.5 : 1). The catalyst (0.1 mmol WCl_6, 0.2 mmol $PhNH_2$, 0.4 mmol Et_3N, in 100 mL PhCl) was prepared *in situ* for 30 min at 45 °C. The vessel was briefly evacuated, then back filled to 1 bar with premixed C_2H_4/C_2D_4. EADC (1.5 mmol, 1.8M in toluene) was then added and the vessel pressurised to 7 bar with premixed C_2H_4/C_2D_4. An exotherm to 47 °C was observed. Over the course of 9 min the pressure dropped to 2 bar, and the reaction was quenched with Pr^iOH and H_2O (40 mL), and cooled to 1 °C. Toluene (100 mL) was added to assist in separation of the organic and aqueous phases *in situ*. A sample was taken for GC-FID and GC-MS analysis, extractive ion trace methods being used to accurately quantify the amounts of each isotopomer present.

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