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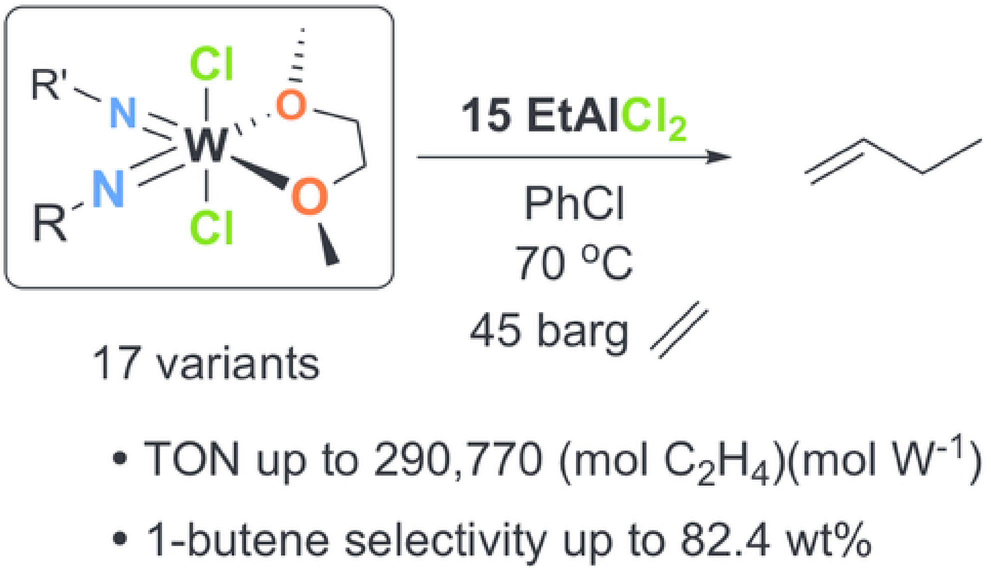

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bis(Imido) tungsten complexes: efficient pre-catalysts for the homogeneous dimerization of ethylene

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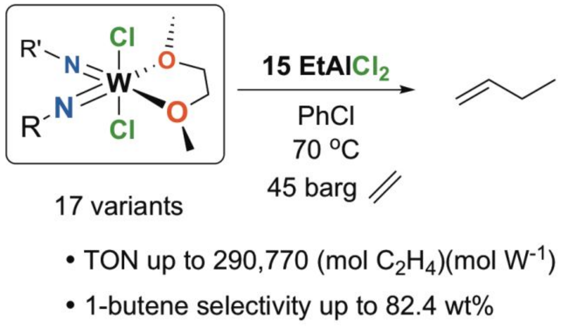
ABSTRACT: The ethylene dimerization performance of a range of bis(imido)tungsten pre-catalysts, after activation with aluminum co-catalysts, has been assessed. The best performing system achieved an activity of 409,410 (mol C_2H_4)(mol W)$^{-1}$h^{-1} [79.6 wt% 1-butene] with a 1-butene selectivity of 82.4 wt% [290,770 (mol C_2H_4)(mol W)$^{-1}$h^{-1} activity]. In addition to selected previously reported variants, the symmetrical bis(imido)tungsten(VI) complexes [$WCl_2(NPh)_2$(tmeda)] (**3**) and [$WCl_2(NR)_2$(dme)] [R = 2,4,6-trifluorophenyl, **7**; 2,4,6-triphenylphenyl, **8**; 2,4,6-tris(trifluoromethyl)phenyl, **9**], were prepared. A series of unsymmetrical bis(imido)tungsten(VI) complexes [WCl_2(NDipp)(NR)(dme)] (R = ^{i}Pr, **11**; ^{t}Bu, **12**; 2,4,6-trimethylphenyl, **13**; 2,4,6-trichlorophenyl, **14**; 2,4,6-trifluorophenyl, **15**; 2,6-dinitrophenyl, **16**; 2,4,6-triphenylphenyl, **17**) were also synthesized using an improved version of a previous preparative route that eases purification. The molecular structures of complexes **5**-**13** and **15**-**17** were determined by X-ray crystallographic analysis. Catalysis employing complexes **1**-**17** unveils a complicated relationship between steric and electronic factors that affects activity and catalyst lifetime, however selectivity is dominated by electronic considerations. Higher reaction temperatures were shown to favor 1-butene selectivity and higher activity, whilst replacement of $EtAlCl_2$ with $MeAlCl_2$ as co-initiator was found to be detrimental. Tungsten(IV) species were demonstrated to be unlikely as the active species during catalysis. Studies of catalysis runs undertaken to varying productivities found that during the nascent phase of reaction a notably lower activity is observed, whilst the selectivity favors C_{8+} formation during this period, most likely due to activation processes still occurring. The rate of formation of 1-butene was shown to increase with productivity, as a result of the greater solubility of ethylene in the 1-butene generated compared to the chlorobenzene solvent. The formation of C_6 by-products was shown to be independent of 1-butene concentrations, consistent with a mechanism whereby 1-butene is only incorporated into secondary products when it reacts prior to dissociation from the tungsten center.

KEYWORDS: dimerization, ethylene, 1-butene, catalysis, tungsten, imido

TOC GRAPHIC



- TON up to 290,770 (mol C_2H_4)(mol W^{-1})
- 1-butene selectivity up to 82.4 wt%

INTRODUCTION

Ethylene oligomerization is an important example of homogenous catalysis applied within the commodity chemicals industry, being used for the production of linear alpha olefins (LAOs).[1] The majority of ethylene oligomerization processes commercialized prior to 2000 had broad range selectivities, producing LAOs from C_4 to C_{20+}.[2] However, more recent capacity additions have included a much higher proportion of 'selective' ethylene oligomerization technologies, specifically dimerization to 1-butene, trimerization to 1-hexene, and tetramerization to 1-octene, as this allows companies to better match supply of specific LAOs with market and geographic demands.[2,3]

Considering ethylene dimerization in particular, the primary commercial process for this conversion is AlphaButol,[4] which is licensed by Axens; approximately 24 plants have been constructed with a cumulative capacity of ~500 ktpa.[2b,5] This process uses a soluble titanium complex, $Ti(OBu)_4$, in conjunction with triethylaluminum as co-catalyst at 50-55 °C and 20-27 bar ethylene pressure, giving typical activities in the range 100-9,700 g/gTi/h [170-16,550 $(mol\ C_2H_4)(mol\ Ti)^{-1}h^{-1}$].[2b,3b,4,5,6] The suppression of polymer formation is of key importance for the commercial AlphaButol process, with values <0.5 wt% being reported for the better performing examples.[4,5,6] An ethylene conversion of 80-85%

per pass is achieved with a reaction selectivity to 1-butene of 93-95%.[2b,3b,4] The degree of isomerization to internal butenes is cited as being very low, such that the main by-product is C_6 material.[2b,3b,4] This is of key importance as the separation of C_4 components is costly, whereas separation of C_4 and C_6 fractions is trivial, such that 1-butene is readily obtained from the AlphaButol process with an overall purity of >99.7%, and free from isobutene and 1,3-butadiene, which are poisons when 1-butene is used for polymer applications.[2b,3b,5]

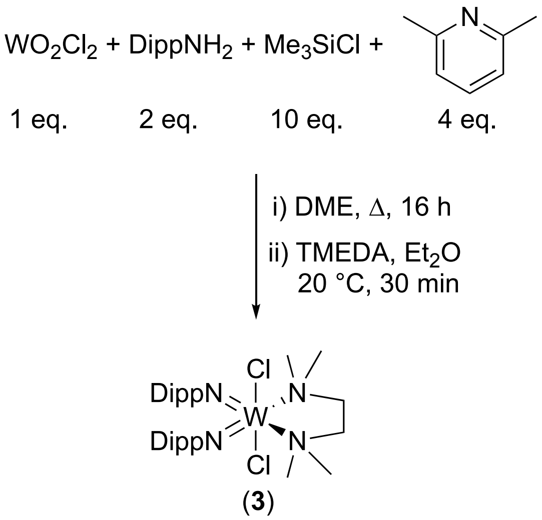
Other systems for the dimerization of ethylene include various catalysts based upon aluminum, cobalt, nickel and tungsten. For example, based on modifications to the Aufbau ethylene polymerization reaction,[7] Dow disclosed that at high temperatures trialkylaluminum reagents mediated dimerization of ethylene.[8] In 1967 it was demonstrated that ethylene dimerization could be achieved over a heterogeneous cobalt oxide/carbon system,[9] work that has been extended more recently with the report of a co-catalyst-free heterogeneous chromium-promoted cobalt oxide on carbon system.[10] Nickel-based catalysts also have a long history that has been well reviewed previously: from their origins in the 1960s using a simple format based upon a nickel salt, aluminum activator, and a phosphine ligand, through to the development of catalysts bearing carefully refined bidentate ligands.[11] The tungsten systems also have their origins in the 1960s when Goodyear reported that WCl_6 in combination with various protic additives, including anilines or phenols, when activated with aluminum alkyl co-catalysts gave systems capable of olefin dimerization.[12] Improvements to this 'in situ' formed catalyst involved active removal of HCl during pre-catalyst formation,[13] which led to the conclusion that tungsten imido species were being formed. This was first exemplified by researchers at IFP who used discreet tungsten imido complexes prepared ex situ for ethylene and propylene dimerization.[14] We subsequently showed that removal of HCl via sequestration with an organic base during formation of the in situ catalyst led to improved selectivities to mono-methyl-branched products from α-olefins substrates.[15] Others have examined the use of immobilized tungsten imido pre-catalysts.[16]

In the course of further studies using pre-formed imido complexes, we have previously reported on the use of group 6 metal imido species for the dimerization of ethylene and α-olefins.[17,18,19] The molybdenum complexes, which are only accessible as bis(imido) compounds, are capable of dimerizing ethylene to 1-butene with selectivities in the range 50-80 wt% and activities of 11,000-64,000 $(mol\ C_2H_4)(mol\ Mo)^{-1}h^{-1}$,[20] the selectivity being limited by both isomerization of 1-butene and C_6 formation.[17] In comparison, both mono- and bis-(imido) tungsten complexes may be synthesized.

We have reported in detail on the catalytic ability of the former to dimerize ethylene with typical overall selectivities to 1-butene of 70-80 wt% and activities in the range of 150,000-320,000 (mol C_2H_4)(mol W)$^{-1}$h^{-1},[21] with little to no associated polymer formation.[19] For the bis(imido) tungsten species we have presented detailed studies of their activation chemistry with various aluminum activators, and shown on NMR tube scales that such species can mediate ethylene dimerization.[18] Herein, we complete the picture reporting the catalytic potential of bis(imido)tungsten complexes for ethylene dimerization under stirred-tank reactor conditions. This is supplemented by studies that provide unique insight into the mechanism and active species present during catalysis, highlighting the likely role of tungsten(V) species.

RESULTS AND DISCUSSION

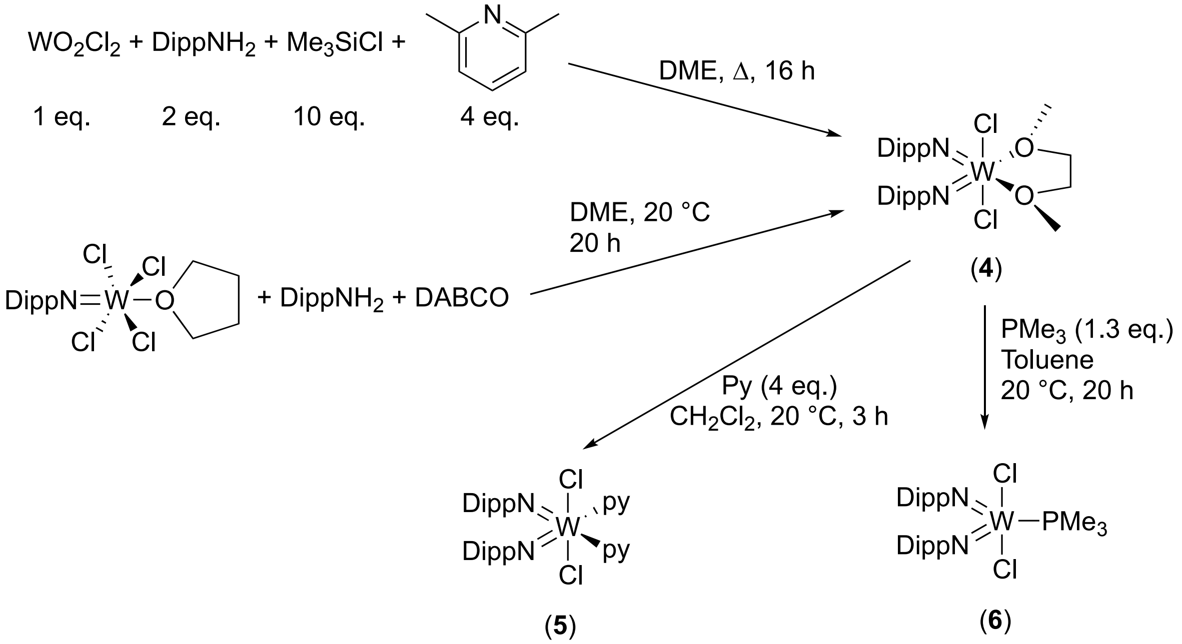
1. Synthesis and characterization of complexes. A range of bis(imido)tungsten complexes were prepared following literature methods, improvements thereof, or analogous procedures. [W(NH^{t}Bu)$_2$(N^{t}Bu)$_2$] (**1**) and [WCl$_2$(N^{t}Bu)$_2$(py)$_2$] (**2**) were prepared according to known protocols.[22,23] Attempts to prepare [WCl$_2$(NPh)$_2$(dme)] using an equivalent method to that used for **4** (vide infra) were unsuccessful as the dme ligand readily dissociates, resulting in formation of an insoluble material. In contrast, $[WCl_2(NPh)_2(tmeda)]$ (**3**) was easily prepared and isolated (Scheme 1) and is analogous to previously-reported $[WCl_2(NPh)_2(4,4'\text{-bpy})]$.[24]



Scheme 1. Preparation of complex **3.**

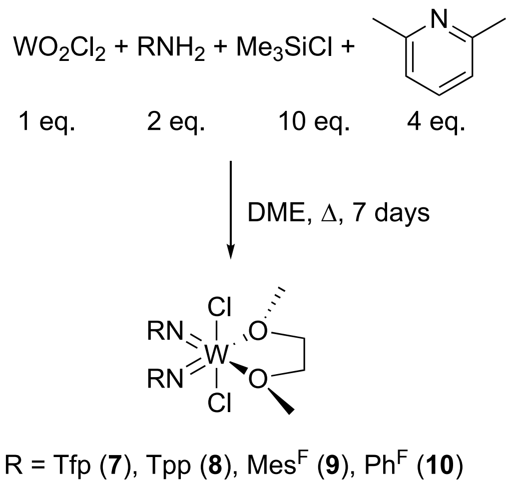
The known symmetrical bis(imido)complex $[WCl_2(NDipp)_2(dme)]$ (**4**) was prepared according to the procedure reported by Schrock and co-workers starting from WO_2Cl_2.[25] An alternative route to **4** also reported by Schrock *et al.* through reaction of $[WCl_4(NDipp)(thf)]$ with $DippNH_2$ and Et_3N in DME/Et_2O was attempted.[25] However, for this latter case purification proved challenging due to the partial solubility of the $[Et_3NH]Cl$ by-product in the solvent mixture, so a modified procedure was developed that uses dme as solvent and DABCO (1,4-diazabicyclo[2.2.2]octane) in place of Et_3N as base; this allowed isolation of the target product free from ammonium salts (Scheme 2). Complexes $[WCl_2(NDipp)_2(py)_2]$ (**5**) and

$[WCl_2(NDipp)_2(PMe_3)]$ (**6**) were prepared via addition of pyridine and PMe_3, respectively, to solutions of **4** (Scheme 2). The analytical data collected for these complexes were unremarkable, except that whilst the pyridine ligands in **5** are tightly bound, giving sharp resonances in its ^1H NMR spectrum, the PMe_3 ligand in **6** is labile in solution, which was confirmed by variable temperature (VT) NMR spectroscopy (see SI for ^1H and $^{31}P\{^1H\}$ spectra and brief discussion).



Scheme 2. Preparation of complexes **4, 5** and **6.**

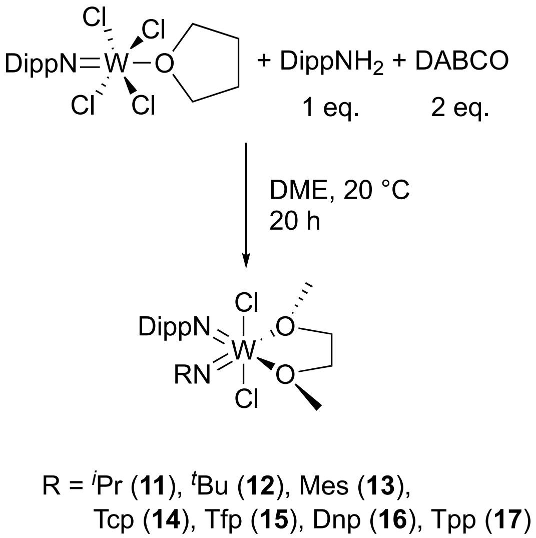
The remaining symmetrical bis(imido) complexes $[WCl_2(NR)_2(dme)]$ (R = Tfp, **7**; Tpp, **8**; Mes^F, **9**; Ph^F, **10**), were prepared via an analogous procedure to that used to synthesize $[WCl_2(NDipp)_2(dme)]$ (Scheme 3).[25] An alternative synthesis of complex **10** has been reported.[26]



Scheme 3. Preparation of the symmetrical bis(imido)tungsten(VI) complexes **7-10.**

A range of unsymmetrical bis(imido) complexes featuring one Dipp-substituted imido moiety were prepared from [WCl_4(NDipp)(thf)] by reaction with the relevant primary amine and DABCO in DME at 20 °C (Scheme 4); the complexes [WCl_2(NDipp)(NR)(dme)] (R = ^{i}Pr, **11**; ^{t}Bu, **12**; Mes, **13**; Tcp, **14**; Tfp, **15**; Dnp, **16**; Tpp, **17**) were all obtained in good yield. Whilst this synthetic methodology proved successful for a wide range of alkyl and aryl imido groups, a limitation was discovered for more electron withdrawing substituents. Attempts to prepare [WCl_2(NDipp)(NMes^F)(dme)] led to the isolation of [WCl_2(NDipp)$_2$(dme)], and a range of products that could not be identified, suggesting scrambling of the imido functionalities occurs readily, facilitated presumably by destabilization of the imido complexes by the electron withdrawing substituent. In order to explore this phenomenon further, d_5-PhCl solutions of the isolated unsymmetrical *bis*(imido) complexes bearing electron withdrawing and electron donating aryl substituents, **15** and **12**, respectively, were heated at 60 °C and monitored by NMR spectroscopy. After 3 hours complex **15** had undergone complete scrambling to give a mixture of $[WCl_2(NDipp)_2(dme)]$ (**4**), $[WCl_2(NDipp)(NTfp)(dme)]$ (**15**), and $[WCl_2(NTfp)_2(dme)]$ (**7**). In contrast, complex **12** remained unchanged after 24 hours at 60 °C; subsequent heating at 110 °C for a further 1 hour led to complete loss of **12** and the formation of products resulting from decomposition.

A further limitation to the synthetic strategy employing $[WCl_4(NDipp)(thf)]$ as a starting point was discovered in terms of the steric bulk permissible, with attempts to prepare the sterically-demanding derivative $[WCl_2(NDipp)(NTtbp)(dme)]$ leading to recovery of more than 50% of the starting $TtbpNH_2$ and a range of unidentifiable products. Conversely, too little steric bulk, combined with unfavorable electron withdrawing groups prevents isolation of monomeric symmetrical *bis*(imido)complexes via this avenue. Indeed, attempts to prepare $[WCl_2(NPh)_2(dme)]$, $[WCl_2(NDipp)(NPh)(dme)]$, $[WCl_2(NPh)(N^tBu)(dme)]$, $[WCl_2(NDipp)(NPh^F)(dme)]$ and $[WCl_2(NNPh^F)(N^tBu)(dme)]$ all led to complex mixtures of products. Bridged-imido complexes are known to form with sterically undemanding substituents, and it is suspected that such species were present in the mixture of products obtained.[25]



Scheme 4. Preparation of the unsymmetrical bis(imido)tungsten(VI) complexes **11**-**17**.

All of the complexes described thus far incorporate a W^{VI} center. However, since we and others have previously investigated the role of oxidation state in ethylene dimerization mediated by tungsten mono(imido) complexes,[14,19] the bis(imido) tungsten(IV) complex, $[W(NDipp)_2(PMe_3)_3]$ (**18**) was prepared according to the previously reported method and tested as a potential dimerization pre-catalyst.[27]

The molecular structures of the symmetrical bis(imido) complexes **5**–**10** (Figure 1), along with those of the unsymmetrical derivatives **11**–**17** (Figure 2), were determined by X-ray crystallographic analysis (see Table 1 for selected metric parameters).[18] All complexes of the type [WCl_2(NR)(NR′)(dme)] (with R = R′ or R ≠ R′) examined herein adopted a distorted octahedral coordination with the chloride atoms located *trans* to each other and bent away from the imido substituents, something consistent, in part, with steric constraints (Σ_{ang} N(1)-W-X {X = N(2), Cl, O(1)} and N(2)-W-Y {Y = N(1), Cl, O(2)} is between 389 – 395°). These observations are in accordance with those made for previously reported tungsten bis(imido) complexes.[18,28] The W-N interatomic distances in each of the symmetrical and unsymmetrical bis(imido) complexes are in the range 1.738(2)-1.787(3) Å, distances that are slightly longer than those for their mono(imido) analogues (W-N = 1.685-1.727 Å).[19] The W-N bond distances for these symmetrical and unsymmetrical bis(imido) complexes are consistent with a W-N bond order of between two and three in each case. This elongation of the W-N interatomic distances in the bis(imido) complexes compared to their mono(imido) analogues is a result of the absence of available tungsten π-symmetry orbitals for π-bonding with all four *p* orbitals provided by the two imido substituents, making the bis(imido) complexes electronically saturated.[18] Note, since complex **6** is five-coordinate, direct comparison of its crystallographically-determined metric parameters with those of the six-coordinate complexes is precluded.

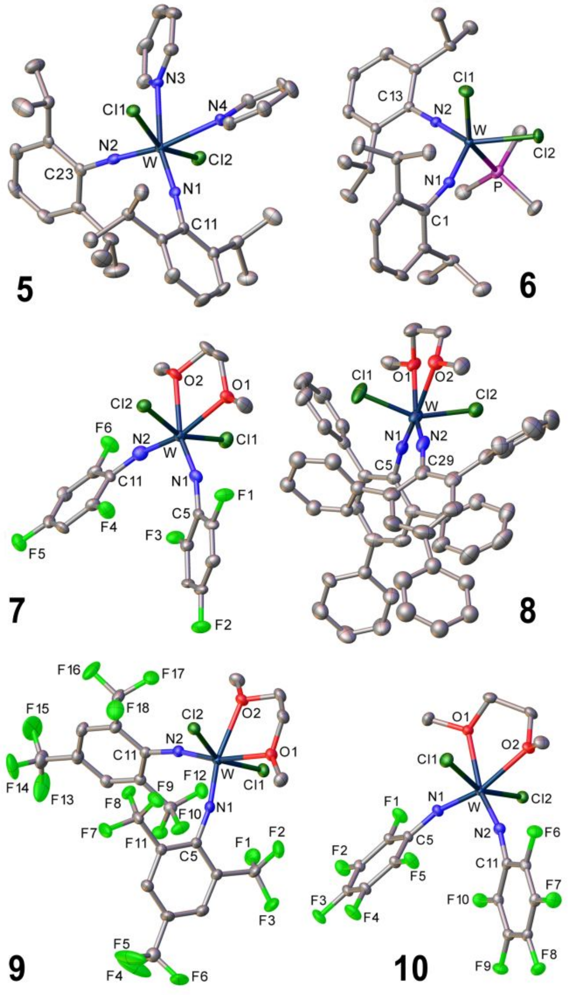


Figure 1. Molecular structures of complexes **5**–**10.** Thermal ellipsoids are drawn at the 50% probability level; the disorder in **5**, **8** (see Fig. S43) and **9** and all H atoms are omitted for clarity.

For the symmetrical bis(imido) complexes the W-N(1) and W-N(2) bond distances are equipollent within experimental error. Although the W-N(1)-C(1) and W-N(2)-C(2) angles for each bis(imido) complex differ slightly (1.5-7°), depending on the nature of the imido substituent, these differences can be attributed to crystal packing forces rather than to specific structural properties of the bis(imido) complexes.[18,28] The W-N interatomic distances of complexes **4**, **7**, **8** and **10** are found to be the same within experimental error (~1.760 Å), despite the completely different electronic properties of the substituent at nitrogen (electron withdrawing imido substituents are expected to exhibit longer W-N bonds). Notably, only for complex **9** (NMes^F) is a slightly longer W-N bond (by ~0.01 Å) observed. This similarity in the W-N bond lengths between complexes **4, 7-10** is rationalized by considering the electronic saturation of the tungsten center in bis(imido) complexes: the lack of π-symmetry orbitals available in the cis bis(imido) framework results in what can be regarded as a delocalized cis-[(RN)W(NR)] arrangement.[18]

Based on the differences in the W-O bond distances determined for the symmetrical bis(imido) complexes (**8** > **4** > **7** > **10** = **9**), an ordering of the *trans* influence of the different imido ligands can be inferred: NMes^F = NPfp < NTfp < NDipp < NTpp. However, this ranking must be treated with caution. Firstly, it deviates from the ordering that would be expected based on the electronic character of the organo substituents.[19] Secondly, the notable deviation away from octahedral coordination (vide supra) will distort the σ-bonding framework through which *trans* influence effects are principally transmitted (Tables 1 and 2).[29] This latter effect will be further magnified by the established electronic coupling between the cis imido motifs across the C-N-W-N-C framework.[30] Together, these factors make it difficult to quantify the electronic impact of a particular organoimido substituent reliably in the cis bis(imido) coordination manifold.

Table 1. Selected bond distances (Å) and angles (°) in symmetrical bis(imido) complexes.

	4[a]	**5**	**6**	**7**	**8**	**9**	**10**
W-N(1)	1.7598(17)	1.772(4)	1.762(3)	1.759(15)	1.762(3)	1.7749(16)	1.7593(16)
W-N(2)	1.7599(17)	1.759(4)	1.765(3)	1.749(15)	1.770(4)	1.7695(16)	1.7570(16)
W-O(1)	2.3494(15)	2.393(4) [b]	2.5257(12)	2.306(12)	2.392(12) [e]	2.2918(14)	2.3115(13)
W-O(2)	2.3446(15)	2.361(4) [c]	---	2.324(13)	2.368(18) [e]	2.3179(13)	2.2901(13)
W-Cl(1)	2.3841(7)	2.3873(13)	2.3727(12)	2.370(5)	2.3631(12)	2.3516(5)	2.3791(5)
W-Cl(2)	2.3878(9)	2.3938(13)	2.4363(11)	2.377(5)	2.3749(11)	2.3589(5)	2.3663(5)
N(1)-C	1.393(3)	1.387(6)	1.406(5)	1.38(2)	1.397(5)	1.377(2)	1.371(2)
N(2)-C	1.395(3)	1.390(7)	1.387(5)	1.38(2)	1.376(5)	1.380(2)	1.371(2)
W-N(1)-C	163.06(15)	175.5(4)	164.4(3)	159.6(15)	166.0(3)	165.22(14)	158.62(14)
W-N(2)-C	161.47(15)	173.0(4)	178.6(3)	162.9(17)	162.0(3)	166.82(14)	165.55(14)
N(1)-W-Cl(1)	99.73(6)	99.84(13)	105.37(12)	97.2(5)	100.52(11)	99.38(5)	95.45(5)
N(1)-W-O(1)	89.35(7)	86.36(17) [b]	102.54(12)	92.5(6)	95.0(4)	92.50(6)	91.24(6)
N(2)-W-O(1)	166.75(7)	167.98(18) [b]	83.74(12) [d]	163.5(7)	160.0(4) [e]	164.68(6)	163.65(6)
N(1)-W-O(2)	159.36(7)	165.72(17) [c]	---	162.8(6)	163.8(3) [e]	163.53(6)	161.83(6)
N(1)-W-Cl(2)	97.11(6)	97.14(13)	112.92(12)	97.8(5)	95.67(11)	98.84(5)	97.66(5)
N(1)-W-N(2)	103.89(8)	105.6(2)	110.61(16)	103.9(8)	104.30(15)	102.81(7)	104.91(7)
N(2)-W-Cl(2)	97.19(6)	94.33(15)	135.36(11)	96.4(5)	101.30(11)	97.48(5)	97.73(5)
N(2)-W-O(2)	96.69(7)	88.17(18) [c]	---	93.2(7)	91.6(3) [e]	93.65(6)	93.26(6)
N(2)-W-Cl(1)	97.45(6)	96.66(14)	95.15(12)	97.5(5)	96.77(11)	98.38(5)	95.10(5)

[a] From reference 18 one of the two independent molecules; [b] For O(1) read N(4); [c] For O(2) read N(3); [d] for O(1) read P; [e] weighted average for the disordered O atoms

Table 2. Selected bond distances (Å) and angles (°) in unsymmetrical bis(imido) complexes.

	11	**12**	**13**	**14**	**15**	**16**	**17**
W-N(1)	1.738(2)	1.744(2)	1.751(2)	1.7713(13)	1.7680(16)	1.787(3)	1.771(2)
W-N(2) [a]	1.757(2)	1.766(2)	1.760(2)	1.7541(13)	1.7500(15)	1.745(3)	1.751(2)
W-O(1)	2.304(2)	2.319(2)	2.3459(18)	2.3445(11)	2.3290(14)	2.278(3)	2.350(2)
W-O(2)	2.405(2)	2.375(2)	2.3366(18)	2.3053(11)	2.3397(13)	2.317(2)	2.355(2)
W-Cl(1)	2.3935(7)	2.3901(7)	2.4003(7)	2.3880(4)	2.3699(5)	2.3701(9)	2.3752(6)
W-Cl(2)	2.3882(7)	2.3917(7)	2.3905(6)	2.3878(4)	2.4003(5)	2.3889(8)	2.3703(7)
N(1)-C	1.445(4)	1.450(4)	1.383(3)	1.370(2)	1.375(2)	1.369(5)	1.393(3)
N(2)-C	1.387(3)	1.387(4)	1.385(3)	1.394(2)	1.388(2)	1.389(5)	1.393(3)
W-N(1)-C	157.1(2)	159.4(2)	168.70(18)	162.06(12)	154.52(14)	152.3(3)	150.7(2)
W-N(2)-C	173.1(2)	173.5(2)	167.08(18)	168.23(11)	169.75(13)	174.0(3)	167.8(2)
N(1)-W-Cl(1)	97.78(9)	98.68(8)	95.90(7)	96.41(4)	98.59(5)	98.78(10)	100.17(6)
N(1)-W-O(1)	93.89(10)	92.32(10)	91.97(8)	94.89(5)	91.68(6)	92.29(12)	94.06(8)
N(2)-W-O(1)	160.82(9)	161.30(10)	161.32(8)	159.91(5)	163.94(6)	163.68(18)	162.66(9)
N(1)-W-O(2)	163.45(10)	161.48(10)	161.77(8)	164.96(5)	161.80(6)	163.28(18)	163.54(9)
N(1)-W-Cl(2)	96.30(9)	95.26(9)	97.77(7)	96.57(4)	95.85(5)	96.51(10)	96.35(6)
N(1)-W-N(2)	105.26(11)	106.34(12)	106.31(10)	105.17(6)	104.39(7)	103.89(14)	103.27(9)
N(2)-W-Cl(2)	97.89(8)	97.68(8)	94.35(7)	97.65(4)	96.66(5)	95.05(10)	98.10(7)
N(2)-W-O(2)	91.29(9)	92.14(9)	91.79(8)	89.88(5)	93.62(6)	92.70(13)	92.90(9)
N(2)-W-Cl(1)	95.46(8)	98.68(8)	98.39(7)	98.80(4)	97.17(5)	98.16(10)	97.06(7)

[a] The N-Dipp imido ligand.

X-Ray crystallographic analysis of the unsymmetrical bis(imido) complexes revealed that the W-N(1) interatomic distances in complexes **11**-**13** lie in the range 1.738(2)-1.751(2) Å, with those for complexes **14**, **15** and **17** being slightly longer, 1.768(2) to 1.771(2) Å (Table 2). The W-N(1) bond of the DnpN-complex **16** is longer still at 1.787(3) Å. These data reflect the electron withdrawing character of the imido substituents, with the strongly electron withdrawing Tfp, Tpp, and Dnp groups resulting in a lengthening of the W-N(1) imido bond. The impact of strongly electron withdrawing imido groups was also evident in the structures of the unsymmetrical imido complexes **14**-**17** where the W-NDipp (W-N(2)) bond distances are shorter than that for complex **12** (Table 2). This bond shortening results from significant N→W lone pair donation from the Dipp imido group, which is enhanced due to the poor nitrogen-to-tungsten donor character of the second imido ligand bearing the electron withdrawing groups Tfp, Tpp and Dnp.

The W-O(1) and W-O(2) bond distances in the mixed bis(imido) complexes **11**-**17** vary significantly with no readily apparent trend (Table 2). Even the W-O(1) bond, which is *trans* to the Dipp group in all six mixed bis(imido) complexes and hence expected to be similar for complexes **11**-**17**, assumes different values between 2.278(3) and 2.350(2) Å (Table 2).

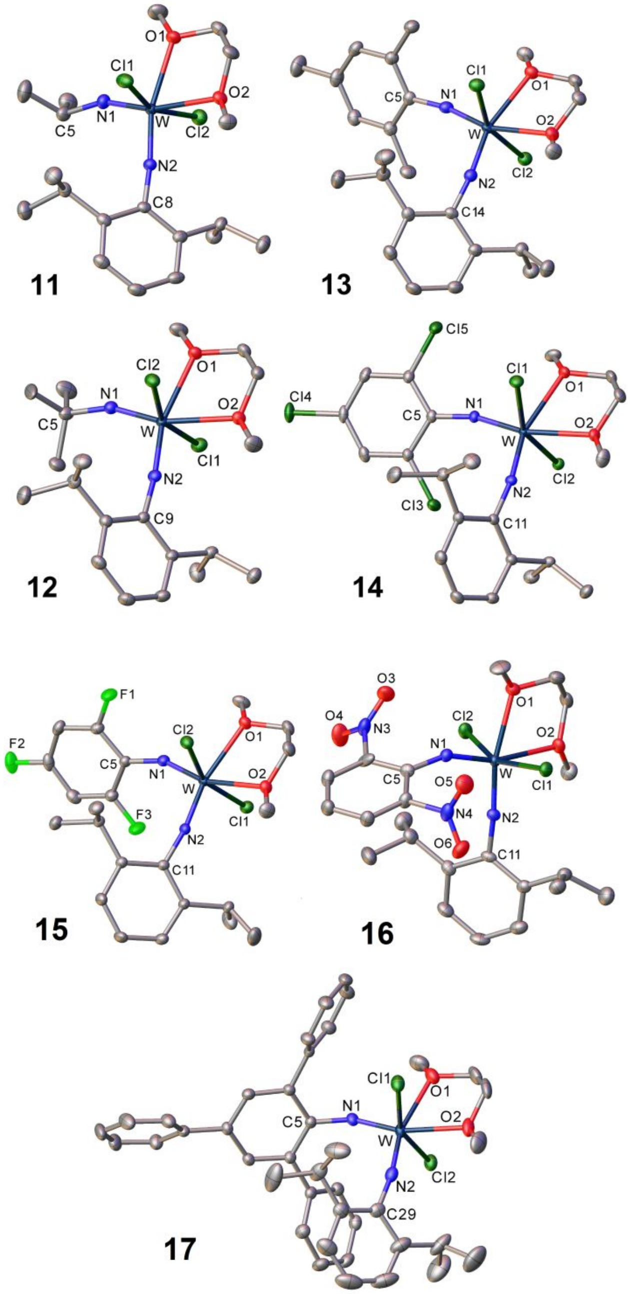


Figure 2. Molecular structures of complexes **11**–**17.** Thermal ellipsoids are drawn at the 50% probability level. Solvent molecules in **13** (see Fig. S44), **14** and **16,** and all H atoms are omitted for clarity.

2. Catalysis. bis(Imido) tungsten complexes **1-17** were screened for catalytic ethylene dimerization performance in combination with $EtAlCl_2$ as co-catalyst at 40 barg ethylene pressure and 60 ℃ in chlorobenzene solution (Table 3). In all cases 1-butene was the major product formed (52.0-87.8 wt%), but significant differences in selectivity and activity were observed as a function of the pre-catalyst. Repeat runs were performed in order to assess the inherent experimental error present, and full details of this analysis are given in the SI. The error in the activity values is ±6.8 % (one standard deviation expressed as a percentage of the mean) and for most of the selectivity values the error is < 2 % of value, on the same basis.

2.1. Impact of the imido substituent – symmetrical pre-catalysts. The pre-catalysts featuring only alkyl-substituted imido groups, complexes **1** and **2**, were amongst the least active and selective for both the C_4 fraction and within the C_4 fraction to 1-butene, such that the overall amount of 1-butene was the lowest observed. This poor performance of alkyl- compared with the aryl-substituted imido systems is consistent with that observed for mono(imido) tungsten complexes under identical conditions.[19] Moving to phenyl imido substituents, complex **3**, lead to a more than three-fold increase in activity, although the catalyst lifetime was still very short, resulting in a low productivity (Table 3, entry 3). Compared to that achieved using **1** and **2**, the selectivity to 1-butene was also increased from ~20 wt% to 74.0 wt% on moving to phenyl imido derivative **3**. This was attributed to a reduction in both the levels of C_6 and C_{8+} products, although a small amount of polymer was still formed.

Replacing the phenyl imido derivative **3** by complex **4**, which bears the more sterically demanding Dipp-substituted imido ligands, resulted in a doubling in activity and a near fifty-fold increase in catalyst lifetime. Indeed, the catalyst generated from **4** never fully deactivated, with the productivity determined being limited by the volume of the reaction vessel. Although the selectivity to 1-butene within the C_4 fraction was marginally greater with pre-catalyst **4** compared to that with **3**, the selectivity to the C_4 fraction decreased, meaning that the overall selectivity to 1-butene was lower for **4** by 8.5 wt%. No polymer formation observed with pre-catalyst **4**.

To explore the effect of the neutral donor ligand (L) of the bis(imido) pre-catalysts of composition $[WCl_2(NR)_2L_2]$, whilst maintaining the same tungsten $WCl_2(NDipp)_2$ core, catalytic tests with complexes $[WCl_2(NDipp)_2(dme)_2]$ (**4**), $[WCl_2(NDipp)_2(py)_2]$ (**5**), and $[WCl_2(NDipp)_2(PMe_3)]$ (**6**) were undertaken. Replacement of a bound dme by two pyridine ligands gave a significant reduction in both catalytic activity and productivity, with the liquid fraction showing a lower selectivity to 1-butene, primarily through increased formation of C_{8+} by-products and trace polymer (0.1 wt%). The performance of pre-catalyst **6** possessing a single PMe_3 ligand in place of dme was similar to that determined for complex **4**, giving the same activity within error, but a slightly increased yield of 1-butene 72.0 vs 65.5 wt%. In related imido-based alkene dimerization systems possessing oxygen-based donor scaffolds, the removal and complete sequestration by the aluminum co-catalyst has previously been shown to be the first step of the activation process.[18] Whether the differences in performance between complexes with dme, py and PMe_3 as supporting ligands arise as a result of how easily they dissociate (or are abstracted) from tungsten initially, or due to variation in how effectively these ligands are sequestered by the aluminum co-catalyst, remains unproven. Although both these factors may be at work here, an examination of the E-Al bond lengths for complexes **5**, **6** and $Cl_3Al \leftarrow E$ (E=PMe_3, py) suggests that ease of dissociation from tungsten may dominate over effective sequestration, consistent with the lability of the PMe_3 ligand of **6**.[31]

Table 3. Ethylene dimerization catalysis at 40 barg ethylene pressure and 60 °C using bis(imido)tungsten(VI) pre-catalysts.[a]

Entry	**Pre-catalyst**	**Rxn Time {min}**	**TON** [b]	**Activity** [c]	**C_4** [d] **{wt%} (% 1-C_4)**	**1-C_4** [d] **{wt%}**	**C_6** [d] **{wt%} (% 1-C_6)**	**Linear C_6 {% of C_6}**	**MPs {% of C_6}**	**C_{8+}** [d] **{wt%}**	**PE** [e] **{wt%}**
1	$[W(NH^tBu)_2(N^tBu)_2]$ (**1**)	4.0	720	10,800	54.3 (95.7)	52.0	23.4 (4.9)	7.8	92.2	22.3	1.4
2	$[WCl_2(N^tBu)_2(py)_2]$ (**2**)	4.0	730	10,990	55.4 (95.9)	53.1	32.7 (3.4)	4.9	95.1	11.9	0.0
3	$[WCl_2(NPh)_2(tmeda)]$ (**3**)	4.1	2,460	36,030	76.1 (97.2)	74.0	17.3 (6.2)	8.8	91.2	6.6	1.8
4	$[WCl_2(NDipp)_2(dme)]$ (**4**)	98.0	113,400	69,790	66.6 (98.3)	65.5	32.0 (0.4)	5.4	94.6	1.4	0.0
5	$[WCl_2(NDipp)_2(py)_2]$ (**5**)	9.5	4,170	26,330	58.7 (97.3)	57.1	34.3 (2.0)	4.3	95.7	7.0	0.1
6	$[WCl_2(NDipp)_2(PMe_3)]$ (**6**)	133.1	139,330	62,820	73.3 (98.2)	72.0	25.2 (1.6)	4.1	95.9	1.5	0.0
7	$[WCl_2(NTfp)_2(dme)]$ (**7**)	43.0	144,190	201,420	79.7 (97.6)	77.8	19.4 (3.7)	5.1	94.9	0.9	0.0
8	$[WCl_2(NTpp)_2(dme)]$ (**8**)	5.8	1,640	17,090	66.4 (97.7)	64.9	30.3 (3.1)	10.3	89.7	3.3	0.9
9	$[WCl_2(NMes^F)_2(dme)]$ (**9**)	13.7	870	3,820	76.0 (84.3)	64.1	3.0 (33.7)	49.1	50.9	21.0	11.3

10	[WCl$_2$(NPh^F)$_2$(dme)] (**10**)	62.7	141,340	135,350	84.7 (97.8)	82.8	14.7 (5.2)	3.6	96.4	0.6	0.0
11	[WCl$_2$(NDipp)(N^{i}Pr)(dme)] (**11**)	64.0	29,200	27,460	60.6 (97.2)	58.9	36.7 (1.8)	4.6	95.4	2.7	0.0
12	[WCl$_2$(NDipp)(N^{t}Bu)(dme)] (**12**)	166.0	99,240	35,980	67.6 (98.0)	66.2	29.8 (1.6)	3.7	96.3	2.6	0.1
13	[WCl$_2$(NDipp)(NMes)(dme)] (**13**)	59.0	47,590	37,390	71.6 (97.9)	70.1	24.6 (2.1)	5.2	94.8	3.8	0.0
14	[WCl$_2$(NDipp)(NTcp)(dme)] (**14**)	10.7	5,330	29,810	59.8 (97.7)	58.4	29.6 (2.1)	4.7	95.3	10.6	0.1
15	[WCl$_2$(NDipp)(NTfp)(dme)] (**15**)	67.0	125,970	113,070	67.1 (98.1)	65.8	31.2 (1.6)	3.8	96.2	1.7	0.0
16	[WCl$_2$(NDipp)(NDnp)(dme)] (**16**)	13.0	1,640	7,780	63.7 (96.7)	61.6	21.5 (3.9)	8.1	91.9	14.8	0.1
17	[WCl$_2$(NDipp)(NTpp)(dme)] (**17**)	72.9	144,740	119,070	74.4 (98.4)	73.2	24.3 (1.8)	4.1	95.9	1.3	0.0
18	WCl$_6$ / 2 PhNH$_2$ / 4 Et$_3$N [f]	3.3	1,500	27,070	90.4 (97.3)	88.0	9.6 (19.5)	19.5	80.5	0.0	85.4
19	WCl$_6$ / 2 DippNH$_2$ / 4 Et$_3$N [f]	2.6	1,480	34,170	93.2 (100.0)	93.2	6.8 (0.0)	0.0	100.0	0.0	96.3

[a] General conditions: 20 μmol W pre-catalyst; 300 μmol EtAlCl$_2$ (15 eq to W); 74 mL PhCl (solvent); 60 °C; 40 barg C$_2$H$_4$ pressure (41 bara); stirrer speed 1000 rpm; nonane standard (1.000 mL). Full details of catalysis procedures, including ethylene uptake data, are available in the SI. Unless stated otherwise, catalytic runs were performed until consumption of C$_2$H$_4$ dropped below 0.2 g min^{-1} or until the reactor was filled. [b] TON (productivity) is reported in (mol C$_2$H$_4$)(mol W)$^{-1}$. [c] Activity is reported in (mol C$_2$H$_4$)(mol W)$^{-1}$h^{-1}. [d] Wt% of liquid fraction. [e] Wt% of total product. [f] Data taken from reference 19.

The symmetrical bis(imido) tungsten(VI) complexes **7**–**10** were tested for ethylene dimerization catalytic performance in order to examine the effect of changing the imido moiety in isolation (Fig. 3). Complex **7** bearing the more electron-withdrawing, but less bulky 2,4,6-trifluorophenyl (Tfp) exhibited a three-fold improvement in catalytic activity, whilst maintaining equally good catalyst stability compared with Dipp-substituted complex **4** (Table 3, entry 7). Further increasing the electron withdrawing nature of the imido substituents using bis(imido) pre-catalysts **9** (perfluorophenyl, Ph^F) and **10** (2,4,6-tris(trifluoromethyl)phenyl, Mes^F), led to a reduction in activity (Figure 3), with **10** proving almost inactive and non-productive (Table 3, entry 9). This overall trend in activity as a function of imido substituent is consistent with electronic factors predominating since the steric demands vary according to DippN > Mes^FN > Ph^F (see reference 19).

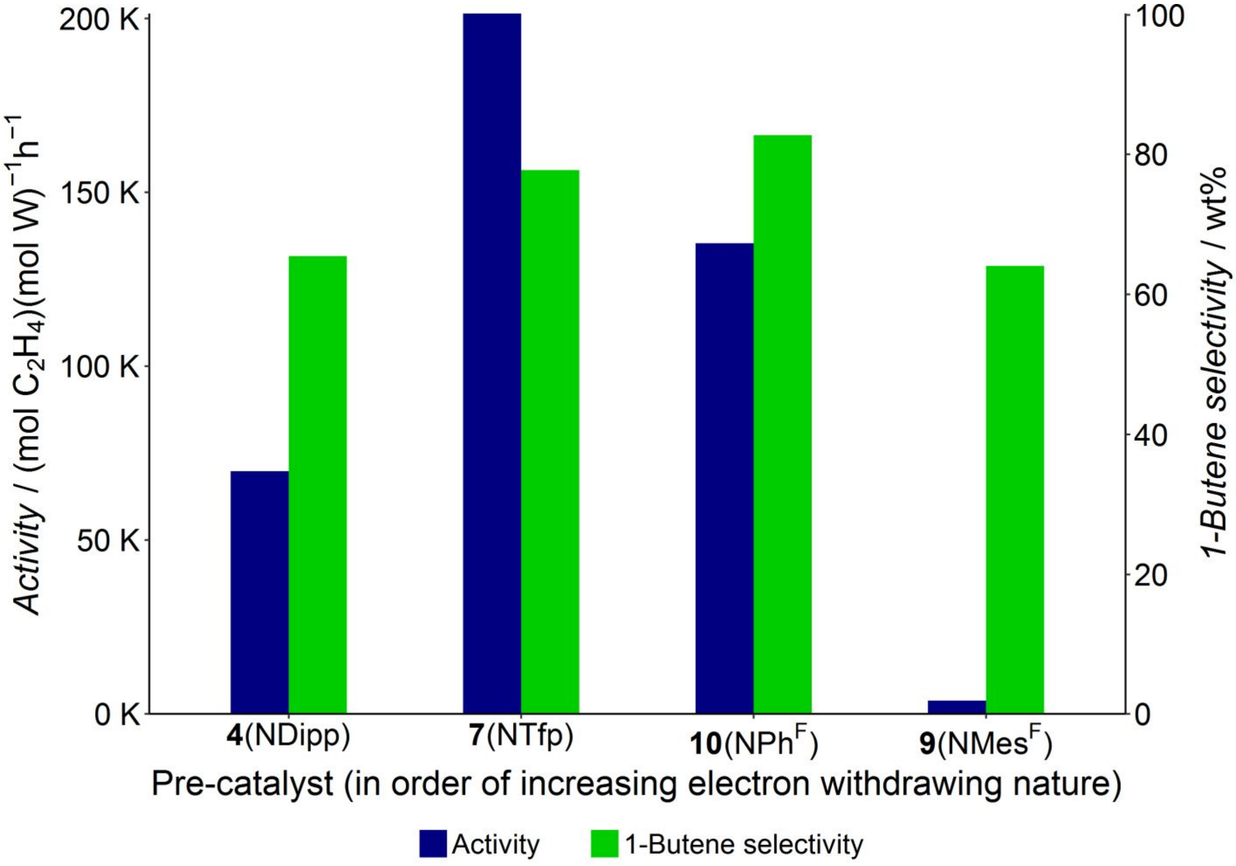


Figure 3. Graphical representation of the trends in activity and selectivity as the electron withdrawing nature of the imido substituents is increased with symmetrically-substituted pre-catalysts **4, 7, 9,** and **10** undertaken with 40 barg ethylene pressure at 60 ℃.

The nature of the imido substituents also impacts on the lifetime of the different catalytic systems. Catalysts generated from complexes **8** and **9** deactivated quickly and gave ethylene up-take traces quite different from those obtained in tests using pre-catalysts **4, 7** and **10.** For each of the tests using complexes **4, 7** and **10** catalytic activity increased over the course of reaction before product filling the autoclave vessel halted reaction (see Figures S14 and S15 vs S10, S13 and S16). The performance of pre-catalysts **4**, **7** and **10** is consistent with that observed for the best-performing mono(imido) pre-catalysts.[19]

To further examine steric influences of the imido substituents, complex **8** featuring the bulky 2,4,6-tri(phenyl)phenyl (Tpp) group was tested (Table 3, entry 8). Compared to the performance achieved using **4** (entry 4), pre-catalyst **8** showed both a four-fold reduction in activity and a truncated catalyst lifetime, hence a very low productivity.

Together the results from tests with pre-catalysts **4**, **7-10** suggest that both electronic and steric factors influence the activity and catalyst stability (manifested as productivity), as also observed for mono(imido) tungsten(VI) pre-catalysts.[19] In contrast, the product selectivities obtained using pre-catalysts **4**, **7-10** were largely unaffected by steric factors, with complexes **4** and **8** giving rise to very similar amounts of 1-butene. However, on moving from complex **4** to **7** to **10**, i.e. on increasing the electron withdrawing nature of the imido substituent,[19] a significant increase in selectivity to 1-butene (65.5 versus 77.8 versus 82.8 wt%) was observed resulting from a reduction in the formation of C_6 products (Figure 3). In contrast, pre-catalyst **9** bearing the most electron withdrawing imido substituent (Mes^F) gave a reduced 1-butene selectivity similar to that obtained using complex **4.**

Analysis of the C_6 products formed in tests with pre-catalysts **4**, **7**, **9**, and **10** revealed very little 1-hexene was formed. Instead, methylpentenes (MPs) were the primary products (predominantly equal proportions of 2-ethyl-1-butene and 3-methyl-1-pentene), observations that together are indicative of 1-butene incorporation. This behavior again agrees with observations made for the mono(imido) pre-catalysts.[19] The C_6-product selectivity achieved starting with complex **9** was markedly different to that from all the other pre-catalysts, giving a roughly 50:50 split between linear and branched material, with the linear fraction being almost exclusively 1-hexene. None of the pre-catalysts **4, 7** and **10** gave any polymer by-product, while systems derived from complexes **8** and **9** gave only trace quantities.

2.2. Impact of the imido substituent – unsymmetrical pre-catalysts. To further explore the steric and electronic influence of imido substituents on catalytic performance, a series of unsymmetrical bis(imido) tungsten(VI) complexes **11**–**17** was prepared. These complexes feature one Dipp-substituted imido moiety and a second imido group, which was varied in a systematic fashion.

Pre-catalysts [WCl_2(NDipp)(NR)(dme)] (**11:** R=^{i}Pr; **12:** R=^{t}Bu) bearing an alkyl imido motif were only half as active as the bis(Dipp) derivative **4**; the more sterically encumbered variant **12** was slightly more active than **11**. Despite their low activity, both complexes **11** and **12** afforded very stable systems, which showed minimal deactivation over the reaction course (see Figures S17 and S18).[32] The liquid fraction selectivity achieved with complex **12** was almost identical to that afforded using **4**, but the performance of **11** was slightly inferior. The catalytic performance of pre-catalyst [WCl_2(NDipp)(NMes)(dme)] (**13**) was similar to that achieved using complexes **11** and **12** (Table 3, entry 13). Deactivation of the system derived from **13** was faster than that for either pre-catalysts **11** or **12**, resulting in low overall productivity. The liquid fraction selectivity was slightly better using **13** with 4.6 wt% more 1-butene being formed relative to that with **4**; again, no polymer by-product was detected.

Inclusion of the electron-withdrawing 2,4,6-trichlorophenyl (Tcp) and 2,6-dinitrophenyl (Dnp) substituents, pre-catalysts [WCl_2(NDipp)(NR)(dme)] (**14:** R= Tcp; **16:** R= Dnp), gave systems with low initial catalytic activities that deactivated quickly; the selectivities to 1-butene were also low (Table 3, entries 14 and 16). In contrast, the N-Tfp-substituted pre-catalyst **15** gave a ~60% increase in activity compared to that achieved using complex

4.[33] This behavior was consistent with that of the equivalent symmetrical pre-catalysts (**7** versus **4**), where such a change in substituent led to increased activity. As for symmetrically-substituted pre-catalysts **4,7-10**, complex **15** also demonstrated increasing activity over the course of the test reaction (see Figure S21). The liquid fraction selectivities obtained using pre-catalysts **4** and **15** were almost identical however. In contrast, for the symmetrical complexes increasing the electron withdrawing nature of the imido substituent gave an increased selectivity to 1-butene. Within experimental error, the activity of pre-catalyst [WCl_2(NDipp)(NTpp)(dme)] (**17**) bearing the bulky N-Tpp group (Table 3, entry 17) was the same as that of the most active of the unsymmetrical bis(imido)-based system **15** at 60 °C. However, the selectivity achieved with **17** (73.2 wt% 1-butene) is greater than that demonstrated by either pre-catalysts **4** and **15**; again, no polymer by-product was obtained using pre-catalyst **17.** The ethylene up-take trace associated with pre-catalyst **17** showed that activity increased during the early part of reaction, and then plateaued (see Figure S23). The reasonable catalytic performance that resulted from use of pre-catalyst [WCl_2(NDipp)(NTpp)(dme)] (**17**) contrasts with the very low activity and short lifetime achieved when starting from [$WCl_2(NTpp)_2$(dme)] (**8**). This change in catalytic behavior again highlights that there is a very delicate balance of factors required to give optimal catalytic performance, as already described for the symmetrical systems [$WCl_2(NMes^F)_2$(dme)] (**9**) vs. [$WCl_2(NTfp)_2$(dme)] (**7**) and [$WCl_2(NPh^F)_2$(dme)] (**10**), which if pushed to an extreme, can lead to a dramatic loss of performance.

To obtain a picture of the way in which the various imido substituents influence the performance of each catalytic system formed on activation with $EtAlCl_2$, the catalytic activity and selectivity obtained using each catalyst system was plotted against a variety of structural (bond lengths and angles, % buried volume of ligands), spectroscopic (^1H and ^{13}C NMR chemical shifts), and electronic (imido ligand parent amine pK_a) characteristics (see section S11 in SI). However, no correlations were established. This lack of relationship between the various pre-catalyst parameters and the observed catalytic activities or selectivities is consistent with both the complex electronic nature of the cis bis(imido) framework (strong electronic coupling across the C-N-W-N-C skeleton) and the difficulty in varying just a single parameter.[30] Therefore, only generalized structure/activity correlations can be made meaningfully in this context (vide supra).

2.3. Comparison of the catalytic performance of the well-defined pre-catalysts versus 'in situ' catalysts. Table 3 entries 18 and 19 present data for the catalytic system generated in situ,[15] and tested under the same conditions. These tests revealed that, as with the mono(imido) complexes,[19] the performance of catalysts generated from pre-formed bis(imido) complexes was much superior to that of systems prepared in situ (i.e. $WCl_6/2RNH_2/4NEt_3$). Specifically, the activities and productivities were much lower for the 'in situ' system, which also formed polymer as the primary product. However, within the albeit small liquid fraction, the selectivity to 1-butene was higher than for the pre-formed imido complexes.

2.4. The effect of temperature. Selected pre-catalysts were screened at reaction temperatures of both 60 and 70 °C (Figure 4). In order to maintain the same concentration of ethylene in solution at the two reaction temperatures, thus ensuring that the effect of temperature was examined in isolation, the ethylene pressure was increased from 40 barg (60 °C) to 45 barg for the tests undertaken at 70 °C.[34] With the exception of pre-catalysts **8** and **9** (Table 4 entries 4 and 5), all other systems gave significantly increased activity (generally approximately double) on raising the reaction temperature, with **7** remaining the most active at both temperatures. Notably, at 70 °C the activity of pre-catalyst $[WCl_2(NDipp)_2(py)_2]$ (**5**) increased by ten-fold. This difference has been attributed to the pyridine ligands being more labile at the higher temperature compared with dme.[18]

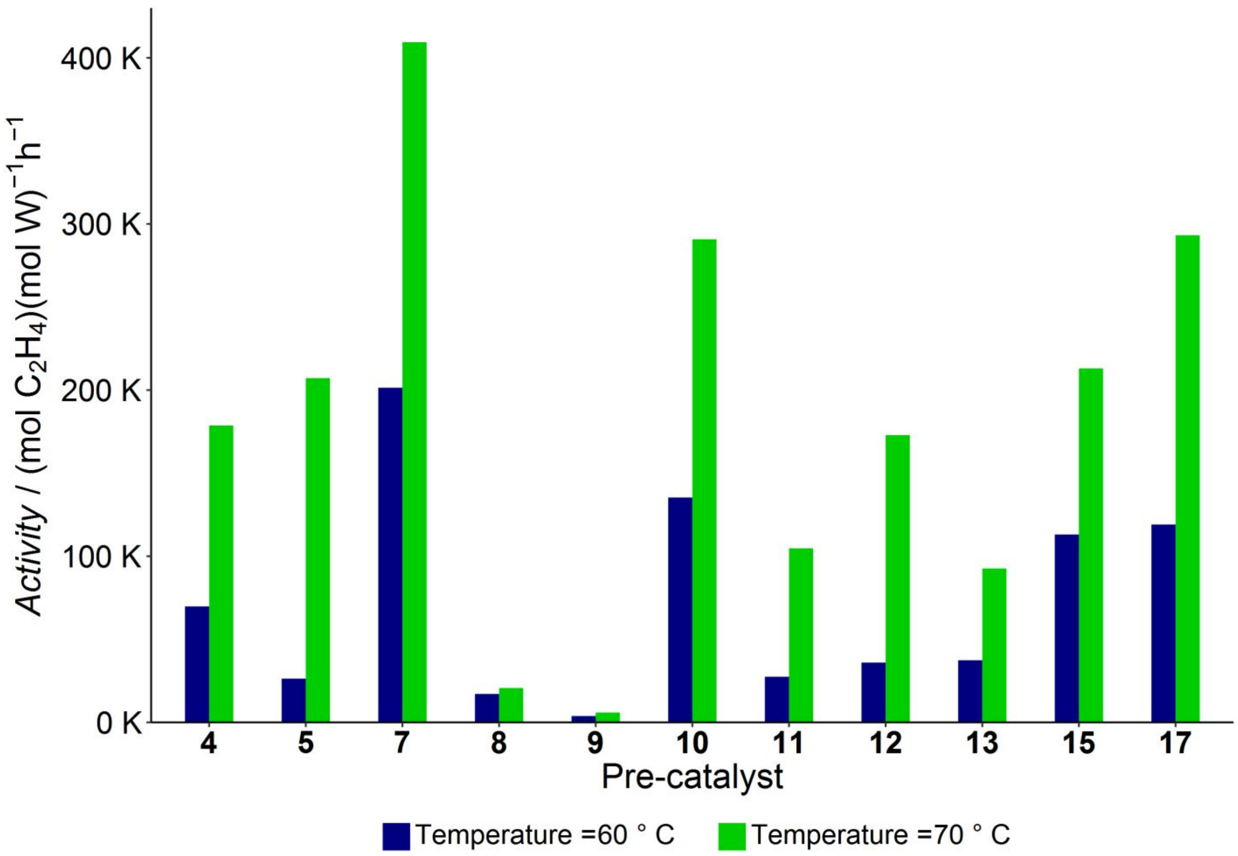


Figure 4. Comparison of the activities of selected pre-catalysts achieved in tests undertaken at 60 ([C_2H_4] = 3.56 M) versus 70 ℃ ([C_2H_4] = 3.58 M).

On raising the reaction temperature from 60 to 70 ℃ all of the pre-catalysts, with the exception of **12**, performed either with no change or with an increased selectivity to 1-butene (in the range 0.7 and 13.1 wt%), Figure 5.[35] In contrast, the selectivity achieved with pre-catalyst **12** decreased slightly by −5.3 wt%. Pre-catalyst **9** gave the highest selectivity to 1-butene at both 60 and 70 ℃ (82.8 and 82.4 wt%, respectively).

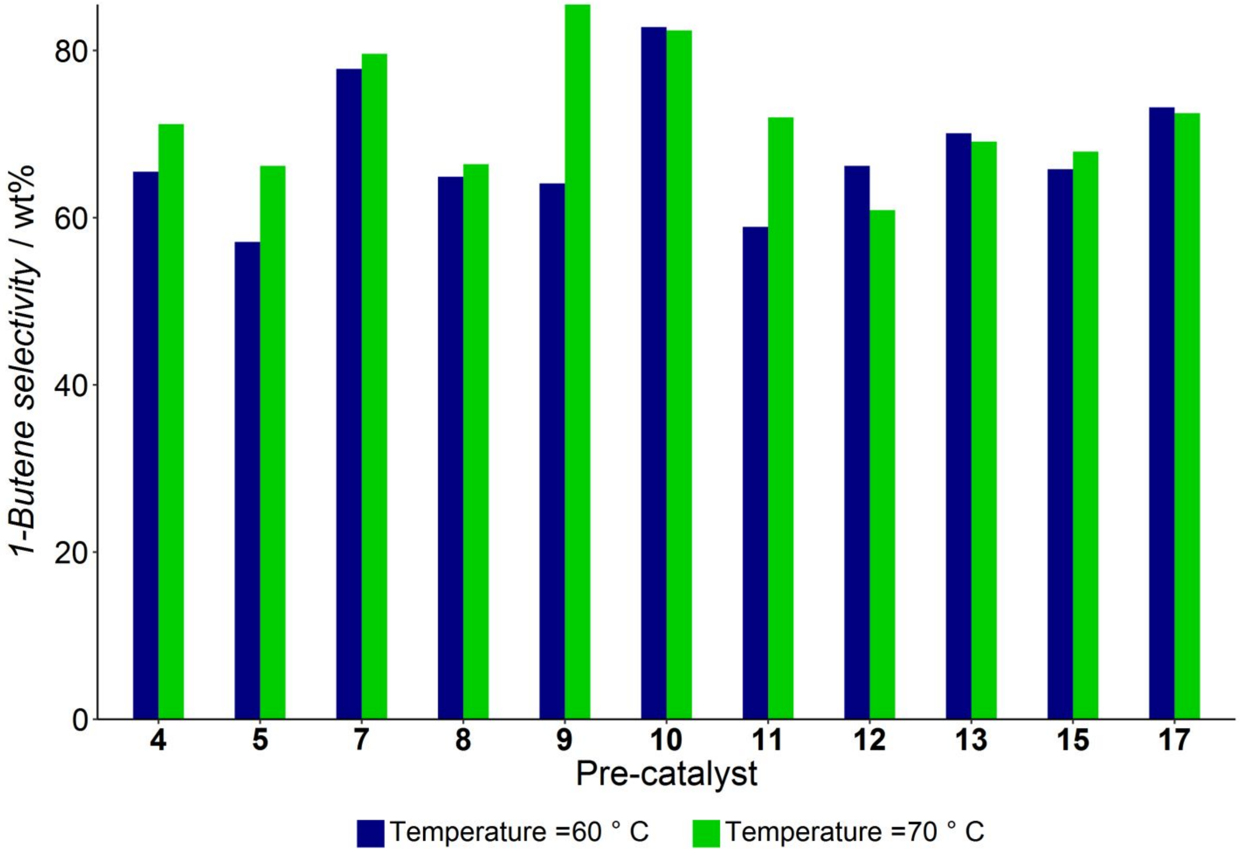


Figure 5. Comparison of the pre-catalyst selectivities achieved in tests run at 60 ℃ ([C_2H_4] = 3.56 M) versus 70 ℃ ([C_2H_4] = 3.58 M).

At 70 ℃ the catalytic activity and selectivity followed the same trends as for the tests carried out at 60 ℃, with complex **7** remaining the most active (Figure 3 versus Figure 6). In contrast, the selectivity trend differed slightly for tests at 70 ℃, with complex **9** no longer being an outlier. Thus, at 70 ℃, as the electron withdrawing character of the imido substituent was raised, so the selectivity to 1-butene increased. Note, complex **9** remains an ineffectual pre-catalyst as indicated by the low activity and productivity that ensued. The selectivity within the C_6 fraction is very similar at 60 and 70 °C, with methylpentenes (MPs) being the major products in all cases, except again for complex **9** (Table 4, entry 5).

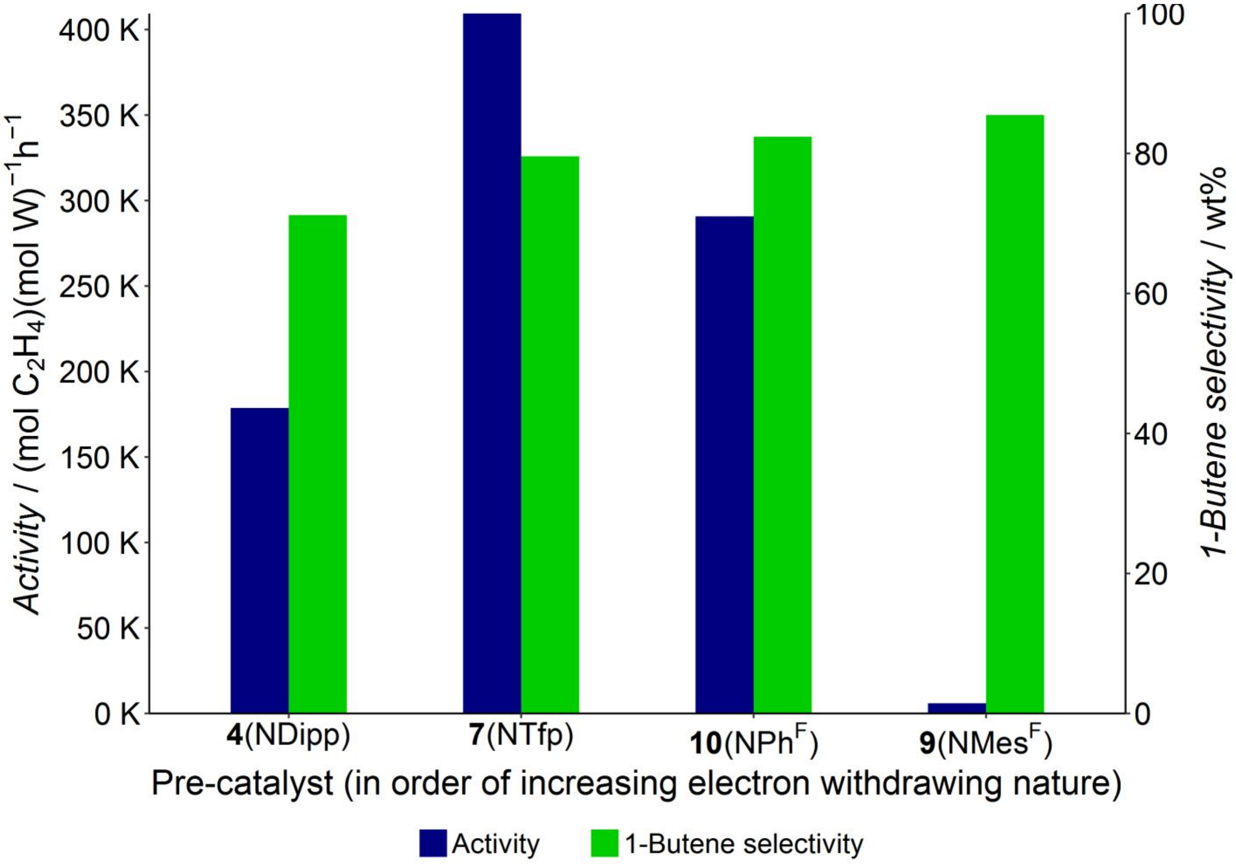


Figure 6. Trends in activity and selectivity as the electron withdrawing nature of the imido substituents are increased (left to right) with symmetrical pre-catalysts at 70 °C.

Given the increases in catalytic activity and selectivity observed on raising reaction temperature from 60 to 70 ℃, a number of tests were attempted at 80 ℃. However, for reactions run at 80 ℃ it proved impossible to keep the system isothermal. This led to runaway exotherms occurring, which necessitated that the reactions were terminated. This contrasts with all the tests performed at 60 and 70 ℃ where the internal autoclave temperature was readily maintained within ±1 ℃ of the set point. A single example of a reaction undertaken at 80 ℃ with pre-catalyst [WCl_2(NDipp)(N^tBu)(dme)] (**12**) is included in the SI for reference (Table S4). Despite achieving a comparatively high activity, the internal reactor temperature rose from 80 to 163 ℃ during the course of this reaction making the data uninformative.

Table 4. Ethylene dimerization catalysis at 45 barg ethylene pressure and 70 °C using bis(imido)tungsten(VI) pre-catalysts.[a]

Entry	Pre-catalyst	Rxn Time {min}	TON [b]	Activity [c]	C_4 [d] {wt%} (% 1-C_4)	1-C_4 [d] {wt%}	C_6 [d] {wt%} (% 1-C_6)	Linear C_6 {% of C_6}	MPs {% of C_6}	C_{8+} [d] {wt%}	PE [e] {wt%}
1	[$WCl_2(NDipp)_2$(dme)] (**4**)	45.1	134,340	178,680	72.6 (98.1)	71.2	25.9 (1.3)	6.3	93.7	1.5	0.0
2	[$WCl_2(NDipp)_2(py)_2$] (**5**)	36.4	125,670	207,210	67.5 (98.0)	66.2	30.8 (1.7)	4.0	96.0	1.7	0.0
3	[$WCl_2(NTfp)_2$(dme)] (**7**)	21.2	141,610	409,410	81.6 (97.6)	79.6	17.7 (3.8)	5.2	94.9	0.8	0.0
4	[$WCl_2(NTpp)_2$(dme)] (**8**)	82.9	28,570	20,680	68.2 (97.4)	66.4	28.4 (2.6)	10.3	89.7	3.4	0.1
5	[$WCl_2(NMes^F)_2$(dme)] (**9**)	22.8	2,260	5,940	89.9 (95.1)	85.5	3.2 (41.0)	63.7	36.3	6.9	4.0
6	[$WCl_2(NPh^F)_2$(dme)] (**10**)	29.0	140,300	290,770	84.4 (97.6)	82.4	15.1 (5.2)	3.7	96.3	0.5	0.0
7	[WCl_2(NDipp)(N^iPr)(dme)] (**11**)	57.0	99,030	104,750	73.7 (97.7)	72.0	24.7 (1.7)	4.6	95.4	1.6	0.0
8	[WCl_2(NDipp)(N^tBu)(dme)] (**12**)	34.5	99,420	172,900	62.0 (98.2)	60.9	36.0 (1.9)	4.2	95.8	2.0	0.0
9	[WCl_2(NDipp)(NMes)(dme)] (**13**)	81.0	124,330	92,630	70.7 (97.7)	69.1	28.2 (1.5)	4.1	95.9	1.1	0.1

10	$[WCl_2(NDipp)(NTfp)(dme)]$ (**15**)	36.1	128,340	213,060	69.3 (98.0)	67.9	28.4 (1.7)	3.9	96.1	2.3	0.0
11	$[WCl_2(NDipp)(NTpp)(dme)]$ (**17**)	29.4	143,360	293,210	73.8 (98.4)	72.5	25.0 (1.9)	4.6	95.5	1.3	0.0

[a] General conditions: 20 μmol W pre-catalyst; 300 μmol $EtAlCl_2$ (15 eq to W); 74 mL PhCl (solvent); 70 °C; 45 barg C_2H_4 pressure (46 bara); stirrer speed 1000 rpm; nonane standard (1.000 mL). Full details of catalysis procedures, including ethylene uptake data, are available in the SI. Unless stated otherwise, catalytic runs were performed until consumption of C_2H_4 dropped below 0.2 g min^{-1} or until the reactor was filled. [b] TON (productivity) is reported in (mol C_2H_4)(mol $W)^{-1}$. [c] Activity is reported in (mol C_2H_4)(mol $W)^{-1}h^{-1}$. [d] wt% of liquid fraction. [e] wt% of total product.

2.5. Catalysis test by-product formation. For most ethylene oligomerization systems, the amounts of secondary products formed by incorporation are first order in the concentration of primary products.[36] Generally, when catalytic oligomerization tests are performed in batch mode, the concentration of the primary product increases over time, which leads to a faster rate of incorporation and hence to increasing amounts of secondary products. In turn, this leads to a reduction in the relative selectivity for the primary product. An exception to this first order dependence was first highlighted during investigation of a Cr-pyrrole-based trimerization catalyst.[37] Study of these chromium-based systems showed that the formation of branched decenes occurred via two routes: one that was related directly to 1-hexene concentration, and one that was independent. This latter observation suggested that there is a pathway by which 1-hexene is formed and re-incorporated (to give secondary products) without its dissociation from the chromium center. In this case the formation of branched decenes is still positive order in 1-hexene, albeit a fractional order less than one.[37]

In other work involving mono(imido) tungsten pre-catalysts, we have shown that the ethylene oligomerization selectivity is independent of productivity. Thus, we sought here to explore if such a selectivity/productivity relationship held for the bis(imido) tungsten pre-catalysts.[19] To this end, two tests employing complex **4** (45 barg ethylene pressure, 70 °C) were undertaken with different ethylene contact times giving 'low' and 'moderate' productivities (Table 5, entries 1 and 2, respectively). The results from these two tests were compared to a standard 'high' productivity run (i.e. Table 4, entry 1). Consistent with the situation observed for the mono(imido)tungsten complexes, the reactions stopped at 'low' and 'moderate' productivities both made less of the primary product 1-butene rather than more (as would be expected if incorporation was dependent upon the concentration of primary product) or the same (as would be expected if incorporation was independent of the concentration of primary product).[19] Indeed, the selectivity to 1-butene rose markedly from 59.2 to 66.2 to 71.2 wt%, as the productivity increased.

In order to understand this observation, the formation of products other than 1-butene as a function of time must be considered. The catalysis described herein was performed such that the bis(imido)tungsten pre-catalysts were activated in the reaction vessel by addition of aluminum co-catalyst followed by immediate pressurization of the autoclave with ethylene. Inspection of the ethylene uptake traces (see SI) reveals that pressurization was complete typically within 1-2 minutes. However, during this initial time window catalysis would be occurring at an ethylene concentration[38] that was substantially lower than that during the remainder of the reaction. Furthermore, although fast during this initial reaction period,[17] transformation of the pre-catalyst into the true catalytically active species will be ongoing, giving rise to transitory species that are likely to perform differently from the fully-activated catalyst.

For the reaction with pre-catalyst **4** (45 barg ethylene pressure, 70 °C) stopped at 'low' productivity there was an increased selectivity towards C_{8+} materials (Table 5, entry 1, 10.1 wt%) compared with the standard run (Table 4, entry 1). This indeed suggested that during the early stages of reaction a transitory species was present that supported enhanced chain growth, despite the lower ethylene concentration. Comparing the 'moderate' and 'high' productivity runs (Table 5, entry 2 vs Table 4, entry 1) the level of C_{8+} formation was almost identical (reduced by 0.2 wt%), with the further enhancement in 1-butene selectivity resulting from reduced C_6 formation; the composition of the C_6 and C_{8+} fractions remained invariant with productivity. The absolute amounts of C_{8+} material made for the 'low', 'moderate' and 'high' productivity reactions (Table 6) increased with productivity, consistent with C_{8+} products forming continuously during reaction. However, the average calculated rate of formation of the C_{8+} product fraction was initially much higher than those calculated for the C_4 or C_6 fractions (Table 6). In contrast, the rate of formation of the C_6 fraction was initially low, but roughly equal for the reactions run to 'moderate' and 'high' productivities. Taken together these data are consistent with the rates of C_6 and C_{8+} formation being independent of 1-butene concentration. This indicated that the route through which C_6 products formed was almost exclusively through reaction of 1-butene prior to its dissociation from the metal. Once dissociated, 1-butene is essentially unable to re-coordinate to the tungsten center.

The overall activity of the reaction of **4** stopped at 'low' productivity (and that quenched at 'low' productivity, *vide infra*) was roughly half that for the reactions of **4** run to 'moderate' and 'high' productivities, which were the same within experimental error. This again indicated that in the nascent stages of the reaction there is less tungsten in the active form and/or that species that are present, which mediate catalysis to the heavier products, have lower activity than those in the final fully activated form. However, inspection of the rate of formation of 1-butene specifically (Table 6) revealed that this rate increased consistently with productivity. Hence, the increased selectivity observed with productivity is not just due to an ever-decreased weighting of the initial high levels of C_{8+} formation, but also due to an increase in the rate of catalysis towards the primary product, 1-butene (1-C_4). This is further highlighted by the ratio of C_6:1-C_4 products, which decreased with productivity. Thus, the rate of 1-butene formation will depend primarily upon the concentration of active tungsten species and the ethylene concentration in solution. One possible explanation for the increasing rate of 1-butene formation over time is that gradually more tungsten species reach the active state. However, this can be ruled out, as the data showed that activation was complete long before the time the reaction run to 'moderate' productivity was stopped.

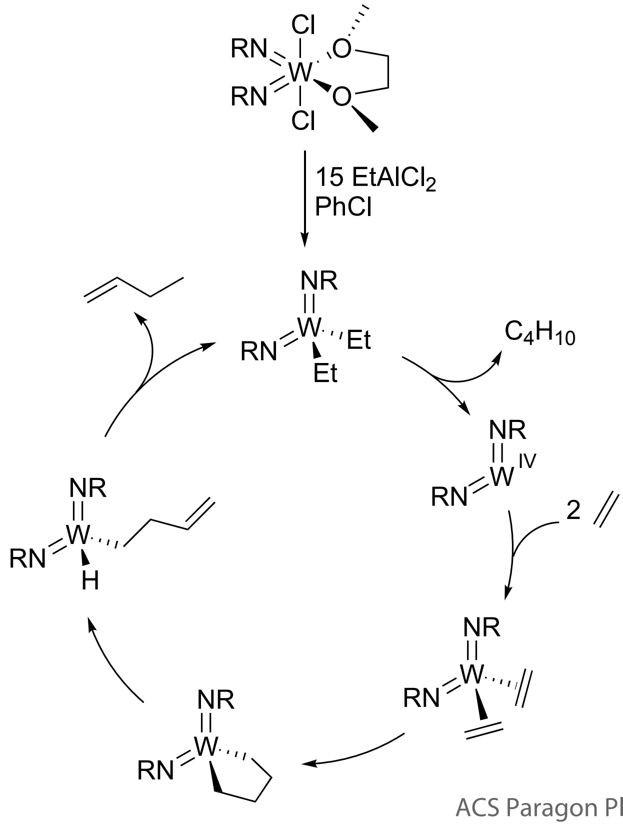
Together, these observations indicated that the ethylene concentration in solution must increase with time, although the pressure was kept constant during reaction. To explore this effect, a series of experiments were conducted to measure the solubility of ethylene in chlorobenzene and in mixtures of chlorobenzene and 1-butene in varying ratios (see SI for full details). This study revealed that on a volumetric basis, ethylene is twice as soluble in liquefied 1-butene as in chlorobenzene. Consequently, a substantial increase in ethylene concentration will occur over the course of a batch reaction as 1-butene is formed. This, in turn, explains the observed increase in rate of 1-butene formation and the improved selectivity as higher productivities were reached.

Since we have demonstrated that differences in catalytic performance occurring during the very early stages of a test reaction lead to the formation of reaction by-products (vide supra), it was important to establish whether effects of changes in temperature/pressure as a test run was terminated also had an impact. For all the catalysis tests reported herein, reactions were terminated by closing the ethylene supply and cooling the reactor to −5 °C; initial cooling was rapid, with the reactor reaching ~30 °C within 2-3 minutes. Note, that at 30 °C catalysis has been shown to proceed very poorly.[19] However, to probe the extent of further catalysis taking place within this cooling regime, the reaction involving $[WCl_2(NDipp)_2(dme)]$ (**4**) run to low productivity (Table 5, entry 1) was repeated, but immediately after the ethylene supply was closed, an aliquot of water was added to the reactor from a burette using an over-pressure of inert gas (Table 5, entry 3). These two test runs afforded extremely similar selectivities after experimental variability was considered, which confirmed that minimal further catalysis occurred after the ethylene supply was closed and rapid cooling applied.

2.6. The influence of co-catalyst. Previous studies of related tungsten-based oligomerization catalysts have examined the influence of the aluminum co-catalyst on performance.[14,15,18,19] Consequently, a brief study was undertaken here in which $EtAlCl_2$

was replaced with $MeAlCl_2$ with pre-catalysts $[WCl_2(NDipp)_2(dme)]$ (**4**) and $[WCl_2(NDipp)(N^tBu)(dme)]$ (**12**); see Table 7 versus Table 3, entries 4 and 12 for the equivalent $EtAlCl_2$ examples). Consistent with previous findings, the activity and catalyst lifetime (manifested as productivity) were both reduced dramatically on replacing $EtAlCl_2$ by $MeAlCl_2$.[15,19] For the pre-catalyst **4** the selectivity to C_4 was markedly lower with $MeAlCl_2$ (−23.3 wt%), with the selectivity within the C_4 fraction also having decreased appreciably (−16.7%). These changes were accompanied by a reduction in the C_6 fraction of −22.3 wt%, such that the overall amount of 1-butene produced increased by 7.9 wt% (cf. $[WCl_4(NDipp)(thf)]$ in previous work).[19] In contrast, much smaller variations in performance were observed using the pre-catalyst **12** in combination with $MeAlCl_2$ (C_4, +6.4 wt%; 1-C_4 in C_4, −0.6%; C_6, −3.8 wt%), although overall the amount of 1-butene increased by nearly the same extent (+5.9 wt%), see $[WCl_4(NPh)(thf)]$ (**2d**) in previous work.[19] The reason why differing pre-catalysts respond so differently to replacement of $EtAlCl_2$ with $MeAlCl_2$ remains unclear.

2.7. Probing the role of tungsten oxidation state. For many selective ethylene oligomerization catalysts considerable debate still surrounds the oxidation state of the catalytically-relevant transition metal species.[14,39,40b] Exploring electronic reaction manifolds is a challenging task, not least because using complexes of preset oxidation state can be problematic since the sequence of reaction steps required to form the active catalyst may simply not be available to the chosen pre-catalysts of a particular oxidation state. However, for the bis(imido) systems of interest here, there is a body of evidence that points to olefin dimerization proceeding through a metallacyclic pathway involving oxidative ethylene coupling at a tungsten(IV) center (Scheme 5).[18,40] Consequently, here we have screened the catalytic performance of the bis(imido)tungsten(IV) complex $[W(NDipp)_2(PMe_3)_3]$ (**18**), a potential precursor to the coordinatively- and electronically-unsaturated W^{IV} bis(imido) species necessary for a metallacyclic pathway, under a variety of conditions. The performance of **18** has been compared with that of the related tungsten(VI) pre-catalyst **4**.



Scheme 5. A possible mechanism for catalytic production of 1-butene via a tungsten bis(imido) metallacyclic intermediate based on previous computational studies; see reference 40c.

In the absence of an aluminum-based co-catalyst no reaction between **18** and ethylene was detected (Table 8, entry 3). This is consistent with strong coordination of PMe_3 to the tungsten center, which was not displaced by ethylene, and the coordinative and electronic saturation of **18** in this five-coordinate cis bis(imido) manifold.[41]

Activation of complex **18** with $EtAlCl_2$ (W:Al 1:15) at both 60 or 70 ℃ gave systems that had low activity and very short lifetimes compared with those achieved with **4**/$EtAlCl_2$ (Table 8, entries 1 and 2).[42] Tests conducted using **18** at 60 ℃ gave a slightly different selectivity to that using **4**, but at 70 ℃ the selectivity achieved with **18** was indistinguishable from that achieved with **4**. In order to enhance the displacement and sequestration of the PMe_3 from **18**, tests were performed using more Lewis acidic $AlCl_3$ (Table 8, entries 4 and 5). No reaction with ethylene was detected at an aluminum loading of 0.1 equivalents, while with 10 equivalents only a trace amount of 1-butene was detected (20 turnovers).

Together these results present a complicated scenario. Partial abstraction and weak sequestration of PMe_3 by $EtAlCl_2$,[31] followed by ethylene dimerization via an oxidative coupling/metallacyclic pathway (as proposed computationally, i.e. Scheme 5),[40] would account for the observed ethylene dimerization mediated by **18**/$EtAlCl_2$. However, such a pathway is at odds with the lack of catalysis achieved with **18**/$AlCl_3$. Consequently, in the absence of further investigations, a reaction manifold in which $EtAlCl_2$ plays a more complex role such as alkylation and subsequent β-hydride elimination forming a tungsten hydride species (something supported by the comparatively poor performance of $MeAlCl_2$ activator) cannot be ruled out.

2.8. Comparison with the AlphaButol process. Since the titanium-based AlphaButol process (using $Ti(OBu)_4/Et_3Al$) is the only commercialized ethylene dimerization protocol, a comparison of its performance against the results obtained herein with tungsten-centered systems was pertinent. From the studies above, the overall best performing bis(imido)tungsten(VI) pre-catalysts were complexes **7** and **10**, when deployed at 70 °C. The activity achieved using **7** (409,410 (mol C_2H_4)(mol W)$^{-1}$h^{-1}), Table 4, entry 3, is twenty-five-times higher than the best values reported for the AlphaButol process, which lie in the range 170-16,550 (mol C_2H_4)(mol W)$^{-1}$h^{-1}.[2b,3b,4,5,6] Comparing on a mass rather than on a mole basis, the activity of pre-catalyst **7** (62,490 g(gW)$^{-1}$h^{-1}) is nevertheless still six-times greater than that of AlphaButol (100-

9,700 g(gTi)$^{-1}$h^{-1}).[2b,3b,4,5,6] Both the Ti- and W-based catalyst systems have the capability of operating to high productivities.[4,5,6] The other relevant parameter in calculating the economics of catalyst usage is the cost per mole or mass of the pre-catalyst. Whilst tungsten is a relatively cheap metal, in this regard it is clear that tungsten-imido species would be more expensive than the relatively simple titanium-containing pre-cursors employed by AlphaButol.

From an industrial stance, catalyst selectivity is the most important parameter, as high activity is worthless if undesired products are generated. In this regard both pre-catalysts **7** and **10** performed less well compared to AlphaButol systems, giving only 79.6 (**7**) and 82.4 (**8**) wt% 1-butene compared to the 93-95% of AlphaButol.[2b,3b,4,5,6] Notably, neither pre-catalyst **7** nor **10** produced any polymeric products, which is a major advantage, although despite early reports of trace polymer formation occurring with AlphaButol, later reports document examples free from polymer,[2b,3b,4,5,6] and so it may be assumed that the commercially applied configuration already avoids polymer formation.

Table 5. Ethylene dimerization catalysis at 45 barg ethylene pressure and 70 °C using bis(imido)tungsten(VI) pre-catalyst **4** operated to differing productivities by intentionally stopping the reaction at varying times before the reaction vessel filled.[a]

Entry	**Pre-catalyst**	**Rxn Time {min}**	**TON** [b]	**Activity** [c]	**C_4** [d] **{wt%} (% 1-C_4)**	**1-C_4** [d] **{wt%}**	**C_6** [d] **{wt%} (% 1-C_6)**	**Linear C_6 {% of C_6}**	**MPs {% of C_6}**	**C_{8+}** [d] **{wt%}**	**PE** [e] **{wt%}**
1	[$WCl_2(NDipp)_2$(dme)] (**4**)	4.2	4,390	62,850	60.4 (98.0)	59.2	29.5 (2.2)	5.1	94.9	10.1	0.0
2	[$WCl_2(NDipp)_2$(dme)] (**4**)	20.7	56,730	164,450	67.4 (98.2)	66.2	30.9 (1.7)	4.1	95.9	1.7	0.0
3	[$WCl_2(NDipp)_2$(dme)] (**4**) [f]	3.7	5,080	83,170	64.0 (98.0)	62.7	28.7 (2.3)	5.5	94.5	7.3	0.1

[a] General conditions: 20 μmol W pre-catalyst; 300 μmol $EtAlCl_2$ (15 eq to W); 74 mL PhCl (solvent); 70 °C; 45 barg C_2H_4 pressure (46 bara); stirrer speed 1000 rpm; nonane standard (1.000 mL). Full details of catalysis procedures, including ethylene uptake data, are available in the SI. Unless stated otherwise, catalytic runs were performed until consumption of C_2H_4 dropped below 0.2 g min^{-1} or until the reactor was filled. [b] TON (productivity) is reported in (mol C_2H_4)(mol $W)^{-1}$. [c] Activity is reported in (mol C_2H_4)(mol $W)^{-1}h^{-1}$. [d] Wt% of liquid fraction. [e] Wt% of total product. [f] Quenched with water.

Table 6. Masses, rates of formation and concentrations, of individual fractions made during reactions operated to varying productivities for Table 4, entries 1 and 2, and Table 3, entry 1, using pre-catalyst **4** (45 barg ethylene, 70 °C).[a]

Entry	**Rxn Time {min}**	**Total mass of product {g}**	**Mass of individual components {g}**				**Average rate of formation of component {(mol product)(mol W)$^{-1}$s^{-1}}**			**C_6 : 1-C_4**
			1-C_4	**C_4**	**C_6**	**C_{8+}**	**1-C_4**	**C_6**	**C_{8+}**	
1	4.2	2.463	1.458	1.488	0.727	0.249	5.16	1.71	0.44	0.50
2	20.7	31.830	21.071	21.453	9.835	0.541	15.12	4.70	0.19	0.47
3	45.1	75.374	53.667	54.722	19.522	1.131	17.67	4.29	0.19	0.36

[a] General conditions: 20 μmol W pre-catalyst; 300 μmol $EtAlCl_2$ (15 eq to W); 74 mL PhCl (solvent); 70 °C; 45 barg C_2H_4 pressure (46 bara); stirrer speed 1000 rpm; nonane standard (1.000 mL). Full details of catalysis procedures, including ethylene uptake data, are available in the SI.

Table 7. Ethylene dimerization catalysis at 40 barg ethylene pressure and 60 °C using bis(imido)tungsten(VI) pre-catalysts activated with $MeAlCl_2$ as aluminum co-catalyst.[a]

Entry	**Pre-catalyst**	**Rxn Time {min}**	**TON**[b]	**Activity**[c]	**C_4**[d] **{wt%} (% 1-C_4)**	**1-C_4**[d] **{wt%}**	**C_6**[d] **{wt%} (% 1-C_6)**	**Linear C_6 {% of C_6}**	**MPs {% of C_6}**	**C_{8+}**[d] **{wt%}**	**PE**[e] **{wt%}**
1	$[WCl_2(NDipp)_2(dme)]$ (**4**)	30.1	18,220	36,320	89.9 (81.6)	73.4	9.7 (22.4)	95.3	6.5	0.4	0.0
2	$[WCl_2(NDipp)(N^tBu)(dme)]$ (**12**)	10.0	1,590	9,250	74.0 (97.4)	72.1	26.0 (5.5)	92.0	8.0	0.0	0.6

[a] General conditions: 20 μmol W pre-catalyst; 300 μmol $MeAlCl_2$ (15 eq to W); 74 mL PhCl (solvent); 60 °C; 40 barg C_2H_4 pressure (41 bara); stirrer speed 1000 rpm; nonane standard (1.000 mL). Full details of catalysis procedures, including ethylene uptake data, are available in the SI. Unless stated otherwise, catalytic runs were performed until consumption of C_2H_4 dropped below 0.2 g min^{-1} or until the reactor was filled. [b] TON (productivity) is reported in (mol C_2H_4)(mol $W)^{-1}$. [c] Activity is reported in (mol C_2H_4)(mol $W)^{-1}h^{-1}$. [d] Wt% of liquid fraction. [e] Wt% of total product.

Table 8. Ethylene dimerization catalysis using [W(NDipp)$_2$(PMe$_3$)$_3$] (**18**) as pre-catalyst under varying reaction conditions.[a]

Entry	**Pre-catalyst**	**Rxn Time {min}**	**TON** [b]	**Activity** [c]	**C_4** [d] **{wt%} (% 1-C_4)**	**1-C_4** [d] **{wt%}**	**C_6** [d] **{wt%} (% 1-C_6)**	**Linear C_6 {% of C_6}**	**MPs {% of C_6}**	**C_{8+}** [d] **{wt%}**	**PE** [e] **{wt%}**
1	[W(NDipp)$_2$(PMe$_3$)$_3$] (**18**) [f]	10.0	500	3,010	76.2 (100.0)	76.2	23.8 (0.0)	0.0	100.0	0.0	0.4
2	[W(NDipp)$_2$(PMe$_3$)$_3$] (**18**)	10.1	1,860	11,090	74.8 (97.4)	72.9	24.7 (4.1)	4.1	95.9	0.5	0.2
3	[W(NDipp)$_2$(PMe$_3$)$_3$] (**18**) [g]	6.7	0	0	-	-	-	-	-	-	-
4	[W(NDipp)$_2$(PMe$_3$)$_3$] (**18**) [h]	7.5	0	0	-	-	-	-	-	-	-
5	[W(NDipp)$_2$(PMe$_3$)$_3$] (**18**) [i]	8.7	20	110	100.0 (100.0)	100.0	0.0 (0.0)	-	-	0.0	27.0

[a] General conditions: 20 μmol W pre-catalyst; 300 μmol EtAlCl$_2$ (15 eq to W); 74 mL PhCl (solvent); 70 °C; 45 barg C_2H_4 pressure (46 bara); stirrer speed 1000 rpm; nonane standard (1.000 mL). Full details of catalysis procedures, including ethylene uptake data, are available in the SI. Unless stated otherwise, catalytic runs were performed until consumption of C_2H_4 dropped below 0.2 g min^{-1} or until the reactor was filled. [b] TON (productivity) is reported in (mol C_2H_4)(mol W)$^{-1}$. [c] Activity is reported in (mol C_2H_4)(mol W)$^{-1}$h^{-1}. [d] Wt% of liquid fraction. [e] Wt% of total product. [f] 60 °C; 40 barg C_2H_4 pressure (41 bara). [g] No co-catalyst. [h] AlCl$_3$ (0.1 eq to W) in place of EtAlCl$_2$. [i] AlCl$_3$ (10 eq to W) in place of EtAlCl$_2$.

SUMMARY AND CONCLUSIONS

A range of symmetrical and unsymmetrical bis(imido)tungsten(VI) complexes have been prepared and, in most cases, their molecular structures determined. Along with a number of previously known variants, the potential of such complexes in combination with a chloroaluminum co-catalyst to mediate catalytic ethylene dimerization to 1-butene has been explored. The results reveal a complicated relationship between the steric and electronic factors imparted by the imido substituents, which affect both catalyst activity and lifetime. Product selectivity, however, is dominated principally by electronic considerations. In contrast, studies of the electronic influence of the imido moieties revealed that increasing their electron withdrawing character leads to enhanced selectivity to 1-butene, but that an optimum exists in terms of catalyst activity and lifetime. However, it must be noted that it is difficult to vary systematically either the steric or electronic demands of the organoimido substituents in isolation from one another. In particular, the strong electronic coupling of the two multiply bonded imido motifs in a cis orientation has a significant structural and electronic impact on the characteristics of the pre-catalysts.

It was found that catalytic tests performed at 70 °C provided significant enhancements in both 1-butene selectivity and activity over tests performed at 60 ℃, whilst maintaining similarly good catalyst lifetimes (manifested as high productivities). A comparison of the performance of $EtAlCl_2$ versus $MeAlCl_2$ as co-catalyst revealed that better performance was achieved using $EtAlCl_2$, something consistent with previous studies of related tungsten-based systems. Investigation of the catalytic performance of $[W^{IV}(NDipp)_2(PMe_3)_3]$ with $EtAlCl_2$ and $AlCl_3$ as co-catalysts revealed a complex picture. Thus, it is clear that the mechanism for ethylene dimerization is more complicated than the previously proposed metallacyclic pathway in which oxidative coupling of ethylene occurs at a coordinatively-unsaturated tungsten(IV) bis(imido) moiety. Together our results implicate the pivotal role of an aluminum ethyl species during tungsten-based pre-catalyst activation.

For all catalytic tests undertaken with bis(imido)tungsten(VI) pre-catalysts, the rates of formation of each of the C_4, C_6 and C_{8+} product fractions, selectivity, and by-product formation as a function of productivity were all investigated and outcomes related to pre-catalyst's substitution pattern. These studies showed that during the nascent phase of catalytic reaction a notably lower activity is observed, with selectivity to the C_{8+} fraction being favored during this period, most likely due to on-going catalyst activation processes. The rate of formation of 1-

butene was shown to increase with productivity as a result of the greater solubility of ethylene in 1-butene compared to the chlorobenzene solvent. Generation of C_6 by-products was found to be independent of 1-butene concentration, something consistent with a mechanism whereby 1-butene is only incorporated into secondary products when it reacts prior to dissociation from the tungsten center.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge *via* the Internet on the ACS Publications website at http://pubs.acs.org.

Full synthetic methods, characterizing data, catalysis procedures, experimental reproducibility studies, ethylene uptake data, and crystallographic data in CIF format.

Accession Codes

CCDC 1847022-1847034 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by email data_request@ccdc.cam.ac.uk, or by contacting The Cambridge

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Notes

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ABBREVIATIONS

Ph^F, perfluorophenyl; Dipp, 2,6-diisopropylphenyl; Dnp, 2,6-dinitrophenyl; Mes, 2,4,6-trimethylphenyl; MPs, methylpentenes; Tpp, 2,4,6-triphenylphenyl; Tfp, 2,4,6-trifluorophenyl; Tcp, 2,4,6-trichlorophenyl; Mes^F, 2,4,6-*tris*(trifluoromethyl)phenyl; Ttbp, 2,4,6-tri(*tert*-butyl)phenyl; py, pyridine; bipy, 2,2'-bipyridine; dme, 1,2-dimethoxy ethane; tmeda, *N*,*N*,*N'*,*N'*-tetramethyl-1,2-ethylenediamine; TON, turnover number (productivity)..

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33 Due to the observed behavior of complex **15** to undergo rapid scrambling of the imido groups in solution, this pre-catalyst was prepared as a stock solution immediately prior to use, with less than 5 minutes elapsing before use in catalysis.

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