Exploring the reactivity of tungsten *bis*(imido) dimethyl complexes with methyl aluminium reagents: implications for ethylene dimerization†

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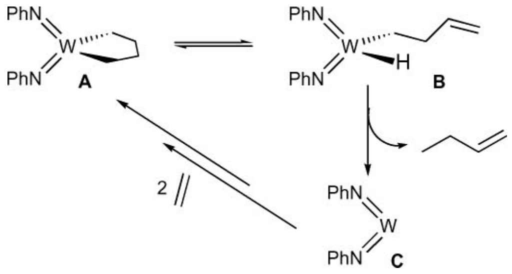
The reaction of [$WCl_2(NAr)_2(DME)$] (**1**) with excess Me_3Al affords the dimethyl complex [$WMe_2(N\{Ar\}AlMe_2\{\mu\text{-}Cl\})(NAr)$] (**2**), which on treatment with THF or $MeAlCl_2$ yields [$WMe_2(NAr)_2(THF)$] (**3**) and [$WMe_2(N\{Ar\}AlMe(Cl)\{\mu\text{-}Cl\})(NAr)$] (**5**), respectively. Complex **3** is unstable in solution dissociating to form [$WMe_2(NAr)_2$] (**4**) that may be isolated as an adduct with PMe_3, [$WMe_2(NAr)_2(PMe_3)$] (**6**). While complex **2** is inert towards ethylene, complex **3** reacts rapidly to afford a mixture of methane and but-1-ene (1 : 4). Neither complex **2** nor **3** react with propylene. Reaction of **3** with a C_2H_4/C_2D_4 (1 : 1) affords a mixture of isotopomers that is consistent with complete isotopic scrambling. The structures of complexes **1**, **2**, and **3** have been determined by X-ray diffraction.

Introduction

Since the pioneering work of Ziegler in the mid-1950s metal-catalysed alkene oligomerisation has attracted an overwhelming research effort from both academia and industry.[1–3] An area of particular importance is the catalytic dimerization of alkenes, which provides a straightforward and economical route for the manufacture of higher olefinic feedstocks for industry.[4] Here, amongst the most desirable products are the linear, short-chain materials (C_4–C_{20}) that are finding increasing use as comonomers in polyethylene manufacture, as plasticizers, and as synthetic lubricant base oils.[5] For these applications, the design of catalysts that engender high levels of control over the selectivity and extent of chain branching remains a crucial goal.

Although a number of metal-based dimerization initiator systems have been reported,[4,6] of particular interest are those derived from WCl_6, which display a desirable selectivity for the head-to-tail and tail-to-tail products resulting from α-olefin coupling.[7] In general, these tungsten-based initiators are generated *in situ* by sequential reaction of WCl_6 with an aryl amine at elevated temperatures, followed by addition of a co-initiator, typically $EtAlCl_2$ (EADC) or $Et_3Al_2Cl_3$ (W : amine : Al 1 : 2 : 10).[8,9] While the exact nature of the resulting active initiator species is unknown, it is well documented that efficient removal of HCl is one key feature in ensuring high catalytic activity.[10,11] This observation strongly suggests that either amido and/or imido tungsten complexes are generated during pro-initiator preparation. Such a notion is supported by the reports that, in combination with EADC, discrete imido complexes of the type [$WCl_4(NAr)$] (W : Al 1 : 11) are active for propylene dimerization, while related tungsten *bis*(imido) pro-initiators [$WCl_2(NAr)_2$] exhibit ethylene dimerization behaviour (W : Al 1 : 15) at elevated pressures (40 bar).[11–13]

Recently, the nature of the interplay between Me_2AlCl and various *bis*(imido) tungsten species of relevance to ethylene dimerization *via* a concerted metallacyclic coupling cycle, has been explored computationally.[14] In particular, this study probed the key degradation manifold of the metallacyclopentane (**A**) *via* a combined β-hydride/reductive elimination pathway (Scheme 1). This revealed an unexpectedly high barrier to reductive elimination from **B** (72.4 kcal mol^{-1}), something accounted for by the presence of the two strongly donating imido ligands.



Scheme 1 Proposed metallacyclic β-hydride elimination and reductive elimination/olefin dissociation steps of *bis*(imido) tungsten-initiated ethylene dimerization.

In order to attenuate the electron density at the tungsten centre and hence facilitate reductive elimination, coordination of the Lewis acidic alkyl aluminium to the nitrogen lone pairs of the imido fragments was investigated. The lowest energy arrangements were computed to be those in which there is both imido-N→Al and Cl→W coordination (Fig. 1). As anticipated the double Lewis acid adduct **A-Al₂** achieves the most significant lowering of the energy barrier to reductive elimination, by 24.3 kcal mol^{-1} relative to that determined for **A**. Clearly the overall free energy of activation for metallacycle degradation remains rather high, something that is at odds with the observed catalytic performance of such systems.[11]

Together, these contradictory observations inspired us to investigate model reactions between discrete tungsten *bis*(imido)

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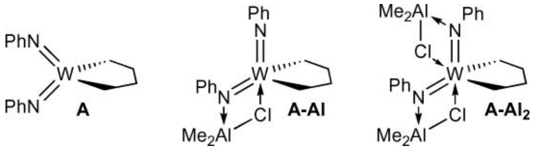


Fig. 1 Computed modes of Me_2AlCl coordination to the metallacyclic *bis*(imido) tungsten complex **A**.[14]

Table 1 Selected bond distances (Å) and angles (°) in **1**

Molecule	*A*	*B*
W–N(1)	1.7598(17)	1.7571(18)
W–N(2)	1.7599(17)	1.7579(17)
W–Cl(1)	2.3841(7)	2.3852(8)
W–Cl(2)	2.3878(9)	2.3873(7)
W–O(1)	2.3494(15)	2.3307(16)
W–O(2)	2.3446(15)	2.3539(16)
N(1)–C	1.393(3)	1.393(3)
N(2)–C	1.395(3)	1.393(3)
N(1)–W–N(2)	103.89(8)	104.91(8)
Cl(1)–W–Cl(2)	154.28(2)	154.89(2)
O(1)–W–O(2)	70.06(6)	70.33(6)
N(1)–W–Cl(1)	99.73(6)	98.64(6)
N(1)–W–Cl(2)	97.11(6)	97.24(6)
N(2)–W–Cl(1)	97.45(6)	97.38(6)
N(2)–W–Cl(2)	97.19(6)	97.18(6)
W–N(1)–C	163.06(15)	164.93(15)
W–N(2)–C	161.47(15)	168.14(15)

complexes and Me_xAlCl_{3-x} reagents *in vitro* in order to gain a greater understanding of the role of Lewis acidic activators in ethylene dimerization.

Results and discussion

Preparation and structural characterisation of $[WCl_2(NAr)_2(DME)]$ (1)

The starting point for this investigation was the previously reported complex $[WCl_2(NAr)_2(DME)]$ (**1**), which was prepared according to the known procedure.[15] To provide a comparison with the structures of the various tungsten alkyl complexes described below, the molecular structure of complex **1** was determined and found to possess an asymmetric unit comprising two molecules (*A* and *B*) of similar conformation (Fig. 2, Table 1).

The tungsten atom adopts a strongly distorted octahedral coordination with the two chloride and two imido ligands occupying mutually *trans* and *cis* positions, respectively, as found for the related complex $[WCl_2(NPh)_2(bipy)]$ reported by Bradley *et al.*[16] As is the case for the majority of *cis*-octahedral d^0 *bis*(imido) complexes, the π-donor chlorides of **1** are tilted away from the two multiply bonded ligands due to electronic factors.[17,18] The metric parameters associated with the two imido nitrogen atoms of either of the independent molecules *A* or *B* are identical to within experimental error, with a mean W–N–C angle of 164.4° and an average W–N distance of 1.759(2) Å, data that are comparable with the parameters determined for $[WCl_2(NPh)_2(bipy)]$ (165.8° and 1.78(1) Å, respectively). In line with established precedent, the W–N bond distances of **1** are best regarded as being intermediate between those for X_2 (2-electron) and LX_2 (4-electron) imido binding as a result of the limited π-bonding capacity of the tungsten centre.[19–22]

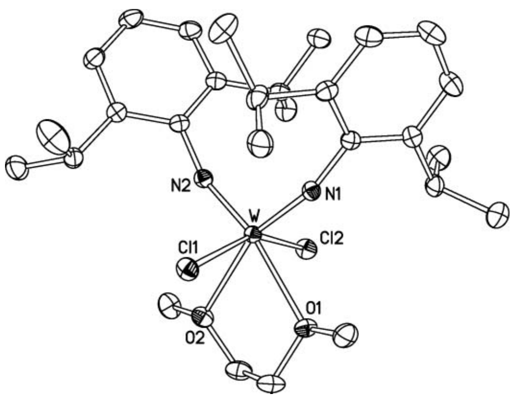
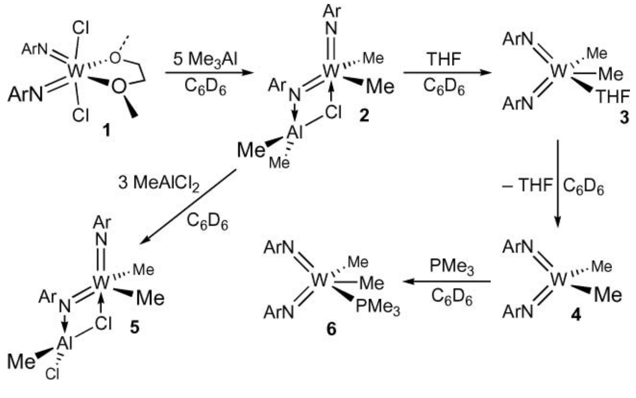


Fig. 2 Molecular structure of $[WCl_2(NAr)_2(DME)]$ (**1**), showing independent molecule *A* only. Henceforth H atoms are omitted for clarity and the thermal ellipsoids set at the 50% level.

Reactions of $[WCl_2(NAr)_2(DME)]$ (1) with Me_xAlCl_{3-x}

It has long been established that the nature of aluminium- and boron-based co-initiators has a pronounced impact upon the activity and selectivity of homogeneous early transition metal-catalysed alkene polymerisation.[23] As would be anticipated similar effects have recently also been exemplified for the tungsten-based dimerisation systems of interest here.[9] Consequently, an examination of the reaction of the dichloride complex **1** with variously-substituted alkyl aluminium reagents was carried out. Initially, the reaction with Me_3Al (W : Al 1 : 5) was undertaken and cleanly afforded a single tungsten-containing product $[WMe_2(N\{Ar\}AlMe_2\{\mu\text{-}Cl\})(NAr)]$ (**2**), which was obtained following complete conversion of **1** (Scheme 2). Complex **2** presents two inequivalent aryl imido environments together with distinct resonances attributable to the Al- and W-bound methyl groups according to ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The observed asymmetry results from coordination of an Me_2AlCl fragment (generated *in situ* during transmetallation) to one of the imido ligands. Excess Me_3Al was found to be essential for clean generation of **2**, since in this reaction stoichiometric amounts of the alkyl aluminium are sequestered by the DME liberated from **1**.[24]



Scheme 2 Summary of the synthesis and reactivity of $[WMe_2(N\{Ar\}AlMe_2\{\mu\text{-}Cl\})(NAr)]$ (**2**).

An X-ray diffraction study was used to confirm the connectivity of **2** (Fig. 3, Table 2). The complex has an approximate non-crystallographic C_s symmetry, with the mirror plane passing through the W, Al, Cl, and both N atoms. While the aryl substituent at N(1) lies in this plane, the ring at N(2) is perpendicular to it (with an angle between the ring planes of 85.4°). The coordination geometry of tungsten is intermediate between trigonal bipyramidal (with N(1) and Cl axial) and square-based pyramidal (with N(2) apical), but much closer to the former, as indicated by Reedijk's parameter $\tau = 0.77$ (1 for an ideal TBP and 0 for SBP).[25] There is an additional 'umbrella' distortion,[26] whereby all three equatorial ligands are bent away from the axial terminal imido ligand, N(1)Ar, which forms the highest-order bond with the central atom. The equatorial sites are occupied by two methyl groups and an unsymmetrically-bridging imido ligand, N(2)Ar, which is a constituent of a four-membered –W–N–Al–Cl- metallacycle, with a dative (Al)Cl→W interaction completing the tungsten's coordination sphere. Consequently, the Al atom acquires a near-tetrahedral geometry, with N(2) being trigonal planar ($\sum_{\text{ang}}$ N(2) ~ 360°). Such a bonding scheme is supported by the inequivalence of the two W–N bond distances, which differ by 0.12 Å. The shorter W–N(1) bond has a degree of *pseudo*-triple bond character arising from lone pair donation to tungsten (LX_2 binding) and, as expected, is significantly shorter than the W–N bonds of the parent complex **1** (average 1.759(2) Å); the slight bending at N(1) results from steric repulsion between the aryl substituents.[22] Clearly, coordination of the Lewis acid to one of the two imido ligands of [$WMe_2(NAr)_2$] alleviates competition for the limited π-bonding capacity of the tungsten centre.[27] The Me_2AlCl-bound imido ligand has a W–N(2)-C(21) bond angle of 133.24(12)° and a relatively long W–N(2) bond distance of 1.8613(15) Å. Notably, the structure predicted computationally (**A-Al**) very reliably reproduces that determined experimentally for **2**.[14]

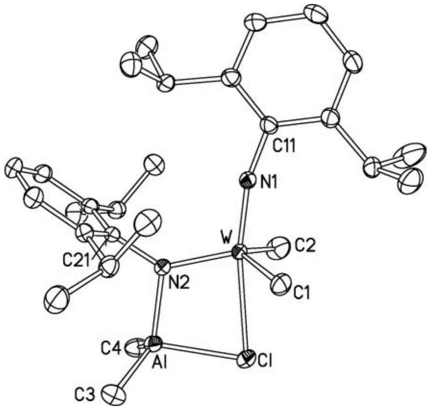


Fig. 3 Molecular structure of [WMe_2(N{Ar}$AlMe_2${μ-Cl})(NAr)] (**2**).

Table 2 Selected bond distances (Å) and angles (°) for [WMe_2(N-{Ar}$AlMe_2${μ-Cl})(NAr)] (**2**) and [$WMe_2(NAr)_2$(THF)] (**3**)

	2	**3**, *A*	**3**, *B*	**3**, *C*
W–N(1)	1.7402(15)	1.764(4)	1.746(4)	1.757(4)
W–N(2)	1.8613(15)	1.784(4)	1.771(4)	1.773(4)
W–C(1)	2.129(2)	2.157(5)	2.173(5)	2.151(5)
W–C(2)	2.139(2)	2.159(5)	2.151(5)	2.159(5)
W–X[a]	2.6440(6)	2.322(3)	2.305(3)	2.311(4)
N(1)–C	1.399(2)	1.391(6)	1.396(6)	1.397(6)
N(2)–C	1.439(2)	1.387(6)	1.395(6)	1.386(6)
N(1)–W–X[a]	169.63(5)	156.0(2)	159.7(2)	158.7(2)
N(1)–W–N(2)	108.27(7)	111.1(2)	110.8(2)	111.4(2)
N(1)–W–C(1)	94.95(8)	97.2(2)	96.5(2)	96.8(2)
N(1)–W–C(2)	96.81(9)	94.0(2)	94.0(2)	94.1(2)
X–W–N(2)[a]	82.00(5)	88.8(2)	89.4(2)	89.8(2)
X–W–C(1)[a]	79.20(7)	76.9(2)	77.3(2)	76.8(2)
X-W–C(2)[a]	79.68(7)	76.3(2)	76.5(2)	76.0(2)
N(2)–W–C(1)	113.16(8)	111.0(2)	111.8(2)	110.3(2)
N(2)–W–C(2)	114.7(1)	109.6(2)	108.9(2)	109.6(2)
C(1)–W–C(2)	123.6(1)	130.2(2)	130.7(2)	130.9(2)
W–N(1)–C	165.9(1)	176.9(4)	178.1(4)	178.2(4)
W–N(2)–C	133.2(1)	154.7(3)	150.1(3)	153.0(3)
Al–Cl	2.2757(8)			
Al–N(2)	1.958(2)			
Al–C(3)	1.947(2)			
Al–C(4)	1.951(2			
Cl–Al–N(2)	90.47(5)			
Cl–Al–C(3)	107.94(8)			
Cl–Al–C(4)	106.32(8)			
N(2)-Al–C(3)	112.55(9)			
N(2)-Al–C(4)	114.93(9)			
C(3)-Al–C(4)	119.9(1)			
W–Cl–Al	78.07(2)			
W–N(2)-Al	109.10(8)			
Al–N(2)-C	117.6(1)			

[a] X = Cl (**2**); X = O(1) (**3**).

Structurally related –M–N–Al–Cl– metallacycles have been observed previously in the complexes [Cp_2ZrC(Ph)=C(Ph)-C(Me)=NAl(Cl)Me_2][28] and [Cp_2ZrCH(Ph)N(Ph)Al(Cl)Me_2].[29] The Al–N bonds of **2** (1.958(2) Å) and of the two Zr complexes (1.888(2) and 1.952(7) Å, respectively), are shorter than those of traditional donor–acceptor adducts, *e.g.* $Me_3N\cdot AlClMe_2$ (2.010(1) Å)[30] or 5,6-benzoquinoline·$AlClMe_2$ (2.016(3) Å),[31] while the Al–Cl bond of **2** is longer than the (terminal) single bonds in NAl(Cl)Me_2 moieties (2.14–2.20 Å).[32] The Cl→W bond (2.6440(6) Å) is marginally longer than previously reported aryl-Cl→W dative bonds, which lie in the range 2.57–2.61 Å, as a consequence of the high *trans* influence of the imido ligand.[33] An analogous –M–N–B–Cl– metallacycle has also been reported in the complex [Os(Cl){HB(pz)$_3$}{N(Ph)-B(Cl)Ph_2}].[34]

Reactivity of [WMe_2(N{Ar}$AlMe_2${μ-Cl})(NAr)] (2)

Although complex **2** is prepared in the presence of excess $AlMe_3$ (W : Al 1 : 5) the formation of products comparable to the double Lewis adduct **A-Al₂** proposed computationally are not observed.[14] Indeed, a previously isolated sample of complex **2** does not react with $AlMe_3$ (W : Al 1 : 5) even at elevated temperatures (60 °C). Nevertheless, **2** reacts rapidly with $MeAlCl_2$ (W : Al 1 : 3) at RT, resulting in complete displacement of the coordinated Me_2AlCl and the clean formation of [WMe_2(N{Ar}Al(Cl)Me{μ-Cl})(NAr)] (**5**) (Scheme 2); again, no evidence of the formation of the double Lewis adduct was obtained. Clearly the creation and retention of –W–N–Al–Cl– metallacycles is a key requirement for Lewis acid coordination to the imido residues of these types of tungsten complex. Once formed, the resulting Lewis acid–Lewis base adducts are quite stable as exemplified by a variable temperature ^{1}H NMR spectroscopic study (+25 to 60 °C; C_6D_5Cl) of **2**, which gave no indication of either decomposition or dissociation of Lewis acid.

It has recently been shown that dimerization initiators generated *in situ* from $WCl_6/ArNH_2/R_xAlCl_{3-x}$ (60 °C) are only active when the aluminium co-initiator bears both an alkyl and a halide group such as for $MeAlCl_2$, $EtAlCl_2$, and $EtAlCl_2$; use of $AlEt_3$, $AlMe_3$, or MAO (methyl aluminoxane) all fail to promote dimerization.[9] Furthermore, it was shown that the activity of the initiator system decreases as a function of the aluminium reagent in the order $EtAlCl_2 > Et_3Al_2Cl_3 > Et_2AlCl$. Collectively, these observations closely parallel our findings for the well-defined imido complexes reported here: not only is $N \rightarrow Al$ and $(Al)Cl \rightarrow W$ coordination facile, but also $MeAlCl_2$ displaces Me_2AlCl (**2**→**5**, Scheme 2). Hence, as inferred computationally, formation of –W–N–Al–Cl– metallacycles is likely to be a key feature of these tungsten-based dimerisation initiators.[14]

In order to further probe the strength and nature of the Me_2AlCl coordination in **2**, reactions with Lewis bases were undertaken. Treatment of **2** with excess THF affords $[WMe_2(NAr)_2(THF)]$ (**3**), accompanied by elimination of $[Me_2AlCl(THF)]$, as apparent from ^1H NMR analysis of the reaction mixture (Scheme 2). Following recrystallisation from diethyl ether, single crystals of **3** suitable for X-ray diffraction analysis were obtained. The asymmetric unit comprises three molecules *A*, *B*, and *C* of similar geometry (Fig. 4, Table 2).

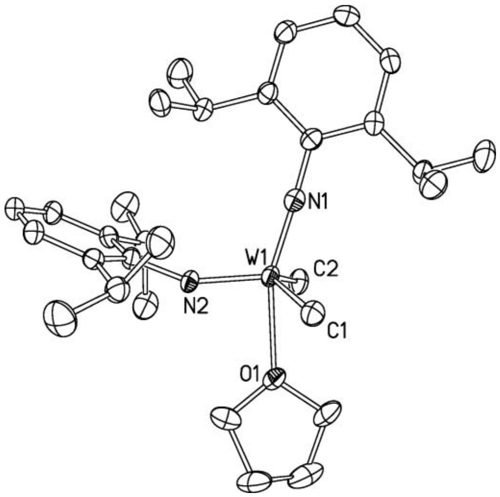


Fig. 4 Molecular structure of $[WMe_2(NAr)_2(THF)]$ (**3**), showing independent molecule *A* only.

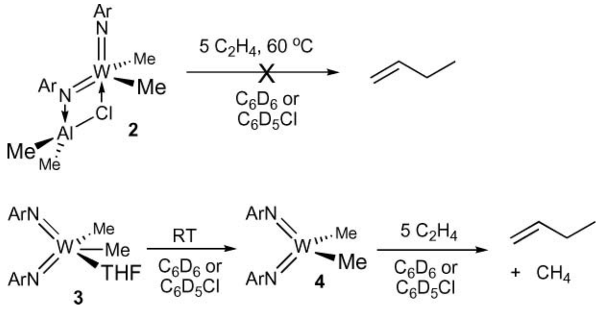
The tungsten's coordination geometry in **3** is broadly similar to that in **2** (with the THF occupying the position of the chloride ligand) although slightly more distorted towards SBP (mean τ = 0.46) with the N(2)Ar ligand in the *pseudo*-apical position and the W, O and both N atoms lying in one plane. The shift to SBP geometry is even more pronounced in the related dimethyl molybdenum complex $[MoMe_2(NAr)_2(PMe_2Ph)]$[35] (τ = 0.26), probably due to bigger steric demands of PMe_2Ph compared with THF.[18b] The arene ring bonded to N(1) of **3** is inclined to this plane by 16.7° (molecule *A*), 7.8° (*B*) and 3.7° (*C*), while the ring at N(2) is nearly perpendicular to it (dihedral angles 84.9, 83.8 and 70.9°, respectively). The W–C bond distances of **3** at 2.157(5) and 2.159(5) Å are unremarkable, and are comparable to those of **2**.[36] Despite the differences in W–N–C bond angle, the two W–N bond distances of 1.764(4) and 1.784(4) Å again indicate that the imido ligands of **3** adopt a bonding arrangement that is intermediate between that of an LX_2 and X_2 donor.[22]

In C_6D_6 solution the THF ligand of **3** is labile at RT, immediately dissociating to give what appears to be the base-free complex $[WMe_2(NAr)_2]$ (**4**) and apparently uncoordinated THF as indicated by ^1H NMR spectroscopic analysis (Scheme 2).‡ Identical behaviour is observed for **3** in C_6D_5Cl solution, with no ^1H NMR spectral changes being apparent over the temperature window −40 °C to RT. Complex **4** may also be prepared quantitatively through reaction of **3** with one equivalent of $(C_6F_5)_3B$ in C_6D_6, which liberates an equimolar quantity of the known adduct $[(C_6F_5)_3B(THF)]$.[37]§ However, although complex **4** is stable in solution for days, all attempts at its isolation resulted in its decomposition. This is consistent with the observation that exposure of a crystalline sample of **3** to vacuum (30 min) results in the removal of THF and subsequent degradation. This contrasts with the analogous molybdenum complex $[MoMe_2(NAr)_2(THF)]$, which is stable under reduced pressure.[35] In contrast, reaction of THF complex **3** with trimethyl phosphine cleanly affords $[WMe_2(NAr)_2(PMe_3)]$ (**6**), which is stable in the solid state even on prolonged exposure to vacuum.

It is important to note that although complex **3** may be prepared in high yield by sequential reaction of **1** with $AlMe_3$ followed by THF, all attempts to prepare **3** through reaction of **1** with a slight excess of MeMgCl in THF, resulted in the formation of an intractable mixture of products, none of which could be assigned to **3**. This contrasts with the analogous molybdenum system where $[MoMe_2(NAr)_2(THF)]$ may be prepared in good yield from reaction of $[MoCl_2(NAr)_2(DME)]$ with methyl magnesium chloride in THF solution.[22]

Reactions of complexes 2 and 3 with C_2H_4 and C_3H_6

An evaluation of the role of Me_2AlCl coordination upon the reactivity of tungsten *bis*(imido) species of relevance to alkene dimerization has been undertaken by comparing the behaviour of complexes **2** and **3**/**4** with ethylene (5 eq.) (Scheme 3). Notably, no reaction occurred between the tungsten-alkyl aluminium adduct **2** even on prolonged heating (48 h, 60 °C), irrespective of the solvent (C_6D_6 or C_6D_5Cl). Similarly, complex **2** does not initiate propylene dimerization, with no reaction taking place. This lack of reactivity



Scheme 3 Behaviour of complexes **2** and **3**/**4** towards ethylene.

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‡ Upon dissolution in C_6D_6 the THF moiety of complex **3** gives rise to resonances at 3.47 and 1.40 ppm by ^1H NMR spectroscopy, which are identical to those found for an authentic sample of free THF.

§ The formation of $[(F_5C_6)_3B(THF)]$ was confirmed spectroscopically by comparison with the data from an authentic sample.

Table 3 Isotopomer distributions predicted by theory and observed following reaction of complex **3** with C_2H_4/C_2D_4 (1 : 1)

	Predicted			
Isotopomer	Chain-growth	Metallacycle	Fully Scrambled	Observed [a]
C_4H_8	1	1	1	1.08
C_4H_7D	1	0	8	1.71
$C_4H_6D_2$	0	0	28	2.70
$C_4H_5D_3$	1	0	56	3.80
$C_4H_4D_4$	2	2	70	4.29
$C_4H_3D_5$	1	0	56	3.68
$C_4H_2D_6$	0	0	28	1.13
C_4HD_7	1	0	8	1.00
C_4D_8	1	1	1	>0.2

[a] GC-MS.

of complex **2** towards alkenes has been attributed to the strong coordination of the Me_2AlCl fragment to the imido moiety and tungsten, which prevent initial alkene association (the LUMO of the 14e$^-$ $W(NAr)_2Me_2$ fragment being occupied by $(Al)Cl\rightarrow W$ donation).[38] Clearly these observations are at odds with the high dimerization activity demonstrated by the R_xAlCl_{3-x}/WCl_6-based systems derived *in situ*. One possible explanation for this behaviour is that *bis*(imido) species are not in fact generated in the reaction of WCl_6 and $ArNH_2$ as proposed,[12,14] rather that mixed *mono*(imido)/amido systems are formed as suggested previously.[11]

In contrast to the behaviour of **2**, addition of ethylene (5 eq.) to solutions of complex **4** (generated upon dissolution of **3**) results in an immediate reaction at RT. Analysis of the reaction mixture after 5 min by ^1H NMR spectroscopy confirms the complete disappearance of **3** and **4** and the appearance of a number of unattributable new resonances. After 48 h at RT ethylene conversion is complete, yielding but-1-ene, but-2-ene (trace), and methane (alkene : alkane 4 : 1 by integration).¶ Further quantities of ethylene (2 × 10 eq.) added to the reaction mixture are slowly converted (days) to but-1-ene. Although reproducible, the origin of the methane evolved during the reaction of **4** with C_2H_4 remains unaccounted for. No C_6 components are observed (which would arise from co-dimerisation of C_2 and C_4 alkenes) in agreement with the failure of these discrete W-species **3**/**4** to initiate dimerisation of propene.

As stated, it has been widely proposed that W-imido-promoted selective alkene dimerization occurs *via* a metallacycle mechanism,[12,39] something that is consistent with the mode of action of discrete chromium-based alkene trimerisation catalysts.[40] Hence, it was decided to probe this assumption *via* the now well-established C_2H_4/C_2D_4 co-oligomerisation experiment.[41–45] To this end, a C_6D_6 solution of complex **3** was treated with a 1 : 1 mixture of C_2H_4/C_2D_4 and the resulting products analysed. As shown in Table 3, the observed distribution of isotopomers is characteristic of a system in which significant scrambling has occurred.[46] This result implies that rather than the expected metallacycle mechanism a chain-growth process (Cossee-type mechanism) may be in operation. While we have not conclusively proven here that a chain-growth process is in operation, the observed scrambling must result from insertion of an alkene into a W–H bond that would be inherent in such a process. This is supported by recent observations made for the *in situ*-generated systems, which gave rise to identical isotopmer scrambling together with the formation of linear decenes that resulted from dimerisation of 1-pentene.[9] As such we feel that a chain growth mechanism must be given the same theoretical considerations granted to the metallacycle (oxidative coupling) pathway for tungsten-mediated alkene dimerization.

Conclusions

Discrete tungsten imido complexes in the presence of aluminium-based Lewis acids are now firmly established as pro-initiators in alkene dimerization, yet the nature of the actual active species remains unclear. A recent computational study proposed that the formation of bimetallic complexes of the type $[WMe_2(N\{Ar\}AlMe(X)\{\mu\text{-}Cl\})(NAr)]$ could be implicated in the catalytic process since coordination of the Lewis acid in this manner significantly lowered the activation barrier for one of the key catalytic steps, namely tungstenacyclopentane degradation.[14] However, it has been demonstrated here that although transmetallation reactions between methyl aluminium reagents and tungsten *bis*(imido) dihalide complexes such as **1** occur readily to afford bimetallic complexes of the type $[WMe_2(N\{Ar\}AlMe(X)\{\mu\text{-}Cl\})(NAr)]$, where X = Me (**2**), Cl (**5**), such compounds do not react with either ethylene or propylene.

In contrast, the labile dialkyl derivative $[W(NAr)_2Me_2(THF)]$ (**3**), generated through displacement of the Lewis acid moiety of **2** by THF, reacts rapidly with ethylene to generate a mixture of, as yet, unidentified species that initiate catalytic dimerization of ethylene affording methane and but-1-ene in a 1 : 4 ratio, respectively. The methane evolved during the initial stages of the reaction is suggestive of initial ethylene insertion into a tungsten–methyl bond, followed by β-hydride elimination and reductive elimination sequence delivering the catalytically active species, rather than oxidative coupling.

Together with the findings of Tobisch's recent computational study,[14] the observations made here strongly suggest that simple discrete tungsten *bis*(imido) complexes, of the type outlined in Fig. 1 are unlikely to be the true active components in homogeneous catalytic alkene dimerization. With this in mind, further detailed studies of the reactions of complexes **2** and **3** with Lewis acids and alkenes are being actively pursued.

Experimental

All operations were conducted under an atmosphere of dry nitrogen using standard Schlenk and cannula techniques, or in a nitrogen-filled Saffron Scientific glove box. NMR-scale reactions were conducted using NMR tubes fitted with Young's tap valves. Bulk solvents were purified using an Innovative Technologies SPS facility and degassed prior to use. NMR solvents (C_6D_6 and C_6D_5Cl) were dried over P_2O_5, distilled and degassed before use. DME (Aldrich) was distilled under nitrogen from sodium/benzophenone. When appropriate, liquid reagents were dried, distilled and deoxygenated. Nitrogen gas was passed through a drying column ($silica/CaCO_3/P_2O_5$) and ethylene and propylene were dried using a column of P_2O_5 and a *c.*H_2SO_4 gas washing bottle. The known compound $[WCl_2(NAr)_2(DME)]$ (**1**)

¶ Comparison was made against an authentic sample of methane dissolved in C_6D_6 in a sealed NMR tube, which gives a resonance at 0.30 ppm. The formation of but-1-ene was verified by GC analysis of the volatile components from the reaction of **3** with C_2H_4 after 48 h at RT.

was prepared using standard literature procedures,[15] while neat Me_3Al was purchased from Albermarle R & D centre. $MeAlCl_2$ was obtained by slow evaporation of hexane from $MeAlCl_2$ solutions obtained from Aldrich.

GC analyses were performed on an Agilent Technologies 6890 N GC system equipped with PONA (50 m × 0.020 mm × 0.50 μm) and MDN12 (60 m × 0.025 mm × 0.25 μm) columns. GC-MS analyses were performed on an Agilent Technologies 6890 N GC system equipped with a MDN12 (60 m × 0.025 mm × 0.25 μm) column, coupled to an Agilent Technologies 5973 N MSD Mass Spectrometric instrument. Elemental analyses were performed by the Analytical Services Department of the Chemistry Department, Durham University. Routine NMR spectra were collected on a Varian Unity 200, Varian Mercury 400 or an Avance 400 MHz Bruker spectrometer. Chemical shifts were referenced to residual protio impurities in the deuterated solvent (^{1}H) or the ^{13}C shift of the solvent (^{13}C). Solvent proton shifts (ppm): C_6D_6, 7.15; C_6D_5Cl, 7.13, 6.98, 6.95. Solvent carbon shifts (ppm): C_6D_6, 128.3. ^{13}C NMR spectra were assigned with the aid of DEPT 135 and gHMQC ^{1}H/^{13}C correlation experiments. Chemical shifts are reported in ppm and coupling constants in Hz.

Preparation of [W(N{Ar}$AlMe_2${μ-Cl})(NAr)Me_2] (2)

To a solution of [W$(NAr)_2Cl_2$(DME)] (**1**) (50 mg, 0.07 mmol) in C_6D_6 (0.8 mL) was added Me_3Al (25 mg, 0.34 mmol). Removal of volatile components from the C_6D_6 solution *in vacuo* gave a small quantity of a tan brown solid. This material was recrystallized from the minimal amount of hexane (–5 °C) to give single crystals of W(N{Ar}$AlMe_2${μ-Cl})(NAr)Me_2 (**2**) of sufficient quality for X-ray diffraction analysis. ^{1}H NMR (C_6D_6, 200 MHz): δ 6.96 (6H, b, H_{meta} and H_{para}), 3.50 (2H, septet, $CH_3C\mathit{H}$, $^3J_{HH} = 6.8$ Hz), 2.65 (2H, septet, $CH_3C\mathit{H}$, $^3J_{HH} = 6.6$ Hz), 1.56 (6H, s, $W(C\mathit{H}_3)_2$), 1.17 (6H, d, $C\mathit{H}_3CH$, $^3J_{HH} = 6.8$ Hz), 1.03 (6H, d, $C\mathit{H}_3CH$, $^3J_{HH} = 6.8$ Hz), 0.89 (12H, d, $C\mathit{H}_3CH$, $^3J_{HH} = 6.6$ Hz), 0.15 (6H, s, $Al(C\mathit{H}_3)_2Cl$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 125.6 MHz): δ 151.3 (C_{ipso}), 149.2 (C_{ortho}), 140.8 (C_{meta}), 124.8 (C_{para}), 71.1 ($CH_3O\mathit{C}H_2$), 61.3 ($\mathit{C}H_3OCH_2$), 50.9 ($W(\mathit{C}H_3)_2$), 29.4 ($CH_3\mathit{C}H$), 28.6 ($CH_3\mathit{C}H$), 26.3 ($\mathit{C}H_3CH$), 24.2 ($\mathit{C}H_3CH$), –6.80 ($Al(\mathit{C}H_3)_3$) ppm. Despite repeated attempts, satisfactory elemental analyses for **2** could not be obtained.

Preparation of [$WMe_2(NAr)_2$(THF)] (3) and [$WMe_2(NAr)_2$] (4)

Complex **1** (0.80 g, 1.15 mmol) was dissolved in CH_2Cl_2 (30 mL) and Me_3Al (414 mg, 5.75 mmol) also dissolved in CH_2Cl_2 (10 mL) was added. The combined solution was allowed to stir for approximately five minutes before the volatile components were then removed *in vacuo* to give a dark brown solid, which was then re-dissolved in hexane (40 mL). To this hexane solution was added THF (0.41 mL, 5.76 mmol) and, after 5 min, the mixture was concentrated *in vacuo*. This resulted in the immediate formation of a yellow precipitate that was collected *via* filtration and recrystallized from diethyl ether (–15 °C), giving light brown crystals (which were dried under a flow of N_2) of sufficient quality for X-ray diffraction analysis; yield 200 mg (27%). Anal. calcd. for $C_{30}H_{48}N_2OW$: C 56.60, H 7.60, N 4.40; found: C 56.80, H 7.52 N 4.70.

Dissolution of **3** in either C_6D_6 or C_6D_5Cl leads to spontaneous dissociation of THF affording [$WMe_2(NAr)_2$] (**4**), which is only stable in solution and was hence characterised by NMR spectroscopy *in situ*. ^{1}H NMR (C_6D_6, 400 MHz): δ 7.07 (6H, b, H_{meta} and H_{para}), 3.62 (4H, septet, $CH_3C\mathit{H}$, $^3J_{HH} = 7.2$ Hz), 1.25 (6H, s, $W(C\mathit{H}_3)_2$, $^2J_{WH} = 7.6$ Hz), 1.17 (24H, d, $C\mathit{H}_3CH$, $^3J_{HH} = 7.2$ Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 175.9 MHz): δ 152.8 (C_{ipso}), 143.1 (C_{ortho}), 126.0 (C_{meta}), 123.0 (C_{para}), 48.6 ($W(\mathit{C}H_3)_2$), 29.3 ($CH_3\mathit{C}H$), 23.9 ($\mathit{C}H_3CH$) ppm.

Preparation of [$WMe_2(NAr)_2(PMe_3)$] (7)

To a C_6D_6 solution of [$WMe_2(NAr)_2$(THF)] (40 mg, 0.06 mmol) was added PMe_3 (0.19 mmol) by vacuum transfer. After 20 min, the volatile components were removed *in vacuo*, giving **6** as a light brown solid. ^{1}H NMR (C_6D_6, 700 MHz): δ 7.12 (4H, d, H_{meta}, $^3J_{HH} = 7.7$ Hz), 7.02 (2H, t, H_{para}, $^3J_{HH} = 7.7$ Hz), 3.88 (4H, septet, $CH_3C\mathit{H}$, $^3J_{HH} = 7.7$ Hz), 1.25 (24H, d, $C\mathit{H}_3CH$, $^3J_{HH} = 7.7$ Hz), 1.08 (6H, s, $W(C\mathit{H}_3)_2$, $^2J_{WH} = 5.2$ Hz), 0.93 (9H, d, $P(C\mathit{H}_3)_3$, $^2J_{PH} = 7.7$ Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6, 175.9 MHz): δ 154.1 (C_{ipso}), 144.2 (C_{ortho}), 125.1 (C_{meta}), 123.0 (C_{para}), 28.8 ($CH_3\mathit{C}H$), 24.4 ($\mathit{C}H_3CH$), 21.9 ($W(\mathit{C}H_3)_2$), 13.4 ($P(\mathit{C}H_3)_3$, $^1J_{PC} = 18$ Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6, 283.2 MHz): δ –25.0 ppm.

Preparation of [$(C_6F_5)_3$B(THF)]

A sample of $B(C_6F_5)_3$ (200 mg, 0.39 mmol) was dissolved in THF (5 mL) and allowed to react for 20 min before all volatile components were removed *in vacuo* to give [$(C_6F_5)_3$B(THF)] as a white solid in quantitative yield. ^{1}H NMR (C_6D_6, 400 MHz): δ 3.19 (4H, br, $\nu_{\frac{1}{2}} = 9.4$ Hz, OCH_2), 0.92 (4H, br, $\nu_{\frac{1}{2}} = 11.0$ Hz, CH_2); ^{19}F{^{1}H} NMR (C_6D_6, 376 MHz): δ –132.9 (2F, d, $^3J_{FF} = 21$ Hz, *o*-$C_6\mathit{F}_5$), –154.8 (1F, $^3J_{FF} = 21$ Hz, *p*-$C_6\mathit{F}_5$), –162.7 (2F, br t, $^3J_{FF} = 19$ Hz, *m*-$C_6\mathit{F}_5$). Anal. Calcd for $C_{22}H_8BF_{15}O$: C, 45.24; H, 1.38. Found: C; 45.00, H; 1.21.

Reaction of [W(N{Ar}$AlMe_2${μ-Cl})(NAr)Me_2] (2) with C_2H_4

Complex **1** (50 mg, 0.07 mmol) was dissolved in C_6D_6 or C_6D_5Cl (0.8 mL), followed by the addition of Me_3Al (25 mg, 0.34 mmol) to both solutions. ^{1}H NMR spectroscopic analysis confirmed the formation of **2** *in situ* in each case. The samples were then allowed to contact ethylene (5 eq., 0.15 mmol) prior to heating at 60 °C for 1 h. Irrespective of the solvent, no reaction between ethylene and **2** was found to occur (verified using ^{1}H NMR spectroscopy). A similar lack of reaction was found when samples of **2** were heated at 60 °C for 1 h under ethylene (1 atm).

Reaction of [W(N{Ar}$AlMe_2${μ-Cl})(NAr)Me_2] (2) with $MeAlCl_2$

Complex **1** (30 mg, 0.04 mmol) was reacted with Me_3Al (18 mg, 0.25 mmol) in C_6D_6. This solution was then treated with $MeAlCl_2$ (0.14 mmol, 1 M in hexanes, 0.14 mL) and, after a 30 min reaction period, the resulting mixture was dried *in vacuo*. This material was analyzed using ^{1}H NMR spectroscopy. The resulting spectrum presented signals assignable to complex **5**, together with resonances attributable to an unknown [Me_xAlCl_{3-x}(DME)] adduct, a by-product of the reaction of [$W(NAr)_2Cl_2$(DME)] (**2**) and Me_3Al. ^{1}H NMR (C_6D_6, 400 MHz): δ 6.95 (6H, b, H_{meta} and H_{para}), 3.58 (2H, $CH_3C\mathit{H}$, septet $^3J_{HH} = 6.8$ Hz), 2.59 (2H, $CH_3C\mathit{H}$,

Table 4 Crystal data and X-ray experimental details

	1	**2**	**3**
CCDC no.	769100	769101	769102
Formula	$C_{28}H_{44}Cl_2N_2O_2W$	$C_{28}H_{46}AlClN_2W$	$C_{30}H_{48}N_2OW$
Formula weight	695.40	656.95	636.55
T/K	120	120	120
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group (no.)	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14^b)	$P2_1/c$ (no. 14)
a/Å	10.5913(14)	11.691(2)	19.506(2)
b/Å	16.009(2)	17.983(3)	16.994(2)
c/Å	18.714(3)	14.342(2)	26.404(3)
α (°)	80.84(3)	90	90
β (°)	87.75(3)	92.64(1)	95.20(2)
γ (°)	76.79(2)	90	90
V/Å^3	3049.5(7)	3012.1(8)	8716(2)
Z and ρ_c/g cm^{-3}	4, 1.515	4, 1.449	12, 1.455
μ(Mo-Kα)/mm^{-1}	3.99	3.97	4.00
Crystal size/mm	0.20 × 0.30 × 0.35	0.11 × 0.26 × 0.34	0.15 × 0.23 × 0.26
Transmission factor, min-max	0.2419–0.4314	0.4874–0.6692	0.1700–0.4323
Reflections collected, unique	43557, 17064	35373, 8025	121256, 25037
2θ max. (°)	60	58	60
R_{int} before and after correction	0.098, 0.024	0.144, 0.028	0.103, 0.046
R_1 [$I > 2\sigma(I)$] and wR_2 (all data)^a	0.020, 0.046	0.018, 0.038	0.045, 0.119

^{a} $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$, $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$. ^{b} Non-standard space group.

septet $^3J_{HH} = 6.8$ Hz), 1.60 (6H, s, W(C$\boldsymbol{H}_3$)$_2$), 1.26 (6H, d, C$\boldsymbol{H}_3$CH, $^3J_{HH} = 6.4$ Hz), 1.01 (6H, d, C$\boldsymbol{H}_3$CH, $^3J_{HH} = 6.8$ Hz), 0.87 (12H, d, C$\boldsymbol{H}_3$CH, $^3J_{HH} = 6.8$ Hz), 0.14 and 0.13 (3H, s, Al(C$\boldsymbol{H}_3$)$_2$Cl).

Reaction of [WMe$_2$(NAr)$_2$(THF)] (3) with C_2H_4

[WMe$_2$(NAr)$_2$(THF)] (**3**) (20 mg, 0.03 mmol) was dissolved in C_6D_6 (0.8 mL) and the resulting solution then allowed to contact ethylene (5 eq., 0.17 mmol) and analyzed using ^{1}H NMR spectroscopy. After a 48 h reaction period but-1-ene was observable in the ^{1}H NMR spectrum. The presence of but-1-ene was confirmed using GC analysis.

Reaction of [WMe$_2$(NAr)$_2$(THF)] (3) with C_2H_4/C_2D_4

In an NMR tube fitted with a J. Young's valve [WMe$_2$(NAr)$_2$(THF)] (**3**) (20 mg, 0.03 mmol) was dissolved in C_6D_6 (0.8 mL) and then frozen (−78 °C). The resulting frozen solution was allowed to contact C_2H_4 (0.17 mmol) and C_2D_4 (0.17 mmol). After 48 h at RT, the mixture was analyzed using ^{1}H NMR spectroscopy and by GC and GC-MS.

X-Ray crystallography

Diffraction experiments (Table 4) were carried out on a Siemens 3-circle diffractometer with a SMART 1000 CCD area detector, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and Cryostream (Oxford Cryosystems) open-flow N_2 cryostats. Reflection intensities were corrected for absorption by semi-empirical method based on Laue equivalents;[47] the structures were solved by Patterson method and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[48]

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