α-Olefin Dimerization by a Mono(imido) Tungsten Catalyst: Computational Evidence for the Role of Lewis Acid Chelates in Effective Catalysis

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Summary: The computational mechanistic survey of α-olefin dimerization by a mono(imido) tungsten/Lewis acid catalyst system disclosed that the Lewis acid plays a prominent role in the effective catalytic cycle. This DFT study aids in unveiling the identity of the catalytically active species and in rationalizing observed catalysts' abilities.

The catalytic dimerization of low-number α-olefins represents an attractive method for producing specific higher olefins.[1] This process has witnessed significant research efforts in both academia and industry.[2] Most of the catalyst systems yield branched dimers, but some late transition metal based systems exhibit abilities for linear dimerization.[3–6] Despite the recent development of several chromium systems to selectively trimerize ethylene[7] and to show selectivity toward formation of 1-octene,[8] applications of group 6 metals in olefin dimerization are scarce.[2,9]

Tungsten imido complexes are one of the rare examples. These compounds, when exposed to Lewis acids of $AlCl_nR_m$ type, have been recently reported as selective catalyst systems for dimerization of α-olefins.[10] As an example, treatment of WCl_6 with 1 equiv of aniline and the required amount of base leads in the presence of the cocatalyst presumably *in situ* to the $[W(NPh)R_2Cl_2]$ (**1**) mono(imido) tungsten compound. The {**1** + Lewis acid} catalyst system is reported to be highly selective to dimerization and moderately active.[10] One noteworthy aspect is that a distinct amount of the Lewis acid (~15 mol equiv) is required, this in contrast to the more usual huge excess of activators for various other oligomerization and polymerization catalyst systems.[2] This suggests a specific role being played by the cocatalyst, thereby extending its presumed function in precatalyst activation.

This prompted us to employ DFT calculations as a powerful tool capable of aiding in understanding the Lewis acid's function in the effective dimerization. The present study gauges, first, the strength of possible Lewis acid complexation onto mono(imido) tungsten intermediates and evaluates, second, how the associated cocatalyst does affect the energy profile of relevant elementary steps. Dimerization of prototypical ethylene has been scrutinized for $[W(NC_6H_5)Cl_2(C_2H_4)_2]$ and $AlClMe_2$ components, which closely mimic the real catalyst system. DFT calculations (TPSS[11]/SDD[12]+Ahlrichs-TZVP[13])[14] have simulated the authentic reaction conditions by treating bulk effects of the chlorobenzene solvent by a consistent polarizable continuum model.[15] All the stationary points were fully located with inclusion of solvation (see the Supporting Information for full details).

Two different mechanistic scenarios are possible for olefin dimerization; on one hand, to involve subsequent migratory olefin insertion into metal−H and metal−alkyl bonds followed by β-H elimination, or alternatively to follow the metallacycle mechanism. The high selectivity toward dimerization (with %(higher oligomers + polymers) < 1) together with the observed characteristic substitution pattern of generated α-olefin dimers, which is barely influenced by product isomerization,[10,16] points toward an operative metallacycle mechanism, although a strict proof via labeling experiments is still missing. Metallacycle intermediates have furthermore been unequivocally identified as participating in the chromium-mediated selective ethylene oligomerization.[17]

The present DFT study thus focuses on the metallacycle mechanism shown in Scheme 1. After transformation of **1** into the $[W(NPh)Cl_2(olefin)_2]$ active catalyst species **2**, oxidative

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(10) (a) Hanton, M. J.; Tooze, R. P. WO 2005089940 (Sasol Technology (UK) Ltd), September 29, 2005. (b) The {**1** + Lewis acid} catalyst system is highly selective to dimerization (with %(higher oligomers + polymers) <1) and moderately active (N_t ~36 (mol olefin)(mol W)$^{-1}$ h^{-1}, 60 °C).

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Scheme 1. Catalytic Cycle for α-Olefin Dimerization by Mono(imido) Tungsten Compounds, Exemplified for Ethylene

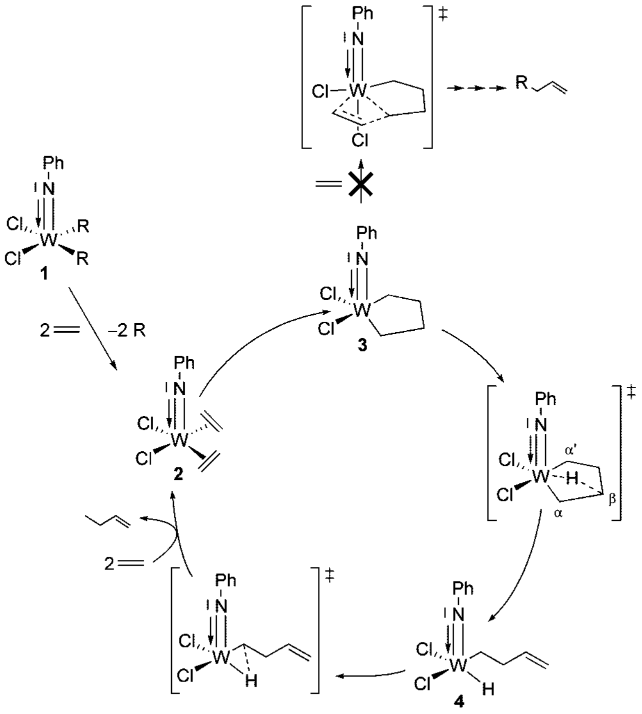

Table 1. Calculated Energy Profile (in kcal mol^{-1}) for Relevant Steps

Lewis acid association^a	oxid coupling $\Delta G^{\ddagger}\Delta G^{b}$	β-H abstraction $\Delta G^{\ddagger\,c}$	RE-CH $\Delta G^{\ddagger\,c}$
3–0	7.0/−2.3	31.4	42.4
3-IA	13.6/1.7	18.9	29.2
3-IB	17.0/4.1	27.6	26.3
3-IIA	13.3/−1.3	20.7	18.1
3-IIB	16.3/3.9	30.7	17.9
3-IIIA	15.9/2.9	18.2	13.0
D3–0	14.8/−9.4	20.2	47.2
D3-IB	13.5/−9.0	25.0	53.6

^{a} See Figure 1. ^{b} Energies relative to **2**, **D2**. ^{c} Energies relative to **3**, **D3**.

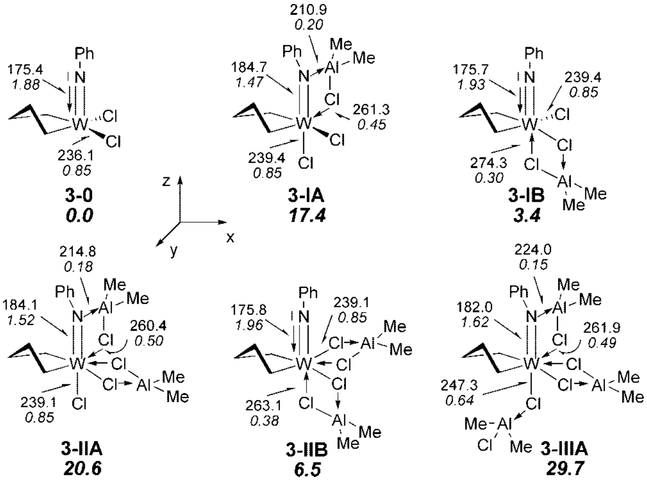

Figure 1. Most stable forms of various modes of Lewis acid association onto **3**. Bond distances (pm), Wiberg bond orders[22] (*italic type*), and relative stability (ΔG in kcal mol^{-1}) are given.

coupling of the two olefin moieties affords the tungstana(VI)cyclopentane intermediate **3**. Degradation of the conformationally rigid five-membered metallacycle following the favorable stepwise mechanism[18] (comprising consecutive β-H abstraction and reductive CH elimination with an intervening W-H-alkenyl intermediate **4**) leads to the dimer product. Repeated olefin insertion into successively enlarged metallacycle fragments and subsequent degradation would lead to larger oligomers.

It is instructive to first analyze the situation where the Lewis acid does not participate in the productive dimerization cycle. The energy profiles of relevant elementary steps are summarized in Table 1 (entry 1).[19] The oxidative coupling has a low barrier and is slightly exergonic, thus being a facile, reversible step. Degradation of **3** is predicted to be distinctly more expensive kinetically. Of the two consecutive steps, the second RE step has the higher barrier, thereby determining the overall degradation kinetics. The almost insurmountably high barrier of 42.4 kcal mol^{-1} does not correlate with the observed activity. Moreover, **3** is predicted as exhibiting a greater propensity to grow than to degrade, as the olefin insertion barrier is significantly smaller (Table S1, Supporting Information), such that the dimer-generating channel should remain closed. This clearly indicates that "bare" mono(imido) tungsten species are not responsible for dimerization catalysis.

We next evaluated the aptitude of the Lewis acid for complexation onto **3**. Restricting this to the immediate proximity of the tungsten center, up to three $AlClMe_2$ moieties have been considered. The most stable form of various imaginable association modes located are depicted in Figure 1. This shows the clear preference for four-membered chelating interactions. One $AlClMe_2$ moiety can lead to **3-IA** or **3-IB** bridging the imido N or Cl and W atoms, respectively. Similarly, **3-IIA**, having the Lewis acid complexed across tungsten−imido and tungsten−chlorine bonds, and **3-IIB**, with two chelated W−Cl bonds, are possible in the presence of two $AlClMe_2$ moieties, while **3-IIIA** differs from **3-IIA** by an additional monodentate Lewis acid association at the second W−Cl bond. There are only a few such adducts reported in the literature.[20,21] Noteworthy, cocatalyst association via dative W→Me interactions are found to be less stable.

The adducts are characterized structurally and electronically in Figure 1. The dianionic imido ligand acts as a net six-electron donor to the electron-deficient tungsten center, formally adopting a $\sigma^2\pi^4$ configuration.[23] For **3-IA** to be formed, the nitrogen lone pair has to redirect toward the Al center, which comes at the expense of the tungsten−imido bond. Hence, the strength of the tungsten−imido bond diminishes as indicated by its substantial lengthening and the smaller bond order. Chelation at the W−Cl bond, however, as seen for example in **3-IB**, causes significantly less pronounced structural distortions and the tungsten−imido bond is slightly strengthened. Overall, Lewis acid association at the imido group provokes substantial

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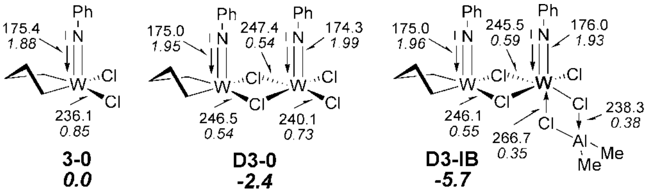

Figure 2. Most stable form of Lewis acid association onto the tungsten dimer form **D3**. Bond distances (pm), Wiberg bond orders[22] (*italic type*), and relative stability (ΔG in kcal mol^{-1}) are given.

electronic reorganizations at the nitrogen center, effectively attenuating the tungsten−imido bond. This is only partially compensated for by the newly formed N→Al and Cl→W dative bonds. Adducts **3-IA**, **3-IIA**, and **3-IIIA** are predicted to be highly unfavorable, following a regular trend (Figure 1). The less effective π-donor Cl centers are clearly seen as the preferred target for Lewis acid association. The weakening of an equatorial W−Cl bond is largely balanced by the new dative bonds, such that **3-IB** and **3-IIB** are only of moderately higher energy.

The relevance of tungsten dimers, which could be formed during **1** → **2** transformation, has been probed computationally for the W(μ-Cl)$_2$W-bridged species **D3-0**, representing a likely candidate (Figure 2). The investigation of Lewis acid adduct formation concentrates on **D3-IB**, where one AlClMe$_2$ moiety bridges a W−Cl bond (Figure 2), thus resembling the most stable adduct **3-IB** of the tungsten monomer. The AlClMe$_2$ moiety forms a four-membered chelate with the ancillary tungsten atom, while the alternative association at a μ-Cl bridge is distinctly disfavored by 14.4 kcal mol^{-1}. The aptitude of the Lewis acid to preferably complex at the “spectator” tungsten center holds true also for the various species being involved in relevant elementary steps. As shown in Figure 2, the unbound tungsten dimer **D3-0** is slightly more stable than **3-0**. The comparison of the most stable adducts (**IB**) reveals that AlClMe$_2$ complexation onto **D3-0** is exergonic by 3.3 kcal mol^{-1}, but somewhat endergonic for **3-0** (Figure 1). This is understandable from the lower donor ability of the W(μ-Cl)$_2$W-bridging Cl atoms in **D3-IB**, when compared to the metallacycle fragment in **3-IB**.

Besides the thus far analyzed thermodynamics of adduct formation, the detailed understanding of the cocatalyst’s role necessitates the elucidation of its role in individual steps.[19] The energy profiles are summarized in Table 1 for the various association modes. The barrier for oxidative coupling roughly doubles in size upon cocatalyst association. This reversible step is, nevertheless, the most facile of relevant steps for metallacycle growth and degradation, thus not likely affecting the catalytic behavior.

The Lewis acid has a profound influence on metallacycle degradation. The effective β-H abstraction requires a vacant metal acceptor orbital. The suitable tungsten d$_{xz}$ and d$_{yz}$ orbitals (see Figure 1), however, are unavailable in **3-0**, **3-IB**, and **3-IIB**, as they are occupied by electrons donated by the imido group. Accordingly, the thermodynamically favorable Lewis acid association at W−Cl bonds does affect the kinetics of hydride abstraction only to a modest extent. The calculated barrier is similar for these association modes (**0**, **IB**, **IIB**) and amounts to ~28–31 kcal mol^{-1}. The situation, however, is different for **3-IA**, **3-IIA**, and **3-IIIA**. Lewis acid chelation at the arylimido group, although thermodynamically unfavorable, alleviates the blockage of tungsten dπ orbitals to some extent, thereby accelerating the β-H abstraction. This is revealed from the significantly reduced barrier of ~18–21 kcal mol^{-1}, which again is nearly uniform. On the other hand, the kinetics of reductive elimination appears to be largely dictated by the saturation of the coordination sphere around the tungsten center by AlClMe$_2$ complexation, thereby amplifying the metal’s electrophilicity. Starting from an almost prohibitive barrier in the absence of the cocatalyst (Table 1, entry 1), a regular, steady decrease of the activation energy is predicted upon increasing the number of coordinating AlClMe$_2$ moieties, irrespective of the association mode. The stabilizing role of additionally coordinated olefin molecules has been explicitly probed, but found to be less effective than the cocatalyst.

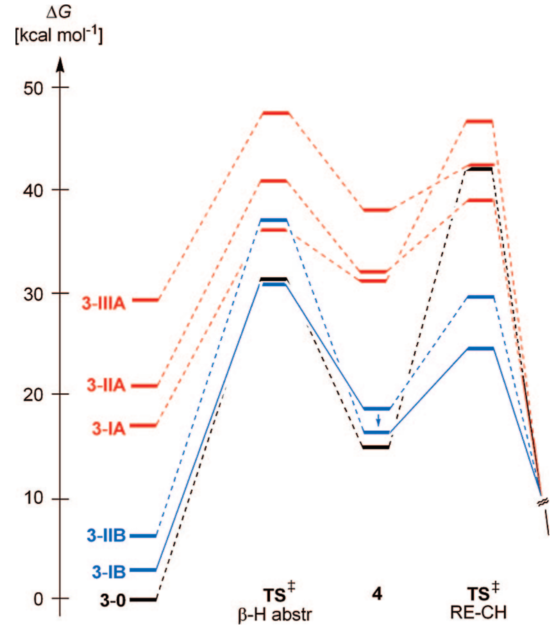

Figure 3. Calculated energy profile for dimer generation.[24]

Concerning tungsten dimers, unbound **D3-0** benefits from electronic interactions between the tungsten atoms, rendering it more susceptible to β-H abstraction, when compared to **3-0**. These interactions, however, leave the electrophilicity of the reacting tungsten center nearly unaffected, thereby giving rise to a prohibitively high barrier for reductive elimination that is of similar size to that calculated for **3-0** (Table 1). Lewis acid chelation of the ancillary tungsten is seen to raise the barrier for both steps by about 5–6 kcal mol^{-1} (Table 1, last entry). This leads to the conclusion that **D3-0** and **D3-IB** are dormant species and that tungsten dimers are not likely to participate in the productive olefin dimer generation cycle. These species are thus excluded from further discussion.

Taking the relative stability of the precursors **3** (Figure 1) into account, Figure 3 summarizes the absolute kinetics for the olefin dimer product-generating channel, with **3-0** chosen as reference.[24] As it can be seen from Figure 2, **3-IB** is the precursor for the most accessible pathway. The pathway from **3-IIB** is disfavored by a barrier for discriminating β-H abstraction that is 6.2 kcal mol^{-1} higher. All the other pathways, in which species with the cocatalyst complexed at the arylimido functionality participate, are kinetically inaccessible. It thus appears that Lewis acid association at the chlorine center is pivotal for an effective catalysis. Metallacycle degradation does involve one AlClMe$_2$ moiety in the first step (**IB**), while subsequent RE-CH does benefit from two activator moieties

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(24) The various modes of AlClMe$_2$ Lewis acid association are color-coded as follows: unbound (*black*), exclusive association at chlorine centres (*blue*), chelates with the arylimido group (*red*). Solid lines indicate the most accessible pathway. The displayed pathways have been restricted to tungsten monomer species for the sake of clarity.

(**IIB**).[25] The β-H abstraction is rate-determining with a barrier of 31.0 kcal mol^{-1} along the most accessible route. The alternative path for metallacycle growth stays almost entirely closed owing to the kinetically more difficult olefin insertion (Table S1, Supporting Information), such that the dimer product should be exclusively formed.

In summary, the presented computational mechanistic survey on a realistic catalyst model and the authentic reaction conditions unveiled that the Lewis acid component plays an integral role in the productive dimerization cycle and is pivotal for achieving effective catalysis. The predicted energy profile of the process is consistent with reported activity and selectivity. This study aids in rationalizing observed catalysts' abilities and in unravelling the identity of the catalytically active species. It also suggests that the complexed Lewis acid component may exert a significant influence on the regulation of the selectivity in α-olefin dimerization and can serve as a direct handle for modifications to improve the catalyst's abilities.

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Supporting Information Available: Text giving full details of the employed computational methodology and tables giving computed Cartesian coordinates and energies of all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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[25] Lewis acid uptake in **4** is indicated as being facile, to not be linked with a significant enthalpic barrier. Given the relative stability of **4** (Figure 2), association of a further $AlClMe_2$ moiety seems to be possible at this stage of the process.