From Ethene to 1-Hexene

Why Trimerization? Computational Elucidation of the Origin of Selective Trimerization of Ethene Catalyzed by $[TaCl_3(CH_3)_2]$ and An Agostic-Assisted Hydride Transfer Mechanism**

*Zhi-Xiang Yu and K N. Houk**

Transition-metal-catalyzed alkene oligomerizations usually yield mixtures of alkenes in the C_4–C_{26} range.[1] It is tedious to separate these mixtures into pure compounds. Consequently, much effort from both industrial and academic communities has been devoted to the search for more efficient catalysts that will produce terminal alkenes of specific lengths. The trimerization of ethene to 1-hexene is of special industrial significance since 1-hexene is an important comonomer in the preparation of linear low-density polyethylene.[2] Most catalysts known today are based on chromium compounds.[3,4] Recently, Sen and co-workers discovered that $[TaCl_3R_2]$, generated in situ by the reaction of $TaCl_5$ with alkyl metal compounds such as CH_3Li, can also function as trimerization catalysts under mild conditions (47.6 atm, 40–60 °C).[5] It has been postulated that metallacycles are involved in alkene trimerizations,[3e,f,6–8] but there has not been detailed information about the potential energy surfaces (PESs) and the structures of the transition states (TSs) and intermediates. Here we report MP2 and B3LYP calculations on the detailed mechanism of the olefin trimerization catalyzed by Sen's catalyst $[TaCl_3(CH_3)_2]$.[9,15] We also explored why this catalyst selectively trimerizes rather than dimerizes or polymerizes alkenes, and have uncovered a novel mechanism for the decomposition of dialkyl complexes of tantalum.

Dialkyltantalum complexes $[TaCl_3(R^1)(R^2)]$ (R^1 and R^2 are alkyl groups) are most stable as trigonal bipyramids with two electronegative Cl ligands in the axial positions (TB-1 conformation, see **1** in Figure 1 and Supporting Information). The TSs and intermediates (except **9**, see below) involved in the trimerization process adopt similar TB-1 conformations.

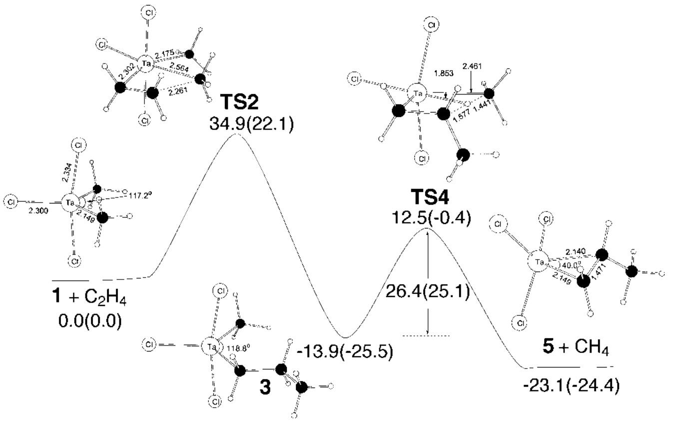
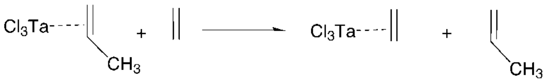


Figure 1. Free energy (ΔG_{298}) surface for the generation of catalytic precursor **5**. Potential energies (ΔE_0) are in parentheses. Energies in kcal mol^{-1}, distances in Å.

The insertion of ethene into **1** proceeds directly via **TS2** to give **3** (Figure 1). No complex of ethene with **1** was found, in contrast to the usual Cossee mechanism.[16] The lack of ethene complexation may be explained by the crowded TB-1 conformation, the coordinately saturated Ta center of **1**, and the lone-pair–π repulsion between Cl ligands and the incoming ethene. Subsequently, **3** undergoes β elimination to afford **5** with liberation of methane. This step is a novel agostic-assisted hydride shift (see below), and no minimum for a metal-hydride intermediate could be found. A similar mechanism was proposed by Negishi et al. for the transformation of dialkylzirconocenes to zirconocene–alkene complexes.[17a,b]

The catalytic cycle shown in Figure 2 starts with the coordination of a second ethene molecule to the tantalum–ethylene complex **6**, producing **7**. Subsequently, facile ring closure via **TS8** transforms **7** to a tantalacyclopentane intermediate, which initially has the TB-1 conformation of **9*** but easily converts into the more stable **9** with a pseudo-square-pyramidal structure. Intermediate **9** is transformed to tantalacycloheptane **11** by ethene insertion via **TS10**. The activation energy (in terms of ΔE_0) of this step is 13.0 kcal mol^{-1} (25.6 kcal mol^{-1} in terms of ΔG_{298}). **TS10** is 14.6 kcal mol^{-1} higher than **TS8** in terms of ΔG_{298}, suggesting that **6**, **7**, and **9** can all equilibrate before they are irreversibly converted to tantalacycloheptane **11**. Because of this equilibrium process, ligand exchange reactions between $[TaCl_3(alkene)]$ complexes and ethene (Scheme 1) favor $[TaCl_3(ethene)]$, **6**, that can enter the trimerization cycle. Complex **6** is more stable than **5** and **13** ($\Delta G_{298}/\Delta E_0$ for Equations (1) and (2) are −0.7/0.3 and −2.8/−1.5 kcal mol^{-1}, respectively).



5 **6** (1)

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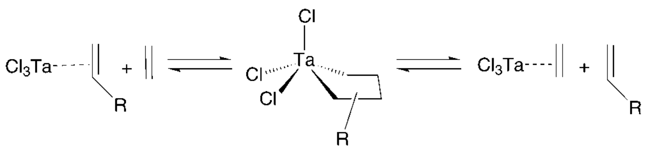


Scheme 1. Ligand exchange reactions between [$TaCl_3$(alkene)] and ethene.

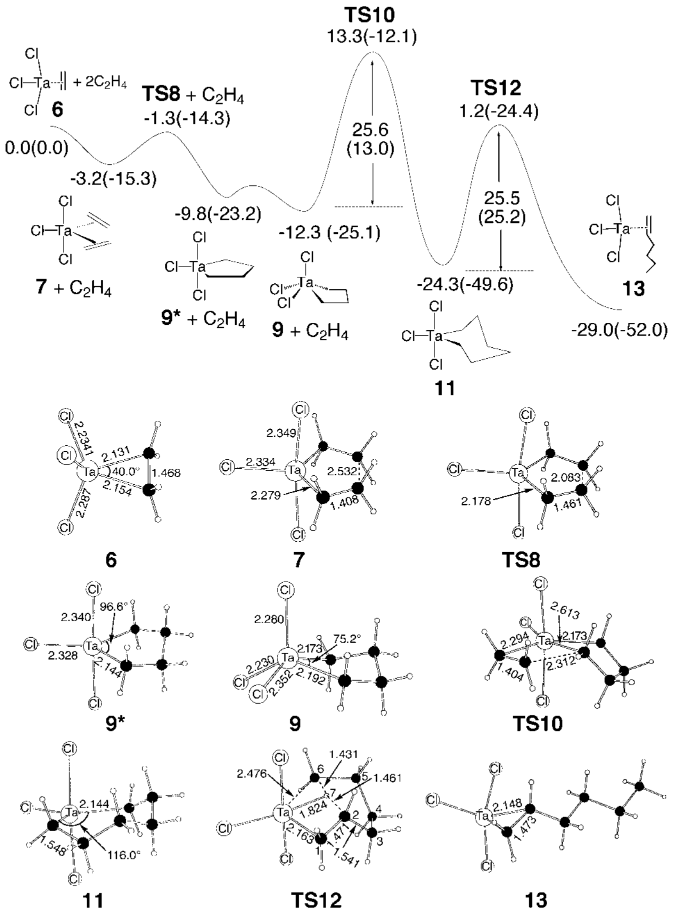
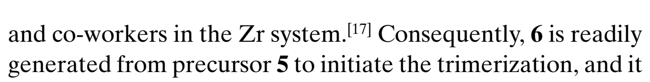


Figure 2. Top: ΔG_{298} surface for the trimerization of ethene; ΔE_0 values in parentheses. Bottom: B3LYP optimized structures of the stationary points involved in this trimerization. Energies in kcal mol^{-1}, distances in Å.

The preference of the ethene–$TaCl_3$ complex over the terminal alkene–$TaCl_3$ is of steric origin. Similar ready ligand-exchange reactions have been observed by Negishi



(2)

13 6

and co-workers in the Zr system.[17] Consequently, **6** is readily generated from precursor **5** to initiate the trimerization, and it is readily regenerated from **13** upon completion of one catalytic cycle. As shown in Figure 2, the activation free energies for the ligand exchange processes are estimated to be about 12.3 kcal mol^{-1} (**9**→**6** + C_2H_4), which is significantly less than that (25.6 kcal mol^{-1}) for the insertion of ethene into tantalacyclopentane **9**. This preference of ethene coordination to $TaCl_3$ contributes to the selective generation of 1-hexene instead of branched oligomers.

The barrier for ethene addition to **9** is about 9 kcal mol^{-1} lower than for ethene addition to **1**, because of the ring strain in **9**. The ideal 120° of the C-Ta-C angle in [$TaCl_3R_2$] cannot be achieved in **9** and **9***, but an angle near this is found in **11**. This is a key element that favors trimerization; conversion of **9** into **11** is much more facile than formation of higher complexes. The reaction of **11** with a fourth ethene molecule to form a tetramer requires an activation energy of 23.1 (see Figure 3) instead of the 13.0 kcal mol^{-1} for the formation of the trimer.

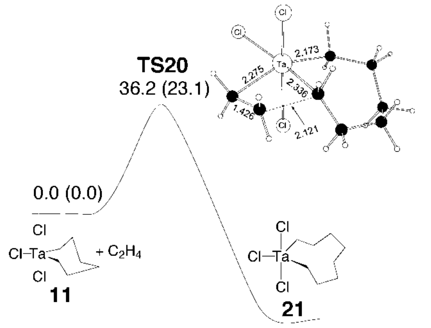


Figure 3. ΔG_{298} surface and calculated TS for the tetramerization of ethene; ΔE_0 values in parentheses. Energies in kcal mol^{-1}, distances in Å.

By contrast to the activation free energy of 36.2 kcal mol^{-1} for the formation of **21**, the conversion of **11** into **13** occurs as a concerted process with an activation free energy of only 25.5 kcal mol^{-1}.[18] This is a novel hydrogen shift related to the well-known metal–hydrogen interaction called β-agostic interaction. The reaction involving **TS12** is called an agostic-assisted hydride shift. Intrinsic reaction coordinate (IRC)[19] calculations demonstrate that distorted geometries of **11** involve a β-agostic interaction of C-H with Ta. These structures are not minima of **11** since too much ring strain is required to achieve the appropriate geometry. But nevertheless this interaction facilitates the conversion of **11** into **13**.[20] The alternate two-step process involving β-H abstraction and reductive elimination, which has been proposed for the Cr and Pt systems,[21,22] requires a higher activation energy to form the metastable intermediate, and a very unfavorable second reductive elimination step (Figure 4a). The overall trimerization cycle from **6** to **13** is highly exothermic and has activation free energies around 26 kcal mol^{-1} for the two most difficult steps.

The agostic-assisted hydride shift leading to reductive elimination requires the dihedral angle H7-C2-C1-Ta to be near 0°, as shown by **TS12** (Figure 2 bottom). The geometry required for the TS of the concerted reductive elimination could not be achieved in **9**. Instead, only a two-step mechanism was found for the transformation of tantalacyclopentane **9** to 1-butene (Figure 4b). The PES of this process is very similar to that shown in Figure 4a, implying that dimerization is disfavored not because of the ring strain in **9**, but because of the nonexistence of a concerted reductive elimination process in the smaller ring size.

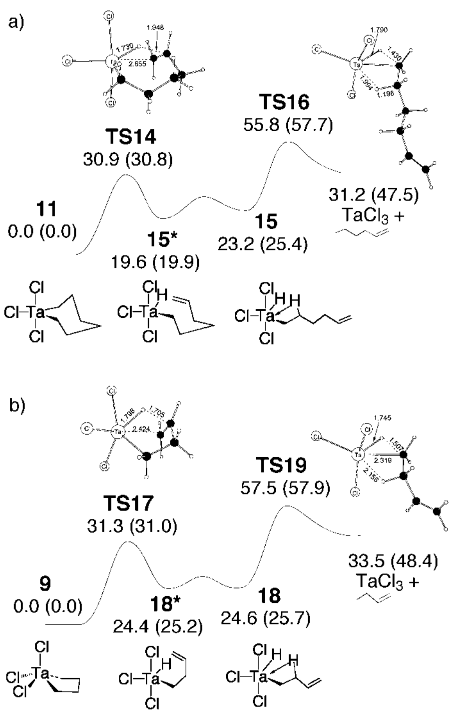


Figure 4. ΔG_{298} surfaces of the β-H abstraction and reductive elimination processes from a) **11** and b) **9**; ΔE_0 values in parentheses. Energies in kcal mol^{-1}, distances in Å.

These theoretical results confirm the intermediacy of tantalacycloalkanes in the trimerization process. The convertion of tantalacycloheptane **11** to tantalum–(1-hexene) complex **13** is a novel concerted process. The dimerization is disfavored by the nonexistence of this kind of concerted reductive elimination process for the tantalacyclopentane, whereas the bimolecular processes of tetramerization and possible higher oligomerization cannot compete with the facile reductive elimination. A similar trimerization mechanism is likely to be shared by the Cr-based catalysts and is under investigation.

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