

## Spin-crossover in Chromium-catalyzed Ethylene Trimerization: Density Functional Theory Study

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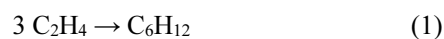
Industrially important linear alpha-olefins are commonly produced by oligomerization of ethylene or by Fischer-Tropsch synthesis followed by purification. Biggest challenge for the linear alpha olefin industry is a Schultz-Flory distribution of products made by most of the processes.<sup>1</sup> With 8-10 products being made at the same time, with most of them sold into different markets with different dynamics, it is difficult to balance the supply and the demand for all or even most products.

Recent findings of selective ethylene trimerization catalysts (mostly based on chromium,<sup>2</sup> even though other titanium,<sup>3</sup> nickel,<sup>4</sup> and tantalum<sup>5</sup> are also known) prompted many scientists to study the reaction mechanism to figure out the high selectivity towards trimerization of ethylene with these catalysts. Experimental and theoretical investigations led to widely accepted redox reaction/ring-expansion mechanism.<sup>2,6</sup>

Chromium complexes are the catalyst precursors that are most commonly used since these complexes give most selective and active transformations. For example, a catalyst system comprising Ar<sub>2</sub>PN(Me)PAr<sub>2</sub> (Ar = 2-methoxyphenyl, abbreviated as PNP) and [CrCl<sub>3</sub>(THF)<sub>3</sub>], activated with methyl aluminoxane (MAO) yields 99.9 wt % 1-hexene in C<sub>6</sub> fraction and 89.9 wt % 1-hexene overall with activity of over 1 million g<sub>1-hexene</sub>/g<sub>Cr</sub> h<sup>-1</sup>. Because of the unpaired electrons in the valence shell of the chromium, it is difficult to examine the characteristics of the paramagnetic Cr catalysts using usual NMR method. Therefore, X-ray crystallography is the only acceptable method experimentally. The need for open shell calculation also impeded theoreticians from studying the reactions computationally due to SCF convergence problems and long computing time.

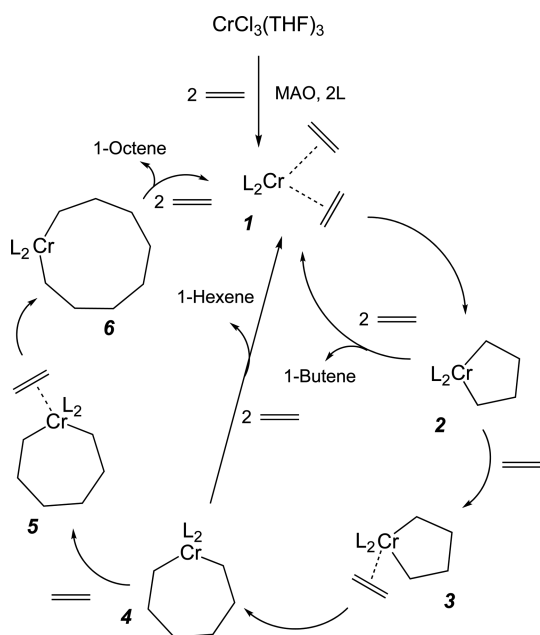
The effect of ligand in the electron pairing energy of Cr(III) complexes was studied by Cacelli *et al.*,<sup>7</sup> quartet being the ground state. Also the study by Blom *et al.*<sup>8</sup> on the cyclopentadienyl chromium complexes showed quartet is always the most stable state. However, the multiplicity of Cr catalyst changes during the reaction because of the oxidation state change. Until now, the change in the multiplicity in the chromium-catalyzed ethylene trimerization has not been studied in detail. In order to study this kind of spin crossing phenomenon during the catalytic cycle, it is imperative to examine all possible spin states of important intermediates.

In this paper, we studied the entire catalytic cycle for chromium-catalyzed ethylene trimerization focusing on the spin-crossover using density functional theory (DFT) method.



DFT calculation was performed using Gaussian 03 program.<sup>9</sup> Among various ligands, we chose PNP-type ligand as a model since it is the most active and selective ligand. Specifically, we used H<sub>2</sub>PNHPH<sub>2</sub> since it is the simplest form to resemble our catalytic system. The anion fragment is proposed to consist of Cl-MAO unit, which remains elusive because of complexity of its structure, and omitted in the discussion for simplicity. The geometry optimizations and thermodynamic corrections were performed with unrestricted hybrid Becke 3-Lee-Yang-Parr (UB3LYP) exchange-correlation functional with the 6-31+G\* basis sets for C, H, N, and P and LanL2DZ(ECP) basis sets for Cr. All stationary points were verified as minima or transition states by full calculation of the Hessian and a harmonic frequency analysis. The calculated number of imaginary frequency (N<sub>Imag</sub>) is 0 for energy minimum structures and 1 for transition states. The magnitude of imaginary frequency and corresponding eigenvectors were analyzed for all transition states to verify involvement of require atoms. Intrinsic reaction coordinate (IRC)<sup>10</sup> calculation were used to confirm the connectivity between transition structures and minima.

The proposed mechanism for ethylene oligomerization with a PNP-based system is illustrated in Figure 1. Catalyst initiation is proposed to involve reduction of Cr(III) to Cr(I) by MAO, ligand exchange, and coordination of two ethylene molecules to yield species **1** as the first active intermediate in the catalytic cycle. Metallacycle formation from **1** involves oxidative addition of two ethylene fragments to yield a five-membered Cr(III) metallacycle, **2**. At this stage, 1-butene can be liberated by reductive eliminative intramolecular  $\beta$ -hydrogen migration to the  $\delta$ -carbon and regeneration of the active catalytic Cr(I) species, **1**, upon coordination of two ethylene molecules. On the other hand, the energetically more favorable coordination of a third ethylene molecule can be followed to yield **3** if 1-butene generation is energetically demanding. Subsequent metallacycle growth results from insertion of the third ethylene molecule into the five-

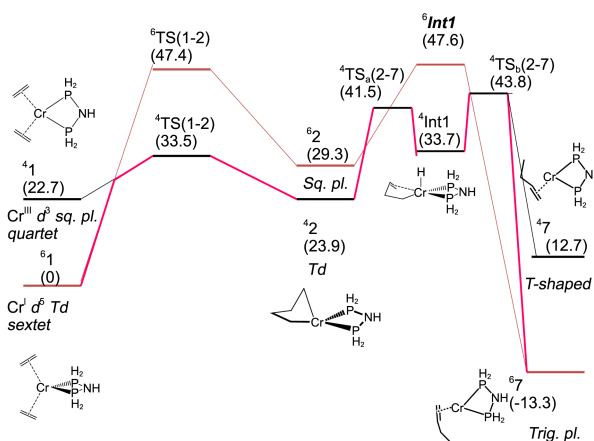


**Figure 1.** Catalytic cycle for ethylene oligomerization with a PNP-based chromium catalyst system.  $L_2 = H_2PNHPh_2$ .

membered metallacycle ring to yield the seven-membered metallacycle species **4**. At this time, 1-hexene can be liberated *via* reductive eliminative intramolecular  $\beta$ -hydrogen migration to the  $\zeta$ -carbon and regeneration of the active catalytic Cr(I) species, **1**, upon coordination of two ethylene molecules. Depending on the energetics of coordinating another ethylene molecule, further expansion of metallacyclic ring can occur.

The first possibility of spin-crossover was tested for 1-butene formation. The reaction intermediates and transition states involved in the first catalytic cycle for the formation of 1-butene are shown in Figure 2. Two spin states for Cr(I) and Cr(III) complexes (quartet and sextet) were considered. As shown in Figure 2, the sextet state is more stable than the quartet state for Cr(I) and the reverse is true for Cr(III). The structure of starting intermediate **1** is tetrahedral for the more stable sextet state and square planar for the less stable quartet state. In case of five-membered Cr(III) metallacycle, **2**, the structure is square planar for the less stable sextet state and tetrahedral for the more stable quartet state. Therefore, the spin state crossing occurs at the transition state (TS(1-2)) where quartet TS is more stable than sextet TS. In other words, it starts as a sextet tetrahedral structure and changes to a quartet square planar structure at the TS(1-2) of the oxidative coupling step and changes back to a quartet tetrahedral structure of the metallacycle. Because of the strain of the five-membered metallacycle, a two-step process involving  $\beta$ -hydrogen abstraction (TS<sub>a</sub>(2-7)) and reductive elimination (TS<sub>b</sub>(2-7)) ensues to produce 1-butene *via* 3-butenylhydrido intermediate (*Int1*). Here once again, spin state changes from quartet Cr(III) TS to sextet trigonal planar Cr(I) product (**7**).

Whether to proceed to make a larger metallacycle **4** from **2**

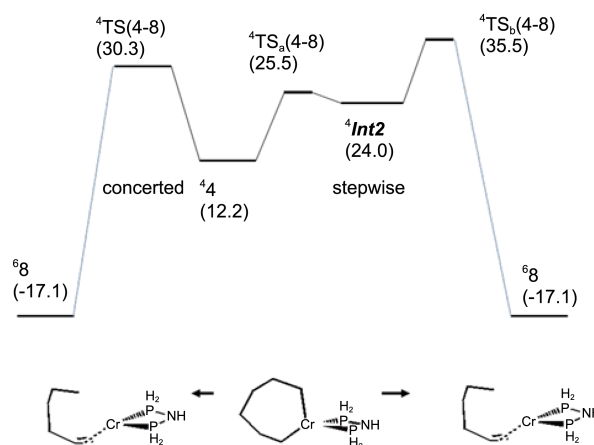


**Figure 2.** Energy profile calculated for ethylene dimerization with a PNP-based chromium catalyst system showing spin-crossover. The relative Gibbs free energies are given in kcal/mol in parenthesis.

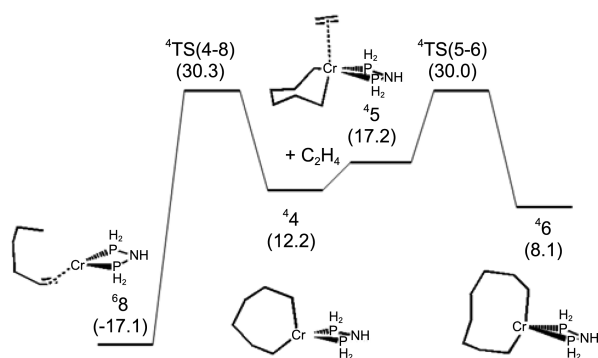
by insertion of another ethylene molecule or to produce 1-butene depends on the relative energetics. The free energy of activation for the formation of metallacycloheptane **4** is 10.5 kcal/mol (Figure S1) whereas the conversion of metallacyclopentane into 1-butene occurs with an activation free energy of 19.9 kcal/mol as shown in Figure 2. This preference of ethylene insertion contributes to the eventual generation of 1-hexene instead of 1-butene.

To produce 1-hexene from **3**, two different routes are possible, one *via* ethylene insertion followed by intramolecular  $\beta$ -hydrogen migration and the other *via* alkyl transfer followed by reductive elimination. The former route is calculated to be preferable to the latter route by 21.5 kcal/mol as shown in Figure S1.

With metallacycloheptane **4**, a concerted process called an agostic-assisted hydride shift occurs instead of a two-step process.<sup>6c</sup> As shown in Figure 3, this concerted process is with an activation free energy of only 18.1 kcal/mol compared with a stepwise process of 23.3 kcal/mol. As the case for 1-



**Figure 3.** Energy profile calculated for the production of 1-hexene from the seven-membered metallacycle species *via* two different routes showing spin-crossover. The relative Gibbs free energies are given in kcal/mol in parenthesis.



**Figure 4.** Calculated energy profile comparing the production of 1-hexene with the formation of metallacyclononane. The relative Gibbs free energies are given in kcal/mol in parenthesis.

butene, spin state crossing occurs at the transition state as shown in Figure 3 and the reaction is highly exergonic with a free energy of  $-17.1$  kcal/mol.

Whether to expand ring size further to nine also depends on the relative energetics. The free energy of activation for the formation of metallacyclononane **6** is  $17.8$  kcal/mol and the conversion of metallacycloheptane into 1-hexene occurs with an activation free energy of  $18.1$  kcal/mol as shown in Figure 4. Since both processes are similar in energetics, co-production of 1-hexene and 1-octene occurs with this type of simple Cr-PNP catalysts, which is consistent with experimental results. Therefore, to produce 1-hexene selectively a delicate control of the ligand structure is needed.

Production of 1-octene *via* agnostic-assisted hydride transfer occurs with a spin state change from quartet Cr(III) TS to sextet trigonal planar Cr(I) product. Further expansion of ring size is not favored to 1-octene production by  $2.8$  kcal/mol. So metallacyclic ring expansion stops at nine.

As a whole, the rate-determining step is oxidative coupling step ( $^4\text{TS}(1-2)$ ) to make a metallacyclopentane which is consistent with the kinetics of the reaction showing second-order dependence of the rate on the concentration of ethylene.

In conclusion, the density functional study on the mechanism of Cr-PNP catalyzed ethylene trimerization including spin state change has shown the co-production of 1-hexene and 1-octene.

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**Supporting Information Available.** Figure S1 and a table giving Cartesian coordinates of all optimized structures of reaction intermediates and transition states involved in the reaction pathway.

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