

Evidence for a Stable Ti(IV) Metallocene Dihydrogen Complex from *ab Initio* Molecular Dynamics

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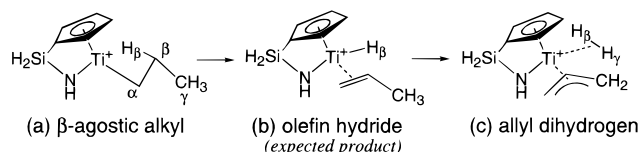
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The Car–Parrinello (CP)^{1,2} *ab initio* molecular dynamics (AIMD) method is maturing into a powerful predictive tool for chemical processes, as it is one of the select few first-principles methods that are able to sample large regions of configuration space with reasonable expense of computer time. Recent applications in chemical catalysis show the potential power of the method, allowing glimpses of real-time reaction simulations,³ studies of subpicosecond fluxionality,^{4,5} reaction path scans,^{6–8} and free energy calculations.^{9,10} In this communication, we present an unexpected example of the ability of CP dynamics to reveal novel reaction pathways, particularly those that traditional “static” methods may overlook. Previous computational investigations in our lab have concerned themselves with systematic studies of chain propagation⁸ and chain termination steps¹⁰ for the constrained-geometry catalyst (CGC) (CpSiH₂NH)Ti^{IV}-R⁺ (Scheme 1a). This metallocene-type compound is a promising new single-site olefin polymerization catalyst that is being commercialized to produce so-called “next-generation” polyolefins.¹¹ The present communication presents evidence for a surprising side reaction of CGC-catalyzed olefin polymerization, which was discovered during an AIMD simulation of β -hydrogen elimination,¹⁰ namely the formation of a stable dihydrogen ligand at a Ti(IV) center.

As the precise computational details of our simulation are similar to those previously published,¹⁰ we here confine ourselves to a few essentials. To model the β -hydrogen elimination reaction of the system shown in Scheme 1, a simulation was done with the CP-PAW package,^{12,13} using the BP86^{14–16} gradient-corrected density functional to derive forces on the atoms. An NVT ensemble was maintained at 300 K by a Nosé¹⁷ thermostat. Atomic mass rescaling¹⁸ was employed to speed up configurational ensemble averaging as detailed in an earlier work.¹⁰ A constraint was imposed upon the reaction coordinate, which in the present case is the distance between the β -carbon and the

Scheme 1



centroid of the β -hydrogen atoms and which was varied in slow-growth fashion.^{19,20} The intent behind a slow-growth simulation is to let the system undergo normal dynamics orthogonal to the reaction coordinate (RC), while keeping the RC itself constrained to slowly move from the starting point of the reaction path to the end point over a period of several picoseconds. In this case the RC was varied from 0.73 to 2.04 Å over a period of 3.5 ps. Moreover, since the system moves freely orthogonal to the RC, a broad region of configuration space is spanned at each point along the RC, allowing the system to search regions of phase space that would remain unexplored in a less expansive search, for instance an intrinsic reaction path following Scheme 1.²¹ Thus, the system may slip from the originally intended reaction path into an alternative one, which might prove unforeseen and—above all—energetically more favorable.

Our original intention¹⁰ was to determine the free energy change for a change from a β -agostic propyl chain (Scheme 1a) to an olefin hydride complex (Scheme 1b) by thermodynamic integration.^{9,19} This β -elimination, where an olefin hydride complex is produced, is the most commonly assumed unimolecular chain termination process in Ziegler–Natta type ethylene polymerization.²² In line with this assumption, initial “static” calculations with the ADF program package²³ had projected these two configurations as the starting and end point for β -hydrogen elimination.¹⁰

Our AIMD simulation at first proceeded in the expected direction, as shown in Figure 1, where various descriptive quantities are graphed as a function of the slow growth RC. As the RC is dilated from its starting value of ≈ 0.75 Å to ≈ 1.5 Å—where formation of the hydride sets in—no unexpected events take place: Figure 1c shows that the biggest noticeable change in the system is in the partial charge of the β -hydrogen atom that is being abstracted, which becomes more negative as the hydridic state is approached. Also, the mobility of the chain increases as it switches from tight binding (through a Ti–C and a β -agostic bond) to lose binding (through olefin π -complexation), as evidenced by the enhanced fluctuations of the Ti–H _{γ} distance (Figure 1b).

The additional mobility of the chain thus incurred allows for large-amplitude rotations of the chain around the Ti–olefin π -bond, which bring the γ -hydrogen atoms close to the hydridic hydrogen (Figure 1a). At an RC value of ≈ 1.6 Å, γ -hydrogen and hydridic hydrogen approach each other closely enough so that a close-range binding interaction can occur, which leads to formation of a dihydrogen molecule bonded to the Ti center (Scheme 1c). This switch is accompanied by major structural changes: the H _{β} –H _{γ} distance drops to ≈ 0.8 Å—which is a typical value for a dihydrogen ligand—and at the same time the C _{γ} –H _{γ} distance rises as the γ -hydrogen is removed from the alkyl chain (Figure 1a). Similarly, the Ti–H _{γ} and Ti–H _{β} distances become

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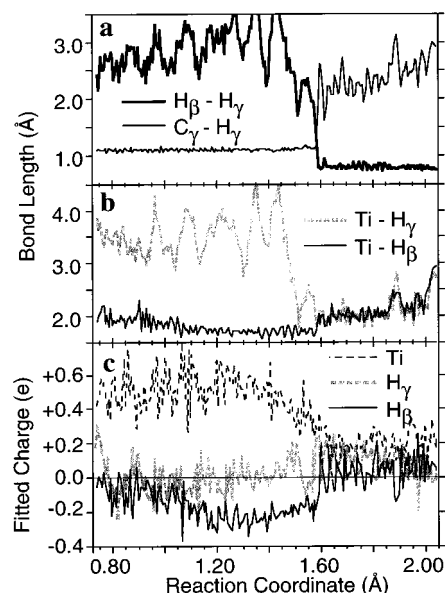


Figure 1. Characteristic bond lengths (a–b) and CP-PAW partial charges (c) as a function of the RC. Onset of dihydrogen formation at RC \approx 1.6 Å. The reaction coordinate is defined as the distance between the β -carbon and the centroid of the two β -hydrogen atoms.

equivalent as the rapidly spinning dihydrogen ligand is formed. As the alkyl chain undergoes transformation into an allyl ligand, all Ti–C distances become equivalent (not shown). In terms of ionicity, the change from olefin hydride to allyl dihydrogen coordination brings on a dramatic deionization of the Ti atom and the hydrogen atoms involved in dihydrogen formation (Figure 1c). The Ti–H₂ bond is obviously nonpolar and, in total, slightly electron deficient since the allyl moiety bears a formal negative charge. Figure 1 shows that the final dihydrogen complex is stable during the remainder of the simulation and is therefore likely a stable minimum. To verify the stability of the dihydrogen complex, a dynamics simulation of the complex was performed with no constraints imposed. The 1.0 ps simulation shows that the dihydrogen complex is stable in the gas phase at 300 K. (Details and results of the simulation are provided in the Supporting Information.)

To quantify the novel reaction pathway obtained by AIMD, a series of “static” DFT calculations²³ were undertaken with the ADF 2.2 quantum chemistry package. A triple- ζ plus polarization basis on the Ti atom and double- ζ plus polarization basis sets^{24,25} on all nonmetal atoms were utilized.²⁶ A series of geometry optimizations with gradients derived from the BP86^{14–16} functional were done for several points along the AIMD trajectory to obtain a zero-temperature energy profile (Figure 2).

Our static calculations show indeed that the olefin hydride, although the expected final product of β -hydrogen elimination, is by no means very stable and is liable to either revert into the alkyl (with a barrier of only 13 kJ/mol) or to rearrange over an even lower barrier (3 kJ/mol) into the allyl dihydrogen complex, which is 26 kJ/mol more stable than the olefin hydride. The binding energy of the H₂ moiety to the allyl complex is calculated to be 46.2 kJ/mol. To our knowledge, no stable dihydrogen complex at a group 4 metal center has yet been structurally characterized either experimentally or theoretically.²⁷ Apart from the fact that the observation of such a compound is of fundamental

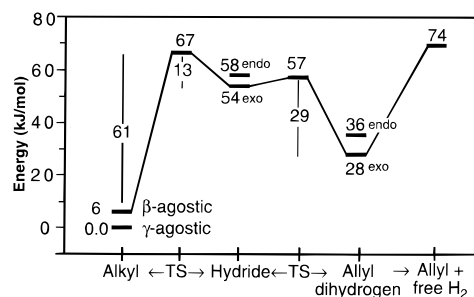


Figure 2. Reaction profile for β -hydrogen abstraction and dihydrogen formation. Energies given relative to the γ -agostic alkyl species. Endo and exo refer to the orientation of the mouth of the allyl group relative to the Cp ring.

interest, it is of practical importance that in the special case at hand—namely Ti(IV) catalyzed olefin polymerization—this feature might give rise to H₂ evolution if the dihydrogen ligand is dissociated. It should be noted that our previous calculations show that, in the presence of monomer, the dominant termination process involves a β -hydrogen transfer to the monomer and not the formation of the allyl dihydrogen complex.¹⁰ Therefore, we would only expect significant amounts of hydrogen gas to be produced in monomer-poor polymerization conditions.

There is experimental evidence for such a side reaction that produces H₂ coming from gas-phase mass spectroscopy experiments on Zr metallocenes,^{28,29} where also the existence of a stable H₂ complex has been inferred.²⁹ However, after completion of our calculations we have been made aware³⁰ of recent work that shows that there is sometimes a significant amount of H₂ detectable in the headspace of slurry, ethylene/1-hexene copolymerizations with certain metallocene-type catalysts.³¹ This and other experimental observations have been attributed to the elimination mechanism involving the formation of an allyl complex as described above.³¹

Concluding, it is important to state that the actual thermodynamic product of β -hydrogen elimination—namely the allyl dihydrogen complex—was first located by AIMD simulations and would not have been found otherwise by us. This shows the uniquely powerful ability of ab initio molecular dynamics to search configuration space in a more global fashion compared to traditional static methods which tend to sample only the immediate region of a single minimum. Thus, it has a greater chance to hit unexpected—but important—reaction paths and products. This is particularly true in studying reaction pathways in systems with high configurational variability, such as the constrained geometry catalyst, whose “flat” potential surface is difficult and tedious to explore with conventional “static” methods.

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Supporting Information Available: A listing of all Cartesian coordinates and results and computational details of the constraint free dynamics simulation of the allyl–dihydrogen complex and Figure 3 showing optimized “static” structures of olefin–hydride and allyl dihydrogen complexes (5 pages). See any current masthead page for ordering and Internet access instructions.

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