



Calculating accurate barriers for olefin insertion and related reactions



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ABSTRACT

Highly accurate (extrapolated CCSD(T)/aug-cc-pwCVQZ) reference energies have been calculated for olefin insertion in a set of simple models for olefin polymerization catalysts, and also for related reactions (hydrogen transfer to metal and to monomer, allyl formation). The model systems cover early (groups 3 and 4, 10 basic systems, 216 geometries) and late (group 10, 3 basic systems, 51 geometries) transition metals. The reference energies were then used to evaluate the performance of 22 commonly used density functional, as well as several ab-initio methods. Dispersion corrections (either implicit or explicit) are essential in getting the olefin complexation energy right, but are less important for describing further reactions from the olefin π -complex stage on. No functional performs entirely satisfactorily (within ~ 1 kcal/mol) for both early and late transition metals. Of the functionals tested, TPSSh-D0 shows the best “across-the-board” performance (important if chemistry involving more than a single metal needs to be described e.g. chain shuttling, bimetallic complexes, bifunctional systems), but M06-2X performs somewhat better specifically for early transition metals. A subsequent benchmark on 21 experimentally known π -coordination enthalpies and barrier heights for early, middle and late TM systems yielded an MAD of 0.60 kcal/mol using our recommended protocol. Finally, we revisited prototypical catalysts systems studied in early computational work, and conclude that insertion of ethene is nearly barrierless for titanocenes, and has a slightly higher barrier for constrained-geometry catalysts and for Zr analogs.

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Introduction

Olefin insertion in a metal–carbon bond is the basis for metal-catalyzed olefin polymerization, and hence for a major petrochemical-based industry. The mechanism of olefin polymerization is well-understood in general terms. The catalyst has an empty coordination site *cis* to the growing chain. The olefin is captured at this empty site, and then the chain migrates to one of the two sp^2 carbon atoms of the olefin in a four-center transition state. This idea was first proposed by Cossee [1]; a refinement of the model emphasizing the role of α -agostic interactions in assisting chain migration has become known as the modified Green-Rooney mechanism or variation [2–5]. Based on this understanding, one could expect modeling to play an important role in analyzing and even predicting catalyst performance. Indeed, major progress has been made in understanding and predicting stereochemistry and –

to a lesser extent – molecular weight of the polymers produced, in particular for well-defined “single-site” homogeneous catalysts [6,7]. However, calculating the *rate* of catalysis seems to be much more difficult. On the experimental side, one should note that good catalysts can be incredibly effective: turnovers of $3 \times 10^5 \text{ s}^{-1}$ are not unusual for ethene polymerization [8]. This implies very low activation energies, but it is not a priori clear to which step(s) the observed barriers correspond. It is possible the insertion step itself is rate-limiting, but one can also make a reasonable case for olefin capture/anion displacement or internal chain rearrangement to be rate-limiting [9–12]. On the computational side, the magnitude of the insertion barrier for simple model systems has been a matter of intense study from the moment computational methods were able to tackle such systems. Morokuma studied the MeTiCl_2^+ system by optimizing geometries at the Restricted Hartree-Fock (RHF) level followed by improved single-point energies at the Møller-Plesset perturbation level with double spin projection (DPUMP2) [13]. The calculated barrier at this level was sizable (~ 4 kcal/mol), but the barrier at the RHF level is much higher (11.3 kcal/mol), in agreement with the general observation that Hartree-Fock overestimates such barriers. This rather large error of HF may imply that the HF *geometry* is also significantly in error and may not be reliable as a

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basis for subsequent post-HF energy calculations. In addition to this, Morokuma made the relevant observation that the HF wavefunctions of coordinatively unsaturated transition metal complexes frequently suffer from triplet instability, and that this Ti model system is no exception. As a consequence, post-HF methods based on an RHF wavefunction may be problematic [13]. In a subsequent study, Morokuma reported calculated barriers of ~ 6 kcal/mol for insertion in $\text{H}_2\text{SiCp}_2\text{ZrMe}^+$ (a minimal *ansa*-metallocene model) using a similar computational approach [14]. Around the same time, Density Theory Functional (DFT) studied by Ziegler predicted virtually barrierless insertion (barriers < 1 kcal/mol) for ethene insertion in Cp_2ZrMe^+ (metallocene) and $\text{H}_2\text{SiCp}_2\text{ZrMe}^+$ using the BP86 functional [15], but BP86 is known to overestimate the stability of compact molecules [16,17]. Ahlrichs and Weiss reported barrierless insertion for $\text{Cp}_2\text{TiCH}_3^\ddagger$ using MP2 [18], but their result was later suggested to be due to MP2 not being an appropriate method for titanium [19]; in addition, post-HF methods require the use of large basis sets to reduce basis set superposition error, which otherwise results in artificial attraction between the olefin and catalyst. On the one hand, these examples indicate that the true insertion barrier for ethene in e.g. Cp_2TiMe^+ and Cp_2ZrMe^+ is likely modest, but on the other hand they demonstrate that there is no consensus about its magnitude (or even on whether there really is a barrier). Both the real insertion barrier and its relation to experimentally observed “activation energies” are uncertain, and different computational methods produce rather different predictions. This constitutes a serious impediment to the use of computational methods for polyethylene catalyst design and optimization. Judging from the more recent literature, there appears to be consensus that for *propene* polymerization the barrier is substantial (in the order of 5 kcal/mol [6]) and insertion is usually rate-limiting even for efficient catalysts, making computational studies of propene polymerization catalysis more meaningful.

In a previous paper, we evaluated the performance of DFT methods for the prediction of dimerization and complexation energies, and concluded that there are few methods that appear to produce consistently reliable results [20]. In Part 1 of the present paper, we address the issue of calculating reliable *barriers*, focusing on olefin insertion and related reactions. Ideally, we would like to identify an efficient DFT method which would produce energy differences with a Maximum Average Deviation (MAD) of < 1 kcal/mol and fewer than 10% of the values off by 2.5 kcal/mol or more. The strategy followed here is the same as that in Ref. [20]: generate highly reliable reference energies for simple model systems using state-of-the-art post-HF methods, followed by benchmarking against a range of functionals, with or without dispersion corrections, leading to a proposed computational protocol for calculating reliable barriers.

Although numerous publications have aimed to evaluate the performance of density functional methods in transition metal catalyzed reactions, we are unaware of any publication that has identified a promising DFT approach with across the board capability for reliable calculation of barrier heights for TM catalyzed reactions. To illustrate the problem, Chen published a series of papers, each focusing on a very specific and limited area of chemistry. PBE0 was found to outperform most methods for π -coordination energies of Au complexes [21]. Cycloisomerizations, Friedel–Crafts reactions, propargyl acetate rearrangements using Au are also well described [22]. Similarly, CH activation using Ir or Pt pincer complexes is well described, although PBE0 is outperformed by B2GP-PLYP [22]. When focusing on C–H activation energies of group 10 metal pincer complexes the recommendation changes to B3LYP followed by several functionals including PBE0 [23]. Ruthenium catalyzed water oxidation was found to be ill described by all tested DFT methods with PBE0 being

recommended as the least poor method [24]. For Zr activation energies all Minnesota functionals were recommended [25] while Re catalyzed activation reactions are best described by ω B97XD [26]. Finally, for hydrogen abstraction from methane using high-valent nonheme iron(IV)-oxo complexes B3LYP and TPSSh were found to give appropriate results [27]. In summary, current recommendations often vary from metal to metal or even reaction to reaction.

Ultimately, we aim to identify a computational procedure that reliably predicts barrier heights for transition-metal-catalyzed reactions across the periodic table. Across-the-board performance is obviously convenient when starting in a new area, or when catalysts containing different metals are to be compared. It becomes essential when studying systems involving more than a single metal, such as bimetallic clusters or bifunctional systems. In the context of olefin polymerization, several important reactions involve more than a single metal: transition metal alkylation, formation of cations by alkyl abstraction, and chain shuttling.

In Part 2 of this work, we test our protocol against a number of experimentally determined reaction energies and activation energies. Since very little reliable experimental data is available for olefin insertion, this part covers a wider range of organometallic reactions. Finally, in Part 3 of this paper we apply the recommended computational approach to prototypical metallocenes and constrained-geometry catalysts.

Methods

Following the protocol proposed in Refs. [20], all compounds were fully optimized using the Gaussian 09 software package [28] at the density functional level of theory employing the TPSS/TPSS functional in combination with correlation-consistent polarized valence- ζ (Dunning) basis sets [29–36], from the EMSL basis set exchange library [37,38], with (m)aug-cc-pVTZ-(PP) quality and accompanying small core relativistic pseudopotentials (ECP) for Zr, Hf, Pd and Pt [39–42]. Wherever available minimally augmented instead of fully augmented basis sets were used to reduce the computational cost [43].

All structures represent either true minima (as indicated by the absence of imaginary frequencies) or transition states (with exactly one imaginary frequency corresponding to the reaction coordinate). Details on quality settings, grid size, TS search methods [44–46], tested DFT methods (for an overview see Table 1) and dispersion corrections [47,48], tested post Hartree-Fock methods [49–51], minimally acceptable basis sets [20], extrapolated reference energies [52,53], T1 diagnostics [54], and BSSE correction [55] can be found in the [supporting information](#).

Results and discussion

Part 1: benchmarking against accurate calculated data

How bad is the problem, anyway?

The main parameters relevant to olefin polymerization catalyst performance are the insertion (propagation) barrier, which in principle determines catalyst activity, and the height of the chain transfer barrier *relative* to propagation, which determines the average degree of polymerization and hence the Molecular Weight (MW). Scheme 1 presents a brief summary of the results obtained for these two key parameters for the simple system Cl_2TiEt^+ + ethene. The insertion barriers produced by various DFT methods cover a range of about 6 kcal/mol, with the reference CCSD(T,FULL) value in the middle of the range. Even worse, the calculated barriers for chain transfer *relative* to insertion range from 1 kcal/mol (corresponding to low-MW oligomers) to 11.5 kcal/mol (essentially

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