

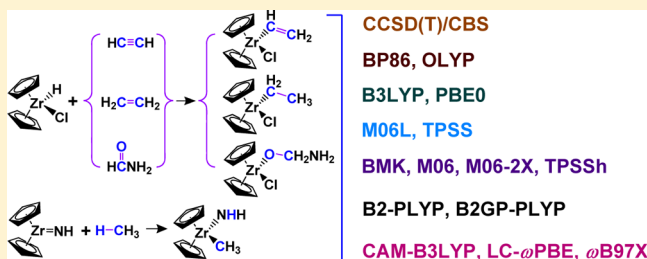
Performance of Density Functionals for Activation Energies of Zr-Mediated Reactions

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Supporting Information

ABSTRACT: Coupled cluster CCSD(T) calculations with core–valence correlation and complete basis set (CBS) limit extrapolation are used to benchmark the performance of commonly used density functionals in computing energy barriers for Zr-mediated reactions involving zirconocene species. These reactions include (a) insertions of the Zr–H bond of $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ into $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, and $\text{C}=\text{O}$ bonds and (b) C–H activations by $\text{Zr}=\text{N}$ bond in $\text{Cp}_2\text{Zr}=\text{NH}$. The best performing functionals are M06-L, M06, and M06-2X in the M06 series, all having mean unsigned deviations (MUD) less than 2 kcal/mol. The worst performing functional is OLYP, with a distinctly large MUD of more than 10 kcal/mol. Considering also the trends in barrier heights and the systematic barrier height deviation, our best recommended functional is M06-2X. In this work, DFT empirical dispersion correction (DFT-D3) is found to improve the performance of barrier height values for most functionals (especially of OLYP and B3LYP). With DFT empirical dispersion correction, we also recommend M06-2X for reaction barrier calculations of Zr-mediated reactions.

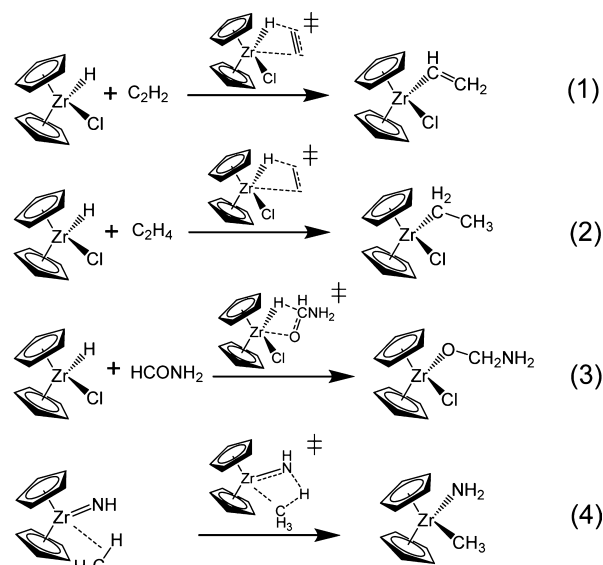


INTRODUCTION

Zirconium is one of the most widely used early transition metals (groups 3 to 6) in organometallic chemistry.^{1–25} Interestingly, the great majority of organozirconium compounds used in organic and organometallic chemistry are zirconocene complexes with a “clamshell” Cp_2Zr fragment structure wherein two cyclopentadienyl (Cp) rings are not parallel.^{1–23} Similar “clamshell” structures of metallocene also exist and are useful in the organometallic chemistry of some other early transition metals like Ti and Sc.^{3,5,19,26–28}

The most well-known zirconocene-mediated reaction in organometallic chemistry is probably the Schwartz hydrozirconation. It is defined by the addition of unsaturated CC bonds (alkenes and alkynes) to zirconocene hydrochloride $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ to generate alkylzirconium and alkenylzirconium compounds (see eqs 1 and 2 in Scheme 1).²² Schwartz pioneered the discovery of $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ reactivity with a wide range of substrates and developed it as a useful reagent for organic synthesis, and thus $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ is also called the “Schwartz reagent,”²² which was first prepared by Wailes and Weigold by the reduction of Cp_2ZrCl_2 .²³ The insertion of a Zr–H bond into C–C double and triple bonds can take place at room temperature and is usually combined with transmetalation to other useful organometallic compounds.^{9,15} The insertion of Zr–H into $\text{C}=\text{C}$ is also involved in the very important olefin polymerization catalysis by zirconocene complexes.¹¹ Besides the addition to alkenes and alkynes, the Schwartz reagent also deoxygenates carbonyl compounds,^{14,18} so amides can be reduced to imines with $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$. As

Scheme 1. The Zr-Mediated Reactions Studied in This Work



zirconium is “oxo-philic” like its congener titanium, this type of reaction occurs by linking the oxygen atom to the metal center of $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$. Thus, the first-step of the deoxygenation is hydrozirconation of the $\text{C}=\text{O}$ bond (see eq 3 in Scheme 1).

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In addition to the insertion of a Zr–H bond into multiple bonds as shown above, the zirconocene complex was also found to be reactive in C–H single bond activation. For imidozirconocene $\text{Cp}_2\text{Zr}=\text{NR}$, the reactive $\text{Zr}=\text{N}$ bond induces cleavage of the C–H bond in benzene, leading to the phenyl-substituted product $\text{Cp}_2\text{Zr}(\text{NHR})(\text{Ph})$.¹² In a similar complex $\text{Cp}_2\text{Zr}=\text{NR}$, *n*-hexane and *n*-pentane were found to be reactive substrates in C–H activation,⁸ while methane with the stronger C–H bond did not react.¹² On the contrary, the reverse reaction, 1,2-methane elimination, was proposed to occur from $\text{Cp}_2\text{Zr}(\text{NHR})(\text{CH}_3)$ to generate $\text{Cp}_2\text{Zr}=\text{NR}$ and CH_4 upon heating,^{8,12} which indicates that activating methane is very demanding in reactivity of this transition metal complex. Despite this, some nonmetallocene imidozirconium species such as $(\text{RNH})_2\text{Zr}=\text{NR}$ were found capable of activating methane to form $(\text{RNH})_3\text{ZrCH}_3$.²⁵

Density functional theory (DFT) has been successfully applied in the modeling of reactivity and in generating insight into the chemistry of a variety of transition-metal complexes. It thus underscores the immense role played by computational chemistry in better understanding of chemistry.^{29–40} However, because the performance of DFT depends on the identity of the functional, it has become customary to calibrate various approximate functionals for particular applications, both for the sake of choosing more appropriate functionals as well as for assisting the development of new and better functionals.^{41–149}

The reference data for DFT calibration can be either from experimental results or from high level ab initio calculation. The latter approach is often the more popular one. Among the high level ab initio methods, CCSD(T) model chemistry is now a “gold standard” and often the method of choice for systems without significant multireference character. There has been a plethora of DFT calibration studies employing CCSD(T) reference values, which covers a wide range of transition metal chemistry parameters, like reaction energy,^{41–58,142} reaction barriers,^{43–51,55–60,138,140–142} dipole moments,⁶¹ geometric structure,^{61–63,139,145,148} electron detachment energy,^{64–67} spin and electronic state energetics,^{66,68–72,135,136} binding energy,^{73–78,139,144} thermochemistry,^{43,67,79,80} etc. Recently, we initiated a DFT calibration program for reactions barriers of transition metal-mediated reactions and have published a series of studies for complexes of Fe,¹³⁸ Au,¹⁴⁰ Ir,^{140,141} Pt,^{140,141} Rh,¹⁴¹ Pd,¹⁴¹ and Ru.¹⁴² All these transition metals are late (groups 9 to 12) or middle (groups 7 to 8) transition metals.^{135–142} Our ultimate goal is to generate systematic knowledge and provide a complete picture of evaluation for DFT performance in the important chemical reactions involving various transition metals in the entire d block of the periodic table. As such, the present work extends our DFT calibration research to early transition metals by choosing zirconium as our target. It would be interesting to compare the early and late transition metals and find out if systematic differences exist between them as far as the choice functionals. To the best of our knowledge, the only two DFT calibration studies on zirconium-mediated reactions are hydrolysis reactions of inorganic compounds ZrCl_4 and ZrO_2 recently published by Dixon and co-workers,^{43,46} and there is still no DFT calibration study on organometallic zirconocene-mediated reaction barriers available in the literature.

In this paper, we study the reaction barriers of typical organometallic Zr-mediated reactions in Scheme 1. These reactions include the Schwartz hydrozirconations of ethene, ethyne, and formamide, representing the addition of multiple

bonds of $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, and $\text{C}=\text{O}$ to Schwartz reagent $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$, separately. In addition, due to our continuous interest in the C–H activation process,^{138,140,141,150–158} we also studied the C–H bond activation in methane by $\text{Cp}_2\text{Zr}=\text{NH}$ (eq 4 in Scheme 1). Although experimentally $\text{Cp}_2\text{Zr}=\text{NH}$ cleaves the C–H bond in benzene but not in methane,¹² due to observed C–H activation of saturated hydrocarbons such as *n*-hexane by other imidozirconocene analogues⁸ and C–H activation of methane by nonmetallocene imidozirconium $(\text{RNH})_2\text{Zr}=\text{NR}$,²⁵ we naturally infer that it is only the reactivity issue that makes $\text{Cp}_2\text{Zr}=\text{NH}$ inactive in methane C–H activation. Hence, it is relevant to include this reaction of $\text{Cp}_2\text{Zr}=\text{NH}$ with CH_4 in our reaction set as prototype Zr-mediated C–H activation. Our high level reference CCSD(T) values were computed with complete basis set (CBS) limit extrapolation to address the basis set incomplete error (BSIE) issue in valence-only electron correlation, and with the Zr 4s4p outer-core electron-correlation effect included to address the core–valence electron-correlation issue. The density functionals (DFs) employed in our study cover many of the commonly used ones, including PBE0,¹⁵⁹ M06,¹⁶⁰ M06-L,^{160a} M06-2X,¹⁶⁰ TPSS,¹⁶¹ TPSSH,¹⁶¹ B3LYP,¹⁶² B2GP-PLYP,¹⁶³ B2-PLYP,¹⁶⁴ ωB97X ,¹⁶⁵ OLYP,^{162b,166} BMK,¹⁶⁷ BP86,^{162a,168} CAM-B3LYP,¹⁶⁹ and LC- ωPBE .¹⁷⁰ These selected functionals form a wide spectrum of modern DFs. Among them, BP86 and OLYP are pure-GGA, while M06L and TPSS are pure meta-GGA. B3LYP and PBE0 are hybrid GGAs, with different amounts of Hartree–Fock (HF) exchange of 20% and 25%, respectively. TPSSH, M06, BMK, and M06-2X are hybrid meta-GGAs, also with different amounts of HF exchange of 10%, 27%, 42%, and 54%, respectively. CAM-B3LYP, ωB97X , and LC- ωPBE are all long-range corrected functionals. B2GP-PLYP and B2-PLYP are two double hybrid functionals, which contain not only exact HF exchange but also MP2-type perturbative correlation contribution.

■ COMPUTATIONAL DETAILS

All DFT calculations were performed using the Gaussian 09 software package.¹⁷¹ The geometric structures of all minima and transition states of the reactions under study were fully optimized by the PBE0 functional, which had been repeatedly found to generate good geometries for transition metal complexes.^{113,139,143,145,149} In these optimizations, we used cc-pVTZ¹⁷² and cc-pVTZ-PP¹⁷³ basis sets on the main group elements (H, C, N, O, Cl) and 4d transition metal (Zr), respectively. Correspondingly, the Stuttgart new relativistic energy-consistent small-core pseudopotential (PP) ECP28MDF was used throughout in conjunction with the above basis set for Zr to account for the scalar relativistic effect.¹⁷³ Due to nonbonded reactant clusters of the substrates in reactions 1–3 (Scheme 1) with the Schwartz reagent $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$, the reaction barriers for these three reactions were calculated as the difference between transition state energy and sum of the corresponding substrate and $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ (separated reactants) energies. Differently, for reaction 4, CH_4 can be weakly bonded to Zr in $\text{Cp}_2\text{Zr}=\text{NH}$. To be consistent with the other three reactions in this work, and to be comparable also with our previous work on other C–H activation reactions,^{140,141,153} for reaction 4 we took references of both the reactant complex and the separated reactants to gauge the reaction barrier. Vibrational analysis was performed to verify the minima and transition states.

Hereafter, we use the abbreviations DZ/TZ/QZ to represent double/triple/quadruple- ζ quality basis sets used in this work, such as cc-pVDZ/cc-pVTZ/cc-pVQZ. In order to test the convergence of basis sets in DFT calculations, the differences of the reaction barriers at the single point B3LYP level between TZ (cc-pVTZ/cc-pV(T+d)Z/cc-pVTZ-PP for H,C,N,O/Cl/Zr) and QZ (cc-pVQZ/cc-pV(Q+d)Z/cc-pVQZ-PP for H,C,N,O/Cl/Zr) basis sets were computed using the PBE0-optimized geometries. The maximum difference found is up to 0.9 kcal/mol (this largest value is from reaction 3, the values from the other three reactions are less than 0.3 kcal/mol, see Table S1 in the SI for details). Therefore, the QZ rather than the TZ basis set was used in the following single point calculations by various DFs in order to alleviate the basis set incompleteness problem. The DFT empirical dispersion correction DFT-D3 of Grimme et al.¹⁷⁴ was used with zero short-range damping denoted as DFT-D3(0).^{174,175} For the ω B97X functional that is not included in the DFT-D3 approach, the empirical dispersion corrected functional ω B97XD designed by its original developers was used instead.¹⁷⁶

All single-point calculations using coupled cluster methods (CCSD(T) and CCSD(T)-F12) were carried out within the MOLPRO program package.¹⁷⁷ To address the valence shell BSIE issue, the two-point CBS limit extrapolations were performed with valence-only correlated CCSD(T) calculations. In these CCSD(T) two-point CBS limit extrapolations, the DZ-TZ basis set pair (cc-pVXZ/cc-pV(X+d)Z/cc-pVXZ-PP for H, C, N, O/Cl/Zr, X = D, T) were used. The two-point CBS limit extrapolations were done for Hartree–Fock and correlation energies separately. For CBS limit extrapolation of HF energy, we used the formula proposed by Martin and Karton:^{178,179}

$$E_{\text{HF},n} = E_{\text{HF,CBS}} + A \exp(-\alpha\sqrt{n}) \quad (1)$$

For the correlation energy, the equation proposed by Truhlar was used:¹⁸⁰

$$E_{\text{corr},n} = E_{\text{corr,CBS}} + \frac{A}{n^\beta} \quad (2)$$

wherein the available values of parameters α and β are 4.42 and 2.46 for DZ-TZ extrapolation,¹⁸¹ while n is the cardinal number of the basis sets ($n = 2/3$ for DZ/TZ).

To alleviate the potential BSIE problem in Zr 4s4p outer-core electron-correlation calculations, an explicitly correlated coupled cluster approach CCSD(T)-F12 was employed.^{182,183} The CCSD(T)-F12 approach used herein employs the CCSD(T)-F12b method with the diagonal fixed amplitude 3C(FIX) ansatz.^{182,183} There is no direct F12 correction to perturbative triples (T), and the triples energy contribution is not scaled by a factor of MP2-F12/MP2 in all CCSD(T)-F12b calculations.

The 4s4p electron-correlation correction ($\Delta\Delta E_{4s4p}^\ddagger$) was determined by the difference of two CCSD(T)-F12b single point calculations with and without Zr 4s4p electrons correlated, using the same basis set. The basis set used here is different from the DZ basis set used in valence-only CCSD(T) calculations by adopting cc-pwCVDZ-PP for Zr, which is specially designed for core–valence correlation treatment.¹⁷³

In CCSD(T)-F12b calculations, density fitting of the Fock and exchange matrices used the auxiliary basis sets (ABSs) of def2-QZVPP/JKFIT¹⁸⁴ and cc-pVTZ/JKFIT¹⁸⁵ for Zr and the rest atoms, respectively, while density fitting of the other two-

electron integrals employed ABSs of cc-pVTZ/MP2Fit¹⁸⁶ (H,C,N,O), cc-pV(T+d)Z/MP2Fit¹⁸⁶ (Cl), and cc-pwCVTZ-PP/MP2Fit (Zr). As suggested in MOLPRO, the resolution of the identity (RI) approximation with the complementary auxiliary basis set (CABS) approach¹⁸⁷ also employed the same JKFIT ABSs used in density fitting of the Fock and exchange matrices. Consistent with previous computational practices,^{142,188} the value of the geminal Slater exponent in these core–valence correlated CCSD(T)-F12b calculations was chosen to be $1.4 a_0^{-1}$.

Combining our valence-only electron-correlation calculation and Zr 4s4p core–valence electron-correlation calculation, our final reference value of activation energy barrier $\Delta E_{\text{final}}^\ddagger$ is the sum of these two parts, as in the following equation:

$$\Delta E_{\text{final}}^\ddagger = \Delta E_{\text{CBS}}^\ddagger + \Delta\Delta E_{4s4p}^\ddagger \quad (3)$$

where $\Delta E_{\text{CBS}}^\ddagger$ is obtained from the valence-only correlated CCSD(T) after DZ-TZ CBS limit extrapolation by eqs 1 and 2, and $\Delta\Delta E_{4s4p}^\ddagger$ is obtained from CCSD(T)-F12 Zr 4s4p outer-core electron-correlation correction for the activation energy barrier.

RESULTS AND DISCUSSION

The optimized structures of the transition states are depicted in Figure 1, and the activation energies are shown in Table 1. As

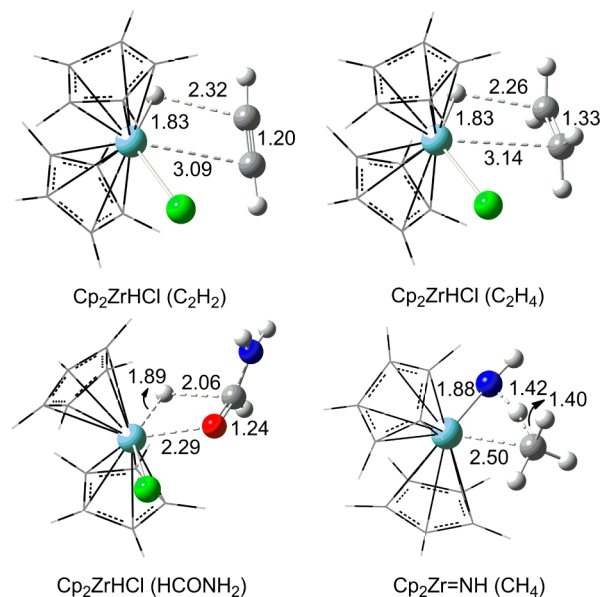


Figure 1. Optimized structures of transition states for the four Zr-mediated reactions in Scheme 1 at the PBE0/TZ level (bond length in Å). Cl ligands are green.

seen from Figure 1, all of the reactions occur through a four-member ring transition state, and the geometries for the three transition states for the reactions of hydrosilylation of ethene, ethyne, and formamide by $\text{Cp}_2\text{Zr}(\text{H})\text{Cl}$ are quite early, having short bond lengths of activated multiple bonds $\text{C}=\text{C}$, $\text{C}\equiv\text{C}$, and $\text{C}=\text{O}$ in substrates. The activation energies change by no more than 2 kcal/mol from DZ to TZ basis set, and CBS limit values are all within 1 kcal/mol from the TZ values, both indicating that the BSIE problem in the target systems is not severe. This weak basis set dependence of the results is similar to those in most of our previous studies,^{139–141} but in sharp contrast to recent findings revealing very strong basis set

Table 1. Activation Energies at the Various CCSD(T) Levels and Zr 4s4p Correlation Corrections for the Four Zr-mediated Reactions in Scheme 1 (in kcal/mol)^a

reaction	$\Delta E_{\text{DZ}}^{\ddagger}$	$\Delta E_{\text{TZ}}^{\ddagger}$	$\Delta E_{\text{CBS}}^{\ddagger}$	$\Delta \Delta E_{4s4p}^{\ddagger}$	$\Delta E_{\text{final}}^{\ddagger}$
1	5.38	4.13	3.12	0.23	3.35
2	6.75	5.10	3.91	0.16	4.07
3	−2.28	−0.45	−0.11	−1.90	−2.01
4	13.93	12.57	11.68	−1.50	10.17
4 ^b	18.48	17.59	17.05	−0.84	16.21

^aUnless otherwise denoted, separated reactants are used as a reference to gauge the reaction barrier for all four reactions. ^bActivation energy is measured with respect to the reactant complex rather than the separated reactants.

dependence in water oxidation reactions both from Baerends' group for Ir catalysis⁴² and from our group for Ru catalysis.¹⁴² The values of 4s4p electron-correlation corrections $\Delta \Delta E_{4s4p}^{\ddagger}$ are positive for hydrozirconation of ethene and ethyne (reactions 1 and 2), and the magnitudes are quite small (<0.3 kcal/mol). Differently, the $\Delta \Delta E_{4s4p}^{\ddagger}$'s of hydrozirconation of formamide and methane C–H activation reaction (reactions 3 and 4) are negative, whose absolute values (up to 1.90 kcal/mol) are relatively larger than those of reactions 1 and 2. The magnitudes of all 4s4p core–valence correlation corrections in this work are generally comparable with our previous core–valence correlation effect calculations in middle (Ru) and late (Ir, Pt) transition metals.^{142,153} Overall, activation energies $\Delta E_{\text{final}}^{\ddagger}$ are lower than about 4 kcal/mol for the three hydrozirconation reactions, which is in line with the fact that these reactions can occur readily at room temperature. For the C–H bond activation in methane by $\text{Cp}_2\text{Zr}=\text{NH}$, the barrier height of 10.17 kcal/mol is significantly higher than hydrozirconation reactions.

With the activation energies $\Delta E_{\text{final}}^{\ddagger}$ obtained from the above coupled cluster calculations serving as a reference, we calibrated various approximate DFT functionals, and the results are summarized in Table 2 and depicted in Figure 2a. As we can see from Table 2 (values in bold), among all tested functionals there are three whose mean unsigned deviations (MUDs) are below 2 kcal/mol. These functionals are three of the Minnesota M06 series. Clearly shown in Figure 2a, the largest MUD over four reactions is produced by OLYP (MUD = 13.29 kcal/mol), due to its extremely poor performance in all the reactions. Thus, its use in Zr-mediated reactions should be avoided without further empirical dispersion correction (discussed later). MUDs of most other functionals lie between 2 and 5 kcal/mol, in the increasing order of B2GP-PLYP < PBE0 <

TPSS < ω B97X < TPSSh < B2-PLYP < BP86 < LC- ω PBE. Apparently, the performance of B2GP-PLYP is better than its parent functional B2-PLYP. The MUD values of PBE0 and B2GP-PLYP are between 2 and 3 kcal/mol, which are similar to their MUD values in reaction barrier calculations involving Rh, Pd, and Ir.¹⁴¹ From the mean signed deviations (MSD) in Figure 2a (blue bar), it can be seen that on average all functionals tend to overestimate the activation energies of the four studied reactions. Together with diverse MSD results in our previous DFT calibration studies for reaction activation barriers of late (Au, Ir, Pt, Rh, Pd) and middle (Fe, Ru) transition metals,^{138,140–142} we can hardly generalize about any trend concerning the barrier underestimation/overestimation behavior of a certain functional, which suggests that this aspect of DFT performance is system- and transition-metal-dependent.

Concerning the C–H activation reaction 4, when separated reactants are employed in barrier measurement, the two functionals having the largest deviations (about 8–12 kcal/mol) are OLYP and B3LYP. Interestingly, when the reactant complex is used as in our previous work,^{140,141} the largest deviation is greatly reduced to 3.46 kcal/mol (coming from M06L). PBE0 was found previously to be one of the best performing functionals for C–H activation barriers by late transition metals Rh, Pd, Ir, and Pt.^{140,141} Despite the fact that PBE0 is not among the best performing functionals for Zr-mediated C–H activation, its absolute value of deviation (2.29 kcal/mol) is still close to the corresponding MUD values (about 1–2 kcal/mol) for Rh, Pd, Ir, and Pt,^{140,141} which represents the stable performance of PBE0. Considering both the separated reactants and reactant complex cases, M06 and M06-2X give the best results (both deviations <2 kcal/mol). The current good performance of the typical “kinetic” functional M06-2X that has a very high ratio of HF exchange (54%) is somewhat surprising, especially considering that it did not perform well for C–H activation reaction barriers involving late transition metals Rh, Pd, Ir, and Pt.¹⁴¹ This interesting difference between early and late transition metals is noteworthy and deserving of future exploration. We also note that as far as the C–H activation reaction is concerned, in the reactant complex case the popular B3LYP functional performs quite well with a deviation of 1.62 kcal/mol, being consistent with its very good performance (MUD of about 1.1–1.2 kcal/mol) for C–H activation by late transition metals Rh, Pd, Ir, and Pt.^{140,141} As will be discussed below, this different performance of B3LYP between the reactant complex and

Table 2. Deviations of DFT-Computed Activation Energies (without Empirical Dispersion Correction) ΔE^{\ddagger} (kcal/mol) from the Reference Coupled Cluster Data $\Delta E_{\text{final}}^{\ddagger}$

barrier ^a	B3LYP	PBE0	BMK	BP86	CAM-B3LYP	M06-L	M06	M06-2X	TPSS	TPSSh	ω B97X	B2GP-PLYP	B2-PLYP	OLYP	LC- ω PBE
$\Delta E^{\ddagger}(1)$	6.54	2.32	4.63	4.05	5.28	−1.10	0.66	−0.18	2.15	2.35	2.17	1.98	3.05	11.53	3.79
$\Delta E^{\ddagger}(2)$	7.65	3.12	5.91	4.97	6.37	−0.72	0.67	0.20	3.12	3.32	3.12	2.43	3.61	12.85	4.69
$\Delta E^{\ddagger}(3)$	8.13	4.03	6.23	6.27	5.52	−0.12	1.50	0.01	3.52	3.61	3.65	2.50	3.85	16.40	5.11
$\Delta E^{\ddagger}(4)$	7.98	1.15	3.85	1.56	5.94	2.93	0.18	0.54	3.70	4.17	3.94	3.58	4.55	12.36	3.33
MSD	7.58	2.66	5.16	4.21	5.78	0.25	0.75	0.14	3.12	3.36	3.22	2.62	3.77	13.29	4.23
MUD ^b	7.58	2.66	5.16	4.21	5.78	1.22	0.75	0.23	3.12	3.36	3.22	2.62	3.77	13.29	4.23
$\Delta E^{\ddagger}(4)^c$	1.62	−2.29	−0.11	−3.01	1.15	3.46	0.46	1.40	−0.43	−0.12	1.94	1.41	1.49	−0.31	−1.16

^aThe labels in parentheses after reaction ΔE^{\ddagger} denote the corresponding reaction labeling number in Scheme 1. ^bMUD values less than 2.0 kcal/mol are shown in bold. ^cActivation energies are calculated as the difference between the transition state energy and the reactant complex energy.

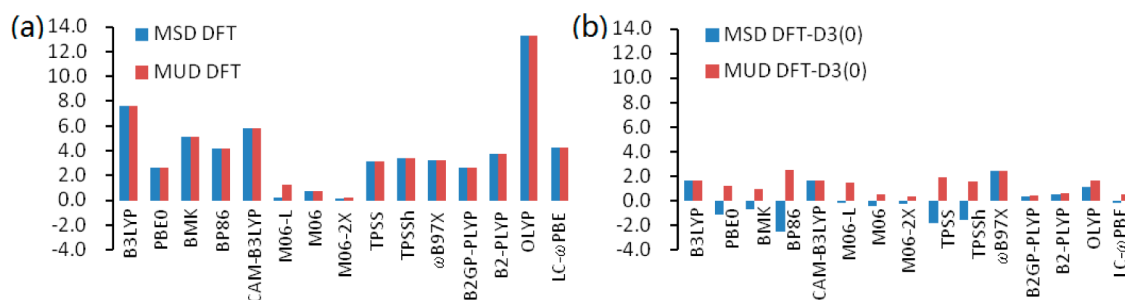


Figure 2. Mean unsigned and signed deviations (in kcal/mol) of calculated activation energies of all reactions through various DFT methods (a) without and (b) with empirical dispersion correction, taking $\Delta E_{\text{final}}^{\ddagger}$ as a reference.

Table 3. Deviations of DFT-Computed Activation Energies (with Empirical Dispersion Correction) ΔE^{\ddagger} (kcal/mol) from the Reference Coupled Cluster Data $\Delta E_{\text{final}}^{\ddagger}$

barrier ^a	B3LYP	PBE0	BMK	BP86	CAM-B3LYP	M06-L	M06	M06-2X	TPSS	TPSSH	ω B97X	B2GP-PLYP	B2-PLYP	OLYP	LC- ω PBE
$\Delta E^{\ddagger}(1)$	1.41	-0.92	-0.48	-1.63	1.66	-1.45	-0.31	-0.48	-2.02	-1.81	2.17	0.03	0.26	0.09	-0.05
$\Delta E^{\ddagger}(2)$	0.78	-1.22	-0.91	-2.71	1.55	-1.22	-0.62	-0.23	-2.55	-2.28	3.12	-0.19	-0.11	-1.07	-0.41
$\Delta E^{\ddagger}(3)$	2.13	0.14	0.57	-0.48	1.31	-0.64	0.15	-0.44	-1.56	-1.38	3.65	0.28	0.65	4.77	0.64
$\Delta E^{\ddagger}(4)$	2.08	-2.55	-1.97	-5.29	1.87	2.56	-0.88	0.23	-1.35	-0.71	0.81	1.37	1.40	0.70	-0.98
MSD	1.60	-1.14	-0.70	-2.53	1.60	-0.19	-0.41	-0.23	-1.87	-1.55	2.44	0.37	0.55	1.12	-0.20
MUD ^b	1.60	1.21	0.98	2.53	1.60	1.47	0.49	0.34	1.87	1.55	2.44	0.47	0.61	1.66	0.52
$\Delta E^{\ddagger}(4)^c$	0.79	-2.74	-1.14	-3.92	0.58	3.48	0.46	1.42	-1.03	-0.73	1.94	1.05	1.01	-1.77	-1.77

^aThe labels in parentheses after reaction ΔE^{\ddagger} denote the corresponding reaction labeling number in Scheme 1. ^bMUD values less than 1.0 kcal/mol are shown in bold. ^cActivation energies are calculated as the difference between the transition state energy and the reactant complex energy.

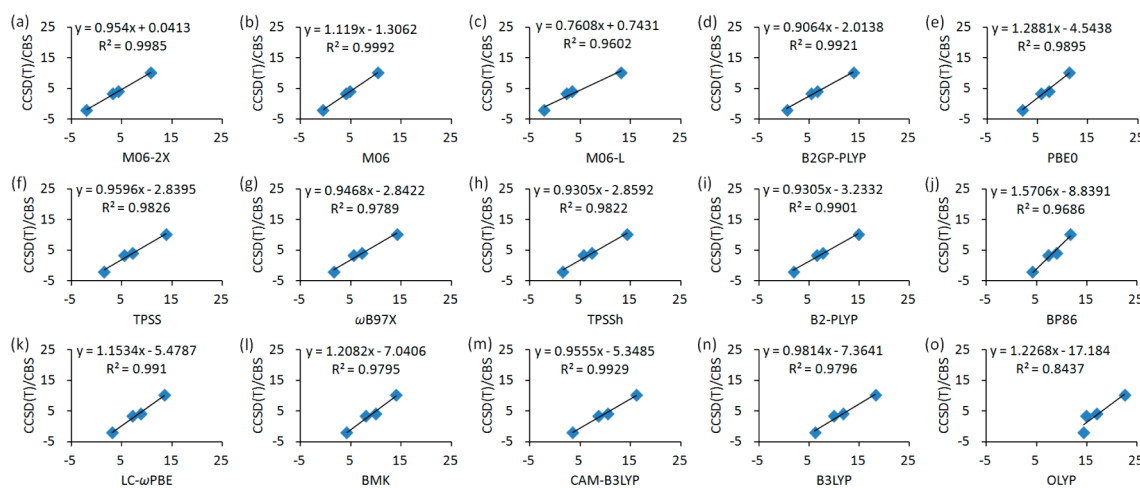


Figure 3. The correlations of the calculated barriers (kcal/mol) for all reactions in Scheme 1 between $\Delta E_{\text{final}}^{\ddagger}$ and various DFT values without DFT dispersion corrections.

separated reactants cases is related to the dispersion interactions.

The results after adding the empirical dispersion corrections are collected in Table 3 and depicted in Figure 2b. As shown in Figure 2b, after taking account of the empirical dispersion correction for DFT, the magnitudes of MUDs decrease to different extents for almost all tested functionals except M06-L and M06-2X, the MUDs of which are slightly increased. Most notable changes are the large improvements of B3LYP and OLYP results after including DFT-D3 correction, by about 6.0 and 11.6 kcal/mol, respectively, which impressively shows the beneficial aspect of DFT dispersion correction. In contrast to the separated reactants cases, when the reactant complex is used in barrier calculation as for reaction 4, the effect of adding dispersion correction is much smaller, even for the above most

affected DFs of B3LYP and OLYP in the separated reactants case. This is because the transition state and reactant complex contain, in principle, a larger fraction of dispersion interactions as compared to their constituting noninteracting subunits. In the reactant complex case, the errors from missing dispersion to the reactant complex and to the transition state largely cancel. While in the separated reactants case, this error canceling is not possible. Hence, the generated barrier from the reactant complex reference is less affected by dispersion. In other words, as mentioned before in this paper, this apparent difference between reactant complex and separated reactants cases concerning B3LYP and OLYP just reflects the fact that these two DFs severely fail to properly account for dispersion interactions. The effect of DFT-D3(0) corrections on the M06 series are quite small (<0.3 kcal/mol) compared with many

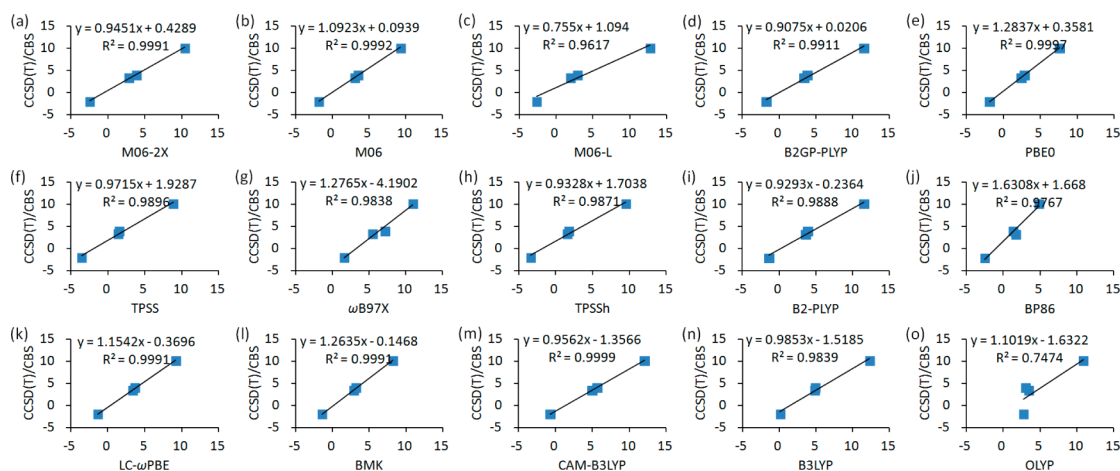


Figure 4. The correlations of the calculated barriers (kcal/mol) for all reactions in Scheme 1 between $\Delta E_{\text{final}}^\ddagger$ and various DFT values with DFT dispersion corrections.

other functionals, which is consistent with the observations in our previous works.^{139–142} This result implies the fact that to a certain extent this M06 series of DFs accounts for dispersion interactions due to the method of its parametrization.¹⁶⁰ Generally for the reactions under study, the magnitudes of MUD changes by empirical dispersion correction are relatively larger than those observed in our previous work,^{139–142} which is not only due to the issue of separated reactants but also in line with the fact that the coordination space is quite compact around the Zr atom by two “clamshell” Cp rings. After adding DFT dispersion correction, the variation of the performance between different functionals becomes apparently smaller, as seen from Figure 2b. With empirical dispersion correction, MUDs of all tested functionals are all less than 3 kcal/mol. Functionals of best performance with a MUD less than 2 kcal/mol are M06-2X < B2GP-PLYP < M06 < LC- ω PBE < B2-PLYP < BMK < PBE0 < M06-L < TPSSH < B3LYP = CAM-B3LYP < OLYP < TPSS (in MUD-increasing order), which can be compared to the corresponding order of functionals before DFT-D3 correction, i.e., M06-2X < M06 < M06-L (MUD less than 2 kcal/mol).

Since barrier height trends from DFT can be more insightful than the barrier height value, it is of great importance to explore the trends of DFT calculated barriers. To investigate this aspect of DFT performance, we separately plotted the barriers from 15 DFTs with the reference coupled cluster data $\Delta E_{\text{final}}^\ddagger$ in Figure 3. We can see that the correlations R^2 for six functionals (M06, M06-2X, B2GP-PLYP, B2-PLYP, LC- ω PBE, and CAM-B3LYP) are very close to 1.0 ($R^2 > 0.99$), and the correlations R^2 for the rest of the functionals are larger than 0.96 except OLYP with $R^2 = 0.84$, indicating that DFT is able to follow the trend in barrier height calculations. The slope of the correlation line can measure the error in relative reaction barriers between different reactions that is useful in quantitatively describing the reactivity difference and trend, while the intercept of the correlation line can measure the systematic barrier underestimation/overestimation by the DFT method. As shown in Figure 3a, the slope and intercept of the correlation line of M06-2X are close to ideal 1.0 (deviation within 0.05 from 1.0) and to ideal zero (deviation within 0.05 kcal/mol from zero), respectively. Both points indicate that the barrier trend is well followed and systematic deviations (underestimation/overestimation) of barriers by this functional are small. In view of

this result as well as performance (MUD) of the barrier height value, without adding dispersion correction, M06-2X is recommended from the above three well-performing functionals of M06 series for reaction barrier calculation of Zr-mediated reactions. Notably, barrier correlation from OLYP is the poorest ($R^2 = 0.84$ from Figure 3o), which is in line with its worst performance in barrier height value calculations. However, when OLYP is greatly improved and is not the worst-performing one in terms of MUD after adding the DFT-D3(0) dispersion correction, as shown in Figure 4, its correlation is still the worst one ($R^2 = 0.75$ from Figure 4o) and becomes even worse than without DFT-D3 correction. These results indicate that OLYP should not be used for Zr-mediated reactions either with or without empirical dispersion correction. As shown in Figure 4, considering the two factors of slope and intercept of the correlation line, M06-2X with DFT-D3 correction is notably the best choice because the slope (0.95) is close to the ideal value of 1.0 and the intercept value (0.43 kcal/mol) is also close to the ideal value of zero. This good performance as well as its good correlation ($R^2 = 0.999$, see Figure 4a) and its MUD being the smallest, as shown in Table 3, all indicate that after DFT-D3 correction, M06-2X is also the most suitable functional to study Zr-mediated reaction barriers. Thus, for dispersion corrected DFTs by DFT-D3, we recommend M06-2X for reaction barrier calculations of Zr-mediated reactions.

CONCLUSIONS

This work calibrates the performance of 15 commonly used DFT methods in the reaction barrier calculations of important Zr-mediated reactions involving zirconocene complexes. Using reference values from coupled cluster calculations at the CCSD(T)/CBS level with the Zr 4s4p core–valence correlation effect included, we find that the best-performing functionals for the barrier height values (<2 kcal/mol) include three functionals of the M06 series. Due to a distinctly large average error of more than 10 kcal/mol before adding DFT-D3 empirical dispersion correction, as well as the bad barrier height trend kept after adding DFT-D3 correction, OLYP should be avoided in this type of application for Zr-mediated reactions. Considering also the performance of the barrier height trend, and without DFT dispersion correction, our recommendation of a functional is M06-2X. Except a slight detrimental effect on

M06-L and M06-2X results, empirical dispersion correction for DFT is found to be beneficial in improving the performance on barrier height values for most functionals, especially for B3LYP and OLYP. After adding DFT dispersion correction, functional variation in performance becomes much smaller, and only two functionals, namely BP86 and ω B97X, have errors larger than 2 kcal/mol, but still smaller than 3 kcal/mol. All these results are encouraging for the use of dispersion correction in zirconocene-mediated reactions. With DFT-D3 dispersion correction, M06-2X is also recommended for reaction barrier calculations of Zr-mediated reactions.

■ ASSOCIATED CONTENT

Supporting Information

Three tables of computational results and Cartesian coordinates of all species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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