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Benchmark Energetic Data in a Model System for Grubbs II Metathesis Catalysis and Their Use for the Development, Assessment, and Validation of Electronic Structure Methods

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Abstract: We present benchmark relative energetics in the catalytic cycle of a model system for Grubbs second-generation olefin metathesis catalysts. The benchmark data were determined by a composite approach based on CCSD(T) calculations, and they were used as a training set to develop a new spin-component-scaled MP2 method optimized for catalysis, which is called SCSC-MP2. The SCSC-MP2 method has improved performance for modeling Grubbs II olefin metathesis catalysts as compared to canonical MP2 or SCS-MP2. We also employed the benchmark data to test 17 WFT methods and 39 density functionals. Among the tested density functionals, M06 is the best performing functional. M06/TZQS gives an MUE of only 1.06 kcal/mol, and it is a much more affordable method than the SCSC-MP2 method or any other correlated WFT methods. The best performing meta-GGA is M06-L, and M06-L/DZQ gives an MUE of 1.77 kcal/mol. PBEh is the best performing hybrid GGA, with an MUE of 3.01 kcal/mol; however, it does not perform well for the larger, real Grubbs II catalyst. B3LYP and many other functionals containing the LYP correlation functional perform poorly, and B3LYP underestimates the stability of stationary points for the *cis*-pathway of the model system by a large margin. From the assessments, we recommend the M06, M06-L, and MPW1B95 functionals for modeling Grubbs II olefin metathesis catalysts. The local M06-L method is especially efficient for calculations on large systems.

1. Introduction

The ground-breaking advances in catalytic olefin metathesis[1−3] have revolutionized organic synthesis and greatly broadened the scope of its applicability to medicine, biology, and materials science as well as promoting green chemistry. As a result of its impact, the Nobel Prize in Chemistry 2005 was awarded to Chauvin,[4] Grubbs,[5] and Schrock[6] "for the development of the metathesis method in organic synthesis".[7] Schrock's Mo-based olefin metathesis catalysts are air sensitive but generally more active than air-stable Grubbs' Ru-based catalysts, and they are complementary in relativities and other properties.[2,8] Grubbs second-generation (Grubbs II) Ru metathesis catalysts[9−16] are a hundred to a thousand times more active than first-generation Ru metathesis catalysts, and they also exhibit greater thermal and chemical stability with significant functional group tolerance.[9−11] The difference between the Grubbs I and II catalysts is the substitution of one of the phosphine ligands, usually tricyclohexylphospine, PCy_3, of the bisphosphine first-generation precatalyst, $(PCy_3)_2Cl_2Ru=CHPh$, by a *N*-heterocyclic carbene (NHC), usually 1,3-dimesityl-4,5-dihydro-2-ylidene, which is abbreviated as H_2IMes.

Together with experimental studies,[1−3,9−16] density functional theory (DFT) has been used in the past decade to model the mechanisms in Grubbs catalysts;[17−32] most of the computational studies employed the BP86 or B3LYP functionals. BP86 was chosen due to its early success in describing metal−carbonyl compounds,[33−35] whereas B3LYP

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Benchmark Energetic Data

J. Chem. Theory Comput., Vol. 5, No. 2, 2009 **325**

Table 1. Basis Sets Employed in the Present Study

| basis sets | Ru | | H | C,N,P,Cl | N^a |
	ECP	valence basis			
DZQ	CEP[b]	CEP[b]	6−31+G(d,p)[c]	6−31+G(d,p)[c]	260
TZQS	CEP[b]	CEP+d3f[b,d]	MG3S[e]	MG3S[e]	522
ATZQ	aug-cc-pVTZ-PP[f]	aug-cc-pVTZ-PP[f]	cc-pVTZ[g]	aug-cc-pVTZ[g]	668
AQZQ	aug-cc-pVQZ-PP[f]	aug-cc-pVQZ-PP[f]	cc-pVQZ[g]	aug-cc-pVQZ[g]	1197
AQZQ+d	aug-cc-pVQZ-PP[f]	aug-cc-pVQZ-PP[f]	cc-pVQZ[g]	aug-cc-pV(Q+d)Z[h]	1212

[a] N is the number of contracted basis functions for **1**, and "valence basis" denotes the basis set used for the 16 electrons of Ru that are treated explicitly. The other 28 electrons (a [Ar]$3d^{10}$ core) of Ru are replaced by a relativistic ECP. [b] Reference 58. [c] Reference 57. [d] References 55 and 56. [e] Reference 59. [f] Reference 62. [g] Reference 61. [h] The aug-cc-pVQZ is used for C and N atoms, and the aug-cc-pV(Q+d)Z basis set[63] is used for P and Cl atoms.

is the most popular DFT method; many users have used B3LYP as a "reliable" black-box computational tool. However, evidence delineating poor performance of popular density functionals in several areas in chemistry has been presented by many research groups.[36−52] Indeed, BP86 and B3LYP are not accurate for the description of Grubbs metathesis catalysis, as shown by Tsipis et al.[23] and us;[30,53] both functionals fail to predict the trend of the phosphine binding energies between the first- and second-generation Grubbs' ruthenium precatalysts for olefin metathesis.[30,31,53] Moreover, Piacenza et al.[31] assessed the performance of five density functionals against benchmark energetic data for $RuCl_2(PH_3)_2CH_2$, a small model system for the first-generation Grubbs catalysts. They found that B3LYP gives the worst performance with a maximum error of 17.8 kcal/mol. Thus, we think that it is now important to scrutinize the strength and limitation of popular and new-generation density functionals for the description of Grubbs olefin metathesis catalysis.

In order to assess the performance of density functionals for olefin metathesis, one needs to use accurate benchmark data. Unfortunately, there are very few experimental data[16] that one can directly compare to. Therefore we generate high-quality data by using the most reliable available levels of wave function theory (WFT). For real catalysts having the size of the Grubbs olefin catalysts, state-of-the-art correlated WFT methods (for example, CCSD(T)[54]) are prohibitively expensive. Alternatively, one can use CCSD(T) on small model systems for the Grubbs olefin metathesis catalysts. One objective of the present study is to use high-level CCSD(T) theory to develop benchmark energetic data for ethene metathesis reactions catalyzed by a model system $[(PH_3)(C_3H_6N_2)Cl_2Ru=CH_2]$ (**1**) that mimics the coordinate covalent bonding in Grubbs second-generation catalysts.

Another goal of our study is to validate a number of low-cost density functional theory (DFT) methods and to determine if there are DFT methods that can describe the energetics of coordinate covalent bonding in Grubbs second-generation olefin metathesis catalysis sufficiently well for practical simulations.

This paper is organized as follows. The computational details and DFT methods are described in Section 2, and results and discussion are in Section 3. Section 4 presents concluding remarks.

2. Computational Methods

2.1. Basis Sets. In the present study we employed five basis sets, and they are listed in Table 1. The DZQ basis set was defined elsewhere;[55,56] it uses the 6−31+G(d,p)[57] basis set for main-group elements and uses the relativistic effective core potential and valence basis set of Stevens et al.[58] for Ru. The TZQS basis set is slightly different from the TZQ basis used in our previous studies;[55,56] TZQS uses the MG3S[59] basis set (for comparison, TZQ uses MG3[59]) for main-group elements and the same basis set for Ru as in the TZQ basis set. The MG3[59,60] and MG3S[59] basis sets are triple-ζ quality basis sets, and they have been defined in previous studies. The ATZQ basis set is also of a triple-ζ quality, and it employs the cc-pVTZ[61] basis for H, the aug-cc-pVTZ[61] basis for C, N, P, and Cl, and the aug-cc-pVTZ-PP[62] relativistic effective core potential and basis set for Ru. The AQZQ basis set is of a quadruple-ζ quality; it employs the cc-pVQZ[61] basis for H, the aug-cc-pVQZ[61] basis for C, N, P and Cl, and the aug-cc-pVQZ-PP[62] relativistic effective core potential and basis set for Ru. The fifth basis set, labeled AQZQ+d, differs from the fourth by the use of aug-cc-pV(Q+d)Z[63] for P and Cl. Note that the MG3S and aug-cc-pV(Q+d) Z basis sets for P and Cl include tight d functions, but the other basis sets used for P and Cl do not.

2.2. Geometries and Energies. The geometries of all stationary points in the catalytic cycle (Figure 1) of the model system $[(PH_3)(C_3H_6N_2)Cl_2Ru=CH2]$ (**1**) were optimized at the M06-L/TZQS level. For the purpose of comparison, we also carried out geometry optimizations at the M06-L/DZQ, M06/TZQS, BP86/TZQS, and B3LYP/TZQS levels.

All energies in the present paper are Born−Oppenheimer electronic energies including nuclear repulsion but not including zero-point vibrational energies or thermal vibrational−rotational energy.

2.3. Benchmark Calculations. Even for the model system $[(PH_3)(C_3H_6N_2)Cl_2Ru=CH_2]$ (**1**), the CCSD(T)/AQZQ level of theory is too computationally demanding. We estimated the CCSD(T)/AQZQ+d relative energies for all stationary points by using a composite approach:

$$E(\text{est. CCSD(T)}/\text{AQZQ}+d) = E(\text{MP2}/\text{AQZQ}+d) + (E(\text{CCSD(T)}/\text{ATZQ}) - E(\text{MP2}/\text{ATZQ})) \quad (1)$$

2.4. Optimization of a Spin-Component-Scaled Second-Order Møller−Plesset Perturbation Theory for Olefin Metathesis. Second-order Møller−Plesset (MP2)[64,65] perturbation theory is the simplest and least expensive first-
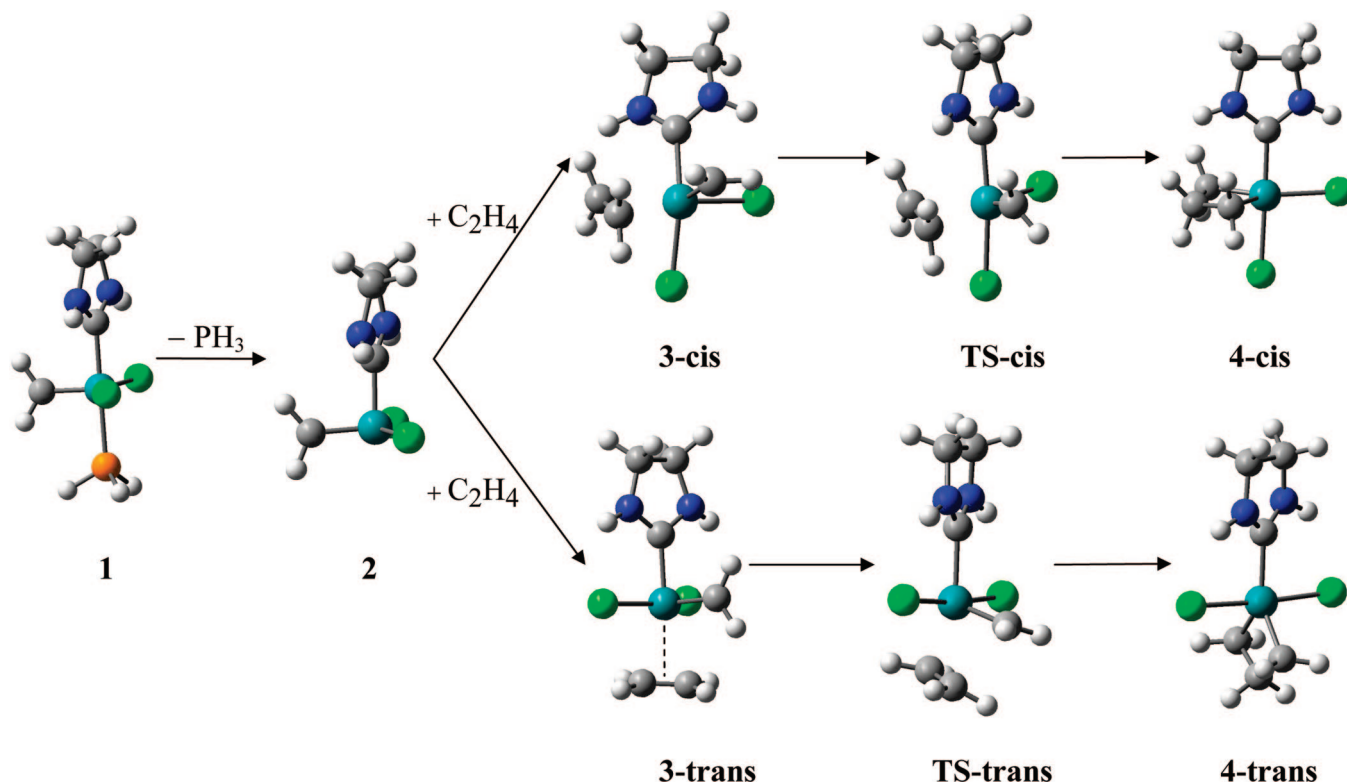
Figure 1. Structures of the stationary points in the catalytic cycle of the model Grubbs II catalyst [(PH₃)(NHC)Cl₂Ru=CH₂] (**1**).

principles WFT method that incorporates dynamical electron correlation in a systematic way. Recently Grimme[66] developed a spin-component-scaled MP2 (SCS-MP2) method by separate scaling of parallel- and antiparallel-spin pair correlation energies, in order to improve the accuracy over standard MP2 theory. (This represents a generalization of the SAC-MP2 method[67] in which both components of the MP2 correlation energy are scaled with the same factor.) The total SCS-MP2 energy can be written as

$$E_{\text{SCS-MP2}} = E_{\text{HF}} + p_S E_S + p_T E_T \qquad (2)$$

where E_{HF} is the Hartree−Fock energy, E_S is the singlet (antiparallel spin) pair correlation energy, and E_T is the triplet (parallel spin) correlation energy. The scaling factors used by Grimme are $p_S = 6/5$ and $p_T = 1/3$. Subsequently Hill and Platts[68] reoptimized these two parameters for weak and stacking interaction energies, and they obtained a method called SCSN-MP2, with $p_S = 0$ and $p_T = 1.76$. More recently Distasio and Head-Gordon[69] optimized p_S and p_T for intermolecular interaction energies with different basis sets, and they named the new methods SCS(MI)-MP2, in which MI stands for molecular interaction. In the present study, we reoptimized p_S and p_T by least-squares fitting to high-level CCSD(T) energetic data in the model Grubbs II metathesis reactions with the AQZQ basis set. We used both the relative energies and absolute total energies in the optimization because we found that the optimization would produce unphysical parameters if the total energies were not included in the training set. Thus the final training set has 10 absolute energies and 7 relative energies. The resulting new parameters are $p_S = 1.363$ and $p_T = 0.568$, and we call the new method SCSC-MP2, which stands for SCS-MP2

optimized for catalysis. The p_S and p_T parameters in SCS(MI)-MP2 or SCSN-MP2 have been optimized against the main-group noncovalent interaction energies, so these parameters are weighted toward the prediction of noncovalent relative energies. The training data for SCSC-MP2 include energetic data for covalent and noncovalent interactions and for transition states involving transition metals. Thus the SCSC-MP2 model chemistry is optimized against a more diverse set of data than SCS(MI)-MP2 or SCSN-MP2, and the optimized values of p_S and p_T look very reasonable in magnitude.

2.5. Tested Methods. We test 17 WFT methods, including HF, MP2, SCS-MP2, SCSC-MP2, SCS(MI)-MP2, SCSN-MP2, CCSD, and CCSD(T) with three basis sets.

We tested 39 density functionals with the M06-L/TZQS geometries. The tested functionals can be classified according to various rungs of "Jacob's ladder"[70] The lowest rung is the local spin density approximation (LSDA), in which the density functional depends only on spin densities, and the second rung is the generalized gradient approximation (GGA, in which the density functional depends on spin densities and their reduced gradient). The third rung is meta-GGA, in which the functional also depends on the spin kinetic energy densities. The fourth rung is hyper GGA,[70] which employs full or partial exact Hartree−Fock (HF) exchange. There are two types of hyper GGAs on the fourth rung, namely the hybrid GGAs (HF + GGA) and hybrid meta-GGAs (HF + meta-GGA). In this work, the tested functionals include 8 GGAs (BLYP,[71,72] BP86,[71,73] G96LYP,[72,74] HCTH,[75] mPWLYP,[72,76] mPWPW,[76] OLYP,[72,77] and PBE[78]), 6 meta-GGAs (BB95,[79] M06-L,[80] mPWB95,[76,79] TPSS,[81,82]

Benchmark Energetic Data

J. Chem. Theory Comput., Vol. 5, No. 2, 2009 **327**

Table 2. WFT Relative Energetics (kcal/mol)[a]

method	cost[b]	1	3-*cis*	3-*trans*	TS-*cis*	TS-*trans*	4-*cis*	4-*trans*	MSE	MUE
best estimate[c]		−25.15	−7.69	−17.64	−7.22	−8.84	−20.39	−19.21		
CCSD(T)/ATZQ	250	−24.91	−9.13	−18.73	−8.78	−10.07	−21.73	−20.27	−1.07	1.14
SCSC-MP2/AQZQ[d]	92	−25.37	−6.80	−16.39	−6.52	−4.87	−23.28	−22.08	0.12	1.83
SCSC-MP2/AQZQ+d[d]	93	−25.55	−6.74	−16.36	−6.45	−4.79	−23.21	−22.00	0.15	1.87
SCSC-MP2/ATZQ[d]	1.5	−25.45	−8.44	−17.65	−8.24	−6.15	−24.78	−23.21	−1.11	1.88
CCSD/ATZQ	113	−22.56	−3.58	−15.50	−4.55	−8.26	−18.73	−18.92	2.01	2.01
SCS-MP2/ATZQ[e]	1.5	−21.79	−1.04	−13.17	−1.99	−3.72	−17.36	−18.24	4.12	4.12
SCS-MP2/AQZQ[e]	92	−21.72	0.41	−12.06	−0.48	−2.56	−16.04	−17.22	5.21	5.21
SCS-MP2/AQZQ+d[e]	93	−21.88	0.47	−12.03	−0.41	−2.48	−15.98	−17.14	5.24	5.24
MP2/AQZQ+d	93	−29.75	−14.51	−21.03	−14.54	−10.09	−31.27	−27.11	−6.02	6.02
MP2/AQZQ	92	−29.54	−14.58	−21.05	−14.62	−10.16	−31.34	−27.18	−6.05	6.05
MP2/ATZQ	1.5	−29.50	−15.95	−22.12	−16.10	−11.31	−32.62	−28.17	−7.09	7.09
SCS(MI)-MP2/AQZQ[f]	92	−32.78	−20.26	−24.44	−21.80	−16.30	−37.45	−30.80	−11.10	11.10
SCSN-MP2/AQZQ[g]	92	−35.49	−25.26	−27.44	−27.20	−20.06	−42.67	−34.07	−15.15	15.15
SCSN-MP2/ATZQ[g]	1.5	−35.18	−25.84	−27.91	−27.94	−20.77	−43.24	−34.60	−15.62	15.62
SCS(MI)-MP2/ATZQ[h]	1.5	−35.74	−27.15	−28.73	−28.65	−20.48	−44.48	−35.51	−16.37	16.37
HF/ATZQ	1.0	−12.67	18.39	−1.31	12.21	−1.25	1.67	−5.06	16.88	16.88
HF/AQZQ	85	−12.80	18.69	−1.06	12.54	−0.83	1.92	−4.71	17.13	17.13

[a] All energies are relative to the 14-electron active catalyst **2**. M06-L/TZQS geometries are used for the calculations involved in this table. [b] The cost for each method is measured by the computer time for a single point energy calculation of **1** divided by the computer time for an HF/AVTZ energy calculation with the *NWChem* program and 512 processors on the MPP2 computer of EMSL. [c] The best estimates for the relative energies are obtained with eq 1. [d] The optimized scaling factors for SCSC-MP2 are $p_S = 1.363$ and $p_T = 0.568$. [e] The scaling factors for SCS-MP2 are $p_S = 1.2$ and $p_T = 1/3$.[66] [f] The scaling factors used for SCS(MI)-MP2/AQZQ are $p_S = 0.31$ and $p_T = 1.46$. Note that these parameters were optimized for the cc-pVQZ basis set.[69] [g] The scaling factors for SCSN-MP2 are $p_S = 0$ and $p_T = 1.76$.[68] [h] The scaling factors used for SCS(MI)-MP2/ATZQ are $p_S = 0.17$ and $p_T = 1.75$. Note that these parameters were optimized for the cc-pVTZ basis set.[69]

VSXC,[83] and τ-HCTH[84]), 13 hybrid GGAs (B3LYP, B97−1,[75] B97−2,[85] B97−3,[86] B98,[87] BHandH,[88] BHandH-LYP,[88] MPW1K,[89] mPW1PW,[76] MPW3LYP,[72,76,90] O3-LYP,[77,91] PBEh,[78] X3LYP[92]), and 12 hybrid meta-GGAs (B1B95,[79] BB1K,[93] BMK, M05,[94] M05−2X,[95] M06,[96] M06−2X,[96] M06-HF,[97] MPW1B95,[90] MPWB1K,[90] TPSSh,[81,82] and τ-HCTHh[84]).

2.6. Software. All DFT calculations were carried out using a locally modified *Gaussian03*[98,99] program, and the MP2, SCS, and CCSD(T) calculations were performed with the *NWChem*[100] program.

2.7. Timings. Although computer timings are only approximate measures of cost because their exact value depends on the computer program, the computer, the computer's load, and other uncontrolled variables, relative timings calculated with the same program on the same number of processors of the same computer for the same system can be useful for approximately gauging the additional effort required for going to a higher level or different level of theory. Therefore, for each method (a method is a model chemistry,[101] that is, a combination of a theory level and a basis set), for structure **1**, we computed the ratio of the computer time for the single-point energy calculation at hand and a single-point energy calculation at the HF/AVTZ level with the same program on the same number of processors of the same computer. The relative timings are included in the tables where they are labeled as "cost". One technical issue that has a significant effect on the timings is that the computer programs we used (see Section 2.6) employ the resolution of the identity[102,103] for nonhybrid DFT but not for MP2. If one employed a program such as TURBOMOLE for the MP2 and SCS-MP2 calculations, their timings would be smaller. In addition to all the above caveats, the user should be aware that the ratios of timings also depend on the size of the molecule (with the slower methods usually scaling less

efficiently with system size than the faster methods). In light of these considerations, a factor of 1.5 or 2 between two such costs is not very significant, but a factor of more can 2 be a very significant consideration in choosing a method.

3. Results and Discussion

3.1. WFT Calculations. Table 2 presents the results for WFT methods. As discussed in Section 2.3, the best estimates in Table 2 are calculated with a composite approach (eq 1). The best estimates in Table 2 employ the AQZQ+d basis set (fifth basis of Table 1) for the MP2 component. We also carried out a full set of calculations (not presented in detail) in which we used the AQZQ basis set (fourth basis set of Table 1) for the MP2 step. Comparing these two composite calculations, the largest difference in the seven numbers in the first row of Table 2 is 0.20 kcal/mol, with a mean unsigned deviation of 0.09 kcal/mol. The benchmark relative energetics are illustrated in Figure 2. Figure 2 shows that the *trans*-bounded π complex (**3-trans**) is energetically more favorable than the *cis*-bounded π complex (**3-cis**), and the energy of **3-trans** is lower than **3-cis** by 10 kcal/mol. Furthermore the transition state for the *cis* pathway (**TS-cis**) is energetically less favorable than the *trans*-pathway by 1.6 kcal. The results for the π complexes and transition states seem to favor the *trans*-pathway. Actually the experimental NMR study of Romero and Piers[14] supports the *trans*-bound Ru-cyclobutane model compound. However, as shown in Figure 2, the energy of the *cis*-Ru-cyclobutane (**4-cis**) is energetically more favorable than the *trans* one (**4-trans**) by about 1.2 kcal/mol. Thus one cannot rule out the *cis*-pathway from the high-level WFT calculations on the small gas-phase model system for Grubbs II olefin metathesis catalysts. Indeed, an experimental paper by Ung et al.[13] supported the *cis*-pathway. From the results in Figure 2, we can say that
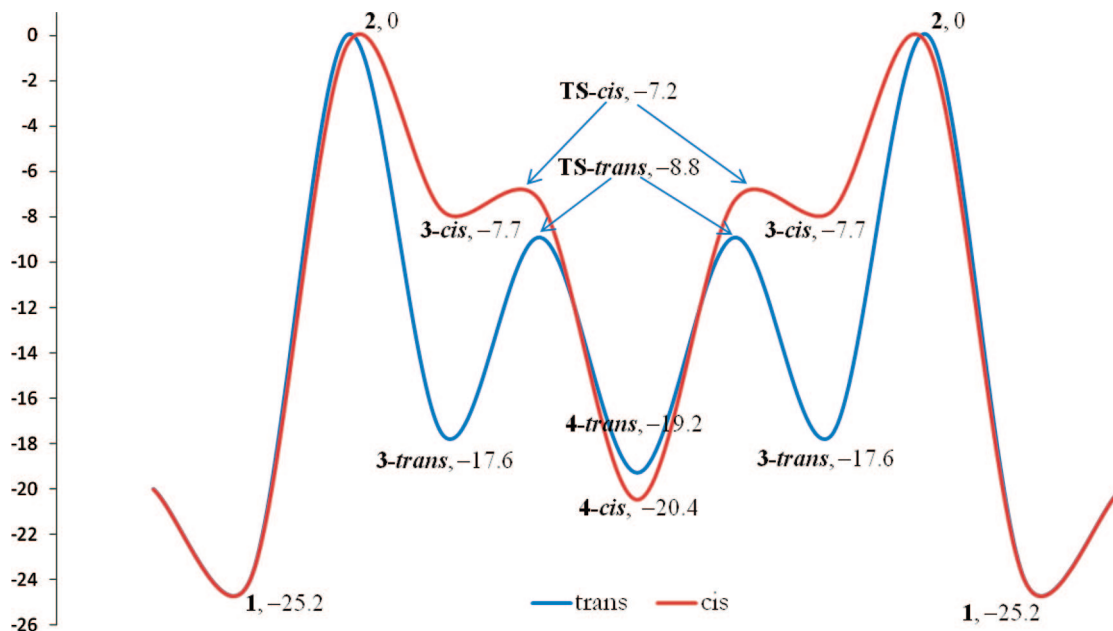
Figure 2. Estimated CCSD(T)/AQZQ potential energy surface (kcal/mol) for the metathesis reaction of the model Grubbs II catalyst $[(PH_3)(NHC)Cl_2Ru=CH_2]$ (**1**).

the *trans*-path way is kinetically more favorable (E(**3-cis**) > E(**3-trans**); E(**TS-cis**) > E(**TS-trans**)) but thermochemically less favorable (E(**4-cis**) < E(**4-trans**)).

We now turn to the performance of the lower-cost WFT methods. The best performing WFT method is CCSD(T)/ATZQ, which gives a small mean unsigned error of 1.05 kcal/mol. However, the computational cost of CCSD(T)/ATZQ is still prohibitively high to be applied to real Grubbs II catalysts. The SCSC-MP2 method optimized in this work gives the second best performance. This is not surprising since we optimized two scaling parameters in SCSC-MP2 against the reference data. A somewhat surprising (but very encouraging) result is that although the two parameters in SCSC-MP2 were optimized with the AQZQ basis set, they work equally well for the ATZQ basis set.

Table 2 also shows that CCSD/ATZQ is slightly worse than SCSC-MP2, but it performs much better than SCS-MP2. Comparing the results of canonical MP2 to those of SCS-MP2, we found that standard MP2 overestimates the stability of all intermediate stationary points on the potential energy surface (PES), whereas SCS-MP2 overcorrects the MP2 method and it underestimates them. The MUE of SCS-MP2 is smaller than that for the canonical MP2 method. Perhaps because the SCS(MI)-MP2 and SCSN-MP2 methods have been optimized only for noncovalent interactions, both methods overestimate the stabilities of all stationary points much more severely than the standard MP2.

3.2. DFT Calculations. Table 3 presents the results for DFT methods. Table 3 also includes an *X* column for the percentage of Hartree−Fock (HF) exchange in each functional and a rung column that assigns each functional to a rung of Jacob's ladder. The best performer in Table 3 is M06, which gives an MUE of 1.18 kcal/mol, surprisingly comparable to the performance of CCSD(T)/ATZQ (MUE = 1.14 kcal/mol). Note that M06 is a much more affordable method than CCSD(T) or MP2.

The second best method is MPW1B95, which is available in all versions of the *Gaussian 03* program. The best performing hybrid GGA is PBEh, which performs very well for this data set, although previous tests[81] have shown PBEh performs worse than B3LYP for main-group thermochemistry. The M06-L local functional, which does not have HF exchange, performs almost as well as PBEh. This is encouraging, since local functionals are well suited for calculations on large molecules where more efficient algorithms[102,104−111] can be employed in the absence of Hartree−Fock exchange. Indeed, with the resolution-of-identity algorithm, the M06-L/AQZQ calculation on the precatalysts $[(PH_3)(C_3H_6N_2)Cl_2Ru=CH_2]$ (**1**) is 48 times faster than M06/AQZQ on the same molecule with 4 cores on an IBM BladeCenter Linux cluster.

Our previous tests[55,56,95,96] have shown that high-Hartree−Fock functionals sometimes perform poorly for transition-metal compounds, because the small unsaturated transition-metal species used as test cases often have large near-degeneracy correlation effects. However, for the systems in the present study, the high-HF functionals, such as MPWB1K, BB1K, M06-HF, M05−2X, MPW1K, and M06−2X perform quite well for modeling the model Grubbs II catalyst; they have an MUE less than 4 kcal/mol. This is probably due to the fact that near-degeneracy correlation effects are not dominant in any of the species in the present study. Nevertheless, we originally recommended[96] using M06 or M06-L rather than M06-HF or M06−2X for systems containing transition metals, and the results in Table 3 confirm that that was a good recommendation.

As can be seen from Table 3, the best performing GGA is PBE, and the MUE of PBE is 2.5 kcal/mol smaller than that of BP86.

Another surprising result in Table 3 is that the LYP correlation functional is problematic for describing the relative energetics in the model Grubbs II olefin metathesis

Benchmark Energetic Data

J. Chem. Theory Comput., Vol. 5, No. 2, 2009 **329**

Table 3. DFT Relative Energetics (kcal/mol)[a]

method	X	rung[b]	cost[c]	1	3-*cis*	3-*trans*	TS-*cis*	TS-*trans*	4-*cis*	4-*trans*	MSE	MUE
best estimate[d]				−25.15	−7.69	−17.64	−7.22	−8.84	−20.39	−19.21		
M06	27	4 (HM)	0.27	−22.58	−5.76	−16.62	−6.17	−8.65	−19.82	−20.17	0.91	1.18
MPW1B95	31	4 (HM)	0.27	−20.93	−3.12	−14.16	−4.81	−9.68	−20.64	−21.64	1.60	2.60
PBEh	25	4 (HG)	0.24	−21.08	−2.42	−12.93	−3.73	−7.83	−19.39	−20.70	2.58	3.01
M06-L	0	3	0.12	−19.68	−4.84	−14.66	−4.36	−5.18	−18.87	−17.49	3.01	3.01
MPWB1K	44	4 (HM)	0.27	−21.77	−2.71	−14.82	−5.63	−11.90	−22.57	−24.09	0.38	3.27
BB1K	42	4 (HM)	0.27	−20.56	−1.35	−13.37	−4.10	−10.20	−20.79	−22.32	1.92	3.31
M06-HF	100	4 (HM)	0.27	−24.68	−2.61	−18.60	−7.59	−19.61	−19.81	−25.60	−1.77	3.52
M05−2X	56	4 (HM)	0.27	−21.48	−1.30	−15.83	−4.15	−12.74	−17.79	−22.50	1.48	3.53
B1B95	28	4 (HM)	0.27	−19.42	−1.50	−12.39	−2.92	−7.51	−18.36	−19.32	3.53	3.56
MPW1K	42	4 (HG)	0.24	−21.13	0.06	−12.26	−2.92	−9.18	−19.31	−21.71	2.81	3.62
TPSSh	10	4 (HM)	0.27	−20.77	−3.11	−12.86	−3.34	−6.77	−15.86	−16.71	3.82	3.82
PBE	0	2	0.10	−20.12	−4.30	−12.75	−3.28	−4.52	−16.51	−16.40	4.04	4.04
mPWB95	0	3	0.12	−19.24	−4.76	−13.20	−3.58	−4.83	−16.21	−15.51	4.12	4.12
M06−2X	54	4 (HM)	0.27	−18.34	0.90	−13.78	−1.88	−8.89	−16.92	−20.63	3.80	4.22
TPSS	0	3	0.12	−20.53	−3.98	−12.92	−3.30	−5.62	−14.71	−14.97	4.30	4.30
mPW1PW91	25	4 (HG)	0.24	−20.05	−0.62	−11.51	−1.90	−6.27	−16.80	−18.45	4.36	4.36
BMK	42	4 (HM)	0.27	−20.02	0.64	−13.12	−6.83	−14.25	−24.87	−29.15	−0.21	5.46
VSXC	0	3	0.12	−25.06	−15.09	−25.79	−14.16	−15.03	−26.30	−23.53	−5.55	5.57
τ-HCTHh	15	4 (HM)	0.27	−19.47	−0.13	−11.11	−0.84	−5.10	−13.59	−15.67	5.75	5.75
B97−1	21	4 (HG)	0.24	−19.01	0.85	−10.66	−0.36	−5.16	−13.32	−15.75	6.10	6.10
mPWPW	0	2	0.10	−18.80	−2.09	−10.94	−1.04	−2.54	−13.41	−13.66	6.24	6.24
BB95	0	3	0.12	−17.44	−2.38	−10.96	−1.22	−2.52	−13.69	−13.12	6.40	6.40
M05	28	4 (HM)	0.27	−15.88	1.90	−8.91	0.87	−2.98	−16.52	−18.37	6.61	6.61
BP86	0	2	0.10	−18.49	−1.79	−10.77	−0.77	−2.39	−12.65	−12.98	6.61	6.61
B98	21.98	4 (HG)	0.24	−18.40	2.01	−9.82	0.75	−4.31	−11.63	−14.28	7.21	7.21
BHandH	50	4 (HG)	0.24	−29.24	−10.92	−22.57	−14.48	−20.64	−33.12	−34.42	−8.46	8.46
BHandHLYP	50	4 (HG)	0.24	−18.22	6.59	−8.70	3.43	−5.31	−9.02	−13.83	8.73	8.73
B97−2	21	4 (HG)	0.24	−16.68	4.00	−7.44	3.14	−1.31	−10.64	−12.87	9.19	9.19
MPW3LYP	20	4 (HG)	0.24	−17.63	3.52	−8.92	3.17	−2.11	−7.58	−10.80	9.40	9.40
X3LYP	21.8	4 (HG)	0.24	−17.26	4.15	−8.44	3.61	−1.86	−7.30	−10.61	9.77	9.77
B97−3	26.93	5 (HG)	0.24	−15.86	5.35	−6.82	3.91	−1.04	−9.70	−12.44	9.93	9.93
B3LYP	20	4 (HG)	0.24	−16.33	5.23	−7.31	4.85	−0.46	−5.78	−9.09	11.04	11.04
mPWLYP	0	2	0.10	−15.75	3.40	−7.56	4.98	1.82	−3.10	−5.41	12.08	12.08
τ-HCTH	0	3	0.12	−14.72	4.43	−5.76	5.53	2.97	−5.71	−7.18	12.24	12.24
BLYP	0	2	0.10	−13.97	5.74	−5.36	7.28	4.09	−0.63	−3.07	14.32	14.32
O3LYP	11.61	4 (HG)	0.24	−11.11	9.42	−1.10	9.43	6.14	−4.39	−6.34	15.46	15.46
HCTH	0	2	0.10	−11.53	8.53	−1.59	9.95	7.77	−3.24	−4.95	15.87	15.87
G96LYP	0	2	0.10	−11.91	8.13	−2.71	9.42	6.52	0.78	−1.37	16.43	16.43
OLYP	0	2	0.10	−8.95	10.56	1.13	11.60	9.75	−1.51	−2.73	18.00	18.00

[a] All energies are relative to the 14-electron active catalyst **2**. The structures of all stationary points are shown in Figure 2. M06-L/TZQS geometries are used for the calculations involved in this table, and the basis set used for the single-point energies is TZQS. [b] GGAs are rung 2, meta functionals that contains spin kinetic energy density are rung 3, hybrid GGAs and hybrid meta functionals are rung 4. On rung 4, hybrid meta GGAs are denoted 4 (HM), and hybrid GGA are denoted 4 (HG). [c] The cost for each method is measured by the computer time for a single point energy calculation of **1** divided by the computer time for an HF/AVTZ energy calculation with the *Gaussian03* program and 4 cores on a IBM BladeCenter Linux cluster. [d] Taken from Table 2.

catalysts; all functionals containing LYP perform poorly. B3LYP gives an MUE of 11.04 kcal/mol, and it underestimates the stability of the stationary points for the *cis*-pathway by a large margin. A similar failure of the LYP correlation functional for Ag clusters has also been reported by Zhao et al.[112]

It is interesting to note that whereas the M06 functional is a many-parameters functional,[96] the MPW1B95 and PBEh functionals were each obtained[78,90] by starting with the exchange and correlation component of previously existing functionals[76,78,79] and combining them with only one new parameter. Although the PBEh functional performs well for the model system, it performs poorly for the real Grubbs catalyst considered in Section 3.4. Therefore it will not be highly recommended for further use in studies of olefin metathesis catalysis.

It is especially striking to compare the cost columns of Tables 2 and 3. Excluding the cost of HF/ATZQ, the costs in Table 3 are a factor of 6−15 times lower than the smallest

cost value in Table 2 and 930−2500 times smaller than the largest cost value in Table 2. This makes the good performance of M06, MPW1B95, and M06-L particularly striking.

3.3. Effect of Geometries and Basis Sets. In previous sections, we based our discussions on single-point energies calculated with the M06-L/TZQS geometries and the TZQS basis set. In this section we compare results with the geometries optimized at the M06-L/DZQ, M06/TZQS, BP86/TZQS, and B3LYP/TZQS levels of theories. We also examine the sensitivity to the size of basis set. The results are shown in Table 4.

As shown in Table 4, M06/TZQS//opt gives a MUE of 1.06 kcal/mol, which is comparable to the CCSD(T)/ATZQ//M06-L/TZQS level. M06/TZQS//M06-L/DZQ gives a slightly smaller MUE than M06/TZQS//M06-L/TZQS, and this is also encouraging because M06-L/DZQ is a much faster method for optimization than the M06-L/TZQS method. Another encouraging result is that M06-L/DZQ gives an MUE of 1.75 kcal/mol, which is smaller than the MUE of

Table 4. Effects of Geometries and Basis Sets

method	cost[b]	1	3-*cis*	3-*trans*	TS-*cis*	TS-*trans*	4-*cis*	4-*trans*	MSE	MUE
best estimate[a]		−25.15	−7.69	−17.64	−7.22	−8.84	−20.39	−19.21		
M06/TZQS// opt[c]	0.27	−22.59	−6.25	−16.69	−6.20	−8.85	−19.91	−20.15	0.78	1.06
M06/TZQS//M06−L/DZQ	0.27	−22.46	−5.85	−16.63	−6.26	−9.01	−19.99	−20.33	0.80	1.17
M06/TZQS// M06-L/TZQS	0.27	−22.58	−5.76	−16.62	−6.17	−8.65	−19.82	−20.17	0.91	1.18
M06-L/DZQ//opt[c]	0.03	−20.61	−5.98	−16.44	−5.16	−7.99	−18.60	−19.15	1.75	1.75
M06−L/AQZQ//M06-L/TZQS[d]	0.30	−19.11	−4.45	−13.44	−4.44	−5.97	−19.43	−18.88	2.92	2.92
M06-L/TZQS//M06-L/TZQS	0.12	−19.68	−4.84	−14.66	−4.36	−5.18	−18.87	−17.49	3.01	3.01
BP86/TZQS//opt[c]	0.10	−18.42	−1.73	−12.25	−0.74	−2.30	−12.84	−13.20	6.38	6.38
BP86/AQZQ//BP86/TZQS[d]	0.18	−17.55	−1.33	−10.72	−0.65	−2.65	−13.43	−14.21	6.51	6.51
BP86/TZQS//M06-L/TZQS	0.10	−18.49	−1.79	−10.77	−0.77	−2.39	−12.65	−12.98	6.61	6.61
B3LYP/TZQS//opt[c]	0.24	−16.20	4.71	−7.50	4.51	−1.07	−6.20	−9.19	10.74	10.74
B3LYP/TZQS//M06-L/TZQS	0.24	−16.33	5.23	−7.31	4.85	−0.46	−5.78	−9.09	11.04	11.04

[a] Taken from Table 2. [b] The cost for each method is measured by the computer time for a single point energy calculation of **1** divided by the computer time for an HF/AVTZ energy calculation with the *Gaussian03* program and 4 cores on a IBM BladeCenter Linux cluster. [c] //opt denotes a consistently optimized geometry. [d] The calculations with the AQZQ basis set employ the resolution of identity (or density fitting) algorithm.

Table 5. Phosphine Dissociation Energies (kcal/mol) in the Real Grubbs II Catalyst
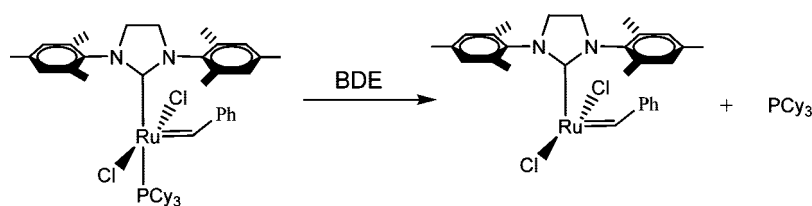
	Expt: BDE = 40.2 kcal/mol[a]	
	noCp[b]	Cp[b]
M06	42.84	40.29
M06-L	41.80	39.40
MPW1B95	32.13	30.38
PBEh	25.11	23.20
PBE	20.49	18.64
TPSS	17.80	15.93
BP86	14.49	12.69
B3LYP	12.59	10.84

[a] Obtained from the experimental[16] collision-induced dissociation energy (36.9 kcal/mol) and the scaled vibrational zero-point-energy correction and thermal vibrational−rotational energy at the M06-L/MIDI! level (scale factor = 0.982, which is determined by an approach described in ref 96). [b] noCP denotes the results that are calculated without counterpoise (Cp) correction for basis set superposition error, whereas Cp denotes counterpoise corrected results. All DFT calculations in this table employ the TZQS basis set and M06-L/DZQ geometries.

the WFT-based SCSC-MP2 method. Note that this good performance might due in part to the cancelation of errors, because M06-L/AQZQ//M06-L/TZQS gives an MUE of 2.94 kcal/mol, just slightly better than the M06-L/TZQS method.

For B3LYP and BP86, the difference in MUEs is small (<0.5 kcal/mol) between the calculations with consistently optimized geometries and the calculations with the M06-L/TZQS geometries.

3.4. Extension to Real Catalysts. Although the model catalyst studied here provides a useful model for coordinate covalent bonding in Grubbs II catalysts, it does not include the bulky and polarizable substituents of real Grubbs catalysts. Therefore we also carried out some single point calculations for the analog of the **1** → **2** step in a real Grubbs II catalyst. The best estimate was made by removing zero-point vibrational energy and thermal vibrational rotational energy from the experimental value of Torker et al.[16] As shown in Table 5, only M06-L and M06 give good performance for the phosphine dissociation energy in the real

Grubbs II catalyst. The counterpoise corrected M06 gives an error of 0.1 kcal/mol, and M06-L gives an error of −0.8 kcal/mol. All other functionals give much larger errors (>8 kcal/mol). Strikingly, the popular BP86 and B3LYP functionals give errors larger than 25 kcal/mol; therefore, they are not reliable for the studies of mechanisms in the Grubbs catalysts.

The fact that functionals like PBEh, PBE, TPSS, BP86, and B3LYP become worse for large molecules is not completely surprising since several previous studies[36−38,42−44,47−49] have shown a deterioration in performance of several density functionals for large molecules; the M06 family of functionals has been shown though not to suffer from this problem of deteriorating for larger-size molecules.[30,53,113−115]

4. Concluding Remarks

In the present study, we developed a benchmark data set for relative energetics in the catalytic cycle of a model system

Benchmark Energetic Data

J. Chem. Theory Comput., Vol. 5, No. 2, 2009 **331**

for Grubbs second-generation olefin metathesis catalysts. The benchmark data were determined by a composite approach, and they are of CCSD(T)/QZ quality. The benchmark data were used as a training set to develop a new SCSC-MP2 method designed for catalysis. We employed the benchmark data and experimental data on a real Grubbs catalyst to test 17 WFT methods and 39 density functionals. We found the following:

1) The SCSC-MP2 method has improved performance for modeling Grubbs II olefin metathesis model catalysts as compared to canonical MP2 or SCS-MP2.

2) Among the tested density functionals, M06 is the best performing functional. M06/TZQS//M06-L/DZQ gives an MUE of only 1.15 kcal/mol for the benchmark data on model compounds and 0.1−0.6 kcal/mol for the phospine dissociation energy in the real Grubbs catalyst, and it is a much more affordable method than the SCSC-MP2 method or any other correlated WFT method.

3) The best performing meta-GGA is M06-L; M06-L/DZQ gives an MUE of only 1.77 kcal/mol for the benchmark data on model compounds and 0.8−1.6 kcal/mol for the real Grubbs catalyst.

4) PBEh is the best performing hybrid GGA, with an MUE of 3.01 kcal/mol for the benchmark data on model compounds, but this error increases to 16−18 kcal/mol for the real Grubbs catalyst.

5) B3LYP and BP86 are not accurate for modeling Grubbs II olefin metathesis catalysts; BP86 perform relatively better than B3LYP. B3LYP underestimates the stability of the *cis*-pathway by a large margin and has an error of 28−29 kcal/mol for the real Grubbs catalyst.

From the assessments, we recommend the M06 and M06-L functionals for modeling Grubbs II olefin metathesis catalysts. The local M06-L method is especially efficient for calculations on large systems. BP86, B3LYP, and eight other functionals containing the LYP correlation functional should be avoided.

We have shown that M06-class functionals also give a good performance for describing interactions in zeolite model complexes[115] and adsorptions of CO on the Mg(001) surface[116] as well as performing well here. Thus the M06 functional suite has been shown to be broadly used for modeling catalysis.

Supporting Information Available: Cartesian coordinates for all molecular systems. This material is available free of charge via the Internet at http://pubs.acs.org.

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