

# How Accurate Can a Local Coupled Cluster Approach Be in Computing the Activation Energies of Late-Transition-Metal-Catalyzed Reactions with Au, Pt, and Ir?

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## Supporting Information

**ABSTRACT:** To improve the accuracy of local coupled cluster (LCC) methods in computing activation energies, we propose herein a new computational scheme. Its applications to various types of late-transition-metal-catalyzed reactions involving Au, Pt, and Ir indicate that the new corrective approach for LCC methods can downsize the mean unsigned deviation and maximum deviation, from the CCSD(T)/CBS reference, to about 0.3 and 0.9 kcal/mol. Using this method, we also calibrated the performance of popular density functionals, with respect to the same test set of reactions. It is concluded that the best functional is the general-purpose double hybrid functional B2GP-PLYP. Other well-performing functionals include the “kinetic” functionals M06-2X and BMK, which have a large percentage of HF exchange, and general-purpose functionals like PBE0 and wB97X. Comparatively, general-purpose functionals like PBE0 and TPSSH perform much better than the tested “kinetic” functionals for Pt-/Ir-catalyzed reactions, while the opposite is true for Au-catalyzed reactions. In contrast, wB97X performs more uniformly in these two classes of reactions. These findings hint that even within the scope of late transition metals, different types of reactions may require different types of optimal DFT methods. Empirical dispersion correction of DFT was found to have a small or no effect on the studied reactions barriers.

## I. INTRODUCTIONS

Homogeneous transition metal (TM) catalysis is central to organometallic chemistry.<sup>1</sup> Among the TMs used for catalysis, the late TMs play important roles in many types of reactions. For instance, Pt and Ir catalysts are frequently employed in C–H activation, which is an important goal in current organic chemistry;<sup>2</sup> gold catalysis, often proceeding under mild conditions with both high yields and chemoselectivities, has become very promising in the field of organic transformations starting from the unsaturated C–C bonds.<sup>3</sup> Correspondingly, density functional theory (DFT) has enabled chemists to reveal reaction mechanisms and to calculate the kinetic parameters by locating the critical points along the reaction pathway, such as minima and transition states. These DFT methods are widely applied in theoretical studies and have often turned out to be complementary to the related experimental work.<sup>4</sup> The quantitative aspect of such theoretical studies concerns mainly the barrier heights of elementary steps for the reactions. However, our current knowledge of the accuracy of calculated barrier heights coming from approximate density functionals for TM-catalyzed reactions is still very limited. Often, the biggest obstacle to clearing up the doubts is the lack of accurate barrier height data for reactions under study. High level ab initio wave function theory (WFT) computations such as coupled cluster (CC) methods<sup>5</sup> have been shown to be capable of achieving high accuracy for closed-shell TM systems.<sup>6</sup> However, their applications are restricted to relatively small systems due to

their high scaling of computational cost with system size. For example, CCSD(T) (the coupled cluster method with single and double excitations and a perturbative treatment of triple excitations),<sup>7</sup> which has been taken as a “gold standard” in modern quantum chemistry calculation for closed-shell systems devoid of severe multiconfigurational character, scales as the seventh-order of the molecular size.

Considerable efforts had been made to reduce the high computational scaling of ab initio WFT methods. There are two main approaches toward this end. One is of the divide-and-conquer type,<sup>8</sup> which is characterized by fragmentation of the system to smaller subsystems; the other one is of the local approximation type, which exploits the overriding local character of electron correlation by using localized molecular orbitals (MOs).<sup>9–11</sup> The former approach is suitable for systems that can be easily fragmented, like main-group systems without extensive conjugation, such as polypeptides and proteins. TM-containing systems are not ideal objects for this approach because it is often not obvious to divide the systems due to very complex interaction between TM and the rest of the system. On the contrary, a local correlation approach can naturally be a practical method in TM-containing systems by employing the localized MOs. Local coupled cluster (LCC) approaches like LCCSD and LCCSD(T) had been developed

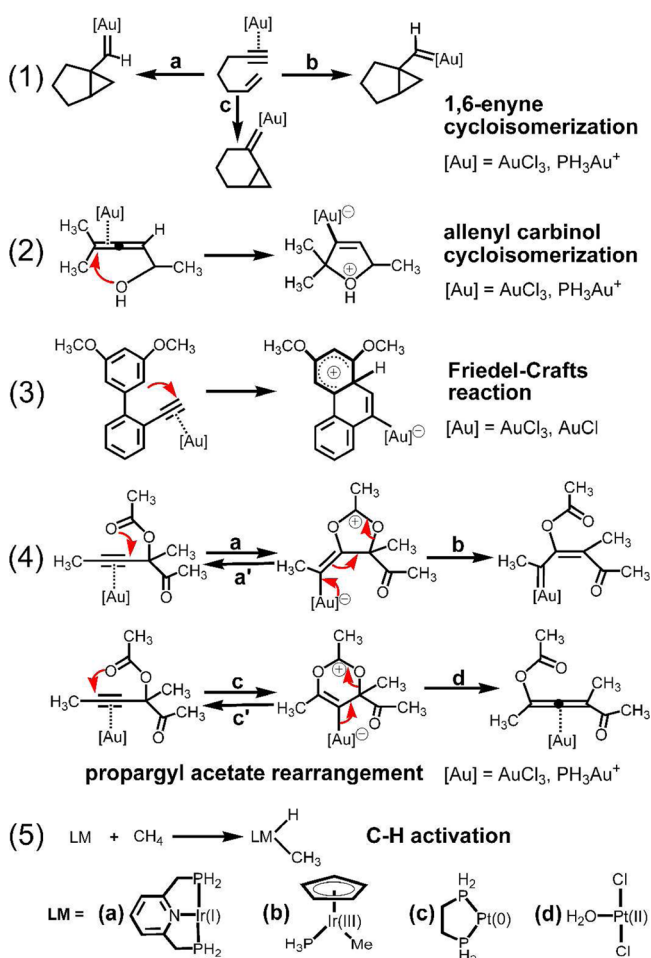
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and made available in popular quantum chemistry software for over a decade,<sup>11</sup> but they are not as widely used as the canonical coupled cluster methods like CCSD(T),<sup>12</sup> perhaps due to the lack of extensive performance verification. Hence, clarifying and improving the accuracy of the LCC approach during activation energy calculations are of essential importance. In this work, we propose a new computational scheme to improve the accuracy of LCC methods in barrier height computations. The performance of the new approach is tested for many late-TM-catalyzed reactions, including four typical gold catalysis involving C–C and C–heteroatom bonds' formation/breakage,<sup>13</sup> and prototype reactions of Pt- and Ir-catalyzed C–H activation,<sup>14</sup> whose wide range is seen in Scheme 1. We hope that this new scheme for improving the

**Scheme 1. Various TM-Catalyzed Reactions Calculated in This Work**



accuracy of the LCC methods can widen the applicability of LCC methods and stimulate more high-level WFT treatments in computational TM catalysis, for which the corresponding canonical CC calculations are often prohibitively costly except in small model systems.

As is typical in WFT methods, LCC methods exhibit significant basis set incompleteness errors (BSIE). Therefore, if accurate results ( $\pm 1$  kcal/mol) are sought, the BSIE should be alleviated by usage of a hierarchy of basis sets, built systematically with an improving degree of completeness, like correlation consistent basis sets, with subsequent extrapolation

to the complete basis set (CBS) limit.<sup>15</sup> An alternative new way to improve the basis set convergence, and thereby reduce the BSIE, is the usage of explicitly correlated methods.<sup>16</sup>

Another source of error, in those LCC methods that are based on local correlation domains, is called domain error. This error originates from the local approximation. The domain of a localized MO is a set of atoms on which the localized MO is mainly spanned. There are two approximations in LCC: first, the excitations from one localized MO are restricted to a virtual subspace associated with the corresponding domain, and second, on the basis of certain criteria, the pairs of localized MOs, which are involved in more than single excitations, can be classified as several types that are treated at different levels such as CCSD or MP2. These two local approximations lead to significant savings of computational costs and can even achieve linear scaling for LCC methods. At the same time, these approximations also introduce domain errors that are not present in canonical CC methods. In principle, domain extension finally will converge the LCC method to a canonical one, but the computational cost along this line increases with the fourth power of domain size and becomes prohibitively expensive quite soon during the domain extension. As such, one has to choose the appropriate domains to balance the cost and the accuracy. The combined BSIE and domain error is the main source of deviation of LCCSD(T) results from the corresponding canonical CCSD(T)/CBS results. Any systematic improvement for LCC accuracy has to take both these two sources of error into account.

## II. METHODS

Our proposed scheme for improving LCC accuracy consists of correcting the LCC/DZ energy  $E_{\text{LCC/DZ}}$  (DZ/TZ represent double/triple- $\zeta$  quality basis set such as cc-pVDZ/cc-pVTZ)<sup>6d,e,17</sup> by adding a correction  $\Delta E = E - E_{\text{LCC/DZ}}$ , which contains both domain error (from DZ calculations) and BSIE ( $\Delta E_{\text{CBS}}$ , from DZ-TZ extrapolation) corrections. We propose the following two ways of computing the correction  $\Delta E$ :

$$\begin{aligned} \Delta E(\text{LCC} - \text{LCC}) \\ = (E_{\text{CC/DZ}} - E_{\text{LCC/DZ}}) + \Delta E_{\text{CBS-LCC}} \end{aligned} \quad (1)$$

$$\begin{aligned} \Delta E(\text{LMP2} - \text{LCC}) \\ = (E_{\text{MP2/DZ}} - E_{\text{LMP2/DZ}}) + \Delta E_{\text{CBS-LCC}} \end{aligned} \quad (2)$$

Equation 1 treats domain error at the LCC level ( $E_{\text{CC/DZ}} - E_{\text{LCC/DZ}}$ ). Because the domain errors are considered to be very similar at the LMP2 and LCCSD levels,<sup>18</sup> in our proposed alternative scheme of eq 2, it is treated at the LMP2 level ( $E_{\text{MP2/DZ}} - E_{\text{LMP2/DZ}}$ ). Both eq 1 and eq 2 treat BSIE at the LCC level ( $\Delta E_{\text{CBS-LCC}}$ ), while employing an explicitly correlated method instead is also possible in principle.<sup>16</sup> Equation 2 has computational advantage over eq 1 because canonical CC/DZ calculation is avoided, and instead the much cheaper canonical MP2/DZ is employed. Recently, Werner and Schütz proposed the correction scheme to improve performance of the LCC method for thermodynamic properties, as shown in eq 3, which is a reformulation of the original expression.<sup>19</sup> Equation 3 is different from eqs 1 and 2 in the fact that domain error and BSIE are addressed at the LMP2 and MP2 levels, respectively.

**Table 1.** Calculated Activation Energies  $\Delta E^\ddagger$  (kcal/mol) for Reaction 5d in Scheme 1 Using CCSD(T)/CBS and CCSD(T)-F12b/CBS Methods at Various Levels

	CCSD(T)/CBS (DZ-TZ)	CCSD(T)/CBS (TZ-QZ)	CCSD(T)/CBS (ADZ-ATZ)	CCSD(T)- F12b/TZ	CCSD(T)- F12b/ADZ	CCSD(T)- F12b/ATZ	CCSD(T)-F12b/CBS (ADZ-ATZ)
$\Delta E^\ddagger$	2.29 (2.59) <sup>a</sup>	2.01	2.09	2.03	2.11	2.06	2.04

<sup>a</sup>BSSE corrected value.

$$\Delta E(\text{LMP2} - \text{MP2})$$

$$= (E_{\text{MP2/DZ}} - E_{\text{LMP2/DZ}}) + \Delta E_{\text{CBS-MP2}} \quad (3)$$

In addition to eqs 1 and 2, in this work we also tested the performance of eq 3 in barrier height calculations, all taking CCSD(T)/CBS values from DZ-TZ extrapolation as a reference. It should be noted that while only TM-catalyzed reactions are treated here, the extension to main group reactions is straightforward. In addition, the corrective approaches proposed in this work are not limited to LCC methods based on local correlation domains but should be effective also for correcting errors introduced by any local approximation in other LCC methods. More generally, the currently proposed corrective scheme can be applied to any energetic calculation using LCC methods to improve its accuracy, whose performance is subject to future investigations.

### III. COMPUTATIONAL DETAILS

All DFT calculations were carried out with the Gaussian 09 program package.<sup>20</sup> Barrier height calculations for the TM-catalyzed reactions shown in Scheme 1 were tested with various functionals including PBE0,<sup>21</sup> M06,<sup>22</sup> M06-L,<sup>22a</sup> M06-2X,<sup>22</sup> TPSS,<sup>23</sup> TPSSH,<sup>23</sup> B3LYP,<sup>24</sup> B2GP-PLYP,<sup>25</sup> B2-PLYP,<sup>26</sup> wB97X,<sup>27</sup> and BMK.<sup>28</sup> Due to the good performance of PBE0 in previous calibrations for 5d TM systems,<sup>29,30</sup> the geometry optimizations of all minima and transition states (for optimized structures, see Figure S1–S3 in the SI) were performed with this functional coupled with the cc-pVTZ/cc-pV(T+d)Z and cc-pVTZ-PP basis sets on main group (C, H, O, N/Cl, P) and TM elements.<sup>6d,e,17</sup> Vibrational analyses were performed to verify that the optimized structures are transition states or minima by having one or no imaginary frequencies. The empirical dispersion correction of Grimme et al.,<sup>31</sup> called DFT-D3, was used with zero short-range damping denoted as DFT-D3(0).<sup>31,32</sup> There are no DFT-D3(0) parameters for the wB97X functional; thus the empirical dispersion corrected functional wB97XD designed by its original developers was used instead.<sup>33</sup>

All ab initio single-point calculations, employing MP2,<sup>34</sup> SCSMP2,<sup>35</sup> CCSD(T),<sup>7</sup> LMP2,<sup>36</sup> and LCCSD(T0)<sup>11</sup> methods, were done using the MOLPRO program package.<sup>37</sup> For C, H, O, N/Cl, P/TM, cc-pVXZ/cc-pV(X+D)Z/cc-pVXZ-PP (X = D, T) basis sets were used.<sup>6d,e,17</sup> These basis sets are abbreviated as XZ hereafter. The scalar relativistic effects of the late TM (Au, Pt, Ir) species were included through the used relativistic pseudopotential (PP).<sup>6e,f</sup> We also tested the effect of adding diffuse basis functions, and the results show that the effect on barrier height is very small in the studied group of reactions, and the results were relegated to the Supporting Information (SI) document (see Table S1). To reduce the computational cost of two-electron integrals, all local MP2 and CC calculations use the density fitting approximation, which has a negligible effect on computational accuracy. To minimize fitting errors in density fitting calculations, auxiliary basis sets were employed.<sup>38</sup> For integrals with up to two external orbitals

in LMP2 and LCCSD calculations, the corresponding cc-pVnZ/MP2FIT auxiliary basis set is used with the cc-pVnZ orbital basis set. As suggested by MOLPRO, to minimize the fitting errors, the next larger fitting basis for the orbital basis was used for integrals over three and four external orbitals in LCCSD calculations (e.g., the cc-pVTZ/MP2FIT auxiliary basis was used to pair with cc-pVDZ orbital basis).

The two-point extrapolations to the complete basis set limit (CBS) were done for Hartree–Fock (HF) and correlation energies separately. For HF energy, we used the formula proposed by Martin et al.,<sup>15e,f</sup> as shown in eq 4. For correlation energy, eq 5 proposed by Truhlar was used.<sup>15c</sup> DZ and TZ basis sets were employed in two-point CBS limit extrapolations. The predetermined optimal parameters  $\alpha$  and  $\beta$  are available for DZ-TZ extrapolation ( $\alpha = 4.42$ ,  $\beta = 2.46$ ).<sup>15d</sup> For pure MP2 and SCSMP2 computations, an optimal  $\beta$  of 2.2 is used.<sup>15c</sup> It should be noted that since uniform CBS limit extrapolations for local and corresponding canonical electron correlation methods are used, the main conclusions of this work are not likely to be affected by the choice of any specific extrapolation scheme.

$$E_{\text{HF},n} = E_{\text{HF,CBS}} + A \exp(-\alpha\sqrt{n}) \quad (4)$$

$$E_{\text{corr},n} = E_{\text{corr,CBS}} + \frac{A}{n^\beta} \quad (5)$$

To have an estimate of the accuracy of our reference CCSD(T)/CBS values, which is based on DZ-TZ CBS limit extrapolation, we have carried out some additional calculations on reaction 5d using more accurate methods. These methods are CCSD(T)/CBS based on ADZ-ATZ extrapolation (AXZ represents corresponding augmented bases of XZ, i.e., aug-cc-pVXZ/aug-cc-pV(X+D)Z/aug-cc-pVXZ-PP for C, H, O/Cl/Pt) and TZ-QZ extrapolation (QZ represents corresponding quadruple- $\zeta$  correlation consistent basis set of TZ), and the CCSD(T)-F12/CBS method based on ADZ-ATZ extrapolation.<sup>6e,17</sup> These highly costly methods cannot be applied to any other reactions in Scheme 1 except for reaction 5d. The ADZ-ATZ and TZ-QZ extrapolation of CCSD(T)/CBS uses eqs 4 and 5 with predetermined optimal parameters ( $\alpha = 4.30$ ,  $\beta = 2.51$  for ADZ-ATZ;  $\alpha = 5.46$ ,  $\beta = 3.05$  for TZ-QZ).<sup>15d</sup> The CCSD(T)-F12 approach used herein employs the CCSD(T)-F12b method with the diagonal fixed amplitude 3C(FIX) Ansatz.<sup>39</sup> In the CCSD(T)-F12 calculations, density fitting (DF) of the Fock and exchange matrices used the auxiliary basis set, def2-AQZVPP/JKFIT<sup>40</sup> and aug-cc-pVTZ/JKFIT<sup>41</sup> for Pt and the rest of the atoms, respectively. DF of the other two-electron integrals, and resolution of the identity approximation, employed aug-cc-pVTZ-PP/MP2FIT<sup>38c</sup> for Pt and aug-cc-pVTZ/MP2FIT<sup>38a</sup> for the rest of the atoms. The optimal values of the geminal Slater exponent in CCSD(T)-F12b calculations were taken from the previous work,<sup>42</sup> i.e.,  $1.0 a_0^{-1}$  for the ADZ basis set and  $1.2 a_0^{-1}$  for the ATZ basis set. The CCSD(T)-F12b/CBS procedure was adapted from the previous work of Hill et al., with CCSD-F12b and the perturbative triples contribution (T) extrapolated separately by Schwenke's two-



Table 2. Deviations ( $D$ ) of Activation Energies  $\Delta E^\ddagger$  (kcal/mol) from the Benchmark Data CCSD(T)/CBS at Various Levels<sup>a</sup>

reaction/ catalyst <sup>b</sup>	$D(\text{LCCSD(T)}/\text{DZ})^c$	$D(\text{LCCSD(T)}/\text{TZ})^d$	$D(\text{LCCSD(T)}/\text{CBS})^e$	$D(\Delta E^\ddagger(\text{LMP2-MP2}))^f$	$D(\Delta E^\ddagger(\text{LMP2-LCC}))^g$	$D(\Delta E^\ddagger(\text{LCC-LCC}))^h$	$D(\text{CCSD(T)}/\text{DZ})^i$	$D(\text{CCSD(T)}/\text{TZ})^j$	$\Delta E^\ddagger(\text{CCSD(T)}/\text{CBS})^k$
1a/Au(III)	0.30	0.98	1.01	0.76	0.23	−0.59	−1.30	−0.25	7.10
1a/Au(I)	−0.85	0.45	0.94	0.37	0.55	0.04	−1.75	−0.47	7.14
1b/Au(III)	−0.68	0.32	0.47	0.66	−0.35	<b>−0.85</b>	−2.00	−0.46	14.12
1b/Au(I)	−0.91	0.42	0.87	0.54	0.37	−0.25	−2.03	−0.54	14.79
1c/Au(III)	0.89	1.22	1.09	0.25	−0.04	−0.66	−0.86	−0.12	7.49
1c/Au(I)	0.57	1.32	<b>1.50</b>	0.28	0.39	−0.25	−1.18	−0.27	8.31
2/Au(III)	−2.76	<b>−1.52</b>	−1.23	0.00	<b>−0.89</b>	−0.57	−2.10	−0.50	2.28
2/Au(I)	<b>−3.08</b>	−1.27	−0.61	0.27	0.23	0.00	<b>−2.46</b>	<b>−0.66</b>	4.48
4b/Au(I)	−2.21	−1.20	−1.02	−0.55	−0.61	−0.33	−1.52	−0.30	19.27
5a/Ir(I)	−1.68	−0.80	−0.42	−0.68	−0.35	0.09	−1.17	−0.35	2.40
5b/Ir(III)	1.46	1.03	0.75	−0.89	−0.32	−0.10	0.62	0.24	8.57
5c/Pt(0)	0.07	−0.06	−0.09	0.28	0.09	0.10	0.25	0.07	8.70
5d/Pt(II)	−1.10	−0.28	0.10	<b>−0.97</b>	0.00	0.13	−1.07	−0.33	2.29
MUD <sup>l</sup>	1.27	0.83	0.78	0.50	0.34	0.30	1.41	0.35	

<sup>a</sup>MaxD values are shown in bold. <sup>b</sup>Reactions are shown in Scheme 1, and various catalysts are Au(III): AuCl<sub>3</sub>; Au(I): [PH<sub>3</sub>Au]<sup>+</sup>; Ir(I): PNP-Ir(I); Ir(III): Cp(PH<sub>3</sub>)MeIr(III); Pt(0): (dpe)Pt(0); Pt(II): (H<sub>2</sub>O)Cl<sub>2</sub>Pt(II). <sup>c</sup>Calculated with the LCCSD(T) method using the DZ basis set. <sup>d</sup>Calculated with the LCCSD(T) method using the TZ basis set. <sup>e</sup>The CBS limit was extrapolated from LCCSD(T) calculated with DZ and TZ basis sets. <sup>f</sup>LCCSD(T)/DZ results corrected with eq 3. <sup>g</sup>LCCSD(T)/DZ results corrected with eq 2. <sup>h</sup>LCCSD(T)/DZ results corrected with eq 1. <sup>i</sup>Calculated with the CCSD(T) method using the DZ basis set. <sup>j</sup>Calculated with the CCSD(T) method using the TZ basis set. <sup>k</sup>Activation energies calculated by CCSD(T) extrapolated to the CBS limit with DZ and TZ basis sets, which are taken as the benchmark data in this paper. <sup>l</sup>Mean Unsigned Deviation.

point CBS scheme<sup>43</sup> with corresponding optimal parameters for the ADZ-ATZ case in CCSD(T)-F12b.<sup>42</sup> The HF basis set limit in the CCSD(T)-F12/CBS datum was not obtained from extrapolation but was approximated by the SCF+CABS-singles energy<sup>44</sup> calculated with the largest basis set (ATZ) used in CCSD(T)-F12 calculations. Using the standard counterpoise approach, we also tested the basis set superposition error (BSSE) for reaction 5d at the CCSD(T)/CBS level based on DZ-TZ extrapolation.

The calculated activation energies  $\Delta E^\ddagger$  of reaction 5d by CCSD(T) and CCSD(T)-F12 methods with various CBS limit extrapolations are summarized in Table 1. It can be seen that CCSD(T)/CBS with DZ-TZ extrapolation ( $\Delta E^\ddagger = 2.29$  kcal/mol) yields a value only 0.25 kcal/mol away from the best estimate ( $\Delta E^\ddagger = 2.04$  kcal/mol) coming from CCSD(T)-F12b/CBS with ADZ-ATZ extrapolation. This provides an estimate of accuracy of our CCSD(T)/CBS reference values employed in this work. In addition to other tests (see Table S1 for Au-catalyzed reactions), it can also be seen from Table 1 that a diffuse basis set is not important in the studied reactions. From the BSSE corrected value in Table 1, we find that BSSE is small and has detrimental effect on CBS result as found also in our previous work on Au-substrate binding,<sup>30</sup> hence we do not consider BSSE further in this work.

For local correlation computations, the standard orbital domains are determined automatically by the procedure of Boughton and Pulay<sup>45</sup> using the default thresholds in MOLPRO. To improve the domain consistency, we manually merged the standard domains generated automatically with DZ and TZ basis sets. The distance criteria ( $R_{\text{CLOSE}}$  and  $R_{\text{WEAK}}$ ) that control the pair classification were chosen to be converged or almost converged (for details, see Table S2 in the SI). In Au-catalyzed reactions, the  $R_{\text{CLOSE}}$  and  $R_{\text{WEAK}}$  are 5 and 6 bohr, respectively, while for Pt- and Ir-catalyzed C–H activations, they are 7 and 8 bohr, respectively. For Au-catalyzed reactions, we tested also 5s5p outer core–valence correlation, and the result (see Table S4 in the SI) reveals that they are very small and negligible, presumably because Au is not directly involved

in the bond formation and breakage but only acts as a Lewis “soft” acid. Since our previous calculations showed that for Ir- and Pt-catalyzed C–H activation the 5s5p outer core–valence correlation effect is very small,<sup>46</sup> we did not consider the outer core–valence correlation effect in this work.

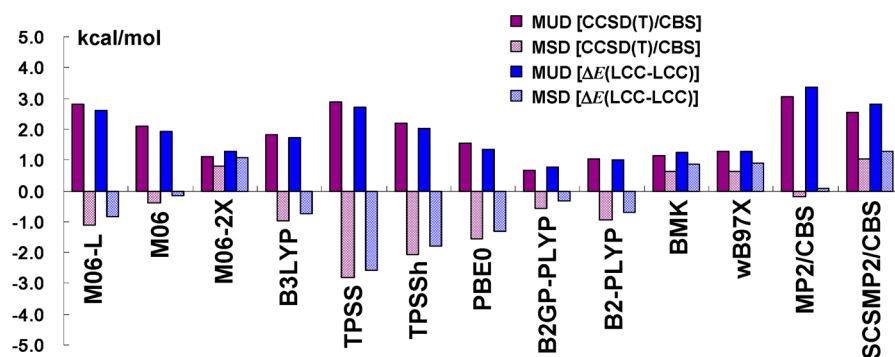
## IV. RESULTS AND DISCUSSION

**LCC Calibrations.** The reactions in Scheme 1 are representative and are catalyzed with various late TMs and their oxidation states including Au(III), Au(I), Ir(III), Ir(I), Pt(II), and Pt(0). Table 2 summarized the activation energy deviations for these reactions, except for reaction 3, for which corresponding benchmark CCSD(T)/CBS reference calculations are too expensive to be feasible.

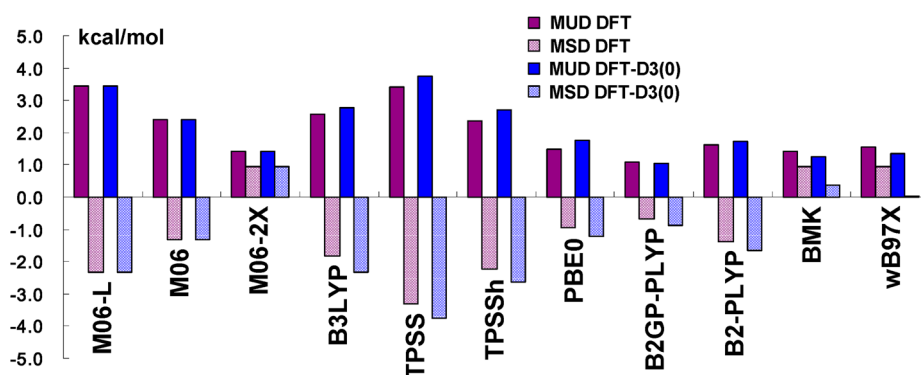
From the values in Table 2, it is clear that results from the LCCSD(T) method can have significant BSIE. When the basis set changes from DZ to TZ, the mean unsigned deviation (MUD)/maximum deviation (MaxD) decrease from 1.27/−3.08 kcal/mol to 0.83/−1.52 kcal/mol. By doing extrapolation to the CBS limit based on DZ and TZ results, the MUD and MaxD are further slightly reduced to 0.78 and 1.50 kcal/mol, respectively. Though extrapolating to the CBS limit can significantly improve the accuracy of the local methods from DZ values by about 0.5 kcal/mol in MUD, there is still space for further improvement because the domain error is not yet considered.

By considering domain error in addition to BSIE, we have the three options shown above in eqs 1–3. According to eq 3 proposed by Werner et al., which corrects LCCSD(T)/DZ results by adding both domain error and BSIE from the second-order perturbation theory treatment, the accuracy of LCCSD(T) has been apparently improved. Compared with the LCCSD(T)/DZ values, the MUD decreased by 0.77 kcal/mol, and now MUD/MaxD are 0.50/−0.97 kcal/mol.

Different from eq 3, eq 2 addresses the BSIE with LCCSD(T), which is an obviously higher level than second-order perturbation theory. As expected, MUD decreases, by 0.16 kcal/mol, which is about a 30% improvement in accuracy



**Figure 1.** Mean unsigned (MUD) and signed (MSD) deviations of activation energies of the reactions in Table 2 for which CCSD(T)/CBS is affordable, calculated with various DFT/TZ and two ab initio methods taking both CCSD(T)/CBS and corrected LCCSD(T) values (by eq 1) as references.



**Figure 2.** Mean unsigned (MUD) and signed (MSD) deviations of calculated activation energies of all reactions in Scheme 1, calculated with various DFT/TZ methods without and with dispersion correction taking corrected LCCSD(T) values (by eq 1) as a reference.

over eq 3. The calculated MUD/MaxD are 0.34/−0.89 kcal/mol now with eq 2.

Equation 1, which is an alternative procedure proposed here for treating both the domain error and BSIE with the LCC method, gets MUD/MaxD of 0.30/−0.85 kcal/mol. This accuracy is slightly higher than that of eq 2 and is about a 40% improvement over eq 3 tested above. Despite this slight improvement over eq 2, we also note that, for reaction 5 of Ir-/Pt-catalyzed C–H activation, eq 1 is much better than eq 2 for both MUD and MaxD. From the MUD values shown in Table 2, we can see that LCCSD(T) results corrected with either eq 1 or 2 are comparable or even slightly better than CCSD(T)/TZ results, which means that the corrective LCC method with the TZ basis set has the potential to approach the accuracy of the corresponding canonical CC/TZ level.

Compared with eq 2, eq 1 gains only a slight accuracy improvement in terms of both MUD and MaxD by 0.04–0.05 kcal/mol, which may not offset the expensive computational cost for using the canonical CCSD(T)/DZ method. Clearly, the significant computational advantage of eq 2 over 1 is that it can treat larger systems by correcting the domain error with much cheaper second-order perturbation theory but with only a slight loss of accuracy. As demonstrated in Table 2, although eq 3 can also lead to computational time savings due to its usage of second-order perturbation theory for both domain error and BSIE corrections, the accuracy is obviously less than those achieved by eq 1 or eq 2, especially for reaction 5 (Scheme 1). This result is due to the direct involvement of the TM d-valence shell in the C–H activation reactions of the reaction 5 series. On the other hand, reactions 1–4 are considered to be

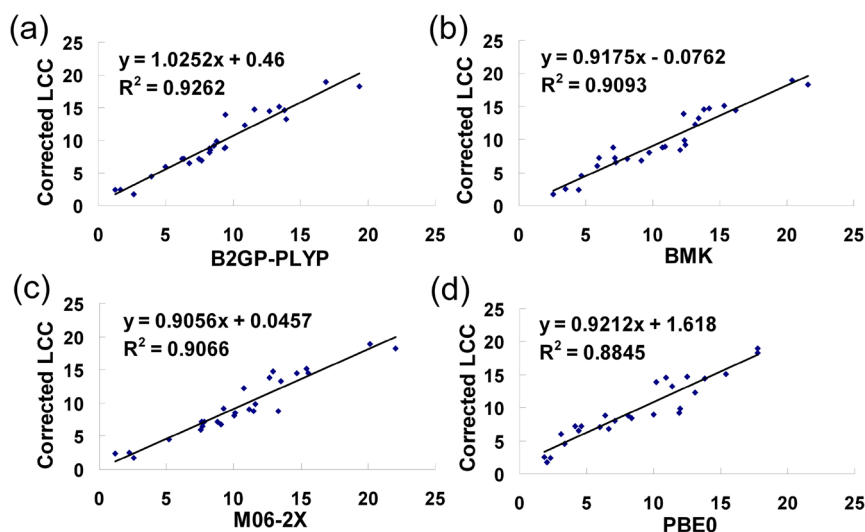
Lewis “soft” acid catalysis by gold cations without direct involvement of the TM d-valence shell in bond formation and breakage. It is well-known that single-reference perturbation theoretic treatments of many TM-containing systems are problematic,<sup>47</sup> which is also the case here because the MUD of MP2/CBS activation energies from the CCSD(T)/CBS reference for the reaction 5 series is 5.26 kcal/mol, compared with the corresponding MUD of 2.09 kcal/mol for reactions 1–4. We note that the poor result of MP2/CBS extrapolation to model CCSD(T)/CBS was also observed before in the 3d TM system,<sup>48</sup> although this way of obtaining CCSD(T)/CBS is widely and successfully used in main group element systems.<sup>49</sup> We also note that eq 2 and eq 1 produce slightly different deviations (D) in Table 2, with the mean absolute difference between them being ~0.3 kcal/mol. This in turn means that the two ways of computing domain error in eqs 2 and 1 are not equivalent and produce somewhat different results. However, the similarity of their MUDs here does not enable us to determine which procedure is better.

**DFT Calibrations.** Following our previous DFT calibration on Au-substrate binding,<sup>30</sup> we also explore the DFT performance of the TM-catalyzed reactions under study. As shown at the bottom of Table 2, for either eq 1 or eq 2 the MUD of the corrective LCCSD(T) methods is only ~0.3 kcal/mol. With such small deviation from the CCSD(T)/CBS reference, we can safely rely on these methods to assess the performance of a series of DFT or other ab initio methods. As expected, in Figure 1 by employing both the CCSD(T)/CBS reference and LCCSD(T) reference corrected by eq 1 for reactions for which CCSD(T)/CBS is affordable, it is seen clearly that both

**Table 3.** Various DFT/TZ Calculated MUD and MaxD (inside Brackets) of the Activation Energies  $\Delta E^\ddagger$  (kcal/mol) of All Reactions Shown in Scheme 1 Taking the Corrected LCCSD(T)/DZ Results with eq 1 as Reference<sup>a</sup>

	M06-L	M06	M06-2X	B3LYP	TPSS	TPSSh	PBE0	B2GP-PLYP	B2-PLYP	BMK	wB97X
HF% <sup>b</sup>	0	27	54	20	0	10	25	65	53	42	15
[Au] <sup>c</sup>	3.58 (3.58) [−10.90]	2.33 (2.35) [−7.30]	<b>1.32</b> (1.33) [3.76]	2.81 (3.11) [−8.64]	3.81 (4.22) [−9.48]	2.66 (3.03) [−6.98]	<b>1.62</b> (1.91) [−3.66]	<b>1.16</b> (1.10) [−4.44]	<b>1.78</b> (1.90) [−6.34]	<b>1.28</b> (1.08) [3.30]	<b>1.57</b> (1.41) <sup>f</sup> [5.62]
[Pt,Ir] <sup>d</sup>	2.70 (2.70) [5.60]	2.73 (2.71) [3.96]	<b>1.89</b> (1.90) [4.49]	<b>1.14</b> (0.94) [3.01]	<b>1.14</b> (1.15) [−1.78]	<b>0.84</b> (0.87) [−1.44]	<b>0.82</b> (0.94) [−2.43]	<b>0.69</b> (0.77) [−1.20]	<b>0.69</b> (0.73) [−1.22]	2.08 (2.06) [3.56]	<b>1.46</b> (0.99) <sup>f</sup> [2.95]
total <sup>e</sup>	3.44 (3.44)	2.39 (2.41)	<b>1.41</b> (1.41)	2.56 (2.78)	3.40 (3.75)	2.38 (2.70)	<b>1.50</b> (1.76)	<b>1.09</b> (1.05)	<b>1.61</b> (1.72)	<b>1.41</b> (1.24)	<b>1.55</b> (1.35) <sup>f</sup>

<sup>a</sup>MUD values with DFT-D3(0) are inside parentheses and small MUD values (<2.0 kcal/mol) are in bold. <sup>b</sup>Percentage of HF exchange in various functionals. <sup>c</sup>Deviations of Au-catalyzed reactions. <sup>d</sup>Deviations of Pt- and Ir-catalyzed reactions. <sup>e</sup>Deviations of all reactions from above rows. <sup>f</sup>There is no DFT-D3(0) parameters for wB97X functional, thus wB97XD (empirical dispersion corrected wB97X defined in ref 33) was used instead.

**Figure 3.** The best four correlations of calculated barriers (kcal/mol) for all reactions in Scheme 1 between corrected LCCSD(T) values (by eq 1) vs (a) B2GP-PLYP, (b) BMK, (c) M06-2X, and (d) PBE0 values.

computational schemes generate a very similar assessment of DFT performances in terms of both deviation values and their trend. Thus from Figure 1 we find that the MUD values of the tested functionals from both reference values decrease in the same order, i.e., B2GP-PLYP < B2-PLYP < BMK  $\approx$  M06-2X < wB97X < PBE0 < B3LYP < M06 < TPSSh < M06-L < TPSS. This indicates that the corrective LCC methods applied here are consistent.

As found in previous Au-substrate binding energy calculations,<sup>30</sup> here too, the MP2 and SCSMP2 methods do not show good performance in activation energy calculations compared with the best functionals. Thus, we shall not further assess these two ab initio methods and focus below on the DFT assessment.

Since the CCSD(T)/DZ is affordable for all of the reactions in Scheme 1, in Figure 2, including all reactions, we still can use the results from eq 1, which are of slightly higher accuracy than those of eq 2, as a reference to search the optimal functionals. Figure 2 demonstrates an error order of B2GP-PLYP < BMK  $\approx$  M06-2X < PBE0 < wB97X < B2-PLYP < B3LYP < M06 < TPSSh < M06-L < TPSS, which is almost the same as that from Figure 1 except for double hybrid functional B2-PLYP. This functional gets a four-rank lowering in the MUD decreasing direction, the reason for which will be discussed below. Since we have noted that Au-catalyzed reactions and Pt-/Ir-catalyzed

reactions can be very different, a separate comparison for them as done in Table 3 could be helpful for making a clear assessment. We can see that for Au-catalyzed reactions, there are six functionals with a MUD less than 2 kcal/mol. They are in the increasing order of B2GP-PLYP < BMK < M06-2X < wB97X < PBE0 < B2-PLYP. While for Pt-/Ir-catalyzed C–H activation reactions, there are eight functionals with a MUD less than 2 kcal/mol, which, however, is in the increasing order of B2GP-PLYP  $\approx$  B2-PLYP < PBE0 < TPSSh < TPSS  $\approx$  B3LYP < wB97X < M06-2X. Comparatively, one of the two double hybrid functionals, B2-PLYP (MUD/MaxD of 1.78/−6.34), performs apparently worse than the other one B2GP-PLYP (MUD/MaxD of 1.16/−4.44) in Au-catalyzed reactions, but they do similarly well in Pt-/Ir-catalyzed reactions. It is this difference that makes B2-PLYP on average less good in Figure 2, which includes all the reactions of Scheme 1, compared with Figure 1, which includes only a subset of the reactions in Scheme 1, containing less Au-catalyzed reactions. In addition, for this set of Pt-/Ir-catalyzed reactions, many general-purpose functionals with a medium percentage of HF exchange (10–25%), like popular B3LYP, PBE0, and TPSSh, or no HF exchange, like TPSS, perform very well. For example, the best two among them, PBE0 and TPSSh, have MUD/MaxD of 0.82/−2.43 and 0.84/−1.44 kcal/mol, respectively. In total, from all reactions in Scheme 1, the best five functionals are

B2GP-PLYP < BMK  $\approx$  M06-2X < PBE0 < wB97X, with MUD less than 1.6 kcal/mol. Considering MaxD, the smallest four are BMK < PBE0 < B2GP-PLYP < M06-2X, with an absolute value less than 4.5 kcal/mol.

Among the five best in tested functionals with a MUD less than 1.6 kcal/mol, one is the double hybrid functional B2GP-PLYP, and two (BMK and M06-2X) are “kinetic” functionals. These functionals are all characterized by a high percentage of Hartree–Fock (HF) exchange (65%/42%/54% for B2GP-PLYP/BMK/M06-2X). This observation for the late TM involved reactions is in accord with a previous finding that inclusion of 40–50% of HF exchange in functionals is beneficial for barrier height calculations for pure main-group element systems.<sup>50–52</sup> By introducing MP2-type nonlocal correlation, B2GP-PLYP achieves even better performance than BMK and M06-2X for both Au- and Ir/Pt-catalyzed reactions, which is a promising improvement over “kinetic” functionals. The MaxD values for B2GP-PLYP, BMK, and M06-2X are –4.44 (reaction 4d/Au(III)), 3.56 (reaction 5b/Ir(III)), and 4.49 (reaction 5c/Pt(0)) kcal/mol, respectively. In addition to these three functionals, hybrid GGA PBE0, which is a general-purpose DFT with a medium percentage of HF exchange (25%), also performs well (MaxD of –3.66 kcal/mol for reaction 4d/Au(III)). The well-performing general-purpose functionals B2GP-PLYP and PBE0 deserve more attention considering the fact that they are also good in Au-substrate binding energy calculations,<sup>30</sup> structures, atomization energies, clustering energies, barrier heights, and properties of 3d, 4d, and 5d TM-containing complexes.<sup>29,53–59</sup> The range-separated DFT of wB97X may also be recommended due to its small MUD and uniform performance in the Au- and Pt-/Ir-catalyzed reactions tested in this work. TPSS and TPSSH show relatively poor performance in Au-catalyzed reactions, which may be due to their low percentage of HF exchange (0% and 10%).<sup>60,61</sup>

While above we calibrated the barrier height values, now we wish to explore the trends of DFT barriers, which may be more important. To reveal this aspect of DFTs, we show in Figure 3 the best four correlations between the reference corrective LCCSD(T) and the functionals. It can be seen that the order of performance in the trend is consistent with that in MUD values, which is an interesting result. Thus, we can see a good correlation ( $R^2 = 0.93$ ) of the above best functional B2GP-PLYP, indicating that DFT is able to follow the trend in barrier height calculations. In addition, we also find that the slope of the correlation line for B2GP-PLYP is very close to ideal, 1.0 (1.025), which means that systematic underestimation or overestimation of barriers by this functional is small. The correlations for other DFT methods are relegated to the SI.

Finally, with the DFT empirical dispersion corrections included,<sup>32,33</sup> as shown in Figure 2 and Table 3, only B2GP-PLYP, BMK, and wB97X functionals have slight improvements, and the rest of the functionals are either almost unaffected (M06 series) or made worse (all the rest). This is in line with our previous assessment for Au-substrate binding energies.<sup>30</sup> It should be noted that all of the TM ligands here in this work are neither large nor bulky, which may be the reason for the observed small dispersion effect from DFT methods.

## V. CONCLUSIONS

In this work, we have proposed a new computational scheme to improve the accuracy of LCC methods in computing the reaction activation energies. These schemes were tested with late-TM-catalyzed reactions involving Au, Pt, and Ir.<sup>62–65</sup> The

results show that our corrective approach for LCC can improve the mean unsigned deviation and maximum deviation from the CCSD(T)/CBS reference down to about 0.3 and 0.9 kcal/mol. Using this new method, we subsequently tested the performance of popular density functionals for activation energies of late-TM-catalyzed reactions. The best functional is found to be the general-purpose double hybrid functional B2GP-PLYP, which is best for both Au- and Pt-/Ir-catalyzed reactions. In addition to B2GP-PLYP, some of the other well-performing functionals include the “kinetic” functionals, M06-2X and BMK, which also include a large percentage of HF exchange. This observation is similar to previous conclusions reached for main group reactions. The general-purpose functional PBE0 and the range-separated functional wB97X are also recommended. Comparatively, general-purpose functionals like PBE0 and TPSSH perform much better than the tested “kinetic” functionals in Pt-/Ir-catalyzed reactions, while the opposite is true for Au-catalyzed reactions. In contrast, wB97X performs more uniformly in these two classes of TM-catalyzed reactions. These findings hint that even within the late TMs, it is necessary to distinguish different types of TM-catalyzed reactions in searching the optimal DFT methods. The assessment of barrier correlation between DFT and the corrective LCC approach is consistent with the above found performance order for the various DFT methods. This result indicates that good-performing functionals identified herein are good in both barrier values and trends. DFT empirical dispersion correction was found to only have very small or no effect at all on the late-TM-catalyzed reactions barriers studied herein.

Finally, this work improves the accuracy of the LCCSD(T) method nearer to the CCSD(T) gold standard and is clearly superior, in terms of accuracy, to all of the tested DFT methods, which were chosen to represent most rungs in Jacob's ladder with and without empirical dispersion add-ons. More applications of LCC methods for either direct usage or DFT-calibration purposes in TM catalysis are essential to finally establish this relatively low cost and reliable LCC scheme.

## ■ ASSOCIATED CONTENT

### Supporting Information

Nine tables and four figures of computational results and Cartesian coordinates. 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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