

Assessment of Theoretical Methods for Complexes of Gold(I) and Gold(III) with Unsaturated Aliphatic Hydrocarbon: Which Density Functional Should We Choose?

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 Supporting Information

ABSTRACT: Gold–substrate interaction is essential in gold-catalyzed organic transformations. This study uses high-level coupled cluster calculations with core–valence correlation and complete basis set (CBS) limit extrapolation as a reference, for assessing the performance of popular density functional theory (DFT) approximations for a variety of Au(I)/Au(III) complexes with unsaturated aliphatic hydrocarbon C_nH_m substrates (ethene, ethyne, and allene). The tested functionals cover from LDA to GGA and meta-GGA, and to hybrids and double hybrids (LSDA, PBE, M06-L, TPSS, B3LYP, PBE0, M06, M06-2X, TPSSH, B2-PLYP, B2GP-PLYP). Both the geometry and bond dissociation energy (D_e) of the Au– C_nH_m complexes are studied. Our findings show that B2GP-PLYP, PBE0, and B2-PLYP are the best performing functionals for this set of Au– C_nH_m complexes. DFT dispersion correction (DFT-D3), though very helpful for some functionals (e.g., B3LYP and B2-PLYP), does not uniformly improve the results of all functionals. Ab initio methods like MP2 and SCSMP2 are also tested. MP2 is found to be the worst performing method, and while SCSMP2 greatly improves the results, still its accuracy is lower than that of the best functionals, B2GP-PLYP, PBE0, and B2-PLYP.

1. INTRODUCTION

There has been a surge of interest in recent years in gold-catalyzed organic reactions with the concomitant rapid development and discovery of many new transformations in the field.^{1–11} The catalyzed reactions often involve unsaturated substrates with C=C, C=C=C, and C≡C functional groups. It is thought that the Au coordination to these functional groups is a key step in activating the substrates during these gold-catalyzed transformations.^{2,12} Due to the importance of these Au–substrate interactions, many theoretical and computational studies have been carried out to explore the interactions and bonding in Au–alkene^{13–21} and Au–alkyne complexes.^{19–24}

Density functional theory (DFT), which has had significant success in the transition metal chemistry area,^{25–38} has also been widely used for exploring many Au-catalyzed reaction mechanisms.^{39–71} However, what is still missing is a systematic study that assesses the performance of various approximate density functionals in reproducing the geometries and interactions between Au^I/Au^{III} and unsaturated aliphatic hydrocarbons. In this study, we employ coupled cluster CCSD(T) computations with an aim of achieving such a systematic assessment of the widely used DFT and some ab initio methods (e.g., MP2 and its variants) in reproducing geometries and bond dissociation energies (D_e) of Au–substrate complexes. As shown in Scheme 1, the target molecules AuL_x– C_nH_m used in the study are unsaturated substrates (C_nH_m) including ethene, ethyne, and allene, in

combination with a variety of Au^I/Au^{III}-ligated species related to real catalysts ($C_nH_m = C_2H_2, C_2H_4, C_3H_4$; AuL_x = Au^I, Au^ICl, Au^{III}Cl₃, Au^INHC, Au^IPH₃).

The coupled cluster benchmark data will rely on calibrated complete basis set (CBS) limit extrapolations including core–valence correlation effects, which is probably the highest ab initio level to have ever been applied to these Au– C_nH_m complexes. Useful knowledge about both the Au– C_nH_m interaction and its ab initio treatment is gained in this study, which would be helpful to future DFT and ab initio studies of Au-catalyzed organic transformations.

2. COMPUTATIONAL DETAILS

Treatment of Scalar Relativistic Effect. To take the scalar relativistic effects into account, we employed the new Stuttgart/Köln small-core relativistic pseudo-potential (PP)⁷² for gold, for both DFT and ab initio computations. To test whether such ECP treatment of scalar relativistic effects is sufficient, we performed MP2 calculations on naked Au(I) complexes using Stuttgart/Köln PP and compared the results to the calculations using the full electron third-order Douglas–Kroll–Hess (DKH) Hamiltonian.^{73,74} The DKH and PP calculations both included the Au-5s5p core–valence

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Scheme 1. The Complexes Studied in This Work

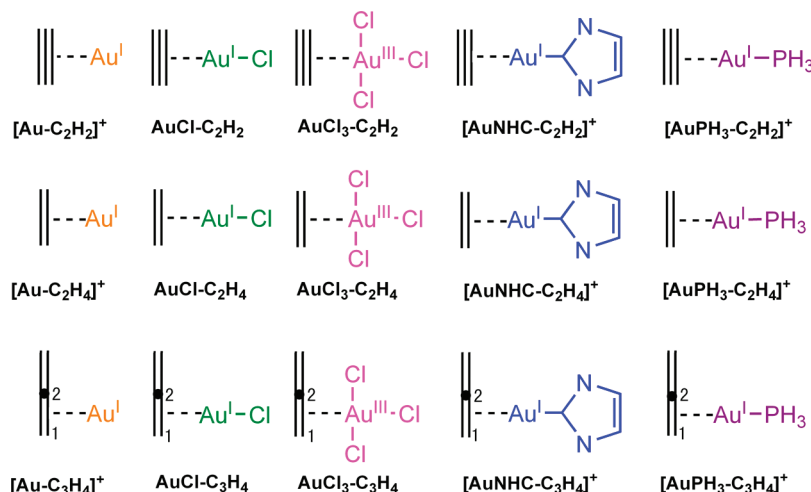


Table 1. Various Basis Sets and Their Abbreviations in This Work

elements	basis set ^a	abbreviation ^a	ref
Au	(aug-)cc-pVXZ-PP	(A)XZ	75
	(aug-)cc-pwCVXZ-PP	(A)wXZ	75
	(aug-)cc-pwCVTZ-DK	(A)wTZ-DK	75
C,H	(aug-)cc-pVTZ-DK	(A)TZ-DK	77
C,N,H	(aug-)cc-pVXZ	(A)XZ	76
Cl,P	(aug-)cc-pV(X+d)Z	(A)XZ	78
C,N,Cl,P	cc-pwCVXZ	wXZ	76, 79

^a X represents the cardinal number of the correlation consistent basis set and could be D, T, Q, or 5 in this work.

correlation effect (note that the Au 5s orbital is lower in energy than the 4f orbitals in the DKH scheme at the Hartree–Fock level). The Au 5s5p core–valence correlation in the PP and DKH schemes used the corresponding correlation consistent weighted core–valence triple- ζ basis sets of (aug-)cc-pwCVTZ-PP and (aug-)cc-pwCVTZ-DK.⁷⁵ For the remaining main group elements (C, H), we adopted the (aug-)cc-pVTZ basis set⁷⁶ in the PP scheme and (aug-)cc-pVTZ-DK⁷⁷ in the DKH scheme. The results (see Tables S1 and S2 in Supporting Information (SI)) show that these two approaches generate similar geometries (maximal Au–C bond distance deviation of 0.002 Å) and D_e 's (maximal deviation of 0.96 kcal/mol). Considering the fact that the scope of this work is mainly the comparative study of different quantum chemical electronic structure methods, we can safely rely on the PP adopted for scalar relativistic effect. Because many basis sets are used in this work, we summarized their designations and our corresponding abbreviations in Table 1. “A” represents prefix “aug-” for a basis augmented by diffuse functions. “w” denotes the weighted core–valence correlated basis set. “X” is the cardinal number of the correlation consistent basis set, which could be D, T, Q, or 5. For third row p elements Cl and P, we used the “(X+d)” basis set that includes an additional set of d orbitals to improve the basis set extrapolation behavior. For clarity, we do not use the suffix “-PP” in our abbreviation for the basis set on the Au atom.

Density Functional Methods. All DFT calculations were done using the Gaussian 09⁸⁰ program. We employed 11 functionals which cover the range from LDA to (hybrid) GGA, (hybrid) meta-GGA, and double-hybrid functionals: LSDA,⁸¹ PBE,⁸² M06-L,⁸³ TPSS,⁸⁴ B3LYP,^{85–87} PBE0,^{82,88,89} M06,^{83,90} M06-2X,^{83,90} TPSSH,⁸⁴ B2-PLYP,⁹¹ and B2GP-PLYP.⁹²

Geometric performance tests were carried out only for the smaller naked Au(I) complexes $[\text{Au}^I-\text{C}_n\text{H}_m]^+$ ($\text{C}_n\text{H}_m = \text{C}_2\text{H}_2$, C_2H_4 , and C_3H_4), for which we could perform geometry optimization at the CCSD(T)/CBS level including Au 5s5p correlation. On the basis of the previous assessment of DFT optimized geometries of 5d transition-metal-containing complexes,⁹³ we selected five functionals, i.e., LSDA, B3LYP, PBE0, M06, and B2-PLYP, to test the optimized geometries, employing DZ and TZ basis sets.^{75,76} In double hybrid B2-PLYP geometry optimizations, the 1s electrons of C atoms were not correlated in MP2-type correlation treatments. In addition to these geometry tests, we also performed geometry optimizations for all complexes in Scheme 1 at the B3LYP/DZ level, which can be compared with the CCSD/DZ results (shown in Table S8 in the SI), and thereby provide a more general comparison between these two levels.

A test of D_e values obtained with B3LYP/AQZ^{75,76} showed a difference of up to 0.3 kcal/mol compared with the B3LYP/ATZ (see Table S3 in SI), hence indicating that the ATZ basis set gives values close to convergence for DFT. Therefore, all D_e calculations were done for all complexes in Scheme 1, using 10 of the functionals (excluding LSDA), in combination with the ATZ basis set.^{75,76} In addition, we tested the effect of dispersion correction using Grimme's DFT-D3 method,⁹⁴ and we employed two different short-range damping schemes, the original DFT-D3(0)^{94,95} and the Becke–Johnson scheme, DFT-D3-(BJ).^{96–100} We also tested for basis set superposition error (BSSE) correction for DFT using the B3LYP functional, and the results (Table S9 in the SI) indicate that the BSSE corrections are very small and thus can be neglected.

Ab Initio Methods. Four ab initio methods were employed using the Molpro2010 package.¹⁰¹ Two of these are coupled cluster methods (CCSD and CCSD(T)),^{102–104} and two are the perturbative methods, MP2¹⁰⁵ and SCMP2.¹⁰⁶ Basis set convergence in ab initio methods is not as fast as in DFT, and it

Table 2. $D_e/\text{CBS}_{\text{val}}$ (Valence Correlated CBS Limit, in kcal/mol) of $\text{AuCl}-\text{C}_2\text{H}_2$ Obtained by Extrapolation with Different Two-Point Extrapolation Formulas

D_e	eqs 3 and 4		eqs 1 and 2		
	CBS (ADZ-ATZ)	CBS (ATZ-AQZ)	CBS (ADZ-ATZ)	CBS (ATZ-AQZ)	CBS (AQZ-ASZ)
$\text{AuCl}-\text{C}_2\text{H}_2$	41.66	41.76	41.47	41.77	41.82
D_e	CBS (DZ-TZ)	CBS (TZ-QZ)	CBS (DZ-TZ)	CBS (TZ-QZ)	CBS (QZ-SZ)
$\text{AuCl}-\text{C}_2\text{H}_2$	40.04	41.35	39.78	41.37	41.82

requires extrapolation to the complete basis set (CBS) limit. We therefore selected the D_e datum for $\text{AuCl}-\text{C}_2\text{H}_2$ for calibration and performed extensive CBS limit extrapolation using a series of valence correlated basis sets from (A)DZ through (A)TZ and (A)QZ all the way to (A)SZ.^{75,76} Thus, we obtained a series of two-point extrapolation data from consecutive pairs of basis set extrapolation, denoted as (A)DZ–(A)TZ, (A)TZ–(A)QZ, and (A)QZ–(A)SZ. For two-point CBS limit extrapolations of Hartree–Fock (HF) and correlation energy, we tested a few proposed formulas. The first one is based on Helgaker’s inverse cubic scaling dependence of the correlation energy on the basis set,¹⁰⁷ shown in eq 1.

$$E_{\text{corr},n} = E_{\text{corr,CBS}} + \frac{A}{n^3} \quad (1)$$

wherein two parameters A and $E_{\text{corr,CBS}}$ are to be determined by calculations with two basis sets, like (A)DZ–(A)TZ, while n is the cardinal number of the basis sets ($n = 2/3/4/5$ for (A)DZ/(A)TZ/(A)QZ/(A)SZ).

For the HF CBS limit extrapolation, a similar fifth power scaling dependence in eq 2¹⁰⁸

$$E_{\text{HF},n} = E_{\text{HF,CBS}} + \frac{A}{n^5} \quad (2)$$

was used in combination with eq 1

It was found before by Truhlar¹⁰⁹ that for CBS limit extrapolation involving a small basis like (A)DZ, which is the only affordable choice for the large complexes in this study, higher accuracy can be achieved by using the more general eq 3:

$$E_{\text{corr},n} = E_{\text{corr,CBS}} + \frac{A}{n^\beta} \quad (3)$$

The predetermined optimal parameter β is available for ADZ–ATZ ($\beta = 2.51$), DZ–TZ ($\beta = 2.46$), and (A)TZ–(A)QZ ($\beta = 3.05$) extrapolation.¹¹⁰ In combination with eq 3, we used the exponential scaling for HF CBS limit extrapolation,^{111,112} shown in eq 4

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

wherein predetermined optimal parameter α is available for ADZ–ATZ ($\alpha = 4.30$), DZ–TZ ($\alpha = 4.42$), ATZ–AQZ ($\alpha = 5.79$), and TZ–QZ ($\alpha = 5.46$) CBS limit extrapolation.¹¹⁰

As summarized in Table 2, taking (A)QZ–(A)SZ extrapolation from eqs 1 and 2 as a reference, we find that (a) for the (A)DZ–(A)TZ extrapolation, eqs 3 and 4 produce better CBS limits for D_e than the values obtained from eqs 1 and 2 and (b) for the (A)TZ–(A)QZ extrapolation, eqs 3 and 4 generate almost the same CBS limit of D_e as that from eqs 1 and 2, which is a conceivable result since the optimal $\beta = 3.05$ in eq 3 for (A)TZ–(A)QZ extrapolation is very close to the theoretical

value of 3.0 in eq 1, and the difference of extrapolated absolute HF energies between eqs 4 and 2 with the (A)TZ–(A)QZ basis is already very small ($<0.4 \text{ mE}_h$). Thus, in this work, we used eqs 3 and 4 for (A)DZ–(A)TZ and (A)TZ–(A)QZ extrapolations, while for (A)QZ–(A)SZ extrapolation, we used eqs 1 and 2.

The above CBS limit extrapolation procedures are usable for CCSD(T) calculations. Thus, for MP2 and SCSMP2, only (A)DZ–(A)TZ extrapolations were done, employing eqs 3 and 4 with an optimal parameter β for MP2 ($\beta = 2.2$), as determined by Truhlar.¹⁰⁹

The highest level ab initio geometry optimizations for naked Au(I) complexes $[\text{Au}^1-\text{C}_n\text{H}_m]^+$ ($\text{C}_n\text{H}_m = \text{C}_2\text{H}_2, \text{C}_2\text{H}_4$, and C_3H_4) were performed with CCSD(T), MP2, and SCSMP2 with the wDZ/DZ and wTZ/TZ bases on Au/C,H atoms. The calculations include the Au 5s5p core–valence correlation. CCSD(T), MP2, and SCSMP2 CBS limit extrapolation was done then using eq 3 with the wDZ/DZ–wTZ/TZ basis set pair, as described above for the DZ–TZ basis set.

D_e Calculations. The geometries are uniformly optimized at the CCSD/DZ level for all of the complexes in Scheme 1 and used routinely for D_e calculations. Three ab initio methods, CCSD(T), MP2, and SCSMP2, and 10 functionals were employed in the D_e calculations for all of the complexes in Scheme 1.

The ab initio values were corrected to produce the final $D_e/\text{CBS}_{\text{final}}$ data based on eq 5:

$$D_e/\text{CBS}_{\text{final}} = D_e/\text{CBS}_{\text{val}} + \Delta D_e/\text{CBS}(\text{5s5p}) + \Delta D_e/\text{CBS}(\text{CV}) \quad (5)$$

Here, $D_e/\text{CBS}_{\text{val}}$ is the D_e value resulting from the ADZ–ATZ valence correlated CBS limit using eqs 3 and 4. $\Delta D_e/\text{CBS}(\text{5s5p})$ is the Au 5s5p core–valence correlation correction for D_e from the wDZ/DZ–wTZ/TZ (in the order, Au/Cl,P,C,N,H) CBS limit extrapolation using eq 3. Lastly, $\Delta D_e/\text{CBS}(\text{CV})$ is the core–valence correlation correction from other non-hydrogen atoms for D_e calculated from the wDZ/DZ–wTZ/TZ (in the order, Au,C,N,Cl,P/H) CBS limit extrapolation using eq 3, and excluding the correlation of the 1s electrons for Cl and P. All of the core–valence correlation corrections were calculated by the difference of two single point calculations, with and without the corresponding core–valence correlation using the same (A)wXZ basis set. Three ab initio methods, CCSD(T), MP2, and SCSMP2, were employed in D_e calculations for all of the complexes in Scheme 1. Ten functionals with the ATZ basis set were tested on the DFT side, as described above in the DFT subsection. In single point calculations with double-hybrid functionals, the core electrons of non-hydrogen atoms were correlated in an MP2-type correlation treatment.

The CBS D_e calculations were also corrected for basis set superposition error (BSSE) using the standard counterpoise

Table 3. D_e (kcal/mol) of AuCl–C₂H₂ Calculated at the CCSD(T) Level with Various Valence Correlated Basis Sets and CBS Limit Extrapolations, with and without BSSE Correction

D_e	ADZ	ATZ	AQZ	ASZ	CBS _{val} ^a (ADZ-ATZ)	CBS _{val} ^a (ATZ-AQZ)	CBS _{val} ^b (AQZ-ASZ)
without BSSE correction	39.48	40.87	41.40	41.61	41.66	41.76	41.82
with BSSE correction	35.35	39.11	40.69	41.22	41.13	41.73	41.75

^a CBS was obtained from eqs 3 and 4. ^b CBS was obtained from eqs 1 and 2.

Table 4. Key Bond Lengths (in Å) of Naked Au(I) Coordinate Complexes Optimized with Different Basis Sets at CCSD and CCSD(T) Levels

complex	parameter	CCSD/DZ	CCSD/ADZ	CCSD/TZ	CCSD/wDZ	CCSD(T)/DZ	CCSD(T)/CBS ^a (wDZ-wTZ)
[Au–C ₂ H ₂] ⁺	$r_{\text{Au–C}}$	2.191	2.191	2.179	2.168	2.175	2.135
	$r_{\text{C–C}}$	1.253	1.254	1.235	1.256	1.262	1.236
[Au–C ₂ H ₄] ⁺	$r_{\text{Au–C}}$	2.201	2.207	2.189	2.182	2.188	2.151
	$r_{\text{C–C}}$	1.404	1.408	1.392	1.408	1.413	1.399
[Au–C ₃ H ₄] ⁺	$r_{\text{Au–C1}}$	2.157	2.164	2.146	2.142	2.149	2.117
	$r_{\text{Au–C2}}$	2.217	2.221	2.212	2.188	2.190	2.158
	$r_{\text{C1–C2}}$	1.388	1.391	1.374	1.392	1.397	1.380

^a CCSD(T)/CBS was obtained by the extrapolation with eq 3 using wDZ/DZ-wTZ/TZ basis sets on Au/C,H to include the Au 5s5p correlation effect.

approach.^{113,114} The results for the AuCl–C₂H₂ complex shown in Table 3 indicate that BSSE corrected D_e values are consistently smaller than the corresponding ones without BSSE correction. As expected, with the larger basis sets like ATZ–AQZ or AQZ–ASZ, the BSSE corrections for the CBS limit are very small. While at the ADZ–ATZ CBS limit level, which is the only practical level for some relatively large complexes we studied here, and taking the (A)QZ–(A)SZ CBS limit extrapolation value as the reference, the calculations without BSSE correction generate much closer results than those with BSSE correction, in accord with a previous study of BSSE effect on interaction energy.¹¹⁵ This is a reflection that BSSE and basis set incompleteness error (BSIE) are oppositely signed for D_e . Thus, a favorable error cancellation occurs without BSSE correction. Therefore, in what follows, we show ADZ–ATZ CBS limit results without BSSE correction, while the BSSE corrected data are relegated to the Supporting Information (see Table S5 in the SI).

3. RESULTS AND DISCUSSION

3.1. Molecular Structures. *Naked Au(I) Coordinate Complexes.* To explore the factors that affect the geometries of Au–alkene/alkyne/allyene complexes, we first optimized the [Au^I–C_nH_m]⁺ (C_nH_m = C₂H₂, C₂H₄, and C₃H₄) complexes at various CCSD/DZ levels. To address the geometric influence of basis-set augmentation, we tested basis sets with diffuse functions (ADZ), a valence triple- ζ basis (TZ), and wDZ that considers the Au 5s5p correlation effects. In addition, CCSD(T) was also employed in geometry optimization combined with DZ to check the effect of perturbative triples (T) in the coupled cluster method. Key geometric parameters in these naked Au(I) coordinate complexes were collected in Table 4.

Basis Set and Au 5s5p Correlation Effect in Coupled Cluster Calculations. Inspection of the Au–C bond lengths in the three [Au^I–C_nH_m]⁺ complexes in Table 4 shows that augmenting the DZ basis set in CCSD with diffuse basis functions, from DZ to ADZ, results in minor Au–C bond lengthening (by 0.007 Å at most). However, improvement of the valence part, from DZ to

TZ, changes the bond lengths more significantly, e.g., shortening by up to 0.012 Å. Inclusion of the 5s5p electron correlation effect for gold, with the wDZ basis set, leads to maximal Au–C shortening, by 0.029 Å. Adding the triples (T) in CCSD(T)/DZ shortens the Au–C bond lengths by up to 0.027 Å compared with CCSD/DZ.

The above tests demonstrate that the quality of valence correlated basis set and the addition of Au 5s5p core–valence correlation and triples (T) all impart significant effects on the coupled cluster optimized geometries, while adding diffuse basis functions has a minor effect. Thus, we performed CCSD(T)/CBS calculations with the wDZ–wTZ basis set including the Au 5s5p correlation to obtain the most accurate and reliable geometric parameters of these [Au^I–C_nH_m]⁺ complexes, as shown for reference in the last column of Table 4. Comparing CCSD(T)/CBS Au–C bond lengths with CCSD/DZ ones, the former are shorter by about 0.040–0.059 Å than the latter.

Performance of DFT Methods. Having the reference geometric parameters for these [Au^I–C_nH_m]⁺ complexes, we can now assess the performance of DFT methods. To this end, we selected B3LYP, LSDA, M06, PBE0, and B2-PLYP to optimize the naked Au(I) complexes with DZ and TZ bases. The key bond lengths of these complexes optimized with TZ basis sets are collected in Table 5, while the results with DZ basis sets are reported in the Supporting Information (see Table S4 in the SI).

The best results using the CCSD(T)/CBS (wDZ-wTZ) reference are indicated in Table 5 by the bold font. Thus, PBE0 is the best method in the test set, with deviations of the Au–C bond lengths being only about –0.002 to +0.023 Å. This good performance of the PBE0 conforms to the previous geometry calibration of 5d transition metal complexes.⁹³ However, in contrast to the previous finding that LSDA is the best DFT in 5d transition metal complexes,⁹³ here, LSDA underestimates the Au–C bond lengths significantly (the deviations are about –0.062 to –0.077 Å). This conforms to the known tendency of LSDA to underestimate metal–ligand bond lengths in 3d and 4d transition metal species,^{116,117} a tendency that seems to persist here in the 5d transition metal complexes. B3LYP, which is the most popular functional in many areas,

Table 5. Key Bond Lengths (in Å) of Naked Au(I) Coordinate Complexes Optimized at Various DFT/TZ and ab Initio CBS Levels^a

		B3LYP/TZ	LSDA/TZ	M06/TZ	PBE0/TZ	B2-PLYP/TZ	SCSMP2/ CBS(wDZ-wTZ) ^b	MP2/CBS (wDZ-wTZ) ^b	CCSD(T)/ CBS(wDZ-wTZ) ^c
[Au–C ₂ H ₂] ⁺	<i>r</i> _{Au–C}	2.177	2.058	2.204	2.133	2.149	2.109	2.069	2.135
	<i>r</i> _{C–C}	1.233	1.250	1.227	1.237	1.241	1.240	1.247	1.236
[Au–C ₂ H ₄] ⁺	<i>r</i> _{Au–C}	2.203	2.086	2.222	2.158	2.171	2.127	2.092	2.151
	<i>r</i> _{C–C}	1.396	1.408	1.383	1.396	1.401	1.404	1.410	1.399
[Au–C ₃ H ₄] ⁺	<i>r</i> _{Au–C1}	2.148	2.053	2.161	2.115	2.126	2.094	2.062	2.117
	<i>r</i> _{Au–C2}	2.246	2.096	2.303	2.181	2.186	2.113	2.073	2.158
	<i>r</i> _{C1–C2}	1.375	1.388	1.363	1.377	1.382	1.386	1.392	1.380

^a The best bond distances compared with reference CCSD(T)/CBS values are denoted in bold. ^b The CBS limit extrapolation was obtained according to eq 3 ($\beta = 2.2$), with the wDZ/DZ-wTZ/TZ basis on Au/C₂H. ^c The CBS limit extrapolation was obtained according to eq 3 ($\beta = 2.46$), with the wDZ/DZ-wTZ/TZ basis on Au/C₃H.

Table 6. *D_e* (kcal/mol) of AuCl–C₂H₂ Calculated from CCSD(T) with Various Valence Correlated Basis Sets and CBS Limit Extrapolations

	DZ	TZ	QZ	SZ	CBS ^a (DZ-TZ)	CBS ^a (TZ-QZ)	CBS ^b (QZ-SZ)
<i>D_e</i>	37.74	39.29	40.51	41.17	40.04	41.35	41.82
	ADZ	ATZ	AQZ	ASZ	CBS ^a (ADZ-ATZ)	CBS ^a (ATZ-AQZ)	CBS ^b (AQZ-ASZ)
<i>D_e</i>	39.48	40.87	41.40	41.61	41.66	41.76	41.82

^a Extrapolating to the CBS limit according to eqs 3 and 4. ^b Extrapolating to the CBS limit according to eqs 1 and 2.

including gold catalysis, overestimates Au–C bond lengths by about 0.031–0.088 Å. The M06 functional also overestimates the Au–C bond lengths by about 0.044–0.145 Å. It is noteworthy that the double-hybrid functional B2-PLYP produces the second lowest deviation among all tested functionals, with Au–C bond lengths overestimated by about 0.009–0.028 Å. Considering the basis set dependence of the double-hybrid functional (due to MP2 correlation component) compared with other functionals, B2-PLYP still has the potential to reach higher accuracy with a larger basis set than the used TZ basis set (see Table S4 in the SI for the trend of geometric change with increasing bases).

Performance of MP2 and SCSMP2. Geometric parameters obtained from the MP2/CBS level and SCSMP2/CBS level for the same naked Au(I) coordinate complexes are listed in Table 5. Compared with the CCSD(T)/CBS (wDZ-wTZ) reference values in Table 5, all Au–C bond lengths obtained with both MP2 and SCSMP2 are consistently shorter. Deviations of the Au–C bond lengths in these complexes are about –0.055 to –0.085 Å at the MP2/CBS level, while at the SCSMP2/CBS level, the deviations are significantly smaller, –0.023 to –0.045 Å, indicating the improvement of SCSMP2 over MP2.

3.2. Bond Dissociation Energies (*D_e*). We begin to discuss our extensive calibrations on AuCl–C₂H₂, for assessment of the accuracy of our adopted CCSD(T)/CBS procedure; then we show the results for all of the complexes at various ab initio and DFT levels.

Calibration with the AuCl–C₂H₂ Complex. Convergence of Valence-Correlated Basis Set. Table 6 summarizes these *D_e* results of AuCl–C₂H₂, calculated with CCSD(T) using the DZ-TZ-QZ-SZ and ADZ-ATZ-AQZ-ASZ basis sets, along with the corresponding CBS limit extrapolations.

It is seen that when the basis set quality improves, generally the *D_e* value increases, indicating that BSIE leads to underestimation

of *D_e*. Taking the highest-level CBS(AQZ-ASZ) value as a reference, it is clear that CBS extrapolation is absolutely necessary to overcome the BSIE problem, and the extrapolation improves the result even when it is performed from the low-end basis sets, such that the ADZ-ATZ extrapolation is better than the expensive ASZ *D_e* without CBS extrapolation, a situation that was frequently encountered in many previous high-level ab initio studies on various systems.^{109,118,119} It is noteworthy that the *D_e* value resulting from CBS(ADZ-ATZ) extrapolation (41.66 kcal/mol) is only 0.16 kcal/mol away from the CBS-(AQZ-ASZ) reference (41.82 kcal/mol), indicating a satisfactory balance between computational accuracy and the cost of the former approach. The beneficial effect of diffuse basis functions on *D_e* decreases along with the increasing quality of the valence basis set (1.74–1.58–0.89–0.44 kcal/mol along DZ–TZ–QZ–SZ series), which is understandable since the basis is becoming more complete and, hence, the role of the diffuse basis vanishes. The highest CBS(QZ-SZ) and CBS(AQZ-ASZ) values are identical to the second digit, which is a convincing indication that basis set convergence is achieved to a satisfactory level in the CBS extrapolation. At the double- ζ /triple- ζ CBS level, the effect of diffuse functions is still significant (1.62 kcal/mol). One interesting point is that if we add the *D_e* improvement from DZ to CBS(DZ-TZ) to the ADZ value, we get *D_e* = 41.78 kcal/mol, which is very close to the CBS(ADZ-ATZ) value (41.66 kcal/mol). This means we can use CBS(DZ-TZ) and ADZ single point, all of which are from a smaller basis set compared with ATZ, to get similar quality results of the CBS(ADZ-ATZ) value with a larger basis set. This CBS procedure could be very useful in those cases where diffuse functions are necessary but the ATZ calculation for large systems is prohibitively expensive in CBS extrapolation procedures.

Au 5s5p Correlation. Except for the valence correlation, we also explored the effects of Au 5s5p core–valence correlation

Table 7. Au 5s5p Core–Valence Correlation Corrections to D_e (kcal/mol) of AuCl–C₂H₂ from CCSD(T) with Different Basis Sets^a and CBS Limit Extrapolations

ΔD_e (AwDZ)	ΔD_e (AwTZ)	ΔD_e (AwQZ)	$\Delta D_e/\text{CBS}^b$ (AwDZ–AwTZ)	$\Delta D_e/\text{CBS}^b$ (AwTZ–AwQZ)
3.08	2.22	1.90	1.73	1.67
ΔD_e (wDZ)	ΔD_e (wTZ)	ΔD_e (wQZ)	$\Delta D_e/\text{CBS}^b$ (wDZ–wTZ)	$\Delta D_e/\text{CBS}^b$ (wTZ–wQZ)
2.68	2.05	1.81	1.70	1.64

^a (A)wXZ represents (A)wXZ/(A)XZ basis set on Au/Cl,C,H. ^b Extrapolating to the CBS limit with eqs 3, 4.

Table 8. CCSD(T)/CBS Calculated D_e (kcal/mol) of All Complexes, and Correction Components from Au–5s5p and Other Core–Valence Correlation Calculations

complex	D_e /ADZ	D_e /ATZ	$D_e/\text{CBS}_{\text{val}}$ (ADZ–ATZ) ^a	$\Delta D_e/\text{CBS}$ (5s5p) ^b	$\Delta D_e/\text{CBS}$ (CV) ^c	$D_e/\text{CBS}_{\text{final}}$ (CBS _{val} +5s5p+CV)
[Au–C ₂ H ₂] ⁺	51.84	53.19	53.91	2.61	–0.32	56.20
[Au–C ₂ H ₄] ⁺	60.36	62.30	63.34	2.91	–0.30	65.95
[Au–C ₃ H ₄] ⁺	61.29	62.90	63.73	3.05	–0.34	66.44
AuCl–C ₂ H ₂	39.48	40.87	41.66	1.70	–0.14	43.22
AuCl–C ₂ H ₄	43.95	46.00	47.14	1.75	–0.11	48.78
AuCl–C ₃ H ₄	44.26	45.79	46.65	1.86	–0.16	48.35
AuCl ₃ –C ₂ H ₂	28.37	28.68	29.08	0.56	–0.11	29.53
AuCl ₃ –C ₂ H ₄	38.80	39.21	39.78	0.71	–0.11	40.38
AuCl ₃ –C ₃ H ₄	37.51	37.54	37.88	0.70	–0.13	38.45
[AuNHC–C ₂ H ₂] ⁺	41.65	42.77	43.46	1.21	–0.17	44.50
[AuNHC–C ₂ H ₄] ⁺	45.00	46.55	47.47	1.25	–0.15	48.57
[AuNHC–C ₃ H ₄] ⁺	45.36	46.58	47.31	1.30	–0.19	48.42
[AuPH ₃ –C ₂ H ₂] ⁺	41.60	42.71	43.37	1.22	–0.10	44.49
[AuPH ₃ –C ₂ H ₄] ⁺	45.79	47.14	47.95	1.28	–0.06	49.17
[AuPH ₃ –C ₃ H ₄] ⁺	46.14	47.37	48.09	1.32	–0.09	49.32

^a The CBS_{val} limit was extrapolated from the CCSD(T) valence correlation calculated with the ADZ and ATZ basis sets. ^b Correction of the Au 5s5p core–valence correlation from the CCSD(T) CBS extrapolation with the wDZ/DZ and wTZ/TZ basis sets on Au/Cl,P,C,H,N. ^c Correction of the core–valence correlation of non-hydrogen main group elements (C, N, Cl, P) obtained from CCSD(T) CBS extrapolation with wDZ/DZ and wTZ/TZ basis sets on Au,C,N,Cl,P/H.

systematically with wXZ/XZ (X = D, T, Q) basis sets for Au/Cl, C,H atoms, as well as corresponding diffuse function augmented basis sets. The calculated ΔD_e 's due to the Au 5s5p core–valence correlation with the CCSD(T) method are summarized in Table 7.

First, it is seen that the Au 5s5p core–valence correlation effect computed at all levels consistently increases the D_e values. Second, the Au 5s5p core–valence correlation correction to D_e decreases with the increase in basis set quality. This is in line with the previous computational observation on the Au 5s5p correlation effect.⁷⁵ Last, we note that even though the AwDZ basis set generates a somewhat different ΔD_e value compared with the wDZ basis set, the $\Delta D_e/\text{CBS}$ values of two basis-set series, with and without diffuse basis functions, are quite close (within 0.03 kcal/mol). This result demonstrates that it is not necessary to use a much larger AwXZ basis instead of a wXZ basis to compute the Au 5s5p core–valence correlation effect. In addition, the wDZ–wTZ CBS limit is just 0.06 kcal/mol away from the reference wTZ–wQZ CBS limit, indicating that the wDZ–wTZ CBS limit is already sufficiently accurate.

More Au–C₂H₂/C₂H₄/C₃H₄ Complexes. CCSD(T)/CBS Reference Results. The calibration of the AuCl–C₂H₂ complex led to an appropriate general scheme to calculate the D_e values for other complexes. Table 8 summarizes these D_e values, calculated at the CCSD(T)/CBS_{final} level according to eq 5, in which we also

added the non-Au core–valence correlation correction ΔD_e –(CV)/CBS with wDZ/DZ–wTZ/TZ (basis set on Au,C,N,Cl,P/H) CBS limit extrapolation to reach higher accuracy. Although the magnitudes of the ΔD_e (CV) contributions are small, applying CBS limit extrapolation for this correction can change its signs from all positive at the CCSD(T)/DZ level to all negative, as those in Table 8.

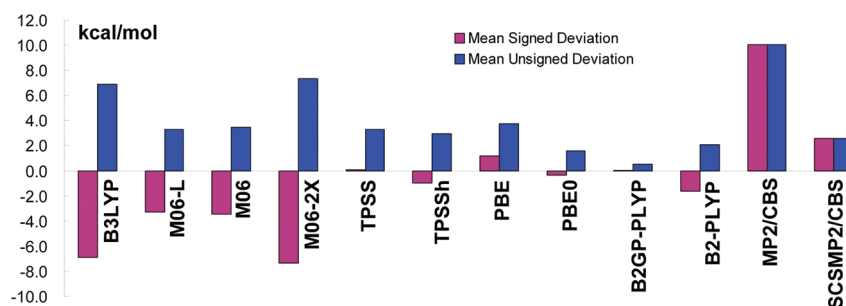
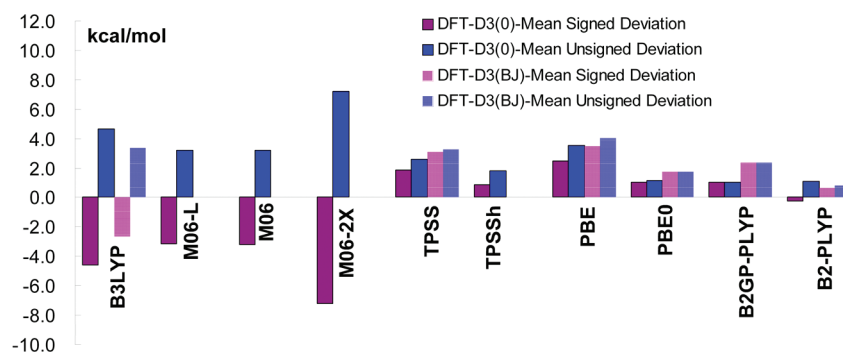
Inspecting the D_e/CBS (5s5p) values in Table 8, it is seen that the Au 5s5p core–valence correlation correction ΔD_e values for Au^{III}Cl₃–C_nH_m are smaller than for the other Au^IL_x–C_nH_m complexes. Just as found above for the group of naked Au^I complexes, the valence correlation extrapolation to the CBS limit is absolutely necessary because the improvements from the ATZ results to the CBS(ADZ–ATZ) limit are usually up to about 1 kcal/mol. Again, the Au^{III}Cl₃–C_nH_m complexes are different from other complexes due to their apparently smaller improvements (0.34–0.57 vs 0.66–1.14 kcal/mol) from the ATZ results to the ADZ–ATZ CBS limit.

Considering the CCSD(T)/CBS_{final} values, the D_e 's for the naked Au^I complexes [Au–C_nH_m]⁺ are the largest among the studied complexes, while the AuCl₃–C_nH_m species have the smallest D_e values. For the complexes with other ligands like AuCl–C_nH_m, [AuNHC–C_nH_m]⁺, and [AuPH₃–C_nH_m]⁺, the variations of the D_e values for the same unsaturated hydrocarbon substrate are no more than about 1 kcal/mol. Concerning the

Table 9. Mean Signed (S) and Unsigned (U) Deviations of Various DFT Methods without and with DFT-D3 Dispersion Corrections from CCSD(T)/CBS_{final}^a

		B3LYP	M06-L	M06	M06-2X	TPSS	TPSSH	PBE	PBE0	B2GP-PLYP	B2-PLYP
without DFT-D3	U	6.91	3.31	3.48	7.33	3.31	2.97	3.72	1.60	0.52	2.07
	S	−6.91	−3.31	−3.48	−7.33	0.10	−0.97	1.22	−0.36	0.05	−1.61
DFT-D3(0) ^b	U	4.71	3.21	3.25	7.25	2.56	1.85	3.52	1.14	0.99	1.08
	S	−4.61	−3.21	−3.25	−7.25	1.83	0.80	2.41	1.00	0.99	−0.30
DFT-D3(BJ) ^c	U	3.36	— ^d	— ^d	— ^d	3.22	— ^e	3.97	1.74	2.35	0.77
	S	−2.69	— ^d	— ^d	— ^d	3.04	— ^e	3.42	1.74	2.35	0.59

^a The smallest three mean unsigned deviations of each set are denoted in bold. ^b Using zero-damping in DFT-D3. ^c Using Becke–Johnson (BJ) damping in DFT-D3. ^d There are no BJ parameters for the M06 series of functionals. ^e Currently, the BJ parameters of TPSSH could have some problem, see ref 120; thus these data are omitted.

**Figure 1.** Mean signed and unsigned deviations of calculated D_e with various DFT/ATZ and ab initio (CBS_{final}) methods taking CCSD(T)/CBS_{final} as a reference.**Figure 2.** Mean signed and unsigned deviations of calculated D_e with various DFT-D3/ATZ methods taking CCSD(T)/CBS_{final} as a reference.

comparison between different C_nH_m 's within one AuL_x , the D_e of C_2H_2 is apparently and consistently smaller than those of C_2H_4 and C_3H_6 , which is in line with previous theoretical calculations favoring the Au–alkene over the Au–alkyne interaction thermodynamically,²⁰ while the difference of D_e between the latter two is usually quite small, except for $AuCl_3$ systems.

In summary of our ab initio treatment of D_e of Au complexes, we note the following:

- ADZ-ATZ CBS is necessary and sufficient for good accuracy (within about 0.2 kcal/mol from (A)QZ-(A)SZ CBS value). Note that diffuse functions are still important at this level (having about a 1–2 kcal/mol effect on D_e).
- Au-5s5p core–valence correlation is important (up to about 3 kcal/mol), and DZ-TZ CBS limit extrapolation is necessary to get the converged values. Here, diffuse functions are not important.

- Non-Au core–valence correlation is not very important (within −0.34 kcal/mol).

Performance of Various DFT Methods. The CCSD(T)/CBS_{final} values of D_e can serve as a benchmark for testing the various DFT functionals, with an aim of hopefully finding one or more that are uniformly better than others for these problems.

For the DFT data of each of the complexes, see Table S6 and S7 in the SI. Table 9 summarizes the statistical analysis of the mean signed/unsigned deviations of various DFT methods without and with dispersion corrections. These deviations are also shown schematically in Figures 1 and 2, where Figure 1 shows also the performance of two tested ab initio methods.

From the D_e values in Table 9 and Figure 1, we find that ranking of the tested functionals without dispersion corrections, in order of increasing mean unsigned deviation, is B2GP-PLYP < PBE0 < B2-PLYP < SCSMP2 < TPSSH < TPSS ≈ M06-L < M06 < PBE < B3LYP < M06-2X < MP2. So it can be seen that good

geometric performances of DFT methods correlate with their good energetic performances. In all of the tested methods, B2GP-PLYP provides the best results compared with CCSD-(T)/CBS_{final}, with the maximal deviation of 1.14 kcal/mol, and a very small mean signed/unsigned deviation of 0.05/0.52 kcal/mol. For this set of Au complexes, B2GP-PLYP, which is a reparametrized B2-PLYP, outperforms its parent. The second best one is PBE0, which is best among all of the tested (hybrid)-(meta)-GGA functionals, with a maximal deviation of -3.79 kcal/mol and a small mean signed/unsigned deviation of -0.36/1.60 kcal/mol. The third best one is B2-PLYP, with a maximal deviation of -3.75 kcal/mol and a small mean signed/unsigned deviation of -1.61/2.07 kcal/mol. The popular B3LYP functional produces the second largest deviations in all tested DFT, with a maximal deviation of -12.49 kcal/mol and mean signed/unsigned deviations of -6.91/6.91 kcal/mol. It is interesting to note that B3LYP, M06-L, M06, and M06-2X consistently underestimate D_e (thus have signed/unsigned deviations of exactly same magnitude but opposite sign), while other tested functionals do not behave similarly. M06-2X performs much worse than the other two in the M06 series, which indicates that a high ratio of exact exchange is not beneficial in these Au complexes of late transition metals.

After adding the DFT-D3 dispersion correction, as shown in Table 9 and Figure 2, the deviations of some tested functionals were consistently reduced, with considerable improvement for B3LYP and B2-PLYP. As found before,^{92,121} the results of the M06 series functionals are almost not affected by adding dispersion corrections. For some tested density functionals, like TPSS, PBE, and PBE0, DFT-D3 corrections do not uniformly improve the results. DFT-D3(0) with zero short-range damping improves the results of TPSS, PBE, and PBE0, while DFT-D3(BJ) with BJ-damping does not. For B2GP-PLYP, both DFT-D3 corrections turn out to spoil an already good performance. After and before DFT-D3 corrections, the best three functionals remain to be PBE0, B2GP-PLYP, and B2P-PLYP, where the first rank depends on the dispersion correction scheme, B2GP-PLYP (no dispersion correction and DFT-D3(0) correction) or B2-PLYP (DFT-D3(BJ) correction).

Performance of MP2 and SCSMP2. As shown in Table 9 and Figure 1, the D_e values obtained at the MP2/CBS_{final} and SCSMP2/CBS_{final} levels are all overestimated compared to the reference values at the CCSD(T)/CBS_{final} level. Especially poor is the MP2/CBS method, which has the largest mean deviation (10.08 kcal/mol) and largest maximal deviation (14.41 kcal/mol) of D_e among all of the tested methods. SCSMP2 significantly reduced the mean deviation to about 2.6 kcal/mol, and the maximal deviation to about 5.3 kcal/mol, but its performance compared with many tested DFT methods is still not impressive, especially considering that it is more computationally costly than most DFT approaches.

4. CONCLUSIONS

We have systematically studied herein the geometries and bond dissociation energies (D_e) of typical AuL_x-C_nH_m complexes (Scheme 1) by employing ab initio coupled cluster, MP2, SCSMP2, and DFT (B3LYP, LSDA, M06, M06L, M06-2X, PBE, PBE0, TPSS, TPSSh, B2-PLYP, and B2GP-PLYP) calculations. Our reference CCSD(T) calculations include the calibrated valence correlation complete basis set (CBS) extrapolation and core-valence correlation corrections, which are shown to be

important for the achievement of high accuracy. For geometry optimization, the best tested DFT method is the hybrid GGA PBE0 followed by the double hybrid B2-PLYP. Unlike LSDA, the extraordinary performance of PBE0 in geometry conforms to the previous calibration on 5d transition metal complexes.⁹³ For D_e , the most accurate DFT methods are the two double-hybrid functionals B2-PLYP and B2GP-PLYP, with ranking order depending on whether one does or does not add dispersion correction and the particular scheme thereof (D3(0) or D3(BJ)). With or without DFT dispersion correction, the smallest mean unassigned deviations of these two double-hybrid methods are all within about 1 kcal/mol. The largest unassigned deviations for them are about 1–3 kcal/mol. Within the tested GGA or hybrid GGA, PBE0 is again the best one, with performance which is just slightly worse than that of the best of the two double hybrids with DFT-D3(0). Thus, the good geometric performance is found to correlate with good energetics of DFT methods in this study. B3LYP is significantly improved by dispersion corrections, but it is still outperformed by PBE0. DFT-D3 dispersion does not yield a uniform improvement for all of the functionals we tested here. For both geometry and D_e , MP2 significantly underestimates/overestimates Au–C bond lengths/ D_e , which is in the opposite direction of most tested DFT functionals like B3LYP. SCSMP2 greatly alleviates the poor performance of MP2, but it is not better than the best performing DFT methods for these Au complexes. All in all, the double-hybrid functionals tested in this study showed very promising performance on these Au(I)/Au(III) complexes with unsaturated molecules.

In general, our recommended cost-effective methods for Au-unsaturated hydrocarbon complexes are three functionals: two double hybrids, B2GP-PLYP and B2-PLYP, and one hybrid GGA, PBE0. It would be interesting to know whether these functionals can keep their good performance in theoretical studies of homogeneous gold-catalyzed reactions, and whether there exist alternative optimal functionals. These studies are underway in our group.

■ ASSOCIATED CONTENT

S Supporting Information. Nine tables and Cartesian coordinates of the studied complexes used in D_e calculations. 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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