Performance of Density Functional Theory and Relativistic Effective Core Potential for Ru-Based Organometallic Complexes

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Supporting Information

ABSTRACT: Herein a performance assessment of density functionals used for calculating the structural and energetic parameters of bimetallic Ru-containing organometallic complexes has been performed. The performance of four popular relativistic effective core potentials (RECPs) has also been assessed. On the basis of the calculated results, the MN12-SX (range-separated hybrid functional) demonstrates good performance for calculating the molecular structures, while MN12-L (local functional) performs well for calculating the energetics, including that of the Ru–Ru bond breaking process. The choice of appropriate density functional is a crucial factor for calculating the energetics. The LANL08 demonstrates the lowest performance of the RECPs for calculating the molecular structures, especially the Ru–Ru bond length.

INTRODUCTION

In recent decades, Ru-based organometallic complexes have attracted special attention from researchers due to their applications in catalysis and dye-sensitized solar cells (DSSCs).1–5 In addition, Ru–carbonyl clusters such as Ru_4(CO)_12 are of interest because of their catalytic properties and as a precursor for the synthesis of organometallic complexes containing Ru–Ru bonds.6 Their properties are directly related to the Ru–Ru interactions, and consequently on the Ru–Ru bond length and Ru–Ru bond energy. The Ru–Ru bond length is readily measured by X-ray crystallography, but measuring the Ru–Ru bond energy is a more difficult task. Theoretical predictions of the molecular properties of organometallic complexes are usually performed using density functional theory (DFT) because of its robustness with a low computational cost.7–14 However, different exchange-correlation functionals can give varying results, creating difficulty when studying these complexes. Therefore, the benchmark studies of exchange-correlation functionals used for calculating the molecular properties of the organometallic complexes have been extensively studied. Most of these studies considered small complexes containing only one transition metal. However, a benchmark study of exchange-correlation functionals for bi- or trimetallic compounds is still lacking. Narendrapurapu et al. investigated the performance of DFT functionals of metal–metal and metal–carbon bond distances in carbonyl complexes of first-row transition metals carbonyl complexes (e.g., Mn_2(CO)_{10}) with the all-electron correlation-consistent (cc) basis sets; the M06-L functional worked well for predicting metal–metal bond distances.12 This kind of study should be expanded to second-row transition metal complexes containing metal–metal bonds. Recent systematic studies for assessing the performance of the DFT functional to predict the molecular structure of two Ru-containing organometallic complexes are reported.15–17 However, the compounds in these studies contain the bridged oxygen between two Ru atoms; the extension of their results to bi- and trimetallic compounds, which has a Ru–Ru bond, is still questionable.

Recently, Laury and Wilson assessed the performance of 22 density functionals combined with the relativistic effective core potential (RECP) for studying small complexes of second-row transition metals complexes.18 They suggested that the double-hybrid functionals that mix the second-order Möller–Plesset perturbation theory (MP2), B2GP-PLYP and mPW2-PLYP, performed well for calculating the enthalpies of formation when compared with experimental data. However, using double-hybrid functionals for studying organometallic complexes can be questionable due to their expensive computation time than other DFT functionals. Therefore, using these methods is limited to only small transition metal complexes. Hence it is necessary to find a suitable DFT functional with lower computational cost to study these organometallic systems.

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Additionally, in the bi- or trimetallic system, the near-degeneracy effect is not negligible. Therefore, in principle, a multireference-based method is needed to calculate the molecular properties; however, using that method is practically impossible for bi- or trimetallic complexes with large ligands. Therefore, using DFT methods is essential, which makes finding suitable exchange-correlation functionals necessary.

Most benchmark studies have been focused on assessing the performance of exchange-correlation functionals for calculating the molecular properties. Since Ru is a heavy element, considering relativistic effects is also crucial for predicting the molecular properties of its complexes. The scalar relativistic effect can be readily considered using RECP, and various RECPs are available for Ru. Therefore, the calculation of molecular properties of Ru-containing organometallic complexes can be performed using a robust combination of exchange-correlation functionals with RECPs.

In the present study, we performed systematic assessment of DFT functionals combined with four popular RECPs for predicting the Ru−Ru, Ru−C, Ru−N, and Ru−S bond lengths and additionally for calculating the energetics of Ru-containing organometallic complexes. A total of 80 models of chemistry (= 20 exchange-correlation functionals × 4 RECPs) are examined in this work. To the best of our knowledge, this is the first assessment of the performance of RECPs for calculating the molecular properties of Ru-containing organometallic complexes. This work will provide a reference for further development of new exchange-correlation functionals and guidance for selecting a reasonable combination of exchange-correlation functional and RECP.

## COMPUTATIONAL DETAILS

The molecular structures of the Ru containing organometallic complexes were optimized using 20 exchange-correlation functionals, BLYP,18,19 BP86,18,20 BPW91,18,21 BE,22,23 N12,24 M06-L,25 M11-L,26 TPSS,27 MN12-L,28 B3LYP,19,29 B3PW91,20,29 B3LYP91,21,29 PBE0,30 M06,31 TPSSh,32 ωB97X,33 ωB97XD,34 M11,35 N12-SX,36 and MN12-SX.36 The harmonic vibrational frequency calculations were performed to identify the minimum energy structure. For all atoms except Ru, the second generation default bases and triple-ζ valence with heavily polarized basis functions (def2-TZVPP) were used. The validation of def2-TZVPP basis sets for the main group atoms (C and O) in the CCSD(T) calculations, respectively. All DFT and CCSD(T) calculations were performed using the Gaussian09 program.40

### RESULTS AND DISCUSSION

#### A. Bond Lengths

Six molecules, Ru2, Ru(CO)5, Ru3(CO)12, [Ru2(CO)6(μ-SCH2CH2S)], [Ru(bpy)(CO)2(COOCH3)]2, and trans-[Cp2Ru2(CO)4], were optimized using 20 DFT functionals with four RECPs (total of 80 models of chemistry), and their molecular structures are shown in Figure 1. Figure 1 shows that all the molecules except Ru(CO)5 contain Ru−Ru bonds. In addition, [Ru(bpy)(CO)2(COOCH3)]2 contains the bipyridine (bpy) ligand that is often used for the design of an efficient DSSC.41,42 The Ru−S bond is also important due to the recent demonstration of the cc-pVTZ-PP (ECP28MDF); the valence basis set of the dhf-TZVPP is reoptimized using the segmented contraction. Therefore, the performance of the dhf-TZVPP may be almost equivalent to that of the cc-pVTZ-PP.

The single-point energy calculations were performed using the coupled-cluster singles and doubles, including the perturbative corrections for triple excitations, CCSD(T) for CO, Ru(CO)5, Ru(CO)3, and Ru3(CO)12 molecules to examine accurate energetics. The CCSD(T) calculations were performed on the optimized structure using MN12-SX/dhf-TZVPP because it gave the smallest mean absolute deviation (MAD) for the Ru−Ru bond lengths. The dhf-TZVPP and def2-TZVPP were used for Ru and main group atoms (C and O) in the CCSD(T) calculations, respectively. All DFT and CCSD(T) calculations were performed using the Gaussian09 program.40

Figure 1. Optimized molecular structures of Ru contained complexes (a) Ru2, (b) Ru(CO)5, (c) Ru3(CO)12, (d) [Ru2(CO)6(μ-SCH2CH2S)], (e) [Ru(bpy)(CO)2(COOCH3)]2, and (f) trans-[Cp2Ru2(CO)4].

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photoisomerization of the Ru–S bond containing organometallic complexes. In summary, the molecules examined in this study are structurally similar to recently popular organometallic complexes. Since all the molecules except Ru₂ have been well characterized by X-ray crystallography, the calculated bond lengths can be readily compared with those of experimental values. For Ru₂, the result of recent high-level ab initio calculations (the second-order multiconfigurational perturbation theory, CASPT2) has been considered as a reference value. The optimized geometrical parameters of the molecular structures are summarized in Tables S2–S7 in the Supporting Information. We have considered 31 bond lengths, including Ru–Ru (5 bonds), Ru–C (17 bonds), Ru–S (1 bond), and Ru–N (8 bonds) for assessing the performance of DFT functionals in this study. The mean absolute deviations (MADs) of the Ru–X (X = C, N, and S), Ru–Ru, and all bond lengths, with respect to the respective experimental values, are shown in Figure 2a, 2b, and 2c, respectively. For clarity the MADs of the Ru–Ru and Ru–X (X = C, N, and S) were split between the figures due to the significance of the Ru–Ru bond of the organometallic complexes.

First, the scales of the vertical axes in Figure 2a and 2b are evidently different; the MADs of the Ru–Ru bonds are much larger than those of the Ru–X bonds. This result clearly demonstrates the error source of all bond lengths (see Figure 2c) originates from the Ru–Ru bond length. This implies that theoretical description of the Ru–Ru bond of organometallic complexes is a difficult task. As seen in Figure 2c, the BLYP shows the worst performance in calculating the bond lengths; it seriously overestimates the Ru–Ru and the Ru–X bond lengths (see Tables S2–S7 in the Supporting Information). Therefore, it is strongly not recommended for calculating the molecular structures of Ru-containing organometallic complexes. The B3LYP, a hybrid version of BLYP, also gives poor performance. This is demonstrated by an overestimation of the Ru–Ru bond lengths, shown in Figure 2b and Tables S2–S7 in the Supporting Information. Additionally, B3LYP gave the poorest results of the Ru–Ru bond lengths among the hybrid DFT functionals. Although the B3LYP is the most popular DFT functional, the results calculated by B3LYP are not promising. Caution should therefore be exercised when using B3LYP for the Ru–Ru bonds containing organometallic complexes. As shown in Figure 2b, the new Minnesota hybrid functionals (M11, N12-SX, and MN12-SX) show good results for the Ru–Ru bond lengths. Especially, M11 and MN12-SX, which give the smallest MAD of the Ru–Ru bond lengths. The MADs of the Ru–Ru bond lengths calculated using the ωB97X and ωB97XD functionals are slightly larger than those of new Minnesota hybrid functionals. The MADs of ωB97X and ωB97XD in Figure 2a show that the inclusion of the empirical dispersion interaction improves the description of the Ru–X bond lengths slightly. However, the same effect is not observed on the Ru–Ru bond length (see Figure 2b), indicating that the dispersion interaction on the Ru–Ru bond is negligible.

Figure 2b shows that hybrid functionals are in general slightly better than their counterpart, generalized gradient approximation (GGA) or meta-GGA functionals, according to the small MAD (e.g., PBE vs PBE0). As shown in Tables S4–S7 in the Supporting Information, the hybrid functionals predict shorter Ru–Ru bond lengths than those calculated by their counterpart GGA or meta-GGA functionals, leading to the smaller MAD value. It is well-known that the Hartree–Fock (HF) method tends to underestimate the bond lengths of molecular structures. Therefore, mixing some amount of HF exchange (i.e., hybrid functional) also tends to give a shorter bond length. Similar results can be found in recent theoretical investigations on Ru₂ and Os₂.

Figure 2 demonstrates the LANL08 RECP has poor performance for calculating the structural parameters; LANL08 overestimates all bond lengths compared with the reference values (see Tables S2–S7 in the Supporting Information). This observation correlates with the results of the recent study on the performance of DFT and MP2 methods for determining the structural parameters of Ru-containing organometallic complexes. This study showed that
LANL2DZ RECP was inadequate for predicting the structural parameters. It is noteworthy that the pseudo-potential part of LANL08 is the same as that of LANL2DZ. Therefore, the LANL08 performance is similar to LANL2DZ. In addition, LANL2DZ shows poor performance in calculating the bond lengths and vibrational frequencies of MX (M = Zn, Cd; X = S, Se, Te) quantum systems. According to these results, LANL08 (and LANL2DZ) is not recommended for calculating the structural parameters of organometallic complexes. Other RECPs give similar results; no RECP gave a remarkably small MAD. In summary, with the exception of LANL08, recently developed Minnesota functionals with RECPs (especially MN12-SX) are recommended for predicting the molecular structure of Ru-containing organometallic complexes.

B. Energetics. The performance of exchange-correlation functionals for calculating the energetics of Ru-containing organometallic complexes was assessed. The experimental bond dissociation energy (BDE) of Ru–CO in Ru(CO)$_3$ was selected as the reference value. To the best of our knowledge the BDE of the Ru–Ru bond is not available in the literature, with the exception of Ru$_2$ (see ref 50, references therein). However, we replace the experimental value of BDE of Ru$_2$ as the recent multireference configuration interaction including the Davidson correction (MRCI+Q) result because of the discrepancy (see ref 50 for the details). To circumvent the lack of experimental data for the BDE of the Ru–Ru bond, we calculate the reaction energies for two reactions (eqs 1 and 2) using the high-level CCSD(T) method (CCSD(T)/dihf-TZVPP//MN12-SX/dhf-TZVPP). It should be noted that some DFT functionals are more accurate than CCSD(T) for calculating the dissociation energy of 3d transition metal containing diatomic molecules. However, Ru is a 4d transition metal and Ru$_5$(CO)$_{12}$, Ru(CO)$_3$, and Ru(CO)$_4$ in eqs 1 and 2 are well described by a single reference method. For example, the BDE ($D_0$) of Ru(CO)$_5$ (Ru(CO)$_5$ $\rightarrow$ Ru(CO)$_4$ + CO) calculated by CCSD(T)/dihf-TZVPP//MN12-SX/dhf-TZVPP (ZPEs calculated by MN12-SX/dhf-TZVPP are used) is 28.6 kcal/mol, which is very close to the experimental value (27.6 ± 0.4 kcal/mol; see Table S3 in the Supporting Information) even if it is obtained by single-point calculations. Therefore, it is readily expected that reaction energies of eqs 1 and 2 calculated by CCSD(T)/dihf-TZVPP//MN12-SX/dhf-TZVPP will be reasonably close to the true values.

\[
\text{Ru}_5\text{(CO)}_{12} + 3\text{CO} \rightarrow 3\text{Ru(CO)}_5 \tag{1}
\]

\[
\text{Ru}_3\text{(CO)}_{12} \rightarrow 3\text{Ru(CO)}_4 \tag{2}
\]

As these two reactions include the Ru–Ru bond breaking process, they can serve as a model to estimate the BDE of the Ru–Ru bond. The four energy values (BDE of the Ru–CO in Ru(CO)$_3$, BDE of Ru$_2$, reaction energies of eqs 1 and 2) are considered the reference values for assessing exchange-correlation functionals. The four calculated energy values are summarized in Tables S2, S3, and S8 in the Supporting Information, and the calculated MADs with respect to the reference values are shown in Figure 3. Figure 3a and 3b show the MADs of three (excluding the BDE of the Ru–CO bond in Ru(CO)$_3$ from four energetic values) and four energetic values, respectively. First, the difference between Figure 3a and 3b shows that the large deviation originates from the energetics of the Ru–Ru bond. Therefore, the following discussion will focus on the results in Figure 3a, with the energetics of the Ru–Ru bond. As can be seen from Figure 3a, all DFT functionals except M06-L and MN12-L show large deviations from the reference values. Especially, N12, which shows almost 40 kcal/mol deviation. The MN12-L, a recently developed local DFT functional, demonstrates the best performance for the energetics, with M06-L closely following it. However, although N12 and M11-L are also recently developed local DFT functionals they demonstrate a large deviation. Especially the MAD of N12 is comparable with that of BLYP. These results indicate that local DFT functionals cannot guarantee good performance for calculating the energetics; therefore, selecting the DFT functional itself is crucial. Including the exact exchange energy slightly reduces the MAD. However, the MAD of M11 is still comparable with that of M06-L. Therefore, the M11 family functional is not recommended for calculating the energetics of Ru-containing organometallic complexes. The variation between ωB97X and ωB97XD indicates that including empirical dispersion will slightly improve the prediction of energetic values; however, it is hardly noticeable.

On the basis of the results in Figure 3a, calculating of the energetics of the Ru–Ru bond by DFT is still a difficult task. The deviations in M06-L and MN12-L are smaller than those in other exchange-correlation functionals, but they are still close to
10 kcal/mol. In addition, both M06-L and MN12-L predict the ground state of Ru$_2$ as $^7\Delta_g$ instead of the $^7\Sigma^+_g$ state (see Table S2 in the Supporting Information), although high-level multireference ab initio calculations such as CASPT2 and MRCI+Q have predicted the $^7\Sigma^+_g$ state as the ground state. Table S8 shows that CCSD(T) predicts reaction 1 as endothermic. However, there is no DFT functional to predict reaction 1 as endothermic. Therefore, development of a new exchange-correlation functional giving improved energetics for the Ru–Ru bond breaking process is necessary. One should be careful to select the exchange-correlation functional for calculating the energetics, in particular, the process involving the Ru–Ru bond breaking. We recommend the MN12-L functional for calculating the energetics of the Ru–Ru bond containing organometallic complexes.

Contrary to bond length calculations, LANL08 does not show poor performance when calculating the bond energy. In the calculations with local DFT functionals, LANL08 generally shows the smallest MAD. However, in the calculations with hybrid DFT functionals, the situation is generally opposite; LANL08 shows the largest MAD. In addition, MN12-L with LANL08 shows the smallest MAD, but M06-L with LANL08 shows the largest MAD. A similar situation takes place in the calculations with the de2-TZVPP; generally, the de2-TZVPP shows the largest and smallest MADs, respectively. Therefore, in energetic calculations, the type of RECP is not a crucial factor, whereas the type of DFT functional is crucial for calculating the energetics of Ru-containing organometallic complexes.

**CONCLUSIONS**

The performance of DFT functionals for calculating the structural and energy parameters of bi- and trimetallic Ru-containing organometallic complexes has been investigated. The DFT functionals examined in this study range from GGA to hybrid meta-GGA functionals, along with recently developed Minnesota functionals. In addition, the performance of four popular RECPs has been assessed. Thereby, a total 80 models of chemistry were considered in this work. The recently developed MN12-SX functional performs well for predicting the structural parameters. For energy parameters, including that of the Ru–Ru breaking process, the local DFT functional MN12-L shows the smallest MAD. The M06-L also shows good performance for calculating energy parameters. The LANL08 is the lowest performing RECP for calculating the molecular structures. This result correlates with previous studies. However, all RECPs show similar performance in calculating energetics of the Ru containing organometallic complexes; therefore, when calculating energetics, choosing an appropriate DFT functional is crucial. Although the MN12-L gives the best performance for calculating the energetics, the MAD is over 5 kcal/mol. Therefore, further development of exchange-correlation functionals is necessary and this work should be referenced for that purpose.

**ASSOCIATED CONTENT**

- Supporting Information
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