

# Performance of Density Functional Theory and Møller–Plesset Second-Order Perturbation Theory for Structural Parameters in Complexes of Ru

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**S** Supporting Information

**ABSTRACT:** We assess the performance of density functional theory (DFT) and Møller–Plesset second-order perturbation theory (MP2) for predicting structural parameters in Ru complexes, in particular, a Ru(IV) allyl dicationic complex with the formula  $[\text{Ru}(\eta^5\text{-Cp}^*)(\eta^3\text{-CH}_2\text{CHCHC}_6\text{H}_5)(\text{NCCH}_3)_2]^{2+}$  and the molecules  $\text{RuO}_4$  and  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ , where  $\text{Cp}^*$  denotes  $\text{C}_5\text{Me}_5$  and Me denotes methyl. The density functionals studied are B3LYP, B3PW91, M05, M06, M06-L, MOHLYP, MPW3LYP, PBE0, PW6B95, SOGGA,  $\tau\text{HCTHhyb}$ ,  $\omega\text{B97X}$ , and  $\omega\text{B97X-D}$ , in combination with three different basis sets, namely, LANL2DZ, def2-SVP, and def2-TZVP. The theoretically computed Ru–C distances corresponding to the phenylallyl complex are especially well predicted by the SOGGA (pure DFT) and  $\omega\text{B97X-D}$  (DFT plus an empirical molecular mechanics term) methods. This contrasts with an article in this Journal [Calhorda, M. J.; Pregosin, P. S.; Veiros, L. F. *J. Chem. Theory Comput.* **2007**, 3, 665–670] in which it was found that DFT cannot account for these Ru–C distances. Averaging over four Ru–C distances in the allyl complex and three unique Ru–O distances in  $\text{RuO}_4$  and  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ , the SOGGA and  $\omega\text{B97X-D}$  methods have both a smaller mean unsigned error than MP2 and the same maximum error. The M06, PW6B95, PBE0, M06-L, and  $\omega\text{B97X}$  density functionals also have a smaller or the same mean unsigned error as MP2.

## INTRODUCTION

The organometallic chemistry of ruthenium is very interesting from both synthetic and theoretical points of view. Ruthenium catalysts are used in a wide range of applications including hydroamination,<sup>1</sup> metathesis,<sup>2</sup> hydrogenation,<sup>3</sup> selective transformation of alkynes,<sup>4</sup> and allylic alkylation.<sup>5</sup> Quantum chemical modeling of such catalytic systems is a key step in the rational design and understanding of the detailed mechanisms of catalytic processes. The large size of catalytic systems makes their study with reliable wave function theory (WFT) difficult. Density functional theory (DFT) offers an affordable and efficient alternative if one uses an accurate enough exchange–correlation functional and a suitable large basis set.

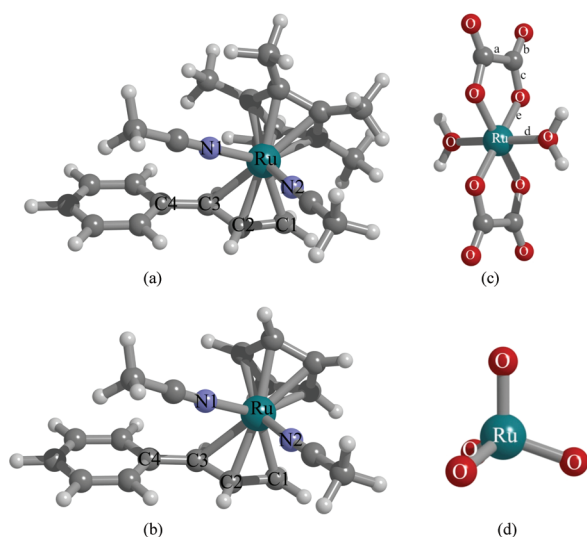
Fomine et al.<sup>6</sup> performed DFT studies on ruthenium-alkylidene-mediated metathesis of various olefins using a variety of functionals, in particular, B3LYP,<sup>7</sup> M05,<sup>8</sup> and PBE0,<sup>9</sup> and they discussed stereoselectivity and the steric effect on activation energy. Mathew et al.<sup>10</sup> used B3LYP to study the structural and energetic features of decomposition pathways of a Grubbs second-generation olefin metathesis catalyst. Occhipinti et al.<sup>11</sup> studied various Ru–L bonds in  $\text{L}-(\text{PCy}_3)_2\text{Ru}=\text{CH}_2$  complexes, where L is a dative ligand. Noncovalent interactions in a Ru-triphenyl phosphine complex were studied by Sieffert and Büehl<sup>12</sup> using the B3LYP, BP86,<sup>13</sup> B3LYP-D,<sup>14</sup> B97-D,<sup>15</sup> M05,<sup>8</sup> M05-2X,<sup>16</sup> M06-L,<sup>17</sup> M06-HF,<sup>18</sup> and M06-2X<sup>19</sup> functionals. According to their study, B97-D, M06-HF, M06-L, M06, and M06-2X produce the best agreement with the experimental<sup>20</sup> binding enthalpies. Piacenza et al.<sup>21</sup> assessed the performance of the B3LYP, BP86, B97-D, TPSSH,<sup>22</sup> and B2-PLYP<sup>23</sup> functionals

for ruthenium-catalyzed olefin metathesis. The popular B3LYP has the largest overall error. Tsepis et al.<sup>24</sup> and Zhao and one of the authors<sup>25,26</sup> also applied DFT to ruthenium olefin catalysts, and M06-L and M06 were found to perform better than older functionals such as BP86, B3LYP, and TPSSH. Pandian et al.<sup>27</sup> found the M06 functional to be useful for studying ruthenium-catalyzed ring-closing metathesis. Diesendruck et al.<sup>28</sup> showed how BP86 and M06-L calculations can predict the configuration of chelated ruthenium complexes. Sliwa and Handzlik<sup>29</sup> evaluated 31 different density functionals for reaction energies of model Grubbs-type ruthenium complexes and found the best performance with M06 and  $\omega\text{B97X-D}$ . They also examined 20 density functionals for reproduction of the  $\text{PCy}_3$  dissociation energy of a Grubbs catalyst and found the best performance with M06-L, M06, and M06-2X. Dutta et al.<sup>30</sup> studied reactions of alkynes with cyclopentadienyl-ruthenium half-sandwich compounds, and M06 calculations were in excellent agreement with the bond lengths and bond angles and with the orientation of the alkyne ligand; they could rationalize steric effects and relative stabilities of mechanistic intermediates.

In light of these successes, we became interested in a paper in this Journal entitled “Geometry Optimization of a Ru(IV) Allyl Dicationic Complex: A DFT Failure?”<sup>31</sup> That paper concluded that popular density functionals, namely B3LYP, BLYP,<sup>13a,32</sup> BPW91,<sup>13a,33</sup> B3PW91,<sup>7a</sup> BP86, PW91,<sup>33</sup> PBE,<sup>34</sup> PBE0,<sup>34,35</sup> and mPW1PW91,<sup>35</sup> even with reasonably large basis sets, greatly

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**Figure 1.** Structures of (a) Complex-1, (b) Complex-2, (c)  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ , and (d)  $\text{RuO}_4$ . Color conventions: hydrogen, light gray; carbon, black; nitrogen, blue; oxygen, red; and ruthenium, green.

overestimate the weak Ru–C bond length involving a phenylallyl ligand in the catalytic dication  $[\text{Ru}(\eta^5\text{-Cp}^*)(\eta^3\text{-CH}_2\text{CHCHC}_6\text{H}_5)(\text{CH}_3\text{CN})_2]^{2+}$ , abbreviated here as Complex-1. Here, the acetonitrile ligands are coordinated at the nitrogen, and  $\text{Cp}^*$ , as usual, denotes  $\text{C}_5\text{Me}_5$  where Me is a methyl group. The experimental structure was obtained by X-ray diffraction from the salt crystal. The DFT overestimates that they found for Ru–C bond distances are 0.38–0.46 Å, and Hartree–Fock theory overestimates the key Ru–C bond length (called Ru–C3 in Figure 1) by 0.60 Å. The authors also concluded that WFT in the form of Møller–Plesset second-order perturbation theory (MP2) is more accurate than DFT and yields results that agree with the experimental ones within 0.07 Å. However, they did not test more recently developed density functionals such as M05, M06, M06-L, SOGGA,<sup>36</sup>  $\omega\text{B97X}$ ,<sup>37</sup> and  $\omega\text{B97X-D}$ .<sup>38</sup> Thus, it was the initial goal of the present study to test these functionals on the problem studied by Calhorda et al.<sup>31</sup> To make the process more complete, we also tested seven other density functionals and Hartree–Fock theory.

In order to test the generality of our conclusions, we also consider bond lengths in two other Ru complexes,  $\text{RuO}_4$  and  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ .

## METHODOLOGY

We have employed 15 levels of electronic structure theory, in particular, Hartree–Fock theory, MP2 theory, and 13 density functionals, namely, B3LYP, B3PW91, M05, M06-L, M06-2X, MOHLYP,<sup>39</sup> MPW3LYP,<sup>40</sup> PW6B95,<sup>41</sup> PBE0, SOGGA,  $\tau\text{HCTHhyb}$ ,<sup>42</sup>  $\omega\text{B97X}$ , and  $\omega\text{B97X-D}$ .

The SOGGA and M06-L functionals are particularly interesting because previous work<sup>36</sup> has shown that they have good accuracy for geometries, and furthermore, because they do not involve any Hartree–Fock exchange, they are particularly efficient for geometry optimization of large systems.

We combine these levels with a variety of basis sets, namely, LANL2DZ,<sup>43</sup> def2-SVP,<sup>44</sup> and def2-TZVP,<sup>44</sup> for a total of 45 model chemistries. Use of the LANL2DZ basis set also implies usage of its associated effective core potential (ECP) to replace

the 28-electron inner core of Ru, whereas calculations with the def2-class basis sets replace the 28-electron inner core of Ru with the Stuttgart ECPs.<sup>45</sup> Both the LANL2DZ and Stuttgart ECPs account for scalar relativistic effects (they are therefore sometimes called relativistic ECPs, i.e., RECPs). Gaussian 09<sup>46</sup> and a locally modified version, MNGFM4.1,<sup>47</sup> were used for the geometry optimization calculations with the option “scf=tight”. The integration grid employed is “ultrafine” as defined in Gaussian 09.<sup>46</sup> The calculations on the odd-electron anion were carried out with spin unrestricted methods (UHF and spin-polarized DFT). The atomic charges were computed employing ChelpG,<sup>48</sup> Merz–Kollman,<sup>49</sup> and natural bond orbital (NBO) analysis<sup>50</sup> schemes. For ChelpG and Merz–Kollman methods, we set the radius of Ru to 2.07 Å.<sup>51</sup>

## STRUCTURES

We will consider two Ru dication structures. The experimental structure<sup>52</sup> that forms the basis for the comparison of Calhorda et al.<sup>31</sup> is  $[\text{Ru}(\eta^5\text{-Cp}^*)(\eta^3(\text{CH}_2\text{CHCHC}_6\text{H}_5)(\text{CH}_3\text{CN})_2)]^{2+}$ , abbreviated here as Complex-1. However, Calhorda et al. modeled this as  $[\text{Ru}(\eta^5\text{-Cp})(\eta^3\text{-CH}_2\text{CHCHC}_6\text{H}_5)(\text{CH}_3\text{CN})_2]^{2+}$  (which we call Complex-2), where Cp denotes  $\text{C}_5\text{H}_5$ . We will compare the calculated structural parameters of Complex-1 to experimental results and discuss unsigned errors and mean unsigned errors (MUEs). Coordinates of calculated structures are in the Supporting Information. For Complex-2, we will compare the calculated structure to the calculated structure for Complex-1. In this case, we discuss the results as unsigned deviations and mean unsigned deviations (MUDs). The comparisons for Complex-1 and Complex-2 are focused on Ru–C distances and C–C–C bond angles in the allyl ligand.

To test the performance of the theoretical models used in this study beyond Ru–C bonding, we have also selected two structures containing Ru–O bonds, namely,  $\text{RuO}_4$ <sup>53</sup> and the molecular fragment  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$  from the *trans*-dimethylammonium bis(oxalato) diaquaruthenate (III) tetrahydrate<sup>54</sup> complex. The coordinates of these systems were taken from their experimental crystal structures available at ICSD.<sup>55</sup> Figure 1 depicts the structures of Complex-1, Complex-2,  $\text{RuO}_4$ ,<sup>53</sup> and  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ .<sup>54</sup>

## RESULTS AND DISCUSSION

Figure 1 shows that Complex-1 and Complex-2 involve coordination of a phenylallyl ligand to ruthenium. For a structural analysis of Complex-1 and Complex-2, we select all of the Ru–C bond lengths, namely, Ru–C1, Ru–C2, and Ru–C3, where C1, C2, and C3 are identified in Figure 1, and Ru–CR, where CR denotes one of the carbons of the cyclopentadienyl ligand. In all cases, we use the average of the five Ru–CR values and treat this average as a single variable. We also consider the C1–C2–C3 bond angles in the allyl portion of the phenylallyl ligand, denoted by  $\angle\text{C1–C2–C3}$ . In order to test the ability of the model chemistries to reproduce the geometrical parameters, we compute the errors and mean unsigned errors (MUEs) for these parameters with respect to the experimental parameters.<sup>52</sup>

In assessing the qualities of HF, MP2, and the density functionals, we consider only the largest basis set, namely, def2-TZVP. We will, however, also discuss basis set effects.

Tables 1 and 2 show that the new-generation functionals, namely, SOGGA, M05, M06, M06-L, PW6B95,  $\omega\text{B97X}$ , and  $\omega\text{B97X-D}$ , when used with the def2-TZVP basis set, yield small

**Table 1. Unsigned Error and Mean Unsigned Error (both in Å) Computed for Complex-1 Employing Different Model Chemistries with Respect to the Experimental Values**

bond distance	basis set	B3LYP	B3PW91	HF	M05	M06	M06-L	MOHLYP	MP2
Ru–C1	LANL2DZ	0.044	0.025	0.092	0.011	0.017	0.007	0.040	0.067
	def2-SVP	0.007	0.086	0.005	0.016	0.007	0.012	0.015	0.010
	def2-TZVP	0.007	0.015	0.001	0.019	0.007	0.012	0.013	0.020
Ru–C2	LANL2DZ	0.114	0.098	0.154	0.084	0.068	0.043	0.179	0.032
	def2-SVP	0.078	0.034	0.101	0.035	0.032	0.025	0.125	0.063
	def2-TZVP	0.088	0.044	0.106	0.042	0.039	0.028	0.142	0.074
Ru–C3	LANL2DZ	0.360	0.335	0.555	0.311	0.234	0.203	0.618	0.011
	def2-SVP	0.306	0.194	0.409	0.193	0.138	0.148	0.523	0.078
	def2-TZVP	0.337	0.227	0.424	0.216	0.159	0.160	0.563	0.073
Ru–CR <sup>a</sup>	LANL2DZ	0.088	0.040	0.088	0.040	0.052	0.043	0.102	0.076
	def2-SVP	0.035	0.011	0.035	0.011	0.003	0.016	0.045	0.027
	def2-TZVP	0.029	0.015	0.029	0.015	0.000	0.021	0.039	0.040
MUE <sup>b</sup>	LANL2DZ	0.15	0.12	0.22	0.11	0.09	0.07	0.23	0.05
	def2-SVP	0.11	0.08	0.14	0.06	0.05	0.05	0.18	0.04
	def2-TZVP	0.12	0.08	0.14	0.07	0.05	0.06	0.19	0.05

<sup>a</sup> Average over five Ru–C distances for C atoms in the cyclopentadienyl ring. <sup>b</sup> Mean unsigned error: average over four previous values.

**Table 2. Unsigned Error and Mean Unsigned Error (both in Å) Computed for Complex-1 Employing Different Model Chemistries with Respect to the Experimental Values**

bond distance	basis set	MPW3LYP	PBE0	PW6B95	SOGGA	τHCTHhyb	ωB97X	ωB97X-D
Ru–C1	LANL2DZ	0.033	0.010	0.018	0.004	0.025	0.013	0.023
	def2-SVP	0.008	0.018	0.013	0.024	0.002	0.020	0.008
	def2-TZVP	0.008	0.023	0.016	0.029	0.006	0.022	0.011
Ru–C2	LANL2DZ	0.117	0.059	0.059	0.025	0.098	0.066	0.059
	def2-SVP	0.072	0.016	0.020	0.017	0.051	0.018	0.017
	def2-TZVP	0.083	0.022	0.025	0.014	0.059	0.024	0.021
Ru–C3	LANL2DZ	0.384	0.222	0.196	0.137	0.335	0.172	0.148
	def2-SVP	0.280	0.123	0.115	0.052	0.228	0.066	0.056
	def2-TZVP	0.320	0.149	0.129	0.066	0.260	0.088	0.074
Ru–CR <sup>a</sup>	LANL2DZ	0.084	0.053	0.049	0.048	0.076	0.040	0.043
	def2-SVP	0.033	0.002	0.004	0.004	0.024	0.009	0.002
	def2-TZVP	0.031	0.002	0.010	0.007	0.020	0.010	0.004
MUE <sup>b</sup>	LANL2DZ	0.15	0.09	0.08	0.05	0.13	0.07	0.07
	def2-SVP	0.10	0.04	0.04	0.02	0.08	0.03	0.02
	def2-TZVP	0.11	0.05	0.05	0.03	0.09	0.04	0.03

<sup>a</sup> Average over five Ru–C distances for C atoms in cyclopentadienyl ring. <sup>b</sup> Mean unsigned error: average over four previous values.

**Table 3. Error (in degrees) Computed for ∠C1–C2–C3 for Complex-1**

basis set	B3LYP	B3PW91	HF	M05	M06	M06-L	MOHLYP	MP2
LANL2DZ	0.9	0.5	1.4	0.5	0.1	0.8	2.1	3.7
def2-SVP	0.9	0.3	1.3	0.1	0.8	0.8	1.9	4.6
def2-TZVP	1.0	0.2	1.1	0.1	0.7	0.9	1.9	4.9

MUE values typically in the same range as those for MP2 calculations. The older PBE0 functional also does well. For Ru–C bond lengths, the popular functionals B3LYP and B3PW91 yield larger MUEs of ~0.12 and 0.08 Å, respectively. It is also encouraging that Tables 3 and 4 show that *all* of the density functionals studied here have much smaller errors in ∠C1–C2–C3 than does MP2.

The key issue in the article by Calhorda et al. was the weak Ru–C3 bond. They defined 0.07 Å as an “acceptable” error for this bond but found that all density functionals tested had an error of at least 0.23 Å. Tables 1 and 2 show eight functionals with an error less than 0.23 Å for this bond. Four of these (PW6B95, SOGGA, ωB97X, and ωB97X-D) have an error of 0.13 Å or less, and two (SOGGA and ωB97X-D) have an acceptable error of 0.07 Å or less.

**Table 4.** Error (in degrees) Computed for  $\angle C1-C2-C3$  for Complex-1

basis set	MPW3LYP	PBE0	PW6B95	SOGGA	$\tau$ HCTHhyb	$\omega$ B97X	$\omega$ B97X-D
LANL2DZ	1.1	0.5	1.2	2.0	0.5	1.0	1.3
def2-SVP	0.7	0.6	1.4	2.5	0.1	1.8	1.9
def2-TZVP	0.9	1.0	1.6	3.4	0.2	1.5	1.8

**Table 5.** Unsigned Deviations and Mean Unsigned Deviations (both in Å) Computed for Complex-2 Employing Different Model Chemistries with Respect to the Original Complex, Complex-1

bond distance	basis set	B3LYP	B3PW91	HF	M05	M06	M06-L	MOHLYP	MP2
Ru–C1	LANL2DZ	0.044	0.025	0.092	0.011	0.017	0.007	0.040	0.067
	def2-SVP	0.007	0.086	0.005	0.016	0.007	0.012	0.015	0.010
	def2-TZVP	0.007	0.015	0.001	0.019	0.007	0.012	0.013	0.020
Ru–C2	LANL2DZ	0.114	0.098	0.154	0.084	0.068	0.043	0.179	0.032
	def2-SVP	0.078	0.034	0.101	0.035	0.032	0.025	0.125	0.063
	def2-TZVP	0.088	0.044	0.106	0.042	0.039	0.028	0.142	0.074
Ru–C3	LANL2DZ	0.360	0.335	0.555	0.311	0.234	0.203	0.618	0.011
	def2-SVP	0.306	0.194	0.409	0.193	0.138	0.148	0.523	0.078
	def2-TZVP	0.337	0.227	0.424	0.216	0.159	0.160	0.563	0.073
Ru–CR <sup>a</sup>	LANL2DZ	0.103	0.087	0.101	0.048	0.056	0.043	0.114	0.085
	def2-SVP	0.035	0.012	0.035	0.011	0.003	0.016	0.045	0.027
	def2-TZVP	0.033	0.009	0.029	0.015	0.000	0.021	0.039	0.040
MUD <sup>b</sup>	LANL2DZ	0.155	0.136	0.226	0.114	0.094	0.074	0.238	0.049
	def2-SVP	0.106	0.082	0.138	0.064	0.045	0.050	0.177	0.045
	def2-TZVP	0.116	0.074	0.140	0.073	0.051	0.055	0.189	0.052

<sup>a</sup> Average over five Ru–C distances for C atoms in the cyclopentadienyl ring. <sup>b</sup> Mean unsigned error: average over four previous values.

**Table 6.** Unsigned Deviations and Mean Unsigned Deviations (both in Å) Computed for Complex-2 Employing Different Model Chemistries with Respect to the Original Complex, Complex-1

bond distance	basis set	MPW3LYP	PBE0	PW6B95	SOGGA	$\tau$ HCTHhyb	$\omega$ B97X	$\omega$ B97X-D
Ru–C1	LANL2DZ	0.033	0.010	0.018	0.004	0.025	0.013	0.023
	def2-SVP	0.008	0.018	0.013	0.024	0.002	0.020	0.008
	def2-TZVP	0.008	0.023	0.016	0.029	0.006	0.022	0.011
Ru–C2	LANL2DZ	0.117	0.059	0.059	0.025	0.098	0.066	0.059
	def2-SVP	0.072	0.016	0.020	0.017	0.051	0.018	0.017
	def2-TZVP	0.083	0.022	0.025	0.014	0.059	0.024	0.021
Ru–C3	LANL2DZ	0.384	0.222	0.196	0.137	0.335	0.172	0.148
	def2-SVP	0.280	0.123	0.115	0.052	0.228	0.066	0.056
	def2-TZVP	0.320	0.149	0.129	0.066	0.260	0.088	0.074
Ru–CR <sup>a</sup>	LANL2DZ	0.090	0.062	0.055	0.055	0.087	0.050	0.052
	def2-SVP	0.033	0.002	0.004	0.004	0.024	0.009	0.002
	def2-TZVP	0.031	0.002	0.010	0.007	0.020	0.010	0.004
MUD <sup>b</sup>	LANL2DZ	0.16	0.09	0.08	0.06	0.14	0.08	0.07
	def2-SVP	0.10	0.04	0.04	0.02	0.08	0.03	0.27
	def2-TZVP	0.11	0.05	0.05	0.03	0.09	0.04	0.03

<sup>a</sup> Average over five Ru–C distances for C atoms in the cyclopentadienyl ring. <sup>b</sup> Mean unsigned error: average over four previous values.

For Ru–C bond distances, Tables 1 and 2 show that the popular LANL2DZ basis set gives larger MUEs than the other two basis sets, def2-SVP and def2-TZVP, and we judge it to be unreliable. The other valence double- $\zeta$  basis set studied here, namely, def2-SVP, performs as well as the valence triple- $\zeta$  basis set def2-TZVP.

In addition to the fact that they used older density functionals and an inadequate basis set, one reason for the different conclusions here and in ref 31 is that the model system, Complex-2,

selected by Calhorda et al.<sup>31</sup> is not a good choice for modeling the original system, Complex-1. Tables 5 and 6 list the absolute deviation and MUD computed for Ru–C bond lengths for Complex-2 with respect to the original complex (Complex-1); Tables 7 and 8 list the deviation computed for  $\angle C1-C2-C3$  in Complex-2 with respect to Complex-1. It may be seen from these tables that the substituents (five methyl groups) present on the cyclopentadiene ring play an important role in the modification



**Table 7.** Deviation (in degrees) Computed for  $\angle \text{C1} - \text{C2} - \text{C3}$  in Complex-2 with Respect to Complex-1

basis set	B3LYP	B3PW91	HF	M05	M06	M06-L	MOHLYP	MP2
LANL2DZ	0.9	0.5	1.4	0.5	0.1	0.8	2.1	3.7
def2-SVP	0.9	0.3	1.3	0.1	0.8	0.8	1.9	4.6
def2-TZVP	1.0	0.2	1.1	0.1	0.7	0.9	1.9	4.9

**Table 8.** Deviation (in degrees) Computed for  $\angle \text{C1} - \text{C2} - \text{C3}$  in Complex-2 with Respect to Complex-1

basis set	MPW3LYP	PBE0	PW6B95	SOGGA	$\tau\text{HCTHhyb}$	$\omega\text{B97X}$	$\omega\text{B97X-D}$
LANL2DZ	1.1	0.5	1.2	2.00	0.5	1.0	1.3
def2-SVP	0.7	0.6	1.4	2.5	0.1	1.8	1.9
def2-TZVP	0.9	1.0	1.6	3.4	0.2	1.5	1.8

**Table 9.** MUE<sup>a</sup> (Å) Computed for Ru–O Distance in  $\text{RuO}_4$  and  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ 

basis set	B3LYP	B3PW91	HF	M05	M06	M06-L	MOHLYP	MP2
LANL2DZ	0.056	0.045	0.054	0.059	0.055	0.054	0.074	0.075
def2-SVP	0.042	0.036	0.071	0.055	0.042	0.048	0.064	0.040
def2-TZVP	0.042	0.034	0.066	0.054	0.041	0.048	0.062	0.040

<sup>a</sup> Mean unsigned error: average over three Ru–O values.**Table 10.** MUE<sup>a</sup> (Å) Computed for Ru–O Distance in  $\text{RuO}_4$  and  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ 

basis set	MPW3LYP	PBE0	PW6B95	SOGGA	$\tau\text{HCTHhyb}$	$\omega\text{B97X}$	$\omega\text{B97X-D}$
LANL2DZ	0.055	0.038	0.041	0.033	0.048	0.046	0.045
def2-SVP	0.041	0.034	0.027	0.014	0.034	0.046	0.044
def2-TZVP	0.040	0.031	0.027	0.012	0.033	0.045	0.043

<sup>a</sup> Mean unsigned error: average over three Ru–O values.**Table 11.** Overall Mean Unsigned Errors and Largest Errors in Ru–C and Ru–O Bond Lengths (Å) for def2-TZVP Basis Set

functional	MUE (Ru-allyl) <sup>a</sup>	MUE (Ru-X) <sup>b</sup>	largest <sup>c</sup>
SOGGA	0.04	0.02	0.07
$\omega\text{B97X-D}$	0.04	0.03	0.07
$\omega\text{B97X}$	0.04	0.04	0.09
MP2	0.06	0.05	0.07
PW6B95	0.06	0.04	0.13
PBE0	0.06	0.04	0.15
M06	0.07	0.05	0.16
M06-L	0.07	0.05	0.16
M05	0.09	0.07	0.22
B3PW91	0.10	0.06	0.23
$\tau\text{HCTHhyb}$	0.11	0.06	0.26
MPW3LYP	0.14	0.08	0.32
B3LYP	0.14	0.09	0.34
HF	0.18	0.11	0.42
MOHLYP	0.24	0.13	0.56

<sup>a</sup> Average over three Ru–C distances in which C is an allyl carbon.<sup>b</sup> Average over seven values for X = C or O; equivalent to a 4:3 weighted average of the bottom rows of Tables 1 and 2 with the bottom rows of Tables 9 and 10. <sup>c</sup> Largest absolute error for any of the four Ru–C or three Ru–O distances.

of all Ru–C bond lengths; the MUDs with def2-TZVP are as large as 0.19 Å. In fact, Calhorda et al. had studied this effect of the methyl groups, but they reported bond length differences smaller than 0.1 Å with the LANL2DZ basis set for Ru. We find larger differences even with LANL2DZ. They found large errors in Ru–C distances just as we find in Table 1 for B3LYP/LANL2DZ, where the error is 0.36 Å. These errors are reduced to 0.14 Å by SOGGA/LANL2DZ and to 0.07 Å with SOGGA/def2-TZVP.

For  $\text{RuO}_4$  and  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ , we focus our attention on the Ru–O bond lengths. The four Ru–O bonds in  $\text{RuO}_4$  are equivalent and symmetric: for  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ , two Ru–O distances involving the water ligands are identical, and four Ru–O distances involving oxalates are identical. Therefore, we computed the MUEs as unweighted averages over the three unique values. Tables 9 and 10 show the resulting MUE computed for the Ru–O distances in these molecules with various model chemistries. These tables show that the MUE in the DFT bond lengths is typically 0.03–0.07 Å, with the best results obtained by SOGGA (0.01 Å) and PW6B95 (0.03 Å). For Ru–O bond lengths, the def2-SVP basis set is almost as good as def2-TZVP, and LANL2DZ is again significantly less accurate.

Finally, in Table 11, we present an overall assessment of the density functionals for computed bond distances. For this table, we report the results with the most complete basis set, namely, def2-TZVP, and we average over the errors in the seven Ru–C

**Table 12.** Difference between the ChelpG Charges of Complex-1 and Complex-2 Calculated with the def2-TZVP Basis Set for the Five Model Chemistries with the Smallest Errors in Geometries ( $q_{\text{difference}} = q_{\text{Complex-1}} - q_{\text{Complex-2}}$ )

atoms	M06	M06-L	PW6B95	PBE0	$\omega$ B97X
Ru	0.38	0.33	0.29	0.31	0.42
$\text{C}_{\text{Cp}^*-\text{Cp}}^a$	0.03	0.05	0.07	0.06	0.01
$-\text{C}_6\text{H}_5$	−0.05	−0.05	−0.05	−0.09	−0.04
$-\text{N1CCH}_3$	−0.22	−0.21	−0.18	−0.15	−0.17
$-\text{N2CCH}_3$	0.02	0.04	0.03	−0.02	−0.04
Allyl	−0.15	−0.15	−0.15	−0.12	−0.18
C1	−0.18	−0.12	−0.07	−0.07	−0.16
C2	−0.33	−0.37	−0.38	−0.42	−0.38
C3	0.15	0.19	0.18	0.20	0.18

<sup>a</sup> Difference of sum over all of the atoms of  $\text{Cp}^*$  and Cp rings.**Table 13.** Difference between the MK Charges of Complex-1 and Complex-2 Calculated with the def2-TZVP Basis Set for the Five Model Chemistries with the Smallest Errors in Geometries ( $q_{\text{difference}} = q_{\text{Complex-1}} - q_{\text{Complex-2}}$ )

atoms	M06	M06-L	PW6B95	PBE0	$\omega$ B97X
Ru	0.33	0.10	0.20	0.33	0.37
$\text{C}_{\text{Cp}^*-\text{Cp}}^a$	0.04	0.14	0.10	0.05	0.02
$-\text{C}_6\text{H}_5$	−0.08	−0.08	−0.10	−0.07	−0.07
$-\text{N1CCH}_3$	−0.23	−0.18	−0.15	−0.16	−0.17
$-\text{N2CCH}_3$	0.05	0.10	0.03	−0.02	−0.02
Allyl	−0.11	−0.07	−0.09	−0.14	−0.14
C1	−0.04	−0.05	−0.04	−0.08	−0.05
C2	−0.02	0.00	−0.01	0.03	0.00
C3	0.01	0.02	0.04	−0.03	0.01

<sup>a</sup> Difference of sum over all of the atoms of  $\text{Cp}^*$  and Cp rings.**Table 14.** Difference between the NBO Charges of Complex-1 and Complex-2 Calculated with the def2-TZVP Basis Set for the Five Model Chemistries with the Smallest Errors in Geometries ( $q_{\text{difference}} = q_{\text{Complex-1}} - q_{\text{Complex-2}}$ )

atoms	M06	M06-L	PW6B95	PBE0	$\omega$ B97X
Ru	0.02	0.01	0.01	0.01	0.02
$\text{C}_{\text{Cp}^*-\text{Cp}}^a$	0.13	0.14	0.13	0.13	0.12
$-\text{C}_6\text{H}_5$	−0.07	−0.07	−0.08	−0.08	−0.06
$-\text{N1CCH}_3$	−0.01	−0.01	0.00	−0.01	0.00
$-\text{N2CCH}_3$	−0.02	−0.03	−0.02	−0.02	−0.02
Allyl	−0.07	−0.06	−0.06	−0.06	−0.07
C1	−0.03	−0.02	−0.02	−0.55	−0.54
C2	0.01	0.01	0.02	−0.49	−0.48
C3	−0.05	−0.04	−0.05	−0.28	−0.27

<sup>a</sup> Difference of sum over all of the atoms of  $\text{Cp}^*$  and Cp rings.

and Ru–O bond distances. For every density functional, we tabulate the mean unsigned error and the maximum error; the latter is usually, but not always, the error in the Ru–C3 distance (in a few cases, namely, MP2, SOGGA,  $\omega$ B97X, and  $\omega$ B97X-D, it is an error in a Ru–O distance). Table 11 shows that seven

functionals have an average error smaller than or equal to that of MP2, and of these seven functionals, two also have the same maximum error. The two functionals that outperform MP2 in MUE and do not have a larger maximum error than MP2 are SOGGA and  $\omega$ B97X-D. Although  $\omega$ B97X-D contains an empirical molecular mechanics term, SOGGA is simply a density functional, as are all other methods in Table 11 except HF and MP2. Because density functional calculations are much less expensive than MP2 for large systems, it is very encouraging that some of the density functionals outperform MP2. As an example of the cost differential, with the def2-TZVP basis set, we found for Complex-1 that a geometry optimization step with the SOGGA, M06-L, or PBE0 density functionals is about 40 times faster than one with MP2, and a geometry optimization step with M06,  $\omega$ B97X-D, or PW6B95 is about 30 times faster than with MP2.

In order to understand the effect of methyl groups on  $\text{Cp}^*$ , we used three schemes for electrostatic fitting to determine the partial charges on the atoms of Complex-1 and Complex-2. In particular, we used ChelpG,<sup>48</sup> Merz–Singh–Kollamn,<sup>49</sup> and natural bond orbital (NBO)<sup>50</sup> methods. Tables 12–14 show the differences in partial atomic charges between Complex-1 and Complex-2 as determined by these analyses for the five model chemistries with smallest errors in geometries. (The charges themselves are given in the Supporting Information.) It is well-known that  $\text{Cp}^*$  is a better electron donor than Cp, and Tables 12–14 (row 2) confirm this in that the sum of the charges on all of the atoms in  $\text{Cp}^*$  in methylated Complex-1 is more positive than that for Cp from Complex-2. However, the Ru atoms in Complex-1 are also more positive, by 0.02–0.4 au depending on the method. The extra electron density donated by  $\text{Cp}^*$  ends up on the phenyl group, the  $\text{NCCCH}_3$  ligand on the phenyl side, and the allyl group (especially C1), which are all less positive or more negative in Complex-1 than in Complex-2.

## CONCLUSIONS

In the present study, we employed 45 different model chemistries to assess the performance of density functional methods in predicting the structural parameters of Ru bonds to C and O. The important highlights of our study are as follows:

- 1 Ru–C distances in Complex-2 are quite different from those of Complex-1, contrary to a previous<sup>31</sup> assumption.
- 2 Selection of the model chemistry is an important step for obtaining accurate geometries in studying catalytic complexes.
- 3 The popular B3LYP functional does not yield accurate Ru–C bond lengths.
- 4 The popular LANL2DZ basis set is found to be inadequate for studying the structural parameters.
- 5 Seven density functionals, namely, SOGGA,  $\omega$ B97X-D, PW6B95, M06, M06-L,  $\omega$ B97X-D, and PBE0, have an average error in Ru–X bond lengths, where X is C or O, that is smaller than or equal to that of the more expensive MP2 method. Hence, we recommend these functionals with the def2-SVP or def2-TZVP basis set for calculating Ru–C and Ru–O bond lengths.
- 6 The presence of methyl groups on the Cp ring modifies the electronic environment of the Ru center, making that environment more negative.

The progress of DFT since the Callhorda et al. study of four years ago is very encouraging.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** The coordinates computed by SOGGA/def2-TZVP and M06/def2-TZVP model chemistries and tables of the structural parameters (bond lengths and bond angles) of Complex-1, Complex-2,  $\text{Ru}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2^-$ , and  $\text{RuO}_4$ , computed for all of the model chemistries employed herein, as well as a discussion exploring additional ruthenium complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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