

## Evaluation of Functionals O3LYP, KMLYP, and MPW1K in Comparison to B3LYP for Selected Transition-Metal Compounds

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**Abstract:** We have investigated the performance of the hybrid density functionals O3LYP, KMLYP, and MPW1K in comparison to B3LYP for predicting geometrical parameters of selected transition-metal compounds. We used different combinations of ECPs and basis sets (Stuttgart/Dresden 1997, LANL2DZ, 6-31G(d), 6-311++G(d,p)) to analyze the effect on selected transition-metal compounds. B3LYP is superior to the other three density functionals for the split valence double- $\zeta$  basis set 6-31G(d), contrary to what was reported for organic reactions. But in combination with the split valence triple- $\zeta$  basis set 6-311++G(d,p) O3LYP was clearly superior to all the other functionals. LANL2DZ performed worse in every case.

### Introduction

During the past decades, density functional theory (DFT)<sup>1,2</sup> has become the most widely used method in computational quantum chemistry. It has been proven in many cases that it is the most suitable method for calculating transition-metal compounds.<sup>3–8</sup> An exchange-correlation matrix replaces the exchange term in standard Hartree–Fock (HF)<sup>9</sup> theory, and the progress in density functional theory is based on the development of better approximations toward the “real” exchange-correlation functional.

The exchange-correlation density functional  $f^{\text{xc}}(\rho)$  is written as the sum of individual exchange  $f^{\text{x}}(\rho)$  and correlation  $f^{\text{c}}(\rho)$  components in nearly all functionals used in the last years. Thereby the approximations are made separately for each of the contributions.

One of the most common and widely used density functionals is the hybrid functional B3LYP,<sup>10</sup> which is a combination of Becke’s 1988 nonlocal exchange functional B88,<sup>11</sup>  $\rho^{4/3}$  Dirac Slater exchange term,<sup>12</sup> about 20% of Hartree–Fock exchange functional,<sup>10</sup> Vosko, Wilk, and Nusair’s local correlation functional (VWN),<sup>13</sup> and Lee, Yang, and Parr’s nonlocal correlation functional (LYP).<sup>14</sup>

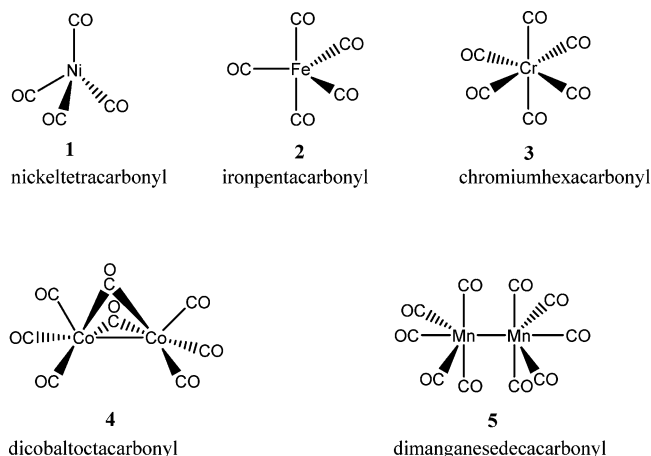
Though B3LYP usually gives reliable results, there have been cases where the results from B3LYP density functional calculations showed some discrepancies to experimentally measured values. Therefore the search for improved density functionals is ongoing. Lately Handy and Cohen have developed the new exchange functional OPTX.<sup>15</sup> By replacing B88 through OPTX the density functional O3LYP is obtained. It is claimed to be superior to B3LYP in predicting geometries of organic molecules and heats of reactions as well as activation parameters for organic reactions.<sup>16–20</sup> Contrary to these results, it was reported that O3LYP is improper for the calculation of dispersion-bond homomolecular dimers.<sup>21</sup> But this study did not compare the results against those of the density functional B3LYP. Studying the performance of O3LYP for anticipating bond dissociation energies, geometries, and vibrational frequencies for first-row transition metals, Baker and Pulay<sup>22</sup> found that the values obtained with O3LYP are of equal quality as those achieved with B3LYP, while for predicting atomic excitation energies and ionization potentials they obtained worse results with O3LYP compared to B3LYP.<sup>22</sup> Calculating the activation barriers for hydrocarbon pericyclic reactions, Guner et al.<sup>23</sup> found that the results obtained with O3LYP were comparable to the B3LYP results.

Another new density functional, developed by Musgrave and co-workers,<sup>24</sup> is the hybrid KMLYP. Here the exchange

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functional is a similar combination of the Slater exchange functional<sup>12</sup> and the HF<sup>9</sup> exchange functional, while for the correlation part the functionals of Lee, Yang, and Parr<sup>14</sup> and of Vosko, Wilk, and Nusair are combined.<sup>13</sup> The KMLYP functional has been shown to be a tool of higher precision for calculating enthalpies of reaction and transition-state barriers than the B3LYP method, G2 theories, QCISD(T), and CCSD(T).<sup>24</sup> Studying the geometry as well as the electron affinity of SF<sub>6</sub>, Brinkmann et al.<sup>25</sup> found that calculations with the KMLYP functional provided good geometrical parameters for SF<sub>6</sub> and for the corresponding anion. They also observed an improved electron affinity in comparison to standard DFT functionals. Structures and energetics for transition states for H-abstraction reactions are also anticipated well using the KMLYP functional.<sup>26</sup> Predicting the cumulene/poly-yne isomerization energies Pomerantz et al.<sup>27</sup> obtained clearly better results with KMLYP than with B3LYP. KMLYP was also observed to be much better than B3LYP in modeling the aromaticity of 10 $\pi$ -annulenes,<sup>28</sup> while for pericyclic reactions of hydrocarbons, Guner et al.<sup>29</sup> found that KMLYP tends to overestimate activation enthalpies. They could also show that the calculated bond lengths of the transition states are only comparable to the accuracy of those calculated with the B3LYP functional when using high-quality basis sets.

Recently the MPW1K hybrid density functional was developed by Truhlar and co-workers.<sup>30</sup> It uses the modified Perdew-Wang gradient-corrected exchange functional and the correlation functionals of Adamo and Barone.<sup>31</sup> Comparing MPW1K to B3LYP,<sup>10</sup> it is notable that it includes a larger proportion of the HF<sup>9</sup> exchange functional.<sup>30,32,33</sup> It was shown that geometries and vibrational frequencies of stationary points, enthalpies, and barrier heights for organic reactions obtained with the MPW1K method are in good agreement with experimental values or with higher order calculations.<sup>19,29,30,32–48</sup> MPW1K is claimed to be especially superior to other DFT methods for the calculation of large systems.<sup>35</sup> Li et al.<sup>37</sup> investigated several hydrogen atom transfer reactions involved in atmospheric chemistry with hybrid DFT methods. They found that MPW1K provides very accurate stationary point geometries and energetics also in combination with small basis sets. Studying the unimolecular decomposition reaction of C<sub>2</sub>H<sub>5</sub>O, Zhang et al.<sup>49</sup> could show that MPW1K is also well suited for the calculation of reaction rates. Predicting the structures and B–N bond dissociation energies of amine-boranes with various DFT methods, Gilbert found that using B3LYP poor results were obtained, whereas the MPW1K functional gave good results.<sup>50</sup> It was also shown that using MPW1K the predicted potential energy surface for S<sub>N</sub>2 reactions was in good agreement with the one achieved with G2 theory and slightly better than applying the B3LYP functional.<sup>43</sup> Iron et al.<sup>51</sup> demonstrated that the reactivities of organometallic complexes obtained with the MPW1K functional are of comparable accuracy with experimental results, while Kuwata et al.<sup>52</sup> reported the observation that MPW1K/6-31+G-(d,p) calculations are less accurate and often disagree with model chemistry predictions investigating the reactivity of syn acetaldehyde oxide. Saeys et al. came to a similar result



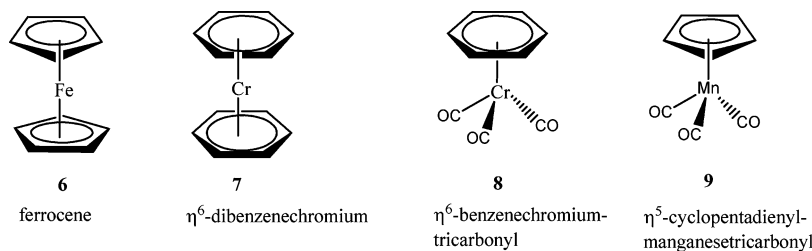
**Figure 1.** Structures of the selected transition-metal carbonyl compounds.

studying radical reactions of hydrocarbons.<sup>53</sup> Using different DFT functionals including MPW1K, Cohen et al. estimated an inaccurate heat of formation of diazomethane compared to experimental results.<sup>54</sup>

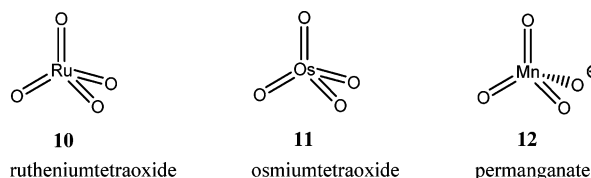
As described above, many investigations have been published on the suitability of the new hybrid functionals O3LYP, KMLYP, and MPW1K for the calculation of organic molecules and organic reactions. Most of these studies showed that these relatively new functionals are clearly superior to B3LYP, but so far their usefulness for the calculation of geometries and reactivities of transition-metal compounds by these functionals was not clear. Therefore we decided to study the geometries and vibrational frequencies of several transition-metal compounds using the density functionals O3LYP, KMLYP, MPW1K, and B3LYP in comparison to experimental results. Because of the large body of experimental data available, carbonyl complexes are especially well suited for this test,<sup>55</sup> e.g. the calculation of the CO frequencies as an indication for the quality of the method.<sup>56,57</sup>

## Computational Details

All calculations were carried out using Gaussian 03.<sup>58</sup> B3LYP, O3LYP, KMLYP, and MPW1K were combined with the split valence double- $\zeta$  (DZ) basis set 6-31G(d),<sup>59,60</sup> with the split valence triple- $\zeta$  (TZ) basis set 6-311++G-(d,p),<sup>61–63</sup> and with LANL2DZ.<sup>64–67</sup> LANL2DZ consists of the D95V<sup>64</sup> basis set for the first- and second-row elements and a double- $\zeta$  basis set containing ECP-representations of core electrons for third-row elements and beyond. For ruthenium and osmium the split valence double- $\zeta$  (DZ) basis set 6-31G(d)<sup>59,60</sup> and the split valence triple- $\zeta$  (TZ) basis set 6-311++G(d,p)<sup>61–63</sup> were used in combination with the Stuttgart/Dresden 1997 ECP.<sup>68,69</sup> To examine the influence of additional diffuse and polarization functions we also calculated selected transition-metal compounds for comparison. Details are given in the Supporting Information together with a complete list of the basis sets used. No symmetry or internal coordinate constraints were applied during optimizations. Vibrational frequency calculations were carried out for all structures to verify them as true minima by the absence of imaginary eigenvalues, and additionally the stability of



**Figure 2.** Structures of the selected transition-metal sandwich complexes and semisandwich complexes.



**Figure 3.** Structures of the selected transition-metal tetraoxides.

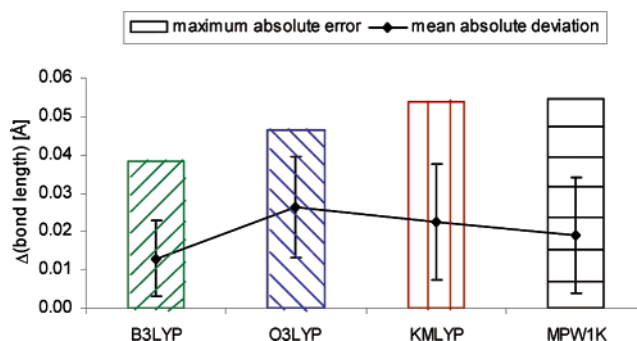
the wave function was checked. Different multiplicities were evaluated, and all systems proved to be in the singlet state.<sup>55,56</sup>

## Results and Discussion

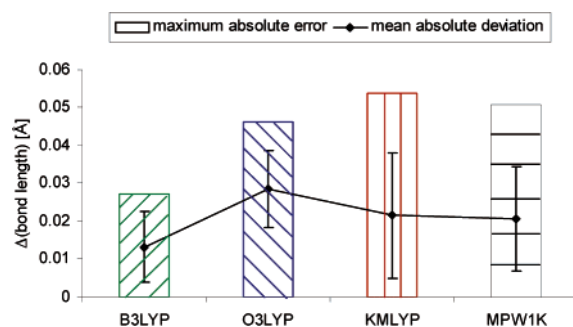
The suitability of the hybrid density functionals O3LYP, KMLYP, and MPW1K for the prediction of the geometry of transition-metal compounds was investigated. Selected geometrical parameters of the transition-metal carbonyl compounds, transition-metal sandwich complexes, transition-metal semisandwich complexes, and transition-metal tetraoxides were compared to experimental data;<sup>70–82</sup> details are available as Supporting Information. We chose nickel(0)-tetracarbonyl,  $\text{Ni}(\text{CO})_4$  (**1**), iron(0)pentacarbonyl,  $\text{Fe}(\text{CO})_5$  (**2**), chromium(0)hexacarbonyl,  $\text{Cr}(\text{CO})_6$  (**3**), dicobalt(0)-octacarbonyl,  $\text{Co}_2(\text{CO})_8$  (**4**), and dimanganese(0)decacarbonyl,  $\text{Mn}_2(\text{CO})_{10}$  (**5**) as examples for transition-metal carbonyl compounds (Figure 1), and ferrocene  $\text{Fe}(\text{C}_5\text{H}_5)_2$  (**6**) and  $\eta^6$ -dibenzenechromium,  $\text{Cr}(\text{C}_6\text{H}_6)_2$  (**7**) as  $\pi$ -coordinated transition-metal sandwich complexes, while  $\eta^6$ -benzene(0)-chromiumtricarbonyl,  $\text{Cr}(\text{C}_6\text{H}_6)(\text{CO})_3$  (**8**) and  $\eta^5$ -cyclopentadienylmanganese(I)tricarbonyl,  $\text{Mn}(\text{C}_5\text{H}_5)(\text{CO})_3$  (**9**) represent the transition-metal semisandwich complexes (Figure 2) as well as ruthenium tetraoxide,  $\text{RuO}_4$  (**10**), osmium tetraoxide,  $\text{OsO}_4$  (**11**), and permanganate,  $\text{MnO}_4^-$  (**12**) as transition-metal tetraoxides (Figure 3).

We refrained from discussing individual bond lengths and angles. Instead we decided to use a statistical description of the different methods. All details on bond lengths, angles, and frequencies are given in the Supporting Information (Tables S1–S18).

The mean absolute deviations (MAD) and the standard deviations as well as the largest absolute errors for the bond lengths calculated by the split valence double- $\zeta$  basis set 6-31G(d) are illustrated in Figures 4–8. A graphical representation of the performance of the four different density functionals together with 6-31G(d) for all calculated compounds except  $\text{RuO}_4$  (**10**) and  $\text{OsO}_4$  (**11**) is shown in Figure 4. We did not include the differences between computational and experimental values for  $\text{RuO}_4$  (**10**) and  $\text{OsO}_4$  (**11**) in the overall picture because these two compounds have been calculated using ECPs.



**Figure 4.** Performance of different hybrid density functionals in combination with 6-31G(d) for the prediction of the bond lengths of compounds **1–9** and **12** in comparison to experimentally observed values.

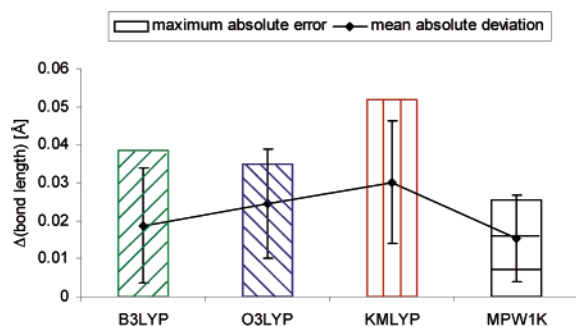


**Figure 5.** Performance of different functionals in combination with 6-31G(d) for the prediction of the bond lengths of selected first-row transition-metal carbonyl compounds (**1–5**) in comparison to experimentally observed values.

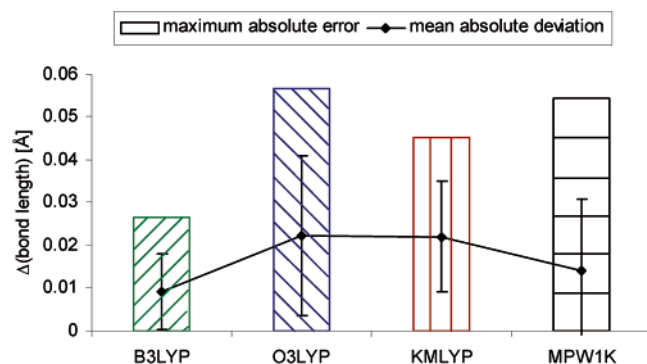
Figure 4 shows the overall mean absolute deviation and the maximum absolute error from experimental values for the calculated bond lengths of compounds **1–9** and **12** for all four different density functionals in combination with 6-31G(d). B3LYP is clearly superior compared to the other functionals for the calculation of transition-metal compounds together with the basis set 6-31G(d).

The individual results for the different groups of investigated transition-metal compound are summarized below (Figures 5–8), and numerical values are given in the Supporting Information (Table S19).

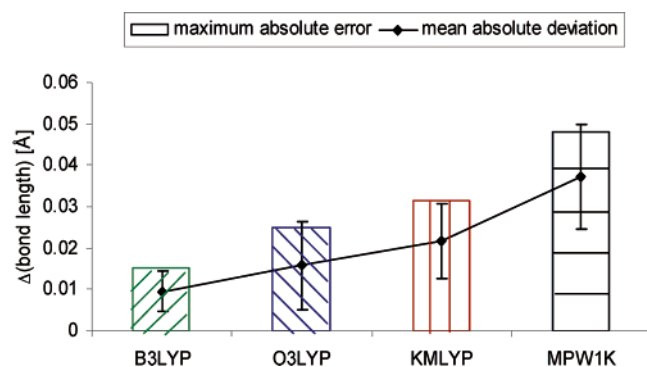
During this study it was observed that the new hybrid functionals O3LYP, KMLYP, and MPW1K in combination with 6-31G(d) do not perform better than B3LYP in predicting geometries of transition-metal compounds. Instead it could be shown (Figures 5, 7, and 8) that using B3LYP better predictions for almost all bond lengths were obtained. In all cases but for **6** and **7** significantly better results are obtained with B3LYP. For calculating geometries of transi-



**Figure 6.** Performance of different functionals in combination with 6-31G(d) for the prediction of the bond lengths of selected first-row transition-metal sandwich complexes (**6**, **7**) vs experimentally observed values.

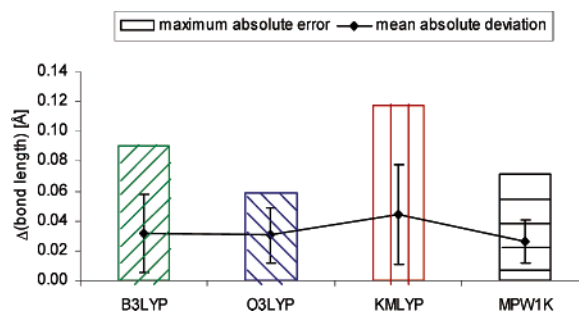


**Figure 7.** Performance of different functionals in combination with 6-31G(d) for the prediction of the bond lengths of selected first-row transition-metal semisandwich complexes (**8**, **9**) vs experimentally observed values.

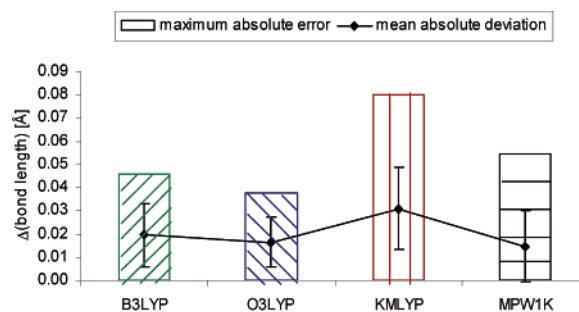


**Figure 8.** Performance of different functionals in combination with 6-31G(d) for the prediction of the bond lengths of selected transition-metal tetraoxides (**10–12**) vs experimentally observed values.

tion-metal sandwich complexes (**6**, **7**) MPW1K performs similar to B3LYP (Figure 6). The maximum absolute errors of the bond lengths of selected first-row transition-metal carbonyl compounds (**1–5**) and first-row transition-metal semisandwich complexes (**8**, **9**) using B3LYP are relatively small (in the range of about 0.03 Å, Figures 5 and 7). Applying B3LYP for calculating the bond lengths of transition-metal tetraoxides the maximum error is small, too ( $\approx 0.01$  Å, Figure 8). For O3LYP or MPW1K the maximum errors of the bond lengths of the compounds studied are in an acceptable range (most 0.06 Å, Figures 5–8). KMLYP



**Figure 9.** Performance of different functionals in combination with LANL2DZ for the prediction of the bond lengths of compounds **1–9** and **12** in comparison to experimentally observed values.



**Figure 10.** Performance of different functionals in combination with 6-311++G(d,p) for the prediction of the bond lengths of compounds **1–9** and **12** in comparison to experimentally observed values.

shows large deviations for the transition-metal carbonyl compounds with up to 0.13 Å (Figure 5).

## Basis Set Effects

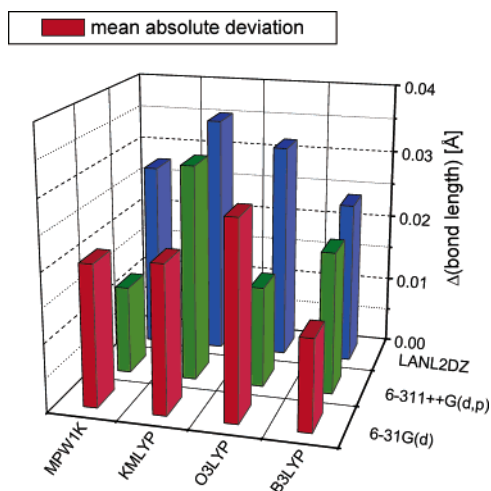
In addition to 6-31G(d), we also used LANL2DZ and 6-311++G(d,p) as basis sets in combination with the four density functionals. On selected compounds we also checked the influence of additional diffuse and polarization functions (see Supporting Information, Table S20). A statistical description of the LANL2DZ results for compounds **1–9** and **12** is given in Figure 9.

In comparison to the results calculated with 6-31G(d) (Figure 8), one notices that a medium-quality basis set like LANL2DZ leads to significant deviations in all cases. They are always larger than the same functional in combination with the split valence double- $\zeta$  basis set 6-31G(d) (Figure 4) or the triple- $\zeta$  basis set 6-311++G(d,p) (Figure 10).

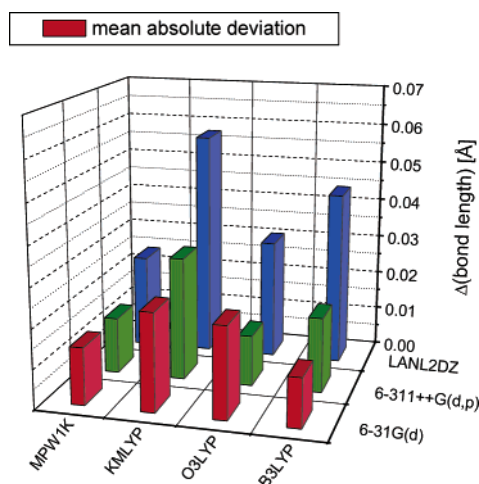
In combination with 6-311++G(d,p) (Figure 10) the best results were obtained with O3LYP. In agreement with the 6-31G(d) and LANL2DZ results, the largest mean absolute deviation from the experimentally observed values is achieved when using KMLYP.

The results obtained by using the double- $\zeta$  basis sets 6-31G(d,p), 6-31+G(d), and 6-31+G(d,p) are similar to those obtained with the double- $\zeta$  basis set 6-31G(d), while those achieved with the triple- $\zeta$  basis set 6-311+G(3df,2p) are comparable to the results from the calculations with the triple- $\zeta$  basis set 6-311++G(d,p). Details of that evaluation are given in the Supporting Information (Table S20).





**Figure 11.** Mean absolute deviation of the calculated bond lengths of selected first-row transition-metal carbonyl compounds (**1–5**) from experimentally observed values.

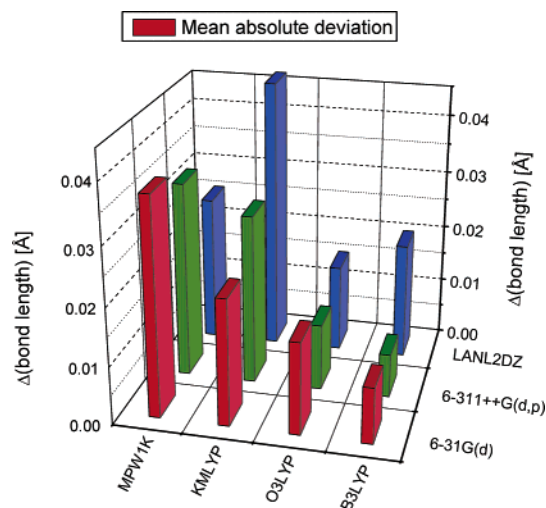


**Figure 12.** Mean absolute deviation of calculated bond lengths of selected first-row transition-metal sandwich (**6, 7**) and semisandwich (**8, 9**) complexes from experimentally observed values.

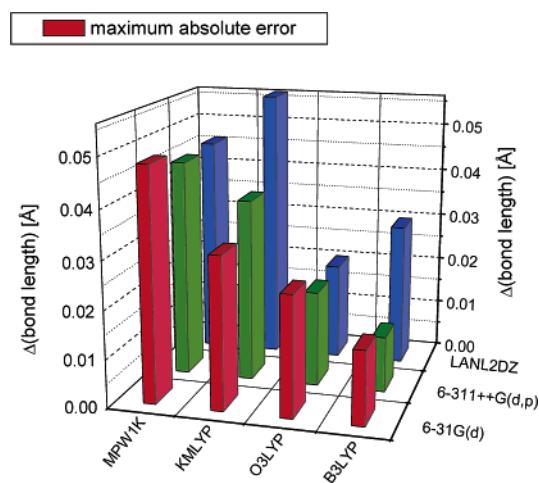
Taking into account the significant increase in computation time, we recommend to use B3LYP in combination with 6-31G(d) or O3LYP together with 6-311++G(d,p) for calculating transition-metal compounds. Graphical representations of the results are given in Figures 11–13.

**Transition-Metal Carbonyl Compounds 1–5.** A comparison of the performance of B3LYP, O3LYP, KMLYP, and MPW1K in combination with three different basis sets for the prediction of the bond lengths of selected first-row transition-metal carbonyl compounds (**1–5**) is illustrated in Figure 11. The functional/basis set combination B3LYP/6-31G(d) is clearly the best choice for predicting the bond lengths of the transition-metal carbonyl compounds **1–5**.

**Transition-Metal Sandwich (6, 7) and Semisandwich (8, 9) Complexes.** Figure 12 shows the performance of B3LYP, O3LYP, KMLYP, and MPW1K in combination with three different basis sets for the calculation of the bond lengths of the selected transition-metal sandwich (**6, 7**) and semisandwich (**8, 9**) complexes. B3LYP/6-31G(d) is the best combination for calculating the geometries of the selected



**Figure 13.** Mean absolute deviation of the calculated bond lengths of selected transition-metal tetraoxides (**10–12**) from experimentally observed values.

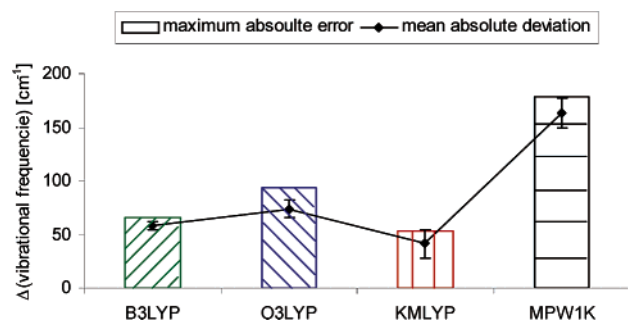


**Figure 14.** Maximum absolute error of the calculated bond lengths of the investigated transition-metal compounds (**1–12**) vs experimentally observed values.

transition-metal sandwich (**6, 7**) and semisandwich (**8, 9**) complexes, but together with 6-311++G(d,p), O3LYP and MPW1K are superior to B3LYP. Guner et al.<sup>23,29</sup> already observed a similar effect of higher quality basis sets in combination with the B3LYP functional when they predicted the heats of reactions of hydrocarbon pericyclic reactions with B3LYP, KMLYP, and O3LYP together with double- $\zeta$  and triple- $\zeta$  basis sets.

**Transition-Metal Tetraoxides (10–12).** Figure 13 shows the results for the transition-metal tetraoxides (**10–12**) for all four functionals in combination with all three basis sets. For compounds **10–12** B3LYP/6-31G(d) and B3LYP/6-311++G(d,p) are the favorable combinations.

**Maximum Absolute Error.** Not only the mean absolute deviation but also the maximum absolute error shows the same trends, given in Figure 14. Applying the split valence double- $\zeta$  basis set 6-31G(d), one obtains the smallest maximum absolute error for B3LYP, while in combination with the triple- $\zeta$  basis set 6-311++G(d,p) the smallest maximum absolute error is found for O3LYP.



**Figure 15.** Performance of different functionals with 6-311++G-(d,p) for the prediction of the CO frequencies of selected transition-metal carbonyl compounds (1–5) vs experimentally observed values.

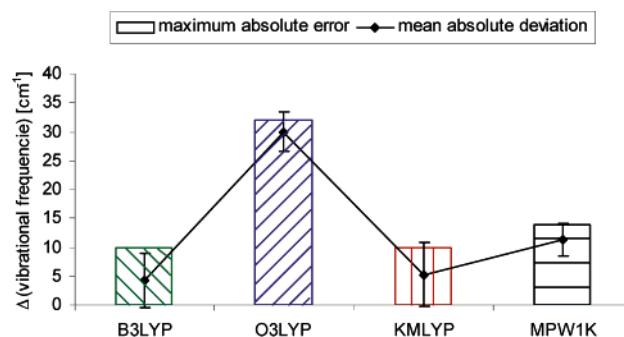
The maximum negative and positive errors obtained for the different compounds in dependence of functional and basis set are listed in the Supporting Information (Tables S19 and S20). In combination with 6-31G(d) and 6-311++G-(d,p) O3LYP and MPW1K tend to underestimate the bond lengths of the transition-metal compounds, while KMLYP and B3LYP incline to overestimate them.

**Vibrational Frequencies.** In addition we studied the vibrational frequencies of the selected transition-metal carbonyl compounds (1–5). Although the accuracy of the calculated frequencies is not perfect, they are still a good indication for the quality of the method used. We compared these calculated frequencies to experimental values from gas-phase data. Selected vibrational frequencies of the transition-metal carbonyl compounds (1–5) compared to experimental data<sup>83–87</sup> are available as Supporting Information. It is obvious that for the double- $\zeta$  calculations larger errors result; therefore, we recommend to use basis sets of triple- $\zeta$  quality for these types of calculations. The mean absolute deviations (MAD) and the standard deviations as well as the largest absolute errors of the calculated CO frequencies in comparison to the experimentally obtained values are shown in Figure 15.

For KMLYP/6-31G(d) and KMLYP/6-311++G-(d,p) the smallest errors in the CO frequencies were calculated, B3LYP being only the second best method. This result can be explained because the transition-metal atom is not involved in the CO vibration.

Looking at the values in the Supporting Information, Tables S4 and S5, it is obvious that for the triple- $\zeta$  basis set the experimentally measured metal–carbon vibrations are reproduced, while the errors in the double- $\zeta$  metal–carbon vibrational values are quite large. This is a direct result of the better description of the metal–carbon bonding situation in the higher quality basis set. Only for KMLYP no difference in the quality of the basis sets is observed.

The mean absolute deviations (MAD) and the standard deviations as well as the largest absolute errors of selected metal–carbon vibrational frequencies of Ni(CO)<sub>4</sub> (1), Fe(CO)<sub>5</sub> (2), and Cr(CO)<sub>6</sub> (3) in comparison to experimentally determined values are illustrated in Figure 16. For the transition-metal carbonyl compounds 4 and 5 no experimental data of the metal–carbon vibrational frequencies could be found in the literature.



**Figure 16.** Performance of different functionals in combination with 6-311++G-(d,p) for the prediction of selected metal–carbon vibrational frequencies of Ni(CO)<sub>4</sub> (1), Fe(CO)<sub>5</sub> (2), and Cr(CO)<sub>6</sub> (3) vs experimentally observed values.

Figure 16 shows the performance of the four density functionals together with the split valence triple- $\zeta$  basis set 6-311++G-(d,p) for the calculation of the metal–carbon frequencies of Ni(CO)<sub>4</sub> (1), Fe(CO)<sub>5</sub> (2), and Cr(CO)<sub>6</sub> (3).

Comparing the results obtained with the split valence double- $\zeta$  and the triple- $\zeta$  basis set, one notices that in combination with 6-311++G-(d,p) the errors are smaller for all functionals. B3LYP and KMLYP in combination with 6-311++G-(d,p) show similar mean absolute deviations from the experimentally observed values. For B3LYP/6-311++G-(d,p) the mean absolute deviation is slightly smaller. MPW1K and O3LYP show significant mean absolute deviations from the experimentally obtained values, clearly larger than for B3LYP and MPW1K.

The maximum positive and negative errors obtained when predicting the CO and metal–carbon vibrational frequencies of selected transition-metal carbonyl compounds are listed in the Supporting Information (Tables S21 and S22). B3LYP, O3LYP, and MPW1K tend to overestimate the CO vibrational frequencies, while KMLYP tends to underestimate these.

## Conclusion

We have investigated the performance of the O3LYP, KMLYP, and MPW1K density functionals in combination with different basis sets for the geometry optimization of several transition-metal compounds as well as for the calculation of the vibrational frequencies of selected transition-metal carbonyl compounds in comparison to the B3LYP density functional. The reliabilities of these methods were evaluated based on their ability to reproduce known geometrical parameters and experimental data.

While O3LYP, KMLYP, and MPW1K have been reported to generally show a better performance than B3LYP for the calculation of organic molecules and organic reactions, this is not true for predicting geometrical parameters of the transition-metal compounds we selected. O3LYP, KMLYP, and MPW1K together with the split valence double- $\zeta$  basis set 6-31G(d) gave generally inferior results to B3LYP for the geometry optimization of all transition-metal compounds examined in this study. Only in combination with the split valence triple- $\zeta$  basis set 6-311++G-(d,p) the results obtained with O3LYP were superior to B3LYP for all investigated

transition-metal compounds. For all studied functionals and transition-metal compounds the mean absolute deviation and the maximum absolute error of the calculated bond lengths is clearly larger when using LANL2DZ as the basis set than for 6-31G(d) or 6-311++G(d,p). Comparing the results obtained with 6-31G(d) and with 6-311++G(d,p) as basis sets, it is important to note that the prediction of the calculated bond lengths of the transition-metal carbonyl compounds (**1–5**) in combination with O3LYP and MPW1K as functionals is more precise with 6-311++G(d,p) than with 6-31G(d).

Calculating the CO frequencies of the transition-metal carbonyl compounds (**1–5**) together with the split valence double- $\zeta$  basis set 6-31G(d) and with the split valence triple- $\zeta$  basis set 6-311++G(d,p) the best results were obtained using the KMLYP functional. The prediction of the metal–carbon frequencies of selected transition-metal carbonyl compounds using the B3LYP and KMLYP functionals together with 6-311++G(d,p) we obtained very small deviations from the experimental values, while the results obtained with O3LYP and MPW1K were slightly inferior.

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**Supporting Information Available:** Details on calculated and experimentally observed individual bond lengths, angles, and frequencies and maximum absolute errors of the calculated bond lengths in comparison to experimental values as well as a list of the basis sets used. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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