

# Performance of Density Functional Theory for 3d Transition Metal-Containing Complexes: Utilization of the Correlation Consistent Basis Sets

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The performance of 44 density functionals used in conjunction with the correlation consistent basis sets (cc-pVnZ where  $n = T$  and  $Q$ ) has been assessed for the gas-phase enthalpies of formation at 298.15 K of 3d transition metal (TM) containing systems. Nineteen molecules were examined: ScS, VO, VO<sub>2</sub>, Cr(CO)<sub>6</sub>, MnS, MnCl<sub>2</sub>, Mn(CO)<sub>5</sub>Cl, FeCl<sub>3</sub>, Fe(CO)<sub>5</sub>, CoH(CO)<sub>4</sub>, NiCl<sub>2</sub>, Ni(CO)<sub>4</sub>, CuH, CuF, CuCl, ZnH, ZnO, ZnCl, and Zn(CH<sub>3</sub>)<sub>2</sub>. Of the functionals examined, the functionals that resulted in the smallest mean absolute deviation (MAD, in parentheses, kcal mol<sup>-1</sup>) from experiment were B97-1 (6.9), PBE1KCIS (8.1), TPSS1KCIS (9.6), B97-2 (9.7), and B98 (10.7). All five of these functionals include some degree of Hartree–Fock (HF) exchange. The impact of increasing the basis set from cc-pVTZ to cc-pVQZ was found to be slight for the generalized gradient approximation (GGA) and meta-GGA (MGGA) functionals studied, indicating basis set saturation at the triple- $\zeta$  level. By contrast, for most of the generalized gradient exchange (GGE), hybrid GGA (HGGA), and hybrid meta-GGA (HMGGA) functionals considered, improvements in the average MAD of 2–3 kcal mol<sup>-1</sup> were seen upon progressing to a quadruple- $\zeta$  level basis set. Overall, it was found that the functionals that include Hartree–Fock exchange performed best overall, but those with greater than 40% HF exchange exhibit significantly poor performance for the prediction of enthalpies of formation for 3d TM complexes. Carbonyl-containing complexes, a mainstay in organometallic TM chemistry, are demonstrated to be exceedingly difficult to describe accurately with all but 2 of the 44 functionals considered. The most accurate functional, for both CO-containing and CO-free compounds, is B97-1/cc-pVQZ, which is shown to be capable of yielding results within 1 kcal mol<sup>-1</sup> of high-level ab initio composite methodologies.

## Introduction

Density functional theory (DFT)<sup>1</sup> has seen increasing use in transition metal (TM) computational chemistry over the past decade.<sup>2</sup> The reason for this growth is primarily its low computational cost and success in predicting molecular properties (i.e., geometries, thermodynamics, infrared spectroscopy, etc.). Such successes have made the development and improvement of density functionals a very active area of research.<sup>3–12</sup> Although a large number of density functionals are available, problems remain in selecting the appropriate functional for a particular scientific problem of interest. The choice of a specific DFT method should be guided by careful consideration of the original calibration and further, system-specific testing of the selected functional. For example, although many common density functionals have been developed and even parametrized for a limited set of molecules (such as main group molecules), these functionals are often applied to TM complexes without subsequent validation of their applicability.

To assess the appropriateness of DFT methods for TM systems, comprehensive studies must be carried out where a wide variety of functionals are tested for a diverse set of TM molecules, as has been explicitly called for in one recent study.<sup>13</sup> Notable work along these lines includes studies by Zhao and Truhlar,<sup>14–19</sup> in which the M05 and M06 suite of functionals (i.e., M05, M05-2X, M06, M06-2X, M06-L, M06-HF) were developed and evaluated. Fitting parameters in these functionals

were optimized for a robust database that included main group atomic and molecular properties, as well as properties for TM atoms, complexes, and reactions. Zhao and Truhlar have recommended that M06 and M06-L be used for the calculation of TM atomization energies, metal–ligand bond energies, and reaction energies, based on comparison with the 3d transition metal reaction energies (TMRE48) database that includes 9 TM dimer atomization energies, 21 metal–ligand bond dissociation energies (BDE), and 19 TM reaction energies.<sup>18,19</sup> The average mean absolute deviation (AMAD) was approximately 6 kcal mol<sup>-1</sup> for both M06 and M06-L using this database. They noted that to reduce calculated errors in reaction barrier heights, a “high” percentage of Hartree–Fock (HF) exchange should be included; for example, M05-2X incorporates twice the percentage of HF exchange (56%) as compared to M05. However, such an increase in the percentage of HF exchange included in a functional can adversely affect the accuracy of calculated ground-state properties, such as atomization energies, for TM systems.

In another recent study,<sup>6,7</sup> the performance of 57 functionals for evaluating TM properties was examined with double- and triple- $\zeta$  basis sets. The study suggested that G96LYP, MPWLYP1M, XLYP, BLYP, MOHLYP, and mPWLYP be used for modeling TM–ligand BDEs, metal–metal and metal–ligand bond lengths, and both binding and atomization energies for TM dimers. A study by Furche and Perdew of 62 transition metal-containing compounds has also been reported.<sup>12</sup> In their study, the performance of six functionals paired with triple- and occasion-

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ally quadruple- $\zeta$  basis sets was examined for dissociation energies, bond lengths, and vibrational frequencies of 3d TM systems including TM dimers, monohydrides, monoxides, mononitrides, and monofluorides;<sup>12</sup> BP86 and TPSS were recommended.

Few studies, however, have analyzed the use of DFT methods in determining enthalpies of formation,  $\Delta H_f^\circ$ , of TM systems,<sup>20,21</sup> even though this fundamental thermodynamic quantity is not only of great experimental importance, but also provides a rigorous test of the accuracy of a computational method. In a study of calculated  $\Delta H_f^\circ$  by Riley and Merz for 94 TM systems,<sup>20</sup> 12 functionals were examined using two different basis sets, 6-31G\*\* and TZVP. The lowest mean absolute deviation (MAD) for the compounds in their test set was 9.1 kcal mol<sup>-1</sup> using the TPSS1KCIS functional with the TZVP basis set, which is well above the traditional definition of “chemical accuracy” (i.e.,  $\pm 1$  kcal mol<sup>-1</sup>). On the basis of recent, high-level ab initio calculations of the enthalpies of formation of TM complexes by DeYonker et al.,<sup>21</sup> it was suggested that a target for “transition metal accuracy” for calculated enthalpies of formation should be set at  $\pm 3$  kcal mol<sup>-1</sup>, due to the larger experimental uncertainties common to such complexes. In the study by Riley and Merz,<sup>20</sup> the average error in the experimental enthalpies of formation was  $\pm 3.6$  kcal mol<sup>-1</sup>, roughly one-third the calculated MAD of TPSS1KCIS. They also observed that the functional that produced the lowest MAD was dependent upon the TM, the number of ligands, the type of ligands, and the basis set utilized.

In similar studies about the relative efficacies of ab initio methods (such as MP2 and CCSD(T)), insight has often been gained through the utilization of the correlation consistent basis sets (e.g., cc-pVnZ, aug-cc-pVnZ, cc-pCvNz, aug-cc-pCvNz, where  $n = D, T, Q, 5, 6$ ).<sup>22–29</sup> Due to the unique construction of this family of basis sets, systematic, monotonic convergence in the description of molecular properties is observed upon increasing the quality of the basis set.<sup>30–32</sup> At the complete basis set (CBS) limit, the remaining source of error can therefore be attributed solely to the selected method, thereby providing a gauge of the error inherent in a methodology. Such a relationship is not necessarily guaranteed for DFT, however,<sup>3,5,33–36</sup> as it has been shown<sup>4,37,38</sup> that there are some molecules for which basis sets should be recontracted to ensure monotonic convergence to the Kohn–Sham (KS) limit. Despite this caveat, the correlation consistent basis sets span an array of sizes, and thus the common assumption that DFT calculations exhibit basis set convergence at the triple- $\zeta$  level<sup>3–5,34,35</sup> can be assessed through use of the cc-pVQZ basis set. Indeed, some prior work<sup>33,35,39</sup> has suggested that larger basis sets may be required for saturation in DFT. This behavior of DFT may be especially pronounced for TM species, which have been shown by ab initio methods<sup>40</sup> to be particularly sensitive to basis set size. In any event, the all-electron correlation consistent basis sets designed specifically for TMs<sup>41,42</sup> have not yet been extensively studied for DFT calculations, and thus the present work provides a succinct means to guide the selection of not only the most accurate density functional, but also the appropriate accompanying basis set.

One trend that emerges from previous DFT studies<sup>6,7</sup> of TM species is that certain properties, including metal–metal and metal–ligand BDEs, bond lengths, and ionization potentials, are poorly described by hybrid functionals, inarguably the most popular type of functional in use in molecular quantum chemistry, presumably due to the inclusion of HF exchange. In Riley and Merz’s study,<sup>20</sup> errors from calculations utilizing

hybrid functionals for metal–metal bonded systems are in excess of 30 kcal mol<sup>-1</sup>. In this study, we seek to evaluate the degree to which extant density functionals, including those with HF exchange, can accurately calculate enthalpies of formation. Additionally, the present work carefully considers the extent to which basis set saturation impacts calculated properties of TM complexes. The findings of this work are expected to be of use in computational applications on systems of real interest, as it provides a gauge of method performance with respect to basis set for TM species using  $\Delta H_f^\circ$ , a fundamental physical property that not only determines the stability of a molecule, but can also be used to evaluate the amount of energy needed or released in any reaction, ranging from catalytic cycles to detonation.

## Computational Methods

All calculations in this study were carried out using the *Gaussian03* package.<sup>43</sup> Geometry optimizations were carried out at both the triple- $\zeta$  and quadruple- $\zeta$  levels (cc-pVTZ and cc-pVQZ, respectively) for all functionals, and frequency calculations were carried out at the triple- $\zeta$  level for each functional to determine the zero-point energy and enthalpy corrections for the molecules. These corrections were not scaled, as many of the functional/basis set combinations listed below lack published scaling factors, and it has been shown<sup>44</sup> that both these factors and their attendant uncertainties vary from method to method. Moreover, concerns have previously been identified<sup>45</sup> about differences in scaling behavior between diatomic and polyatomic molecules, both of which are present in the test set described below. Previous studies on calculated enthalpies of formation<sup>13</sup> and vibrational frequencies<sup>12</sup> have also eschewed these empirical corrections.

For calculations involving sulfur and chlorine, the cc-pV( $n+D$ )Z ( $n = T, Q$ ) basis sets for sulfur and chlorine<sup>46</sup> were utilized in place of cc-pVnZ, as it has been shown by Wilson et al.<sup>23,33,35,46–49</sup> that these modified basis sets can result in substantial improvements in the evaluation of energetic properties. For some of the compounds in the test set, the cc-pVTZ basis set was uncontracted; results are presented in Supporting Information but overall have an effect on the MAD of less than 0.2 kcal mol<sup>-1</sup>. The enthalpy of formation was determined with a standard procedure<sup>50</sup> from the calculated atomization energy of each molecule, calculated enthalpy corrections (from absolute zero to 298.15 K) for each molecule, experimental enthalpies of formation of the constituent atoms,<sup>51,52</sup> and experimental enthalpy corrections for the constituent atoms.<sup>51,52</sup>

Previous computational work<sup>53</sup> on 4s to 3d excitations has suggested that, even for the 3d series, relativity must be considered to obtain meaningful results with DFT. For calculations on large TM systems of interest, such as catalytic intermediates, these effects are typically incorporated via an effective core potential (ECP), such as in the LANL2DZ ECP and valence basis set.<sup>54</sup> However, ECPs have only been published within the correlation consistent framework for Cu and Zn.<sup>55</sup> The all-electron results discussed in this work can therefore serve as an upper limit of accuracy, against which future efforts in 3d TM ECP development can be gauged. In the meantime, the magnitude of scalar relativistic effects here have been investigated with a second-order Douglas-Kroll (DK) Hamiltonian<sup>56</sup> (and accompanying cc-pVTZ-DK basis set<sup>57</sup>) for the functional that gives the lowest MAD of calculated enthalpies of formation in this work, B97-1.<sup>58</sup> The results are presented in full as Supporting Information, but overall the MAD for this functional is improved by the inclusion of relativistic effects by less than 0.5 kcal mol<sup>-1</sup>. Thus, it appears that  $\Delta H_f^\circ$

**TABLE 1: Experimental Gas-Phase Enthalpy of Formation [ $\Delta H_f^\circ$  (298.15 K)], Electronic Ground State, Uncertainty, and the Average Uncertainty for the Set of TM Species, Reported in kcal mol<sup>-1</sup>**

	ground state	$\Delta H_f^\circ$	uncertainty	ref
CuF	$^1\Sigma^+$	1.1	3	61
CuH	$^1\Sigma^+$	65.9	2	62
CuCl	$^1\Sigma^+$	19.262	2	62
Cr(CO) <sub>6</sub>	$^1A_{1g}$	-240	1.1	62
FeCl <sub>3</sub>	$^6A_1$	-60.5	1.2	51
Fe(CO) <sub>5</sub>	$^1A_1'$	-173	2.0	62
CoH(CO) <sub>4</sub>	$^1A_1$	-136	0.5	62
MnCl <sub>2</sub>	$^6\Sigma_g$	-63	0.5	62
MnCl(CO) <sub>5</sub>	$^1A_1$	-219.5	3.1	51
MnS	$^6\Sigma^+$	63.31	2.0	62
NiCl <sub>2</sub>	$^3B_1$	-17.7	0.05	51
Ni(CO) <sub>4</sub>	$^1A$	-144	2.5	51
ScS	$^2\Sigma^+$	41.747	3.1	62
VO	$^4\Sigma$	31.8	2	63
VO <sub>2</sub>	$^2A_1$	-41.6	3.3	63
Zn(CH <sub>3</sub> ) <sub>2</sub>	$^1A$	12.6	1.4	51
ZnCl	$^2\Sigma^+$	6.5	1.0	62
ZnH	$^2\Sigma^+$	62.909	0.5	62
ZnO	$^1\Sigma^+$	52.8	0.9	62
avg uncertainty			1.7	

may be less sensitive to relativity than s/d splitting,<sup>53</sup> which might be expected given the known difference<sup>59</sup> between s orbital contraction and d orbital expansion under the influence of relativity. Previous work on calculated BDEs for zinc compounds has also shown<sup>60</sup> that the functionals that perform best with relativistic effects included also perform best in nonrelativistic calculations. Given this past finding, as well as the small and unsystematic effect of relativity found in this work, we expect our conclusions about functional accuracy to remain the same irrespective of the inclusion of relativistic effects. Therefore, results presented in this work do not include these effects.

The set of transition metal species examined comprises 19 species with 1–6 coordinating groups, different metal–ligand bonding types, and different ligand sizes: ScS, VO, VO<sub>2</sub>, Cr(CO)<sub>6</sub>, MnS, MnCl<sub>2</sub>, MnCl(CO)<sub>5</sub>, FeCl<sub>3</sub>, Fe(CO)<sub>5</sub>, CoH(CO)<sub>4</sub>, NiCl<sub>2</sub>, Ni(CO)<sub>4</sub>, CuH, CuF, CuCl, ZnCl, ZnH, ZnO, and Zn(CH<sub>3</sub>)<sub>2</sub>. These species, although generally smaller than TM systems typically studied, still experience many of the difficulties pervasive in TM chemistry, such as low-lying, nearly degenerate electronic states, partial d shell occupancies, and so forth. However, as these compounds have both published experimental  $\Delta H_f^\circ$  values with low experimental error bars and well-established experimental ground states (Table 1), they serve as a suitable data set for comparison. The spin state of each system was matched with the reported experimental ground state, regardless of whether or not the functional/basis set combinations predicted a lower-energy electronic state.

The 44 functionals utilized in this study are listed in Table 2 and can be grouped into three categories: generalized gradient approximation (GGA), meta-GGA (MGGA), and generalized gradient exchange (GGE) methods. The GGA functionals depend on both the electron density and the gradient of that density, while MGGA functionals also depend on the kinetic energy. These two groups can also include HF exchange, giving rise to the hybrid GGA (HGGA) and hybrid MGGA (HMGGA) classes of functionals. The GGE functionals proposed by Hertwig and Koch<sup>88</sup> are similar to GGA functionals, except that the GGA correlation functional is replaced with a local spin density approximation (LSDA) correlation functional that

depends only on the density. Because previous studies on TMs using DFT methods<sup>7,20,84</sup> have shown that hybrid functionals are better suited to assess the  $\Delta H_f^\circ$  of the metal–ligand systems, we have included more HGGA and HMGGA functionals than pure functionals. Table 2 provides the percent of HF exchange included for the hybrid functionals, as well as references for all functionals. All told, the functionals chosen here fulfill a previously published request<sup>13</sup> to investigate additional functionals for evaluating enthalpies of formation.

## Results and Discussion

**A. Effect of Basis Set.** To determine the effect of the quality of the basis set on predicted thermochemistry, triple- $\zeta$  and quadruple- $\zeta$  quality correlation consistent basis sets (cc-pVTZ and cc-pVQZ, respectively) were combined with all 44 functionals to calculate the enthalpies of formation of all species. As shown in Table 3, only a limited improvement was seen when the basis set quality was increased from cc-pVTZ to cc-pVQZ for all pure GGA and MGGA functionals, except HCTH. In fact, only about half of the pure GGA and MGGA functionals showed a concomitant increase in accuracy upon increasing the basis set size. Indeed, for BP86, mPWPBE, mPWPW91, BB95, mPWB95, mPWKCIS, and PBEKCIS, the MAD actually increased upon improving the basis set. In contrast, all GGE, HGGA, and HMGGA functionals showed improved accuracy when the basis set quality increased from triple- to quadruple- $\zeta$ . For the GGE functionals, this decrease in MAD ranges from 1.5 kcal mol<sup>-1</sup> for PBEVWN5 to 2.8 kcal mol<sup>-1</sup> for OVWN5; from 1.2 kcal mol<sup>-1</sup> for B3P86 to 3.8 kcal mol<sup>-1</sup> for B97-1 for the HGGA functionals; and from 1.8 kcal mol<sup>-1</sup> for MPW1KCIS to 4.1 kcal mol<sup>-1</sup> for M05-2X for the HMGGA category. Therefore, for this set of molecules, the hybrid functionals are more dependent upon the basis set size than pure functionals.

**B. Accuracy of Pure vs Hybrid Functionals.** Among the 44 functionals studied in this work, there are a number of pairs of functionals that differ only with respect to the inclusion of HF exchange (e.g., BLYP and B3LYP, mPWPW91 and mPW1PW91, TPSSKCIS and TPSS1KCIS, etc.). In almost all cases, there is a significant reduction in the MAD when HF exchange is included. For example, the MAD of the pure functional BB95 is 37.3 kcal mol<sup>-1</sup>, whereas the MAD of the corresponding hybrid functional B1B95 is 8.9 kcal mol<sup>-1</sup> (at the cc-pVQZ level). The sole exception is for the OLYP and O3LYP pair of functionals: OLYP has a MAD of 11.0 and 9.3 kcal mol<sup>-1</sup> for cc-pVTZ and cc-pVQZ basis sets, respectively, whereas O3LYP has a MAD of 14.1 and 11.0 kcal mol<sup>-1</sup> for cc-pVTZ and cc-pVQZ, respectively. Overall, the AMAD of the pure GGA and MGGA functionals at the cc-pVQZ basis set level is 24.9 kcal mol<sup>-1</sup>, while the AMAD of the HGGA and HMGGA functionals is a significantly lower 16.2 kcal mol<sup>-1</sup>.

The present results also show that this reduction in MAD upon inclusion of HF exchange is far more significant for the MGGA functionals than it is for the GGA functionals. With the cc-pVQZ basis set, the AMAD for the HGGA functionals is 16.4 kcal mol<sup>-1</sup> (cf. 21.2 kcal mol<sup>-1</sup> for the GGA functionals), while the AMAD for the HMGGA functionals is 16.0 kcal mol<sup>-1</sup> (cf. 31.2 kcal mol<sup>-1</sup> for the MGGA functionals).

Figure 1 shows the calculated MAD (with the cc-pVQZ basis) for the test set of 3d metal complexes plotted against the percentage of HF exchange included in each DFT functional. There is an obvious dichotomy in the accuracy of the calculated enthalpies of formation between the functionals with a lower percentage HF exchange (defined



**TABLE 2: Generalized Gradient Approximation (GGA), Meta-GGA (MGGA), Generalized Gradient Exchange (GGE), Hybrid GGA (HGGA), and Hybrid MGGA (HMGGA) Functionals Utilized in This Study and the Percent Hartree–Fock Exchange Included in the Hybrid Functionals**

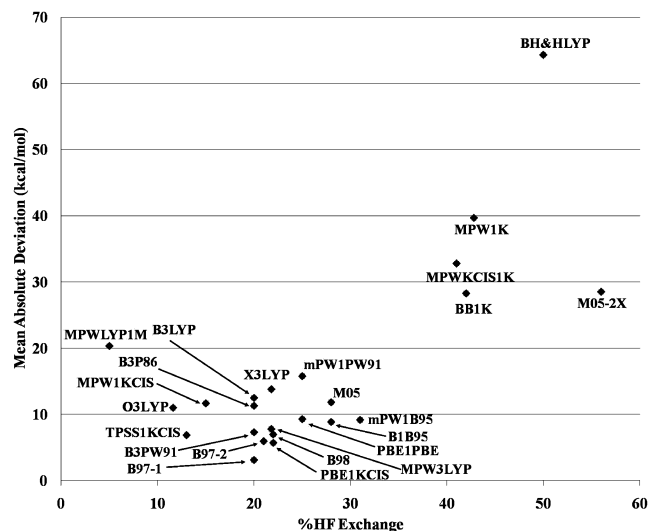
class	functional	ref	class	functional	% HF	ref
<b>GGA</b>	BLYP	64, 65	<b>HGGA</b>	B3LYP	20.00	64–66
	BP86	64, 67		B3P86	20.00	64, 67
	BPBE	64, 68		B3PW91	20.00	64, 69, 70
	BPW91	64, 70		B97-1	21.00	58
	G96LYP	65, 71		B97-2	21.00	72
	HCTH	58, 73		B98	21.98	74
	mPWLYP	65, 75		BH&HLYP	50.00	43, 64, 65
	mPWPBE	68, 75		MPW1K	42.80	70, 75, 76
	mPWPW91	70, 75		mPW1PW91	25.00	70, 75
	OLYP	77		MPW3LYP	21.80	7, 65, 75
<b>MGGA</b>			<b>HMGGA</b>	MPWLYP1M	5.00	6
	BB95	64, 79		O3LYP	11.61	78
	mPWB95	64, 75, 79		PBE1PBE	25.00	68, 80, 81
	mPWKCIS	75, 83, 84		X3LYP	21.80	65, 82
	PBEKCIS	68, 83				
	TPSSKCIS	83, 85		B1B95	28.00	64, 79
<b>GGE</b>	VSXC	86		BB1K	42.00	64, 79, 84
				M05	28.00	14, 87
	BVWN5	6, 64		M05-2X	56.00	15
	G96 VWN5	6, 71		mPW1B95	31.00	64, 75, 79, 84
	mPWVWN5	6, 75		MPW1KCIS	15.00	75, 83, 84
	OVWN5	6		MPWKCIS1K	41.00	75, 83, 84
	PBEVWN5	6, 68		PBE1KCIS	22.00	68, 83
				TPSS1KCIS	13.00	70, 83–85

**TABLE 3: Mean Absolute Deviations (MAD) from Experiment and the Deviations between cc-pVTZ and cc-pVQZ Calculations ( $\Delta$ ) for all 44 Functionals, in kcal mol<sup>-1</sup> for all 19 Molecules**

		cc-pVTZ	cc-pVQZ	$\Delta$			cc-pVTZ	cc-pVQZ	$\Delta$
GGA	Avg. MAD	22.2	21.2	-1.0	HGGA	Avg. MAD	19.3	16.4	-2.9
	BLYP	17.3	16.2	-1.2		B3LYP	15.9	12.5	-3.3
	BP86	33.6	34.0	0.4		B3P86	12.5	11.3	-1.2
	BPBE	25.1	25.1	-0.1		B3PW91	11.0	7.3	-3.6
	BPW91	24.2	24.1	-0.1		B97-1	6.9	3.1	-3.8
	G96LYP	13.4	12.2	-1.1		B97-2	9.7	6.0	-3.7
	HCTH	13.4	8.3	-5.0		B98	10.7	7.0	-3.7
	mPWLYP	22.6	21.6	-1.0		BH&HLYP	66.4	64.3	-2.1
	mPWPBE	30.9	31.1	0.2		MPW1K	42.2	39.7	-2.5
	mPWPW91	30.0	30.1	0.2		mPW1PW91	18.5	15.8	-2.7
MGGA	OLYP	11.0	9.3	-1.8		MPW3LYP	11.2	7.8	-3.4
						MPWLYP1M	21.7	20.4	-1.4
	Avg. MAD	31.1	31.2	0.1		O3LYP	14.1	11.0	-3.0
	BB95	36.7	37.3	0.6		PBE1PBE	12.5	9.3	-3.2
	mPWB95	43.0	43.8	0.8		X3LYP	17.1	13.8	-3.3
	mPWKCIS	38.6	39.1	0.5	HMGGA	Avg. MAD	19.1	16.0	-3.1
	PBEKCIS	37.3	37.6	0.3		B1B95	12.4	8.9	-3.5
GGE	TPSSKCIS	19.7	19.2	-0.5		BB1K	31.5	28.3	-3.2
	VSXC	11.5	9.9	-1.6		M05	15.6	11.9	-3.8
						M05-2X	32.6	28.5	-4.1
	Avg. MAD	16.8	14.7	-2.1		mPW1B95	12.7	9.2	-3.5
	BVWN5	16.0	13.5	-2.5		MPW1KCIS	13.5	11.7	-1.8
	G96 VWN5	21.5	19.1	-2.4		MPWKCIS1K	35.6	32.8	-2.8
	mPWVWN5	11.6	9.8	-1.8		PBE1KCIS	8.1	5.7	-2.4
	OVWN5	23.1	20.3	-2.8		TPSS1KCIS	9.6	6.9	-2.7
	PBEVWN5	12.0	10.6	-1.5					

ad hoc as 5–31%) and those with a higher percentage (>40%). The hybrid functionals in the former category all have calculated MADs under 21 kcal mol<sup>-1</sup>, whereas those in the latter group all have MADs in excess of 28 kcal mol<sup>-1</sup>. Within the low range of HF exchange, there is no obvious correlation between the amount of HF exchange included and accuracy. It can be conjectured that lowering the amount of HF exchange below 10% leads to an increase in MAD, as indicated by both the larger MAD of MPWLYP1 M (5%)

and the behavior of the GGAs and MGGA in general, but further investigation along these lines is warranted. Within the high range of included HF exchange, the functional with the most included HF exchange, M05-2X (56%), is only 0.2 kcal mol<sup>-1</sup> less accurate than BB1K, the most accurate functional in this regime. It should be noted that M05<sup>14</sup> was parametrized against 3d TM dimer atomization energies and metal–ligand bond energies (in addition to various main group molecular and reaction properties); M05-2X<sup>15</sup> is



**Figure 1.** Pictorial representation of the mean absolute deviation from experiment in  $\text{kcal mol}^{-1}$  versus the percent Hartree–Fock (HF) exchange of the hybrid functionals utilizing the cc-pVQZ basis set. (Table 2 lists each hybrid functional and its corresponding percent HF exchange.)

identical to M05, save for a doubling of the HF exchange, and thus its (relative, i.e., in the high HF exchange category) accuracy for calculating  $\Delta H_f^\circ$  is not unexpected.

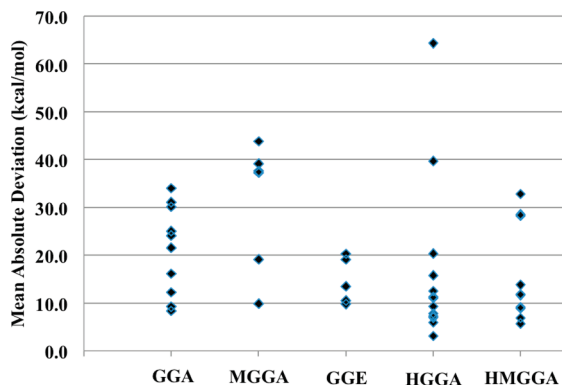
**C. Carbonyl-Containing Compounds.** Compounds containing the carbonyl ligand are ubiquitous in TM chemistry, and so it is of great concern that earlier ab initio studies of transition metal compounds have shown that the deviation from experiment for calculated enthalpies of formation for  $\text{M}(\text{CO})_n$  systems can be on the order of tens of  $\text{kcal/mol}$ , with a particularly large sensitivity to basis set size.<sup>21</sup> For that reason, we scrutinized the performance of the functionals used in this study when

applied to carbonyl-containing compounds. Table 4 details the comparison between the calculated accuracy for the carbonyl-containing species [i.e.,  $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{CO})_5$ ,  $\text{CoH}(\text{CO})_4$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{MnCl}(\text{CO})_5$ ] and those complexes without CO ligands. For nearly every functional, the carbonyl-containing compounds have a much higher MAD than the noncarbonyl species. The most pronounced example of this is for the MGGA group, where four of the six studied functionals show calculated MADs over  $100 \text{ kcal mol}^{-1}$  for the five carbonyl-containing molecules. The HGGA B97-1 results in the overall lowest MAD for the carbonyl compounds,  $3.2 \text{ kcal mol}^{-1}$  (with the cc-pVQZ basis). Table 4 also demonstrates that the improvement seen (vide supra) with the cc-pVQZ basis set can be directly attributed to the increased accuracy of calculated enthalpies of formation of the carbonyl species. For example, the change upon progressing from cc-pVTZ to cc-pVQZ with the B3PW91 functional results in a reduction in MAD for the carbonyl species from 20.8 to  $15.8 \text{ kcal mol}^{-1}$ , whereas the non-CO species show no improvement upon increasing the basis set size.

From the poor performance in evaluating  $\Delta H_f^\circ$  for carbonyl-containing TM species, it seems DFT may have difficulties describing the metal–carbonyl bond environment. Conversely, a Furche and Perdew study<sup>12</sup> suggested that DFT can perform adequately in the determination of carbonyl BDEs for  $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{CO})_5$ , and  $\text{Ni}(\text{CO})_4$ . A possible explanation for why DFT performs better for these BDEs than for enthalpies of formations is that, in the determination of BDEs, the error generated is often similar in magnitude for both the parent molecule and its constituent fragments [e.g.,  $\text{Ni}(\text{CO})_4 \rightarrow \text{Ni}(\text{CO})_3 + \text{CO}$ ]. However, the enthalpies of formation determined in this study utilize the atomization energy approach,<sup>50</sup> where reactant and product chemical states are starkly different (e.g.,  $\text{Ni}(\text{CO})_4 \rightarrow \text{Ni} + 4\text{C} + 4\text{O}$ ), and therefore fortuitous cancellation of errors should not be expected.

**TABLE 4: Mean Absolute Deviations (MAD) from Experiment for the Five Carbonyl Containing Species versus Those without Carbonyls for all 44 Functionals, in  $\text{kcal mol}^{-1}$**

		carbonyl containing		noncarbonyl				carbonyl containing		noncarbonyl	
		cc-pVTZ	cc-pVQZ	cc-pVTZ	cc-pVQZ			cc-pVTZ	cc-pVQZ	cc-pVTZ	cc-pVQZ
GGA	avg. MAD	51.2	52.3	9.5	9.4	HGGA	avg. MAD	43.3	40.9	7.3	7.1
	BLYP	35.2	36.8	8.2	8.2		B3LYP	36.2	33.4	4.9	4.7
	BP86	89.0	91.1	12.6	12.7		B3P86	19.0	22.4	6.8	6.9
	BPBE	62.3	64.3	10.2	10.3		B3PW91	20.8	15.8	4.0	4.0
	BPW91	59.4	61.5	10.0	10.1		B97-1	5.9	3.2	3.1	2.9
	G96LYP	17.3	19.6	9.0	9.0		B97-2	16.5	13.3	3.2	3.1
	HCTH	15.5	12.4	7.8	6.4		B98	20.9	17.9	3.0	2.9
	mPWLYP	55.8	56.8	8.4	8.4		BH&HLYP	187.7	184.1	20.6	20.1
	mPWPBE	83.2	84.8	11.0	11.1		MPW1K	121.5	117.9	11.3	11.0
	mPWPW91	80.2	81.9	10.7	10.9		mPW1PW91	39.8	37.2	7.5	7.6
	OLYP	13.7	14.1	6.9	7.0		MPW3LYP	21.4	19.0	3.7	3.6
MGGA	avg. MAD	83.3	85.1	11.1	11.1	HMGGA	avg. MAD	44.5	42.0	6.4	6.3
	BB95	102.7	104.7	12.2	12.3		B1B95	25.7	22.2	4.0	3.8
	mPWB95	123.4	124.9	13.8	13.9		BB1K	86.5	82.5	8.7	8.3
	mPWKCIS	112.9	114.5	11.4	11.4		M05	31.5	29.1	5.9	5.3
	PBEKCIS	103.4	104.8	12.7	12.7		M05-2X	86.6	80.2	9.5	9.4
	TPSSKCIS	40.4	42.0	10.2	10.3		MPW1B95	26.8	23.5	3.9	3.8
	VSXC	17.0	19.6	6.0	6.0		MPW1KCIS	25.1	26.6	6.1	6.0
							MPWKCIS1K	97.7	94.4	10.4	10.1
GGE	avg. MAD	30.7	29.2	8.9	8.8		PBE1KCIS	8.1	9.0	4.2	4.3
	BVWN5	25.6	23.2	9.5	9.4		TPSS1KCIS	12.3	10.3	5.3	5.3
	G96 VWN5	44.0	41.0	10.7	10.5						
	mPWVWN5	11.4	11.8	8.5	8.5						
	OVWN5	58.3	53.8	8.0	7.8						
	PBEVWN5	14.3	16.1	8.0	8.0						



**Figure 2.** Mean absolute deviation spread of GGA, MGGA, GGE, HGGA, and HMGGGA functionals in kcal mol<sup>-1</sup>.

**D. Performance Evaluation of All Functionals.** The spread of MADs for the five groups of functionals is represented in Figure 2. At first glance, it appears that most of the functional categories, except GGE, cover a large range of accuracy ( $\approx 30$  kcal mol<sup>-1</sup>). However, the two obvious outliers for HGGA are BH&HLYP and MPW1K, two functionals (Figure 1) with a high amount of HF exchange. Similarly, the three higher-lying points in Figure 2 for the HMGGAs (which appear as two points due to overlap) are the high HF exchange functionals MPWKIS1K, BB1K, and M05-2X. If these poorly performing functionals are removed from consideration, then the HGGA and HMGGGA functionals are both quite closely spaced (standard deviations in MAD of 4.7 and 2.5 kcal mol<sup>-1</sup>, respectively), comparable to GGE (with a standard deviation of 4.8 kcal mol<sup>-1</sup>). This behavior stands in contrast to the GGA and MGGA functionals, which show much larger spreads with respective standard deviations of 9.3 and 13.4 kcal mol<sup>-1</sup>.

Overall, the density functionals that had the lowest MAD (in kcal mol<sup>-1</sup>) are B97-1 (6.9), PBE1KCIS (8.1), TPSS1KCIS (9.6), B97-2 (9.7), and B98 (10.7) at the cc-pVTZ basis set level and B97-1 (3.1), PBE1KCIS (5.7), B97-2 (6.0), TPSS1KCIS (6.9), and B98 (7.0) at the cc-pVQZ basis set level. These functionals all include of HF exchange, ranging from 13% for TPSS1KCIS to 22% for PBE1KCIS. The best performance by a pure functional was found for HCTH, which, when paired with the cc-pVQZ basis set, yielded a MAD of 8.3 kcal mol<sup>-1</sup>. (This functional, also referred to as HCTH/407,<sup>73</sup> was fitted against, among other properties, TM complex dissociation energies.) To further illustrate the importance of the inclusion of HF exchange, PBE1KCIS had the second-lowest MAD, but its pure counterpart PBEKCIS had the fifth-highest MAD. The same five functionals are the most accurate for this data set for both the cc-pVTZ and cc-pVQZ bases. The five least accurate DFT methods (in kcal mol<sup>-1</sup>, with the cc-pVQZ basis) are PBEKCIS (37.6), mPWKCIS (39.1), MPW1K (39.7), mPWB95 (43.8), and BH&HLYP (64.3). Three of these functionals are MGGA, whereas the other two possess  $>42\%$  HF exchange.

As the B97-1 functional resulted in the lowest MADs by far for calculated enthalpies of formation with both basis sets, it is worth noting its development. The B97-1 functional<sup>58</sup> was made from the B97 functional,<sup>89</sup> which was designed by Becke and was parametrized for the G2/97 test set.<sup>90</sup> The G2/97 test set includes atomization energies, ionization potentials, and electron and proton affinities of more than 100 first- and second-row atomic and molecular species. The B97-1 functional, developed by Hamprecht et al., resulted from a self-consistent reoptimization of the original B97 parameters; it was found that 21% HF exchange was optimal. Though the functional was not

parametrized for transition metal species, it has been used to predict metal–ligand bond energies of Cr(CO)<sub>6</sub>, Fe(CO)<sub>5</sub>, Ni(CO)<sub>4</sub>, CrO<sub>2</sub>F<sub>2</sub>, CrO<sub>2</sub>Cl<sub>2</sub>, and Fe(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>, and it was found to be more accurate than B97 and B3LYP.<sup>58</sup> A similar functional, B97-2,<sup>72</sup> also performed well for these species. In earlier studies, the B97-2 functional was found to outperform B97-1 when used for the prediction of first- and second-row main group atomization energies, bond lengths, bond angles, static isotropic polarizabilities, and isotropic NMR shielding constants. B97-2 was less accurate than B97-1 for total energies and ionization potentials, and it is less accurate than its predecessor B97-1 in the current study as well, although both are among the most accurate functionals.

Previous work<sup>13</sup> by Riley and co-workers determined that TPSS1KCIS was the best functional for their 3d test set and the triple- $\zeta$  basis set TZVP,<sup>91</sup> with a MAD of 9.1 kcal mol<sup>-1</sup>. For our test set with the comparable cc-pVTZ basis set, we find a similar MAD for TPSS1KCIS of 9.6 kcal mol<sup>-1</sup>, which is outperformed by both B97-1 and PBE1KCIS (MADs of 6.9 and 8.1 kcal mol<sup>-1</sup>, respectively). Additionally, each of these functionals shows improved accuracy when the basis set is increased in size to cc-pVQZ.

As a final test of the accuracy achievable with DFT for TM complexes, the most accurate functional in this study—B97-1 paired with a cc-pVQZ basis set—was compared against two recent highly accurate ab initio studies. The G4(MP2) method<sup>92</sup> and the ccCA-tm approach<sup>21</sup> are both composite model chemistries that utilize coupled cluster calculations and basis set extrapolation schemes to approximate the results of a prohibitively expensive high-level/large basis set calculation; G4(MP2) also includes an empirical correction. These two methods have been applied to different TM test sets that contain eight (G4(MP2)) and six species (ccCA-tm) in common with the current work. The G4(MP2) calculations yield a MAD of 2.3 kcal mol<sup>-1</sup> for CuCl, CuH, FeCl<sub>3</sub>, MnS, NiCl<sub>2</sub>, VO, ZnMe<sub>2</sub>, and ZnH; B97-1/cc-pVQZ gives a MAD of 3.0 kcal mol<sup>-1</sup> for this subset. The ccCA-tm results for VO, VO<sub>2</sub>, FeCl<sub>3</sub>, NiCl<sub>2</sub>, CuF, and ZnMe<sub>2</sub> show a MAD of 2.8 kcal mol<sup>-1</sup>, while B97-1 gives a MAD of 3.8 kcal mol<sup>-1</sup>. Thus, for both subsets, B97-1 paired with a quadruple- $\zeta$  basis set yields results within one kcal mol<sup>-1</sup> of more accurate methodologies. Work is underway to evaluate the performance of this functional for a far larger set of TM compounds.

## Conclusions

The performance of 44 density functionals has been examined with respect to their accuracy in predicting enthalpies of formation at 298.15 K for a set of 19 3d TM-containing molecules. For this set of complexes, which spans the entire 3d series, the effect of improving the basis set quality from cc-pVTZ to cc-pVQZ was examined; for GGE, HGGA, and HMGGGA functionals, this increase in basis set quality leads to a noticeable reduction in the deviation from experiment, in some cases leading to results improved by over 3 kcal mol<sup>-1</sup>. This finding illustrates that the calculation of TM energetic properties with DFT are more sensitive to basis set size than main group species. This behavior can almost entirely be attributed to the accuracy of calculated enthalpies of formation of carbonyl systems. Not only are these species much more sensitive to the basis set size, but they are also poorly described (MAD  $> 10$  kcal mol<sup>-1</sup>), even at the quadruple- $\zeta$  level, by every functional except B97-1 and PBE1KCIS.

The inclusion of Hartree–Fock exchange within the functional is also shown to be important for the accurate prediction



of  $\Delta H_f^\circ$  of transition metal–ligand bonded systems. For example, the MAD for the calculated  $\Delta H_f^\circ$  for the pure functional BPW91 utilizing the cc-pVQZ basis set is 24.1 kcal mol<sup>-1</sup>, whereas its hybrid counterpart B3PW91 shows a MAD of 7.3 kcal mol<sup>-1</sup>. However, the inclusion of too much exchange, defined in this study as >40%, leads to a precipitous decline in accuracy. For the entire set, the functionals with the lowest MAD for the enthalpy of formation are B97-1, PBE1KCIS, and B97-2, which have MADs of 3.1, 5.7, and 6.0 kcal mol<sup>-1</sup>, respectively, at the cc-pVQZ basis set level. The most accurate functional, B97-1, can produce calculated enthalpies of formation for 3d TM species within 1 kcal mol<sup>-1</sup> of high-level ab initio methods. Work is currently in progress to evaluate the behavior of this functional with a larger set of TM species.

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**Supporting Information Available:** Enthalpies of formation for all 44 functionals and 19 molecules with the cc-pVTZ and cc-pVQZ basis sets. Also, results for the uncontracted cc-pVTZ basis set and B97-1, as well as results for B97-1/cc-pVTZ-DK (for relativistic effects). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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