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## Troubles in the systematic prediction of transition metal thermochemistry with contemporary out-of-the-box methods

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# Troubles in the systematic prediction of transition metal thermochemistry with contemporary out-of-the-box methods.

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KEYWORDS: DLPNO-CCSD(T), DFT, Transition Metals, Reaction Enthalpies.

ABSTRACT. The recently developed DLPNO-CCSD(T) method and 7 popular DFT functionals (B3LYP, M06, M06L, PBE, PBE0, TPSS and TPSSh) with and without an empirical dispersion term have been tested to reproduce 111 gas phase reaction enthalpies involving 11 different transition metals. Our calculations, corrected for both relativistic effects and basis set incompleteness, indicate that most of the methods applied with default settings perform with acceptable accuracy on average. Nevertheless, our calculations also evidenced unexpected and non systematic large deviations for specific cases. For group 12 metals (Zn, Cd, Hg) most of the methods provided mean unsigned errors (MUE) less than 5.0 kcal/mol, with DLPNO-CCSD(T) and PBE methods performing excellently (MUE lower 2.0 kcal/mol). Problems started with group 4 metals (Ti and Zr). Best performer for Zr complexes with a MUE of 1.8 kcal/mol, PBE0-D3, provides a MUE larger than 8 kcal/mol for Ti. DLPNO-CCSD(T) provides a reasonable

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3 MUE of 3.3 kcal/mol for Ti reactions, but gives MUE a larger than 14.4 kcal/mol for Zr  
4 complexes, with all the larger deviations for reactions involving  $ZrF_4$ . Large and non-systematic  
5 errors have been obtained for group 6 metals (Mo and W), for 8 reactions containing Fe, Cu, Nb  
6 and Re complexes. Finally, for the whole set of 111 reactions, the DLPNO-CCSD(T), B3LYP-  
7 D3 and PBE0-D3 methods turned out to be the best performers, both providing MUE below 5.0  
8 kcal/mol. Since DFT results cannot be systematically improved and large non-systematic  
9 deviations of 20-30 kcal/mol were obtained even for best performers, our results indicates that  
10 current DFT methods are still unable to provide robust predictions in transition metal  
11 thermochemistry, at least for the functionals explored in this work. The same conclusion holds  
12 for both DLPNO-CCSD(T) and canonical CCSD(T) methods when used entirely as out-of-the-  
13 box. However if careful investigation core correlation is performed, relativistic effects are  
14 properly included and the quality of the reference wave function is properly checked, CCSD(T)  
15 methods can still provide good quality results that might be even used to validate DFT methods,  
16 due to paucity of accurate thermodynamic data for realistic-size transition metal complexes.  
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## 1. Introduction

In silico molecular design leading to better materials, catalysts and enzymes based on transition metals is an emerging field of research<sup>1-26</sup> which can bridge theoretical chemistry and industry.<sup>27</sup> Indeed, dramatic increase in computer power, and the availability of a large number of reliable molecular modeling codes with a variety of electronic structure methods,<sup>28</sup> promote a new strategy in chemistry. Focusing on catalysis, the search for new complexes can be first made by molecular simulations, allowing to focus experimental efforts only on the most promising candidates, within the so called catalysis by design approach. This is opposite to more traditional strategies where potential complexes are searched by trial and error.

The design and discovery of a new catalyst from theory is still a big challenge due to the difficulty to propose a compound that at the same time it is easy to synthesize, shows good catalytic activity, and it is stable under catalytic conditions. The increasing role of electronic structure methods in catalysis of course relies on the capacity of these methods to approach chemical accuracy, which is often not the case. One source of errors might be related to approximate treatment of conformational sampling and solvent effects in existing computational protocols. The accurate estimation of these effects is not affordable since systematic conformational search would require the calculation of  $3^N$  structures (where N is the number of rotatable bonds) at a high level of theory, while reliable treatment of solvent effects would require inclusion of explicit solvent molecules. On the other hand, it could be that the accuracy of the electronic structure method by itself is not approaching chemical accuracy, which prevents a out-of-the-box approach to systematically screen thousands of perspective complexes comprising a large variety of transition metal and ligands in an automatic fashion.

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3 This explains the continuous benchmarking of electronic structure methods towards chemically  
4 more stressful situations, with publications indicating the limitation of a particular method or  
5 group of methods to accurately describe certain molecular properties or reaction energies.<sup>29-51</sup>  
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10 Inspired by these documented failures and challenged by prohibitive costs of some electronic  
11 structure methods, efforts are constantly made to improve methods performance and to reduce  
12 computational costs. This results in two big families of methods recommended for routine  
13 predictions in transition metal chemistry.  
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21 The first group of methods is rooted into density functional theory (DFT).<sup>52-53</sup> Apart from the so-  
22 called double-hybrids,<sup>54</sup> these methods have favorable scaling behavior and quite often lead to  
23 accurate predictions. However, since the exact form of the exchange-correlation (XC) functional,  
24 the core of DFT, is still unknown, there is no single method working equally good across all  
25 known classes of compounds and properties. Further, the accuracy of hundreds of possible  
26 approximations to the exact XC functional is known to be at some extent dependent on the  
27 particular complex or property.<sup>55</sup> This implies that careful testing of functionals vs. particular  
28 complexes and reaction type can highlight those functionals leading to accurate performance, but  
29 any generalization to other reactions or different compound classes is always questionable.  
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43 On the other side, wave function theory (WFT) methods<sup>56</sup> can be systematically improved in  
44 quality, and allow achieving any given level of accuracy, with the huge limitation of exceedingly  
45 high, or even prohibitive, computational costs. Among WFT methods the coupled cluster  
46 approach including single, double and partly triple excitations in perturbative fashion,  
47 CCSD(T)<sup>57</sup> became *de facto* the “gold standard” in contemporary theoretical chemistry. Despite  
48 the promised chemical accuracy, low convergence with respect to the basis set and the large  
49 computational costs (scales as  $N^7$  with  $N$  being the basis set size of the system) kept this method  
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3 away from extensive applications in transition metal chemistry. However, recent advances<sup>58-68</sup>  
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5 made CCSD(T) method affordable up to systems of hundred light atoms. Among these methods,  
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7 the domain based local pair natural orbital (DLPNO)<sup>62-63</sup> CCSD(T) implementation turned out to  
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9 be particularly popular.<sup>69</sup>  
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13 Due to the reduced computational cost of CCSD(T) into these modern variants, whether DFT or  
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15 WFT methods are to be used for meaningful predictions in transition metal chemistry is a hot  
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17 topic of research.<sup>39</sup> As expected, the DFT community advocates strongly for the latest  
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19 functionals, usually the Minnesota or the so-called DFT-D functionals, appealing to low  
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21 computational costs, excellent performance in numerous benchmark studies on transition metal  
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23 complexes,<sup>49,70-89</sup> and some ability to account for difficult-to-handle static correlation.<sup>39,49,90-91</sup>  
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28 On the other hand, recent successful applications of DLPNO-CCSD(T) methods in transition  
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30 metal thermochemistry,<sup>92-95</sup> and the excellent reputation of the parent CCSD(T) method in  
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32 general,<sup>56,96-97</sup> advocates for this method to be used for accurate calculations. Indeed, in a recent  
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34 study we have shown that mean unsigned error below 2.0 kcal/mol can be achieved by the  
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36 DLPNO-CCSD(T) method in the prediction of non-covalent ligands dissociation enthalpies in  
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38 coinage metal complexes, already with the computationally affordable cc-pVTZ basis sets.<sup>98</sup>  
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40 Worth to mention that the performance of the M06 functional on the same reactions turned out to  
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42 be comparable.  
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48 To contribute further to finding the best out-of-the-box approach to be used in transition metal  
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50 thermochemistry in general, we propose 4 new datasets involving 11 different transition metals  
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52 (Ti, Fe, Mo, Re, Nb, Cu, Zr, W, Zn, Cd, Hg) and 111 gas phase reaction enthalpies in total,  
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54 derived from accurate experimental formation enthalpies. We explore the accuracy of the  
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56 CCSD(T) method in its DLPNO implementation as well as other 14 popular DFT methods on  
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3 these datasets. All the systems are in the singlet ground state, since the current implementation of  
4 DLPNO-CCSD(T) can only be applied to closed shell systems. T1 diagnostic<sup>99</sup> as well as largest  
5 amplitudes (T2) were thoroughly monitored to exclude any large influence of multi-reference  
6 effects.  
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## 11 12 13 14 **2. Computational Details**

### 15 16 17 **2.1 Geometry Optimization**

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20 All geometry optimizations were performed with the hybrid GGA PBE0<sup>100-102</sup> functional as  
21 implemented in the Gaussian 09<sup>103</sup> suite of programs. The Grimme's D3(BJ)<sup>90</sup> dispersion  
22 correction was applied to arrive at the PBE0-D3(BJ) functional, to account the possible influence  
23 of the dispersion interaction, not covered by the standard PBE0 functional, on molecular  
24 geometries.<sup>80,104-105</sup> The default values were adopted for the self-consistent-field and geometry  
25 optimization convergence criteria. Numerical integration of the exchange-correlation (XC) terms  
26 was performed using tighter-than-default "ultrafine" option (pruned, 99 radial shells and 590  
27 angular points per shell) to eliminate the potential numerical noise in energy second derivatives.  
28 Geometries were characterized as true energy minima by the eigenvalues of the analytically  
29 calculated Hessian matrix. Translational, rotational, and vibrational partition functions for  
30 thermal corrections to give total enthalpies were computed within the ideal-gas, rigid-rotor, and  
31 harmonic oscillator approximations following standard procedures.  
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50 The all-electron triple- $\zeta$  basis sets augmented with single sets of polarization functions (TZVP)  
51 of Ahlrichs et al.<sup>106-107</sup> were used on all the elements with  $Z \leq 18$ . On all elements with  $Z > 18$   
52 quasi-relativistic effective core potentials (ECPMWB) of the Stuttgart type<sup>108</sup> were used to  
53 describe the core electrons. To get the valence basis sets consistent in quality with the TZVP  
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3 family, the corresponding basis sets<sup>108</sup> were systematically improved: all outermost exponents  
4 were split (s, p and d for d-elements and s and p for p-block elements) and the polarization  
5 functions were added (the two f polarization functions for d-block elements<sup>109</sup> and one d  
6 polarization function (Huzinaga polarization) for p-block elements from the EMSL basis set  
7 library<sup>110-111</sup>).

## 16 2.2 Single-Point Energy Evaluations

19 The ORCA<sup>69</sup> suite of programs was employed for all the single-point DFT and WFT  
20 calculations performed in the present work. First, the DLPNO-CCSD(T)<sup>62-63</sup> method was applied  
21 for all single-point energy evaluations in the current work. The default “NormalPNO” DLPNO  
22 settings (TCutPairs =  $10^{-4}$ , TCutPNO =  $3.33 \cdot 10^{-7}$ , TCutMKN =  $10^{-3}$ ) were used as recommended  
23 for most computational applications in terms of cost/efficiency ratio.<sup>68</sup> In addition, the energy  
24 was reevaluated at the optimized geometry also using the following popular DFT functionals:  
25 GGA PBE,<sup>100-101</sup> hybrid GGA B3LYP,<sup>112-114</sup> PBE0,<sup>100-102</sup> meta-GGA TPSS,<sup>115</sup> M06L,<sup>116</sup> and  
26 hybrid meta-GGA TPSSh<sup>115</sup> and M06.<sup>117-118</sup> Apart from being used standalone, every functional  
27 has been augmented with Grimme’s empirical correction term with zero-damping (M06 and  
28 M06L) and Becke-Johnson damping (B3LYP, PBE, PBE0, TPSS, TPSSh) to arrive at  
29 corresponding DFT-D3 functionals.<sup>90</sup> Numerical integration was performed using tighter-than-  
30 default “Grid 5 FinalGrid 6” option (Lebedev434 and IntAcc=5.01 for SCF iterations and  
31 Lebedev590 and IntAcc=5.34 for the final electronic energy) to eliminate the potential numerical  
32 noise associated with some meta-GGA functionals.<sup>119-121</sup> All the above-mentioned methods were  
33 used with few families of the basis sets as described below.

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3 Few canonical CCSD(T) calculations were done with Gaussian 09 suite of programs to take an  
4 advantage of molecular symmetry.  
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## 7 8 9 **2.2.1 Correlation-Consistent Basis Sets (CCBS)**

10 These basis sets will be abbreviated as CCBS and described below.

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16 **2.2.1.1 Ti and Fe Complexes.** For all the reactions involving Ti and Fe, the all electron basis  
17 sets cc-pVNZ-DK<sup>122-130</sup> contracted to be used with the Douglas-Kroll-Hess (DKH) Hamiltonian  
18 have been used, since relativistic effects are non-negligible for 3d transition metals.<sup>39,92,98,131-134</sup>

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20 E.g. to get the estimates for the reaction  $\text{TiF}_4 + 2\text{I}_2 \rightarrow \text{TiI}_4 + 2\text{F}_2$ , all elements (Ti, F, I) have been  
21 described with the all-electron cc-pVNZ-DK basis sets.  
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29 **2.2.1.2 Other Transition Metal complexes.** For all other transition metal complexes and related  
30 species the following basis sets have been applied. All elements with  $Z \leq 18$  have been described  
31 with standard correlation consistent basis sets (cc-pVNZ) of Dunning et al.<sup>125,130</sup> All other  
32 elements with  $Z > 18$  were described with the correlation consistent basis sets developed by  
33 Peterson et al.<sup>135</sup> (cc-pVNZ-PP) with the fully-relativistic (MDF) small-core Stuttgart-type  
34 effective core potentials<sup>128,135-142</sup> for which these basis sets were optimized. Standard non-  
35 relativistic Hamiltonian has been used with these basis sets. For example, to estimate the reaction  
36 enthalpy of the reaction  $\text{ZrF}_4 + 2\text{I}_2 \rightarrow \text{ZrI}_4 + 2\text{F}_2$ , the cc-pVNZ-PP basis sets and the  
37 corresponding ECPs were used for Zr and I, while the cc-pVNZ basis set was used for F. The  
38 correlation fitting basis sets (cc-pVNZ/C) developed by Hättig et al.,<sup>143</sup> necessary for the  
39 resolution of identity approximation as a part of DLPNO scheme, were used.  
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## 55 56 **2.2.2 Sapporo Basis Sets (SBS)**

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To explore the basis set effect and way to include the scalar relativistic effects (relativistic pseudopotentials vs. DKH<sup>129</sup> Hamiltonian), the all electron basis sets of the Sapporo family have been used for all the complexes and related species. Moreover, since the Sapporo basis sets have been designed to recover core-valence electron correlation, these have been used to estimate the sensitivity of the DLPNO-CCSD(T) reaction energies to the number of the electrons in the frozen core.<sup>144</sup> Gaussian finite nucleus model has been used with Sapporo basis sets. All Sapporo basis sets were downloaded from official web page of Sapporo quantum chemistry group.<sup>145</sup>

### 2.2.3 Complete Basis Set Extrapolation

**2.2.3.1 Correlation Consistent Basis Sets.** To eliminate the effects of basis set incompleteness we used the following extrapolation schemes for HF and correlation energies of individual species suggested by Helgaker et al.<sup>146-148</sup> for two adjacent cc-pVNZ-(PP/DK) level basis sets (N=3 and N=4):

$$E_{HF}^X = E_{HF}^\infty + \alpha e^{-1.63X} \quad (1)$$

$$E_{corl}^X = E_{corl}^\infty + \beta X^{-3} \quad (2)$$

Where X = 3 and 4 for cc-pVTZ and cc-pVQZ basis sets, correspondingly;  $E_{HF}^\infty/E_{corl}^\infty$  HF and correlation energies at CBS limit;  $\alpha/\beta$  are parameters to be obtained from a system of the two equations. The total enthalpy at CBS limit for each reaction ( $A + B \rightarrow C + D$ ) was evaluated via following equation:

$$\Delta H_{DLPNO-CCSD(T)}^0 = E_{HF}^\infty(C) + E_{corl}^\infty(C) + H_{corr}^{PBE0-D3}(C) + E_{HF}^\infty(D) + E_{corl}^\infty(D) + H_{corr}^{PBE0-D3}(D) - (E_{HF}^\infty(A) + E_{corl}^\infty(A) + H_{corr}^{PBE0-D3}(A) + E_{HF}^\infty(B) + E_{corl}^\infty(B) + H_{corr}^{PBE0-D3}(B)) \quad (3)$$

where  $H_{corr}^{PBE0-D3}$  is the correction to the electronic energy to arrive to the enthalpy obtained with standard harmonic oscillator/rigid rotor/ideal gas approximation, see Section 2.1 for the details. For all DFT calculations the following formula has been used to calculate the (A + B → C + D) reaction enthalpy:

$$\Delta H_{DFT}^0 = E_{DFT}^\infty(C) + H_{corr}^{PBE0-D3}(C) + E_{DFT}^\infty(D) + H_{corr}^{PBE0-D3}(D) - (E_{DFT}^\infty(A) + H_{corr}^{PBE0-D3}(A) + E_{DFT}^\infty(B) + H_{corr}^{PBE0-D3}(B)) \quad (4)$$

Where DFT = B3LYP, B3LYP-D3, M06, M06-D3, M06L, M06L-D3, PBE, PBE-D3, PBE0, PBE0-D3, TPSS, TPSS-D3, TPSSh, TPSSh-D3 and  $E_{DFT}^\infty$  has been extrapolated via formula (1).

**2.2.3.2 Sapporo Basis Sets.** The Sapporo basis set family has not been tested to obtain the CBS limit energies. However, the overall basis set design philosophy aimed at reproducing the accurate natural orbitals suggests a behavior for these basis sets similar to that of the correlation consistent basis sets of Dunning et al.<sup>149</sup> Therefore, to extrapolate the results obtained with Sapporo basis sets to the CBS limit, the expressions (1) and (2) have been applied, also for the test purpose.

## 2.3 The Benchmark Set

To accurately benchmark the electronic structure theory methods high quality gas phase experimental data are requested. Gas phase formation enthalpies of many compounds, among which transition metal complexes, are measured and tabulated,<sup>150-151</sup> and are used for benchmarks.<sup>152-158</sup> In this work, however, we do not try to reproduce the absolute formation enthalpies for few reasons. First, direct calculation of heats of formation via atomization schemes cannot be done via DLPNO-CCSD(T) method which is only available for singlet ground states

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3 so far, while many atoms have open-shell ground states. Second, direct calculation of formation  
4 enthalpies via atomization schemes often leads to large errors since electron correlation energies  
5 in atoms and molecules are very different and no error-compensation can be expected.<sup>96</sup> To  
6 overcome these difficulties, we created reaction datasets from experimentally obtained individual  
7 formation enthalpies and validated the electronic structure methods against these datasets.  
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16 The enthalpies used to build the reaction datasets had to satisfy a few requirements. First, they  
17 have to be accurate, since the overall uncertainty for the reaction enthalpy will be the algebraic  
18 sum of the uncertainties of reactants and products. For relatively small non-TM  
19 organic/inorganic molecules the enthalpies are usually quite accurate, since many of them are  
20 gases or volatile liquids at standard conditions and precise spectroscopic or calorimetric  
21 measurements are applicable. Transition metal complexes on the other hand are often solids or  
22 liquids in their standard states, and gas phase formation enthalpies are obtained from  
23 combination of solid/liquid formation enthalpies and enthalpies of sublimation or vaporization.  
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25 The solid formation enthalpies are usually quite accurate and often measured calorimetrically.  
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27 Enthalpies of sublimation/vaporization are more difficult to obtain since related to measurements  
28 of vapour pressures over TM complexes at high temperatures. Many complexes are destroyed  
29 (partially) upon sublimation, and often resulting second and third-law enthalpies have some  
30 uncertainties. Due to these circumstances, in these work we used the experimental formation  
31 enthalpies of TM complexes with an error bar smaller than 6.0 kcal/mol. However, we combined  
32 these enthalpies to obtain the overall uncertainties in reaction enthalpies  $\pm 5$  kcal/mol. In order to  
33 evaluate the error bars for reaction enthalpies we proceed as follows. For every reaction  $A + B$   
34  $\rightarrow C + D$ , first the formation enthalpies of C and D were taken at their upper-estimated values,  
35 while for A and B the formation enthalpies were taken at their under-estimated values. E.g. if  
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3 formation enthalpy of C is  $5.0 \pm 2.0$  kcal/mol, we took it as 7.0 kcal/mol and if formation enthalpy  
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5 of A is  $3.0 \pm 2.0$  we took it as 1.0 kcal/mol. Then, we did the inverse, namely the formation  
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7 enthalpies of C and D were taken at their under-estimated values, while for A and B the  
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9 formation enthalpies were taken at their upper-estimated values. The reaction enthalpies were  
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11 taken at average of these estimates, and uncertainties were corresponded to lowest and highest  
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13 reaction enthalpies. This methodology allows us to consider in all reactions the most pessimistic  
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15 error bars both for highest and lowest uncertainties.  
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21 The second constraint is again related to DLPNO-CCSD(T) method which can only be applied to  
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23 closed shell systems. This puts an important constraint on the reactions to be included in the  
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25 benchmark set: both reactants and products have to be singlets. Since a dominant part of the  
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27 transition metals have unfilled d-shells, there is a high chance that open shell states of the  
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29 complexes formed by these metals might be more stable comparing to closed shell states. To  
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31 verify it, each transition metal complex and related compound (i.e. molecule introducing the  
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33 covalent ligand, e.g.  $F_2$ ) have been optimized with multiplicities 1, 3 and 5 with pure GGA PBE  
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35 functional and relativistically contracted  $\Lambda 1$  basis sets<sup>159</sup> of “cc-pvdz” quality as implemented in  
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37 the PRIRODA code<sup>159-160</sup> to ensure singlet ground states. The formation enthalpies which satisfy  
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39 the above-mentioned constraints are given in Table 1. The chemical reactions generated from  
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41 these formation enthalpies are given in Table 2. Optimized coordinates of all the systems  
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43 composing these reactions are included in the Supporting Information and also available at the  
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45 url: <https://sites.google.com/site/theochemdatasets/reaction-enthalpies>.  
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56 **Table 1.** Experimental gas phase formation enthalpies used to build the reaction database.  
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Entry	Expt. $\Delta H_f(298.15)$ (kcal/mol) <sup>a</sup>	Avg. $\Delta H_f(298.15)$ (kcal/mol) <sup>a</sup>
Br <sub>2</sub>	7.388±0.026 <sup>161</sup>	7.388(-0.026;0.026)
BrCl	3.5±0.3 <sup>151</sup>	3.5(-0.3;0.3)
BrF	-13.97±0.41 <sup>151</sup>	-13.97(-0.41;0.41)
C <sub>2</sub> H <sub>5</sub> Br	-15.6±1.5 <sup>162</sup> ; -14.79±0.24 <sup>163</sup> ; -15.45±0.50 <sup>164</sup>	-15.28(-1.82;1.18)
C <sub>2</sub> H <sub>5</sub> Cl	-26.8 ± 0.2 <sup>165</sup> ; -26.83 ± 0.18 <sup>166</sup> ; -25.74 ± 0.14 <sup>167</sup> ; -26.1 ± 0.4 <sup>168</sup>	-26.37(-0.64;0.76)
C <sub>2</sub> H <sub>5</sub> I	-1.7±0.2 <sup>169</sup> ; -2.1±0.23 <sup>162</sup>	-1.90(-0.43;0.40)
C <sub>2</sub> H <sub>6</sub>	-20.±0.1 <sup>165</sup> ; -20.04±0.07 <sup>170</sup> ; -20.24±0.12 <sup>171</sup>	-20.09(-0.27;0.19)
C <sub>4</sub> H <sub>10</sub> (linear)	-30.03±0.16 <sup>170</sup> ; -30.37±0.16 <sup>172</sup>	-30.2(-0.33;0.33)
C <sub>5</sub> NH <sub>11</sub> (piperidine)	-11.27±0.15 <sup>173</sup>	-11.27(-0.15;0.15)
C <sub>5</sub> NH <sub>5</sub> (pyridine)	33.61±0.36 <sup>174</sup> ; 33.63±0.36 <sup>175</sup>	33.62(-0.36;0.36)
Cd	26.721±0.048 <sup>161</sup>	26.721(-0.048;0.048)
CdC <sub>2</sub> H <sub>6</sub> <sup>a</sup>	24.4±1.0 <sup>176-178</sup> ; 25.05±0.31 <sup>176,179</sup>	24.73(-1.32;0.67)
CdC <sub>4</sub> H <sub>10</sub> <sup>b</sup>	24.1±1.7; 25.17±0.45 <sup>180-182</sup>	24.64(-4.71;5.76)
CH <sub>3</sub> Br	-8.2±0.2 <sup>183</sup> ; -9.0±0.32 <sup>184</sup> ; -8.97±0.35 <sup>163</sup>	-8.72(-0.6;0.73)
CH <sub>3</sub> Cl	-20.0±0.5 <sup>151</sup> ; -19.6±0.36 <sup>165</sup> ; -19.59±0.16 <sup>166</sup> ; -20.53±0.14 <sup>181,185</sup> ; -20.63±0.14 <sup>166</sup>	-19.93(-0.70;0.83)
CH <sub>3</sub> I	3.42±0.34 <sup>186</sup> ; 3.50±0.24 <sup>187</sup> ; 3.8±0.3 <sup>188</sup>	3.57(-0.49;0.53)
CH <sub>4</sub>	-17.89±0.08 <sup>151</sup> ; -17.8±0.07 <sup>165</sup> ; -17.8±0.1 <sup>181</sup> ; -17.889±0.075 <sup>189</sup> ; -17.54±0.26 <sup>181,190</sup>	-17.78(-0.184;0.504)
Cl <sub>2</sub>	0	0(0;0)
ClF	-12.02±0.10 <sup>151</sup>	-12.02(-0.1;0.1)
CO	-26.417±0.041 <sup>151</sup>	-26.417(-0.041;0.041)
CuCl	21.77±0.4 <sup>151</sup>	21.77(-0.4;0.4)
CuF	-3.0±4.0 <sup>151</sup>	-3(-4.0;4.0)
F <sub>2</sub>	0	0(0;0)

1	FeC <sub>5</sub> O <sub>5</sub>	-173.96±1.7 <sup>191</sup> ; -173.0±1.6 <sup>191-192</sup> , 172.9+/-1.9 <sup>193</sup>	-173.3(-2.37;1.88)
2			
3	Fecis-C <sub>4</sub> O <sub>4</sub> I <sub>2</sub>	-151.9±2.2 <sup>194</sup>	-151.9(-2.2;2.2)
4			
5	H <sub>2</sub>	0	0(0;0)
6			
7	H <sub>2</sub> O	-57.7978±0.0096 <sup>161</sup> ; -57.799±0.01 <sup>151</sup>	-57.7984(-0.011;0.0102)
8			
9	HBr	-8.674±0.038 <sup>161</sup> ; -8.709±0.04 <sup>151</sup>	-8.6905(-0.057;0.055)
10			
11	HCl	-22.06±0.024 <sup>161</sup> ; -22.06±0.05 <sup>151</sup>	-22.06(-0.05;0.05)
12			
13	HF	-65.32±0.17 <sup>161</sup> ; -65.141±0.2 <sup>151</sup>	-65.2305(-0.259;0.289)
14			
15	Hg	14.67±0.01 <sup>161</sup>	14.67(-0.01;0.01)
16			
17	HgBr <sub>2</sub>	-20.42±2.0 <sup>151</sup>	-20.42(-2;2)
18			
19	HgC <sub>2</sub> H <sub>5</sub> Br	-7.24±0.36 <sup>181,195-196</sup>	-7.24(-0.36;0.36)
20			
21	HgC <sub>2</sub> H <sub>5</sub> Cl	-16.2±0.36 <sup>181,195-196</sup>	-16.2(-0.36;0.36)
22			
23	HgC <sub>2</sub> H <sub>5</sub> I	3.42±0.36 <sup>181,195-196</sup>	3.42(-0.36;0.36)
24			
25	HgCH <sub>3</sub> Br	-4.45±0.72 <sup>181,196-197</sup>	-4.45(-0.72;0.72)
26			
27	HgCH <sub>3</sub> Cl	-13.2±0.72 <sup>181,196-197</sup>	-13.2(-0.72;0.72)
28			
29	HgCH <sub>3</sub> I	5.16±0.72 <sup>181,196-197</sup>	5.16(-0.72;0.72)
30			
31	HgCl <sub>2</sub>	-34.96±1.50 <sup>151</sup>	-34.96(-1.50;1.50)
32			
33	Hgl <sub>2</sub>	-3.855±0.5 <sup>151</sup>	-3.855(-0.5;0.5)
34			
35	HI	6.334±0.024 <sup>161</sup> ; 6.300±0.05 <sup>151</sup>	6.317(-0.007;0.041)
36			
37	I <sub>2</sub>	14.92±0.02 <sup>161</sup>	14.92(-0.02;0.02)
38			
39	IBr	9.77±0.02 <sup>151</sup>	9.77(-0.02;0.02)
40			
41	ICl	4.185±0.025 <sup>151</sup>	4.185(-0.025;0.025)
42			
43	IF	-22.65±0.9 <sup>151</sup>	-22.65(-0.9;0.9)
44			
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MoF <sub>6</sub>	-372.29±0.22 <sup>151</sup>	-372.29(-0.22;0.22)
MoO <sub>2</sub> Cl <sub>2</sub>	-151.3±3.5 <sup>151</sup>	-151.3(-3.5;3.5)
NbBr <sub>5</sub>	-106.02±3.0 <sup>151</sup>	-106.02(-3.0;3.0)
NbCl <sub>5</sub>	-168.10±2.0 <sup>151</sup>	-168.1(-2.0;2.0)
OCl <sub>2</sub>	19.4±0.5 <sup>151</sup>	19.4(-0.5;0.5)
OF <sub>2</sub>	5.86±0.50 <sup>151</sup>	5.86(-0.5;0.5)
ReC <sub>5</sub> O <sub>5</sub> Br	-204.9±1.8 <sup>198</sup>	-204.9(-1.8;1.8)
ReC <sub>6</sub> H <sub>3</sub> O <sub>5</sub>	-180.9±2.1 <sup>181,199-206</sup> ; -181.2±1.4 <sup>181,199-206</sup> ; -181.1±1.3 <sup>181,199-206</sup>	-181.1(-1.9;2.3)
TiBr <sub>4</sub>	-131.50±1.2 <sup>151</sup>	-131.5(-1.2;1.2)
TiCl <sub>4</sub>	-182.4±0.9 <sup>151</sup>	-182.4(-0.9;0.9)
TiF <sub>4</sub>	-370.8±1.0 <sup>151</sup>	-370.8(-1.0;1.0)
TiI <sub>4</sub>	-66.269±2.0 <sup>151</sup>	-66.269(-2.0;2.0)
TiO <sub>2</sub>	-73.0±3.0 <sup>151</sup>	-73(-3.0;3.0)
WC <sub>10</sub> NH <sub>11</sub> O <sub>5</sub>	-194.8±2.1 <sup>181,199-207</sup> ; -194.2 <sup>181,199-206</sup>	-194.5(-2.4;1.8)
WC <sub>10</sub> NH <sub>5</sub> O <sub>5</sub>	-144.9±2.6 <sup>181,199-207</sup> ; -144.7 <sup>181,199-206</sup>	-144.8(-2.7;2.5)
WC <sub>6</sub> O <sub>6</sub>	-209.7±0.72 <sup>208</sup> 207,209-211; 211.5±1.1 <sup>208-209</sup> 207,210,212; -212.0±0.9 <sup>208</sup> 207,209-210,213-214; -211.9±0.9 <sup>215</sup>	-211.3(-1.6;2.3)
WCl <sub>6</sub>	-118.0±6.0 <sup>151</sup>	-118(-6.0;6.0)
WF <sub>6</sub>	-411.5±0.4 <sup>151</sup>	-411.5(-0.4;0.4)
Zn	31.166±0.096 <sup>161</sup> ; 31.171±0.05 <sup>151</sup>	31.1685(-0.0985;0.0935)
ZnC <sub>2</sub> H <sub>6</sub>	13.2±1.4; 12.6±0.31 <sup>177,181,216</sup> (ref 43,47)	12.9(-1.1;1.7)
ZnC <sub>4</sub> H <sub>10</sub>	14.±1.0 <sup>177,181</sup> 217 218-219	14(-1;1)
ZrBr <sub>4</sub>	-154.1±2.0 <sup>151</sup>	-154.1(-2.0;2.0)
ZrC <sub>10</sub> H <sub>10</sub> Cl <sub>2</sub>	-103.6±0.93 <sup>220-221</sup>	-103.6(-0.93;0.93)
ZrC <sub>12</sub> H <sub>16</sub>	8.89±0.81 <sup>220-222</sup>	8.89(-0.81;0.81)
ZrCl <sub>4</sub>	-207.93±0.5 <sup>151</sup>	-207.93 (-

		0.5;+0.5)
ZrF <sub>4</sub>	-400.00±0.79 <sup>151</sup>	-400.0 (-0.79;+0.79)
ZrI <sub>4</sub>	-86.6±2.0 <sup>151</sup>	-86.6 (-2.0;+2.0)
<sup>a</sup> One significantly different experimental measurement ( $\Delta_f H^\circ_{\text{gas}} = 29.4 \pm 2.9$ ) of Cd(CH <sub>3</sub> ) <sub>2</sub> formation enthalpy was discarded. <sup>b</sup> One significantly different experimental measurement ( $\Delta_f H^\circ_{\text{gas}} = 32.07 \pm 0.81$ ) of Cd(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> formation enthalpy was discarded.		

**Table 2.** Transition metal gas phase reaction enthalpies used to build the datasets.

No	Reaction	Expt. $\Delta H^\circ(298.15)$ (kcal/mol) <sup>a</sup>	Avg.
1	Zn + C <sub>2</sub> H <sub>6</sub> = ZnC <sub>2</sub> H <sub>6</sub>	1.8(-1.36;2.09)	
2	Zn + 2CH <sub>4</sub> = ZnC <sub>2</sub> H <sub>6</sub> + H <sub>2</sub>	17.3(-2.2;2.17)	
3	Zn + C <sub>4</sub> H <sub>10</sub> = ZnC <sub>4</sub> H <sub>10</sub>	13.0(-1.39;1.46)	
4	Zn + 2C <sub>2</sub> H <sub>6</sub> = ZnC <sub>4</sub> H <sub>10</sub> + H <sub>2</sub>	23.0(-1.46;1.65)	
5	Zn + 4CH <sub>4</sub> = ZnC <sub>4</sub> H <sub>10</sub> + 3H <sub>2</sub>	54.0(-3.14;1.81)	
6	ZnC <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>6</sub> = ZnC <sub>4</sub> H <sub>10</sub> + H <sub>2</sub>	21.2(-2.9;2.36)	
7	ZnC <sub>2</sub> H <sub>6</sub> + 2CH <sub>4</sub> = ZnC <sub>4</sub> H <sub>10</sub> + 2H <sub>2</sub>	36.7(-3.74;2.44)	
8	Cd + C <sub>2</sub> H <sub>6</sub> = CdC <sub>2</sub> H <sub>6</sub>	18.1(-1.57;0.99)	
9	Cd + C <sub>4</sub> H <sub>10</sub> = CdC <sub>4</sub> H <sub>10</sub>	28.1(-2.6;1.56)	
10	Cd + 2C <sub>2</sub> H <sub>6</sub> = CdC <sub>4</sub> H <sub>10</sub> + H <sub>2</sub>	38.1(-2.67;1.75)	
11	CdC <sub>2</sub> H <sub>6</sub> + C <sub>2</sub> H <sub>6</sub> = CdC <sub>4</sub> H <sub>10</sub> + H <sub>2</sub>	20.0(-3.1;2.76)	
12	Cd + 2CH <sub>4</sub> = CdC <sub>2</sub> H <sub>6</sub> + H <sub>2</sub>	33.6(-2.41;1.07)	
13	Cd + 4CH <sub>4</sub> = CdC <sub>4</sub> H <sub>10</sub> + 3H <sub>2</sub>	69.04(-4.29;1.97)	

14	$\text{CdC}_2\text{H}_6 + 2\text{CH}_4 = \text{CdC}_4\text{H}_{10} + 2\text{H}_2$	35.5(-3.94;2.84)
15	$\text{Hg} + \text{I}_2 = \text{HgI}_2$	-33.5(-0.47;0.59)
16	$\text{Hg} + \text{Cl}_2 = \text{HgCl}_2$	-49.6(-1.54;1.48)
17	$\text{Hg} + 2\text{HI} = \text{HgI}_2 + \text{H}_2$	-31.2(-0.55;0.68)
18	$\text{Hg} + 2\text{HCl} = \text{HgCl}_2 + \text{H}_2$	-5.5(-1.62;1.6)
19	$\text{Hg} + \text{CH}_3\text{I} = \text{HgCH}_3\text{I}$	-13.1(-1.12;1.12)
20	$\text{Hg} + \text{CH}_3\text{Cl} = \text{HgCH}_3\text{Cl}$	-7.9(-1.54;1.6)
21	$\text{Hg} + \text{CH}_3\text{Br} = \text{HgCH}_3\text{Br}$	-10.4(-1.42;1.3)
22	$\text{Hg} + \text{C}_2\text{H}_5\text{I} = \text{HgC}_2\text{H}_5\text{I}$	-9.4(-1.34;1.47)
23	$\text{Hg} + \text{C}_2\text{H}_5\text{Cl} = \text{HgC}_2\text{H}_5\text{Cl}$	-4.5(-1.76;1.63)
24	$\text{Hg} + \text{C}_2\text{H}_5\text{Br} = \text{HgC}_2\text{H}_5\text{Br}$	-6.6(-1.15;2.73)
25	$\text{Hg} + \text{Br}_2 = \text{HgBr}_2$	-42.5(-2.01;2.06)
26	$\text{Hg} + 2\text{HBr} = \text{HgBr}_2 + \text{H}_2$	-17.7(-2.13;2.12)
27	$\text{HgI}_2 + \text{Cl}_2 = \text{HgCl}_2 + \text{I}_2$	-16.2(-2.01;2.03)
28	$\text{HgI}_2 + 2\text{HCl} = \text{HgCl}_2 + 2\text{HI}$	25.6(-2.19;2.23)
29	$\text{HgI}_2 + \text{CH}_4 = \text{HgCH}_3\text{I} + \text{HI}$	33.1(-1.65;1.34)
30	$\text{HgI}_2 + \text{CH}_3\text{Cl} = \text{HgCH}_3\text{Cl} + \text{I}_2$	25.5(-2.01;2.16)
31	$\text{HgI}_2 + \text{CH}_3\text{Br} = \text{HgCH}_3\text{Br} + \text{I}_2$	23.1(-1.98;1.76)
32	$\text{HgI}_2 + \text{C}_2\text{H}_6 = \text{HgC}_2\text{H}_5\text{I} + \text{HI}$	33.7(-1.75;1.77)
33	$\text{HgI}_2 + \text{C}_2\text{H}_5\text{Cl} = \text{HgC}_2\text{H}_5\text{Cl} + \text{I}_2$	29.0(-2.32;2.09)
34	$\text{HgI}_2 + \text{C}_2\text{H}_5\text{Br} = \text{HgC}_2\text{H}_5\text{Br} + \text{I}_2$	26.8(-2.62;3.29)
35	$\text{HgI}_2 + \text{Br}_2 = \text{HgBr}_2 + \text{I}_2$	-9.0(-2.58;2.51)
36	$\text{HgI}_2 + 2\text{HBr} = \text{HgBr}_2 + 2\text{HI}$	13.5(-2.79;2.65)
37	$\text{HgCl}_2 + \text{CH}_3\text{I} = \text{HgCH}_3\text{I} + \text{Cl}_2$	36.6(-2.68;2.54)
38	$\text{HgCl}_2 + \text{CH}_3\text{Cl} = \text{HgCH}_3\text{Cl} + \text{Cl}_2$	41.7(-3;3.12)
39	$\text{HgCl}_2 + \text{CH}_3\text{Br} = \text{HgCH}_3\text{Br} + \text{Cl}_2$	39.2(-2.88;2.82)
40	$\text{HgCl}_2 + \text{C}_2\text{H}_5\text{I} = \text{HgC}_2\text{H}_5\text{I} + \text{Cl}_2$	40.3(-2.9;2.89)

41	$\text{HgCl}_2 + \text{C}_2\text{H}_5\text{Cl} = \text{HgC}_2\text{H}_5\text{Cl} + \text{Cl}_2$	45.1(-3.22;3.15)
42	$\text{HgCl}_2 + \text{C}_2\text{H}_5\text{Br} = \text{HgC}_2\text{H}_5\text{Br} + \text{Cl}_2$	43.0(-3.61;-3.86)
43	$\text{HgCl}_2 + \text{Br}_2 = \text{HgBr}_2 + \text{Cl}_2$	7.9(-3.57;3.48)
44	$\text{HgCl}_2 + 2\text{HBr} = \text{HgBr}_2 + 2\text{HCl}$	-12.2(-3.71;3.72)
45	$\text{HgCH}_3\text{I} + \text{CH}_3\text{Cl} = \text{HgCH}_3\text{Cl} + \text{CH}_3\text{I}$	5.1(-2.54;2.8)
46	$\text{HgCH}_3\text{I} + \text{CH}_3\text{Br} = \text{HgCH}_3\text{Br} + \text{CH}_3\text{I}$	2.7(-2.52;2.4)
47	$\text{HgCH}_3\text{I} + \text{C}_2\text{H}_5\text{I} = \text{HgC}_2\text{H}_5\text{I} + \text{CH}_3\text{I}$	3.7(-2.44;2.57)
48	$\text{HgCH}_3\text{I} + \text{C}_2\text{H}_5\text{Cl} = \text{HgC}_2\text{H}_5\text{Cl} + \text{CH}_3\text{I}$	8.6(-2.86;2.73)
49	$\text{HgCH}_3\text{I} + \text{C}_2\text{H}_5\text{Br} = \text{HgC}_2\text{H}_5\text{Br} + \text{CH}_3\text{I}$	6.5(-3.25;3.83)
50	$\text{HgCH}_3\text{I} + \text{Br}_2 = \text{HgBr}_2 + \text{CH}_3\text{I}$	-29.4(-3.11;3.16)
51	$\text{HgCH}_3\text{Cl} + \text{CH}_3\text{Br} = \text{HgCH}_3\text{Br} + \text{CH}_3\text{Cl}$	-2.5(-3;2.82)
52	$\text{HgCH}_3\text{Cl} + \text{C}_2\text{H}_5\text{I} = \text{HgC}_2\text{H}_5\text{I} + \text{CH}_3\text{Cl}$	-1.4(-3.02;2.89)
53	$\text{HgCH}_3\text{Cl} + \text{C}_2\text{H}_5\text{Cl} = \text{HgC}_2\text{H}_5\text{Cl} + \text{CH}_3\text{Cl}$	3.4(-3.34;3.15)
54	$\text{HgCH}_3\text{Cl} + \text{C}_2\text{H}_5\text{Br} = \text{HgC}_2\text{H}_5\text{Br} + \text{CH}_3\text{Cl}$	1.3(-3.73;4.25)
55	$\text{HgCH}_3\text{Cl} + \text{Br}_2 = \text{HgBr}_2 + \text{CH}_3\text{Cl}$	-34.5(-3.69;3.48)
56	$\text{HgCH}_3\text{Br} + \text{C}_2\text{H}_5\text{I} = \text{HgC}_2\text{H}_5\text{I} + \text{CH}_3\text{Br}$	1.1(-2.72;2.77)
57	$\text{HgCH}_3\text{Br} + \text{C}_2\text{H}_5\text{Cl} = \text{HgC}_2\text{H}_5\text{Cl} + \text{CH}_3\text{Br}$	5.9(-3.04;3.03)
58	$\text{HgCH}_3\text{Br} + \text{C}_2\text{H}_5\text{Br} = \text{HgC}_2\text{H}_5\text{Br} + \text{CH}_3\text{Br}$	3.8(-3.43;4.13)
59	$\text{HgCH}_3\text{Br} + \text{Br}_2 = \text{HgBr}_2 + \text{CH}_3\text{Br}$	-32.1(-3.29;3.46)
60	$\text{HgC}_2\text{H}_5\text{I} + \text{C}_2\text{H}_5\text{Cl} = \text{HgC}_2\text{H}_5\text{Cl} + \text{C}_2\text{H}_5\text{I}$	4.9(-3.21;2.95)
61	$\text{HgC}_2\text{H}_5\text{I} + \text{C}_2\text{H}_5\text{Br} = \text{HgC}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{I}$	2.8(-3.6;4.05)
62	$\text{HgC}_2\text{H}_5\text{I} + \text{Br}_2 = \text{HgBr}_2 + \text{C}_2\text{H}_5\text{I}$	-33.1(-3.46;3.38)
63	$\text{HgC}_2\text{H}_5\text{Cl} + \text{C}_2\text{H}_5\text{Br} = \text{HgC}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{Cl}$	-2.1(-3.76;4.47)
64	$\text{HgC}_2\text{H}_5\text{Cl} + \text{Br}_2 = \text{HgBr}_2 + \text{C}_2\text{H}_5\text{Cl}$	-38.0(-3.62;3.8)
65	$\text{HgC}_2\text{H}_5\text{Br} + \text{Br}_2 = \text{HgBr}_2 + \text{C}_2\text{H}_5\text{Br}$	-35.9(-4.72;4.19)
66	$\text{TiF}_4 + 2\text{Cl}_2 = \text{TiCl}_4 + 2\text{F}_2$	188.4(-1.9;1.9)
67	$\text{TiF}_4 + 4\text{HCl} = \text{TiCl}_4 + 4\text{HF}$	15.7(-3.12;3.28)

68	$\text{TiF}_4 + 2\text{Br}_2 = \text{TiBr}_4 + 2\text{F}_2$	224.5(-2.23;2.3)
69	$\text{TiF}_4 + 4\text{HBr} = \text{TiBr}_4 + 4\text{HF}$	13.1(-3.41;3.63)
70	$\text{TiF}_4 + 2\text{I}_2 = \text{TiI}_4 + 2\text{F}_2$	274.7(-3.05;3)
71	$\text{TiF}_4 + 4\text{HI} = \text{TiI}_4 + 4\text{HF}$	18.3(-4.16;4.47)
72	$\text{TiF}_4 + 2\text{OF}_2 = \text{TiO}_2 + 4\text{F}_2$	286.1(-5.02;4.98)
73	$\text{TiF}_4 + 2\text{OCl}_2 = \text{TiO}_2 + 4\text{ClF}$	210.92(-5.4;5.4)
74	$\text{TiCl}_4 + 2\text{Br}_2 = \text{TiBr}_4 + 2\text{Cl}_2$	36.1(-2.13;2.18)
75	$\text{TiCl}_4 + 4\text{HBr} = \text{TiBr}_4 + 4\text{HCl}$	-2.6(-2.5;2.56)
76	$\text{TiCl}_4 + 2\text{I}_2 = \text{TiI}_4 + 2\text{Cl}_2$	86.3(-2.95;2.93)
77	$\text{TiCl}_4 + 4\text{HI} = \text{TiI}_4 + 4\text{HCl}$	2.6(-3.24;3.39)
78	$\text{TiCl}_4 + 2\text{OF}_2 = \text{TiO}_2 + 4\text{ClF}$	49.6(-5.3;5.3)
79	$\text{TiCl}_4 + 2\text{OCl}_2 = \text{TiO}_2 + 4\text{Cl}_2$	70.6(-4.9;4.9)
80	$\text{TiBr}_4 + 2\text{I}_2 = \text{TiI}_4 + 2\text{Br}_2$	50.2(-3.32;3.26)
81	$\text{TiBr}_4 + 4\text{HI} = \text{TiI}_4 + 4\text{HBr}$	5.2(-3.6;3.69)
82	$\text{TiBr}_4 + 2\text{OF}_2 = \text{TiO}_2 + 2\text{Br}_2 + 2\text{F}_2$	61.6(-5.3;5.21)
83	$\text{TiBr}_4 + 2\text{OCl}_2 = \text{TiO}_2 + 2\text{Br}_2 + 2\text{Cl}_2$	34.5(-5.28;5.23)
84	$\text{ZrC}_{10}\text{H}_{10}\text{Cl}_2 + \text{C}_2\text{H}_6 = \text{ZrC}_{12}\text{H}_{16} + \text{Cl}_2$	132.6(-1.95;1.99)
85	$\text{ZrF}_4 + 2\text{Cl}_2 = \text{ZrCl}_4 + 2\text{F}_2$	192.1(-1.32;1.26)
86	$\text{ZrF}_4 + 4\text{HCl} = \text{ZrCl}_4 + 4\text{HF}$	19.4(-2.54;2.64)
87	$\text{ZrF}_4 + 2\text{Br}_2 = \text{ZrBr}_4 + 2\text{F}_2$	231.1(-2.82;2.87)
88	$\text{ZrF}_4 + 4\text{HBr} = \text{ZrBr}_4 + 4\text{HF}$	19.7(-4.01;4.22)
89	$\text{ZrF}_4 + 2\text{I}_2 = \text{ZrI}_4 + 2\text{F}_2$	283.6(-2.87;2.79)
90	$\text{ZrF}_4 + 4\text{HI} = \text{ZrI}_4 + 4\text{HF}$	27.2(-3.98;4.23)
91	$\text{ZrCl}_4 + 2\text{Br}_2 = \text{ZrBr}_4 + 2\text{Cl}_2$	39.1(-2.6;2.51)
92	$\text{ZrCl}_4 + 4\text{HBr} = \text{ZrBr}_4 + 4\text{HCl}$	0.4(-2.97;2.89)
93	$\text{ZrCl}_4 + 2\text{I}_2 = \text{ZrI}_4 + 2\text{Cl}_2$	91.5(-2.55;2.53)
94	$\text{ZrCl}_4 + 4\text{HI} = \text{ZrI}_4 + 4\text{HCl}$	7.8(-2.84;2.99)

95	$\text{ZrBr}_4 + 2\text{I}_2 = \text{ZrI}_4 + 2\text{Br}_2$	52.4(-4.06;4.13)
96	$\text{ZrBr}_4 + 4\text{HI} = \text{ZrI}_4 + 4\text{HBr}$	7.5(-4.43;4.46)
97	$\text{MoO}_2\text{Cl}_2 + 4\text{F}_2 = \text{MoF}_6 + \text{OCl}_2 + \text{OF}_2$	-195.7(-4.75;4.69)
98	$\text{MoO}_2\text{Cl}_2 + 6\text{HF} = \text{MoF}_6 + 2\text{HCl} + 2\text{H}_2\text{O}$	10.7(-5.6;5.37)
99	$\text{WC}_6\text{O}_6 + \text{C}_5\text{NH}_{11} = \text{WC}_{10}\text{NH}_{11}\text{O}_5 + \text{CO}$	1.3(-4.54;4.24)
100	$\text{WC}_6\text{O}_6 + \text{C}_5\text{NH}_5 = \text{WC}_{10}\text{NH}_5\text{O}_5 + \text{CO}$	6.1(-5.05;4.77)
101	$\text{WC}_{10}\text{NH}_{11}\text{O}_5 + \text{C}_5\text{NH}_5 = \text{WC}_{10}\text{NH}_5\text{O}_5 + \text{C}_5\text{NH}_{11}$	4.8(-5.61;5.63)
102	$\text{WCl}_6 + 3\text{F}_2 = \text{WF}_6 + 3\text{Cl}_2$	-293.5(-6.4;6.4)
103	$\text{WF}_6 + 6\text{CO} = \text{WC}_6\text{O}_6 + 3\text{F}_2$	359.1(-2.34;2.55)
104	$\text{Fe-cis-C}_4\text{O}_4\text{I}_2 + \text{CO} = \text{FeC}_5\text{O}_5 + \text{I}_2$	19.7(-4.38;4.4)
105	$\text{CuCl} + \text{F}_2 = \text{CuF} + \text{ClF}$	-36.8(-4.49;4.51)
106	$\text{CuCl} + \text{HF} = \text{CuF} + \text{HCl}$	18.4(-4.74;4.71)
107	$\text{NbBr}_5 + 3\text{Cl}_2 = \text{NbCl}_5 + 2\text{Br}_2 + \text{BrCl}$	-43.8(-5.36;5.35)
108	$\text{NbBr}_5 + 5\text{HCl} = \text{NbCl}_5 + 5\text{HBr}$	4.8(-5.58;5.49)
109	$\text{ReC}_5\text{O}_5\text{Br} + \text{CH}_3\text{Br} = \text{ReC}_6\text{H}_3\text{O}_5 + \text{Br}_2$	39.9(-4.44;4.73)
110	$\text{ReC}_5\text{O}_5\text{Br} + \text{CH}_3\text{I} = \text{ReC}_6\text{H}_3\text{O}_5 + \text{IBr}$	30.0(-4.25;4.61)
111	$\text{ReC}_5\text{O}_5\text{Br} + \text{CH}_4 = \text{ReC}_6\text{H}_3\text{O}_5 + \text{HBr}$	32.9(-4.27;4.33)

## 2.4 Calculation of Deviations

To gauge the deviation of the theoretical reaction enthalpies from their experimental counterparts, we used the two common protocols based on the mean unsigned error (MUE =  $|\Delta\text{H}(\text{Exp.}) - \Delta\text{H}(\text{Theo.})|$ ) and the mean signed error (MES =  $\Delta\text{H}(\text{Exp.}) - \Delta\text{H}(\text{Theo.})$ ). Simultaneous analysis of both MUE and MSE is necessary to make a conclusion on ability of the method to provide the absolute reaction enthalpies and on its predictive ability. Clearly, if both

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3 MUE and MSE approach to zero then the method can be recommended for absolute values and  
4 thus predictions. This is the best scenario. If MUE is large and MSE is equally large (either  
5 positive or negative) then the method cannot be recommended for estimation of absolute reaction  
6 enthalpies. However, it still can be used for predictions, since in some instances trends are more  
7 important than absolute values. Finally, the worst scenario is large MUE and vanishing MSE,  
8 when the method cannot be recommended neither for accurate absolute enthalpies nor for the  
9 relative values.  
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### 20 21 **3. Results and Discussion**

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24 This section is organized as follows. First, the performance of the out-of-the-box methods in  
25 reproducing reaction enthalpies involving group 12 elements (Zn, Cd, Hg) is discussed. Then, we  
26 proceed to reaction enthalpies of Ti and Zr (group 4) complexes. After that, the results obtained  
27 for complexes of group 6 metals (Mo and W) are considered. Then, the performance for the  
28 diverse dataset containing few reactions of Fe, Cu, Nb, Re is examined. Next, we comment on  
29 the overall performance obtained for the combined dataset involving all the 11 transition metals  
30 considered. Possible origins of the deviations from experimental values are also discussed.  
31 Practical recommendations on the choice of out-of-the-box methods to be used in transition  
32 metal thermochemistry will be given.  
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#### 46 47 **3.1 Group 12 (Zn, Cd, Hg) Complexes**

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50 Since the number of reactions involving Zn and Cd turned out to be much smaller comparing to  
51 Hg, these two were grouped to combined ZNCDRE14 (Zn and Cd reaction enthalpies, 14 – the  
52 number of reactions) dataset. The reaction enthalpies containing Hg are collected in HGRE51  
53 dataset.  
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### 3.1.1 Zn and Cd Reaction Enthalpies (ZNCDRE14)

The MSE and MUE errors obtained for reaction enthalpies involving Zn and Cd complexes obtained with CCBS basis sets and CBS extrapolation are presented in Chart 1. The results obtained with TZ and QZ basis sets are given in Chart S1 in SI. The lowest errors, MUE/MSE of 0.5/0.1 kcal/mol were obtained with the standalone PBE functional followed closely by DLPNO-CCSD(T) with MUE/MSE of 0.8/-0.2 kcal/mol. The worst performer was B3LYP with a MUE/MSE of 6.2/6.2 kcal/mol, followed closely by M06 with MUE/MSE of 5.2/-5.2 kcal/mol and M06L with MUE/MSE of 5.0/-4.8 kcal/mol. The errors in prediction of the experimental reaction enthalpy obtained with DLPNO-CCSD(T), M06 and PBE0-D3 are given in Table 3. Maximum absolute deviation in DLPNO-CCSD(T) has been detected for reaction 13 and amounted only to -1.6 kcal/mol which is within experimental accuracy. For M06, deviations larger than 5 kcal/mol were documented for reactions 1, 2, 4, 5, 10, 13. However, It should be emphasized that statistics must be taken carefully, since MUEs and MSEs of 4–5 kcal/mol can still be consistent with large experimental uncertainties.

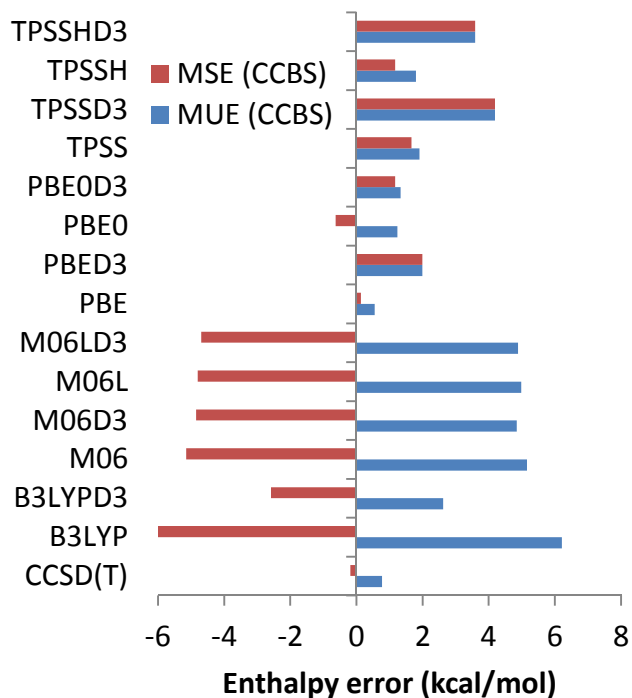
The influence of an empirical dispersion correction on performance is not the same for all the functionals under study. Thus, dispersion correction reduces the MUE error for B3LYP by 3.6 kcal/mol, while the performance of the M06\* family is not influenced. Conversely, for PBE, TPSS and TPSSh inclusion of an empirical dispersion term leads to larger errors. For example, for the standalone TPSS functional in CBS limit the MUE/MSE are 1.9/1.7 kcal/mol while for its dispersion-corrected counterpart MUE/MSE are 4.2 kcal/mol.

**Table 3.** Reaction enthalpies errors in kcal/mol obtained with few popular methods for ZNCDRE14 dataset.



Reaction Number	DLPNO-CCSD(T) $\Delta H$ Error (kcal/mol)	M06 $\Delta H$ Error (kcal/mol)	PBE0-D3 $\Delta H$ (kcal/mol)
1	0.6	-6.1	1.6
2	0.4	-7.0	1.6
3	1.2	-5.3	2.6
4	0.9	-6.9	1.8
5	0.6	-8.9	1.8
6	0.3	-0.9	0.2
7	0.1	-1.8	0.2
8	-1.0	-4.9	1.7
9	-1.0	-5.0	1.9
10	-1.3	-6.6	1.1
11	-0.3	-1.7	-0.6
12	-1.1	-5.9	1.7
13	-1.6	-8.6	1.1
14	-0.5	-2.7	-0.6

Provided a reasonably good quality triple- $\zeta$  basis set is used, the reaction enthalpies obtained with DFT methods are not sensitive to the basis set size, since only minor changes were detected when extrapolating from TZ to CBS. Conversely, DLPNO-CCSD(T) results are more sensitive to the basis set size. Thus, when going from TZ to QZ basis sets the MUE changes from 2.0 to 1.0 kcal/mol, while extrapolating from QZ to CBS reduces the MUE by 0.2 kcal/mol only, showing that results are converged essentially at the QZ level. Results obtained with CCBS are almost identical to those obtained with all-electron relativistic Sapporo basis sets (SBS) and are given in Chart S2 in the Supporting Information.



**Chart 1.** Mean unsigned (MUE) and mean signed (MSE) errors with respect to experimental reaction enthalpies obtained for ZNCDRE14 dataset with CCBS basis sets and CBS extrapolation.

### 3.1.2 Hg Complexes (HGREG51)

The MSE and MUE obtained for 51 reaction enthalpies of Hg complexes obtained with CCBS and CBS extrapolation are presented in Chart 2. The results obtained with TZ and QZ CCBS are given in Chart S3 in SI. The best performer with MUE/MSE of 0.9/0.1 kcal/mol turned out to be the standard hybrid GGA functional PBE0 followed closely by its dispersion-corrected counterpart with MUE/MSE 1.1/0.4 kcal/mol. DLPNO-CCSD(T) method performs similarly well and provides MUE/MSE of 1.6/-1.0 kcal/mol. The largest MUE of 2.8 kcal/mol has been obtained for M06 with or without an empirical dispersion term. The errors in reaction enthalpies

with regard to experiment obtained with DLPNO-CCSD(T), M06 and PBE0-D3 are given in Table 4.

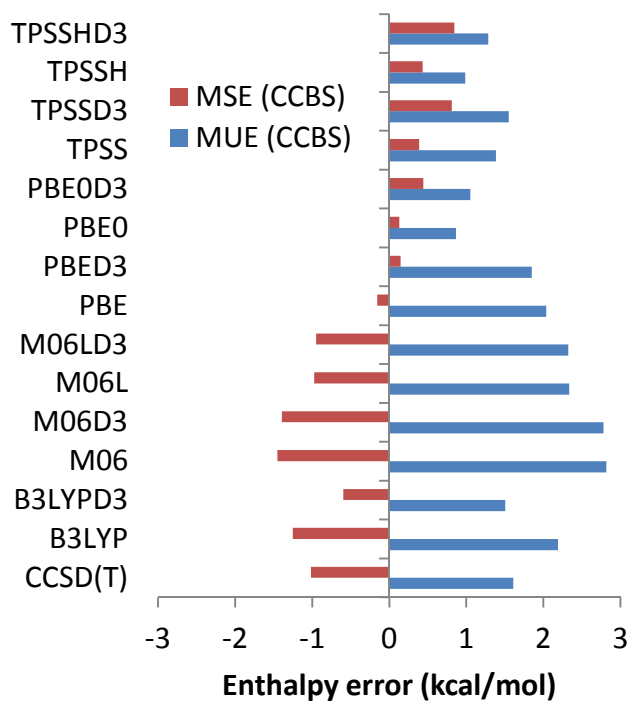
**Table 4.** Reaction enthalpies errors in kcal/mol obtained with few popular methods for HGRE51 dataset.

Reaction Number	DLPNO-CCSD(T) $\Delta H$ Error (kcal/mol)	M06 $\Delta H$ Error (kcal/mol)	PBE0-D3 $\Delta H$ (kcal/mol)
15	-2.4	-8.6	2.0
16	-2.9	-3.7	2.1
17	-2.6	-7.1	1.0
18	-4.6	-2.0	1.7
19	-3.2	-6.3	2.3
20	-3.5	-4.0	2.4
21	-2.6	-4.7	3.2
22	-3.3	-6.5	2.0
23	-5.5	-5.9	0.6
24	-3.7	-5.8	2.1
25	-2.3	-7.9	2.2
26	-2.5	-3.5	3.0
27	-0.5	4.9	0.1
28	-2.0	5.1	0.7
29	-1.0	0.0	0.5
30	-1.1	4.7	0.3
31	-0.2	3.9	1.2
32	-1.1	-0.4	0.4
33	-3.1	2.7	-1.5
34	-1.3	2.8	0.0
35	0.2	0.7	0.2
36	0.1	3.6	2.0
37	-0.3	-2.7	0.2
38	-0.6	-0.3	0.3
39	0.3	-1.0	1.1
40	-0.4	-2.8	-0.1
41	-2.6	-2.3	-1.6
42	-0.8	-2.1	0.0
43	0.7	-4.2	0.1
44	2.1	-1.5	1.3
45	-0.4	2.4	0.0
46	0.6	1.7	0.9
47	-0.1	-0.2	-0.3
48	-2.3	0.4	-1.8

49	-0.5	0.5	-0.2
50	0.9	-1.6	-0.1
51	0.9	-0.7	0.8
52	0.3	-2.5	-0.4
53	-2.0	-2.0	-1.8
54	-0.2	-1.8	-0.3
55	1.3	-3.9	-0.2
56	-0.7	-1.8	-1.2
57	-2.9	-1.3	-2.6
58	-1.1	-1.1	-1.1
59	0.4	-3.2	-1.0
60	-2.2	0.6	-1.5
61	-0.4	0.7	0.1
62	1.0	-1.4	0.2
63	1.8	0.2	1.5
64	3.2	-2.0	1.6
65	1.5	-2.1	0.1

The largest errors for the DLPNO-CCSD(T) method have been obtained for reactions 18 and 23 and amount to 4.6 and 5.5 kcal/mol which partially can be explained by experimental uncertainties of 3-4 kcal/mol. Somewhat larger errors are documented for the M06 functional. An empirical dispersion correction has been found to improve the performance of the B3LYP functional only reducing its MUE by  $\sim 0.7$  kcal/mol. The performance of all other functionals has not been affected by inclusion of an empirical dispersion term.

For all the methods the results are only slightly sensitive to the basis set size. The errors obtained with all-electron relativistic Sapporo basis set correlate perfectly with the CCBS results, however some deviations can be observed. First, when only CBS corrected results are considered the best performer with a MUE of 0.7 kcal/mol turned out to be DLPNO-CCSD(T). The worst performer with a MUE of 2.7 kcal/mol turned out to be M06L with or without an empirical dispersion term. Also, the relative performance of some DFT methods has been changed slightly with SBS comparing to CCBS results, see Chart S4 for more details.



**Chart 2.** Mean unsigned (MUE) and mean signed (MSE) errors with respect to experimental reaction enthalpies obtained for HGRE51 dataset with CCBS basis sets and CBS extrapolation.

### 3.1.3 Practical Recommendations for Group 12 Complexes

Analysis of the cumulative results reported in Table 5 suggests that basically all methods apart from B3LYP-D3, M06\* and TPSSh-D3 provide MUEs below 2 kcal/mol and can be recommended for reactions consistent with those in the ZNCDRE14 and HGRE51 datasets. The DLPNO-CCSD(T) and PBE0-D3 methods are particularly recommended as providing the lowest errors. Both ECP-based correlation consistent basis sets with the non-relativistic Hamiltonian and all-electron Sapporo basis sets with DKH Hamiltonian lead to very accurate results.

**Table 5.** Complete basis set approximated mean unsigned and mean signed errors for several popular methods (DLPNO-CCSD(T), B3LYP-D3, M06, PBE0-D3, TPSSh-D3, PBE, PBE-D3, TPSS) for the ZNCDRE14 and HGRE51 datasets.

	ZNCDRE14		HGRE65	
	MUE (kcal/mol)	MSE (kcal/mol)	MUE (kcal/mol)	MSE (kcal/mol)
DLPNO-CCSD(T)	0.8	-0.2	1.6	-1.0
B3LYP-D3	2.6	-2.6	1.5	-0.6
M06	5.2	-5.2	2.8	-1.5
PBE0-D3	1.3	1.2	1.1	0.4
TPSSh-D3	4.2	4.2	1.3	0.8
PBE	0.5	0.1	2.0	-0.2
PBE-D3	2.0	2.0	1.8	0.1
TPSS	1.8	1.2	1.4	0.4

Other DFT methods, in particular PBE and TPSS, can also provide results that are comparable in accuracy, but these have to be used carefully when large complexes are calculated due to important intramolecular dispersion interactions not fully covered in standard GGA approximations.

### 3.2 Group 4 (Ti, Zr) Complexes

Two separate reaction enthalpies datasets have been composed for Ti and Zr complexes. The first dataset, TIRE18 includes 18 reaction enthalpies related to Ti. The second, ZRRE13 includes 13 reaction enthalpies for Zr complexes. The performance for these two datasets is discussed below.

#### 3.2.1 Ti Complexes (TIRE18)

Inspection of Chart 3, where the MUE and MSE are plotted for all the methods obtained with CCBS and CBS extrapolation scheme, indicates that results for the titanium complexes are

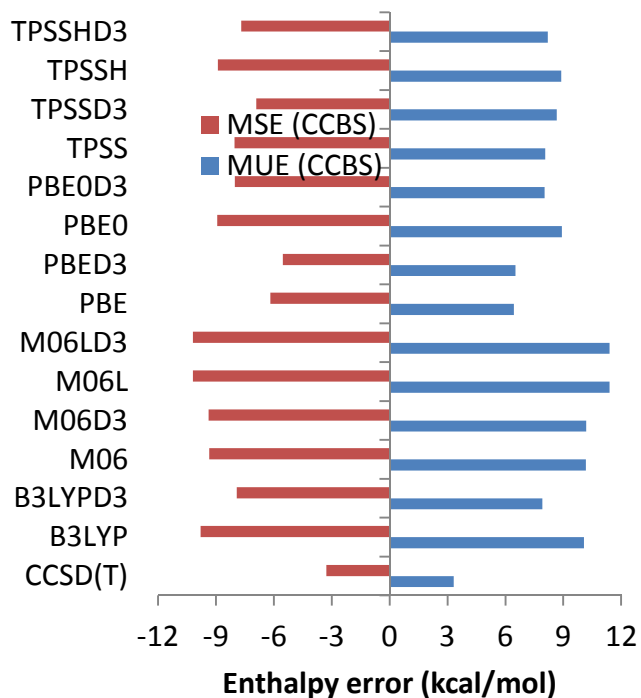
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3 somewhat worse comparing to those for group 12 metals, especially for DFT methods. The  
4 results obtained with TZ and QZ basis sets are given in Chart S5. The best performer with a  
5 MUE/MSE of 3.3/-3.3 kcal/mol is the DLPNO-CCSD(T) method. The worst performer is M06L  
6 method with or without dispersion correction, providing a MUE of 11.4 kcal/mol. It has to be  
7 noticed that comparing to the ZNCDRE14 and HGRE51 datasets, the experimental uncertainties  
8 associated with TIRE18 dataset are higher by 2-3 kcal/mol, and therefore can account for  
9 somewhat larger errors. This indicates that critical understanding of the performance of different  
10 methods is needed. For instance, for reactions 70, 72 and 79, the DLPNO-CCSD(T) predicted  
11 enthalpies are wrong by -6.8, -7.9 and -6.8 kcal/mol, still consistent with the experimental  
12 uncertainties of  $\pm 5$  kcal/mol, as shown in Table 2 and Table 6. On the other hand, deviations up  
13 to 21 kcal/mol obtained with the M06 functionals for reactions 68, 70, 72, 76 and 77 cannot be  
14 considered consistent with experimental uncertainties up to 5.4 kcal/mol in the worst case.

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33 **Table 6.** Reaction enthalpies errors in kcal/mol obtained with few popular methods for TIRE18  
34 dataset.  
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Reaction Number	DLPNO-CCSD(T) $\Delta H$ Error (kcal/mol)	M06 $\Delta H$ Error (kcal/mol)	PBE0-D3 $\Delta H$ (kcal/mol)
66	-2.6	-5.1	-4.0
67	-1.6	5.3	-7.3
68	-5.5	-18.9	-6.2
69	-2.2	-4.2	-8.5
70	-6.8	-20.1	-6.2
71	-3.6	-11.7	-11.9
72	-7.9	-21.1	-22.3
73	-3.6	-8.8	-11.8
74	-2.9	-13.7	-2.2
75	-0.6	-9.5	-1.3
76	-4.3	-15.0	-2.2
77	-2.0	-17.0	-4.6
78	0.5	-8.1	-13.4
79	-6.8	-11.6	-12.7

80	-1.3	-1.3	0.0
81	-1.4	-7.5	-3.4
82	-2.4	-2.3	-16.1
83	-3.9	2.1	-10.5

When going from TZ to CBS limit the MUE/MSEs are improved by few kcal/mol practically for all the methods, as it normally should be upon extending the basis set. All results obtained at CCBS are similar to those obtained with the Sapporo basis sets, see Chart S6 in Supporting Information. The best performer is again DLPNO-CCSD(T), with a MUE/MSE of 3.3/-3.3 kcal/mol. The worst performer is M06L with a MUE/MSE of 10.9/-9.9 kcal/mol for both dispersion-corrected and uncorrected versions.



**Chart 3.** The mean unsigned (MUE) and mean signed (MSE) errors with respect to experimental reaction enthalpies obtained for TIRE18 dataset with CCBS basis sets.



### 3.2.2 Zr Complexes

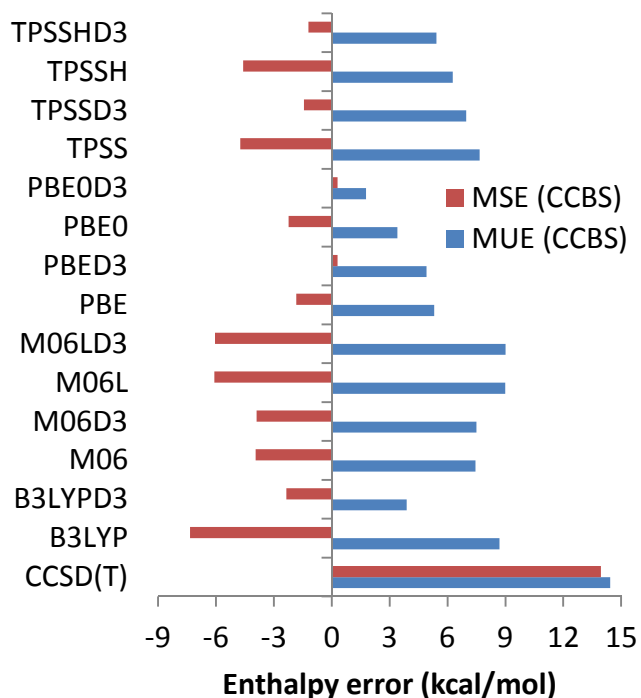
The CCBS results in CBS extrapolation obtained for 13 reactions involving Zr complexes are given in Chart 4. The results obtained with TZ and QZ basis sets are given in Charts S7 and S8 in SI. The best performance with a MUE/MSE of 1.8/0.3 kcal/mol has been obtained for the PBE0-D3 method. Perhaps surprisingly, the worst performer turned out to be DLPNO-CCSD(T)/CBS with a MUE of 14.4/14.0 kcal/mol. From Table 7, which reports the errors for each reaction obtained with the DLPNO-CCSD(T), M06 and PBE0-D3 methods, it can be seen that the largest errors for DLPNO-CCSD(T) are for reactions 85 – 90, and all of them involve ZrF<sub>4</sub>. Considering that experimental uncertainties for these reactions are  $\pm 3$ -4 kcal/mol, errors of more than 30 kcal/mol indicates that either measurements are not precise or there is an error associated with our DLPNO-CCSD(T) estimations. Since PBE0-D3 method predicts errors smaller than 2.5 kcal/mol for these reactions, the second hypothesis is more likely to be the case. The possible sources of errors for these and other reactions will be discussed in Section 3.6.

**Table 7.** Reaction enthalpies errors in kcal/mol obtained with few popular methods for ZRRE13 dataset.

Reaction Number	DLPNO-CCSD(T) $\Delta H$ Error (kcal/mol)	M06 $\Delta H$ Error (kcal/mol)	PBE0-D3 $\Delta H$ (kcal/mol)
84	3.7	8.2	6.8
85	29.1	-0.2	1.3
86	30.2	10.3	-1.9
87	27.7	-11.6	-0.4
88	31.7	4.2	-1.1
89	27.5	-12.0	1.8
90	31.6	-2.0	-2.5
91	-1.4	-11.5	-1.7
92	1.5	-6.1	0.8
93	-1.6	-11.9	0.5
94	1.4	-12.3	-0.6

95	-0.2	-0.4	2.2
96	-0.1	-6.2	-1.5

As previously, an empirical dispersion correction leads to significant improvement on the B3LYP performance. The B3LYP-D3 method results in a MUE of 3.9 kcal/mol, which is 4.8 kcal/mol smaller than the MUE from standard B3LYP/CBS. PBE and in particular PBE0 performance was also improved by inclusion of the empirical dispersion term. The performance of all other functionals was not affected by an empirical dispersion term.



**Chart 4.** The mean unsigned (MUE) and mean signed (MSE) errors with respect to experimental enthalpies obtained for ZRRE13 dataset with CCBS basis sets and CBS extrapolation.

When going from TZ basis set to CBS limit the MUE/MSE of all but DLPNO-CCSD(T) method were improved by 1-2 kcal/mol. Interestingly, the MUE/MSE for DLPNO-CCSD(T) systematically increase when going from TZ to QZ and CBS limit again pointing to systematic

error in calculations or in experimental measurements. When ZF<sub>4</sub>-based reactions (85-90) were removed, the MUE for TZ, QZ and CBS limit turned out to be 2.1, 1.5 and 1.4 kcal/mol, correspondingly. The results obtained with all electron relativistic Sapporo basis set and DKH Hamiltonian are depicted in Chart S8 in SI and in complete agreement with CCBS values, only minor differences can be detected in the absolute MUEs of the methods. This makes us believe that the errors we observe for the ZRRE13 dataset do not come from the use of an ECP. The best performer is again PBE0-D3 method with a MUE of 2.1 kcal/mol. On the opposite side, the DLPNO-CCSD(T) method turned out to perform even slightly worse, providing a MUE of 15.5 kcal/mol.

### 3.2.3 Practical Recommendation for Group 4 Metals

No single method can be recommended when accurate reaction enthalpies of group 4 metals are desired. In principle, DLPNO-CCSD(T) showed good performance for Ti reactions and for all Zr reactions excluding those with ZrF<sub>4</sub>, and could be recommended. But, since quite large deviations are possible, we recommend always use either a careful canonical CCSD(T) calculation (see section 3.6), or other 1-2 DFT methods to verify the DLPNO-CCSD(T) values, in particular PBE0-D3 and PBE-D3 methods.

**Table 8.** Complete basis set approximated mean unsigned and mean signed errors for several popular methods (DLPNO-CCSD(T), B3LYP-D3, M06, PBE0-D3, TPSSh-D3, PBE, PBE-D3, TPSS) for TiRE35 and ZRRE21 datasets.

	Ti		Zr	
	MUE (kcal/mol)	MSE (kcal/mol)	MUE (kcal/mol)	MSE (kcal/mol)
DLPNO-CCSDT	3.3	-3.3	14.4	14.0
B3LYP-D3	7.9	-7.9	3.9	-2.4

M06	10.2	-9.4	7.4	-3.9
PBE0-D3	8.0	-8.0	1.8	0.3
TPSSh-D3	8.2	-7.7	5.4	-1.2
PBE	6.4	-6.2	5.3	-1.8
PBE-D3	6.5	-5.5	4.9	0.3
TPSS	8.1	-8.0	7.7	-4.7

### 3.3 Group 6 (Mo, W) Complexes

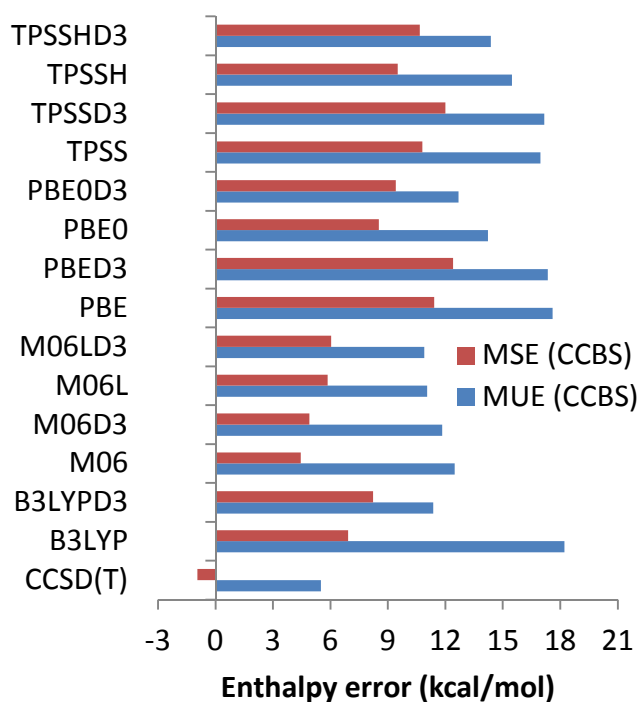
Since only few reliable formation enthalpies were found for Mo, we decided to combine Mo reactions with ones for W in one single dataset MOWRE7 including in total 7 reactions. The performance for this dataset is discussed below.

#### 3.3.1 Mo and W Complexes

The MUE and MSEs errors obtained for 7 reaction enthalpies of Mo and W complexes at the CBS limit are shown in Chart 5. The results obtained with the TZ and QZ basis sets are given in Chart S9 in SI. The smallest MUE/MSE have been obtained with DLPNO-CCSD(T) and amount to 5.5/-0.9 kcal/mol. The largest MUE of 18.2 kcal/mol has been obtained for B3LYP. Again, very heterogeneous performance has been observed for DLPNO-CCSD(T). It works excellently for reactions 97 – 101, providing errors below 5.0 kcal/mol. For reactions 102 and 103 the deviations are 9.3 and -17.0 kcal/mol, respectively. It should be noted that quite large errors were obtained for reactions 102 and 103 with other methods, e.g. M06 and PBE0-D3, see Table 9. Such large errors cannot be explained by experimental uncertainties which are only of  $\pm 3$ -4 kcal/mol and can be attributed to inaccuracy either in the experimental measurements or in the calculations. As it will be shown in Section 3.6.6, large DLPNO-CCSD(T) errors for these two reactions can be remedied by inclusion of core-correlation effects.

**Table 9.** Reaction enthalpies errors in kcal/mol obtained with few popular methods for MOWRE7 dataset.

Reaction Number	DLPNO-CCSD(T) $\Delta H$ Error (kcal/mol)	M06 $\Delta H$ Error (kcal/mol)	PBE0-D3 $\Delta H$ (kcal/mol)
97	1.0	27.3	25.2
98	-1.6	13.4	24.7
99	-3.9	-8.1	-8.2
100	0.9	-2.6	-3.3
101	4.8	5.5	5.0
102	9.3	13.1	6.3
103	-17.0	-17.4	16.3



**Chart 5.** Mean unsigned (MUE) and mean signed (MSE) errors with respect to experimental reaction enthalpies obtained for MOWRE7 dataset with CCBS basis sets.

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3 As previously, an empirical dispersion correction significantly improves the B3LYP  
4 performance, reducing the MUE by almost 7 kcal/mol. The performance of the M06 and M06L  
5 methods is not affected by dispersion correction. The PBE, PBE0, TPSS and TPSSh functionals  
6 demonstrate only minor improvement, within 1-1.5 kcal/mol, upon inclusion of an empirical  
7 dispersion correction term.  
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16 When going from TZ to CBS limit, the MUEs of all but the M06/M06-L methods were  
17 practically not affected. For the M06/M06-L methods improvement in MUEs were obtained  
18 upon increase in the basis set. Result obtained with the all electron relativistic Sapporo basis sets  
19 are given in Chart S10 in SI. The best and worst performers are identical with both basis sets.  
20 Perhaps the only difference with CCBS is the slightly worse performance of the M06/M06-L  
21 methods obtained with the Sapporo basis sets. Thus, the MUE of 18.7 kcal/mol obtained for the  
22 B3LYP functional is quite close to the MUE of 18.3 kcal/mol obtained for the M06 functional  
23 used with the CBS extrapolation scheme.  
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### 36 3.3.3 Practical Recommendation for Group 6 Metals

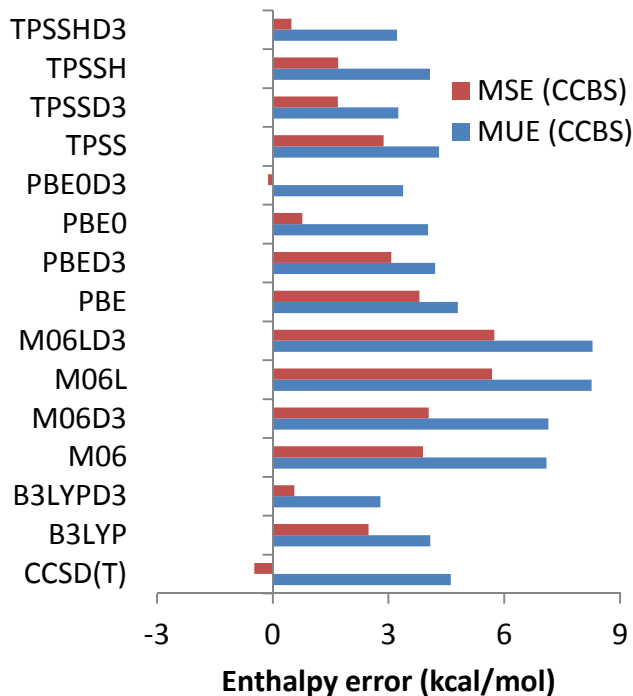
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39 Since large errors have been obtained for all the methods tested for group 6 metals reaction  
40 enthalpies, no single method can be recommended if accurate estimates are needed. The smallest  
41 MUE has been obtained with DLPNO-CCSD(T), and probably this should be the method of  
42 choice until a new better performing method is found.  
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50 **Table 10.** Complete basis set approximated mean unsigned and mean signed errors for several  
51 popular methods (DLPNO-CCSD(T), B3LYP-D3, M06, PBE0-D3, TPSSh-D3, PBE, PBE-D3,  
52 TPSS) for MOWRE7 dataset.  
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	Mo and W	
	MUE (kcal/mol)	MSE (kcal/mol)
DLPNO-CCSDT	5.5	-0.9
B3LYP-D3	11.4	8.2
M06	12.5	4.5
PBE0-D3	12.7	9.4
TPSSh-D3	14.4	10.7
PBE	17.6	11.4
PBE-D3	17.3	12.4
TPSS	17.0	10.8

### 3.4 Fe, Cu, Nb, Re complexes

Due to the scarcity of reliable experimental formation enthalpies involving Fe, Cu, Nb and Re, only 8 reactions could be composed in total. Since no statistically approved conclusions could be made for separate metals, we combined all these reactions into a single dataset, FECUNBRERE8. The performance obtained for this combined dataset with all the methods and CBS extrapolation is presented in Chart 6. The results for all the methods with TZ and QZ basis sets are given in Chart S11 in SI. The best performer with a MUE of 2.8 kcal/mol turned out to be B3LYP-D3, followed closely by TPSSh-D3 with a MUE only 0.4 kcal/mol higher. The worst performer with a MUE of 8.3 kcal/mol was found to be M06L with or without an empirical dispersion correction. The DLPNO-CCSD(T)/CBS provided a MUE of 4.6 kcal/mol which is still below 5.0 kcal/mol and can be related to experimental uncertainties for these reactions about  $\pm 5.0$  kcal/mol. The largest deviation for the DLPNO-CCSD(T) method was obtained for reaction 104 and amounted to 10.4 kcal/mol. As for the Zr dataset, we investigate in section 3.6 the possible sources of errors at the origin of the DLPNO-CCSD(T) deviation for reaction 104, and propose a solution.



**Chart 6.** Mean unsigned (MUE) and mean signed (MSE) errors with respect to experimental enthalpies obtained for FECUNBRERE8 dataset with CCBS basis sets.

**Table 11.** Reaction enthalpies errors in kcal/mol obtained with few popular methods for FECUNBRERE8 dataset.

Reaction Number	DLPNO-CCSD(T) $\Delta H$ Error (kcal/mol)	M06 $\Delta H$ Error (kcal/mol)	PBE0-D3 $\Delta H$ (kcal/mol)
104	10.7	9.8	6.4
105	-3.5	-2.8	-4.3
106	-5.2	-7.5	-4.7
107	4.8	19.4	4.9
108	1.1	11.6	1.7
109	-3.8	1.9	-1.0
110	-4.1	1.2	-1.9
111	-3.8	-2.5	-2.1



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3 As previously, dispersion correction significantly improves the B3LYP performance, leading to a  
4 decrease of the MUE by 3 kcal/mol. The smaller improvement upon inclusion of an empirical  
5 dispersion term has been documented for the PBE, PBE0, TPSS and TPSSh methods. Similarly  
6 to previous results, the performance of the M06/M06-L methods has been found not to be  
7 influenced by dispersion correction. Small improvement amounting to a fraction of kcal/mol in  
8 MUE was noticed when going from TZ basis set to CBS limit. The results obtained with SBS are  
9 given in Chart S12 in SI and essentially mirror the CCBS values described above.  
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### 20 **3.4.1 Practical Recommendations for Fe, Cu, Nb and Re dataset.**

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24 Practically all methods but M06/M06-L can be recommended to evaluate reaction enthalpies  
25 based on the performance obtained for FECUNBRERE8 dataset. Particularly good performance  
26 of B3LYP-D3 method resulting in MUE/MSE of 2.8/0.6 should be noted.  
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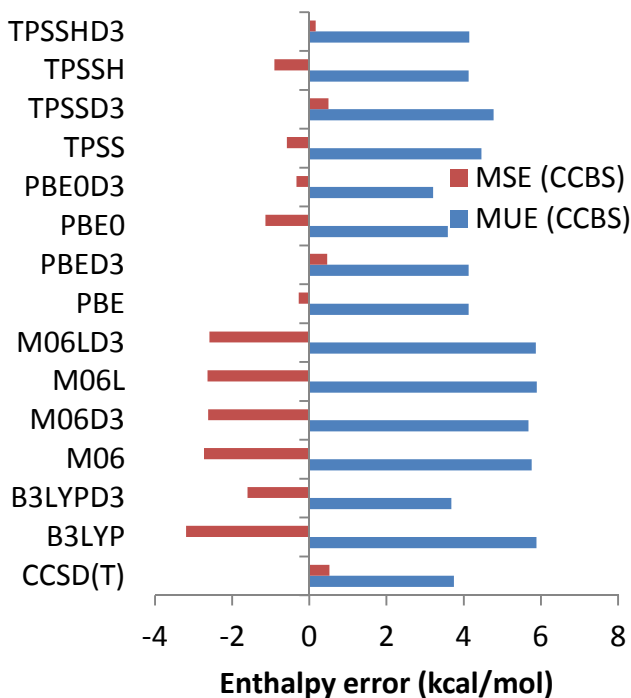
**Table 12.** Complete basis set approximated mean unsigned and mean signed errors for several popular methods (DLPNO-CCSD(T), B3LYP-D3, M06, PBE0-D3, TPSSh-D3, PBE, PBE-D3, TPSS) for the FECUNBRERE8 dataset.

	MUE (kcal/mol)	MSE (kcal/mol)
DLPNO-CCSDT	4.6	-0.5
B3LYP-D3	2.8	0.6
M06	7.1	3.9
PBE0-D3	3.4	-0.1
TPSSh-D3	3.2	0.5
PBE	4.8	3.8
PBE-D3	4.2	3.1
TPSS	4.3	2.9

### 3.5 Overall Performance

The overall performance of the methods and CBS extrapolation for the 6 datasets including 111 reactions is plotted in Chart 7. The results obtained with TZ and QZ are given in Chart S13 in SI. Comparing to results obtained for individual datasets, all methods work more uniformly. Thus, the difference between the best performer, PBE0-D3 with MUE of 3.2 kcal/mol and the worst performer, M06L with a MUE of 5.9 kcal/mol is only 2.7 kcal/mol. The DLPNO-CCSD(T) method provides a MUE of 3.7 kcal/mol, indicating that on average DFT and CCSD(T) provide comparable accuracy for thermochemistry of transition metal complexes. As for the separate datasets, an empirical dispersion correction significantly improves the B3LYP performance, by reducing the MUE by 2.2 kcal/mol. The performance of the other functionals is practically not affected by empirical dispersion correction. Both the DLPNO-CCSD(T) and B3LYP values accurately correlate with experiments, with a  $R^2$  of 0.99, This indicates the excellent

performance of the explored methods on the large scale, and that there is a series of functionals whose performance is rather similar and, as aforementioned, comparable to DLPNO-CCSD(T) results, see Table 13.



**Chart 7.** Mean unsigned (MUE) and mean signed (MSE) errors with respect to experimental reaction enthalpies obtained for combined dataset of 111 reactions involving 11 transition metal complexes with CCBS basis sets.

Since the 111 reactions considered are dominated by Hg reactions, which might bias statistical analysis, as a further indicator of the performance of the various methods, the MUE and MSE obtained by averaging over the single datasets is reported in Table 13 as well as in Charts S15-16. While consistent with MUE and MSE obtained for the 111 reactions, averaging over the datasets results in increased MUE and MSE. While errors obtained for all methods are

comparable to average experimental uncertainty of 3.1 kcal/mol obtained for all 111 reactions, our analysis also indicated that quite large deviations are possible and, in principle, they are difficult to anticipate. In this respect, the main result from this analysis is that none of the methods used here is the real winner, and none of them can be recommended as a out-of-the-box method for predicting transition metals thermochemistry.

**Table 13.** Complete basis set approximated mean unsigned and mean signed errors for several popular methods (DLPNO-CCSD(T), B3LYP-D3, M06, PBE0-D3, TPSSh-D3, PBE, PBE-D3, TPSS) for all 111 reactions involving 11 transition metal complexes.

	Averaging over 111 reactions		Averaged over datasets	
	MUE (kcal/mol)	MSE (kcal/mol)	MUE (kcal/mol)	MSE (kcal/mol)
DLPNO-CCSDT	3.7	0.5	5.0	1.3
B3LYP-D3	3.7	-1.6	5.0	-0.8
M06	5.8	-2.7	7.5	-1.9
PBE0-D3	3.2	-0.3	4.7	0.5
TPSSh-D3	4.1	0.2	6.0	1.1
PBE	4.1	-0.3	6.1	1.2
PBE-D3	4.1	0.5	6.1	2.1
TPSS	4.1	-0.6	6.7	0.5

As final remark, it as to be stressed that in addition to large MUEs obtained for all the methods, vanishing MSEs have been detected. As discussed in section 2.4, this results in poor average predictive power of all the methods on the combined dataset of 111 reaction enthalpies not only in terms of absolute values, but also in terms of relative values, i.e. trends in behavior, making *in silico* screening of catalysts a real challenge.

### 3.6 Possible Sources of Errors

An excellent performance has only been observed for reactions involving group 12 metals, for all other reactions significant errors have been found and need to be explained. Since the accuracy of DFT depends on the particular functional/system under study and cannot be improved systematically, i.e. for some reactions simple GGA can be superior to advanced hybrid-meta GGA or double-hybrids, we concentrate exclusively on explanations of DLPNO-CCSD(T) failures. For this method, the following possible sources of deviations from experimental values can be suggested: the poor quality of the experimental data, the effect of DLPNO truncation, the multi-reference character of the systems under study, poor quality of Hartree-Fock reference wave function, the insufficient basis sets and improper treatment of scalar relativistic effects, improper treatment of core-valence electron correlation and frozen core-approximation.

#### 3.6.1 Experimental Errors and Uncertainties

For many reaction enthalpies (see Table 2) the experimental uncertainties can be as large as  $\pm 5$  kcal/mol. Since for some formation enthalpies only a single measurement is available, inaccuracy of experimental data might account to some extent for the seemingly poor DLPNO-CCSD(T) performance. However, there are still a few reactions for which DLPNO-CCSD(T) errors larger than experimental uncertainties were documented and for which, at the same time, DFT methods performed quite well. For example, for reactions 85-90 of ZRRE13 dataset the DLPNO-CCSD(T) method resulted in errors 25-30 kcal/mol. All these reactions involve  $\text{ZrF}_4$  species. This indicates that either the experimental formation enthalpy of  $\text{ZrF}_4$  is severely wrong or there is something fundamental missing when applying the default DLPNO-CCSD(T)

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3 protocol. The experimental accuracy of  $ZrF_4$  formation enthalpy in the gas phase is claimed to be  
4 quite high.<sup>151</sup> It was obtained as the sum of the formation enthalpy of  $ZrF_4$ (solid) and enthalpy of  
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6 sublimation of the latter, as in the equation below:  
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$$\Delta H_f(ZrF_4, \text{gas}) = \Delta H_f(ZrF_4, \text{solid}) + \Delta H_{\text{subl}}(ZrF_4) \quad (5)$$

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10  
11 For the sublimation enthalpy of  $ZrF_4$ (crystal),  $\Delta H_{\text{subl}}(ZrF_4)$ , there are ten independent  
12 measurements, and the third law sublimation enthalpies perfectly agree with each other.<sup>151</sup> The  
13 only available formation enthalpy of solid  $ZrF_4$  was measured with fluoride bomb calorimetry by  
14 direct combination of the elements, with an estimated uncertainty of only  $\pm 0.25$  kcal/mol.  
15 Furthermore, the overall quite robust PBE0-D3 method gives a MUE of only 1.5 kcal/mol for  
16 reactions 85-90, suggesting that the poor performance of DLPNO-CCSD(T) is in the default  
17 (out-of-the-box) protocol we used. We decided to combine these zirconium reactions as well as  
18 few other reactions, namely reactions 102 – 104, 68, 70, 72, 79 for which large DLPNO-  
19 CCSD(T) errors were documented, into one dataset. Then, we tried to explore possible sources  
20 of inaccuracy in the adopted DLPNO-CCSD(T) protocol before ascribing the failure of DLPNO-  
21 CCSD(T) to inaccuracy in the experiments.  
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### 41 **3.6.2 Basis Set Effect and Relativistic Treatment.**

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43 Insufficient basis sets can be discarded since the CBS extrapolation has been used with quite  
44 reasonable basis sets, correlation consistent triple and quadruple- $\zeta$  quality. Scalar relativistic  
45 effects have been included both via scalar-relativistic ECPs (CCBS results) and via the DKH  
46 Hamiltonian with relativistic basis sets (SBS). Since both ECP and DKH all-electron strategies  
47 have led to almost identical results, this hypothesis can be ruled out as well. This finding also  
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3 rules out the possibility that the ECP and the valence basis set we used are not well balanced, an  
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5 effect discussed in ref. 223.  
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### 8 9 **3.6.3 Multi-Reference Character**

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12 First, we tried to detect possible multi-reference character of the systems under study via the  
13 largely used T1 diagnostic. For each of the reactions in Table 2 the T1 value of all the complexes  
14 was calculated, and the largest T1 value within each reaction was correlated with the DLPNO-  
15 CCSD(T)/CBS error. For all 111 reactions,  $R^2$  turned out to be 0.03. For separate datasets, the  
16  
17 following  $R^2$  were obtained: ZNCDRE14:  $R^2=0.41$ , HGRE51:  $R^2=0.20$ , TIRE18:  $R^2=0.01$ ,  
18  
19 ZRRE13:  $R^2=0.02$ , MOWRE:  $R^2=0.04$ , FECUNBRERE8:  $R^2=0.59$ . Since all  $R^2$  are significantly  
20  
21 small, with the exception of the FECUNBRERE8 dataset, no correlation between T1 values and  
22  
23 errors is obtained. Second, we also tried to correlate largest coupled cluster amplitudes, T2,  
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25 which are also often considered as indication of multi-reference character as discussed in ref.,<sup>92</sup>  
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27 with the DLPNO-CCSD(T) errors. The following correlation coefficients have been obtained: all  
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29 complexes:  $R^2=0.09$ , ZNCDRE14:  $R^2=0.51$ , HGRE51:  $R^2=0.10$ , TIRE18:  $R^2=0.24$ , ZRRE13:  
30  
31  $R^2=0.10$ , MOWRE:  $R^2=0.28$ , FECUNBRERE8:  $R^2=0.33$ . Again, no correlation has been  
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33 detected, also for the FECUNBRERE8 dataset. In particular, T1 and T2 values for the most  
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35 problematic reactions 85-90 are 0.017-0.019 and 0.060-0.136, respectively, which are values  
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37 smaller or equal to those for the similar reactions 97-98 (T1: 0.025 and T2: 0.083-0.136) for  
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39 which errors below 2.0 kcal/mol were obtained. In addition, it has to be stressed that single-  
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41 determinant DFT methods would also have no chance to succeed if the CCSD(T) errors for  
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43 reactions 85 – 90 were caused by the lack of multi-reference treatment. However, since quite  
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45 large T1 and T2 values have been obtained for some complexes, the necessity of multi-reference  
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3 treatment might be responsible for some failures, but only for minor part since no correlation has  
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5 been detected.  
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### 8 9 **3.6.4 Effect of Pair Natural Orbitals Truncation**

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12 The DLPNO truncation has been reported to have only small influence on reaction energies.<sup>68</sup> To  
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14 further check this point, we carried out canonical CCSD(T) calculation for the problematic  
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16 reactions introduced above, namely reactions 68, 70, 72, 79, 104, 85, 86, 87, 88, 89, 90, 102 and  
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18 103. Due to quite large CPU time required for canonical CCSD(T) calculations compared to its  
19  
20 DLPNO counterpart, we limited these tests to TZ basis sets calculations only. In Table 14 we  
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22 compare the deviations in reaction enthalpies with respect to experimental estimates obtained  
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24 with different protocols and TZ quality basis sets. These deviations have to be interpreted  
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26 carefully since TZ basis sets are insufficient for CCSD(T) calculations, and extension of the  
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28 basis set to CBS limit can significantly influence the results. However, comparing the reaction  
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30 enthalpy errors obtained with different protocols is insightful enough to estimate the effect of  
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32 changing the computational scheme.  
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39 In the second column of Table 14 the errors in reaction enthalpies obtained with standard  
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41 DLPNO-CCSD(T)/TZ(ECP) protocol are given. In the third column the errors obtained with  
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43 canonical CCSD(T)/TZ(ECP) basis set are presented. The largest discrepancy between DLPNO-  
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45 CCSD(T) method and its canonical counterpart was detected for reaction 104. The canonical  
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47 CCSD(T) scheme resulted in the reaction enthalpy underestimated by 3.5 kcal/mol, while the  
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49 DLPNO-CCSD(T)/TZ(ECP) value is underestimated by 9.5 kcal/mol. Therefore,  
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51 underestimation of 10.7 kcal/mol obtained for this reaction with DLPNO-CCSD(T)/CBS scheme  
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56 in Section 3.4 can be ascribed to the PNO truncation and can be ameliorated by either tightening  
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the DLPNO settings or switching to canonical CCSD(T). For all other reactions the DLPNO truncation effect turned out to be much smaller. Particularly large errors documented for ZrF<sub>4</sub> reactions 85-90 remained unaffected. Finally, the mean unsigned deviation obtained for reactions in Table 14 with canonical CCSD(T) method is only 0.3 kcal/mol smaller comparing to its DLPNO counterpart, compares columns 2 and 3 in Table 14.

**Table 14.** Errors in reaction enthalpies obtained with different computational schemes: standard DLPNO-CCSD(T)/TZ(ECP), canonical CCSD(T)/TZ(ECP), DLPNO-CCSD(T)/TZ(ECP) on PBE wave function, canonical CCSD(T) with all-electron Sapporo TZ and standard TZ(ECP) basis sets and all electrons included in correlation treatment.

Energy	CCSD(T)	CCSD(T)	CCSD(T)	CCSD(T)	CCSD(T)
DLPNO	Yes	No	Yes	No	No
ECP	Yes	Yes	Yes	No	Yes
FC <sup>a</sup>	Yes	Yes	Yes	No	No
WF <sup>b</sup>	HF	HF	PBE	HF	HF
Reaction	$\Delta H$ dev. <sup>c</sup>	$\Delta H$ dev. <sup>c</sup>	$\Delta H$ dev. <sup>c</sup>	$\Delta H$ dev. <sup>c</sup>	$\Delta H$ dev. <sup>c</sup>
68	-4.8	-3.2	-6.8	-0.7	-
70	-4.6	-2.3	-4.7	1.9	-
72	-4.9	-5.5	-6.7	-9.2	-
79	-4.9	-6.1	-5.9	-11.3	-
85	28.0	28.7	13.3	1.9 (-3.7) <sup>f</sup>	7.2
86	17.9	18.2	3.6	-8.1 (-2.2) <sup>f</sup>	-2.0
87	26.2	27.3	11.4	4.3 (-3.0) <sup>f</sup>	10.3
88	18.1	18.6	3.6	-5.9 (0.6) <sup>f</sup>	-0.4
89	26.6	27.8	12.0	7.3	11.4
90	15.0	15.9	1.1	-6.4	-2.7
102	5.6	4.9	6.7	0.6	2.4
103	-14.6	-15.2	-17.2	8.5	-3.4
104	9.5	3.5	5.5	1.4	-
MUE <sup>d</sup>	<b>13.9</b>	<b>13.6</b>	<b>7.6</b>	<b>5.2</b>	<b>5.0<sup>e</sup></b>

<sup>a</sup> Frozen core approximation. If “Yes”, only valence electrons are included in correlation treatment. The largest noble gas core is frozen. If “No”, all electrons included in the SCF procedure are also included in correlation treatment. <sup>b</sup> Wave function (determinant) used for

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3 CCSD(T) calculation. <sup>c</sup>  $\Delta H(\text{Exp.}) - \Delta H(\text{Theo.})$  <sup>d</sup> The mean absolute deviation from  
4 experimental values in kcal/mol. <sup>e</sup> Calculated only for reactions 85-90, 102-103 <sup>e</sup> DLPNO-  
5 CCSD(T) on the PBE wave function. <sup>f</sup> CBS extrapolated values.  
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### 8 9 10 11 12 13 14 15 **3.6.5 Quality of the HF Determinant as DLPNO-CCSD(T) Reference State** 16

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18 As discussed in ref. <sup>224</sup>, for some transition metal systems the Hartree-Fock wave function is a  
19 poor reference for subsequent coupled cluster calculations. And it would be even more so for  
20 open shell systems which are avoided in the present work. To check the sensitivity of the  
21 reaction enthalpies to the reference determinant, we performed DLPNO-CCSD(T) calculations  
22 on the top of the PBE wave function (fourth column in Table 14). The mean unsigned reaction  
23 enthalpy error for all reactions with respect to experimental enthalpies turned out to be reduced  
24 by 6.3 kcal/mol comparing to default DLPNO-CCSD(T)/TZ(ECP) protocol. This indicates the  
25 choice of reference determinant influences the reaction enthalpies to much larger extent than  
26 PNO truncation. However, influence of reference wave function is not homogeneous. For  
27 reactions 68, 70, 72, 79, 102 and 103 the difference in errors obtained with HF and PBE  
28 reference wave functions is below 2-3 kcal/mol. The most drastic differences have been obtained  
29 for the problematic reactions 85-90. The errors for these reaction enthalpies have been reduced  
30 by 14-15 kcal/mol when PBE determinant was used as reference wave function. This can  
31 partially account for underestimations of 27-32 kcal/mol obtained for those reactions with the  
32 DLPNO-CCSD(T)/CBS method. However, trivial replacement of the HF with a DFT  
33 determinant for subsequent CCSD(T) calculations might introduce another source of errors since  
34 there are many DFT functionals available, and it is unclear to what extent a change of the DFT  
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3 reference function will (and if) influence the resulting properties. This would be a good subject  
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5 for future work.  
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### 8 9 **3.6.6 Correlation of Core Electrons**

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12 By default, in many CCSD(T) codes (e.g. Gaussian 09, ORCA) core electrons are not included in  
13  
14 the correlation treatment giving rise to the so-called “frozen core” approximation. This is done to  
15  
16 improve computational efficiency, and it is usually physically sound since dynamic correlation in  
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18 the core electrons normally affects relative energies minimally. We further investigate the  
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20 validity of this approximation for the most problematic reactions in our set.  
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25 First, we used the all electron Sapporo TZ basis sets in case core electrons covered by ECP turn  
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27 out to be important. Further, canonical CCSD(T) calculations were preferred to the DLPNO  
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29 approximation since the default correlation auxiliary basis sets available in ORCA were  
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31 constructed only to cover valence orbitals correlation effects. Since this approach resulted in a  
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33 large number of electrons included in the correlation treatment, even TZ calculations become  
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35 computationally too much demanding. To overcome this difficulty we decided to run these  
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37 CCSD(T) calculations with Gaussian 09 suite of programs since latter can take an advantage of  
38  
39 the molecular symmetry in CCSD(T) calculations, see the computational details section. In  
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41 particular, we used  $T_d$  symmetry for  $ZrF_4$ ,  $ZrCl_4$ ,  $ZrBr_4$ ,  $ZrI_4$ ,  $TiF_4$ ,  $TiCl_4$ ,  $TiBr_4$ ,  $TiI_4$ ;  $D_{3h}$   
42  
43 symmetry for  $FeC_5O_5$ ,  $C_{2v}$  symmetry for  $Fe-cis-C_4O_4I_2$ ,  $TiO_2$ ; and  $O_h$  symmetry for  $WC_6O_6$ ,  
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45  $WCl_6$ ,  $WF_6$ . The results obtained with this protocol are given in the fifth column of Table 14.  
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51 The reaction enthalpy errors for reaction of 85-90 were found to be different by 20-30 kcal/mol  
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53 comparing to their DLPNO-CCSD(T)/TZ (CCBS) values, and in much better agreement with the  
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55 experimental values, with a reduction of the MUE to 5.2 kcal/mol. This suggests that the large  
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3 discrepancies for these reactions with the standard DLPNO-CCSD(T) method should be rooted  
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5 to lack of correlation treatment of core electrons (the out-of-the-box approach for Zr is to  
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7 correlate only the  $4d^2$  and  $5s^2$  electrons). The error for reaction 102 was decreased by 5 kcal/mol  
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9 comparing to standard DLPNO-CCSD(T)/TZ estimate and essentially matches the experimental  
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11 value. Interestingly, for reaction 103 inclusion of core electrons in the correlation treatment  
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13 resulted in the CCSD(T) value under estimating the experimental value by roughly 17 kcal/mol,  
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15 whereas the DLPNO-CCSD(T)/TZ(ECP) overestimates the experimental value by roughly 8  
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17 kcal/mol. Considering that also DFT methods show scattered and largely wrong prediction for  
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19 reaction 103, it is difficult to ascribe this disagreement between theory and experiments to a  
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21 failure of theoretical methods or to inaccuracy in the experimental measures. The reaction  
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23 enthalpy of other reactions is also influenced by inclusion of the core electrons in the correlation,  
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25 but to significantly smaller extent. For example, for reactions 72 and 79 inclusion of core  
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27 electrons in the correlation treatment improved the reaction enthalpies by 4 and 2.6 kcal/mol,  
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29 respectively, compared to standard DLPNO-CCSD(T)/TZ (ECP) results, whereas for reactions  
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31 72 and 79, the error in reaction enthalpies became larger by 4.3 and 6.4 kcal/mol. Finally, the  
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33 overall MUE was found to be 5 kcal/mol indicating core correlation to be responsible for the  
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35 most of the errors. It should also be noted that this error might be ameliorated if CBS  
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37 extrapolation is used. And indeed, CBS extrapolated enthalpies for reactions 85-88 resulted in  
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39 errors smaller than 3.8 kcal/mol.

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41 To understand the influence of the ECP to describe the core electrons of TM complexes,  
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43 canonical CCSD(T)/TZ (ECP) calculations with all electrons non-covered by ECP (i.e.  
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45  $4s^2 4p^6 4d^2 5s^2$  for Zr and  $5s^2 5p^6 5d^2 6s^3$  for W) were performed for reactions 85 – 90 and 102 –  
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47 103. The results are given in the sixth column of the Table 14. Comparison with estimates  
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3 obtained with the default protocol, where only the outermost electrons (i.e.  $4d^25s^2$  for Zr and  
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5  $5d^26s^3$  for W) were correlated in the DLPNO-CCSD(T)/TZ (ECP) calculations (second column  
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7 in Table 14), indicates that the deviations where all the electrons out of the ECP are included in  
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9 the correlation treatment are much closer to the all electrons canonical CCSD(T) calculations  
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11 (compares columns 2 and 6 with column 5 in Table 14) and very close to the experimental  
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13 reaction enthalpies. This analysis clearly indicates that the experimental formation enthalpy of  
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15  $ZrF_4$  is actually quite precise, and that the initial failure we observed for  $ZrF_4$  including reactions  
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17 can be ascribed to the out-of-the-box application of the standard protocol used in quantum  
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19 chemistry codes to perform CCSD(T) calculations. Further, it highlights the importance of  
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21 extending the numbers of correlated electrons, particularly in those cases where no experimental  
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23 value is available for benchmarking the performance of the method.  
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#### 30 **4. Conclusions**

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33 The recently developed DLPNO-CCSD(T) method and 7 popular DFT functionals with and  
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35 without an empirical dispersion term have been tested to reproduce 111 reaction enthalpies  
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37 derived from experimental gas phase formation enthalpies of 11 transition metals. DLPNO-  
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39 CCSD(T) was found to perform excellently for group 12 transition metals providing MUE below  
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41 2 kcal/mol. Combining these results with the excellent performance for Cu, Ag and Au  
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43 datasets,<sup>98</sup> we can conclude that DLPNO-CCSD(T) leads to accurate thermochemistry for  
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45 reactions involving group 12 metals or group 11 metal ions. DFT functionals perform similarly  
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47 well, providing MUEs close to or below 2 kcal/mol. Much less appealing results were obtained  
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49 when group 4 metals were considered, with DLPNO-CCSD(T) resulting in MUE greater than 3.3  
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51 kcal/mol for Ti and 14.4 kcal/mol for Zr based enthalpies. For Ti complexes DFT performs  
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53 clearly worse, with PBE providing the smallest MUE of 6.4 kcal/mol. For Zr complexes, DFT  
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3 performs clearly better, with PBE0-D3 resulting in MUE and MSE smaller than 1.8 kcal/mol.  
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5 Nevertheless, even this functional should be used with care. For group 6 metals DLPNO-  
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7 CCSD(T) clearly outperforms all DFT methods proving MUE below 5.5 kcal/mol and vanishing  
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9 MSE. Best performing DFT functional for these reactions, M06L-D3 provides MUE of 10.9  
10  
11 kcal/mol. Finally, for combined set containing 8 reactions of Fe, Cu, Nb, Re DLPNO-CCSD(T)  
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13 and DFT methods provide similar errors, in particular MUE of DLPNO-CCSD(T) is 4.6  
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15 kcal/mol and B3LYP-D3 is 2.8 kcal/mol.  
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21 Based on our results, no single DFT method performs equally good across all the reactions of all  
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23 transition metals investigated. Even if some methods were found to be the best performers for  
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25 particular datasets, large errors in general and large non-systematic deviations of 20 – 30  
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27 kcal/mol were obtained for some particular reactions. Aiming at using these methods with a  
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29 systematic accuracy of about 2-3 kcal/mol, which is required for *in silico* screening of new  
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31 catalysts, conclusions from our study are quite disappointing. Indeed, considering that we  
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33 focused on systems in a stable singlet state, even larger discrepancies with experimental data can  
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35 be foreseen for open shell systems.  
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41 While we do not try to decipher the reason of the poor performance of DFT on some of the  
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43 metals, test calculations with the DLPNO-CCSD(T) and canonical CCSD(T) were performed.  
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45 Canonical CCSD(T) calculations on the reactions where DLPNO-CCSD(T) resulted in  
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47 significant deviation from experiment indicated that these large discrepancies cannot be ascribed  
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49 to the PNO truncation. Few attempts to improve the performance of DLPNO-CCSD(T) and  
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51 CCSD(T) on these difficult cases by reducing the number of frozen orbitals, by pushing the  
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53 quality of the basis set, and by replacing the reference HF wave function with the PBE one were  
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55 also attempted. DLPNO-CCSD(T) calculations on the top of PBE wave-functions also led to  
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3 some improvement, however more tests are needed to recommend this protocol for routine  
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5 calculations on transition metal complexes. The main conclusion of these tests indicated that all  
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7 electron DKH calculations with all electrons included in the correlation treatment led to the most  
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9 significant improvement.  
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13 The DLPNO-CCSD(T) method, apart from the Zr dataset, generally performs either better or  
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15 similarly than DFT methods. Canonical CCSD(T) test calculations indicated that the PNO  
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17 truncation has negligible effects in most of the cases, and that the largest CCSD(T) deviations  
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19 from experiments can be remedied by proper inclusion in correlation of core electrons and taking  
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21 into account of relativistic effects. Further, our results also indicate that benchmarking DFT  
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23 methods towards CCSD(T) results for transition metals, a typical protocol to select the best  
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25 performing functional for the specific problem at hand, *might in principle be possible*. However,  
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27 to be reliable the CCSD(T) numbers must be tested by systematic inclusion of all potentially  
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29 important effects originated from core electrons correlation, relativism, starting wave function,  
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31 basis set quality and multi-reference character.  
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38 As final remark, our calculations highlighted the importance of working with a large or carefully  
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40 built datasets, since unexpected large deviations can occur. In this respect, the datasets we  
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42 introduced could reveal useful for development of new methods for transition metals chemistry.  
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#### 46 ASSOCIATED CONTENT

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49 **Supporting Information.** Cartesian coordinates (Å), DLPNO-CCSD(T), B3LYP, B3LYP-D3,  
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51 M06, M06-D3, M06L, M06L-D3, PBE, PBE-D3, PBE0, PBE0-D3, TPSS, TPSS-D3, TPSSh,  
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53 TPSSh-D3 energies with different basis sets, T1 diagnostic values, T2 (largest amplitudes  
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55 values), enthalpic corrections, tabulated enthalpies and errors forming the basis of Charts 1 – 7  
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3 and Charts S1-S16, tabulated absolute enthalpies of all 111 reactions. This material is available  
4  
5 free of charge via the Internet at <http://pubs.acs.org>.  
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28  
29 The manuscript was written through contributions of all authors. All authors have given approval to the final version of  
30 the manuscript. ‡These authors contributed equally. (match statement to author names with a symbol)  
31  
32

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## Material for the Table of Contents

