



Toward Accurate Theoretical Thermochemistry of First Row Transition Metal Complexes

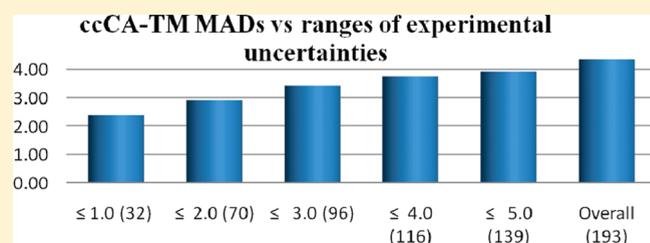
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S Supporting Information

ABSTRACT: The recently developed correlation consistent Composite Approach for transition metals (ccCA-TM) was utilized to compute the thermochemical properties for a collection of 225 inorganic molecules containing first row (3d) transition metals, ranging from the monohydrides to larger organometallics such as $\text{Sc}(\text{C}_5\text{H}_5)_3$ and clusters such as $(\text{CrO}_3)_3$. Ostentatiously large deviations of ccCA-TM predictions stem mainly from aging and unreliable experimental data. For a subset of 70 molecules with reported experimental uncertainties less than or equal to $2.0 \text{ kcal mol}^{-1}$, regardless of the presence of moderate multireference character in some molecules, ccCA-TM achieves

transition metal chemical accuracy of $\pm 3.0 \text{ kcal mol}^{-1}$ as defined in our earlier work [*J. Phys. Chem. A* 2007, 111, 11269–11277] by giving a mean absolute deviation of $2.90 \text{ kcal mol}^{-1}$ and a root-mean-square deviation of $3.91 \text{ kcal mol}^{-1}$. As subsets are constructed with decreasing upper limits of reported experimental uncertainties (5.0, 4.0, 3.0, 2.0, and $1.0 \text{ kcal mol}^{-1}$), the ccCA-TM mean absolute deviations were observed to monotonically drop off from 4.35 to $2.37 \text{ kcal mol}^{-1}$. In contrast, such a trend is missing for DFT methods as exemplified by B3LYP and M06 with mean absolute deviations in the range 12.9–14.1 and $10.5\text{--}11.0 \text{ kcal mol}^{-1}$, respectively. Salient multireference character, as demonstrated by the T_1/D_1 diagnostics and the weights (C_0^2) of leading electron configuration in the complete active self-consistent field wave function, was found in a significant amount of molecules, which can still be accurately described by the single reference ccCA-TM. The ccCA-TM algorithm has been demonstrated as an accurate, robust, and widely applicable model chemistry for 3d transition metal-containing species with versatile bonding features.



INTRODUCTION

Transition metal-containing species play a pivotal role in all major areas of both chemical research and industry, including catalysis, synthesis, combustion, and materials. Quantitative energetic information of these compounds is useful in elucidating the underlying mechanism of chemical processes involving transition metal-containing compounds, as well as providing guidance about synthetic preferences. Unlike main group molecules, accurate bond enthalpies and standard enthalpies of formation (ΔH_f°) are still elusive for many fundamental transition metal-containing molecules in the gas phase. Tabulated values of these thermodynamic quantities^{1–3} are not unequivocal even for some classical metal complexes such as $\text{Cr}(\text{CO})_x$ and $\text{Fe}(\text{CO})_x$.^{4–6} This is due to the age and scarce availability of experimental data, as well as severe difficulties in assessing the quality of this data. Consequently, computational methods are critical and sometimes provide the only means to obtain the energetic profiles of transition metal species. The development of reliable and computationally amenable methods to accurately predict the energetic properties of transition metal species becomes an important task for the computational chemistry community.

Many physical phenomena compound to make the investigation of the electronic structure of transition metal-containing molecules an extremely difficult task. These effects are not limited to competing low-lying excited states, the existence of spin–orbit

coupling, strong relativistic effects, increased electron correlation due to metal–ligand backbonding, and complexity of core–core and core–valence electron interactions. General computational approaches that can be used to efficiently and reliably compute bond energies of transition metal molecules are not well established, even though a great deal of progress has been made recently (see a selected few examples in refs 7–14). Density functional theory (DFT), more efficient as compared to wave function-based electron correlation methods, has been extensively applied to a great variety of transition metal-containing species with growing success for a number of years (see recent reviews^{15,16} and references therein). However, DFT methods that are viable for research on transition metal-containing species are often heavily parametrized, for example, the M06 families.^{17–19} Pure functionals such as PBE do not contain empirical parameters but fail to predict the ground spin states of open shell transition metal-containing systems such as iron complexes.²⁰ Despite their wide applications, DFT methods may fail to provide quantitatively useful information, for example, for the enthalpies of formation calculated via atomization energies for a number of transition metal complexes.⁹ The problems could be alleviated by using

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reaction energies, which are not always available. Multireference methods such as multireference configuration interaction (MRCI) and complete active space perturbation theory (CASPT n)^{21,22} are free of spin contamination and can properly address the multireference character that is prominent in many transition metal compounds. These methods have been commonly used to obtain accurate energetic description of small transition metal compounds. For relatively larger molecules, a complete active space (CAS) that includes all relevant valence electrons and valence molecular orbitals is computationally intractable. The use of restricted active space is more computationally amenable, but is challenging to users²³ as there is no generally applicable strategy of defining truncated active spaces for a well-balanced multiconfiguration reference wave function. While a rigorously size-consistent multireference analogue of coupled cluster theory, especially coupled cluster including singles, doubles, and perturbative treatment of triples [CCSD(T)], has not yet been implemented or fully developed,^{24–26} the well-developed and readily available MRCI (or MRACPF²⁷ and MRAQCC²⁸) and CASPT2 approaches are generally not suitable for accurate predictions of dissociation energies and related quantities such as enthalpies of formation due to the size-consistency error^{29,30} that increases with the system size. Because of the above-mentioned difficulties with MR methods, single reference wave function-based electronic structure theory, particularly CCSD(T), remains a potential method of choice for accurate transition metal thermochemistry.

The scaling order of computational cost increases with the electron excitation level of the employed theory; for example, the cost of MP2 and CCSD(T) scales as N^5 and N^7 , respectively, where N is related to the size of the molecule. Composite approaches can attain accuracy comparable to CCSD(T), coupled cluster theory with excitation levels higher than triple, or full CI with a very large basis set or extrapolated complete basis set (CBS) limit, at only a small fraction of computational cost. Our laboratory has created a composite method, the correlation consistent Composite Approach (ccCA),^{31–33} that achieves “chemical accuracy”, where energies and thermochemical properties of main group-containing species are reliably computed to within 1.0 kcal mol⁻¹ of experimental values on average, but the cost is comparable to only a single point energy evaluation by CCSD(T) with a triple- ζ quality basis set or MP2 with a quadruple- ζ quality basis set. One distinguishable feature of ccCA is that it is an MP2-based model chemistry, but no empirical corrections are included in the energy computations. Consequently, the errors originate only intrinsically from the utilized theories, allowing unbiased performance of ccCA for molecules outside the benchmark. Also, it is expected that ccCA can serve as a pan-periodic model chemistry that is, in principle, applicable for all elements without regard to the block in which they reside in the periodic table, that is, s-block for alkali and alkaline metals,³³ p-block for group IIIA–VIIIA elements,^{31–34} and d-block for transition metals.^{7,8}

Because of the aforementioned issues, the development of an accurate model chemistry for transition metal-containing species has lagged behind their main group counterparts. This was primarily due to significant advances in d-block basis sets^{5,35} occurring over the last 5 years. Our research group^{7,8} pioneered the development of ccCA for computing energies and thermochemical properties of a variety of 3d-containing molecules to be within 3.0 kcal mol⁻¹ of experimental values on average, using the correlation consistent basis sets developed by Peterson and coauthors.³⁵ In earlier work, we have coined the term “transition

metal chemical accuracy” to describe a mean absolute deviation (MAD) of 3.0 kcal mol⁻¹ or better for transition metal species.⁷ This targeted accuracy is larger than for energetics of main group species because greater uncertainties are common in the experimental data for transition metal compounds and greater errors are expected with theory due to a number of factors including increased valence electron space, stronger relativistic effects, and increased complexity of metal–ligand bonding. In a recent study,⁸ the earlier ccCA algorithm was modified to address more effectively the core–valence correlation and scalar relativistic effects. This modified ccCA algorithm for transition metal chemistry is called ccCA-TM. Using ccCA-TM, a MAD of 2.85 kcal mol⁻¹ was achieved for a set of 52 molecules, which represents a variety of metal–ligand bonding and includes species ranging from diatomics to transition metal complexes with organic ligands. Unlike DFT methods,³⁶ ccCA-TM performs consistently for all 10 3d metals without drastic variation. Similar accuracy was also obtained for a subset of 20 molecules in a recent study by Mayhall et al.¹⁰ using the Gaussian 4(MP2)-tm model chemistry. Additionally, Dixon and co-workers have developed a normalized clustering energy approach^{37,38} for small clusters and have performed a series of theoretical studies of bond energies and enthalpies of formation for oxides, clusters, and other oxo-compounds of group IVB and VIB metals.^{37–40} Landis et al.⁴¹ have also investigated bond enthalpies of a large set of d-block transition metal compounds.

Despite the successes achieved recently, many problems in the development of transition metal model chemistries remain to be solved. Given the diversity of the 3d metal-containing compounds, the sets are usually limited or heavily biased. For example, the 20-molecule set employed by Mayhall et al.¹⁰ does not contain any molecules with more than four non-hydrogen atoms, and the important class of organometallics is essentially excluded. The systematic studies by Dixon and co-workers^{37–40} are limited to oxo-compounds and clusters, and most of these molecules do not have an experimentally determined enthalpy of formation. The relatively larger set of 58 molecules in the ccCA-TM study⁸ is still not comprehensive in that only four molecules are presented for Sc and V each, and not all homologous compounds such as MX $_n$ (M = transition metal, X = F, Cl, Br, O, and $n = 1, 2, 3$, etc.) for which experimental data are known have been included. In contrast to most studies that focus on specific types of transition metal compounds, some DFT studies considered quite a few types of molecules such as hydrides, halides, oxides, coordinate compounds, and metal dimers. Furche and Perdew¹² investigated the thermochemical properties of 74 species and systematically compared the performance of DFT methods for homologous compounds. Riley and Merz³⁶ studied the quality of a variety of DFT methods in the prediction of ΔH_f° s for 95 species. As compared to DFT methods, the performance of parameter-free ccCA-TM is generally less dependent on transition metals or bonding in molecules. Nonetheless, a more extensive set is still helpful for evaluating the overall quality of single reference ccCA-TM against experimental data, and for statistical assessment of the applicability, as well as limitations, of ccCA-TM for various subcategories of transition metal molecules. To this end, 225 enthalpies of formation (referred to as the ccCA-TM/11all set) are collected from available thermochemistry compendia and journal literature, regardless of the magnitude of experimental uncertainties. It is impossible to be exhaustive in considering all molecules for which gaseous ΔH_f° values have been experimentally

reported. We have attempted to include (before removal of outliers, vide infra) all existent and computationally tractable 3d metal gas-phase enthalpies of formation from the current literature, JANAF tables, NIST webbook, and Yungman compendia. This large collection of test molecules should provide a more statistically meaningful analysis of ab initio methods than any sets used in previous transition metal model chemistry studies. Given the diversity of the molecules in the set, a number of ccCA-TM predicted enthalpies of formation are found to significantly deviate from reported experimental data. Possible causes for the outliers, for example, the large uncertainty of experimental data and the inappropriateness of single reference methods as indicated by the T_1/D_1 diagnostics^{42,43} and the leading CI coefficient (C_0^2) in CAS CI wave functions, are discussed metal by metal. Unlike the various main group test sets, the only selection criterion for our overall ccCA-TM/11 test set is tractability with the ccCA methodology. As a result, the presence of outlier molecules will drastically change the statistical results. For example, the metal dimer Fe_2 , which is notoriously difficult to study with single and multireference ab initio methods, has a ccCA-TM deviation as large as $-47 \text{ kcal mol}^{-1}$. This statistically masks the possible advantages of applying ccCA-TM toward determining the electronic structure of new iron-containing molecules. To minimize masking effects on the statistical results, the outliers are excluded from the set of 225 entries to give a subset of 193 quantities (referred to as ccCA-TM/11), still large enough for statistically significant analysis. The presence of large deviations but small coupled cluster diagnostics, known severe multireference character, or ambiguous experimental data (vide infra) is the criterion for removing species from the ccCA-TM/11 subset.

The ccCA-TM/11 set of 193 molecules were then divided into different subsets on the basis of ranges of experimental uncertainties, bonding types, and size of molecules. Several extrapolation schemes for complete basis set (CBS) limits were compared for the ccCA-TM/11 set. The T_1 and D_1 coupled cluster diagnostics,^{42,43} along with C_0^2 from viable CASCI calculations, are further discussed to a priori estimate the validity of single reference computations for the overall set, as well as different bonding types.

COMPUTATIONAL METHODS

The general ccCA-TM formulation has been described previously.⁸ Here, it is briefly recapitulated with emphasis on the possible variations of ccCA-TM. The equilibrium geometries are optimized with B3LYP^{44–47} and the cc-pVTZ basis set. The total ccCA-TM energy of a molecular species is calculated by

$$E(\text{ccCA-TM}) = E_0(\text{ccCA-TM}) + \Delta E(\text{CC}) + \Delta E(\text{CV}) + \Delta E(\text{ZPE}) + \Delta E(\text{SO}) \quad (1)$$

where $E_0(\text{ccCA-TM})$ is the reference MP2 energy, $\Delta E(\text{CC})$ is the correction to the dynamic correlations not sufficiently recovered by the MP2 method, $\Delta E(\text{CV})$ is the correction for the core–core and core–valence interactions, $\Delta E(\text{ZPE})$ includes the zero point energy scaled by 0.989⁴⁸ and thermal corrections to 298.15 K, and $\Delta E(\text{SO})$ is the spin–orbit coupling correction, which is only calculated for smaller sized molecules with the FOCI Stuttgart ECP⁴⁹ method. The scalar relativistic correction is considered throughout this study by using the one-electron Douglas–Kroll–Hess Hamiltonian^{50–52} and the DK correlation consistent basis sets³⁵ in all single point energy computations. The atomic energies are calculated in the same

fashion as molecules except that the spin–orbit corrections are taken from experimental data.^{1,3} The ROHF- and UHF-ccCA-TM atomic energies and the additive contributions of ccCA components, as well as the experimental values of atomic enthalpies of formation, are given in Tables S1 and S2.

The reference energy $E_0(\text{ccCA-TM})$ is the extrapolated complete basis set (CBS) limit for MP2 with the aug-cc-pVnZ-DK ($n = 2$ or D, 3 or T, and 4 or Q)³⁵ series of basis sets [aug-cc-V($n+d$)Z-DK for Si, P, S, and Cl].^{53,54} A two-point extrapolation of HF energies with TZ and QZ basis sets has proven to be very effective and is adopted in the ccCA algorithms.^{55,56}

$$E(n) = E(\text{CBS}) + A \exp(-1.63n) \quad (2)$$

The dynamic correlation energy can be either extrapolated with the mixed Gaussian formula by Peterson, Woon, and Dunning,⁵⁷ denoted as “P” in this study:

$$E(n) = E(\text{CBS}) + A \exp[-(n-1)] + B \exp[-(n-1)^2] \quad (3)$$

or the inverse cubic power of l_{max} , the highest angular momentum used in the basis set functions, by Schwartz,^{58,59} by Halkier et al.,⁶⁰ and by Helgaker et al.⁶¹ denoted as “S3”:

$$E(n) = E(\text{CBS}) + Al_{\text{max}}^{-3} \quad (4)$$

or the inverse quartic power of $l_{\text{max}} + 1/2$ by Kutzelnigg et al.⁶² and by Martin and co-worker,^{63,64} denoted as “S4”:

$$E(n) = E(\text{CBS}) + A(l_{\text{max}} + 1/2)^{-4} \quad (5)$$

The value of l_{max} is equal to the cardinal number n for main group elements, denoted as “TQ”, and $n + 1$ for 3d metal elements, denoted as “Q5” in this Article. Preliminary results show that using Q5 for transition metal atoms and transition metal-containing molecules, while using TQ for main group atoms, results in a bias of the main group atomic energies that are not consistent with molecular energies. It is proposed that l_{max} should be equal to either n (TQ) or $n + 1$ (Q5) in an individual ccCA-TM calculation. A compromise was also made to replace l_{max} by $(n + 1/2)$, and two more extrapolations can be defined as

$$E(n) = E(\text{CBS}) + A(n + 1/2)^{-3} \quad (6)$$

$$E(n) = E(\text{CBS}) + A(n + 1)^{-4} \quad (7)$$

These two additional extrapolations are denoted as “S3h” and “S4h”, respectively. An averaged value of the P and S3 extrapolations,⁴⁸ denoted as “PS3”, is also investigated. Different CBS extrapolations of MP2 energies are summarized in Table 1.

The correlation correction $\Delta E(\text{CC})$ is the energy difference between CCSD(T) and MP2 with the same cc-pVTZ-DK basis set.

$$\Delta E(\text{CC}) = E[\text{CCSD(T)/cc-pVTZ-DK}] - E[\text{MP2/cc-pVTZ-DK}] \quad (8)$$

In the main group ccCA algorithm, MP2 is used for the core–core and core–valence correlation corrections. However, our earlier study revealed that MP2 is not sufficient for recovering the core–core and core–valence correlation corrections for larger transition metal compounds.⁸ Significant improvements in accuracy were found when CCSD(T) is applied in place of MP2. The core–core and core–valence correlation corrections were found less dependent on basis sets than the level of theory.⁸

Table 1. Different Variants of the ccCA-TM Algorithm^a

	cc-CA-TM
geometry optimization	B3LYP/cc-pVTZ
ZPE	experimental values for atoms B3LYP/cc-pVTZ harmonic frequencies scaled by 0.989 for molecules
HF/CBS	HF/aug-cc-pVTZ-DK HF/aug-cc-pVQZ-DK $E(n) = E(\text{HF/CBS}) + A \exp(-1.63n)$
MP2/CBS	MP2/aug-cc-pVDZ-DK MP2/aug-cc-pVTZ-DK MP2/aug-cc-pVQZ-DK “P”: eq 3 ^b “S3”: eq 4 ^b “S4”: eq 5 ^b “PS3”: 1/2 (“P” + “S3”) ^b “S3h”: eq 6 “S4h”: eq 7
correlation corrections	CCSD(T)/cc-pVTZ-DK - MP2/cc-pVTZ-DK
core–valence corrections	CCSD(T,FC1)/aug-cc-pCVDZ – CCSD(T)/aug-cc-pCVDZ
spin–orbit corrections	experimental values for atoms when applicable FOCI Stuttgart ECP for molecules when applicable

^aBoth ROHF and UHF references can be considered for open-shell molecules. ^b $I_{\text{max}} = n$ for “TQ” or $(n + 1)$ for “Q5”.

To reduce the computational cost, the aug-cc-pCVDZ-DK basis set is used instead of aug-cc-pCVTZ-DK.

$$\Delta E(\text{CV}) = E[\text{CCSD(T, FC1)/aug-cc-pCVDZ-DK}] - E[\text{CCSD(T)/aug-cc-pCVDZ-DK}] \quad (9)$$

The notation “FC1” indicates that the inner shell closest to the valence shell is included as active, which means, in addition to valence electrons, 1s electrons are correlated for Li–Ne, 2s2p electrons correlated for Na–Ar, 3s3p electrons correlated for K–Zn including 3d transition metals, and 3s3p3d electrons correlated for Ga–Kr. The aug-cc-pCVDZ-DK basis sets are generated by adding the core/valence basis set functions to aug-cc-pVDZ-DK without further optimization. All ccCA-TM variants and their corresponding notations are detailed in Table 1.

The spin–orbit coupling corrections⁶⁵ were calculated for molecules when applicable and tractable. Spin–orbit interactions were approximately considered as the energy difference between the lowest L–S state and the state averaged, where the energies of each L–S state were obtained by diagonalizing the effective spin–orbit Hamiltonian on the basis of contracted CASSCF wave functions.

In this study, all CASSCF computations are performed with the cc-pVTZ-DK basis set, and T_1/D_1 diagnostics and spin contamination are extracted from CCSD/cc-pVTZ-DK calculations on the basis of HF or ROHF canonical orbitals. All computations were performed using MOLPRO 2006.1⁶⁶ except for UHF ccCA-TM energies, which were obtained in Gaussian 03.⁶⁷ In Gaussian 03 DKH calculations, the nuclei are simulated as point charges so that the scalar relativistic energies for closed-shell systems are equivalent to those computed in MOLPRO.⁶⁸

When the experimental enthalpies of formation from various sources are in disagreement, the experimental value with the least experimental uncertainty is usually selected for the molecules. Values from recent literature are adopted when the experimental uncertainties are comparable to earlier data. We note that occasionally experimental data reported with a large uncertainty are found in better agreement with theoretical prediction, for example, the standard enthalpy of CrO_3 as discussed in ref 8. No attempts were generally made to select the experimental data in better agreement with theoretical predictions. Decisions made on the adopted experimental value of specific cases (and the rare exceptions) are explicitly detailed below, and a full listing of all experimental values located in the literature is provided in Tables S3 and S4 of the Supporting Information.

RESULTS AND DISCUSSION

A. Effects of CBS Extrapolation Schemes. The Peterson extrapolation (eq 3) and its averaged PS3 extrapolation with S3 (eq 4) for correlation energies have been used previously in the CCSD(T) CBS^{69,70} and main group ccCA studies.⁴⁸ Although it is inconclusive that one extrapolation is generally superior to others for the CCSD(T) CBS limits, it is beneficial to assess the effectiveness of the possible schemes (Table 1). Consistent with our earlier observations,⁷¹ utilization of the ROHF reference wave function for open-shell molecules gives substantially better results than a UHF reference wave function by minimizing the effect of spin contamination. Only ROHF-ccCA-TM results are discussed below. For the ccCA-TM/11 set, the differences among different extrapolations are less than 0.2 kcal mol^{−1}, except for S3(Q5), which has a MAD of 4.72 kcal mol^{−1}, 0.37 kcal mol^{−1} greater than the ROHF-ccCA-TM-P MAD of 4.35 kcal mol^{−1} (Figure 1). For subsets of different experimental uncertainty ranges, the S3(Q5) MAD is 0.4–1.1 kcal mol^{−1} larger than the best CBS extrapolation scheme. The S4(TQ) and PS3(TQ) schemes remain close to ccCA-TM-P with a difference of less than 0.05 kcal mol^{−1} in MAD for all subsets as well as the overall set, and thus can be considered equivalent alternatives. As the size of set increases, the CBS extrapolations choice has less impact on the accuracy on average. Different patterns are found in mean signed deviation (MSD) of various extrapolation schemes. While the P, S4(TQ) variants have negative MSDs for all subsets, S3(TQ), PS3(TQ), S4h, S4(Q5), and PS3(Q5) show a change from positive MSD to negative MSD as the subset size increases, and S3(Q5) and S3h have positive MSDs for all subsets. Similar to the findings for CCSD(T) CBS energies,^{69,70} historically preferred extrapolations do not show statistically significant differences. In the following, only the ROHF-ccCA-TM results with the mixed Gaussian/inverse exponential form (“P”, eq 3) are discussed. “ROHF” is omitted unless specified otherwise.

B. 3d Transition Metal-Containing Species and Metal Dimers. The ccCA-TM algorithm has been applied to calculate the standard ΔH_f° s for the ccCA-TM/11all set of 225 transition metal species, about 4 times larger than the set in our previous study.⁸ Although numerous theoretical studies have been performed on some of the species in our test set, and the thermodynamic properties and electronic structure of their ground state have been well-established (for examples, see a comprehensive review of the electronic structure of diatomic 3d block molecules by Harrison⁷²), there are also quite a few species for which little information exists on the equilibrium geometry, spin multiplicity,

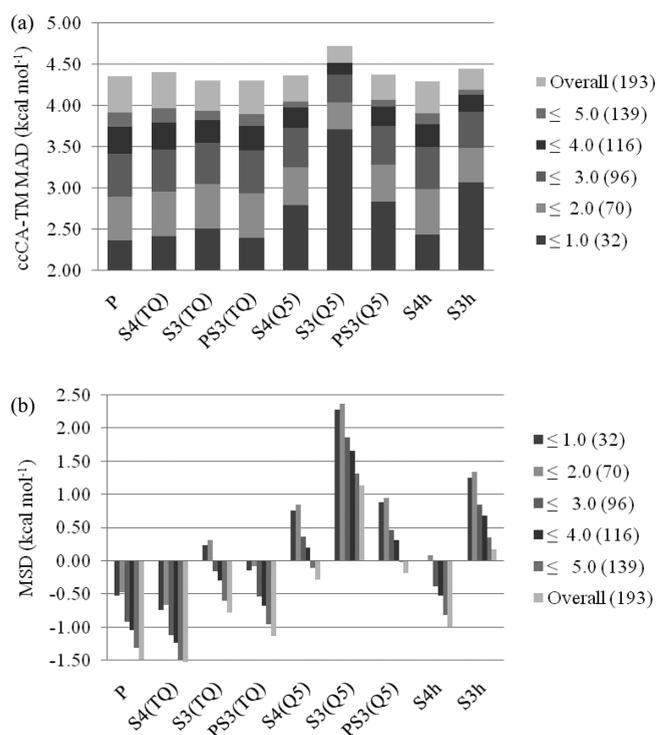


Figure 1. The mean ccCA-TM deviations in kcal mol⁻¹ from the experimental enthalpies of formation for subsets with different ranges of experimental uncertainties: (a) MADs; (b) MSDs. The numbers of quantities are given in parentheses.

and/or electronic configuration. This study may be useful in addressing knowledge gaps in the electronic structure for many small inorganic molecules, which can further guide experimental and theoretical research. The complete listings of ccCA-TM ground electronic states and experimental ground states (when known) are also given in Tables S3 and S4 of the Supporting Information. The deviations of the ccCA-TM predictions from experimental ΔH_f 's (calculated as experimental value minus theoretical value) are collected in Table S5. The overall performance of ROHF-ccCA-TM, by utilizing ROHF, RMP2,⁷³ and R/UCCSD(T)⁷⁴ methods, is better than the UHF counterpart, by utilizing UHF, UMP2, and UCCSD(T)⁷⁴ methods, for open-shell molecular and atomic energies.⁸ However, it has been found that for most molecules, the ΔH_f predictions by both methods agree well with each other, even though both may be in close agreement with or deviate significantly from experimental data (Table S5). Single reference methods such as CCSD(T) and MP2 suffer from the inaccurate or incorrect wave function description of the ground electronic state of molecular systems when the multireference character is prominent. As transition metal compounds are more likely to involve complicated bonding with quasidegenerate orbitals and to harbor a wealth of low-lying electronic states, intrinsic errors rising from the multireference character in the ground electronic state become more prevalent than molecules containing main group elements only. To assess the reliability of the single reference coupled cluster methods in this respect, the weights of leading configurations (C_0^2), T_1/D_1 diagnostics,^{42,43,75} and spin contamination ($\langle S^2 - S_z^2 - S_z \rangle$) are collected in Table 2 for challenging molecules. Given the complexity of the electronic structure of the transition metal containing molecules, in the following paragraphs,

the diagnostics are analyzed and used in determining whether large deviations (or outliers) of theoretical prediction with respect to experimental data originate from inappropriateness of single reference methods or large uncertainty of experiments. Even though the diagnostics should be interpreted qualitatively, stringent requirements have been recommended, especially for accurate study of main group species. However, the size of test set will be seriously restricted even if loose requirements of $T_1 < 0.05$, $D_1 < 0.10$, and $C_0^2 > 0.90$ are reinforced in screening the molecules. Thus, the diagnostics are rather used together with other information in determining possible outliers. The calculations of C_0^2 are restricted due to the exponentially increasing computational cost with increasing CASSCF active space size, and, as such, only molecules of up to three atoms and few tetratomics of high symmetry were considered. For larger sized molecules, only the T_1/D_1 diagnostics are discussed. Another restriction of the C_0^2 diagnostics is that excited configuration(s) including virtual orbitals may be important for the electronic ground-state wave function, for example, the 4p orbital of the transition metal atom. In the following paragraphs, the species in the ccCA-TM/11all set will be discussed metal by metal, followed by a separate description of metal dimers.

1. Sc. In our ccCA-TM/11all set, 16 scandium-containing compounds are included. The single reference ccCA-TM calculation for ScF₂ is expected to be reliable on the basis of the diagnostics by the C_0^2 , T_1 , and D_1 values of 0.975, 0.020, and 0.046, respectively, and t_1 and t_2 amplitudes of less than 0.05. The theoretical prediction (-158.2 kcal mol⁻¹) is within the Yangman value (-157.4 ± 7.0 kcal mol⁻¹) but slightly deviates from the experimental value (-163.7 ± 5.3 kcal mol⁻¹) obtained by Hildenbrand and Lau.⁷⁶ The ccCA-TM prediction (-297.1 kcal mol⁻¹) for ScF₃ agrees well with the value (-300.4 ± 3.6 kcal mol⁻¹) by Hildenbrand and Lau⁷⁶ but outside of the error bar of ref 1 (-302.9 ± 3.2 kcal mol⁻¹). In this study, the experimental data from ref 76 are adopted for both ScF₂ and ScF₃ for consistency.

The ΔH_f 's by Gingerich for TiN and VN were found to be 8–10 kcal mol⁻¹ lower than more recent experimental data.¹ This is somewhat consistent with our ccCA-TM prediction for ScN, which is 27.9 kcal mol⁻¹ higher than the Gingerich experimental ΔH_f . Single reference results are considered acceptable for ScN on the basis of the diagnostic requirements for appropriate utility of single reference methods for transition metal-containing molecules. Experimentally, ScB₂ has been mostly investigated in its solid form⁷⁷ and to our knowledge has not been characterized in the gas phase. We observe that a cyclic geometry with ²A₁ symmetry is more stable than a linear geometry of B–Sc–B. However, neither geometry gives a ΔH_f value as low as the experimental value.¹ Multireference character of ScB₂, as evidenced by the diagnostics, may undermine the reliability of MP2/CCSD-based methods. An equilibrium bent geometry was predicted for Sc₂O, resulting in a ccCA-TM ΔH_f of 14.6 kcal mol⁻¹, which is within the experimental value of -2.81 ± 18 kcal mol⁻¹ by Kordis and Gingerich.⁷⁸ The ccCA-TM ΔH_f of ScBr₃ is 17.8 kcal mol⁻¹ higher than the experimental value.⁷⁹ However, the reliability of the ccCA-TM value is supported by the small T_1 and D_1 diagnostics, and good agreement with experiment is found for the lighter analogues ScF₃ and ScCl₃, with deviations of -3.3 and $+4.4$ kcal mol⁻¹, respectively. The large discrepancy between experiment and theory raises question to the experimental ΔH_f value for ScBr₃.

Table 2. Listing of Possible Outliers with Diagnostics, ccCA-TM Predictions, and Experimental Data of Standard Enthalpy of Formation (in kcal mol⁻¹) for the ccCA-TM/11all Set of 3d Transition Metal-Containing Molecules^a

molecule	C_0^2	T_1	D_1	$t_{1\max}^b$	$t_{2\max}^b$	$\langle S^2 - S_z^2 - S_z \rangle$	ccCA-TM	exp. ^c
ScN	0.895	0.042	0.073		-0.07		118.9	91.0 ± 20
ScB ₂	0.772	0.073	0.186	-0.26	-0.10	0.038	201.3	150.6 ± 21
ScBr ₃		0.016	0.036				-127.1	-109.3 ± 2.6
Sc ₂	0.500	0.119	0.186	0.23	-0.12	0.036	170.8	154.2 ± 5.3
Sc ₂ O		0.026	0.045		-0.07		14.6	-4.5 ± 11
TiB	0.877	0.158	0.283	-0.29	-0.10	0.007	209.3	181.3 ± 15
TiC	0.863	0.045	0.082	-0.06	-0.06	0.005	198.4	169.8
TiF ₂	0.976	0.022	0.053	-0.06		0.004	-133.0	-164.5 ± 10
TiF ₃		0.024	0.052	-0.06		0.002	-265.6	-284 ± 10
TiBr ₂	0.981	0.024	0.060	-0.07		0.005	-23.0	-42.8 ± 5.0
V ₂	0.706	0.097	0.262	0.37	-0.15	0.010	210.3	181.2 ± 4.0
VC	0.840	0.064	0.115	-0.07		0.002	209.7	181.6 ± 15
VF	0.984	0.053	0.170	0.18		0.005	14.4	0.7 ± 15
VBr	0.986	0.061	0.196	0.21		0.006	67.2	46.2 ± 10
VBr ₂	0.984	0.027	0.061	-0.08	0.12	0.011	-7.0	-36.5
VBr ₃		0.040	0.109	0.13	0.10	0.018	-45.0	-61.6
(CrBr ₂) ₂		0.032	0.099	0.13	0.44	0.026	-61.0	-79.8 ± 8.0
Cr(CO) ₅		0.032	0.102	-0.08	-0.08		-168.6	-153.9 ± 3.1
Mn ₂	0.900	0.072	0.242	0.60	-0.08	0.906	154.6	127.5 ± 6.1
Mn(CO) ₅ H		0.041	0.166	0.10	-0.07		-186.8	-176.8 ± 2.2
Mn(CO) ₅		0.047	0.194	0.20	-0.08	0.003	-168.3	-179.4 ± 1.2
MnF ₄		0.037	0.117	-0.17	-0.06	0.030	-215.2	-231.0 ± 17
Fe ₂	0.614	0.045	0.105	0.15	0.23	0.056	218.8	171.0 ± 2.1
Fe(C ₅ H ₅)		0.022	0.064	-0.09	0.05	0.006	106.3	88.0 ± 3.8
Co ₂	0.515	0.037	0.083	0.10	0.13	0.024	192.3	164.2 ± 6.3
(CoBr ₂) ₂		0.040	0.143	-0.15	0.22	0.011	-14.3	-37.5 ± 4.0
(CrCl ₂) ₂		0.047	0.225	-0.29	-0.36	0.009	-54.9	-76.8 ± 4.0
Co(SiF ₃)(CO) ₄		0.046	0.280	0.18			-433.7	-456.0
CuCl ₂	0.993	0.032	0.143	-0.20		0.004	-1.7	-9.0
CuOH	0.973	0.044	0.173	-0.13			13.4	28.0 ± 4.0
(ZnBr ₂) ₂		0.014	0.057				-108.0	-120.3 ± 3.5
(ZnCl ₂) ₂		0.013	0.053				-147.5	-168.0

^aThe values of C_0^2 are obtained from CASCI based on CASSCF natural orbitals. All other data are extracted from the CCSD(T)/cc-pVTZ-DK calculations. ^bThe maximal amplitude is not given when its absolute value is less than 0.05. ^cSee the Supporting Information for the source of experimental data.

The species ScN, ScB₂, Sc₂O, and ScBr₃ are excluded in the pruned ccCA-TM/11 set. All outlier molecules (containing elements Sc–Zn) with diagnostics, ccCA-TM predictions, and experimental data are listed in Table 2.

The ccCA-TM predicted ΔH_f is 13.1 kcal mol⁻¹ lower than the experimental data (-369.0 ± 8.0 kcal mol⁻¹) for the dimeric (ScCl₃)₂. This molecule does not show multireference character ($T_1 = 0.013$ and $D_1 = 0.033$), which suggests that this system requires further study. A cyclic geometry was located for the ground state (²A₁) of ScC₂ and ScC₄,^{80,81} and the ccCA-TM deviations in ΔH_f are -2.7 and $+0.3$ kcal mol⁻¹ as compared to experimental values¹ of 152.7 ± 4.0 and 196.2 ± 5.0 kcal mol⁻¹, respectively. The ccCA-TM method reproduces the experimental ΔH_f (20.0 ± 1.4 kcal mol⁻¹) of Sc(C₅H₅)₃ (the largest molecule in the ccCA-TM/11all set) with a deviation of $+0.3$ kcal mol⁻¹. By excluding the four possible outliers (ScN, ScB₂, Sc₂O, and ScBr₃), ccCA-TM yields a MAD of 4.16 kcal mol⁻¹ for 12 scandium-containing molecules, which is less than the average value of their uncertainties (± 3.8 kcal mol⁻¹).

2. Ti. The subset of 31 titanium-containing molecules provides a versatile and challenging group of systems to examine the effectiveness of the ccCA-TM. It could be fortuitous that excellent agreement was achieved for TiSe (ccCA-TM ΔH_f , 77.7 kcal mol⁻¹; experimental ΔH_f ,¹ 76.8 kcal mol⁻¹) with an experimental uncertainty of 10 kcal mol⁻¹. The ccCA-TM ΔH_f value for TiSe should be treated with caution because TiSe salient multireference character ($C_0^2 = 0.863$, $T_1 = 0.088$, and $D_1 = 0.199$). Large deviations of ccCA-TM predictions were found for species (TiB, TiC, TiF₂, and TiF₃) with either large experimental uncertainties (≥ 10 kcal mol⁻¹) or no error bars reported. In contrast to TiF₂ and TiF₃, TiB and TiC are found to have significant multireference character. Recently, Hildenbrand⁸² revised the standard ΔH_f 's for TiCl_x ($x = 1, 2,$ and 3) on the basis of updated information on the electronic structure, and the newly adopted values (40.9 ± 2.0 , -49.0 ± 2.0 , and -121.5 ± 2.0 kcal mol⁻¹) are substantially higher than those (36.9 ± 10.0 , -56.7 ± 3.0 , and -128.9 ± 1.5 kcal mol⁻¹) from the JANAF table.³ Our ccCA-TM predictions are in much better agreement

with the experiments of Hildenbrand. Speculation that the experimental data for TiF_2 and TiF_3 are questionable is supported by good agreement between ccCA-TM predictions and experimental values for other titanium halides (with the exception of TiBr_2) as well as agreement with large basis set CCSD(T)-DK results.⁷ The ccCA-TM prediction for TiF is $5.7 \text{ kcal mol}^{-1}$, near the outer range of the experimental uncertainty ($-4.0 \pm 8.0 \text{ kcal mol}^{-1}$).¹ By excluding the suspected statistical outliers, that is, TiB , TiC , TiF_2 , TiF_3 , and TiBr_2 , ccCA-TM achieves a MAD of $5.27 \text{ kcal mol}^{-1}$ for 27 Ti-containing species (including Ti_2), as compared to the average experimental uncertainty of $\pm 3.6 \text{ kcal mol}^{-1}$.

Our predictions of electronic ground states are in agreement with previously theoretical and experimental studies for all titanium-containing species except TiC_2 . In both the ccCA-TM geometry optimization step (B3LYP/cc-pVTZ) and previous theoretical studies (B3LYP, BP86, CASSCF, and MRCI),^{83,84} the $^3\text{B}_1$ electronic state of cyclic geometry was predicted to be the lowest in energy for TiC_2 . However, the $^3\text{B}_2$ electronic state is $1.0 \text{ kcal mol}^{-1}$ lower than the $^3\text{B}_1$ state in energy using ccCA-TM, which is consistent with the previous observation that high-level single reference methods predict a lower energy for the $^3\text{B}_2$ state.⁸³ The ccCA-TM prediction ($187.5 \text{ kcal mol}^{-1}$) of the $^3\text{B}_2$ state deviates significantly from the experimental value ($175.4 \pm 3.0 \text{ kcal mol}^{-1}$) for TiC_2 . However, a relatively better agreement was found for TiC_4 (ccCA-TM ΔH_f , $224.1 \text{ kcal mol}^{-1}$; experimental ΔH_f , $217.9 \pm 5.0 \text{ kcal mol}^{-1}$). The ccCA-TM ΔH_f for TiO_2 is $-67.9 \text{ kcal mol}^{-1}$, which agrees with a CCSD(T)-based prediction ($-67.9 \text{ kcal mol}^{-1}$) by Li et al.³⁸ The ccCA-TM ΔH_f for TiOCl_2 , $-143.2 \text{ kcal mol}^{-1}$, agrees well with a recommended value of $-142.9 \pm 4.8 \text{ kcal mol}^{-1}$ by West et al.⁸⁵ and $-141.8 \text{ kcal mol}^{-1}$ by Wang et al.³⁹ based on CCSD(T) composite methods. However, all of the converged theoretical predictions are substantially lower than the experimental value³ ($-130.4 \text{ kcal mol}^{-1}$) by a difference of more than 10 kcal mol^{-1} . The ccCA-TM ΔH_f for bent TiOF is found to be $10.7 \text{ kcal mol}^{-1}$ higher than the experimental value of $-103.5 \text{ kcal mol}^{-1}$ (no error bars). The ccCA-TM prediction of the ΔH_f of $\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3$ ($-138.2 \text{ kcal mol}^{-1}$) is substantially lower than the NIST webbook experimental value² ($-124.5 \pm 1.6 \text{ kcal mol}^{-1}$). However, the coupled cluster diagnostics ($T_1 = 0.020$ and $D_1 = 0.070$) suggest that $\text{Ti}(\text{C}_5\text{H}_5)\text{Cl}_3$ can be accurately described by single reference methods.

3. V. For the vanadium subset, 23 species are considered. For VO and VO_2 , the experimental values (31.8 ± 2.0 and $-41.6 \pm 3.3 \text{ kcal mol}^{-1}$) by Balducci et al.⁸⁶ are adopted. For VCl_x ($x = 1, 2, 3,$ and 4), the experimental ΔH_f values (49.7 ± 2.0 , -34.8 ± 2.0 , -85.6 ± 2.0 , $-126.1 \pm 0.6 \text{ kcal mol}^{-1}$, respectively) are from a very recent study of Hildenbrand et al.⁸⁷ The adopted values for VCl and VCl_2 are in large discrepancy with the previous experimental data¹ (37.9 ± 2.0 and $-51.6 \pm 3.6 \text{ kcal mol}^{-1}$), and the validity of those values has been discussed in ref 87. Five possible outliers (VC, VF, VBr, VBr_2 , and VBr_3) are determined, which are found with either a reported uncertainty $\geq 10.0 \text{ kcal mol}^{-1}$ or no uncertainty reported. While the diagnostics suggest that single reference ccCA-TM predictions for VC, VF, and VBr should be treated with caution, VBr_2 and VBr_3 are more likely single reference systems for which the ccCA-TM results are reliable. The MAD of ccCA-TM is $4.52 \text{ kcal mol}^{-1}$ for 18 vanadium-containing molecules, as compared to $2.6 \text{ kcal mol}^{-1}$, the average value of 14 reported uncertainties.

Similar to TiC_2 (or ScC_2) and TiC_4 (or ScC_4), a cyclic geometry and a fan-like geometry were used for VC_2 and VC_4 , respectively. The lowest electronic states of VC_2 and VC_4 are determined as quartet states in B_1 symmetry, in accordance with a previous theoretical study by Redondo et al.⁸⁸ Among the isomers of tetranuclear vanadium oxide V_4O_{10} , a cage-like structure in the T_d symmetry has been found to be the lowest in energy.⁸⁹ On the basis of this geometry, the ccCA-TM ΔH_f for V_4O_{10} is within the error bars of the experimental value of $-675 \pm 5.0 \text{ kcal mol}^{-1}$.

4. Cr. The chromium subset is the largest one among the metals, including 35 molecules with a significant contribution of experimental ΔH_f data from the systematic and accurate study of chromium halides and oxohalides by Ebbinghaus.^{90,91} The experimental ΔH_f for CrH ($101.7 \pm 1.6 \text{ kcal mol}^{-1}$) by Chen et al.⁹² is quite different from an earlier value¹ of $80.2 \pm 10 \text{ kcal mol}^{-1}$. In comparison to the ΔH_f 's determined by Ebbinghaus,⁹⁰ the ccCA-TM predictions were found to be in good agreement for chromium oxides CrO and CrO_2 , but a large deviation was found for CrO_3 . As discussed earlier, the ccCA-TM calculations for CrO_3 are consistent with enthalpies computed with a CBS CCSD(T)-DK-based composite method,^{7,93} supporting that ccCA-TM can be used as a good approximation to CBS CCSD(T)-DK. However, the possible multireference character in CrO_3 as shown by the diagnostics ($T_1 = 0.051$ and $D_1 = 0.190$) may undermine the reliability of all MP2/CCSD(T)-based methods. In a mass spectroscopy study of metal monochlorides and dichlorides, Hildenbrand⁹⁴ obtained the experimental ΔH_f values for CrCl and CrCl_2 (33.7 ± 1.6 and $-26.3 \pm 1.0 \text{ kcal mol}^{-1}$) close to values (31.1 ± 0.7 and $-28.1 \pm 0.4 \text{ kcal mol}^{-1}$) obtained by Ebbinghaus.⁹¹ The experimental ΔH_f for CrF_3 by Ebbinghaus ($-199.8 \pm 3.4 \text{ kcal mol}^{-1}$) is $15.8 \text{ kcal mol}^{-1}$ higher than the value in the Yungman compendia¹ ($-216.6 \pm 3.2 \text{ kcal mol}^{-1}$). The ccCA-TM prediction of $-196.3 \text{ kcal mol}^{-1}$ agrees with the value by Ebbinghaus, and the validity of single reference calculations is, to some extent, supported by the diagnostics of $T_1 = 0.030$ and $D_1 = 0.087$. As discussed in our earlier study,⁸ the adopted experimental ΔH_f values for $\text{Cr}(\text{CO})_6$ on the NIST webbook² were an average of nine values ($-218 \pm 20 \text{ kcal mol}^{-1}$), and the values for $\text{Cr}(\text{CO})_x$ ($x = 3-5$) were derived directly [for $\text{Cr}(\text{CO})_3$ and $\text{Cr}(\text{CO})_5$] or indirectly [for $\text{Cr}(\text{CO})_4$] from one experimental ΔH_f value of $217.1 \pm 0.62 \text{ kcal mol}^{-1}$ for $\text{Cr}(\text{CO})_6$. The ccCA-TM prediction for $\text{Cr}(\text{CO})_6$ ($-237.8 \text{ kcal mol}^{-1}$) is in close agreement with the lowest experimental value ($-240.4 \pm 1.1 \text{ kcal mol}^{-1}$) posted on the NIST webbook and $-240.0 \pm 1.1 \text{ kcal mol}^{-1}$.¹ The ccCA-TM predictions for $\text{Cr}(\text{CO})_3$ ($-39.0 \text{ kcal mol}^{-1}$) and $\text{Cr}(\text{CO})_4$ ($-103.4 \text{ kcal mol}^{-1}$) are also in good agreement with the ΔH_f values (-44.0 ± 10.0 and $-102.0 \pm 6.0 \text{ kcal mol}^{-1}$, respectively) from the NIST webbook. However, a large deviation was found for $\text{Cr}(\text{CO})_5$, which is thus considered a statistical outlier.

The electronic ground state of CrGe is determined as a septet $^7\Pi$ state, in contrast to the quintet $^5\Pi$ state predicted by Hou et al.⁹⁵ using both CASSCF/CASPT2 and DFT/B3LYP method. Similar to other 3d transition metal-dicarbides, the ground electronic state of CrC_2 was determined to be $^5\text{A}_1$ in a cyclic geometry by ccCA-TM, in agreement with the BPW91/6-311+G* study of Zhai et al.⁹⁶ The electronic ground state of CrC_2 is highly multireference with $C_0^2 = 0.613$, $T_1 = 0.076$, and $D_1 = 0.250$. In contrast to the linear geometry applied to the dihalides of Sc, Ti, and V, the equilibrium geometries of chromium

dihalides (CrF_2 , CrCl_2 , and CrBr_2) are all bent. Our calculations showed that triplet states ($^3\text{A}_1$) are the lowest in energy for CrCl_4 and CrBr_4 in the T_d symmetry. Because no previous theoretical or other experimental studies were found for the dimeric systems $(\text{CrCl}_2)_2$ and $(\text{CrBr}_2)_2$, our assignment of $^9\text{B}_1$ as the ground state should be considered as tentative. The ccCA-TM ΔH_f values of $(\text{CrCl}_2)_2$ ($-105.3 \text{ kcal mol}^{-1}$) and $(\text{CrBr}_2)_2$ ($-61.0 \text{ kcal mol}^{-1}$) are much higher than the experimental values of -116.9 ± 8.0 and $-79.8 \pm 8.0 \text{ kcal mol}^{-1}$, respectively,¹ and the heavier $(\text{CrBr}_2)_2$ with a larger deviation is not considered in the statistical analysis. For the trimeric $(\text{CrO}_3)_3$, our ccCA-TM ΔH_f value ($-382.2 \text{ kcal mol}^{-1}$) based on a C_{3v} symmetry⁹⁷ is within the experimental value ($-389 \pm 10.0 \text{ kcal mol}^{-1}$). It could be fortuitous that the ccCA-TM prediction is in excellent agreement with the experimental ΔH_f of the sizable cluster $(\text{CrO}_3)_3$, which has a large uncertainty of $\pm 10 \text{ kcal mol}^{-1}$. In comparison, the theoretical value from the study of Li et al.³⁸ calculated by a composite approach based on CCSD(T) in combination with relativistic effective core potential basis sets for Cr (and correlation consistent basis sets for O) gave a positive deviation of $32.2 \text{ kcal mol}^{-1}$ as compared to the experimental value. For the monomer CrO_3 , Li et al. obtained a ΔH_f value of $-62.3 \text{ kcal mol}^{-1}$, which is pertinent to their evaluation of ΔH_f , more precisely $\Delta H_{f,0\text{K}}$ of $(\text{CrO}_3)_3$ (see eq 11 in ref 38), but is $2.0 \text{ kcal mol}^{-1}$ less negative than $-64.3 \text{ kcal mol}^{-1}$ obtained in our laboratory using the all electron CBS CCSD(T)-DK composite method.⁷ Assuming the experimental data are accurate, the propagation of error of the monomeric energy amounts to an overestimation of 6 kcal mol^{-1} , which does not justify the large deviation observed for the trimer. By excluding the possible outliers $\text{Cr}(\text{CO})_5$ and $(\text{CrBr}_2)_2$, the ccCA-TM MAD is $4.77 \text{ kcal mol}^{-1}$ for the set of 35 species (including metal dimers Cr_2 and CrCu) with an average experimental uncertainty of $\pm 3.8 \text{ kcal mol}^{-1}$.

5. *Mn*. In the manganese subset, 20 molecules are collected. The experimental ΔH_f value for MnCl_2 ($-62.6 \pm 1.0 \text{ kcal mol}^{-1}$) from a systematic study of monochlorides and dichlorides of Mn, along with other metals Cr, Fe, Co, and Ni, by Hildenbrand⁹⁴ is consistent with the value in ref 1 ($-63.0 \pm 0.5 \text{ kcal mol}^{-1}$). For MnCl , Hildenbrand reported $\Delta H_f = 15.8 \pm 1.6 \text{ kcal mol}^{-1}$, while the Yungman book¹ listed a value of $11.3 \text{ kcal mol}^{-1}$ without error bars. To be consistent, the data by Hildenbrand for both chlorides were used. The experimental ΔH_f value¹ for $\text{Mn}(\text{CO})_5$ used in this study is in agreement with two of the three experimental values posted on the NIST webbook.² For $\text{Mn}(\text{CO})_3(\text{C}_5\text{H}_5)$, the value with the smallest reported uncertainty ($-102.0 \pm 0.7 \text{ kcal mol}^{-1}$) is adopted. To our knowledge, no previous study on the electronic structure of MnF_4 by post-HF ab initio methods has been reported. In this study, the calculations were based on a $^4\text{A}_2$ state in the D_{2d} symmetry, in agreement with the ground state located by Kadasov et al. using HF,⁹⁸ but in contrast to the T_d symmetry found for other metal-tetrahalides or a ^4B ground state in C_2 symmetry by Pradhan et al.⁹⁹ using B3LYP with the 6-311+G(3df) basis set. The obtained ccCA-TM ΔH_f value is within the experimental error bars. However, MnF_4 is regarded as a statistical outlier due to its large experimental uncertainty. Like the analogous dimeric chromium halides, $(\text{MnCl}_2)_2$ and $(\text{MnBr}_2)_2$ may have complicated electronic structure that has not been well studied. The ccCA-TM calculations for $(\text{MnCl}_2)_2$ and $(\text{MnBr}_2)_2$ are based on the tentatively assigned $^{11}\text{B}_2$ ground states by B3LYP/cc-pVTZ. The $^{11}\text{B}_2$ ground states for $(\text{MnCl}_2)_2$ and $(\text{MnBr}_2)_2$ were found

to be single reference with $T_1 < 0.02$ and $D_1 < 0.05$. The ccCA-TM ΔH_f 's for three Mn-containing carbonyls, $\text{Mn}(\text{CO})_5\text{Cl}$, $\text{Mn}(\text{CO})_5\text{Br}$, and $\text{Mn}(\text{CO})_3(\text{C}_5\text{H}_5)$, are in close agreement with experimental data (-219.5 ± 3.1 , -210.9 ± 2.2 , and $-102.0 \pm 0.7 \text{ kcal mol}^{-1}$) from the NIST webbook.² Intriguingly, the ccCA-TM ΔH_f for $\text{Mn}(\text{CO})_5\text{H}$ is 10 kcal mol^{-1} lower, while for $\text{Mn}(\text{CO})_5$, the ccCA-TM prediction is about 10 kcal mol^{-1} higher when compared to respective experimental data. There is essentially no spin contamination for the doublet state of $\text{Mn}(\text{CO})_5$, and its T_1/D_1 diagnostics are similar to those of closed-shell $\text{Mn}(\text{CO})_5\text{H}$. Because of the significant magnitude and opposite sign of the deviations for the structurally alike $\text{Mn}(\text{CO})_5\text{H}$ and $\text{Mn}(\text{CO})_5$, both are not considered in the ccCA-TM/11 pruned set. The ccCA-TM MAD is $4.85 \text{ kcal mol}^{-1}$ for 18 species with an average experimental uncertainty of $\pm 3.5 \text{ kcal mol}^{-1}$.

6. *Fe*. The iron subset includes 26 species, mostly iron halides and carbonyls. To be consistent with other dihalides, the experimental ΔH_f value ($-32.8 \pm 2.0 \text{ kcal mol}^{-1}$) by Hildenbrand⁹⁴ is used for FeCl_2 , which happens to reconcile the experimental data from the Yungman book ($-31.7 \pm 0.2 \text{ kcal mol}^{-1}$) and the NIST/JANAF table ($-33.7 \pm 0.5 \text{ kcal mol}^{-1}$). The experimental ΔH_f values for FeF_2 and FeF_3 from ref 1 (-82.4 and $-178.2 \text{ kcal mol}^{-1}$) are substantially higher than the JANAF table data (-93.1 ± 3.4 and $-196.2 \pm 5.0 \text{ kcal mol}^{-1}$), respectively. The ccCA-TM enthalpies of formation are found to be significantly lower for FeF_2 ($-105.3 \text{ kcal mol}^{-1}$) as compared to both experimental values. Because the ccCA-TM predicted values are in excellent agreement with experimental data for heavier analogues FeCl_2 and FeBr_2 , further theoretical/experimental study of FeF_2 seems necessary to resolve the discrepancy. In addition, the T_1 and D_1 values (0.026 and 0.052, respectively) for FeF_2 also show that the ground state can be well described by single reference methods. In contrast, the ccCA-TM predictions are found significantly higher for FeF_3 ($-170.3 \text{ kcal mol}^{-1}$) as compared to experimental data, even though the T_1 and D_1 values (0.032 and 0.079, respectively) indicate moderate multi-reference character in the electronic ground state of FeF_3 . Tentatively, the experimental value from ref 1 was adopted for FeF_3 , even though the uncertainty is not given. All monomeric chlorides and bromides were found in good to excellent agreement with experiments except for FeBr that has a large experimental uncertainty of 20 kcal mol^{-1} . Essentially the same experimental value for $\text{Fe}(\text{OH})_2$ is given from the JANAF table ($-79.0 \pm 0.5 \text{ kcal mol}^{-1}$) and the Yungman compendia ($-79.5 \pm 3.0 \text{ kcal mol}^{-1}$). Even though the diagnostics ($T_1 = 0.028$ and $D_1 = 0.067$) show moderate multi-reference character for $\text{Fe}(\text{OH})_2$, the ccCA-TM predicted ΔH_f value is $9.3 \text{ kcal mol}^{-1}$ higher than the JANAF experimental value, casting doubts on the reliability of the experimental value.

Surprisingly, ccCA-TM reproduces the experimental ΔH_f for the dimeric halides, $(\text{FeCl}_2)_2$, $(\text{FeF}_3)_2$, and $(\text{FeCl}_3)_2$, with excellent accuracy, while a positive error of $6.6 \text{ kcal mol}^{-1}$ is found for $(\text{FeBr}_2)_2$ as compared to the experimental value ($-60.5 \pm 1.9 \text{ kcal mol}^{-1}$). Equilibrium geometries of all of these dimeric halides were optimized in the D_{2h} symmetry group as determined experimentally.³ The $^9\text{B}_2$ state was determined for $(\text{FeCl}_2)_2$ and $(\text{FeBr}_2)_2$ while $(\text{FeF}_3)_2$ and $(\text{FeCl}_3)_2$ had a $^{11}\text{B}_{3u}$ ground state. Discussion on the iron carbonyls, $\text{Fe}(\text{C}_5\text{H}_5)_2$, and $\text{Fe}(\text{C}_5\text{H}_5)$, can be found in our earlier study,⁸ and $\text{Fe}(\text{C}_5\text{H}_5)$ is treated as an outlier. The ccCA-TM MAD of the iron subset is $4.53 \text{ kcal mol}^{-1}$ for 25 species excluding $\text{Fe}(\text{C}_5\text{H}_5)$,

while the average value of 21 reported experimental uncertainties is ± 3.3 kcal mol⁻¹.

7. *Co.* For the cobalt subset, 16 species were considered. The experimental ΔH_f for CoH (106.6 ± 3.2 kcal mol⁻¹) was calculated on the basis of the dissociation energy (46.6 ± 3.2 kcal mol⁻¹) by Fisher and Armentrout.¹⁰⁰ Similar to mono- and dichlorides of Mn and Fe, the experimental ΔH_f values for CoCl and CoCl₂ were taken from the study of Hildenbrand.⁹⁴ The ΔH_f value¹ for (CoCl₂)₂ (-76.8 ± 4.0 kcal mol⁻¹) used in this study agrees with the JANAF value (-83.8 ± 7.0 kcal mol⁻¹). The NIST webbook ΔH_f value² for Co(CO)₄ (-134.3 ± 1.8 kcal mol⁻¹) reliant on a ΔH_f value for Co₂(CO)₈ is used.

In agreement with the study of metal monosilicides by Wu and Su,¹⁰¹ CoSi and its heavier analogue CoGe were found to have ²Δ ground states. The ccCA-TM predictions of ΔH_f values for these two compounds, 149.3 and 139.6 kcal mol⁻¹, are within the experimental error bars, 145.4 ± 5.0 and 136.4 ± 5.0 kcal mol⁻¹, respectively. Diagnostics indicates that both molecules are of significant multireference character with, for example, $C_0^2 = 0.611$ and 0.504 for CoSi and CoGe, respectively. To our knowledge, no previous study has been done on the electronic structure of (CoCl₂)₂ and (CoBr₂)₂. The electronic ground states of (CoCl₂)₂ and (CoBr₂)₂ are tentatively determined here as ⁷B_{3u} in the D_{2h} symmetry and ⁷A₁ in the C_{2v} symmetry by B3LYP/cc-pVTZ. However, the ccCA-TM predicted ΔH_f values based on the located ground state are much higher than the respective experimental data. Given the complexity of the electronic structure of (CoCl₂)₂ and (CoBr₂)₂, more advanced methods may be needed to characterize their electronic structure. In this study, (CoCl₂)₂ and (CoBr₂)₂ are not considered in the ccCA-TM/11 subset. A large discrepancy in ΔH_f was found for Co(SiF₃)(CO)₄ between the ccCA-TM prediction and the experimental data. The insurmountable obstacles in accurately determining thermochemistry for large organometallic compounds have been emphasized by Simões.¹⁰² Without a proper assessment of the experimental value, Co(SiF₃)(CO)₄ is tentatively considered as a statistical outlier. Finally, the ccCA-TM MAD for 14 cobalt species including CoCu is 4.15 kcal mol⁻¹, while the average value of 12 reported experimental uncertainties is ± 2.9 kcal mol⁻¹.

8. *Ni.* The nickel subset includes 17 species. The experimental ΔH_f value of NiH was calculated on the basis of the dissociation energy D_0 (59.5 ± 3.7 kcal mol⁻¹) by Fisher and Armentrout.¹⁰⁰ The experimentally determined value, 94.4 ± 3.7 kcal mol⁻¹, is substantially higher than the value in ref 1 of 85.7 ± 2.6 kcal mol⁻¹, which is reliant on a dissociation energy D_0 of 68.0 ± 2.5 kcal mol⁻¹. The ccCA-TM ΔH_f value of 91.4 kcal mol⁻¹, or D_0 of 62.5 kcal mol⁻¹, is between the conflicting experimental data, and in agreement with a dissociation energy of about 64 kcal mol⁻¹ obtained with CASPT2.¹⁰³ The experimental ΔH_f value of Ni(CO)₃ listed in the NIST webbook² (-93.0 ± 2.0 kcal mol⁻¹) is higher than the value (-94.5 ± 1.1 kcal mol⁻¹) reported by Sunderlin et al.¹⁰⁴ Overall, there is no outrageous outlier in the nickel subset, and all ccCA-TM absolute deviations are less than 10 kcal mol⁻¹. The theoretical ccCA-TM ΔH_f 's for NiSi¹⁰¹ and NiGe were found to be in excellent agreement with experimental data, despite strong multireference character present in the wave function ($C_0^2 = 0.790$, $T_1 = 0.082$, and $D_1 = 0.208$ for NiSi and $C_0^2 = 0.746$, $T_1 = 0.092$, and $D_1 = 0.230$ for NiGe). The ccCA-TM MAD of the nickel subset is 4.38 kcal mol⁻¹ for 19 species including metal dimers NiCu and Ni₂, while the average value of 18 reported experimental uncertainties is ± 3.2 kcal mol⁻¹.

9. *Cu.* The copper subset contains 13 species. As the 3d-shell is fully filled in copper atom and may have less impact on the bonding of copper-containing molecules than early and mid-transition metals, much smaller deviations of ccCA-TM are found as compared to experimental data. One noticeable exception is CuOH, for which the ccCA-TM ΔH_f is 14.6 kcal mol⁻¹ lower than experimental data.¹ It is unlikely that the deviation is caused by incorrect assignment of the ground-state electron configuration because such error will result in overestimation in theoretical prediction of ΔH_f . However, the large D_1 value may suggest that the ionic CuOH exhibits multireference features, preventing accurate predictions by single reference methods. The experimental ΔH_f of CuCl₂ was derived from a crude dissociation energy by Wang et al.,¹⁰⁵ and thus it is not surprising to find a large discrepancy as compared to the ccCA-TM prediction. Consequently, CuOH and CuCl₂ are possible statistical outliers. For the copper subset including metal dimers, CuCr, CuCo, CuNi, and Cu₂, ccCA-TM achieves a MAD of 2.79 kcal mol⁻¹, which is significantly smaller than the averaged experimental uncertainty of ± 4.4 kcal mol⁻¹.

10. *Zn.* For the zinc subset, 16 species including the weakly bonded Zn₂ were considered. Like copper, zinc atom has a fully filled 3d-shell, and thus its properties are similar to alkaline metals. Szentpály¹⁰⁶ recently revisited the experimental ΔH_f 's for the zinc monochalcogenides, ZnO (55.2 ± 1.0 kcal mol⁻¹), ZnS (62.9 ± 1.0 kcal mol⁻¹), and ZnSe (60.0 ± 1.4 kcal mol⁻¹), and the updated values are found in excellent agreement with our ccCA-TM prediction for ZnS (63.8 kcal mol⁻¹) and ZnSe (59.5 kcal mol⁻¹). For ZnO, however, the ccCA-TM prediction compares better with the experimental value from ref 1 (52.8 ± 0.9 kcal mol⁻¹). Large deviations were found for the dimeric halides (ZnCl₂)₂ and (ZnBr₂)₂, where coupled cluster diagnostics suggest they can be well described by single reference methods. As a result, they are considered as outliers for the statistical analysis of ccCA-TM/11. The ccCA-TM achieves a MAD of 2.19 kcal mol⁻¹ for 14 species, comparable to the averaged experimental uncertainty of ± 2.1 kcal mol⁻¹.

11. *Metal Dimers.* The homonuclear 3d transition metal dimers have been systematically studied by both theoretical methods (see refs 11, 107, 108 for DFT studies) and experimental approaches.^{109–111} The electronic structure of many homonuclear 3d transition metal dimers elaborated in many previous studies is challenging even for multireference methods (see recent examples for Cr₂¹¹² and Mn₂¹¹³ and the experimental determination of double minima on the ground-state potential energy curves of Cr₂¹¹⁴). In this study, the ground electron configurations located for metal dimers by Gutsev and Bauschlicher¹¹⁵ were adopted (see Table S4 in the Supporting Information for details). The homonuclear 3d metal dimers exhibit strong multireference character (except for Cu₂ and Zn₂) and serve as a stringent test for the single reference ccCA-TM method. The ccCA-TM absolute deviations of ΔH_f 's from experimental data are larger than 10 kcal mol⁻¹ for all of the multireference dimers but Ti₂ (a ccCA-TM ΔH_f of 188.3 kcal mol⁻¹ versus an experimental value of 195.0 ± 4.5 kcal mol⁻¹). Five dimers, Sc₂, V₂, Mn₂, Fe₂, and Co₂, have absolute deviations larger than 15 kcal mol⁻¹ and are excluded from the ccCA-TM/11 subset. Additionally, three heteronuclear dimers, CuCr, CuCo, and CuNi, were considered. The ccCA-TM predicted ΔH_f 's for CrCu (137.7 kcal mol⁻¹) and NiCu (135.9 kcal mol⁻¹) are in agreement with experimental data (138.1 ± 6.0 and 133.4 ± 5.0 kcal mol⁻¹), respectively. However, for CoCu,

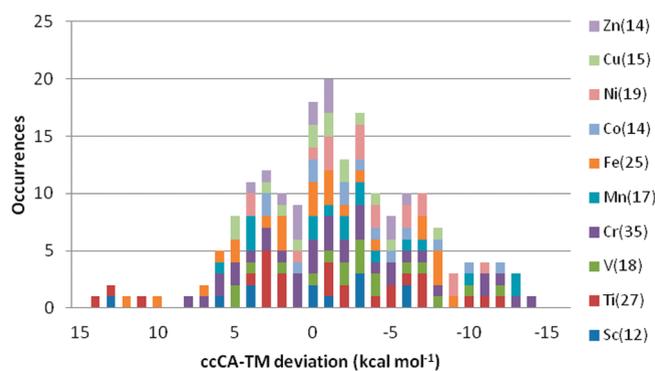


Figure 2. The histogram of the ccCA-TM deviations in kcal mol⁻¹. The numbers of quantities are given in parentheses.

the ccCA-TM ΔH_f (151.4 kcal mol⁻¹) is outside of the experimental error bar of 143.5 ± 5.1 kcal mol⁻¹. The diagnostics suggests that the ground state of CoCu is possibly a single reference system with $C_0^2 = 0.956$, $T_1 = 0.032$, and $D_1 = 0.071$.

12. *Statistical Analysis of Overall Set and Metal Subsets.* The presence of significant outliers (Table 2) has masking effects on the statistical analysis due to the limited number of samples. Some outliers such as metal dimers have salient multireference character. This may undermine the validity of single reference predictions. However, quite a few outliers (ScN, Sc₂O TiF₂, TiF₃, TiBr₂, VBr₂, (ZnCl₂)₂) meet the requirement of $C_0^2 > 0.90$, $T_1 < 0.05$, and $D_1 < 0.10$ for reliable single reference methods, but all of them except TiBr₂ have either a large experimental uncertainty (>10 kcal mol⁻¹) or no experimental uncertainty reported at all. For the ccCA-TM/11 all set including all outlier quantities, the MADs are 6.87 and 11.47 kcal mol⁻¹ for ROHF- and UHF-ccCA-TM, respectively. By excluding the outliers as identified in previous sections based on the experimental uncertainty and the validity of single reference methods, a truncated set of 193 molecules was obtained (ccCA-TM/11). For this truncated set, the MADs decrease to 4.34 and 7.73 kcal mol⁻¹ for ROHF- and UHF-ccCA-TM, respectively.

A histogram for the distribution of ccCA-TM deviations is given in Figure 2 with contributions from different metals in different colors. Overall, no single metal causes any significant problem in the distribution. Linear fitting of the ccCA-TM predictions against experimental data for different metals (Table 3) gives R^2 of 0.9972–0.9997 and slopes of 0.98–1.02, suggesting excellent linearity of our models and no significant systemic error for each metal set. While for most metals, the values of intercept are negative (–3.5 to –0.4) in kcal mol⁻¹, indicating that our theoretical method is overestimating enthalpies of formation, Sc and Cu are the two metals found with positive intercepts (0.1 and 0.9) in the linear fittings. While accurate atomic ΔH_f 's have been experimentally determined and theoretically calibrated, the experimental heats of formation for transition metal atoms still have large uncertainties (Table 3), adding another significant source of error that should be addressed experimentally and/or theoretically. The atomic contribution of uncertainty to ccCA-TM ΔH_f is estimated to be 1.5 kcal mol⁻¹ on average for the ccCA-TM/11 set of 193 quantities. Although the comparison of MADs among metal subset is statistically less significant due to the limited number of experimental quantities and the exclusion of outliers, the relatively large MAD for the Ti subset with comparable experimental accuracy for molecular energies may

be ascribed to the large uncertainty in the atomic ΔH_f value (± 4.0 kcal mol⁻¹) of Ti.

C. Comparisons to ab Initio and DFT Benchmark Studies. Because the full set of 225 molecules encompasses the molecule sets in recent model chemistry^{7,8,10} and DFT studies^{14,36} of gaseous transition metal compounds, it is possible to compare ccCA-TM with previous studies (see Table 4). The ccCA-TM MAD of 2.67 kcal mol⁻¹ is comparable to the 2.84 kcal mol⁻¹ MAD of Gaussian4(MP2)-TM¹⁰ for their set of 20 molecules. However, the Gaussian methods rely on the benchmark molecules to optimize HLC parameters. For example, the G4 theory utilizes six parameters, which may limit their application to species outside the set, especially for transition-metal-containing molecules with exotic bonding features. In a representative DFT study by Riley and Merz,³⁶ TPSS1KCIS in combination with the TZVP basis set provided the smallest MAD (9.1 kcal mol⁻¹) for a large set (referred to as the DFT-TM/07 set in this Article) of 95 molecules. It is noteworthy that the DFT-TM/07 set includes not only molecules with large (>3.0 kcal mol⁻¹) or questionable experimental uncertainties (e.g., TiF₂ and TiF₃), but also species for which single reference methods are not guaranteed to be valid (e.g., Fe₂). Even for such a large, versatile, and challenging set of molecules, the ccCA-TM gives a MAD of 6.87 kcal mol⁻¹, which still outperforms all of the DFT methods considered in ref 36. In a recent assessment of different DFT methods used in combination with the correlation consistent basis sets,¹⁴ the smallest MAD of 3.1 kcal mol⁻¹ was obtained by the functional B97-1 in combination with the cc-pVQZ basis set for a selected small set (referred to as DFT-TM/09) of 19 molecules. The ccCA-TM MAD is found to be 2.2 kcal mol⁻¹, much closer to the averaged experimental uncertainty of 1.5 kcal mol⁻¹ than B97-1.

The calculations of the ccCA-TM MADs are based on the same experimental data used in previous studies, which might contain obsolete data. For example, in the DFT study by Riley and Merz,³⁶ experimental ΔH_f 's for TiCl and TiCl₂ from the Yungman series¹ (24.2 and –57.0 kcal mol⁻¹) were used, while Hildenbrand⁸² recently gave experimental values with improved accuracy. For the DFT-TM/07 set, the ccCA-TM MAD decreases from 6.79 to 5.24 kcal mol⁻¹ when using experimental values adopted in this article (see Table 4). The value of the average experimental uncertainty is lower for the updated experimental data, which also result in a decrease in MAD for other methods; for example, when the updated experimental data were used, TPSS1KCIS in combination with the TZVP basis set gave a MAD of 7.9 kcal mol⁻¹ as compared to 9.1 kcal mol⁻¹ originally reported by Merz et al. The improvements in ccCA-TM MADs (5.24 versus 7.9 kcal mol⁻¹ for the DFT-TM/07 set and 2.24 versus 3.1 kcal mol⁻¹ for the DFT-TM/09 set) indicate that ccCA-TM is a more reliable method for accurate thermochemical quantities and is promising as a benchmark for DFT methods when experimental data are not available and higher level methods are not amenable.

D. Subsets with Different Ranges of Experimental Uncertainties. A high-quality assessment of model chemistries relies on a large set of accurate experimental energetic or structural quantities, which are clearly not available for transition metal-containing molecules. Given the collection of molecules in this study, it is feasible to divide the overall set into different subsets on the basis of the magnitude of reported experimental uncertainties, while keeping the size of the smallest subset large and diverse enough for a statistical analysis. Within the ccCA-TM/11 set, the ccCA-TM MADs of different subsets show a monotonic

Table 3. Atomic Enthalpies of Formation (ΔH_f) at 0 K for Gaseous 3d Metal Atoms and Mean Signed Deviations (MSD), Mean Absolute Deviations (MAD), and Root Mean Square Deviations (rmsd) (in kcal mol⁻¹) of ccCA-TM against the Experimental Enthalpies of Formation, Linear Models, and Experimental Average Uncertainties for the 10 3d Metal Subsets

metal ^a	state	atomic ΔH_f (0 K) ^b	MSD	MAD	rmsd	exp. uncertainty ^c	slope	intercept	R ²
Sc (12)	² D	90.17 ± 0.8	0.51	4.16	5.32	3.8	0.990	0.1	0.9991
Ti (27)	³ F	112.55 ± 4.0	-0.67	5.27	6.55	3.6	0.980	-1.7	0.9984
V (18)	⁴ F	122.4 ± 2.0	-2.75	4.52	5.42	2.6	0.994	-3.1	0.9995
Cr (35)	⁷ S	94.49 ± 1.0	-1.71	4.77	6.03	3.8	0.996	-1.9	0.9978
Mn (17)	⁶ S	67.42 ± 1.0	-2.74	4.85	6.11	3.5	1.016	-1.9	0.9972
Fe (25)	⁵ D	98.73 ± 0.3	-0.18	4.53	5.68	3.3	0.996	-0.4	0.9973
Co (14)	⁴ F	101.6 ± 0.5	-3.22	4.15	5.42	2.9	1.005	-3.0	0.9995
Ni (19)	³ F	102.3 ± 2.0	-3.38	4.38	5.33	3.2	0.993	-3.5	0.9997
Cu (15)	² S	80.4 ± 0.3	-0.49	2.79	3.50	4.4	0.976	0.9	0.9981
Zn (14)	¹ S	31.04 ± 0.05	-0.66	2.19	2.93	2.1	0.992	-0.6	0.9972
overall			-1.49	4.35	5.54	3.4	0.994	-1.7	0.9988

^aThe number of molecules in each subset is given in parentheses. ^bThe averaged value of reported experimental uncertainties for molecules. ^cFrom refs 1 and 3.

Table 4. Mean Signed Deviations (MSD), Mean Absolute Deviations (MAD), and Root Mean Square Deviations (rmsd) (in kcal mol⁻¹) of ccCA-TM against the Experimental Enthalpies of Formation of Different Sets of Molecules in Current and Previous Studies

set	number of molecules	ccCA-TM									
		best results from previous studies		previous exp. ^a				updated exp. ^b			
		MSD	MAD	MSD	MAD	rmsd	error ^d	MSD	MAD	rmsd	error ^d
ccCA-TM/07 ^c	17	-0.8	5.6	-4.31	5.22	9.66	3.3	-4.20	4.85	9.56	3.3
ccCA-TM/09all ^c	58	-2.50	4.78				2.6	-2.22	4.10	6.81	2.7
ccCA-TM/09 ^c	52	-1.15	2.85								
Gaussian 4-TM ^f	20		2.84 ^g					-1.49	2.67	3.31	1.4
DFT-TM/07 ^h	95		9.1(7.9) ^g	-4.30	6.79	10.17	3.7	-2.61	5.24	8.51	3.0
DFT-TM/09 ⁱ	19		3.1					-1.32	2.24	2.70	1.4
ccCA-TM/11all	225							-3.92	6.87	10.40	4.0
ccCA-TM/11 ^j	193							-1.49	4.34	5.54	3.3

^aThe same experimental data as in the corresponding references are used. ^bThe experimental data are updated as in this study. ^cReference 7. ^dThe averaged value of reported experimental uncertainties. ^eReference 8. ^fReference 10. ^gIn parentheses, updated experimental data were used. ^hReference 36. ⁱReference 14. ^jOutliers are excluded from the initial ccCA-TM/11all set.

relationship with the ranges of experimental uncertainties. As illustrated with the *P* variant of ccCA-TM (Figure 1), the MAD for the ≤ 1.0 kcal mol⁻¹ subset is 2.37 kcal mol⁻¹, which increases to 2.90, 3.42, 3.74, and 3.91 in kcal mol⁻¹ as the upper limits of experimental error bars rise to 2.0, 3.0, 4.0, and 5.0 in kcal mol⁻¹, respectively. A list of the 32 molecules with uncertainties ≤ 1.0 kcal mol⁻¹ is given in Table 5. This subset contains all metals except Sc, and a large variety of bond types from diatomics to large complexes. It is surprising to find that for 15 multireference molecular systems, ccCA-TM give predictions as reliable as for the 17 molecules of predominantly single reference character. Although the overall MAD of ccCA-TM exceeds the desired transition metal accuracy of ± 3.0 kcal mol⁻¹, for the subset of 70 molecules with experimental uncertainties ≤ 2.0 kcal mol⁻¹, ccCA-TM practically meets the target accuracy. On the basis of the correlation between the ccCA-TM MAD and ranges of experimental uncertainties, it is possible to find the limit of ccCA-TM accuracy when the ccCA-TM predictions are compared to a

set of experimental quantities with substantially more stringent uncertainties. However, a further division of the set in this study may not generate a statistically sizable subset with better accuracy; for example, only 12 quantities have an experimental uncertainty ≤ 0.5 kcal mol⁻¹.

The ccCA-TM/11 set can be applied to more efficient methods, for example, DFT, MP2, etc., to probe its accuracy in predicting ΔH_f 's for transition metal species. Because B3LYP is employed in the geometry optimization and frequency analysis in ccCA-TM, it is convenient to compare ccCA-TM against this representative hybrid GGA density functional. We also calculated ΔH_f 's with M06, a more recently developed hybrid meta-GGA density functional,¹⁸ with the cc-pVTZ basis set. The MADs of B3LYP and M06 predictions of ΔH_f 's for each subset are plotted against experimental uncertainty ranges in Figure 3. In contrast to ccCA-TM, both B3LYP and M06 do not show any positive correlation with the experimental uncertainty. The B3LYP MADs actually decreases from 14.1 to 12.9 kcal mol⁻¹ as the range of experimental uncertainty increases from 2.0 to

Table 5. Listing of 32 Molecules with Experimental Uncertainty (≤ 1.0 kcal mol $^{-1}$) and Enthalpies of Formation,^a and the Deviations of the ccCA-TM Predictions from Experimental Data^b

molecule	$\Delta H_{f,298K}$	uncertainty	ccCA-TM deviation	C_0^2	T_1	D_1
Ground States Show Significant Multireference Character ^c						
VCl ₄	-126.1	0.6	0.5		0.032	0.106
CrO ₃	-77.3	1.0	-8.0		0.051	0.190
CrCl	31.1	0.7	3.1	0.992	0.134	0.474
CrO ₂ Cl ₂	-124.1	1.0	-1.0		0.038	0.161
Mn(CO) ₃ (C ₅ H ₅)	-102.0	0.7	-3.3		0.042	0.163
FeCl ₃	-60.6	1.0	-1.5		0.045	0.118
FeBr ₃	-30.0	1.0	-3.1		0.055	0.145
Fe(C ₅ H ₅) ₂	57.9	0.6	2.2		0.047	0.188
(FeCl ₂) ₂	-103.1	1.0	-0.2		0.046	0.246
Co(CO) ₄ H	-136.0	0.5	0.5		0.052	0.253
NiCl	43.0	1.0	-1.2	0.470	0.041	0.150
NiCl ₂	-17.4	1.0	-3.6	0.903	0.038	0.120
CuCl	21.8	0.4	0.0	0.995	0.029	0.112
(CuCl) ₃	-61.8	0.5	4.8		0.026	0.123
ZnO	55.2	1.0	2.4	0.846	0.033	0.083
average (15)		0.8	-0.56 (2.36) ^d			
Ground States Do Not Show Multireference Character						
TiF ₄	-182.4	0.5	3.1			
TiCl ₄	-131.0	0.7	2.0			
TiBr ₄	-370.8	0.2	3.9			
VF ₅	-343.2	0.2	2.3			
CrCl ₂	-28.1	0.4	3.2			
MnF ₂	-126.2	1.0	4.0			
MnCl ₂	-62.6	1.0	-2.3			
FeCl ₂	-32.8	1.0	-0.3			
FeBr ₂	-9.9	0.5	-0.1			
Fe(OH) ₂	-79.0	0.5	-9.3			
CoCl ₂	-22.6	1.0	-1.7			
Ni(CO) ₄	-144.0	0.6	-0.6			
Zn(CH ₃) ₂	12.6	0.3	0.8			
ZnH	62.9	0.5	-0.3			
ZnCl	6.5	1.0	-5.1			
ZnCl ₂	-63.5	0.4	-1.0			
ZnS	62.9	1.0	-0.9			
average (17)		0.64	-0.14 (2.41) ^d			
overall average (32)	0.71	-0.52 (2.37) ^d				

^a See Tables S3 and S4 in the Supporting Information for references. ^b All units are given in kcal mol $^{-1}$. ^c Multireference characters are considered significant if $T_1 > 0.05$, $D_1 > 0.10$, or $C_0^2 < 0.90$. ^d The mean absolute deviations are given in parentheses.

5.0 kcal mol $^{-1}$, and increases to 13.3 kcal mol $^{-1}$ for the entire ccCA-TM/11 set. In contrast, the M06 MADs range from 10.5 to 11.0 kcal mol $^{-1}$ without a simple trend with respect to the magnitude of experimental uncertainty.

E. Subsets Based on Bonding Characteristics. Although a small MAD of 1.99 kcal mol $^{-1}$ was observed for the three nitrides, more experimental data are needed for a statistically valid interpretation. Similar accuracy was found for monohydrides and chalcogenides with MADs of 3.65 and 3.63 in kcal mol $^{-1}$, respectively, but the latter has a higher experimental uncertainty on average (Figure 4). The MAD of 80 halides is 4.11 kcal mol $^{-1}$. Transition metal compounds with coordinate ligands such as PF₃ (this subset is collectively labeled “coordination

complexes” herein) can be more challenging than covalent halides, chalcogenides, or hydrides because the size of ligands can be large (e.g., C₅H₅) and ligand-backbonding can be prevalent (e.g., in carbonyls), let alone the controversy in experimental data.¹⁰² The ccCA-TM MAD for the subset of 25 coordination complexes is 4.91 kcal mol $^{-1}$. The subset of metal dimers including the problematic Ti₂, Cr₂, and Ni₂ has the largest MAD among the subsets. Unlike common main group test sets, more open-shell than closed-shell systems comprise our transition metal sets. The ccCA-TM MAD is 4.55 kcal mol $^{-1}$ for the 126 open-shell molecules and 3.98 kcal mol $^{-1}$ for the 67 closed-shell molecules.

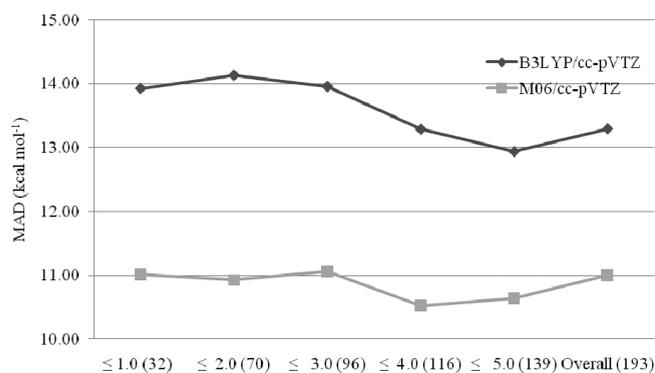


Figure 3. The B3LYP and M06 MADs in kcal mol⁻¹ relative to experimental data for subsets with different ranges of experimental uncertainties.

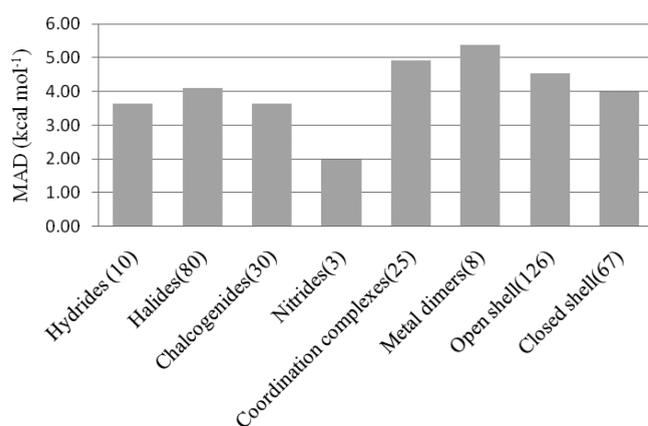


Figure 4. The ccCA-TM MADs in kcal mol⁻¹ relative to the experimental enthalpies of formation for subsets of different bonding types and two subsets of open-shell and closed-shell molecules. The numbers of quantities are given in parentheses.

Subsets of molecules with different numbers of atoms were also considered. The absolute errors in electronic energy may be correlated to the size of molecules because larger molecules have more electrons and, as such, more electronic interactions. The ccCA-TM MADs are 4.02, 3.78, 5.81, and 5.06 in kcal mol⁻¹ for diatomics, triatomics, tetraatomics, and molecules of five or more atoms, respectively. The best accuracy was achieved for the triatomics subset, which is also the subset with the smallest average experimental uncertainty. Because the ccCA-TM MADs are also affected by the experimental uncertainty, the ratios of ccCA-TM MAD against average experimental uncertainty can reflect better the correlation between the accuracy of ccCA-TM and the size of molecules, and a monotonic increase of the ratios from diatomics to tetraatomics is found (Figure 5). However, the ratio for molecules containing five or more atoms decreases, which is probably due to the saturation of bonding on transition metals and the accurate description of functional groups containing only main group elements.

F. Diagnostics for Reliability of Single Reference Methods.

The T_1 and D_1 diagnostics from CCSD calculations and the C_0^2 from the CASSCF wave functions serve as indicators of the multireference character of molecular systems. These data can be used to consider the relevance of single reference ccCA for

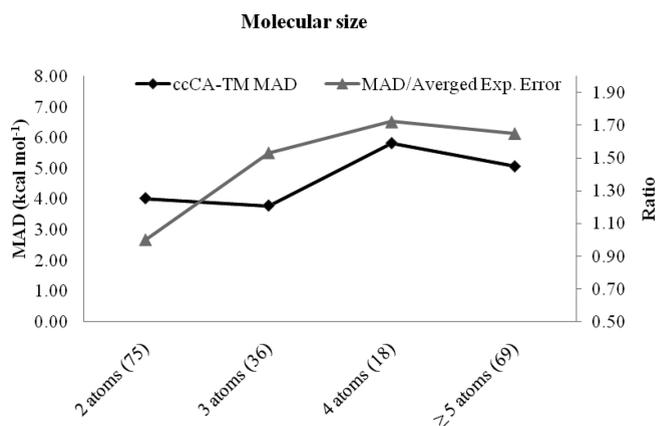


Figure 5. The ccCA-TM MADs in kcal mol⁻¹ (relative to the experimental enthalpies of formation) and their ratios against average values of experimental error bars for subsets of different number of atoms. The numbers of quantities for each subset are given in parentheses.

the molecules studied. Here, the T_1 , D_1 , and C_0^2 values are compared to ccCA-TM deviations from experimental data for the overall set of molecules as well as the various subsets. The scatter plots of T_1 and D_1 diagnostics and spin contamination against the ccCA-TM deviations are given in Figure 6 for the ccCA-TM/11 set. Additional plots illustrating the relationship between the diagnostics and ccCA-TM deviations for each subset of molecules relative to their experimental uncertainties are provided in the Supporting Information. Because CASSCF calculations can become costly for molecules with more than three atoms, only 124 molecules were considered for the C_0^2 diagnostics (see Figure 7 for a scatter plot against ccCA-TM deviation). In most cases, a small value of C_0^2 (≤ 0.90) accompanies relatively larger values in T_1 and D_1 diagnostics. Yet there are curious cases where the value of C_0^2 is not qualitatively consistent with the T_1/D_1 diagnostics. For example, for the $^5\Delta_g$ ground state of Co_2 , $C_0^2 = 0.505$, and quite a number of configuration state functions were found important from the CASSCF/cc-pVTZ-DK calculations. However, $T_1 = 0.037$ and $D_1 = 0.083$ do not reflect the magnitude of the multireference character as much as C_0^2 implies. More often the value of C_0^2 is very close to 1.0, but the T_1/D_1 diagnostics suggest significant multireference character. For example, VH, VF, VCl, and VBr all have $C_0^2 > 0.98$, but it is found that $T_1 > 0.05$ and $D_1 > 0.10$. One possible reason could be that the ground-state molecular wave function has critical contributions from 4p orbitals of the transition metal atoms, which are omitted because only 4s and 3d orbitals of transition metal atom are considered as active orbitals in the default CASSCF wave function used in this study.

The plots demonstrate a possible relationship between the quality of the experimental value and the quality of the computed ccCA enthalpy of formation. As can be seen from Figures 6 and 7, there are clearly visible situations where both diagnostics and error are large, which may indicate “pathological” molecules that are difficult to study with single reference methods. Data points where coupled cluster diagnostics are large, but errors are small, could indicate either fortuitous accuracy using ccCA-TM or success of ccCA-TM in accounting for electronic correlation or basis set effects in inorganic

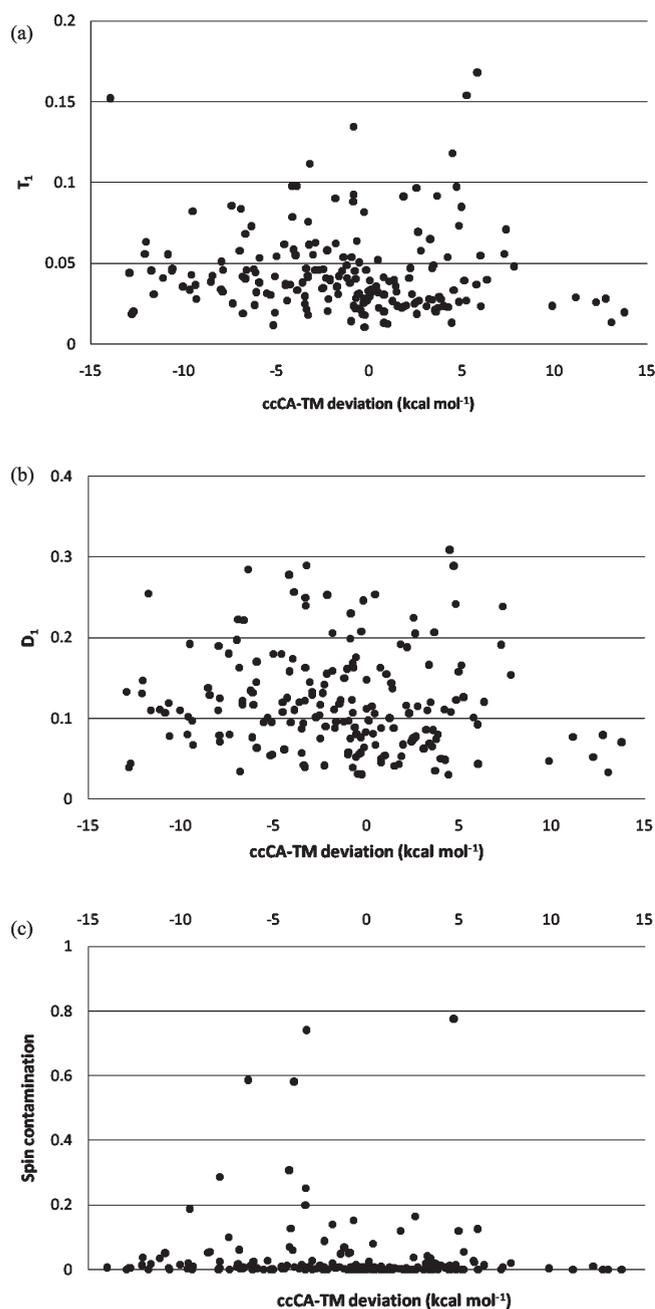


Figure 6. Scatter plot of (a) T_1 diagnostics, (b) D_1 diagnostics, and (c) spin contamination ($\langle S^2 - S_z^2 - S_z \rangle$, open shell molecules only) against the signed deviations of ccCA-TM predictions from experimental enthalpies of formation. All diagnostics results are extracted from the CCSD(T)/cc-pVTZ-DK calculation.

molecules. Last, there are clearly visible data points where errors are large but diagnostics are small. These are situations where the experimental data may be suspect and the value computed with ccCA likely more reliable. In a sense, these plots are representative of the bounty of unanswered questions and future research possibilities in method development and applied inorganic quantum chemistry.

Among 124 molecules for which all diagnostics available, only 42 meet the moderate requirements of $C_0^2 > 0.90$, $T_1 < 0.05$, and $D_1 < 0.10$ for reliable single reference MP2/CCSD calculations.

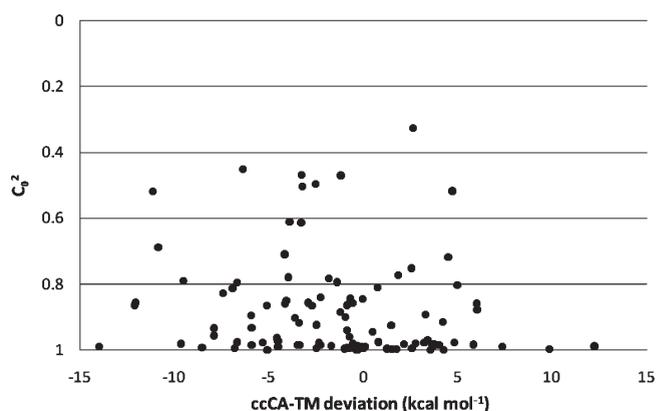


Figure 7. Scatter plot of weights of leading configuration C_0^2 from CASSCF calculations against the signed deviations of ccCA-TM predictions from experimental enthalpies of formation.

The list of the 42 molecules is given in Table S6. No significant spin contamination was found with any of the 42 molecules. Note that the single reference set does not include any larger molecules due to the restriction in C_0^2 calculations.

CONCLUSIONS

An extensive set of 225 transition metal-containing molecules has been used to assess the applicability, as well as limitations, of the recently developed ccCA-TM in the predictions of ΔH_f° 's. Because of the common presence of multireference character, the set is reduced to one-third of its original size even if the molecules are screened by loose requirements of $C_0^2 > 0.90$, $T_1 < 0.05$, and $D_1 < 0.10$. The single reference ccCA-TM was found to be insensitive to multireference character for the prediction of ΔH_f° 's as shown by the T_1/D_1 diagnostics but failed as expected for known multireference systems such as Fe_2 . 32 outliers were determined by careful analysis of the experimental uncertainty, the reliability of single reference methods estimated by the coupled cluster T_1/D_1 diagnostics and CASSCF C_0^2 weight, and comparison between theoretical and experimental results. By excluding the outliers, a truncated set of 193 species was obtained. This truncated set, ccCA-TM/11, as well as its subsets by various categorizations especially the range of experimental error bars, will hopefully see more utilization for future development of ab initio model chemistries.

A monotonic decrease in MAD has been found for ccCA-TM when the upper limits of experimental errors decrease. The ccCA-TM accurately and reliably predicts the ΔH_f° 's of a subset of inorganic compounds with a MAD of $2.90 \text{ kcal mol}^{-1}$, when the accuracy of experimental data is assured by restricting the reported uncertainty to be $\leq 2.0 \text{ kcal mol}^{-1}$. Unlike ccCA-TM, two representative DFT methods, B3LYP and M06, perform poorly. The ccCA MADs are less than the corresponding averaged experimental uncertainties for molecules containing Sc, Zn, and Cu. The discrepancies by different extrapolation schemes for the CBS limits are mostly trivial and the Perterson mixed Gaussian/inverse exponential CBS fit remains as an excellent choice for ccCA-TM computations. Our study supports that ccCA-TM is capable of accurately and reliably predicting ΔH_f° 's for 3d transition metal-containing inorganic compounds.

■ ASSOCIATED CONTENT

S Supporting Information. Calculated ROHF- and UHF-ccCA-TM atomic energies with breakdown contributions, experimental atomic enthalpies of formation at 0 K, thermal corrections and spin-orbit corrections for all atoms considered in this study, experimental enthalpies of formation and their resources for the ccCA-TM/11 set of 225 molecules, calculated ROHF- and UHF-ccCA-TM deviations of enthalpies of formation from experimental data, a list of 42 molecules meeting the diagnostic criteria for insignificant multireference character, and plots illustrating the relationship between the diagnostics and ccCA-TM deviations relative to their experimental data for each subset of different ranges of experimental uncertainty. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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