Benchmarking of Model Core Potentials: Application to the Halogen Complexes of Group 4 Metals

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The reliability of the model core potential (MCP) method was probed in a systematic RHF and MP2 study of the geometries of the group 4 metal halogen complexes (MX_4; M = Ti, Zr, Hf and X = F, Cl, Br, I). The computed bond lengths were compared with experimental values, as well as those predicted using effective core potentials. Provided that electrons from the outermost core shell of the metal atom are treated explicitly in the calculation, both the MCP and ECP methods predict M−X bond lengths within 0.02−0.03 Å of experiment. The reaction energies for a simple set of halogen substitution reactions of the MX_4 complexes leading to the mixed halogen complex, MX_2Y_2, were also studied. Although no experimental values are available for these reactions, comparison was made with the values computed using effective core potentials. The predictability of the different pseudopotential techniques and the importance of the metal atom valence basis set contraction scheme and polarization space are discussed.

INTRODUCTION

The pseudopotential formalism has been very successful in extending computational chemistry to the study of the structures, energetics, properties, and reactions of molecules containing transition metals.[1−6] Two types of pseudopotentials are commonly employed: the model potentials and the effective core potentials (ECPs). Although the two differ in their design and implementation, their principal goal is the same—to reduce the computational expense by replacing the chemically inert core electrons of an atom with an appropriate potential function, thereby treating only the valence electrons explicitly. In addition, pseudopotentials provide a simple mechanism to incorporate relativistic effects into the calculations, which are important for the heavy elements.

The model potential method was originally proposed in 1974 by Huzinaga and co-workers.[3] The development of the model potentials and the current state of the methodology have been recently reviewed.[1−4] There are three versions of the model potential in use: version 1,[7,8] which was used in the present study and will be denoted as the model core potential (MCP) method hereafter; version 2, known as the ab initio model potential (AIMP) method;[9] and version 3.[10] The three differ in the way the core-valence Coulomb and exchange interactions are accounted for. Version 1 represents the core-valence exchange interactions using a local potential, while versions 2 and 3 use a nonlocal representation of the potential function.[1] With the recent publication of the model core potential parameters and associated valence basis sets for the main group elements,[11] the model core potential method may be used in studies involving all of the main

group and transition metal elements. The lanthanides have recently been parametrized,[12] and work on the parametrization of the actinides is currently in progress.

A complete description of the MCP method is available elsewhere,[1−4] and here we shall present only the main assumptions of the method.

In the MCP formalism the one-electron Hamiltonian, $\hat{h}_i$, contains, along with the kinetic energy and nuclear electron attraction terms, two additional terms for each atomic center a: the potential for the core electrons, $\hat{V}_i^\alpha$, and the projection operator, $\hat{P}_i^\alpha$

$$\hat{h}_i = -\frac{1}{2}\nabla_i + \sum_\alpha \left(-\frac{z_\alpha}{r_{i\alpha}} + \hat{V}_i^\alpha + \hat{P}_i^\alpha \right) \qquad (1)$$

where z_α is the core charge on atom α (charge of the bare nucleus minus the number of core electrons).

The spherically symmetric local potential, $\hat{V}_i^\alpha$, approximates the exact atomic nonlocal core potential and has the form

$$\hat{V}_i^\alpha = z_\alpha \left\{ -\sum_I \frac{A_l}{r_{i\alpha}} e^{-\alpha_l r_{i\alpha}^2} - \sum_J A_J e^{-\alpha_J r_{i\alpha}^2} \right\} \qquad (2)$$

where the indices I and J refer to the two sets of parameters $\{\alpha_I, A_I\}$ and $\{\alpha_J, A_J\}$. This potential represents the core Coulomb and exchange potentials, along with the nuclear attraction energy.

The ability of the model potential method to correctly reproduce the nodal structure of the valence orbitals makes it unique and different from its effective core potential counterpart. It is the projection operator $\hat{P}_i^\alpha$ that imparts this property on the model potential method. The projection

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operator is given by

$$\hat{P}_i^\alpha = \sum_{c \in \alpha} B_c |\psi_c(i)\rangle\langle\psi_c(i)| \tag{3}$$

where the parameter B_c is taken as one to two times the absolute value of the atomic orbital energy eigenvalue (ϵ_c) of the core shell c on atom α

$$B_c = F_c |\epsilon_c| \tag{4}$$

The atomic Hamiltonian for the N_v valence electrons is defined as

$$\hat{H}(1, 2, ..., N_v) = \sum_{i=1}^{N_v} \hat{h}_i + \sum_{i>j}^{N_v} \frac{1}{r_{ij}} \tag{5}$$

The values of the model potential parameters $\{\alpha_{I,J}, A_{I,J}\}$ for a given atom are determined from atomic calculations in which the MCP valence orbital shapes and energies are fit to those obtained in all-electron reference calculations. It should be added that scalar relativistic effects may be incorporated into the MCPs if relativistic all-electron calculations are used as the reference.

One of our primary interests is the application of computational chemistry techniques to organometallic chemistry. Pseudopotentials, such as the MCPs, are a necessity in studying such systems, where the molecules are typically large in size and contain a number of heavy atoms, both the metal atoms themselves and the main group elements present in the ligands. In addition, MCPs enable one to efficiently probe the metal-dependent trends commonly observed experimentally, as one descends a column of the periodic table with no increase in computational cost, since all of the metal atoms contain the same number of valence electrons.

Given the nature of the approximations in the MCP method, the parameters and valence basis sets should be thoroughly tested and calibrated before commencing actual studies of organometallics. MCPs have been used in several benchmarking studies as well as in applications focusing on transition metal chemistry. A recent review article[1] gives a comprehensive overview of the studies that have employed MCPs in studies of transition metal compounds. Miyoshi and Sakai carried out a detailed benchmarking of the MCP potentials and valence basis sets for a number of small transition metal complexes at the restricted Hartree−Fock (RHF) level using both large-core (denoted MCP−SD) and small-core (denoted MCP−SPD) metal atom MCPs.[13] They found very good overall agreement between MCP−SPD geometries and harmonic vibrational frequencies and those computed using all-electron basis sets of similar quality. Frenking et al.[14] compared the performance of the SD- and SPD-type MCPs to the corresponding ECPs of Hay and Wadt[15−17] at the restricted Hartree−Fock (RHF) level, in a study involving complexes of the type Ti(CH$_3$)$_n$(Cl)$_{4-n}$. They found the SD-type MCPs and ECPs to be inferior to their respective SPD counterparts, and they found that at the RHF level, without electron correlation effects, the ECP values of geometries, harmonic vibrational frequencies, bond energies, and reaction energies agreed better with experiment than the corresponding MCP values.

The present paper is the second in a series focused on thoroughly benchmarking the MCPs for molecules leading up to the large organometallic species, using techniques that go beyond SCF in order to include the electron correlation energy. In the first paper[18] we focused on the performance of MCPs in the modeling of small molecules that commonly appear as ligands in transition metal complexes, along with their heavier homologues. Here we report the results of benchmarking studies of the simple tetrahalogen complexes of the group 4 transition metals (Ti, Zr, and Hf). These MX$_4$ metal halogen complexes are commonly encountered as starting compounds in organometallic syntheses[19] and are among the simplest coordination complexes. The geometries of these tetrahedral complexes were computed using small-core MCP and ECP approaches and compared, whenever possible, to experiment. The availability of experimental bond lengths for all of the MX$_4$ complexes of the group 4 metals[20−22] enables us to better gauge the predictive power of the MCP method. Reaction energies for a simple set of halogen diatomic substitution reactions of the MX$_4$ complexes, leading to the mixed halogen complex, MX$_2$Y$_2$, were also computed.

COMPUTATIONAL METHODS

The valence space for a pseudopotential of a transition metal atom may comprise either the outermost ns and (n − 1)d shells (an SD or large-core pseudopotential), or the (n − 1)p shell (sometimes accompanied by the (n − 1)s shell) may be also included in the valence space (an SPD or small-core pseudopotential).[5,6] Although the SD-type pseudopotentials offer greater computational savings than their SPD counterparts, Sakai and Miyoshi,[23] as well as Frenking et al.,[14] have shown them to be often inferior in predicting molecular properties of transition metal complexes, particularly when the metal atom is in a high oxidation state. Our preliminary calculations on the MX$_4$ complexes using the MCP−SD and ECP−SD pseudopotentials agree with the previous findings, with computed bond lengths typically deviating from experiment by 0.1 Å or more, especially for fluorides. Hence, the SD pseudopotentials were not used further in the benchmarking study, and the results presented here employed only the SPD-type pseudopotentials.

Comparison of the results obtained with various pseudopotential methods must be made with caution, as the methods differ both in the definition of the core as well as in the structure of the associated valence basis sets for the transition metal atoms. The MCP−SPD potentials treat explicitly the 10 valence electrons from the configuration (n − 1)p^6ns^2 (n − 1)d^2. The number of valence electrons is larger in both the ECPs of Stevens and co-workers,[24−26] denoted ECP1−SPD, and the ECPs of Hay and Wadt,[17] termed ECP2−SPD, and includes the 12 electrons from the configuration (n − 1)s^2(n − 1)p^6ns^2(n − 1)d^2. The default metal basis sets for the ECP potentials include two sets of diffuse p-type functions that represent the np shell and act as polarization functions. In the MCP calculations the polarization functions must be explicitly added. The situation is more uniform for the halogen atoms, where the seven electrons in the ns and np atomic orbitals were included in all of the pseudopotential methods employed. Scalar relativistic pseudopotentials were used for zirconium and hafnium, as well as for iodine.

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Table 1. Summary of the Metal Atom Pseudopotential Valence Basis Sets Employed in Calculations of the MX$_4$ Complexes

	Contraction Scheme		
basis	Ti	Zr	Hf
		MCP−SPD	
DZ	(51/31/41)	(71/41/41)	(71/51/51)
DZ1p	(51/311*/41)	(71/411*/41)	(71/511*/51)
DZ1f	(51/31/41/1*)	(71/41/41/1*)	(71/51/51/1*)
DZ1p1f	(51/311*/41/1*)	(71/411*/41/1*)	(71/511*/51/1*)
TZ	(411/211/311)	(611/311/311)	(611/411/411)
TZ1p	(411/2111*/311)	(611/3111*/311)	(611/4111*/411)
TZ2p	(411/2111*1*/311)	(611/3111*1*/311)	(611/4111*1*/411)
TZ1f	(411/211/311/1*)	(611/311/311/1*)	(611/411/411/1*)
TZ1p1f	(411/2111*/311/1*)	(611/3111*/311/1*)	(611/4111*/411/1*)
TZ2p1f	(411/2111*1*/311/1*)	(611/3111*1*/311/1*)	(611/4111*1*/411/1*)
		ECP1−SPD	
TZ2p	(4211/42*11*/411)	(4211/42*11*/311)	(4111/411*1*/311)
TZ2p1f	(4211/42*11*/411/1*)	(4211/42*11*/311/1*)	(4111/411*1*/311/1*)
		ECP2−SPD	
TZ2p	(4311/31*1*/311)	(4311/32*1*/211)	(4311/32*1*/111)
TZ2p1f	(4311/31*1*/311/1*)	(4311/32*1*/211/1*)	(4311/32*1*/111/1*)

The valence basis set contractions employed for the metal atom are displayed in Table 1. The naming convention adopted to describe the valence basis sets is similar to that used in describing the valence basis sets employed in our calculations of the main group molecules.[18] The terms DZ and TZ denote basis sets of double-ζ and triple-ζ quality, while 1p, 2p, and 1f designate the presence of different numbers of p- and f- type polarization functions, respectively, in the basis set. In the MCP basis sets the basis functions for the p space were contracted in a manner similar to that employed in the default DZ and TZ basis sets of the ECPs. The exponents of the f polarization functions (1.506, 0.875, and 0.784 for Ti, Zr, and Hf) were taken from the compilation of Frenking et al.,[27] while the exponents of the p polarization functions were taken from the compilation of Huzinaga et al.[28] As shown in Table 1, the DZ and TZ basis sets were systematically expanded in the calculations involving the MCP−SPD pseudopotentials. The default metal atom basis sets of TZ2p quality were employed in conjunction with the ECP1− and ECP2−SPD pseudopotentials and further augmented with an f-type polarization function to yield TZ2p1f basis sets. In all of the calculations, the valence basis sets for the halogen atoms were of double-ζ plus polarization quality, with a single d polarization function taken from the compilation of Huzinaga et al.[28] (The exponents were 1.496, 0.514, 0.389, and 0.266 for F, Cl, Br, and I, respectively.)

Molecular geometries were optimized using a modified Powell method[29] at the RHF and MP2 levels of theory, using the development version of the GAMESS package.[30] Some test calculations were performed with the CADPAC program.[31] The MX$_4$ geometries were optimized under T_d symmetry constraints, while C_{2v} symmetry was imposed on the MX$_2$Y$_2$ systems.

RESULTS AND DISCUSSION

A. Geometries. The MCP and ECP bond lengths in the TiX$_4$, ZrX$_4$, and HfX$_4$ complexes (where X = F, Cl, Br, I) are collected in Tables 2−4, along with their respective experimental values. In addition, the deviations between the calculated and experimental bond lengths were averaged over all 12 MX$_4$ complexes for each pseudopotential (M) and

Table 2. Bond Lengths (in Å) for the TiX$_4$ Complexes

method	basis set	r_e(Ti−F)	r_e(Ti−Cl)	r_e(Ti−Br)	r_e(Ti−I)
		MCP−SPD			
RHF	DZ	1.730	2.171	2.327	2.530
	DZ1p	1.734	2.178	2.339	2.552
	DZ1f	1.722	2.170	2.327	2.533
	DZ1p1f	1.725	2.176	2.337	2.550
	TZ	1.714	2.155	2.313	2.517
	TZ1p	1.717	2.160	2.321	2.533
	TZ2p	1.718	2.163	2.325	2.538
	TZ1f	1.704	2.152	2.311	2.517
	TZ1p1f	1.707	2.157	2.318	2.532
	TZ2p1f	1.708	2.159	2.322	2.536
MP2	DZ	1.742	2.168	2.325	2.537
	DZ1f	1.726	2.155	2.314	2.526
	DZ1p	1.749	2.177	2.336	2.551
	DZ1p1f	1.732	2.162	2.321	2.535
	TZ	1.724	2.149	2.305	2.513
	TZ1p	1.730	2.155	2.313	2.524
	TZ2p	1.730	2.156	2.314	2.527
	TZ1f	1.706	2.135	2.293	2.502
	TZ1p1f	1.711	2.140	2.299	2.509
	TZ2p1f	1.711	2.141	2.299	2.511
		ECP1−SPD			
RHF	TZ2p	1.751	2.186	2.337	2.568
	TZ2p1f	1.744	2.184	2.335	2.567
MP2	TZ2p	1.769	2.181	2.328	2.554
	TZ2p1f	1.757	2.171	2.317	2.542
		ECP2−SPD			
RHF	TZ2p	1.728	2.154	2.320	2.533
	TZ2p1f	1.720	2.150	2.317	2.532
MP2	TZ2p	1.746	2.158	2.328	2.546
	TZ2p1f	1.729	2.141	2.312	2.529
		exptl^a			
		1.754	2.170	2.339	2.546

^{a} Experimental distances taken from the Landolt−Börnstein compilations.[20−22]

valence basis set (B) combination, denoted $\sigma_{av}(r_e$:M|B), and compiled in Table 5.

As shown in Tables 2−4, the MCP−SPD bond lengths agree very well with the experimental values with most errors smaller than 0.03 Å. Furthermore, the average errors, σ_{av}-(r_e:MCP−SPD|B), between the MCP−SPD and experimental bond lengths are between 0.02 and 0.03 Å, depending on the basis set employed. Comparison of the accuracy of the MCP−SPD and ECP−SPD bond lengths shows that there

Table 3. Bond Lengths (in Å) for the ZrX_4 Complexes

method	basis set	r_e(Zr−F)	r_e(Zr−Cl)	r_e(Zr−Br)	r_e(Zr−I)
		MCP−SPD			
RHF	DZ	1.932	2.356	2.505	2.702
	DZ1p	1.936	2.363	2.515	2.718
	DZ1f	1.907	2.347	2.500	2.703
	DZ1p1f	1.910	2.352	2.507	2.714
	TZ	1.913	2.349	2.502	2.702
	TZ1p	1.915	2.354	2.508	2.713
	TZ2p	1.916	2.355	2.509	2.714
	TZ1f	1.889	2.338	2.496	2.701
	TZ1p1f	1.891	2.342	2.501	2.707
	TZ2p1f	1.891	2.342	2.501	2.708
MP2	DZ	1.935	2.344	2.491	2.692
	DZ1p	1.941	2.352	2.500	2.701
	DZ1f	1.903	2.319	2.471	2.675
	DZ1p1f	1.907	2.325	2.477	2.680
	TZ	1.920	2.338	2.488	2.687
	TZ1p	1.925	2.343	2.493	2.693
	TZ2p	1.925	2.343	2.493	2.693
	TZ1f	1.886	2.312	2.465	2.668
	TZ1p1f	1.890	2.316	2.469	2.670
	TZ2p1f	1.890	2.316	2.469	2.670
		ECP1−SPD			
RHF	TZ2p	1.917	2.353	2.502	2.729
	TZ2p1f	1.895	2.344	2.495	2.723
MP2	TZ2p	1.931	2.342	2.488	2.707
	TZ2p1f	1.902	2.320	2.466	2.686
		ECP2−SPD			
RHF	TZ2p	1.908	2.344	2.507	2.720
	TZ2p1f	1.889	2.330	2.497	2.713
MP2	TZ2p	1.919	2.331	2.493	2.702
	TZ2p1f	1.891	2.302	2.465	2.676
		exptl[a]			
		1.901	2.323	2.465	2.660

[a] Experimental distances taken from the Landolt−Börnstein compilations.[20−22]

Table 4. Bond Lengths (in Å) for the HfX_4 Complexes

method	basis set	r_e(Hf−F)	r_e(Hf−Cl)	r_e(Hf−Br)	r_e(Hf−I)
		MCP−SPD			
RHF	DZ	1.909	2.337	2.488	2.690
	DZ1p	1.916	2.347	2.504	2.722
	DZ1f	1.885	2.324	2.481	2.688
	DZ1p1f	1.879	2.319	2.484	2.701
	TZ	1.889	2.326	2.480	2.683
	TZ1p	1.895	2.334	2.490	2.697
	TZ2p	1.892	2.334	2.491	2.700
	TZ1f	1.871	2.320	2.479	2.686
	TZ1p1f	1.874	2.325	2.486	2.694
	TZ2p1f	1.873	2.325	2.486	2.696
MP2	DZ	1.912	2.322	2.472	2.675
	DZ1p	1.922	2.331	2.486	2.694
	DZ1f	1.880	2.296	2.450	2.657
	DZ1p1f	1.875	2.286	2.446	2.659
	TZ	1.895	2.313	2.463	2.665
	TZ1p	1.906	2.324	2.475	2.677
	TZ2p	1.901	2.322	2.474	2.678
	TZ1f	1.867	2.293	2.446	2.651
	TZ1p1f	1.874	2.298	2.452	2.655
	TZ2p1f	1.872	2.299	2.454	2.657
		ECP1−SPD			
RHF	TZ2p	1.891	2.333	2.484	2.713
	TZ2p1f	1.879	2.327	2.479	2.709
MP2	TZ2p	1.906	2.322	2.470	2.693
	TZ2p1f	1.885	2.302	2.450	2.673
		ECP2−SPD			
RHF	TZ2p	1.885	2.326	2.494	2.709
	TZ2p1f	1.868	2.313	2.484	2.702
MP2	TZ2p	1.895	2.313	2.478	2.691
	TZ2p1f	1.872	2.288	2.452	2.664
		exptl[a]			
		1.911	2.316	2.450	2.662

[a] Experimental distances taken from the Landolt−Börnstein compilations.[20−22]

is no significant difference in the errors for the two pseudopotential approaches.

The addition of a p polarization function to the MCP−SPD metal atom valence basis set results in an increased bond length by 0.005−0.020 Å. The addition of a second p polarization function to the metal basis set resulted in no significant change to the computed M−X distances when compared to those values obtained with a single p polarization function. On the other hand, the addition of an f polarization function to the MCP−SPD metal atom basis sets reduces the M−X bond length by 0.005 to 0.030 Å, indicating d orbital participation in the bonding between the metal and the halogen and thus the effectiveness of the f-type polarization functions. It must be remembered, however, that with the Cartesian Gaussian functions used in the present study, the addition of the 10-component 4f Gaussian implies the addition of a 4p polarization function as well. As shown in Table 5, the average errors in the bond lengths are not significantly improved by augmenting the metal atom basis set with polarization functions.

The results in Tables 3 and 4 (for ZrX_4 and HfX_4) show that the agreement with experiment improves as the MCP−SPD metal atom basis set is expanded from double-ζ to triple-ζ quality. However, the agreement with experiment for TiX_4 deteriorates as the Ti basis set is expanded, perhaps reflecting fortuitously accurate Ti−X distances when the double-ζ basis set is employed.

The partially filled d shells of the transition metal atom usually lead to several low-lying unoccupied molecular orbitals when ligands coordinate to the metal. The presence of these low-lying excited states requires that electron correlation effects be incorporated into the calculation, either via the wave function approach or via density functional theory.[32−35] For the ZrX_4 and HfX_4 systems we found better agreement between the MCP−SPD and experimental bond lengths when the MP2 method was utilized than when the RHF method was employed, in accord with expectations based on the all-electron calculations. However, the TiX_4 systems exhibit larger errors at the MP2 level than at the RHF level, perhaps again reflecting the accidentally accurate RHF Ti−X distances.

B. Energies of Dihalogen Substitution Reaction. To gauge the ability of the MCPs to model reactions of transition metal complexes, reaction energies, ΔE_{rxn}, were computed for a simple set of dihalogen substitution reactions of the type shown below

$$MX_4 + Y_2 \rightarrow MX_2Y_2 + X_2$$
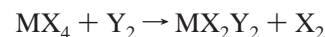
where M = Ti, Zr, or Hf and X, Y = Cl, Br, or I.

The computed bond lengths of the MX_2Y_2 complexes, as well as the dihalides, are shown in Tables 6 and 7. No experimental geometries could be found for the mixed halogen systems for comparison. The agreement between the ECP and MCP results for the halogens is very good (Table

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Table 5. Deviations (in Å) between the Calculated and Experimental Bond Lengths Averaged over All 12 MX_4 Complexes[a]

basis set (B)	$\sigma_{av}(r_e\text{:RHF }|B)^b$	$\sigma_{av}(r_e\text{:MP2 }|B)^b$
MCP−SPD		
DZ	0.023	0.016
DZ1f	0.020	0.015
DZ1p	0.030	0.021
DZ1p1f	0.023	0.016
TZ	0.025	0.019
TZ1p	0.026	0.019
TZ2p	0.026	0.019
TZ1f	0.026	0.025
TZ1p1f	0.026	0.022
TZ2p1f	0.025	0.021
ECP1−SPD		
TZ2p	0.025	0.018
TZ2p1f	0.023	0.012
ECP2−SPD		
TZ2p	0.027	0.012
TZ2p1f	0.025	0.019

[a] Experimental values taken from the Landolt−Börnstein compilation of structural data.[20−22]

$$^b\ \sigma_{av}(P{:}M/B) = \sum_{i=1}^{N} \frac{|P_i^{calc} - P_i^{exp}|}{N},$$

where r_e refers to the bond length, M = RHF or MP2, B is one of the pseudopotentials and corresponding basis sets in Table 1, and N is the number of molecules in the sample (in this case 12).

7). It may be noticed that the MP2 calculations yield bond lengths that are up to 0.05 Å too long, perhaps as the result of the missing core-valence correlation effects, absent in the pseudopotentials that utilize only the s and p valence electrons for the halogens.

The reaction energy, ΔE_{rxn}, was computed as the difference between the total energies of the products (MX_2Y_2 and X_2) and the reactants (MX_4 and Y_2), at their respective optimized geometries. Values of ΔE_{rxn} for all possible reactions involving TiX_4, ZrX_4, and HfX_4, computed using the MCP−SPD, ECP1−SPD, and ECP2−SPD pseudopotentials employing the TZ2p metal basis sets, are collected in Table 8.

At both the RHF and MP2 levels of theory, all of the pseudopotentials predict a negative ΔE_{rxn} value (i.e., the products are more stable than the reactants) for reactions in which the dihalide added, Y_2, is lighter than the one departing, X_2 (for example, $TiBr_4 + Cl_2$). This is in agreement with what one would expect on the basis of the experimental values of the average M−X bond enthalpies for the gas-phase MX_4 complexes. The general trend among the experimental average M−X bond enthalpies is M−Cl (Ti, 103; Zr, 117; Hf, 118 kcal/mol) > M−Br (Ti, 88; Zr, 101; Hf, 103 kcal/mol) > M−I (Ti, 71; Zr, 83; Hf, 86 kcal/mol).[36] The experimental dihalide bond dissociation energies vary as follows: Cl−Cl (58 kcal/mol) > Br−Br (46 kcal/mol) > I−I (36 kcal/mol).[37] The substitution reaction may be summarized as the breaking of two M−X bonds and a Y−Y bond coupled with the formation of two M−Y bonds and an X−X bond. Since two M−X bonds are broken and two M−Y bonds are formed while only a single X−X is broken and a single Y−Y bond is formed during the reaction, the metal−halogen bond strength will determine whether the product is favored or not with respect to the reactants. Thus, from the experimental bond enthalpies, the products will be favored when the halogen being added to the complex, Y,

Table 6. Bond Lengths (in Å) for the MX_2Y_2 Complexes[a]

	M−X		M−Y	
potential	RHF	MP2	RHF	MP2
$TiCl_2Br_2$				
MCP−SPD	2.159	2.157	2.329	2.313
ECP1−SPD	2.186	2.186	2.337	2.325
ECP2−SPD	2.153	2.162	2.322	2.323
$TiCl_2I_2$				
MCP−SPD	2.159	2.162	2.541	2.518
ECP1−SPD	2.183	2.190	2.570	2.548
ECP2−SPD	2.151	2.167	2.539	2.534
$TiBr_2I_2$				
MCP−SPD	2.325	2.320	2.538	2.520
ECP1−SPD	2.334	2.332	2.571	2.551
ECP2−SPD	2.318	2.334	2.536	2.539
$ZrCl_2Br_2$				
MCP−SPD	2.352	2.341	2.512	2.495
ECP1−SPD	2.351	2.341	2.503	2.488
ECP2−SPD	2.340	2.330	2.510	2.496
$ZrCl_2I_2$				
MCP−SPD	2.351	2.341	2.716	2.695
ECP1−SPD	2.347	2.340	2.735	2.710
ECP2−SPD	2.338	2.329	2.726	2.707
$ZrBr_2I_2$				
MCP−SPD	2.509	2.494	2.713	2.693
ECP1−SPD	2.407	2.485	2.733	2.709
ECP2−SPD	2.505	2.492	2.723	2.707
$HfCl_2Br_2$				
MCP−SPD	2.331	2.319	2.494	2.477
ECP1−SPD	2.332	2.321	2.484	2.471
ECP2−SPD	2.323	2.311	2.496	2.480
$HfCl_2I_2$				
MCP−SPD	2.330	2.318	2.703	2.682
ECP1−SPD	2.328	2.318	2.717	2.697
ECP2−SPD	2.321	2.310	2.715	2.694
$HfBr_2I_2$				
MCP−SPD	2.490	2.473	2.700	2.680
ECP1−SPD	2.479	2.466	2.716	2.697
ECP2−SPD	2.491	2.475	2.712	2.693

[a] The TZ2p basis set for each pseudopotential was employed in all of the calculations.

Table 7. Bond Lengths (in Å) for the Dihalides

	Cl_2		Br_2		I_2	
potential	RHF	MP2	RHF	MP2	RHF	MP2
MCP	2.015	2.040	2.301	2.324	2.701	2.728
ECP1	2.010	2.038	2.284	2.312	2.675	2.700
ECP2	2.005	2.028	2.315	2.335	2.687	2.708
exptl[a]	1.987		2.281		2.666	

[a] Experimental values taken from Huber and Herzberg.[38]

is lighter than the departing halogen, X, which our MCP and ECP calculations predict.

The ΔE_{rxn} values computed with the MCP−SPD potential tend to be smaller than those computed using the ECP−SPD potentials. Although a number of exceptions exist, the following trend for the magnitudes of the ΔE_{rxn} values was found: MCP−SPD < ECP1−SPD < ECP2−SPD. The lack of experimental thermodynamic data for these reactions precludes an assessment of the accuracy of the computed ΔE_{rxn} values. The variations among the ΔE_{rxn} values computed using the different pseudopotentials are usually small, on the order of 2−3 kcal/mol, but can be as large as 10 kcal/mol. The inclusion of correlation effects, at the MP2 level,

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Table 8. Computed ΔE_{rxn} Values (in kcal/mol) for the Dihalogen Substitution Reactions of MX$_4$[a]

method	Ti RHF	Ti MP2	Zr RHF	Zr MP2	Hf RHF	Hf MP2
			MCl$_4$ + Br$_2$			
MCP−SPD	20	16	18	16	19	17
ECP1−SPD	24	19	22	20	22	21
ECP2−SPD	30	23	27	24	29	26
			MCl$_4$ + I$_2$			
MCP−SPD	50	39	44	39	46	42
ECP1−SPD	52	40	49	43	50	45
ECP2−SPD	59	46	54	49	57	53
			MBr$_4$ + Cl$_2$			
MCP−SPD	−21	−15	−18	−15	−19	−16
ECP1−SPD	−24	−18	−22	−20	−23	−21
ECP2−SPD	−29	−22	−27	−24	−28	−26
			MBr$_4$ + I$_2$			
MCP−SPD	29	22	26	23	28	25
ECP1−SPD	29	21	27	22	28	24
ECP2−SPD	29	22	27	24	28	26
			MI$_4$ + Cl$_2$			
MCP−SPD	−50	−36	−44	−37	−47	−40
ECP1−SPD	−53	−37	−49	−41	−50	−44
ECP2−SPD	−59	−41	−54	−46	−57	−51
			MI$_4$ + Br$_2$			
MCP−SPD	−29	−21	−26	−22	−28	−24
ECP1−SPD	−29	−20	−27	−22	−28	−24
ECP2−SPD	−30	−21	−27	−23	−28	−25

[a] All ΔE_{rxn} values were computed using the TZ2p metal valence basis set.

results in a decrease in the magnitudes of the computed ΔE_{rxn} values, of about 5−10 kcal/mol, but may be as little as 1 kcal/mol or as large as 20 kcal/mol in some cases.

CONCLUSIONS

The results presented here clearly indicate that the MCP formalism (version 1) works well in modeling these small metal complexes, provided the outermost $(n − 1)$p shell is included in the valence space and treated explicitly. The MCP−SPD methodology typically predicts M−X bond distances to within 0.02−0.03 Å of their experimental values. There appears to be little difference between the accuracies of the bond lengths predicted by the MCP−SPD and the ECP−SPD pseudopotentials of Stevens et al. and Hay and Wadt.

Expanding the MCP−SPD metal atom basis set from double-ζ to triple-ζ quality improves the agreement between computed and experimental bond lengths for the ZrX$_4$ and HfX$_4$ systems, in accord with that expected for all-electron basis sets. However, for the TiX$_4$ systems expanding the Ti atom basis from double-ζ to triple-ζ worsens the agreement between calculated and experimental Ti−X distances. The addition of a 10-component f-type polarization function to the MCP−SPD metal atom valence basis set results in a significant shortening of the bond length, while the addition of a p-type polarization function has the opposite effect.

The inclusion of the electron correlation effects at the MP2 level significantly improves the accuracy of the Zr−X and Hf−X distances over their RHF-computed values, while the opposite trend was found for the Ti−X distances.

The SPD pseudopotentials predict that the direction of the set of dihalide substitution reactions studied is in accord with that expected on the basis of experimental measurements of the M−X and X−X bond strengths. In general, the ΔE_{rxn} values computed using the MCP−SPD potentials were smaller in magnitude than those computed using the ECP1−SPD and ECP2−SPD potentials. The inclusion of correlation effects, at the MP2 level, resulted in a substantial decrease in the magnitude of the reaction energy, by about 5−10 kcal/mol, regardless of the pseudopotential employed.

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CI0000474