

# Combined Pseudopotential and Density Functional Study of Bis- $\eta^6$ -benzene d and f Element Complexes<sup>†</sup>

Michael Dolg<sup>‡</sup>

Institut für Physikalische und Theoretische Chemie, Wegelerstrasse 12, D-53115 Bonn, Germany

Received June 5, 2000

The electronic and molecular structures of selected zerovalent d and f metal bis- $\eta^6$ -benzene sandwich complexes  $M(C_6H_6)_2$  ( $M = Sc, Ti, V, Cr, Y, Zr, Nb, Mo, La, Ce, Gd, Lu, Hf, Ta, Nb, Th$ ) were investigated at the scalar-relativistic level using a combination of energy-consistent ab initio pseudopotentials and gradient-corrected density functionals. The results are compared to previous pseudopotential coupled-cluster and all-electron density functional results based on the zero-order regular approximate Hamiltonian of Chang, Péliissier, and Durand as well as to experimental data.

## 1. INTRODUCTION

An unusual strong metal–arene bonding was observed by Skinner and Connor<sup>1</sup> as well as recently by King et al.<sup>2</sup> for bis- $\eta^6$ -arene sandwich complexes of group 3, 4, and 6 transition metals and a few lanthanides, e.g.,  $M(TTB)_2$  ( $TTB = 1,3,5-(C(CH_3)_3)_3C_6H_3$  or 1,3,5-tri-*tert*-butylbenzene). The measured bond disruption enthalpies range between 39 (Cr) and 73 (W) kcal/mol. Several experimentally still unobserved lanthanide (e.g., Ce, Tb) and actinide (e.g., Th, U) complexes were predicted to be stable. King et al.<sup>2</sup> and later Di Bella et al.<sup>3</sup> carried out scalar-relativistic pseudopotential (PP) Møller–Plesset second-order perturbation theory (MP2) and limited configuration interaction studies including single and double substitutions (CISD) for the group 4 and 6 closed-shell model complexes  $M(C_6H_6)_2$  ( $M = Ti, Zr, Hf; Cr, Mo, W$ ) as well as for the corresponding Y and Gd systems. The theoretical metal–ring binding energies obtained at the MP2 level were in much better agreement with the experimental values than the CISD results, most likely due to a fortunate error compensation of basis set limitations and overestimation of electron correlation effects by the MP2 approach.

Recently we published an ab initio scalar-relativistic PP investigation of group 3 and 4 transition metal, lanthanide, and actinide bis- $\eta^6$ -benzene complexes ( $M = Sc, Y, La; Ti, Zr, Hf; Ce, Nd, Gd, Tb, Lu; Th, U$ ) using besides MP2 the coupled-cluster approach with single, double, and perturbatively treated triple excitation operators (CCSD(T)).<sup>4</sup> Large valence basis sets were applied and MP2 was shown to overestimate significantly the metal–ring binding energy. A corresponding scalar-relativistic all-electron (AE) density functional (DFT) study was also performed.<sup>5</sup> The calculations were based on the zero-order regular approximation (ZORA)<sup>6</sup> for the one-particle Hamiltonian, i.e., the Chang–Péliissier–Durand Hamiltonian,<sup>7</sup> and the gradient-corrected exchange and correlation functionals of Becke<sup>8</sup> and Perdew<sup>9</sup> added to the local density approximation (LDA) with Slater (S) exchange and the Vosko–Wilk–Nusair (VWN) correlation

parametrization.<sup>10</sup> The results for the metal–ring binding energies obtained with these two approaches agreed within 10 kcal/mol; however, although the calculated values for Sc and the group 4 complexes were in accordance with experimental data and empirical estimates, large deviations occurred for Y, the lanthanide and actinide systems, with the theoretical values seemingly being much too low.

Lu and Le-Min Li<sup>11</sup> performed independently of our work an AE DFT investigation on the La, Gd, and Lu complexes including scalar-relativistic effects perturbatively. Their results for metal–ring binding energies were in quite good agreement with both our AE DFT and PP CCSD(T) values. Finally, Jun Li and Bursten<sup>12</sup> found in quasi-relativistic density functional studies that the bis- $\eta^6$ -benzene actinide complexes show significant benzene–metal–benzene bending.

The results published so far support the prediction by King et al.<sup>2</sup> that the actinide compounds should be thermodynamically stable with respect to a dissociation into the metal and the two benzene rings. However, all attempts to synthesize the Th and U systems, e.g., by a metal vapor technique, failed up to now: no evidence for  $U(C_6H_6)_2$  was found, and what was presumably  $Th(C_6H_6)_2$  decomposed above  $-50^\circ C$  and was therefore unisolable.<sup>13</sup>

The goal of the present paper is to combine the use of energy-consistent ab initio PPs and gradient-corrected DFT for the investigation of selected bis- $\eta^6$ -benzene complexes. Such an approach is already routinely used by several groups in computational chemistry and would be economically very attractive for the investigation of larger organometallic complexes. It should be noted, however, that the PPs applied here, and also in many other studies, were not adjusted to DFT reference data, but rather to Hartree–Fock (HF) data including relativistic corrections.

## 2. METHOD

The calculations reported here have been performed with the TURBOMOLE program system<sup>14</sup> of the Karlsruhe group using default sizes of the grids. Grids with higher accuracy lead to changes of the metal–ring binding energy of less

<sup>†</sup> Contribution for the ECP2000 symposium at the 219th National Meeting of the American Chemical Society, San Francisco, March 26–30, 2000.

<sup>‡</sup> E-mail: dolg@thch.uni-bonn.de. FAX: +49-228-73-9066.

than 1 kcal/mol for the hafnium complex. Scalar-relativistic energy-consistent *ab initio* PPs developed in the Stuttgart and Bonn groups<sup>15–20</sup> were used. Small-core PPs for the metal replacing 10 (Sc, Ti, V, Cr), 28 (Y, Zr, Nb, Mo), and 60 (La, Lu, Hf, Ta, W, Th) core electrons, respectively, were applied. For Ce and Gd PPs modeling essentially a fixed 4f occupation of 1 and 7, respectively, has been adopted.<sup>18,19</sup> Note, however, that due to small contributions of the 4f orbitals to chemical bonding, especially for the lighter 4f elements, it was necessary to modify the f projector of the semilocal PP ansatz.<sup>19</sup> The corresponding valence basis sets applied were (7s6p5d1f)/[5s4p3d1f] for the transition metals and lanthanides, (12s11p10d8f)/[9s8p7d5f] for Th, (11s6p1d)/[5s3p1d] for carbon, and (5s1p)/[3s1p] for hydrogen. Possible basis set errors have been investigated for the hafnium complex: additional diffuse functions or polarization functions increased the metal–ring binding energy by less than 3 kcal/mol.

On the basis of the previous investigations discussed above, the electronic ground states in  $D_{6h}$  symmetry result from filling the metal valence electrons into the  $e_{2g}$  and  $a_{1g}$  low-lying empty orbitals formed by the “bonding” linear combination of the unoccupied  $\pi_3$  and  $\pi_4$  orbitals of the two benzene rings. The following ground states were assumed:  $e_{2g}^3 {}^2E_{2g}$  (Sc, Y, La, Lu),  $e_{2g}^4 {}^1A_{1g}$  (Ti, Zr, Hf, Th),  $e_{2g}^4 a_{1g}^1$  (V, Nb, Ta), and  $e_{2g}^4 a_{1g}^1$  (Cr, Mo, W). For Ce and Gd the open, but viewed from its spatial extension rather corelike, 4f shell was assumed to be spherically symmetric and included into the pseudopotential core. In analogy to La and Lu the  $e_{2g}^3 {}^2E_{2g}$  valence substate was considered in the calculations of the Ce and Gd complexes. The calculations are a rigorous model for the concept of a “superconfiguration” introduced by Field<sup>21</sup> into molecular spectroscopy of lanthanide diatomics almost 20 years ago. Quantum chemical calculations on more than 100 lanthanide molecules demonstrate the reliability of this approach.<sup>22</sup>

The open-shell systems were treated using unrestricted Kohn–Sham DFT formalism. The gradient-corrected exchange and correlation functionals of Becke<sup>8</sup> and Perdew<sup>9</sup> were added to the LDA with Slater exchange and the VWN correlation energy parametrization of the homogeneous electron gas.<sup>10</sup> Complete geometry optimizations for the complexes were carried out in the  $D_{2h}$  (Sc, Y, La, Ce, Gd, Lu) and  $D_{6h}$  (Ti, Zr, Hf, Th, V, Nb, Ta, Cr, Mo, W) point groups. The usage of  $D_{2h}$  for the group 3 and lanthanide complexes was necessary since on one hand TURBOMOLE cannot handle symmetry-restricted Kohn–Sham DFT for degenerate ground states, and on the other hand the small (less than 3 kcal/mol change of the metal–ring binding energy) Jahn–Teller distortions reported in a previous article<sup>5</sup> have to be accounted for. Metal–ring bending was not considered, since for the systems investigated here it was found to occur only for the Th complex, where it led to changes of less than 3 kcal/mol of the metal–ring binding energy at the AE DFT and the PP MP2 and CCSD(T) levels of theory.<sup>5,12</sup>

### 3. RESULTS AND DISCUSSION

The qualitative aspects of metal–ring bonding in bis- $\eta^6$ -benzene complexes, possible effects of ring substitution on the metal–ring binding energies, and possible alternative

**Table 1.** Calculated C–C Bond Lengths and Metal–Benzene (M–b) Distances (Å) for Benzene (b) and Bis- $\eta^6$ -benzene Metal Complexes<sup>a</sup> M(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> of Group 3 and 4 Elements as Well as Selected Lanthanides and Th from Pseudopotential (PP) and All-electron (AE) Calculations

M	PP				AE ZORA	
	CCSD(T) <sup>b</sup>		DFT <sup>c</sup>		DFT <sup>d</sup>	
	C–C	M–b	C–C	M–b	C–C	M–b
b	1.420		1.399		1.399	
Sc	1.449	1.927	1.419	1.939	1.427	1.934
Y	1.448	2.169	1.419	2.162	1.427	2.151
La	1.442	2.468	1.416	2.420	1.423	2.421
Ce			1.417	2.380		
Gd			1.418	2.251		
Lu	1.452	2.073	1.421	2.061	1.431	2.028
Ti	1.451	1.728	1.430	1.742	1.429	1.753
Zr	1.452	1.975	1.432	1.960	1.432	1.953
Hf	1.456	1.959	1.435	1.935	1.435	1.882
Th	1.435	2.249	1.429	2.302	1.430	2.305

<sup>a</sup> The C–H distances are  $1.102 \pm 0.002$  Å (PP CCSD(T)),  $1.090 \pm 0.002$  Å (PP DFT), and  $1.088 \pm 0.002$  Å (AE ZORA DFT). The out-of-plane angle of the C–H bond with respect to the C–ring is between 0° and 3°, except for Ti, –2°. <sup>b</sup> Reference 4; the values for the Th complex are MP2 results; C–H distance 1.093 Å. <sup>c</sup> This work. <sup>d</sup> Reference 5.

**Table 2.** Calculated C–C Bond Lengths and Metal–Benzene (M–b) Distances (Å) for Bis- $\eta^6$ -benzene Metal Complexes<sup>a</sup> M(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> of Group 5 and 6 Elements from PP DFT Calculations

M	C–C	M–b
V	1.427	1.676
Nb	1.429	1.873
Ta	1.431	1.872
Cr	1.422	1.614
Mo	1.426	1.791
W	1.427	1.807

<sup>a</sup> The C–H distances are  $1.090 \pm 0.002$  Å. The out-of-plane angle of the C–H bond with respect to the C–ring is between 0° and –1° for Nb, Ta, Mo, and W and between –2° and –3° for V and Cr.

ground states have been extensively discussed in a previous paper.<sup>4</sup> The present contribution will merely focus on the performance of PP DFT studies in comparison to PP CCSD(T) and AE ZORA DFT results as well as experimental data.

The optimized structures of the bis- $\eta^6$ -benzene complexes are reported in Tables 1 and 2. The geometrical parameters for the group 3 and lanthanide complexes, which were calculated in  $D_{2h}$  symmetry, were averaged in order to make a comparison with previous data assuming a  $D_{6h}$  symmetry<sup>4,5</sup> possible. Note that in these previous calculations planar benzene ligands were assumed, partially with fixed C–C and C–H bond lengths, whereas in the current work a full structure optimization in  $D_{2h}$  or  $D_{6h}$  symmetry was performed. Since the out-of-plane angle of the C–H bond with respect to the plane formed by the C atoms is less than 3° for all cases, we would expect only small effects on the bond lengths reported in the previous papers. For all approaches the C–H bond lengths are identical with an accuracy of  $\pm 0.002$  Å for all complexes considered here. Therefore these data are not reported individually in Tables 1 and 2.

A comparison of the current PP DFT results for the group 3 and 4 elements, the lanthanides as well as Th, with those of previous investigations is made in Table 1. The metal–

**Table 3.** Calculated Averaged Metal–Ring Binding Energies (kcal/mol) of Bis- $\eta^6$ -benzene Metal Complexes from Pseudopotential (PP) and All-electron (AE) Calculations in Comparison to Experimental Data (exptl)<sup>1,2</sup> and Estimated Values (estd)<sup>2</sup>

M	PP		AE ZORA DFT <sup>c</sup>	exptl	estd
	CCSD(T) <sup>a</sup>	DFT <sup>b</sup>			
Sc	41.0	36.9	42.6	45	46
Y	49.7	36.3	39.0	72	66
La	37.9	34.2	35.3		69
Ce	35.8	36.4			72
Gd	32.5	32.4		68	69
Lu	32.5	28.6	34.4	62	67
Ti	53.3	48.2	63.8	49	49
Zr	70.5	55.8	66.5	64	65
Hf	69.4	48.6	60.8	67	66
Th	40.1	48.8	48.6		61
V		51.0			52
Nb		64.1		73	73
Ta		56.3			79
Cr	43.1	27.0		39	
Mo	72.4	49.1		59	
W	83.1	55.0		73	

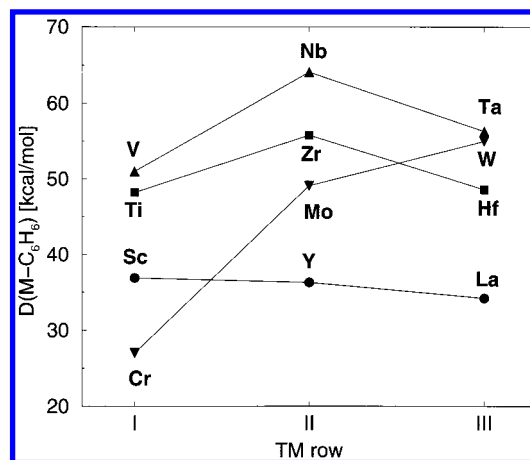
<sup>a</sup> Reference 4; preliminary data for Cr, Mo, and W from ref 28. <sup>b</sup> This work. <sup>c</sup> Reference 5.

ring distances (the term ring denotes the plane of the C atoms of a benzene ligand) as well as the C–C distances derived at the PP DFT and AE ZORA DFT levels agree within 0.01 Å, except for Lu and Hf, where the PP DFT metal–ring distances are 0.03 and 0.05 Å, respectively, larger than the corresponding AE ZORA DFT values. A possible reason for this might be static as well as dynamic polarization of the 4f<sup>14</sup> shell, which is missing in the present PP calculations. Recent studies on the Yb<sub>2</sub> dimer as well as the first and second ionization potentials of the whole lanthanide series demonstrate that the polarization of the 4f shell is indeed important and may be included by a core-polarization potential (CPP).<sup>23</sup> Unfortunately, this approach is currently not implemented in the TURBOMOLE program package.

The agreement with the PP CCSD(T) results is less good, but still acceptable. The C–C bond lengths derived at the CCSD(T) level are typically 0.02–0.03 Å longer than the PP DFT results. The deviation in the metal–ring distances shows no systematic pattern; the agreement is within 0.05 Å. We note that larger basis sets including several f and g functions on the metal had to be used for the PP CCSD(T) calculations in order to get converged results.

The results for the group 5 and 6 complexes summarized in Table 2 are predictions. The C–C distances are by about 0.02 Å shorter than for the group 3 and 4 complexes. The metal–ring distances monotonically decrease from the lighter to the heavier metal in each row and for the first two rows also within each group. Due to the lanthanide contraction the metal–ring distances in the pairs Zr–Hf, Nb–Ta, and Mo–W are almost identical, whereas the one of the La complex is 0.26 Å larger than for the Y complex. The large value of 0.26 Å for the lanthanide contraction derived from the metal–ring distances of the Lu and La systems is in agreement with a “soft” bond<sup>24</sup> and a small f orbital contribution to bonding.<sup>22</sup>

Table 3 summarizes the metal–ring binding energies, i.e., half of the energy necessary to dissociate the complex into the neutral atom and two benzene rings in the gas phase at



**Figure 1.** Metal–ring binding energies (kcal/mol) for selected bis- $\eta^6$ -benzene complexes from pseudopotential density functional calculations.

zero temperature. Solvent effects are estimated to contribute at most a few kcal/mol.<sup>2</sup> Figure 1 displays the trends within each group. For the group 3 and lanthanide systems the AE ZORA DFT values are systematically larger by 1–6 kcal/mol than the PP DFT results. The latter tend also to be smaller than the PP CCSD(T) values by about the same amount. The large PP CCSD(T) value of 50 kcal/mol for the Y complex is obtained in neither PP DFT (36 kcal/mol) nor AE ZORA DFT (39 kcal/mol) calculations; however, the experimental result (72 kcal/mol) and an empirical estimate (66 kcal/mol) point to even stronger metal–ring bonding. Aside from the reasonable agreement between theory and experiment for the Sc complex, the values calculated from experimental data as well as the empirical estimates are roughly a factor 2 (or typically 30 kcal/mol) larger than all values calculated with the three theoretical approaches.

The PP CCSD(T) binding energy of the group 4 complexes was found to be in excellent agreement with the experimental data; i.e., the theoretical values overestimate the experimental ones slightly by up to 7 kcal/mol. The AE ZORA DFT results show larger deviations ranging from an overestimation of 15 kcal/mol at Ti to an underestimation of 6 kcal/mol at Hf. The present PP DFT results are somewhat disappointing, too: although one observes excellent agreement for the Ti complex, the metal–ring binding energies of the Zr and Hf complexes are underestimated by 8 and 18 kcal/mol, respectively. It is noteworthy that both PP and AE ZORA DFT results qualitatively exhibit the same trend within group 4, i.e., similar values for Ti and Hf and a slightly larger value for Zr. The PP values are between 11 and 15 kcal/mol lower than the corresponding AE ZORA results. One possible reason may be suspected in the atomic calculations, where the AE ZORA calculations used spherical functions with a  $d_0^1 d_2^1$  configuration, whereas the present calculations applied Cartesian functions with a  $d_{z^2}^1 d_{x^2-y^2}^1$  configuration. The different shapes of  $d_2$  and  $d_{x^2-y^2}$  result in a different density and therefore in a different energy, which might explain part of the deviations. However, test calculations for various possible  $d^2$  configurations of Hf gave atomic energies differing by up to 5 kcal/mol; i.e., the effect on the metal–ring binding energies is probably 3 kcal/mol or less.

The case of the hafnium complex was considered in more detail. Extension of the basis sets on H, C, and Hf did not



increase the metal–ring binding energy by more than 2 kcal/mol. Therefore, various density functionals implemented in TURBOMOLE<sup>14</sup> were considered. The results discussed in the following always refer to the optimized structures of benzene and the bis- $\eta^6$ -benzene Hf complex in  $D_{6h}$  symmetry, as well as to the lowest energy determinant ( $5d_z^2$   $5d_{x^2-y^2}$   $6s^2$ ) which could be constructed for the ground-state configuration of the Hf atom. Substituting the gradient-corrected Perdew correlation energy functional<sup>9</sup> by the corresponding Lee–Yang–Parr (LYP)<sup>25</sup> functional reduces the metal–ring binding energy from 49 to 36 kcal/mol. Combining the Becke “half-and-half” exchange<sup>26</sup> with the Lee–Yang–Parr correlation energy functional yields 32 kcal/mol, whereas the semiempirical three-parameter B3LYP exchange and correlation energy functional proposed by Becke<sup>27</sup> yields 36 kcal/mol. Slater exchange together with the Becke gradient-corrected exchange functional and the LDA with the VWN parametrization for the correlation energy<sup>10</sup> leads to a value of 27 kcal/mol, whereas using the pure LDA with Slater exchange and the VWN correlation energy functional results in 73 kcal/mol. The presumably worst functional (S–VWN) yields the result closest to the experimental value of 67 kcal/mol<sup>2</sup> and the PP CCSD(T) result of 69 kcal/mol.<sup>4</sup> Since the TURBOMOLE program package does not allow for other functionals, further investigations were not possible. Whereas for the PP MP2, CCSD, and CCSD(T) calculations reported previously<sup>4</sup> it was possible to approach systematically the experimental values by increasing the basis set size and by improving the correlation treatment, such strategy is not possible within DFT.

In case of the Th complex the PP DFT and the AE ZORA DFT results are virtually identical. They are about 8 kcal/mol larger than the PP CCSD(T) value and 12 kcal/mol smaller than the empirical estimate of King et al.<sup>2</sup> All three theoretical approaches indicate that the yet experimentally unknown Th( $C_6H_6$ )<sub>2</sub> complex should be thermodynamically stable with respect to a dissociation onto the Th atom and two benzene rings.

The situation for the group 5 systems is very similar to the one for the group 4 complexes. The PP DFT metal–ring binding energy of the V complex is in excellent agreement with the empirical estimate;<sup>2</sup> however, the values for the Nb and Ta systems are too low by 9 and 23 kcal/mol, respectively. Unfortunately, no other theoretical results are available for comparison.

Finally, for the complexes of the group 6 metals Cr, Mo, and W, the calculated metal–ring binding energies at the PP DFT level are 12, 10, and 18 kcal/mol, respectively, too small when compared to the measured values. On the other hand, preliminary large-scale PP CCSD(T) values are 4, 13, and 10 kcal/mol larger than the experimental results.<sup>28</sup> The PPs used in both studies were identical.

#### 4. CONCLUSIONS

A combination of relativistic pseudopotentials and gradient-corrected density functionals has been applied to study

the structure of zerovalent bis- $\eta^6$ -benzene complexes of group 3–6 transition metals, selected lanthanides, and Th. The results for structures are in very good agreement with those of corresponding all-electron density functional calculations, whereas metal–ring binding energies agree less well. Pseudopotential density functional and coupled-cluster metal–ring binding energies are in reasonable agreement for the group 3 elements and the lanthanides, whereas for the second- and third-row group 4, 5 and 6 elements the density functional values are lower than the coupled-cluster values by up to 28 kcal/mol. Test calculations on the hafnium complex yielded very different results for various modern density functionals. Despite the differences all three approaches considered here indicate that the bis- $\eta^6$ -benzene complex of Th, and possibly also of those of the heavier actinides, should be thermodynamically stable.

#### ACKNOWLEDGMENT

Thanks are due to F. G. N. Cloke (Sussex) for several communications concerning the experimental work and to B. Bursten (Columbus) for providing his results prior to publication. The author is grateful to T. Cundari for the invitation to the ECP2000 symposium, where part of this work was presented.

#### REFERENCES AND NOTES

- (1) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, 57, 79.
- (2) King, W. A.; Di Bella, S.; Lanza, G.; Khan, K.; Duncalf, D. J.; Cloke, F. G. N.; Fragala, I. L.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, 118, 627.
- (3) Di Bella, S.; Lanza, G.; Fragala, I. L.; Marks, T. J. *Organometallics* **1996**, 15, 3985.
- (4) Hong, G.; Schautz, F.; Dolg, M. *J. Am. Chem. Soc.* **1999**, 121, 1502.
- (5) Hong, G.; Dolg, M.; Li, L. *Int. J. Quantum Chem.* **2000**, 80, 201.
- (6) van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J. Chem. Phys.* **1993**, 99, 4597.
- (7) Chang, C.; Péliissier, M.; Durand, P. *Phys. Scr.* **1986**, 34, 394.
- (8) Becke, A. D. *Phys. Rev. A* **1988**, 38, 3098.
- (9) Perdew, J. P. *Phys. Rev. B* **1986**, 33, 8822. Erratum. *Phys. Rev. B* **1986**, 34, 7406.
- (10) Vosko, S. J.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, 58, 1200.
- (11) Lu, H.; Li, L. *Theor. Chem. Acc.* **1999**, 102, 121.
- (12) Li, J.; Bursten, B. E. *J. Am. Chem. Soc.* **1999**, 121, 10243.
- (13) Cloke, F. G. N. Personal communications (May and July, 1999).
- (14) Ahlrichs, R.; et al. *TURBOMOLE*, Version 4 Lehrstuhl für Theoretische Chemie, Universität Karlsruhe, Germany, 1997.
- (15) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, 86, 866.
- (16) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, 77, 123.
- (17) Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1989**, 90, 1730.
- (18) Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* **1989**, 75, 173.
- (19) Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1993**, 85, 441.
- (20) Küchle, W.; Dolg, M.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1994**, 100, 7535.
- (21) Field, R. W. *Ber. Bunsen-Ges. Phys. Chem.* **1982**, 86, 771.
- (22) Dolg, M.; Stoll, H. In *Handbook on the Physics and Chemistry of Rare Earths*; Elsevier: Amsterdam, 1996; Vol. 22, Chapter 152, p 607.
- (23) Wang, Y.; Dolg, M. *Theor. Chem. Acc.* **1998**, 100, 124.
- (24) Wang, S. G.; Schwarz, W. H. E. *J. Phys. Chem.* **1995**, 99, 11687.
- (25) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, 37, 785.
- (26) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 1372.
- (27) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648.
- (28) Ermilov, A. Yu.; Nemukhin, A. V.; Dolg, M. To be published.

CI000050N