

# Ab Initio Study of Metal–Ring Bonding in the Bis( $\eta^6$ -benzene)lanthanide and -actinide Complexes $M(C_6H_6)_2$ ( $M = La, Ce, Nd, Gd, Tb, Lu, Th, U$ )

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**Abstract:** The zerovalent bis( $\eta^6$ -benzene) f-metal sandwich complexes  $M(C_6H_6)_2$  ( $M = La, Ce, Nd, Gd, Tb, Lu, Th, U$ ) were investigated with state-of-the-art quantum chemical ab initio approaches taking into account the effects of electron correlation and relativity. Ground state assignments, optimized metal–ring distances, symmetric metal–ring stretching frequencies, and metal–ring bonding energies are reported. The effects of ring substitution on the metal–ring binding energies are discussed. The complexes of Th and U are predicted to be at least as stable as the corresponding lanthanide systems and form possible synthetic targets. Whereas the lanthanide systems have a  $4f^n e_{2g}^3$  ground state configuration ( $n = 1, 3$  for Ce, Nd), the corresponding actinide compounds should possess, as a consequence of stronger relativistic effects, a  $5f^{n-1} e_{2g}^4$  ground state configuration, with a possible strong admixture of  $5f^{n-1} a_{1g}^2 e_{2g}^2$  ( $n = 1, 3$  for Th, U). The back-donation from the occupied metal  $d_{\pm 2}$  to the empty  $\pi$  orbitals of the benzene ligands is found to be the dominant bonding interaction. Whereas the lanthanide 4f orbitals are essentially localized on the metals and chemically inactive, the actinide 5f shell is partially delocalized and its  $f_{\pm 2}$  components may also take part in the back-donation.

## Introduction

The chemistry of lanthanides and actinides is a very fascinating and active area of research for both experimentalists<sup>1–6</sup> and theoreticians.<sup>7–10</sup> Among the organometallic f-element complexes, those with  $\eta^n$ - $C_nH_n$  ligands, or their hydrogen-substituted derivatives, have attracted much attention due to their highly symmetric structure and the possibility to investigate contributions of individual metal orbitals to metal–ring bonding.<sup>3,4,11–19</sup>

Although much progress has been made to explain the electronic structure and chemical bonding in these compounds on the basis of quantum chemical calculations, some findings are still surprising. Recently, over two decades after the first synthesis, the electronic structure of the ground state of cerocene  $Ce(C_8H_8)_2$ <sup>20</sup> has been revealed to correspond essentially to bis( $\eta^8$ -cyclooctatetraene)cerium(III), first by theoretical<sup>18</sup> and thereafter by experimental<sup>21</sup> investigations, in contrast to the originally expected cerium(IV) complex.

In this contribution, we are interested in the bis( $\eta^6$ -benzene)-lanthanide and -actinide systems  $M(C_6H_6)_2$  ( $M = La, Ce, Nd, Gd, Tb, Lu, Th, U$ ). These systems serve as models for the bis( $\eta^6$ -arene) rare earth metal complexes first synthesized and characterized about a decade ago.<sup>22</sup> Our motivation is the following: (1) In a recent paper, King et al.<sup>23</sup> reported a solution thermochemical investigation of ring-substituted group 3, lanthanide, group 4, and group 6 ( $\eta^6$ -1,3,5- $t$ -Bu<sub>3</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> sandwich complexes (TTB ligand) and derived averaged metal–ligand bond disruption enthalpies  $\bar{D}(M\text{--}arene)$ . It was observed that

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metal–arene bonding in the zerovalent group 3 (Sc, Y), lanthanide (Gd, Dy, Ho, Er), and group 4 (Ti, Zr, Hf) complexes is in no way unusually weak as might have been expected; i.e., bond disruption enthalpies between 45 (Sc) and 72 (Y) kcal/mol were measured. Other lanthanide systems (Ce, Nd) and the corresponding actinide systems (Th, U) were predicted to have similar stabilities (72, 57, 61, and 88 kcal/mol, respectively) by assuming a linear relationship between the sublimation enthalpies of the bulk metal and the bond disruption enthalpies for each group. In addition, a qualitative bonding picture of the closed-shell group 4 and group 6 transition metal complexes  $M(C_6H_6)_2$  ( $M = Ti, Zr, Hf; Cr, Mo, W$ ) based on quantum chemical ab initio calculations has been presented, completing previous considerations by Anderson et al.<sup>22</sup> for the corresponding lanthanide complexes. Later Di Bella et al.<sup>23</sup> extended the theoretical study to rare earth metal complexes  $M(C_6H_6)_2$  ( $M = Y, Gd$ ); however, whereas at the MP2 (Moeller–Plesset second-order perturbation theory) level the  $\bar{D}(M\text{–arene})$  values for the group 4 and 6 complexes were in quite good agreement with available experimental data, only about 50% of the experimental value was typically recovered for the rare earth metal systems. Similarly, in recent relativistic all-electron gradient-corrected density functional theory (DFT) calculations, Lu and Li<sup>19</sup> recovered only 40%–55% of the experimental values for selected lanthanide complexes ( $M = La, Ce, Gd, Lu$ ). Moreover, lanthanide systems predicted to be quite stable, e.g.,  $Ce(TTB)_2$ , were reported to be unisolable<sup>22</sup> and the corresponding actinide systems have been studied neither theoretically nor experimentally to our knowledge. Therefore, high-level ab initio calculations might be useful to obtain a better understanding of the electronic structure and chemical properties of this type of lanthanide and actinide system.<sup>5</sup> (2) Besides their interest in organometallic chemistry,  $Ln(C_6H_6)_2$  and  $An(C_6H_6)_2$  may also serve as the simplest possible model systems for investigating the electronic structure of lanthanide and actinide graphite intercalation compounds.<sup>24</sup> These are of great interest due to their layered, quasi-two-dimensional structure and the resulting large anisotropy of their electric and electronic properties.<sup>24</sup> Bis( $\eta^6$ -benzene) compounds may be a too simple model since graphite intercalation compounds are extended systems; however, detailed knowledge of the electronic structure of  $M(C_6H_6)_2$  will undoubtedly be a valuable first step for further investigations.<sup>25</sup> For example, a similar quantum chemical study of bis( $\eta^8$ -cyclooctatetraene)uranium(IV), uranocene, inspired a new model Hamiltonian for a U  $5f^2$  impurity in a solid leading to unusual low-energy physics.<sup>26,27</sup> (3) By comparing the results for the bis( $\eta^6$ -benzene) complexes of Ce, Nd, Th, and U, one can see the trends within and the differences between the lanthanide and actinide series and discuss them in the framework of relativistic effects, as was successfully done for the corresponding bis( $\eta^8$ -cyclooctatetraene) complexes.<sup>18,26</sup> The present contribution will address mainly general chemical trends; i.e., we will not attempt to calculate spectroscopic properties, for which an inclusion of spin–orbit effects is required. Special emphasis is put hereby on the complexes of Ce, Nd, Th, and U.

The questions to be answered by the present investigation thus are as follows: (1) Are bis( $\eta^6$ -arene)actinide complexes

thermodynamically stable as predicted by King et al.<sup>23</sup>? (2) Which are the electronic ground states and the corresponding electron configurations? (3) What is the main metal–ring bonding mechanism? E.g., what is the relative importance of 4f(5f) and 5d(6d) orbitals? How do relativity and electron correlation affect the results? (4) What changes are to be expected (a) by substituting the central metal by other lanthanides or actinides or (b) by substituting the ring hydrogens by other atoms or groups? (5) Are there characteristic differences for the complexes  $M(C_nH_n)_2$  between  $n = 6$  and  $n = 5, 7, 8$  due to the aromaticity and nonaromaticity, respectively, of the free ligands?

## Computational Details

Quantum chemical ab initio calculations of systems containing lanthanide (Ln) or actinide (An) elements encounter several difficulties; e.g., the large number of electrons and low-lying electronic states as well as non-negligible relativistic effects and significant electron correlation effects require a huge computational effort. The open-shell valence orbitals may extend over three main quantum numbers, i.e.,  $(n - 2)f(n - 1)d ns np$  ( $n = 6$  for Ln,  $n = 7$  for An). For accurate work, at least the  $(n - 1)s(n - 1)p$  semicore shells also have to be included in the valence space. Moreover, especially for actinides, it is also necessary to take into account near-degeneracies resulting from the closeness of the 5f, 6d, 7s, and 7p orbital energies.

Pseudopotentials as a practical and reliable quantum chemical method to overcome some of these difficulties have been developed in the Stuttgart and Dresden groups and are described in detail in previous publications.<sup>28</sup> In the following the method is only briefly summarized. Scalar-relativistic energy-consistent ab initio pseudopotentials treating the f shell explicitly with regard to valence were used to reduce the computational effort by the removal of chemically inactive core electrons and, even more important, to include implicitly the major relativistic effects in an efficient way. Small-core pseudopotentials for lanthanides (Ce, Nd) and actinides (Th, U) replacing 28 and 60 core electrons, respectively, were used to keep frozen-core errors at a minimum. For carbon, the  $1s^2$  core was replaced by a similar pseudopotential.<sup>29</sup> The corresponding valence basis sets applied were (12s11p9d8f)/[5s5p4d4f] with generalized contraction for lanthanides, (12s11p10d8f)/[8s7p6d4f] with segmented contraction for actinides, (5s5p)/[3s3p] for carbon, and (4s)/[2s] for hydrogen. A set of large-core PPs attributing the open lanthanide 4f shell to the inactive core<sup>30</sup> was applied together with (7s6p5d3f)/[5s4p3d3f] valence basis sets. The valence basis sets described so far (basis A) were augmented by three g functions for the metal as well as two d and two p functions for carbon and hydrogen, respectively (basis B).

State-averaged CASSCF (complete active space self-consistent field) calculations were carried out to account for near-degeneracies and to avoid symmetry-breaking problems for spatially degenerate ground states. MRCI (multireference configuration interaction) calculations including the Siegbahn size-extensivity correction (SCC)<sup>31</sup> were performed subsequently to treat dynamical electron correlation effects. The active space comprised 10 orbitals, i.e., formally the metal d orbitals and sd hybrid orbitals in the  $e_{2g}$  and  $a_{1g}$  symmetries, respectively, as well as the seven metal f orbitals. In order to estimate metal–ring binding energies, we also performed MP2 (Moeller–Plesset second-order perturbation theory) and CCSD(T) (singles and doubles coupled-cluster with a perturbative estimate of triples) calculations allowing excitations from all orbitals. In the case of spatially degenerate ground states, a symmetry-broken HF (Hartree–Fock) solution for one component was used as the zeroth-order wave function.

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**Table 1.** Mulliken Population on the Metal for the Most Important Fragment Orbitals Involved in Metal–Ring Bonding, Ligand-to-Metal Donation, and Metal–To-Ligand Back-Donation for the Ground States of  $M(C_6H_6)_2$  ( $M = Ti, Zr, Hf, Th, U, Sc, Y, La, Ce, Nd, Lu$ )<sup>a</sup>

MO	Sc	Y	La	Ce	Nd	Lu	character
e <sub>1u</sub>	0.026	0.048	0.078	0.086	0.076	0.042	$\pi_2 + p_x + p_y$
e <sub>1g</sub>	0.156	0.120	0.056	0.000	0.138	0.182	$\pi_2 + d_{xz} + d_{yz}$
a <sub>1g</sub>	0.014	0.030	0.026	0.040	0.045	0.072	$\pi_1 + d_z^2 + s$
a <sub>2u</sub>	0.049	0.054	0.116	0.112	0.086	0.057	$\pi_1 + p_z$
d	0.245	0.252	0.276	0.238	0.345	0.353	
a <sub>2u</sub>				0.965	0.806		f <sub>z</sub> <sup>3</sup>
b <sub>3u</sub>				0.000	0.244		f <sub>x</sub> <sup>3</sup> –3xy <sup>2</sup>
b <sub>2u</sub>				0.000	0.252		f <sub>3x</sub> <sup>2</sup> y–y <sup>3</sup>
e <sub>1u</sub>				0.000	0.316		f <sub>xz</sub> <sup>2</sup> + f <sub>yz</sub> <sup>2</sup>
e <sub>2u</sub>				0.030	1.376		f <sub>xyz</sub> + f <sub>z</sub> (x <sup>2</sup> –y <sup>2</sup> )
e <sub>2g</sub>	1.140	0.964	1.254	1.293	1.308	0.884	d <sub>xy</sub> + d <sub>x</sub> <sup>2</sup> –y <sup>2</sup> + $\pi_3$
a <sub>1g</sub>				0.076	0.056		d <sub>z</sub> <sup>2</sup> + s + $\sigma^*_{C-C}$
bd	1.860	2.036	1.746	1.636	1.642	2.116	
X → d <sup>3</sup>	96.5	83.7	35.5				

MO	Ti	Zr	Hf	Th	U	character
e <sub>1u</sub>	0.018	0.036	0.038	0.138	0.192	$\pi_2 + p_x + p_y$
e <sub>1g</sub>	0.225	0.192	0.188	0.118	0.212	$\pi_2 + d_{xz} + d_{yz}$
a <sub>1g</sub>	0.004	0.018	0.062	0.062	0.023	$\pi_1 + d_z^2 + s$
a <sub>2u</sub>	0.026	0.036	0.050	0.147	0.139	$\pi_1 + p_z$
d	0.273	0.282	0.338	0.465	0.566	
a <sub>2u</sub>					0.920	f <sub>z</sub> <sup>3</sup>
b <sub>3u</sub>					0.016	f <sub>x</sub> <sup>3</sup> –3xy <sup>2</sup>
b <sub>2u</sub>					0.019	f <sub>3x</sub> <sup>2</sup> y–y <sup>3</sup>
e <sub>1u</sub>					0.032	f <sub>xz</sub> <sup>2</sup> + f <sub>yz</sub> <sup>2</sup>
e <sub>2u</sub>					0.958	f <sub>xyz</sub> + f <sub>z</sub> (x <sup>2</sup> –y <sup>2</sup> )
e <sub>2g</sub>	1.886	1.730	1.490	1.654	1.626	d <sub>xy</sub> + d <sub>x</sub> <sup>2</sup> –y <sup>2</sup> + $\pi_3$
a <sub>1g</sub>				0.129	0.091	d <sub>z</sub> <sup>2</sup> + s + $\sigma^*_{C-C}$
bd	2.114	2.270	2.510	2.217	2.338	
X → d <sup>4</sup>	82.3	62.1		60.5		

<sup>a</sup> The entries under d and bd denote the total donation and back-donation, respectively. The MCSCF wave function was analyzed for the Th, U, Ce, and Nd complexes; the SCF wave function otherwise. Metal valence configurations formally occurring in the complex, i.e., d<sup>4</sup> (Ti, Zr, Hf, Th), f<sup>2</sup>d<sup>4</sup> (U), d<sup>3</sup> (Sc, Y, La, Lu), f<sup>1</sup>d<sup>3</sup> (Ce), and f<sup>3</sup>d<sup>3</sup> (Nd) were used to determine the metal fragment orbitals. Computational details will be presented elsewhere.<sup>25</sup> The experimental atomic excitation energies (kcal/mol)<sup>41–43</sup> from the ground state X to the lowest d<sup>4</sup> or d<sup>3</sup> valence state are also given.

Calculations were performed with the MOLPRO program system<sup>32,33</sup> in the  $D_{2h}$  point group; however, the  $D_{6h}$  symmetry of the sandwich complex was maintained throughout. The metal–ring distances were optimized at CASSCF, MRCI, and MP2 levels while the  $D_{6h}$  ring structure ( $R(C-C) = 1.40 \text{ \AA}$ , and  $R(C-H) = 1.10 \text{ \AA}$ ) was held fixed unless otherwise noted. Jahn–Teller distortions were investigated at the SCF level using the program system TURBOMOLE.<sup>34</sup>

## Results and Discussion

**1. Qualitative Aspects of Bonding.** The outer-shell electronic ground state configurations for the metals (M) studied here are as follows: La, 5d<sup>1</sup> 6s<sup>2</sup>; Ce, 4f<sup>1</sup> 5d<sup>1</sup> 6s<sup>2</sup>; Nd, 4f<sup>4</sup> 6s<sup>2</sup>; Gd, 4f<sup>7</sup> 5d<sup>1</sup> 6s<sup>2</sup>; Tb, 4f<sup>9</sup> 6s<sup>2</sup>; Lu, 4f<sup>14</sup> 5d<sup>1</sup> 6s<sup>2</sup>; Th, 6d<sup>2</sup> 7s<sup>2</sup>; U, 5f<sup>3</sup> 6d<sup>1</sup> 7s<sup>2</sup>. Under  $D_{6h}$  symmetry, the f representation reduces to a<sub>2u</sub>–(f<sub>0</sub>), b<sub>1u</sub>(f<sub>+3</sub>), b<sub>2u</sub>(f<sub>–3</sub>), e<sub>1u</sub>(f<sub>±1</sub>), and e<sub>2u</sub>(f<sub>±2</sub>), the d representation to a<sub>1g</sub>(d<sub>0</sub>), e<sub>1g</sub>(d<sub>±1</sub>), and e<sub>2g</sub>(d<sub>±2</sub>), the p representation to a<sub>2u</sub>(p<sub>0</sub>) and e<sub>1u</sub>(p<sub>±1</sub>), and the s representation to a<sub>1g</sub>. The six occupied (C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> ligand (L)  $\pi$  orbitals belong to the a<sub>1g</sub> and a<sub>2u</sub>( $\pi_1$ ), e<sub>1g</sub> and e<sub>1u</sub>( $\pi_2$ ) irreducible representations, whereas the corresponding unoccupied  $\pi$  orbitals transform according to the e<sub>2g</sub> and e<sub>2u</sub>( $\pi_3$ ), b<sub>1g</sub> and b<sub>2u</sub>( $\pi_4$ ) irreducible representations. The bonding of the group 4 (e<sub>2g</sub><sup>4</sup>, d<sup>4</sup> metal configuration) and group 6 (a<sub>1g</sub><sup>4</sup> e<sub>2g</sub><sup>4</sup>, d<sup>6</sup> metal configuration) transition metal M(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> com-

plexes has been described in terms of a relatively weak L → M donation, involving the filled benzene  $\pi$  orbitals ( $\pi_1$  and doubly degenerate  $\pi_2$  HOMO) and the empty metal-based d<sub>0</sub>, p<sub>0</sub> and d<sub>±1</sub>, p<sub>±1</sub> orbitals, and a strong M → L back-donation from the occupied metal-based d<sub>±2</sub> orbitals to the empty benzene  $\pi$  orbitals (doubly degenerate  $\pi_3$  LUMO and  $\pi_4$ ).<sup>23</sup> These ideas are supported by an analysis of the frontier orbitals (Table 1). In group 4, back-donation increases according to Ti < Zr < Hf, whereas the substantially weaker donation remains almost constant. For group 3 transition metals, lanthanides, and (heavier) actinides, the number of electrons in d valence orbitals is smaller and weaker back-donation and metal–ring bonding (e<sub>2g</sub><sup>3</sup>, d<sup>3</sup> metal configuration) result (Table 1). Back-donation increases similarly to that of group 4 in the order Sc < Y < Lu, and again, donation is less important. La appears to resemble Sc more than Lu. The lighter actinides like Th (e<sub>2g</sub><sup>4</sup>, d<sup>4</sup> metal configuration) and U (f<sup>2</sup>e<sub>2g</sub><sup>4</sup>, f<sup>2</sup>d<sup>4</sup> metal configuration) might behave similarly to group 4 transition metals. However, for lanthanides and actinides, partially occupied f valence orbitals are also available for metal–ring bonding and their role needs to be clarified. Since both metal d and f orbitals are only partially occupied for the cases studied here, the donation from the occupied ligand  $\pi$  orbitals to the empty d (a<sub>1g</sub>, e<sub>1g</sub>) and f (a<sub>2u</sub>, e<sub>1u</sub>) orbitals of the central metal and the back-donation from the occupied metal d (e<sub>2g</sub>) and f (b<sub>2u</sub>, e<sub>2u</sub>) orbitals to the unoccupied ligand  $\pi$  orbitals are possible in principle.

The outer-shell electronic configurations for the systems under investigation can in general be written as (a<sub>2u</sub>b<sub>1u</sub>b<sub>2u</sub>e<sub>1u</sub>e<sub>2u</sub>)<sup>m</sup>–(a<sub>1g</sub>e<sub>2g</sub>)<sup>k</sup>, e.g., with m + k = 4 for Ce(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> and Th(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>

(32) MOLPRO (Version 1996) is a package of ab initio programs written by H.-J. Werner, and P. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. M. Pitzer, A. J. Stone, and P. R. Taylor.

(33) Hampel, C.; Peterson, K.; Werner, H.-J. *Chem. Phys. Lett.* **1992**, *190*, 1–12.

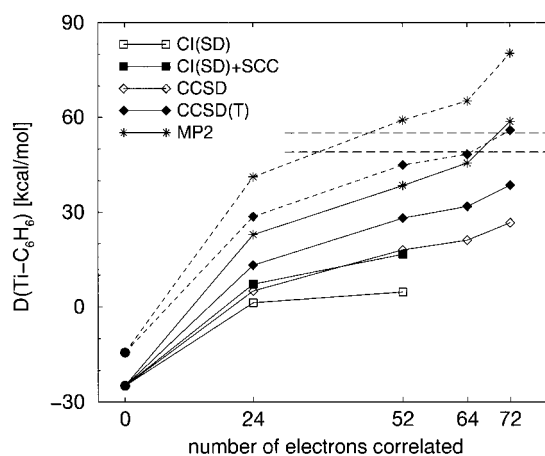
(34) TURBOMOLE ab initio program package: Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169.

and  $m + k = 6$  for  $\text{Nd}(\text{C}_6\text{H}_6)_2$  and  $\text{U}(\text{C}_6\text{H}_6)_2$ . Here the character of the gerade orbitals is similar to those of bis(arene) transition metal complexes; i.e.,  $a_{1g}$  denotes the hybrid of the metal-based  $ns_0$  and  $(n-1)d_0$  orbitals, whereas  $e_{2g}$  results from the interaction between the metal  $d_{\pm 2}$  and the ligand  $\pi_3$  orbitals. In case of the ungerade orbitals, the following two possibilities have to be considered. (1) For strong back-donation from occupied  $f$  orbitals to empty ligand orbitals, one has to consider only those  $f$  orbitals that can interact due to their symmetry, i.e.,  $(b_{2u}e_{2u})^m - (a_{1g}e_{2g})^k$ . A similar configuration would result for strong donation, since the empty  $f$  orbitals which can interact with the occupied ligand orbitals would be raised in energy. (2) In case of very weak donation and back-donation involving the  $f$  orbitals, the  $(n-2)f$  orbitals stay atomic-like; i.e., they are only weakly split by the interaction with the ligands and the possible occupations of the  $f$  shell may give rise to a large number of low-lying electronic states. In this case, one must take all  $f$  orbitals into account and the situation is best described in terms of the superconfiguration model<sup>35</sup> as  $(n-2)f^m(a_{1g}e_{2g})^k$ .

Besides symmetry constraints for orbital interaction, radial extension and energetic aspects determine the degree to which individual orbitals take part in metal–ring bonding. For Ce and Nd, the  $4f$  shell is corelike, both spatially and energetically, whereas for Th and U, the still rather compact  $5f$  shell is energetically almost degenerate with the valence  $6d$  and  $7s$  orbitals (cf. Figures 1–3 in ref 36). From these considerations and from experimental and theoretical investigations of bis(cyclooctatetraene)lanthanide and -actinide complexes, one might expect that the hypothetical  $\text{An}(\text{C}_6\text{H}_6)_2$  derivatives belong to group (1), whereas the experimentally known derivatives of  $\text{Ln}(\text{C}_6\text{H}_6)_2$  rather fall into group (2). The ab initio study of  $\text{Gd}(\text{C}_6\text{H}_6)_2$  by Di Bella et al.<sup>23</sup> confirmed the chemically inert character of the  $\text{Gd } 4f^7$  subshell; nevertheless, additional investigations are needed to explore whether these assumptions are true in general.

**2. Calibration Calculations for  $\text{Ti}(\text{C}_6\text{H}_6)_2$ .** To calibrate our methods, we performed test calculations for the metal–ring binding energy  $\bar{D}$  of  $\text{Ti}(\text{C}_6\text{H}_6)_2$ , which was treated previously by King et al.<sup>23</sup> A relativistic small-core pseudopotential replacing  $1s^2 2s^2 2p^6$  of Ti was applied together with a  $(8s7p6d1f)/[6s5p3d1f]$  valence basis set.<sup>37</sup> The C  $1s^2$  shell was also replaced by a relativistic pseudopotential, and  $(5s5p)/[3s3p]$  and  $(4s)/[2s]$  valence basis sets (basis A) were used for C and H, respectively. The geometrical parameters were taken from King et al. ( $D_{6h}$  symmetry with planar rings;  $R(\text{Ti}-\text{C}_6\text{H}_6) = 2.305$  Å,  $R(\text{C}-\text{C}) = 1.424$  Å,  $R(\text{C}-\text{H}) = 1.068$  Å), and neither geometrical relaxation nor basis set superposition effects were considered.  $\text{Ti}(\text{C}_6\text{H}_6)_2$  appears to be an ideal model system for our goal because, on one hand, the  $[\text{Ar}] 3d^2 4s^2$   $^3F$  ground state of Ti corresponds formally to the  $[\text{Rn}] 6d^2 7s^2$   $^3F$  ground state of Th and similar bonding characteristics of  $\text{Ti}(\text{C}_6\text{H}_6)_2$  and  $\text{Th}(\text{C}_6\text{H}_6)_2$  may be expected and, on the other hand, sufficient experimental information is available for bis(arene)titanium sandwich complexes.<sup>23</sup>

Our results are displayed in Figure 1. The HF (Hartree–Fock) and MP2 (Moeller–Plesset second-order perturbation theory) values for the averaged metal–ring binding energy  $\bar{D}$  of  $-\text{24.8}$  and  $58.7$  kcal/mol, respectively, are in excellent agreement with those of King et al.<sup>23</sup> ( $-\text{26.3}$  and  $58.1$  kcal/mol). The closeness



**Figure 1.** Averaged metal–ring binding energies  $\bar{D}$  (kcal/mol) of  $\text{Ti}(\text{C}_6\text{H}_6)_2$  calculated with different methods. The solid lines refer to the small basis set (A) results; the dashed lines refer to the extended basis set (B) MP2 results or CCSD(T) estimates (cf. text). The long-dashed horizontal line corresponds to the experimental results for  $\text{Ti}(\text{C}_6\text{H}_5\text{Me})_2$  and  $\text{Ti}(\text{TTB})_2$ .<sup>23</sup>

of the MP2 values to the experimental binding energies of related systems (55 kcal/mol for  $\text{Ti}(\text{C}_6\text{H}_5\text{Me})_2$ , 49 kcal/mol for  $\text{Ti}(\text{TTB})_2$ ) however appears to be quite fortuitous, since the present best CCSD(T) (coupled-cluster with single and double excitations and a perturbative estimate of triple excitations) result corresponds only to 70% of the experimental value; i.e., the CCSD(T) correlation contribution to the metal–ring binding energy is 76% of the MP2 value. Triple excitations in CCSD(T) (not contained in MP2) hereby amount to almost 20% of the CCSD(T) correlation contribution. The results are also highly dependent on the number of core orbitals, as is demonstrated at the MP2 level: if the full MP2 correlation contribution is taken to be 100%, one recovers only 84%, 76%, and 57% when freezing 4, 10, and 24 core orbitals, respectively. It is noteworthy that 16% of the correlation contribution stems from the correlation of the Ti  $3s^2 3p^6$  semicore shell and the associated core–valence correlation. Finally, the non-size-extensive CI method, although including the Siegbahn correction and calculating the binding energy with respect to the fragments at large distance, recovers even less correlation contribution than CCSD(T), i.e., 50% in case of 10 inactive orbitals.

The dilemma of ab initio methods becomes especially apparent when the basis sets are increased by two additional  $f$  functions on Ti, two  $d$  functions on C, and two  $p$  functions on H and only SCF and MP2 calculations are still feasible. The SCF and MP2 metal–ring binding energies of  $-\text{14.3}$  kcal/mol and  $80.3$  kcal/mol, respectively, are substantially increased and the latter result overshoots the experimental value by more than 25 kcal/mol (cf. Figure 1).

**3. Large Basis Set Coupled-Cluster Estimates.** Single-point CCSD(T) calculations using the small basis sets described above require 0.5 and 3.5 CPU days on a 80 Mflop workstation for the group 4 and 3 transition metal complexes, respectively. Calculations for lanthanide and actinide complexes demand even more computational resources due to the larger basis sets and higher number of unpaired electrons; i.e., some approximate scheme to obtain large basis set CCSD(T) results has to be applied.

On the basis of the observation that for  $\bar{D}$  of  $\text{Ti}(\text{C}_6\text{H}_6)_2$  the ratio between the MP2 correlation contributions with the small and large basis sets is 0.86–0.88 and the ratio between the CCSD and MP2 correlation contributions with the small basis set is 0.62–0.67, a simple scaling procedure may be applied to

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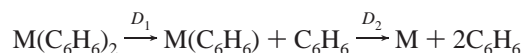
(36) Dolg, M. In *Encyclopedia of Computational Chemistry*; Allinger, N. L., Clark, T., Gasteiger, J., Kollmann, P. A., Schaefer, H. F., III, Eds.; Wiley: New York, 1998; Vol. 2; pp 1478–1486.

(37) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866–872.

estimate a CCSD(T) metal–ring binding energy  $\bar{D}$ (CCSD(T) large) for the large basis set:

$$\bar{D}(\text{CCSD(T) large}) = \bar{D}(\text{SCF large}) + \Delta\bar{D}(\text{T small}) + \Delta\bar{D}(\text{CCSD small}) \times \Delta\bar{D}(\text{MP2 large})/\Delta\bar{D}(\text{MP2 small})$$

Here  $\bar{D}$  denotes the metal–ring binding energy at the level of theory given in parentheses, whereas  $\Delta\bar{D}$  are the correlation contributions to it. We do not scale the contribution of the unlinked triples  $\Delta\bar{D}(\text{T small})$ , since these are not accounted for by MP2. Our estimate for  $\bar{D}(\text{CCSD(T) large})$  of 55.9 kcal/mol is in excellent agreement with the experimental values (55 kcal/mol for  $\text{Ti}(\text{C}_6\text{H}_5\text{Me})_2$ , 49 kcal/mol for  $\text{Ti}(\text{TTB})_2$ ; cf. Figure 1). A similar good agreement is obtained for the heavier homologues  $\text{Zr}(\text{C}_6\text{H}_6)_2$  (67.3 kcal/mol, exp 64 kcal/mol for  $\text{Zr}(\text{TTB})_2$ ) and  $\text{Hf}(\text{C}_6\text{H}_6)_2$  (64.7 kcal/mol, exp 67 kcal/mol for  $\text{Hf}(\text{TTB})_2$ ).<sup>25</sup> Unfortunately, upon adding three g functions to the metal basis set, we obtain estimated CCSD(T)  $\bar{D}$  values of 61.4, 71.1, and 69.0 kcal/mol for Ti, Zr, and Hf, respectively, in less favorable agreement with experiment. Moreover, the application of the scaling procedure to the individual steps of the reaction



does not yield values consistent with  $\bar{D} = (D_1 + D_2)/2$ . Instead of scaling the correlation contributions, we therefore propose to scale the correlation energies  $\Delta E_c$  of the complexes and their fragments itself according to

$$E(\text{CCSD(T) large}) = E(\text{SCF large}) + \Delta E_c(\text{CCSD(T) small}) \times \Delta E_c(\text{MP2 large})/\Delta E_c(\text{MP2 small})$$

The estimated CCSD(T)  $\bar{D}$  values for Ti, Zr, and Hf are now 50.4, 66.8, and 65.1 kcal/mol, respectively, in excellent agreement with the available experimental data. Possible reasons for minor deviations, e.g., structural relaxation or ring substitution effects, will be discussed later.

The problems involved in accurately calculating metal–ring binding energies of transition metal sandwich complexes with ab initio methods are well-known and have been extensively discussed in the literature, e.g., in case of ferrocene,  $\text{Fe}(\text{C}_5\text{H}_5)_2$ .<sup>38</sup> Results comparable in accuracy to those of the best ab initio approaches have been reported for gradient-corrected relativistic density functional theory (DFT),<sup>39</sup> and it might be tempting to apply this computationally efficient method. Unfortunately, in case of the lanthanide and actinide systems studied here, single-reference-based approaches like MP2, CCSD(T), or DFT might provide only a first approximation and multireference techniques like CASSCF + MRCI should be applied instead: in a valence CASSCF for the  $(a_{1g}e_{2g})^4$  case, the  $(e_{2g})^4$  configuration contributes with 94%, 98%, 99%, and 63% for the Ti, Zr, Hf, and Th compounds, respectively, demonstrating the multireference character of the latter system. However, due to the higher complexity of the problem in the presence of an open f shell, a restricted active orbital space must be used in such CASSCF + MRCI studies, resulting in relatively small binding energies which do not allow a discussion of thermodynamical stabilities. Therefore we base the major part of our study on MP2 and CCSD(T) and use CASSCF + MRCI merely to check if this approach is really appropriate.

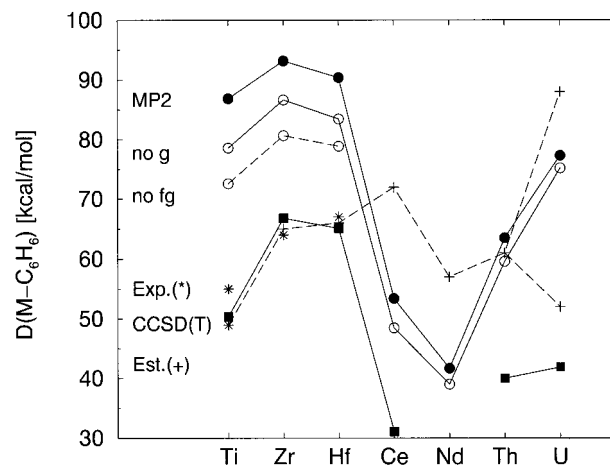
(38) Klopper, W.; Lüthi, H. P. *Chem. Phys. Lett.* **1996**, 262, 546–552 and references cited therein.

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**Table 2.** Metal–Ring Distances (Å)  $d_1$  for  $\text{M}(\text{C}_6\text{H}_6)_2$  and  $d_2$  for  $\text{M}(\text{C}_6\text{H}_6)$ , Benzene Binding Energies (kcal/mol)  $D_1$  for the First Ligand of  $\text{M}(\text{C}_6\text{H}_6)_2$  and  $D_2$  for  $\text{M}(\text{C}_6\text{H}_6)$ , and Vibrational Frequencies ( $\text{cm}^{-1}$ )  $\omega_1$  for the Totally Symmetric Metal–Ligand Stretching Motion in  $\text{M}(\text{C}_6\text{H}_6)_2$  and  $\omega_2$  for the Metal–Ligand Stretching Motion in  $\text{M}(\text{C}_6\text{H}_6)$

$M^a$	MP2						CCSD(T)	
	$d_1$	$d_2$	$D_1$	$D_2$	$\omega_1$	$\omega_2$	$D_1$	$D_2$
Sc <sup>b</sup>	1.861	1.907	82.4	43.7	254	382	52.8	23.9
Y <sup>b</sup>	2.072	2.025	66.6	69.7	253	358	48.4	46.3
La <sup>b</sup>	2.338	2.283	50.3	60.9	227	290	34.5	35.4
Ce <sup>b</sup>	2.310	2.262	53.0	59.5	231	292	37.3	34.2
Nd <sup>b</sup>	2.259	2.222	55.1	36.7	235	292	37.9	11.2
Gd <sup>b</sup>	2.170	2.150	58.5	49.6	244	293	40.7	24.2
Tb <sup>b</sup>	2.148	2.132	58.7	47.3	245	293	40.4	21.8
Lu <sup>b</sup>	2.041	2.040	61.8	41.9	254	298	42.0	15.8
Ti <sup>c</sup>	1.694	1.605	121.3	52.5	283	499	90.0	10.8
Zr <sup>c</sup>	1.894	1.750	113.5	72.9	293	446	85.0	48.5
Hf <sup>d</sup>	1.881	1.837	111.2	66.6	300	358	82.3	47.9
Th <sup>c</sup>	2.265	2.158	70.4	56.5	268	316	42.3	37.8
U <sup>e</sup>	2.090	1.934	78.9	75.7	281	381	39.9	43.8

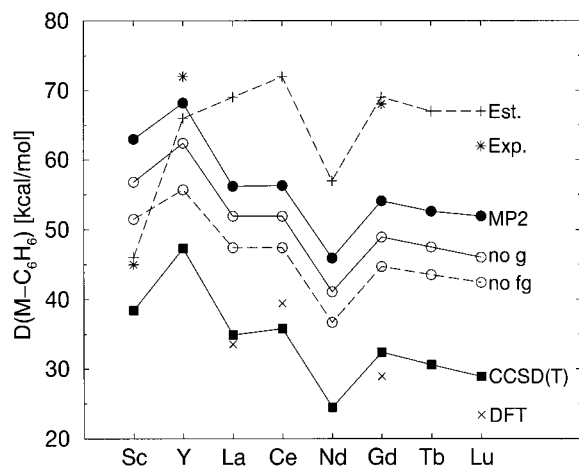
<sup>a</sup> The labels in footnotes *b–e* denote ground substrates for Ce, Nd, Gd, and Tb and ground states otherwise. <sup>b</sup>  $\text{M}(\text{C}_6\text{H}_6)_2$ ,  $^2E_{2g}$ ;  $\text{M}(\text{C}_6\text{H}_6)$ ,  $^4A_{1g}$ . <sup>c</sup>  $\text{M}(\text{C}_6\text{H}_6)_2$ ,  $^1A_{1g}$ ;  $\text{M}(\text{C}_6\text{H}_6)$ ,  $^3E_2$ . <sup>d</sup>  $\text{M}(\text{C}_6\text{H}_6)_2$ ,  $^1A_{1g}$ ;  $\text{M}(\text{C}_6\text{H}_6)$ ,  $^1A_{1g}$ . <sup>e</sup>  $\text{M}(\text{C}_6\text{H}_6)_2$ ,  $^3A_{2g}$ ;  $\text{M}(\text{C}_6\text{H}_6)$ ,  $^3A_1$ .



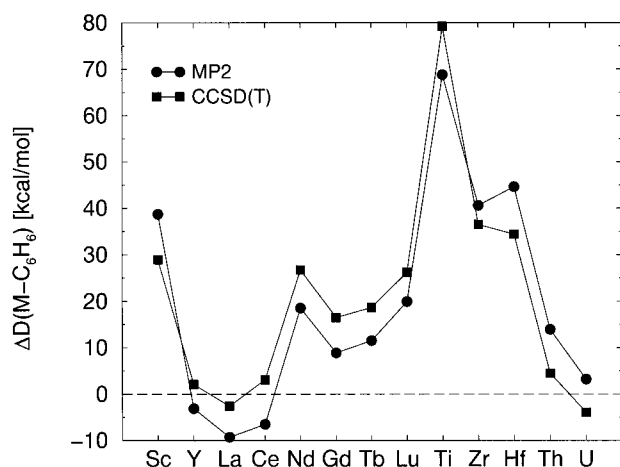
**Figure 2.** Averaged metal–ring binding energies  $\bar{D}$ (kcal/mol) of various bis(arene) complexes with four-valence-electron central metals from MP2 and CCSD(T) calculations (basis B; *no g* and *no fg* denote the neglect of g respectively f and g functions on the metal). The estimated and experimental values are from King et al.<sup>23</sup> The Ce and Nd 4f shells have been treated explicitly.

**4. General Trends.** The general trends in metal–ring distances, metal–ring binding energies, and metal–ring stretching frequencies are summarized in Table 2 and Figures 2–4. The MP2 results are for the largest basis set (basis B), and the corresponding CCSD(T) values have been obtained by the scaling procedure of the correlation energy outlined previously for  $\text{Ti}(\text{C}_6\text{H}_6)_2$ . The electronic states of  $\text{M}(\text{C}_6\text{H}_6)_2$  considered are  $e_{2g}^4$   $^1A_{1g}$  for Ti, Zr, Hf, and Th,  $e_{2g}^3$   $^2E_{2g}$  for Sc, Y, La, and Lu, and  $5f^2e_{2g}^4$   $^3E_{2g}$  for U. In case of the lanthanides, the large-core pseudopotentials attributing the 4f shell to the core were used, unless otherwise noted, and the results for Ce, Nd, Gd, and Tb correspond to the  $^2E_{2g}$  valence substate of the  $4f^n e_{2g}^3$  ( $n = 1, 3, 7, 8$ ) superconfiguration.

Before comparing the metal–ring binding energies  $\bar{D}$  to the experimental values or the corresponding estimates, we want to point out that, in all cases, a significant binding is only achieved by electron correlation effects; i.e., the calculated SCF values  $\bar{D}$  (basis B) are usually close to zero (Sc  $-6.1$ , Y  $3.1$ , La  $5.8$ , Ce  $5.3$ , Nd  $-5.7$ , Gd  $0.6$ , Tb  $-0.3$ , Lu  $-2.7$ , Ti  $-16.9$ ,



**Figure 3.** As Figure 2, but for three-valence-electron central metals. The results for the lanthanides were obtained with pseudopotentials by treating the 4f shell as part of the core. The DFT results were taken from Lu and Li.<sup>19</sup>



**Figure 4.** Differences  $\Delta D$  (kcal/mol) of the metal–ring binding energies  $D_1(M-C_6H_6)$  and  $D_2(M-C_6H_6)$  for the rupture of the first and second benzene rings from the complexes  $M(C_6H_6)_2$  with three- and four-valence-electron central atoms.

Zr 12.5, Hf 7.8, Th 4.1, U –12.4 kcal/mol). Large contributions of higher angular momentum functions have been detected at the MP2 level; i.e., d and p polarization functions on C and H increase  $\bar{D}$  by 15–30 kcal/mol and f and g functions on the central metal are of equal importance and further increase  $\bar{D}$  by about 5 kcal/mol each (Figures 2 and 3). Although our calculations are at the limit of what is currently feasible with the hardware at our disposal (size of integral files up to 25 GB, up to  $10^7$  configuration state functions at the CCSD or MP2 level) and of better quality than those of previous investigations, we have to keep in mind in the following discussion that we have probably still not arrived at the basis set limit.

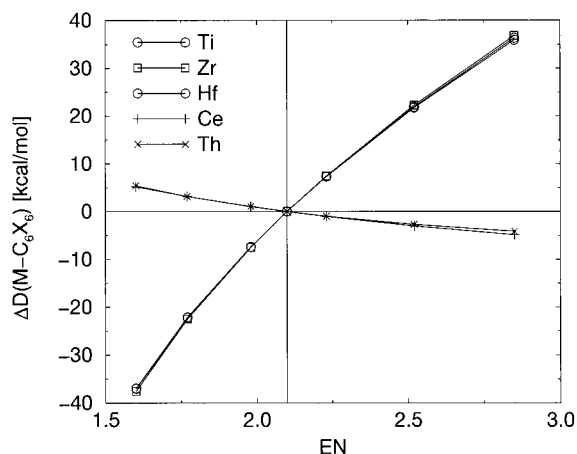
The CCSD(T)  $\bar{D}$  values for the Ti, Zr, and Hf systems are in excellent agreement with the available experimental data (Figure 3), whereas the value for the Th complex is about 20 kcal/mol below the estimate given by King et al.<sup>23</sup> on the basis of the analogy of Th to Ti, Zr, and Hf. The Th system appears to resemble much more the corresponding Ce complex than the group 4 complexes. A similar conclusion results from the discussion of ring substitution effects in the next section. The data given for the U complex should be viewed with some care because, as it will be explained in more detail below, the ground state assignment is not definite. It should be noted, however, that the calculated CCSD(T) value  $\bar{D}(U-C_6H_6)$  is probably a

lower limit for the actual value. In case of Sc, Y, Gd, and Lu, our CCSD(T)  $\bar{D}$  values are only in reasonable agreement with the experimental result for Sc, whereas they are about 25–35 kcal/mol too low for Y, Gd, and Lu (Figure 2). Nevertheless, the calculated values follow quite closely the trend of the estimates given by King et al.<sup>23</sup> for the lanthanide series. Replacing for La and Lu the MP2 treatment by a CASPT2 treatment (second-order perturbation theory based on a CASSCF zeroth-order wave function) with three active electrons in the valence  $e_{2g}$  and  $e_{2u}$  (benzene  $\pi_3$ ) orbitals (basis B), we obtained changes of 0.4 and –0.1 kcal/mol in  $\bar{D}$ . Similarly, treating three active electrons in the valence  $a_{1g}$ ,  $e_{1g}$ , and  $e_{2g}$  (metal d) orbitals (basis B) increases  $\bar{D}$  by only 0.4 and 0.0 kcal/mol. Since the contribution of the reference wave function is between 92% and 98% in all cases, we conclude that the disagreement is not due to a multireference character as was speculated in case of Y and Gd by Di Bella et al.<sup>23</sup> Adding to basis B further diffuse s and p functions for C as well as diffuse p and d functions for La and Lu leads to changes of less than 1 kcal/mol in  $\bar{D}$ . Since, according to our experience, a failure of the applied pseudopotentials is rather unlikely, the only remaining source of error could be an incompleteness in the metal f and g and C d and f basis sets. After completion of the calculations reported here, we became aware of a recent relativistic DFT study on selected lanthanide complexes<sup>19</sup> which reported similarly low  $\bar{D}$  values (cf. Figure 2).

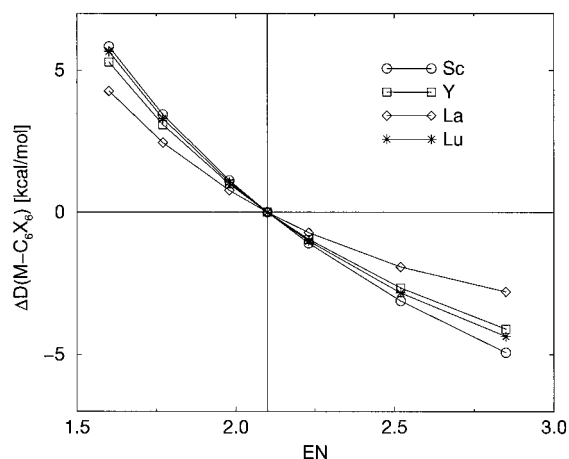
In Figure 4, the difference of the individual metal–ring binding energies  $D_1$  and  $D_2$  is displayed. With the exception of Y, La, and Ce, the removal of the first benzene ligand from the sandwich complex is more difficult than that of the second. It is noteworthy that  $D_1$  is lowest for La and Ce, a fact which might help to explain the experimentally observed instability of the corresponding  $M(TTB)_2$  complexes.<sup>22</sup>

**5. Ring Substitution Effects.** We estimate the influence of substituting the benzene hydrogens by other functional groups in the following way: An attractive (more electronegative substituents) and a repulsive (less electronegative substituents) local pseudopotential of Gaussian form was added to each hydrogen center. The potential was chosen in such a way that the electronegativity, assumed to be proportional to the sum of the ionization potential and the electron affinity according to the Mulliken formula ( $EN = \text{const} \times (IP + EA)$ ), ranges between 1.60 and 2.85 when the value for hydrogen is set to 2.10 per definition. We calculated the metal–ring binding energies of  $M(C_6X_6)_2$  ( $M = \text{Sc, Y, La, Lu, Ti, Zr, Hf, Ce, Th}$ ) at the MP2 level (basis A). The derived changes  $\Delta\bar{D}(M-C_6X_6)$  of the averaged metal–ring binding energies with respect to the unsubstituted systems are displayed in Figures 5 and 6. Electronegative substituents strongly stabilize bis(arene)titanium, -zirconium, and -hafnium complexes, probably by an enhancement of the back-donation from the metal d orbitals to the empty ring  $\pi$  orbitals. This is in agreement with experimental evidence, i.e., the marked increase in  $\bar{D}(M-C_6X_6)$  of 6 kcal/mol upon going from  $Ti(TTB)_2$  to  $Ti(C_6H_5Me)_2$ .<sup>23</sup> The influence of ring hydrogen substitution is less pronounced and is of opposite direction for the other systems; in particular, although Ce and Th formally have four valence electrons, their behavior resembles much more that of Sc and Y.

Our investigation of ring substitution effects accounts only for the “electronic” contributions, not the so-called “steric” ones. Note, however, that neglecting the latter cannot explain the significant underestimation of metal–ring binding energies for the Y and lanthanide complexes.



**Figure 5.** Changes  $\Delta\bar{D}(M-C_6X_6)$  (kcal/mol) of the MP2 metal–ring binding energies of bis(arene) complexes with four-valence-electron central metals upon substitution of H by a pseudoatom X with electronegativity EN (basis A). The EN of H is set to 2.1.



**Figure 6.** As Figure 5, but for three-valence-electron central metals.

**6. Geometrical Relaxation.** All calculations reported so far were performed by imposing  $D_{6h}$  symmetry and a fixed planar ring geometry ( $R(C-C) = 1.40 \text{ \AA}$ ,  $R(C-H) = 1.10 \text{ \AA}$ ). Optimization of the C–C, C–H, and M–B (B: benzene center) distances at the MP2 level (basis B) for  $La(C_6H_6)_2 \ ^2E_{2g}$  ( $R(C-C) = 1.428 \text{ \AA}$ ,  $R(C-H) = 1.095 \text{ \AA}$ ,  $R(La-B) = 2.326 \text{ \AA}$ ) and  $Lu(C_6H_6)_2 \ ^2E_{2g}$  ( $R(C-C) = 1.433 \text{ \AA}$ ,  $R(C-H) = 1.093 \text{ \AA}$ ,  $R(Lu-B) = 2.025 \text{ \AA}$ ) leads to an increase of 3.4 and 3.7 kcal/mol in  $\bar{D}$ , respectively. The corresponding values for  $Th(C_6H_6)_2 \ ^1A_{1g}$  ( $R(C-C) = 1.435 \text{ \AA}$ ,  $R(C-H) = 1.094 \text{ \AA}$ ,  $R(Th-B) = 2.249 \text{ \AA}$ ) and  $U(C_6H_6)_2 \ ^3E_{2g}$  ( $R(C-C) = 1.435 \text{ \AA}$ ,  $R(C-H) = 1.094 \text{ \AA}$ ,  $R(U-B) = 2.071 \text{ \AA}$ ) are 3.9 and 4.1 kcal/mol, respectively. In optimizations for the free benzene ligand ( $R(C-C) = 1.400 \text{ \AA}$ ,  $R(C-H) = 1.090 \text{ \AA}$ ), a relaxation effect in  $\bar{D}$  of  $-0.2$  kcal/mol was found.

The complexes  $M(C_6H_6)_2$  ( $M = Sc, Y, La, Lu$ ) appear to have  $^2E_{2g}$  ground states in  $D_{6h}$  symmetry. According to the Jahn–Teller theorem, at least one of the  $D_{2h}$  components  $^2A_g$  and  $^2B_{1g}$  should possess no minimum at the  $^2E_{2g}$  ground state equilibrium geometry in  $D_{6h}$ . We therefore investigated the possible Jahn–Teller distortions at the SCF level (basis A) for  $La(C_6H_6)_2$  and  $Lu(C_6H_6)_2$ . All four  $D_{6h}$  and ten  $D_{2h}$  respective internal degrees of freedom were optimized (Table 3) with the TURBOMOLE program package.<sup>34</sup> The Jahn–Teller distortion leads to an increase in  $\bar{D}$  of 1.5 and 2.6 kcal/mol for the  $^2B_{1g}$  state of the La and Lu compounds, respectively. The corresponding values for the  $^2A_g$  state are 1.4 and 2.2 kcal/mol. On

the basis of these test calculations, we suppose that our calculated  $\bar{D}$  values are probably too small by about 5 kcal/mol; i.e., geometrical relaxation of the  $D_{6h}$  symmetry with planar rings and fixed C–C and C–H bond lengths cannot explain the discrepancies between the theoretical results and the experimental values or estimates.

**7.  $Ce(C_6H_6)_2$ .** The relative SCF energies of the highest possible multiplicity states for the most probable electronic configurations allowing a significant back-donation from the metal 4f and 5d shells to the ligand  $\pi_3$  LUMOs, i.e.,  $(e_{2u}a_{1g}e_{2g})^4$ , are displayed in Figure 7. It can be seen that the energetically lowest states of the  $e_{2u}^0(a_{1g}e_{2g})^4$  and  $e_{2u}^2(a_{1g}e_{2g})^2$  configurations are higher in energy than the that of  $e_{2u}^1(a_{1g}e_{2g})^3$  by about 3 eV or more and can be excluded from the list of possible ground state configurations. A Mulliken population analysis of the  $e_{2u}^1(a_{1g}e_{2g})^3$  superconfiguration shows that more than 99% of the occupied component of the  $e_{2u}$  orbital is a Ce 4f<sub>±2</sub> orbital. With respect to the 4f occupation of cerium, we find  $Ce(C_6H_6)_2$  to be similar to  $Ce(C_8H_8)_2$ ,<sup>18</sup> and therefore only the  $4f^1(a_{1g}e_{2g})^3$  superconfiguration<sup>35</sup> was considered subsequently.

The  $(a_{1g}e_{2g})^3$  subconfiguration gives rise to the substates  $^4A_{2g}$ ,  $^2A_{1g}$ ,  $^2A_{2g}$ , and three times  $^2E_{2g}$ . The  $4f^1 \ ^2F$  substate reduces to  $^2A_{2u}$ ,  $^2B_{1u}$ ,  $^2B_{2u}$ ,  $^2E_{1u}$ , and  $^2E_{2u}$ . The formation of the direct product between both sets of substates yields 5 quintet, 42 triplet, and 37 singlet states in  $D_{6h}$  symmetry, i.e., a too large number of states to be investigated individually. To determine the  $Ce(C_6H_6)_2$  ground state, we performed for each spin multiplicity CASSCF calculations with a state average, in which only states arising from a coupling of the  $^4A_{2g}$  substate and the lowest  $^2E_{2g}$  substate to the  $^2F$  substate were considered, i.e., 5 quintet, 9 triplet, and 9 singlet states. Our motivation is that  $e_{2g}^3 \ ^2E_{2g}$  and  $a_{1g}e_{2g}^2 \ ^4A_{2g}$  are the states of lowest energy for the complexes of Sc, Y, La, and Lu.<sup>25</sup> It is seen from Figure 8 that the quintet states have similar potential curves and follow well the superconfiguration model, whereas this is not the case for the energetically higher triplet and singlet states. The  $^5A_{1u}$  state is 0.29 and 0.57 eV below the lowest triplet ( $^3E_{1u}$ ) and singlet ( $^1E_{2u}$ ) states, respectively.  $Ce(C_6H_6)_2$  is in this respect completely different from  $Ce(C_8H_8)_2$ , where, due to the mixture of 80%  $4f^1(e_{2u})^3$  and 20%  $(e_{2u})^4$ , a ground state with the lowest possible spin multiplicity ( $^1A_{1g}$ ) but significant open-shell character was found.<sup>18</sup> The main reason is that, for  $Ce(C_6H_6)_2$ , it is not possible to construct an ungerade parity state from the  $4f^0(a_{1g}e_{2g})^4$  and  $4f^2(a_{1g}e_{2g})^2$  superconfigurations which could mix with a low-spin state of the ground state  $4f^1(a_{1g}e_{2g})^3$  superconfiguration.

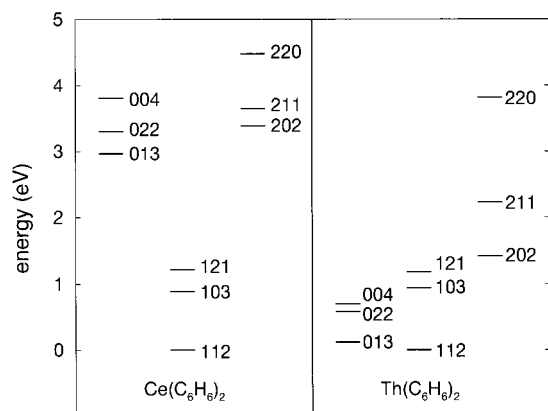
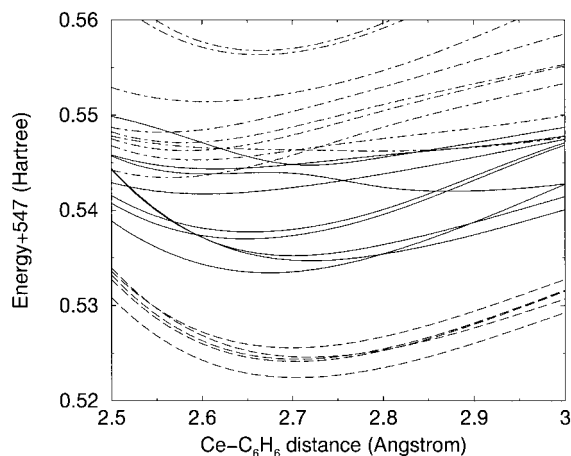
The Ce–ring distance was optimized in state-averaged CASSCF and subsequent valence MRCI calculations (basis A) for the lowest quintet ( $^5A_{1u}$ ) and triplet ( $^3E_{2u}$ ) states, and the corresponding totally symmetric stretching vibrational frequencies were derived (Table 4). Although the quintet–triplet splitting is reduced by dynamical correlation, the  $^5A_{1u}$  state remains 0.20 eV below the  $^3E_{2u}$  state. Using single-reference correlation approaches and correlating all electrons (basis B), we find the  $^3E_{1u}$  state 0.13 eV (0.25 eV) below the  $^5A_{1u}$  state at the MP2 (CCSD(T)) level (basis B) (Table 4). The metal–ring binding energies at the SCF, MP2, and CCSD(T) levels (basis B) are 3.1, 53.4, and 31.1 kcal/mol for the  $^3E_{2u}$  state as well as 9.7, 51.9, and 25.5 kcal/mol for the  $^5A_{1u}$  state. These values are all significantly lower than the estimate of 72 kcal/mol given by King et al.<sup>23</sup>

The main metal–ring bonding interaction arises, as also previously discussed for the transition metal compounds by King et al.,<sup>23</sup> from the rather strong back-donation of the occupied metal  $d_{±2}$  orbitals to the unoccupied  $\pi_3$  orbitals of the rings

**Table 3.** Interatomic Distances (Å) and Out-of-Plane Angle of the C–H Bond for  $M(C_6H_6)_2$  ( $M = La, Lu$ ) from SCF Calculations (Basis A) in  $D_{6h}$  ( ${}^2E_{2g}$  State) and  $D_{2h}$  ( ${}^2A_g$  and  ${}^2B_{1g}$  States) Symmetries<sup>a</sup>

	La( $C_6H_6$ ) <sub>2</sub>			Lu( $C_6H_6$ ) <sub>2</sub>		
	${}^2E_{2g}$	${}^2B_{1g}$	${}^2A_g$	${}^2E_{2g}$	${}^2B_{1g}$	${}^2A_g$
M–C	2.626	2.645, 2.594	2.616, 2.654	2.406	2.434, 2.356	2.390, 2.444
C–C	1.429	1.435, 1.414	1.421, 1.441	1.433	1.436, 1.416	1.423, 1.443
C–H	1.086	1.086, 1.084	1.085, 1.087	1.087	1.087, 1.084	1.085, 1.088
H–H	2.515	2.527, 2.483	2.500, 2.537	2.519	2.534, 2.472	2.499, 2.544
oop <sup>b</sup>	0.5	1.3, 1.9	0.5, 1.0	0.6	2.1, 2.1	1.8, 1.6

<sup>a</sup> The weight factor for the given data in the latter cases is 4:2. <sup>b</sup> oop: out-of-plane angle C(1)–C(4)–H(4) minus 180°.

**Figure 7.** Low-lying electronic states for the  $e_{2u}^i a_{1g}^j e_{2g}^k$  ( $i + j + k = 4$ ) configurations of  $Ce(C_6H_6)_2$  and  $Th(C_6H_6)_2$  from spin- and symmetry-restricted SCF calculations at metal–ring distances of 2.646 and 2.540 Å, respectively (basis A). The states are labeled by  $ijk$ . The full state labels in the  $D_{6h}$  point group are 022  ${}^3A_{2g}$ , 013  ${}^3E_{2g}$ , 004  ${}^1A_{1g}$ , 121  ${}^3A_{1u}$ , 112  ${}^5E_{2u}$ , 103  ${}^3A_{1u}$ , 220  ${}^3A_{2g}$ , 211  ${}^5E_{2g}$ , and 202  ${}^5A_{1g}$ .**Figure 8.** Potential energy curves for low-lying states of  $Ce(C_6H_6)_2$  from state-averaged CASSCF calculations: long-dashed lines, quintet states; solid lines, triplet states; dot-dashed lines, singlet states. The energetic order of the quintet states at 2.7 Å is  ${}^5A_{1u} < {}^5B_{1u} < {}^5B_{2u} < {}^5E_{1u} < {}^5E_{2u}$ . The lowest triplet and singlet states are  ${}^3E_{2u}$  and  ${}^1E_{2u}$ , respectively.

and, to a lesser extent, from the relatively weak donation effects of  $\pi_1$  to  $d_0 + s_0, p_0$  and of  $\pi_2$  to  $d_{\pm 1}, p_{\pm 1}$  (Table 1). The Ce 4f orbitals are almost completely localized on the metal (99.5% in  $e_{1u}$ , 99.6% in  $e_{2u}$ , and 100.0% in  $a_{1u}, b_{1u}$ , and  $b_{2u}$  from a Mulliken population analysis) and do not contribute to metal–ring bonding, whereas the  $e_{2g}$  orbitals have about 60% Ce  $d_{\pm 2}$  and 40% benzene  $\pi_3$  character. Although Ce formally has four valence electrons, only three of them contribute to metal–ring bonding, making the system similar to  $Sc(C_6H_6)_2$  and  $Y(C_6H_6)_2$ ; i.e., the 4f<sup>1</sup> subconfiguration of Ce can safely be included in the pseudopotential core. Within this approximation, we cal-

**Table 4.** Relative Energies, Optimized Metal–Ring Distances  $d_c$  (Å), and Vibrational Frequencies  $\omega_c$  ( $cm^{-1}$ ) of the Symmetric Metal–Ring Stretching Mode for  $M(C_6H_6)_2$  ( $M = Ce, Th$ )

method	$Ce(C_6H_6)_2$				$Th(C_6H_6)_2$			
	state	$T_c$	$d_c$	$\omega_c$	state	$T_c$	$d_c$	$\omega_c$
CASSCF <sup>a</sup>	${}^5A_{1u}$	0.000	2.705	114	${}^3E_{2g}$	0.000	2.548	180
	${}^3E_{2u}$	0.299	2.675	121	${}^1A_{1g}$	0.060	2.536	138
MRCI <sup>a</sup>	${}^5A_{1u}$	0.000	2.658	129	${}^3E_{2g}$	0.000	2.535	187
	${}^3E_{2u}$	0.215	2.626	105	${}^1A_{1g}$	−0.006	2.500	142
MRCI + SCC <sup>a</sup>	${}^5A_{1u}$	0.000	2.656	130	${}^3E_{2g}$	0.000	2.537	186
	${}^3E_{2u}$	0.196	2.636	108	${}^1A_{1g}$	−0.016	2.502	136
SCF <sup>b</sup>	${}^5A_{1u}$	0.000	2.573	213	${}^3E_{2g}$	0.000	2.516	176
	${}^3E_{2u}$	0.579	2.469	208	${}^1A_{1g}$	0.356	2.395	227
MP2 <sup>b</sup>	${}^5A_{1u}$	0.000	2.382	197	${}^3E_{2g}$	0.000	2.340	249
	${}^3E_{2u}$	−0.128	2.297	233	${}^1A_{1g}$	−0.207	2.265	268
CCSD(T) <sup>b</sup>	${}^5A_{1u}$	0.000			${}^3E_{2g}$	0.000		
	${}^3E_{2u}$	−0.252			${}^1A_{1g}$	−0.528		

<sup>a</sup> Basis A; only valence correlation. <sup>b</sup> Basis B; all electrons correlated.

culate at the SCF, MP2, and CCSD(T) levels (basis B) for the  ${}^2E_{2g}$  valence substate metal–ring binding energies of 5.3, 56.3, and 35.8 kcal/mol, respectively. The corresponding values for the  ${}^4A_{2g}$  valence substate are 12.1, 54.0, and 30.2 kcal/mol. These results agree very well with those for an explicit treatment of the Ce 4f shell and therefore further add credibility to the application of the superconfiguration concept in pseudopotential calculations for other lanthanide systems.

The question of the  $Ce(C_6H_6)_2$  ground state cannot be solved definitely by the present calculations; nevertheless, we suggest that the  ${}^3E_{2u}$  state should be the ground state. The MP2 and CCSD(T) metal–ring binding energies are considerably lower than the corresponding values for  $Ti(C_6H_6)_2$   ${}^1A_{1g}$  (−19.4, 86.9, and 47.1 kcal/mol) and comparable to those derived for  $Sc(C_6H_6)_2$   ${}^2E_{2g}$  (−9.2, 63.0, and 38.4 kcal/mol).<sup>25</sup>

**8.  $Nd(C_6H_6)_2$ .** Taking into account the corelike behavior of the 4f orbitals in  $Ce(C_6H_6)_2$  and their increasing core character along the lanthanide series, the superconfiguration model should be even more appropriate for  $Nd(C_6H_6)_2$ . Nevertheless, this complex is much more challenging for an ab initio treatment than  $Ce(C_6H_6)_2$ : because of the presence of two additional valence electrons, a huge number of low-lying near-degenerate electronic states result from the partially occupied 4f shell. To determine the 4f occupation on Nd, three possible low-energy superconfigurations  $4f^4(a_{1g}e_{2g})^2$ ,  $4f^3(a_{1g}e_{2g})^3$ , and  $4f^2(a_{1g}e_{2g})^4$  were investigated in state-averaged CASSCF calculations (basis A) for all possible spin multiplicities. It was found that the energetically lowest septet state ( ${}^7E_{1u}$ ) arising from  $4f^3(a_{1g}e_{2g})^3$  is lower in energy by 0.57 eV than the corresponding quintet state ( ${}^5E_{1u}$ ). It is 1.44 eV below the energetically lowest quintet state ( ${}^5E_{2g}$ ) arising from  $4f^4(a_{1g}e_{2g})^2$ , as well as 1.88 and 2.05 eV, respectively, below the energetically lowest quintet ( ${}^5E_{1g}$ ) and triplet ( ${}^3E_{1g}$ ) states arising from  $4f^2(a_{1g}e_{2g})^4$ . We therefore assign  $4f^3e_{2g}^3$  or  $4f^3a_{1g}^1e_{2g}^2$  as the ground state superconfiguration of  $Nd(C_6H_6)_2$  and postulate that, similar to the case of the Ce compound with its  $4f^1e_{2g}^3$  or  $4f^1a_{1g}^1e_{2g}^2$  ground state super-



**Table 5.** Term Energies (eV) for the Low-Lying Septet States of Nd(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> and U(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> from State-Averaged CASSCF Calculations for the f<sup>3</sup>(a<sub>1g</sub>e<sub>2g</sub>)<sup>3</sup> Superconfiguration (Basis A)<sup>a</sup>

spatial symmetry		Nd(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>	U(C <sub>6</sub> H <sub>6</sub> ) <sub>2</sub>
D <sub>6h</sub>	D <sub>2h</sub>		
A <sub>2u</sub>	B <sub>1u</sub>	0.017	0.000
E <sub>1u</sub>	B <sub>2u</sub> + B <sub>3u</sub>	0.000	0.015
E <sub>1u</sub>	B <sub>2u</sub> + B <sub>3u</sub>	0.020	0.056
A <sub>1u</sub>	A <sub>u</sub>	0.048	0.135
A <sub>2u</sub>	B <sub>1u</sub>	0.048	0.135
E <sub>2u</sub>	A <sub>u</sub> + B <sub>1u</sub>	0.010	0.140
E <sub>2u</sub>	A <sub>u</sub> + B <sub>1u</sub>	0.025	0.173
B <sub>2u</sub>	B <sub>2u</sub>	0.022	0.188
B <sub>1u</sub>	B <sub>3u</sub>	0.025	0.221

<sup>a</sup> Metal–ring distances are 2.646 and 2.540 Å for the Nd and U complexes, respectively. The corresponding lowest state CASSCF (valence MRCI + SCC) equilibrium distances are 2.652 (2.603) and 2.633 (2.525) Å.

configuration, only three valence electrons of the central Nd metal contribute to metal–ring bonding. The results of a Mulliken population analysis of the partially occupied orbitals of a state-averaged CASSCF calculation for all possible 4f<sup>3</sup>-(a<sub>1g</sub>e<sub>2g</sub>)<sup>3</sup> septet states show that the 4f orbitals are perfectly localized on the metal (99.8% in e<sub>1u</sub> and 100% in a<sub>2u</sub>, e<sub>2u</sub>, and e<sub>3u</sub>). Due to their almost negligible mixing with the ligand orbitals and the small splitting by the ligand field, the 4f orbitals are energetically nearly degenerate and a high density of states results already at low energies as is illustrated by the term energies of the lowest septet states summarized in Table 5. A detailed study of the low-energy spectrum and a definite ground state assignment certainly require the inclusion of dynamical correlation effects and simultaneously of spin–orbit coupling; i.e., the entries in Table 5 should merely be considered for a comparison of orbital localization and delocalization effects in Nd(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> with those in U(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>.

The metal–ring bonding in Nd(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> is—quite similar to that in the Ce compound—mainly due to the strong back-donation from the occupied Nd d<sub>±2</sub> orbitals to the empty π<sub>3</sub> orbitals of the rings and the weaker donation from π<sub>1</sub> to d<sub>0</sub> + s<sub>0</sub>, p<sub>0</sub> and from π<sub>2</sub> to d<sub>±1</sub>, p<sub>±1</sub>. However, in case of Nd, a promotion from the 4f<sup>4</sup>6s<sup>2</sup> ground state configuration to the formal 4f<sup>3</sup>e<sub>2g</sub><sup>3</sup> superconfiguration in the metal must be taken into account; i.e., the dissociation energy for Nd(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> should be lower than that for Ce(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>. This argument is in line both with the result of King et al.,<sup>23</sup> who estimated the metal–benzene bond enthalpy to be 72 and 57 kcal/mol for Ce(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> and Nd(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>, respectively, and with our MP2 and CCSD(T) results (Figure 3). Using similar arguments for the other lanthanide elements, a sawtooth behavior of the metal–ring binding energy with maxima at La, Gd, and Lu as well as minima at Eu and Yb is to be expected.<sup>23</sup> Attributing the Nd 4f<sup>3</sup> subshell to the pseudopotential core, we calculate at the SCF, MP2, and CCSD(T) levels (basis B) for the <sup>2</sup>E<sub>2g</sub> valence substate metal–ring binding energies of −5.7, 45.9, and 24.5 kcal/mol, respectively. For the <sup>4</sup>A<sub>2g</sub> valence substate, we obtain −5.3, 43.4, and 19.0 kcal/mol. Unfortunately, CCSD(T) calculations with an explicit treatment of the 4f shell are plagued by convergence problems. For the <sup>5</sup>E<sub>2u</sub> state (corresponding to the <sup>2</sup>E<sub>2g</sub> valence substate), we calculate an MP2 value of 41.6 kcal/mol (basis B).

**9. Th(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>.** The possible low-energy configurations of Th(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> are compared to the corresponding ones of Ce(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> in Figure 7. In contrast to the lanthanide system, the lowest states of e<sub>2u</sub><sup>1</sup>a<sub>1g</sub><sup>2</sup>e<sub>2g</sub><sup>2</sup> and a<sub>1g</sub><sup>1</sup>e<sub>2g</sub><sup>3</sup> are nearly degenerate at the HF level, and a definite decision about the ground state of the

actinide system requires a more sophisticated treatment. Looking merely at the term energies for the three states of the e<sub>2u</sub><sup>1</sup>-(e<sub>2g</sub>a<sub>1g</sub>)<sup>3</sup> configuration, one may be easily misled to the conclusion that the Ce and Th compounds have very similar electronic structures. We note, however, that, in the case of the Th system, the e<sub>2u</sub> orbital corresponds mainly to the ligand π<sub>3</sub> orbital (≈87% for <sup>5</sup>E<sub>1u</sub>), with some contribution of the metal 5f orbital (≈13%), whereas, for the Ce system, the e<sub>2u</sub> orbital corresponds to an almost pure 4f orbital (≈99%). Similar differences in electronic structure between Ce (4f<sup>1</sup>5d<sup>1</sup>6s<sup>2</sup> ground state configuration) and Th (6d<sup>2</sup>7s<sup>2</sup>) are observed, e.g., for the monoxides (CeO 4f<sup>1</sup>σ<sup>1</sup>, ThO σ<sup>2</sup>) or the bis(η<sup>8</sup>-cyclooctatetraene) systems (Ce(C<sub>8</sub>H<sub>8</sub>)<sub>2</sub> 4f<sup>1</sup>π<sup>3</sup>, Th(C<sub>8</sub>H<sub>8</sub>)<sub>2</sub> π<sup>4</sup>).<sup>10</sup> The reason for the tendency of Th to avoid occupied 5f orbitals may be seen in the large indirect relativistic destabilization. Also, the tendency to have Ce with a singly-occupied 4f shell is partly due to the missing orthogonality constraints for this shell with respect to inner shells of the same symmetry, an effect which was named “missing primogenic repulsion”.<sup>40</sup>

In order to establish the ground state, we performed, for each spin-multiplicity (singlet, triplet, quintet) and parity (gerade, ungerade) separate state-averaged CASSCF calculations for the lowest-lying states formally arising from the (5f a<sub>1g</sub>e<sub>2g</sub>)<sup>4</sup> superconfiguration. The lowest odd-parity state arising from the e<sub>2u</sub><sup>1</sup>(a<sub>1g</sub>e<sub>2g</sub>)<sup>3</sup> configuration, <sup>5</sup>E<sub>1u</sub>, is 0.51 eV higher than the two nearly degenerate lowest even-parity states of the (a<sub>1g</sub>e<sub>2g</sub>)<sup>4</sup> configuration, i.e., <sup>1</sup>A<sub>1g</sub> and <sup>3</sup>E<sub>2g</sub>. For the latter two states the metal–ring distance was optimized at the CASSCF and MRCI levels (basis A) and the totally symmetric metal–ring stretching frequencies were determined (Table 4). Due to the very small energy difference between the two states at all levels of theory, no conclusive answer can be given with respect to the question of the Th(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub> ground state. We suggest however, on the basis of our experience, that the correlation treatment of <sup>1</sup>A<sub>1g</sub> is less complete than that of <sup>3</sup>E<sub>2g</sub> and therefore the singlet state most likely is the ground state. At the CASSCF level, this state is best described as a mixture of 63% e<sub>2g</sub><sup>4</sup> and 37% a<sub>1g</sub><sup>2</sup>e<sub>2g</sub><sup>2</sup>. Nevertheless, single-reference MP2 (CCSD(T)) calculations based on the HF wave function (basis B) were carried out and found the e<sub>2g</sub><sup>4</sup> <sup>1</sup>A<sub>1g</sub> state 0.21 eV (0.53 eV) below the a<sub>1g</sub><sup>1</sup>e<sub>2g</sub><sup>3</sup> <sup>3</sup>E<sub>2g</sub> state, in qualitative agreement with the CASSCF/MRCI result (Table 4). The adiabatic term energies of several other low-lying states in Figure 7 were determined at the MP2 level (basis B), i.e., <sup>5</sup>E<sub>2u</sub> (0.59 eV), <sup>3</sup>A<sub>1u</sub> (0.79 eV), <sup>3</sup>A<sub>2g</sub> (1.00 eV), and <sup>5</sup>A<sub>1g</sub> (1.13 eV).

Whereas for Ce, due to the corelike nature of the 4f shell, only three of the four valence electrons participate in metal–ring bonding, all four valence electrons contribute for the Th system. Since the back-donation from the occupied metal d<sub>±2</sub> orbitals to the π<sub>3</sub> LUMO of the rings is the dominating bonding interaction for both complexes (Table 1), metal–ring bonding should be stronger for the Th than for the Ce compound. The higher vibrational frequency for the symmetric metal–ring stretching mode of the Th compound supports this view (Tables 2 and 4). However, the energies of promotion from the atomic ground state configuration to the formal metal configuration in the complex, i.e., Th 6d<sup>2</sup>7s<sup>2</sup> → 6d<sup>4</sup> (60.5 kcal/mol<sup>41</sup>) and Ce 4f<sup>1</sup>5d<sup>1</sup>6s<sup>2</sup> → 4f<sup>1</sup>5d<sup>3</sup> (42.9 kcal/mol<sup>42,43</sup>), may partly compensate

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(43) National Institute of Standards Atomic Spectroscopic Database, <http://aeldata.nist.gov>.

the stronger bonding in the Th complex. For the  $^1A_{1g}$  state of the latter, we obtain metal–ring binding energies of 0.6, 63.5, and 40.0 kcal/mol at the SCF, MP2, and CCSD(T) levels (basis B), respectively, in comparison to 3.1, 53.4, and 31.1 kcal/mol for the  $^3E_{2u}$  state of the Ce system. On the basis of the larger correlation contributions for the Th complex and the likely underestimation of correlation effects due to basis set limitations, we estimate that  $\text{Th}(\text{C}_6\text{H}_6)_2$  should be equally as, if not more stable than,  $\text{Ce}(\text{C}_6\text{H}_6)_2$  (Figure 2); i.e., the ordering given by King et al.<sup>23</sup> should be reversed. These authors estimated values of 72 and 61 kcal/mol for the Ce and Th compounds, respectively. Finally, we note that although the  $\text{Th}(\text{C}_6\text{H}_6)_2$  ground state CASSCF wave function is a mixture of the two configurations  $e_{2g}^4$  and  $a_{1g}^2e_{2g}^2$ , a corresponding CASPT2 calculation yields a  $\bar{D}$  value only 2 kcal/mol higher than the MP2 result for the  $e_{2g}^4$  reference (basis B).

**10.  $\text{U}(\text{C}_6\text{H}_6)_2$ .** Like the 4f shell, the 5f shell tends to become more corelike with increasing nuclear charge. To answer the question if  $\text{U}(\text{C}_6\text{H}_6)_2$  will behave similarly to  $\text{Th}(\text{C}_6\text{H}_6)_2$  and possess a  $5f^2(a_{1g}e_{2g})^4$  ground state superconfiguration or if the U 5f shell is already corelike enough to accommodate a third electron in a  $5f^3(a_{1g}e_{2g})^3$  ground state superconfiguration in analogy to  $\text{Nd}(\text{C}_6\text{H}_6)_2$ , state-averaged CASSCF calculations were performed for both cases. The energetically lowest septet state ( $^7A_{2u}$ ) arising from  $5f^3(a_{1g}e_{2g})^3$  is lower in energy by 0.74 eV than the corresponding quintet state ( $^5E_{1u}$ ), as well as by 1.72 eV and 2.18 eV lower than the energetically lowest quintet ( $^5A_{1g}$ ) and triplet ( $^3E_{2g}$ ) states, respectively, arising from  $5f^2(a_{1g}e_{2g})^4$ . The CASSCF term energies of the lowest septet states of the  $5f^3a_{1g}e_{2g}^2$  ground state superconfiguration are listed in Table 5, together with the corresponding data for the Nd system. The energetic splitting between these states is up to an order of magnitude larger for the U system than for the Nd system. We attribute this to the larger extent to which the U 5f orbitals are involved in metal–ring bonding (localization of 5f on U: 95.6% in  $e_{2u}$ , 97.4% in  $e_{1u}$ , 99.6% in  $a_{2u}$ , and 100.0% in  $b_{1u}$ ,  $b_{2u}$  from a Mulliken population analysis), whereas the Nd 4f orbitals are essentially corelike (cf. above). Despite the observed difference in the state symmetries, i.e.,  $^7E_{1u}$  for  $\text{Nd}(\text{C}_6\text{H}_6)_2$  and  $^7A_{2u}$  for  $\text{U}(\text{C}_6\text{H}_6)_2$ , the strength of metal–ring bonding as measured by the totally symmetric metal–ring stretching frequencies is quite similar in both systems: 116 (132) and 123 (140)  $\text{cm}^{-1}$  at the CASSCF (valence MRCI + SCC) level for the Nd and U complexes, respectively. The slightly higher value for the U system may be due to the somewhat stronger back-donation from the metal  $d_{\pm 2}$  and  $f_{\pm 2}$  orbitals to the ligand  $\pi_3$  LUMOs.

King et al.<sup>23</sup> estimated averaged metal–ring binding energies  $\bar{D}$  for  $\text{U}(\text{C}_6\text{H}_6)_2$  of 88 kcal/mol when U behaves as a group 4 transition metal and 52 kcal/mol when U behaves as a group 3 transition metal or lanthanide element. Unfortunately it was not possible to achieve convergence for MP2 (or CASPT2) calculations with basis B for states of the  $5f^3e_{2g}^3$  (or  $5f^3(a_{1g}e_{2g})^3$ ) superconfiguration in order to derive a reliable value for  $\bar{D}$ . However, we were able to perform such calculations for the  $^3A_{2g}$  state of the  $5f^2e_{2g}^4$  superconfiguration. The metal–ring binding energies are  $-19.0$ ,  $77.3$ , and  $41.9$  kcal/mol at the SCF, MP2, and CCSD(T) level (basis B), respectively. Metal–ring bonding appears to be stronger than in the Th case, possibly due to the additional back-donation by the  $5f^2$  subshell. The total f electron counts are 0.995 and 2.994 for Ce and Nd but only 1.945 for U (Table 1). We note that dynamical correlation has a tremendous effect on the ordering of the  $5f^3e_{2g}^3$   $^7A_{2u}$  and  $5f^2e_{2g}^4$   $^3A_{2g}$  states and strongly favors the latter state as the possible ground state: the  $^3A_{2g}$  term energies with respect to

$^7A_{2u}$  are 2.18 and 0.90 eV at the CASSCF and valence MRCI + SCC levels, whereas at the CCSD(T) level with all electrons correlated we obtain  $-0.72$  eV (basis A). As for the other three more closely investigated  $\text{M}(\text{C}_6\text{H}_6)_2$  complexes ( $\text{M} = \text{Ce}, \text{Nd}, \text{Th}$ ), it is obviously important to correlate all electrons both for the ground state assignment and for the determination of meaningful  $\bar{D}$  values. This is, however, at present not possible at the multireference level with basis sets of reasonable size (at least g functions on the metal and d functions on carbon). Although our calculations do not finally solve the question of the  $\text{U}(\text{C}_6\text{H}_6)_2$  ground state, we find that the U complex should be at least as stable as the Ce and Th compounds (Figure 2).

**11. Comparison to Other f-Element Metallocenes.** The bis-(arene) complexes are obviously unique among the sandwich compounds since the benzene ligand already fulfills the Hückel rule (aromaticity for  $4m + 2\pi$  electrons, i.e., 6 for  $m = 1$ ), whereas the other commonly used ligands  $\text{C}_k\text{H}_k$  ( $k = 5, 7, 8$ ) have the tendency to accept additional electrons from the metal in order to acquire 6 or 10  $\pi$  electrons. Ligands approaching a lanthanide ( $n = 6$ ) or actinide ( $n = 7$ ) atom will first experience mainly the diffuse  $ns$  and  $np$  valence orbitals, then the  $(n - 1)d$  orbitals, and finally the compact  $(n - 2)f$  shell. In contrast to the case of benzene, a formal electron transfer from the metal to the ring is possible for cyclopentadiene or cyclooctatetraene ligands; i.e., the charge separation and the ionic contributions to bonding are especially weak for the bis(arene) complexes. Therefore metal–ring distances are found to be longer for bis-(arene) complexes than in the other cases. As a consequence, the direct role of 5f orbitals in metal–ring bonding is small in the hypothetical and presumably weakly bound  $\text{An}(\text{C}_6\text{H}_6)_2$  complexes studied here, compared to, e.g., the more strongly bound  $\text{An}(\text{C}_8\text{H}_8)_2$  compounds, where  $(n - 1)d$  and  $(n - 2)f$  orbitals are of equal importance.<sup>12–16</sup> In the case of the Ln- $(\text{C}_6\text{H}_6)_2$  systems, a significant direct 4f orbital participation in metal–ring bonding was neither expected nor found in the present calculations.

The possible existence of the complexes  $\text{M}(\text{C}_6\text{H}_6)_3$  or  $\text{M}(\text{C}_6\text{H}_6)_{4-n}\text{X}_n$  ( $n = 0–4$ ,  $\text{M} = \text{Ln}, \text{An}$ ) in analogy to the corresponding cyclopentadienyl compounds is an interesting topic for future research, which is at present probably only feasible with density functional calculations.<sup>44</sup>

## Concluding Comments

The electronic ground state superconfigurations, the corresponding metal–ring distances, and the totally symmetric vibrational frequencies as well as the metal–ring dissociation energies of the bis(benzene) f-metal complexes  $\text{M}(\text{C}_6\text{H}_6)_2$  ( $\text{M} = \text{La}, \text{Ce}, \text{Nd}, \text{Gd}, \text{Tb}, \text{Lu}, \text{Th}, \text{U}$ ) were investigated. In the case of the Ce, Nd, Th, and U systems, large-scale state-averaged multiconfiguration self-consistent field and valence multireference configuration interaction calculations including Siegbahn's size-extensivity correction were applied. Single-reference second-order Møller–Plesset perturbation theory and singles and doubles coupled-cluster results with a perturbative estimate of triples and correlation of all electrons are reported for all elements. Relativistic effects were taken into account by means of energy-consistent quasirelativistic pseudopotentials.

Our main results are the following. (1) All investigated compounds have been found to be thermodynamically stable with respect to a dissociation into the metal and two benzene rings; i.e., the up to now experimentally unknown actinide compounds  $\text{Th}(\text{C}_6\text{H}_6)_2$  and  $\text{U}(\text{C}_6\text{H}_6)_2$  are possible synthetic

(44) Bursten, B. E.; Strittmatter, R. J. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1069–1085.

targets. (2) The electronic ground state superconfigurations are  $4f^n e_{2g}^3$  for the lanthanides ( $n = 0, 1, 3, 7, 8, 14$  for La, Ce, Nd, Gd, Tb, Lu), with rather low-lying  $4f^n a_{1g}^1 e_{2g}^2$  excited superconfigurations.  $\text{Th}(\text{C}_6\text{H}_6)_2$  has an  $e_{2g}^4$  ground state configuration with a significant admixture of  $a_{1g}^2 e_{2g}^2$ , and the  $\text{U}(\text{C}_6\text{H}_6)_2$  ground state superconfiguration is probably  $5f^2 e_{2g}^4$  with an admixture of  $5f^2 a_{1g}^2 e_{2g}^2$ . (3) The back-donation in  $e_{2g}$  symmetry from the occupied metal  $d_{\pm 2}$  orbitals to the empty  $\pi_3$  orbitals of the rings is the principal bonding interaction, in agreement with previous findings. The donation from the occupied benzene  $\pi_1$  and  $\pi_2$  orbitals to the empty metal  $s$ ,  $p_0$ ,  $p_{\pm 1}$ ,  $d_0$ , and  $d_{\pm 1}$  orbitals plays a minor role. The lanthanide  $4f$  orbitals are found to be basically localized on the metal; however, a weak delocalization of some of the U  $5f$  orbitals was observed. The metal–ring binding strength is larger for actinides than for lanthanides ( $\text{Th} > \text{Ce}$ ,  $\text{U} > \text{Nd}$ ), partially due to the relativistically enhanced orbital expansion and the resulting ability of the metal  $d_{\pm 2}$  and  $f_{\pm 2}$  orbitals to participate in back-bonding, partially due to the presence of one more electron in the corelike lanthanide  $4f$  shell. On the other hand, during bond formation, a formal electron promotion from  $ns$  to  $(n - 1)d$  takes place in order to achieve a stronger back-donation. Since relativity usually stabilizes  $ns$  orbitals and destabilizes  $(n - 1)d$  orbitals,

it thus also tends to reduce the dissociation energy. (4) In contrast to the case of the group 4 complexes  $\text{M}(\text{C}_6\text{H}_6)_2$  ( $\text{M} = \text{Ti, Zr, Hf}$ ), substitution of a ring hydrogen by another atom/group will have only a small influence on the strength of metal–ring bonding. Although a substituent with a larger electronegativity will increase the capability of the ring to accept the negative charge and thus will stabilize the system by stronger back-donation, it will at the same time weaken the ability of the ring to donate electrons to the metal. (5) The missing ionic contributions to bonding as a consequence of the closed-shell character of the benzene ligand lead to substantially weaker metal–ring bonding and longer metal–ring distances than, e.g., for the bis(cyclooctatetraene)lanthanide and -actinide complexes. As a consequence of the resulting smaller orbital overlap, the  $4f$  orbitals in bis(benzene)lanthanide complexes do almost not contribute directly to metal bonding, whereas the  $5f$  orbitals of the actinide counterparts contribute weakly. Nevertheless, indirect contributions due to the promotion of an  $f$  electron in the valence shell may occur for some lanthanides and lead to a characteristic sawtooth behavior of the metal–ring binding energies with maxima at La, Gd, and Lu, as well as minima at Eu and Yb.

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