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Density functional study on zerovalent lanthanide bis(arene)-sandwich complexes*

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Abstract. Several zerovalent lanthanide bis(arene)-sandwich complexes, $Ln(\eta^6\text{-}C_6H_6)_2$, Ln = La, Ce, Eu, Gd and Lu, have been studied by means of density functional theory. The calculated geometries are in good agreement with experiment. The calculated dissociation energies of the bond $Ln\text{—}(\eta^6\text{-}C_6H_6)$ may be considerably underestimated, but they correctly reveal the variation regularity. The bonding in these molecules can be described in terms of a relatively weak π-electron donation from benzene to Ln and a stronger electron back-donation from Ln $5d$ to the benzene π^* orbitals. During bond formation, there is electron promotion from Ln $6s$ to $5d$ instead of from $4f$ to $5d$, in opposition to the proposal of Anderson et al. The relativistic effect only slightly influences the molecular geometry, but decreases the bonding energy considerably through lowering the Ln $6s$ level and raising the $5d$ level. It enhances the trend of the bonding energy to decrease along the lanthanide series.

Key words: Lanthanide compound – Density functional theory – Relativistic effect – Electronic structure – Bonding energy

1 Introduction

In recent years, a series of lanthanide bis(arene)-sandwich complexes were synthesized and characterized [1, 2]. The chemical bonding of this new type of organometallic compound is obviously different from that of the usual lanthanide-containing compounds, leading to strong interest in theoretical studies [3, 4]. It is usually emphasized that lanthanides form ionic compounds. However, it is hard to believe that these zerovalent complexes are ionic ones. In the bis(arene)-sandwich complexes of transition metals which are rich in electrons, for example, $Cr(C_6H_6)_2$, the binding between the metal and ligands is realized through ligand-to-metal donation and back-donation from the metal to the ligands. However, the lanthanides have a lack of $5d$ electrons, so is the above-mentioned bonding model still valid? Anderson et al. [5] proposed the $4f$ to $5d$ promotion mechanism by which the lanthanide would possess more $5d$ electrons, but there was no detailed theoretical study to inspect this supposition. It seems worthwhile to study this problem further. Recently Bella et al. [6] accepted the argument of $4f$ to $5d$ electron promotion after carrying out a relativistic effective core potential ab initio study on $Y(C_6H_6)_2$ and $Gd(C_6H_6)_2$ to clarify their electronic structure and bonding.

It has been shown that density functional theory (DFT) is not only a powerful tool for the theoretical study of main-group elements and transition-metal compounds, but is also a useful method for the theoretical study of lanthanide compounds [7–15]. In the present paper, the bis(arene)-sandwich complexes of zerovalent lanthanides, $Ln(TTB)_2$ [Ln = La, Ce, Eu, Gd, and Lu, and TTB is the arene $\eta^6\text{-}(1,3,5\text{-}^tBu)_3C_6H_3]$, are studied by means of DFT to determine their molecular and electronic structures, and to clarify the principal bonding interaction and bonding energetics in these compounds, in particular, to inspect the reasonableness of the $4f$ to $5d$ promotion supposition, as well as to study the influence of relativistic effects on the bonding.

2 Computational details

The principle of DFT and its applications have been described in many publications in detail, for example, in Refs. [16, 17]. The ADF 2.3 package [18] has been used. The frozen-core approximation was adopted with the xenon core of the lanthanides and the helium core of carbon frozen. For the valence orbitals the triple zeta plus polarization STO basis set which was provided by the ADF 2.3 package was used. The local density

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approximation (LDA + VWN correlation functional [19]) was adopted and the gradient corrections for the exchange potential (Becke 88 [20]) and for the correlation potential (Perdew 86 [21]) were taken into account. In order to ensure that the iteration converges to the result with reasonable population in the Ln $4f$ subshell, a positive number is added to the diagonal Fock matrix elements related to the $4f\alpha$ and $4f\beta$ (for La) or $4f\beta$ (for Gd) orbitals [11]. The positive number is selected in such a way that it ensures a correct population when the Ln atom is calculated with the ADF 2.3 program. The influence of the relativistic effect was investigated by means of the pseudo-relativistic correction method [22].

Ln$(C_6H_6)_2$ was taken as the model molecule of Ln(TTB)$_2$ in order to facilitate the calculations. This simplified model molecule has been adopted by Bella et al. [6], and it has been shown to be suitable for a quantitative description of the bonding between Ln and arenes. The preliminary calculations showed that the potential barrier for the opposite rotation of the two benzenes in Ln$(C_6H_6)_2$ is less than 0.01 eV. In the present study, the molecular configuration was constrained to possess D_{6d} symmetry with a C_6 axis on z-and one C_2 axis on x-coordinates.

All calculations were carried out on the SGI Power Challenge XL Super Computation System in the Information Network Center of the Chinese Academy of Sciences.

3 Results and discussion

3.1 The ground state and geometry

Because Ln$(C_6H_6)_2$ is an open system and has unpaired electrons, the spin-unrestricted method was adopted in the calculations. Symmetry-constrained geometric optimization was carried out for the molecules La$(C_6H_6)_2$, Ce$(C_6H_6)_2$, Eu$(C_6H_6)_2$, Gd$(C_6H_6)_2$ and Lu$(C_6H_6)_2$ with different spin multiplicity. The dissociation energies obtained for the Ln-arene bond of these molecules in different multiplet states are presented in Table 1. A part of the optimized molecular geometric data is presented in Table 2. It can be seen from Table 1 that the spin multiplicity of La$(C_6H_6)_2$, Ce$(C_6H_6)_2$, Eu$(C_6H_6)_2$, and Lu$(C_6H_6)_2$ in the ground state is 2, 3, 10, and 2, respectively. For Gd$(C_6H_6)_2$ the energy difference between the states with spin multiplets 11 and 9 is small, and spin-crossing exists near the molecular equilibrium configuration (see Fig. 1).

Comparing the optimized geometry data with the experimental crystal structure, $^9E_2$ should be taken as the ground state of Gd$(C_6H_6)_2$, in accordance with Ref. [6]. However, at higher temperature, the ground state of Gd$(C_6H_6)_2$ may become $^{11}A_1$. Thus Gd$(C_6H_6)_2$ may be a thermo-induced spin-crossing compound; its magnetic property may change abnormally in some temperature range, which remains to be confirmed experimentally.

It can be seen from Table 2 that the optimized distance between Gd and the center of a benzene, BL(Gd-X), is in fairly good agreement with the experimental one. Because of the interaction between Ln and the benzene ring, the C—C bond length of the benzene ring lengthens slightly, but the C—H bond length is unchanged. The relativistic effect makes the distance be-
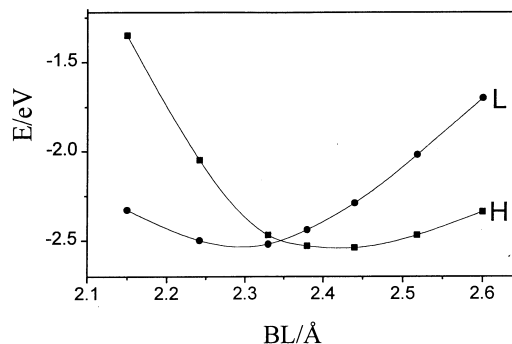

Fig. 1. Potential curve of Gd$(C_6H_6)_2$; L and H refer to the states with the multiplets 9 and 11, respectively; BL is the distance between Gd and the center of C_6H_6; E is the dissociation energy

Table 1. Bond dissociation energies of the high- and low-spin multiplets of Ln$(C_6H_6)_2$ (eV)

Molecules	La$(C_6H_6)_2$		Ce$(C_6H_6)_2$		Eu$(C_6H_6)_2$		Gd$(C_6H_6)_2$		Lu$(C_6H_6)_2$	
Multiplets	2	4	3	5	8	10	9	11	2	4
2D(Ln-C$_6$H$_6$)[a]	2.91	2.72	3.42	2.18	1.41	1.88	2.51	2.54	2.03	1.71

[a] D(Ln—C$_6$H$_6$) is the dissociation energy of the Ln—C$_6$H$_6$ bond

Table 2. Geometry of Ln$(C_6H_6)_2$ in ground states (D_{6d}, in Å). *NR* and *R* denote non-relativistic and relativistic calculations respectively. *BL* denotes bond lengths. *BL(Ln—X)* is the distance between the lanthanide and the center of a benzene. *L* and *H* denote the low- and high-spin multiplets of Gd$(C_6H_6)_2$, respectively

Molecules	La$(C_6H_6)_2$		Ce$(C_6H_6)_2$		Eu$(C_6H_6)_2$		Gd$(C_6H_6)_2$				Lu$(C_6H_6)_2$		C$_6$H$_6$
	R	NR	R	NR	R	NR	R	NR	R	Exp.[2]	R	NR	
BL(Ln—X)	2.49	2.51	2.37	2.43	2.34	2.34	2.30^L	2.33^L	2.44^H	2.22	2.15	2.15	–
BL(C—C)	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.42	1.41	1.43	1.43	1.40
BL(C—H)	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09	1.09	–	1.09	1.09	1.09

Table 3. Energy levels and main components of the molecular orbitals of $Gd(C_6H_6)_2$ in the ground state $^9E_2$

Symmetry	Energy levels (eV)		Main components (%)	
	NR	R	NR	R
$1e_3\alpha$	−11.33	−11.31	38Gdf + 34Hs + 18Cs + 9Cp	56Hs + 29Cs + 12Cp
$2e_3\alpha$	−10.74	−10.73	97Cp	99Cp
$2e_5\alpha$	−10.33	−10.34	63Cp + 37Hs	63Cp + 37Hs
$2e_1\alpha$	−10.26	−10.32	54Cp + 35Hs	54Cp + 36Hs
$3a_1\alpha$	−9.37	−9.50	94Cp + 6Gds	94Cp + 6Gds
$3b_2\alpha$	−8.69	−8.66	100Cp:z	100Cp
$2e_4\alpha$	−8.30	−8.33	60Cp + 36Hs	56Cp + 35Hs + 5Gdf
$2e_2\alpha$	−8.31	−8.31	60Cp + 36Hs	60Cp + 36Hs
$3e_1\alpha$	−11.57	−8.01	97Gdf	93Gdf + 5Cp
$4b_2\alpha$	−11.54	−7.98	98Gdf	100Gdf
$3e_4\alpha$	−11.43	−7.85	100Gdf	94Gdf
$3e_3\alpha$	−11.23	−7.73	61Gdf + 22Hs + 11Cs	100Gdf
$3e_5\alpha$	−7.06	−7.07	82Cp + 11Gdd	82Cp + 11Gdd
$4e_1\alpha$	−6.44	−6.37	96Cp	91Cp + 5Gdf
$3e_2\alpha$	−2.96	−2.96	51Cp + 47Gdd	53Cp + 44Gdd
$4a_1\alpha$	−2.06	−2.12	62Gdd + 38Gds	64Gdd + 26Gds + 8Hs
$1e_3\beta$	−11.28	−11.29	57Hs + 40Cp	57Hs + 40Cp
$2e_3\beta$	−10.73	−10.71	98Cp	98Cp
$2e_5\beta$	−10.32	−10.32	64Cp + 38Hs	64Cp + 38Hs
$2e_1\beta$	−10.28	−10.29	55Cp + 36Hs	55Cp + 36Hs
$3a_1\beta$	−9.23	−9.33	90Cp + 7Gds	90Cp + 7Gds
$3b_2\beta$	−8.60	−8.56	100Cp	100Cp
$2e_2\beta$	−8.30	−8.30	50Cp + 36Hs	50Cp + 36Hs
$2e_4\beta$	−8.30	−8.29	60Cp + 36Hs	60Cp + 36Hs
$3e_5\beta$	−6.88	−6.88	85Cp + 9Gds	85Cp + 8Gds
$3e_1\beta$	−6.37	−6.36	97Cp	97Cp
$3e_2\beta$[a]	−2.47	−2.46	66Cp + 31Gdd	68Cp + 29Gdd
$3e_4\beta$	−1.46	−1.47	100Cp	100Cp

[a] HOMO

tween the Ln atom and the center of one benzene, BL(Ln—X), shorter, but only a little. From La to Lu, BL(Ln—X) decreases monotonously, close to the radius contraction of the two-valent lanthanide ions, which may imply that the lanthanide atoms in these compounds possess electronic configuration similar to that in the two-valent lanthanide compounds.

3.2 Electronic structure and bonding

The levels and components of the molecular orbitals (MOs) for $Gd(C_6H_6)_2$ and $Eu(C_6H_6)_2$ are presented in Tables 3 and 4. It can be seen that the MOs of $Ln(C_6H_6)_2$ can be divided into three groups. The first group of MOs distributes in benzene rings, actually being the linear combination of the MOs of the two benzene ligands. The second group of MOs is highly localized, essentially being the $4f$ atomic orbitals (AOs) of the Ln atom. The levels of the $4f$-like MOs are nearly degenerate and considerably higher than those of the Ln $4f$ AOs, thus they should be considered as nonbonding or antibonding orbitals. The third group includes the $3a_1$, $3e_5$ and $3e_2$ MOs resulting from the interaction between Ln and the ligands, which are the bonding MOs. The main difference between $Eu(C_6H_6)_2$ and $Gd(C_6H_6)_2$ is that in the former case the HOMO possesses higher energy and includes a smaller component of Ln $5d$ orbitals, and the electron in $3e_2\beta$ is absent compared to the latter case. The LUMO consists of Ln $5d$ and $6s$ orbitals. The relativistic effect only slightly influences the levels and composition of the MOs

Table 4. Energy levels and main components of the molecular orbitals of $Eu(C_6H_6)_2$ in the ground state $^8A_1$

Symmetry	Energy levels (eV)		Main components (%)	
	NR	R	NR	R
$3a_1\alpha$	−9.25	−9.46	94Cp + 5Eus	90Cp + 9Eus
$3b_2\alpha$	−8.72	−8.77	98Cp	97Cp
$2e_2\alpha$	−8.25	−8.29	60Cp + 36Hs	60Cp + 36Hs
$2e_4\alpha$	−8.25	−8.29	60Cp + 36Hs	60Cp + 36Hs
$3e_5\alpha$	−6.84	−7.01	87Cp + 8Eud	85Cp + 8Eud
$3e_1\alpha$	−6.52	−6.62	92Cp	93Cp
$3e_4\alpha$	−4.33	−2.96	98Euf	85Euf + 15Cp
$4b_2\alpha$	−4.32	−2.80	100Euf	99Euf
$3e_3\alpha$	−4.27	−2.73	100Euf	99Euf
$4e_1\alpha$	−4.23	−2.72	97Euf	97Euf
$3e_2\alpha$[a]	−2.42	−2.68	66Cp + 32Eud	64Cp + 33Eud
$4a_1\alpha$	−1.49	−1.68	66Eus + 33Eud	72Eus + 26Eud
$3a_1\beta$	−8.91	−9.05	94Cp + 5Eus	92Cp + 8Eus
$3b_2\beta$	−8.33	−8.33	97Cp	97Cp
$2e_2\beta$	−8.20	−8.24	60Cp + 36Hs	60Cp + 36Hs
$2e_4\beta$	−8.20	−8.24	60Cp + 36Hs	60Cp + 37Hs
$3e_5\beta$	−6.47	−6.57	89Cp + 6Eud	88Cp + 5Eud
$3e_1\beta$	−6.12	−6.17	95Cp	94Cp
$3e_2\beta$	−1.86	−2.02	77Cp + 22Eud	76Cp + 23Eud

[a] HOMO

without Ln $4f$ components, but shifts the level of the $4f$-like MOs significantly.

The orbital interaction diagram for $Lu(C_6H_6)_2$ is presented in Fig. 2. It can be seen that the interaction between the Lu $6s$ and the ligand a_1 orbital leads to the

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loss of Lu $6s$ electrons, because the $6s$ orbital is pushed up to become the main component of the LUMO. The interaction between the Ln $5d$ orbital and the ligand e_5 and e_2 (π and π^* of benzene) orbitals results in the formation of a π and a δ bond. The former is a ligand-to-Ln donation bond and the latter is the Ln-to-ligand back-donation bond which is of essential importance for the formation of the stable zerovalent lanthanide bis(arene)-sandwich compounds. The bonding process can be described as follows: The a_1 and e_5 electrons of the ligands coordinate to the Ln atom, and the Ln $6s$ electrons are promoted to $5d$ orbitals which interact with benzene e_2 (π^*) orbitals to form $3e_2$ MO corresponding to the metal-to-ligand back-donation bond. This bonding picture is similar to that obtained by ab initio calculations [6].
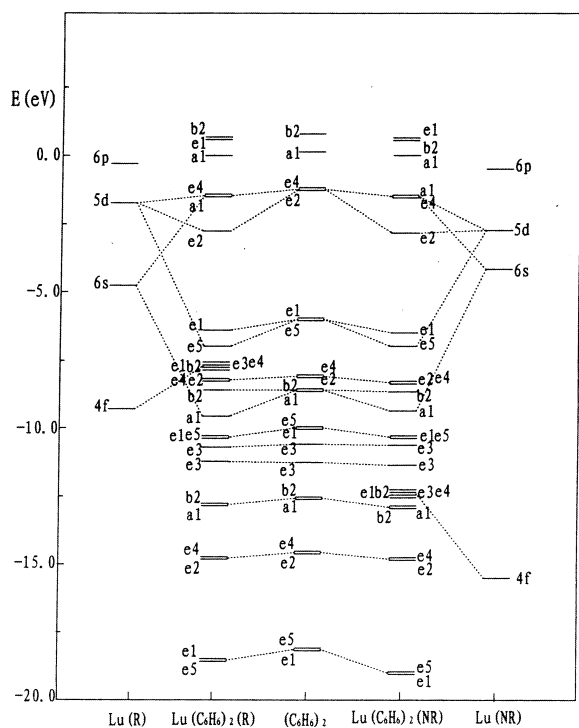
La$(C_6H_6)_2$ and Ce$(C_6H_6)_2$ have a similar electronic structure and bonding characteristics. However, in Ce$(C_6H_6)_2$ the interaction between the $4f$ and benzene π orbitals seems non-negligible, although it is small. The bond dissociation energy of Ce$(C_6H_6)_2$ is a little larger than that of La$(C_6H_6)_2$ (see Table 6), which may correlate to the $4f$ orbitals participating in bonding to a certain extent.

The atomic charge, covalence of Ln—(C_6H_6) bonds, Mulliken population, and bond orders are presented in table 5. The covalence of the Ln—(C_6H_6) bonds was calculated according to Pauling's definition, that is, covalence $= (1 - Q/2) \times 100\%$, where Q is the Mulliken charge on the Ln atom which is assumed in the two-valent state. It can be seen that these compounds possess significant covalent character ($\sim 50\%$). The Mayer bond orders show that there is about one single bond between Ln and one benzene ring. The C—C bonds in the benzene ring are weakened significantly while the C—H bonds are almost unchanged, which shows the reasonableness of the simplified model to imitate TTB with C_6H_6.

Anderson et al. [5] proposed that for the lanthanide atom to form a stable bis(arene)-sandwich complex by back-donation bonding, it should have a $5d^1 6s^2$ configuration in the ground state or an easily accessible excited state. If there is not a $5d$ electron in the ground state, promotion from $4f$ to $5d$ will be required in the formation of the molecule. King et al. [2] found that there is a good linear correlation between the estimated dissociation energies and the Ln $4f^n 6s^2$ to $4f^{n-1} 5d^1 6s^2$ promotion energies of the free lanthanide atoms; however, it can be seen from Table 5 that in Ln$(C_6H_6)_2$ the Ln $4f$ population is the same as that in the free atoms, while most of the Ln $6s$ population loses and the Ln $5d$ population increases by about one electron. This population result is in accordance with the determined magnetic property of these compounds. Thus here there is not a $4f$ to $5d$ electron promotion, but a $6s$ to $5d$ charge transfer. Furthermore, if the $4f$ to $5d$ promotion takes place in the molecular formation, the relativistic effect should in-

Fig. 2. Diagram for the α-spin molecular orbital levels of Lu$(C_6H_6)_2$

Table 5. Valence electronic configuration of Ln in Ln$(C_6H_6)_2$, bond orders, and covalence

Molecules		La$(C_6H_6)_2$		Ce$(C_6H_6)_2$		Eu$(C_6H_6)_2$		Gd$(C_6H_6)_2$		Lu$(C_6H_6)_2$		C_6H_6
		NR	R	NR	R	NR	R	NR	R	NR	R	
Charge on Ln		1.04	1.16	1.06	1.11	0.91	1.10	0.94	1.14	0.93	1.12	
Covalence %		48	42	47	44	54	45	53	43	53	44	
Electronic	Ln $4f$	0.00	0.01	1.20	1.02	6.96	6.69	7.01	6.99	14.00	13.97	
configu-	$5d$	1.97	1.88	1.82	1.90	1.07	1.17	1.91	1.83	1.83	1.76	
ration	$6s$	0.14	0.09	0.05	0.13	0.03	0.02	0.29	0.19	0.32	0.28	
	$6p$	−0.16	−0.16	−0.13	−0.17	0.02	0.01	−0.14	−0.17	−0.09	−0.14	
Mayer	Ln—C_6H_6	1.08	1.02	1.26	1.30	0.90	1.32	1.20	1.08	1.32	1.32	−
bond	C—C	1.24	1.24	1.24	1.23	1.25	1.22	1.22	1.22	1.20	1.19	1.36
order	C—H	1.08	1.08	1.08	1.08	1.07	1.09	1.08	1.08	1.08	1.08	1.06
Mulliken	Ln-C_6H_6	0.18	0.18	0.18	0.20	0.21	0.24	0.24	0.18	0.30	0.30	−
bond	C—C	0.43	0.42	0.43	0.42	0.43	0.40	0.41	0.41	0.40	0.39	0.50
order	C—H	0.44	0.44	0.44	0.44	0.43	0.43	0.44	0.44	0.44	0.44	0.42

crease instead of decrease the bond dissociation energy, because the relativistic effect narrows the 5d-4f energy gap. It seems that an other reason should be found to rationalize the possible linear correlation between the bond dissociation energies and the Ln 4f to 5d promotion energies.

3.3 Dissociation energy and relativistic effects

According to the extended transition-state method proposed by Ziegler [23], the calculated bonding energy (BE) can be decomposed into two terms:

$$BE = \Delta E_{\text{steric}} + \Delta E_{\text{orb-int}}$$

The first term ΔE_{steric} is the total steric repulsion interaction among the components which are going to constitute the molecule. $\Delta E_{\text{steric}} = \Delta E_{\text{Pauli}} + \Delta E_{\text{Coul}}$, where ΔE_{Pauli} is the Pauli repulsion due to the destabilizing two-orbital four-electron interactions among the occupied orbitals on the components of the molecule, and ΔE_{Coul} is the Coulomb interactions among the molecular components without charge deformation. The second term $\Delta E_{\text{orb-int}}$ represents the stabilizing interaction among the occupied and unoccupied orbitals on the molecular components, resulting in bond formation as well as polarization and charge transfer, which can be further divided into the contributions from different symmetry representations. The Ln-arene bond dissociation energy and its decomposition in terms of the above-mentioned scheme are presented in Table 6. For $Gd(C_6H_6)_2$ the bond dissociation energy is close to the ab initio (HF + MP2) result. The calculated dissociation energies may be considerably underestimated, although the experimental data are not properly comparable, for the calculated molecules are free $Ln(C_6H_6)_2$

instead of $Ln(TTB)_2$ in solution. It was pointed out by Bella et al. in the ab initio study of this kind of compound that the underestimation of the BE may mainly come from the single determinant approximation in the Hartree–Fock calculations, but the reason for such an underestimated BE in the DFT calculations remains unclear. Nevertheless, the trend of the dissociation energy to decrease along the lanthanide series is revealed by the calculated results.

Comparing the La, Gd, and Lu compounds which have comparable electronic structural characteristics, it can be found that the dissociation energy decreases along the lanthanide series, even in the nonrelativistic approximation. From La to Lu, the atomic radii decrease due to the lanthanide contraction, and the steric hindrance between the two benzene rings will increase. However, the calculated result shows that the interaction energy between the two benzenes changes very little (less than 0.01 eV) from the distance of 4.40 to 5.02 Å; Thus this is not the factor resulting in weaker bonding in heavier lanthanides. The main fact causing the weaker bonding may be that the 6s level drops down and the 5d level goes up from La to Lu, which would make the coordination of the a_1 and e_5 electrons of benzene to the Ln atom more difficult. Along the lanthanide series, though the attractive Coulomb interaction between Ln and the benzene becomes stronger due to the lanthanide contraction, the Pauli repulsion energy increases more rapidly, resulting in weaker bonding. The decomposition of the BE shows that MOs 3e_2 and 3e_5 contribute the most to the orbital interaction energy, showing that they are the most important bonding orbitals, in accordance with the above-mentioned bonding picture. The BE of $Eu(C_6H_6)_2$ is obviously smaller than that of others. It can be seen from Table 6 that the orbital interaction energies of 3e_2 and 3e_5 in $Eu(C_6H_6)_2$ are only about half

Table 6. The bond dissociation energy (eV) of $Ln(C_6H_6)_2$ and its decomposition

Molecules	$La(C_6H_6)_2$		$Ce(C_6H_6)_2$		$Eu(C_6H_6)_2$		$Gd(C_6H_6)_2$		$Lu(C_6H_6)_2$	
	NR	R	NR	R	NR	R	NR	R	NR	R
Pauli repulsion	30.73	30.12	31.58	35.17	23.35	26.78	32.80	33.41	35.57	35.93
Coulomb interaction	−15.85	−15.48	−16.64	−17.87	−13.72	−15.61	−17.31	−17.29	−18.80	−18.71
Steric repulsion	14.88	14.64	14.93	17.30	9.63	11.17	15.49	16.12	16.77	17.22
a_1	−0.65	−0.49	−1.03	−1.40	−0.07	−0.42	−1.38	−1.42	−2.11	−1.94
a_2	0.18	0.14	0.25	0.19	0.30	0.32	0.25	0.21	0.30	0.28
b_1	0.18	0.15	0.25	0.19	0.30	0.32	0.25	0.21	0.30	0.28
$b_2(f)$	−1.02	−0.76	0.04	−0.02	−2.07	−2.23	−1.13	−0.83	−1.17	−0.78
$e_1(f)$	−2.26	−1.92	−0.90	−1.19	−2.77	−3.06	−2.20	−1.87	−2.24	−1.77
e_2	−11.38	−10.96	−11.20	−11.46	−6.37	−6.36	−11.34	−11.08	−11.38	−11.11
$e_3(f)$	1.20	1.28	3.70	2.87	1.72	2.02	1.84	1.85	2.29	2.50
$e_4(f)$	1.23	1.21	−4.01	−2.45	1.44	1.07	1.55	1.43	1.73	1.68
e_5	−6.15	−6.21	−6.56	−7.54	−4.28	−4.76	−6.82	−7.19	−7.86	−8.49
Total orbital interaction	−18.67	−17.57	−19.45	−20.81	−11.82	−13.10	−18.98	−18.68	−20.14	−19.35
Fitting error	0.02	0.02	0.07	0.08	0.03	0.05	0.05	0.05	0.10	0.11
2D(Ln—C_6H_6)[a]	3.77	2.91	4.45	3.42	2.16	1.88	3.43	2.51	3.28	2.03
R + sp[b]		2.98		3.44				2.52		2.08
Expt.[c]		6.00		6.26				5.91		5.39

[a] The calculated bond dissociation energy 2D(Ln—C_6H_6) refers to the reaction $Ln(C_6H_6)_{2(g)} \rightarrow Ln_{(g)} + 2\,C_6H_{6(g)}$
[b] R + sp means taking the spin-orbit coupling into account
[c] The experimental values refer to the reaction $Ln(TTB)_{2(s)} \rightarrow Ln_{(g)} + 2TTB_{(s)}$, where the subscript "s" indicates that the molecule exists in solution

of those in the other $Ln(C_6H_6)_2$. The $3e_2$ and $3e_5$ orbitals are related to Ln $5d$ orbitals and the bonding MOs. It can be seen from Table 5 that the $5d$ population on the Eu atom in $Eu(C_6H_6)_2$ is about one electron less than that in other compounds; thus the weaker bonding in $Eu(C_6H_6)_2$ originates from the lack of one $5d$ electron. It is interesting to note that the lanthanide bis(arene)-sandwich compounds can be divided into two groups according to their stability, (see Fig. 5 of Ref. [2]). In the relatively more stable group, the Ln element, for example, La, Ce, Gd, Tb, or Lu, has one $5d$ electron in the ground state. In the less stable one, the Ln element, for example, Sm, Eu, Tm, or Yb, does not have $5d$ electrons in the ground state. This fact again shows the important role of the Ln $5d$ orbitals in bonding.

The relativistic effect decreases the dissociation energies by about 0.9, 1.0, 0.3, 0.9, and 1.3 eV respectively for $Ln(C_6H_6)_2$ with Ln = La, Ce, Eu, Gd, and Lu. The spin-orbit coupling influences only slightly the dissociation energy, as expected, because only spin-orbit interaction of Ln $5d$ electrons would contribute to the dissociation energy, for the $4f$ electrons are almost not involved in bonding. The decomposition of the BE shows that the relativistic effect increases the steric repulsion more than it increases the orbital interaction energy, resulting in a decrease in BE. It is obvious that the influence of the relativistic effect on the molecular properties of $Ln(C_6H_6)_2$ mainly originates from the relativistic effect on the Ln atom which lowers the levels of Ln $6s$, and $6p$ orbitals and raises those of the $5d$ and $4f$ orbitals. It was pointed out earlier that about one electron transfers from the Ln $6s$ to $5d$ orbitals in the molecular formation. While the relativistic effect only slightly changes the Ln $6s$ and $5d$ populations, it increases the $6s$ to $5d$ promotion energy by 0.3 to 1.5 eV from La to Lu atoms, which must result in weaker donation and back-donation of electrons and a decrease in BE. Therefore the relativistic effect enhances the trend of the BE to decrease along the lanthanide series.

4 Concluding remarks

1. The calculated geometry of $Ln(C_6H_6)_2$ by DFT is in good agreement with experiment. The calculated bond dissociation energies may be considerably underestimated, though their variation is in line with experiment.

2. $Gd(C_6H_6)_2$ possesses two stable states, the low-spin state $^9E_2$ and the high-spin state $^{11}A_1$. The two potential curves intersect each other near the equilibrium configuration of the molecule, thus $Gd(C_6H_6)_2$ may be a thermo-induced spin-crossing compound.

3. All $Ln(C_6H_6)_2$ molecules possess similar electronic structure except for the Ln $4f$ population. In these molecules the Ln atom always binds the benzene rings by polarized covalent bonds, although the bonding strength is quantitatively a little different. The bonding mechanism is similar to that of the transition metal bis(arene)-sandwich compounds, that is, the ligands donate π electrons to the metal atom and the metal atom back-donates d electrons to the ligand π^* orbitals; however, the Ln $5d$ electrons come from $6s$ to $5d$ instead of from $4f$ to $5d$ promotion. The BE decreases along the lanthanide series due to the increase in the promotion energy.

4. The influence of the relativistic effect on the molecular geometry is relatively small, but its influence on the electronic structure and BE is considerable. It raises the energy of MOs with Ln $4f$ as the main component, and it decreases the BE through increasing the energy needed for the Ln $6s$ to $5d$ electron promotion during molecular formation.

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