Computational study of μ–η^{6}η^6-phenyl, η^5-cyclopentadienyllanthanum(II) complexes and their relative stability

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ABSTRACT

Lanthanum is able to join in η^5 and η^6 fashion to cyclopentadienyl and phenyl rings, yielding known organometallic complexes, where the metal manifests oxidation number 2. A theoretical comparison between these types of molecules and the known cyclopentadienyl derivatives with oxidation number 3 indicates that some kind of extra stabilization takes place in the case of the first compounds and this study attempts to find an explanation for this phenomenon. Besides this, we also present an electronic description of both kinds of organolanthanum complexes.

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1. Introduction

The chemistry of divalent lanthanide compounds was first described considering only three ions; Eu(II), Sm(II) and Yb(II) [1], however the new discoveries of organometallic complexes, where La, Ce and Pr are in 2+ oxidation state have demonstrated that it is possible for stable species to exist in this particular oxidation state [2–7].

Several questions arise relating to this particular feature, because it is a known fact that lanthanide elements and their compounds are commonly found in oxidation state +3 [8], however it seems that the organometallic derivatives demonstrate certain different tendencies. Firstly, it is not common to form sigma joint compounds by combining a lanthanide atom and carbon fragments, but more importantly the π derivatives (more common) depend on a number of geometrical restrictions, which relate to the intrinsically small size of the lanthanide ions. In this sense, ferrocene like derivatives could be prepared [9], although initially for the three elements cited above, this implies elements with a half-full f shell. Nowadays there are also derivatives for lanthanum, cerium and neodymium [10–12], which represent early lanthanide elements and have few electrons in the f shell (or none in the case of lanthanum).

The nature of the chemical bond has been the object of controversy, because originally it was considered to consist solely of ionic bonds among cyclopentadienyl units with trivalent lanthanide ions [12]. However it seems that in fact the bond is a kind of polar covalent [13] because it is entirely directional in nature. The magnetic behavior of each particular compound forms part of the same discussion, as obviously it depends on the electronic occupation of the f shell in this particular case, but in the case of lanthanum, there would have been no discussion because of its intrinsic lack of f electrons; indeed the diamagnetic nature of the Cp$_3$La derivative has been indicated previously [12].

Another important kind of lanthanide organometallic derivative has been studied by Lappert and his co-workers, but in this case, divalent lanthanum compounds have been prepared and these represent thermally stable species [7]. A comparison between these two kinds of lanthanum compounds (i.e. the 3+ oxidation state and the 2+ oxidation state), is the objective of this work.

In this case, a comparison was made between tris(cyclopentadienyl)lanthanum and the [(LnCp″$_2$)$_2$(μ–η^6:η^6-PhMe)] fragment (LanCpPh).

The relative energies yielded by homodesmotic or isodesmic reactions and the nature of the chemical bond and magnetic behavior of each case is studied from a theoretical point of view. The results are very interesting because they indicate the source of the unique thermodynamic behavior, inherent in each one of the different species studied.

2. Methods

All calculations were carried out by applying a pure DFT method for energy evaluations. For the structures of all derivatives, Becke's gradient corrections [14] for exchange and Perdew–Wang's for correlation [15] were applied. This is the scheme for the B3PW91 method which forms part of the GAUSSIAN09 [16] Package. The calculations were performed using the 6-311G** basis set and in the case of the lanthanum, a basis set with TZVP quality SARC [17,18] was

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used for the lanthanum atoms. Full optimizations were carried out for all structures. The reactions were homodesmotic (hyperhomodesmotic [19]) in the case of the tris(cyclopentadienyl)lanthanum and isodesmic in the case of the lanthanum(II) compound, this last reaction is considered isodesmic because of the change in the oxidation state of the lanthanum.
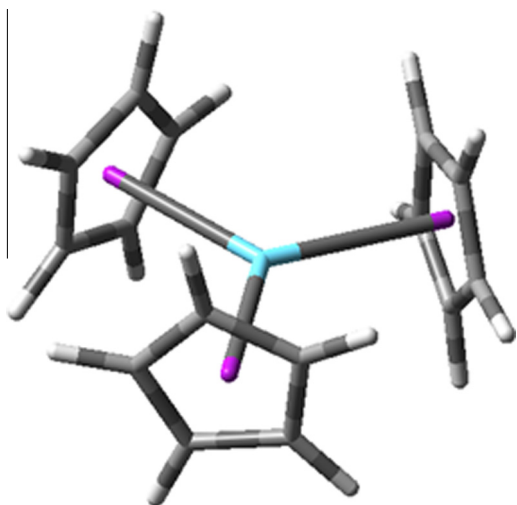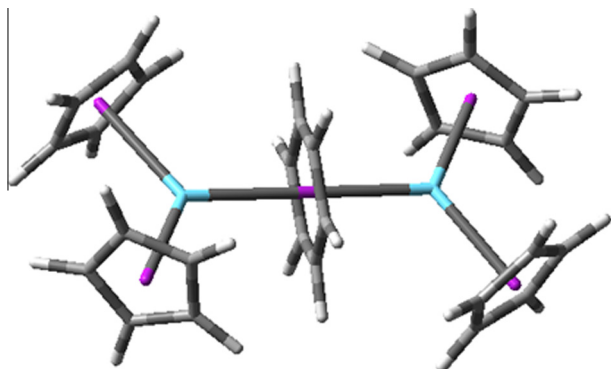

Fig. 1. Tris (cyclopentadienyl) lanthanum(III).
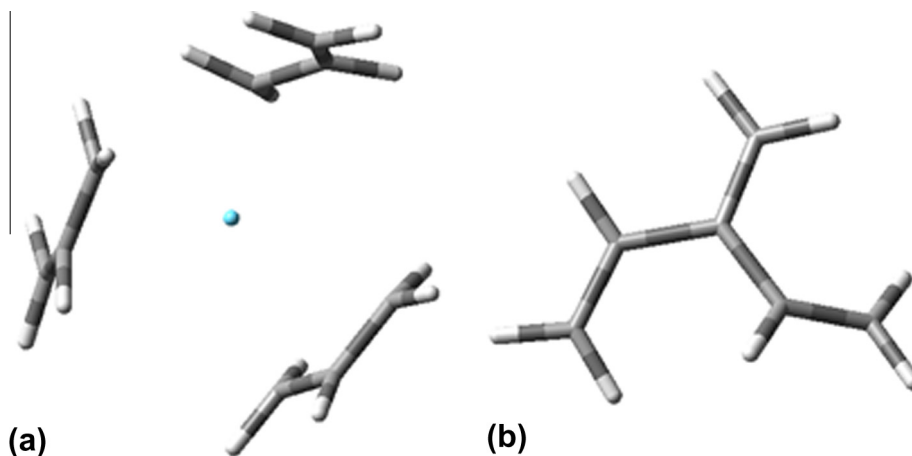

Fig. 2. (LnCp$_2$)$_2$(μ–η^6:η^6-Ph).

3. Results and discussion

In Fig. 1, the shape of the molecule containing the lanthanum(III) ion is presented.

And the molecule with oxidation state 2+ is presented in Fig. 2.

In both cases, the cyclopentadienyl rings have no substituents; this is an important finding because the majority of the prepared known compounds in these molecules contain *n*-methyl-cyclopentadienyl ligands, however the results for homodesmotic and isodesmic reactions are more complicated when they include these fragments, and therefore they are omitted in all the structures.

Homodesmotic (hyperhomodesmotic) and isodesmic reactions were designed for the study of both kinds of molecules. In the case of tris(cyclopentadienyl)lanthanum, the reaction is homodesmotic following Georgés criteria [20,21] as well as with the new one [19], thus there are the same number, type and hybridizations of atoms on both sides of the equation. The parent molecules of these species are tris(allyl)lanthanum and 2-ethyl-butadiene, and these parent molecules can be observed in Fig. 3.

The homodesmotic reaction is presented in Eq. (1).

$$2C_9H_{15}La + 3C_6H_8 \rightarrow C_{15}H_{15}La + 6C_2H_4 \tag{1}$$
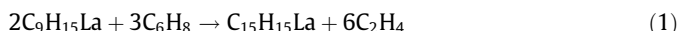
In the case of the oxidation state 2+ molecule, once again the same number, type and hybridizations are found on both sides of the equation; however lanthanum manifests different oxidation states on each side, so that the reaction should be classified as isodesmic. The parent molecules in this case are the same and the corresponding process is depicted in Eq. (2).

$$2C_9H_{15}La + 5C_6H_8 \rightarrow C_{26}H_{26}La_2 + 11C_2H_4 \tag{2}$$
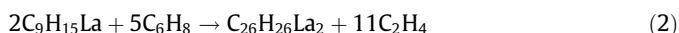
Considering the energy associated with all bonding and considering there are no aromatic rings on the left side of the equation, the enthalpy for the reaction should represent an index that measures the stability of both lanthanum complexes on the basis of the presence of aromaticity on the right side and the change in the oxidation state of the metal atom. In this instance, the definitive results show a surprising pattern.

The result for the tris(cyclopentadienyl)lanthanum is −72.33 kcal/mol, and likewise for the 2+ oxidation state molecule it is −99.266 kcal/mol, therefore there is a difference of 26.9 kcal/mol between these two, and it is possible to assume that this enthalpy difference indicates that the second molecule is thermodynamically more stable than the first one.

It has been suggested that all lanthanide elements and their derivatives are more stable when the oxidation state is +3, however in the present case, the more stable species is that manifesting
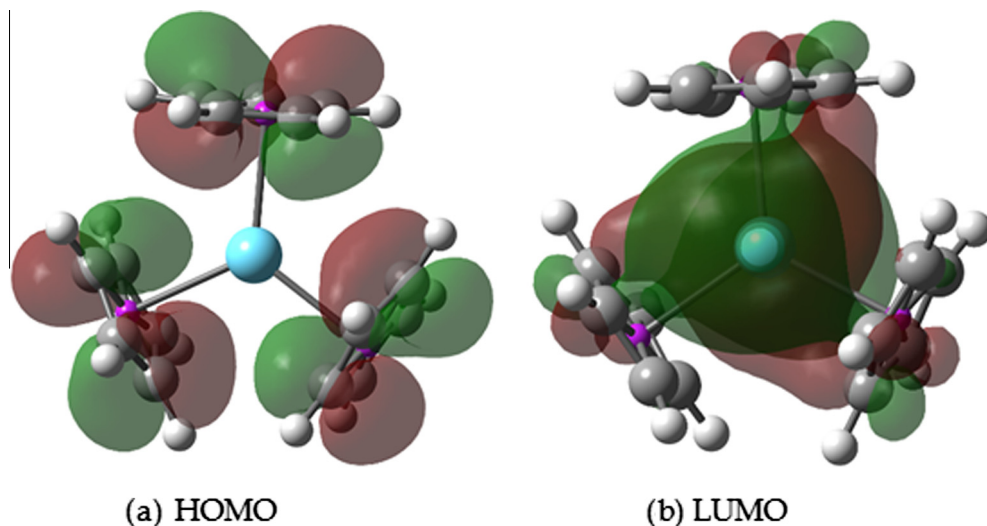

(a)   **(b)**

Fig. 3. Parent molecules of the homodesmotic reactions: (a) tris(allyl)La(III) (b) 2-ethyl-butadiene.

Fig. 4. Frontier molecular orbitals (HOMO–LUMO) for tris(cyclopentadienyl)lanthanum.
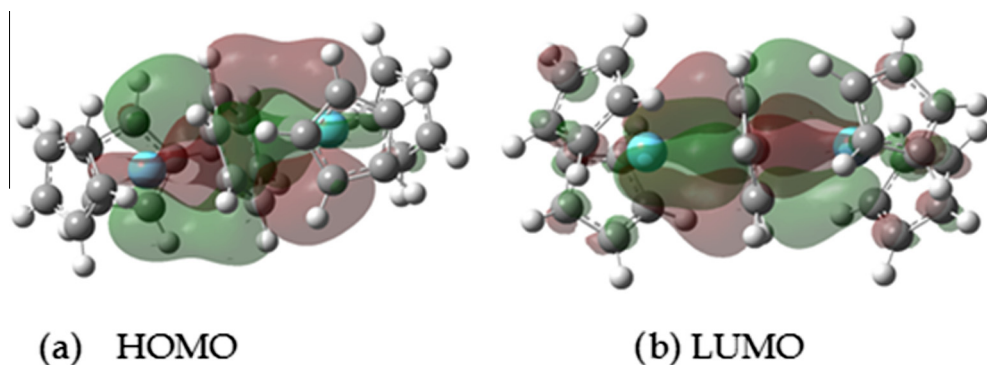

Fig. 5. Frontier molecular orbitals for the LanCpPh compound.

the 2+ oxidation state, obviously the reason of this extra stability should not refer to the difference in the oxidation state, but rather in the nature of the substituents and their bonding. Thus, it is necessary to analyze the electronic structure of both species.

The frontier molecular orbitals of tris(cyclopentadienyl)lanthanum are presented in Fig. 4. This molecule belongs to the C_{3h} point group but neither HOMO nor LUMO present degenerated orbitals.

It is possible to observe classic behavior in this species, where the HOMO only indicates contribution from the charged cyclopentadienyl rings, whereas the LUMO shows a strong interaction among the lanthanum ion and the three rings, with the metal participating more strongly. The energy gap between HOMO and LUMO is 3.905 eV, manifesting very weak semiconductor behavior.

The corresponding frontier molecular orbitals for LanCpPh are presented in Fig. 5.

This compound belongs to the D_2 point group and is a peculiar case pertaining to the δ bond compound. The HOMO comprises a straightforward mix of the molecular orbital from the benzene ring and the b_1 orbitals from the lanthanum, however the LUMO represents a classic interaction between the b_3 orbitals coming from both the lanthanum atoms and the central aromatic ring; the description of the δ bond is presented here. The energy gap between HOMO and LUMO is 1.937 eV, indicating strong semiconductor behavior almost at the limit of conductor behavior.

The answer to the question concerning the extra stability of this last structure lies in the nature of this last molecular orbital. It has been suggested that back-donation takes place between the
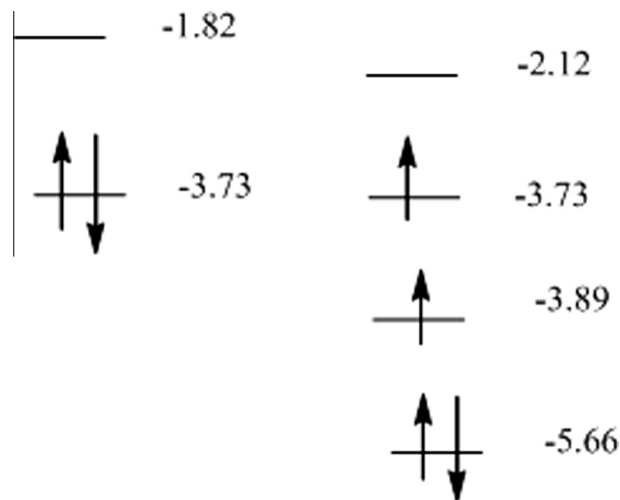

Fig. 6. Comparison of the frontier molecular orbitals of the ground state and the triplet state (values in eV).

frontier molecular orbitals of zerovalent lanthanide bis-arene complexes [22,23], and the present case appears to show a similar phenomenon, as there is a clear case of back-bonding in the LUMO of this compound, where the donation of charge comes from the lanthanum atoms to the low lying antibonding molecular orbitals
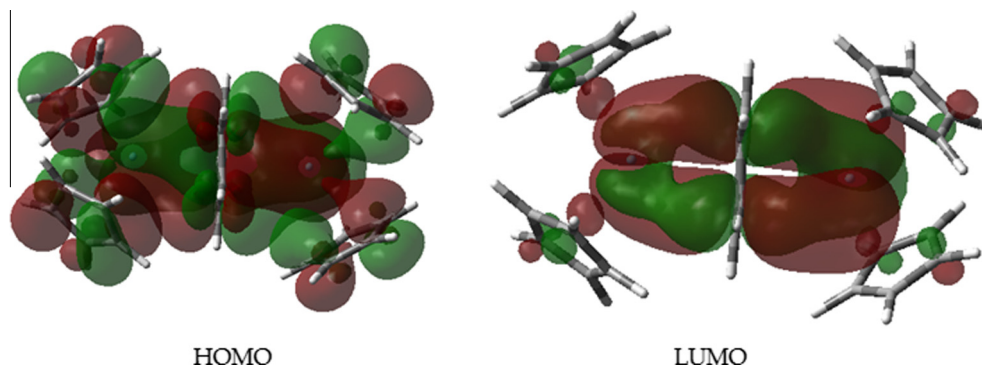
HOMO   LUMO

Fig. 7. Frontier molecular orbitals of the triplet state.

of benzene, and the electrons involved in this kind of current are precisely those lone electrons derived from the La(II) d orbitals.

There are several consequences caused by this effect, (a) the LUMO manifests a very strong electron-acceptor orbital, indeed with respect to this compound the actual known species [7] represents half of an ionic complex and it is an anion that arises for the electro donation coming from K atoms of the cationic moiety; (b) as expected, this species is thermodynamically more stable than the counterpart of the Cp ligands alone, where the back-bonding effect is not apparent and (c) this species is able to reach excited states as discussed below.

The electronic description of both species indicates very marked differences between the two, firstly, the molecule with oxidation state +3 seems to have more ionic behavior, the HOMO manifests only the participation of the charged ligands and the bond length between the lanthanum ion and the center of the cyclopentadienyl rings manifests an average of 2.59 Å; in the HOMO of the second case, the lanthanum atom participates with the carbon atoms on the central benzene ring(although curiously there is little participation on the part of the Cp rings) and the bond length manifests an average of 2.64 Å, however the most important difference lies in the very different multiplicities relating to both species. The first molecule has a closed shell arrangement, whereas in the second case there is a very large possibility of triplet configuration.

Each one of the atoms of lanthanum manifests 2+ oxidation state, indicating that there is a single electron in the 5d orbital, so that it is possible to suggest that the benzene ring becomes negatively charged (2−) and therefore experiences some kind of distortion, as observed by Lappert and his coworkers [24]. The benzene ring has two parallel sides with a short bond length of 1.387 Å; however this distortion is not sufficient to indicate an antiaromatic central ionized benzene ring, even taking into account that the ring is always a planar fragment and that the NBO analysis does not show electronic accumulation on the benzene ring. Lappert himself carried out an interesting EPR study which shows the presence of the free radicals [6,24,25] and the NBO analysis carried out in this work yields an electronic population of 1.15 on each lanthanum atom (6s 0.1, 5d 1.05). This qualitatively concurs with similar results provided by Protchenko [2] and his coworkers (although in the present case the result shows greater electronic richness for the 5d orbital than in the Protchenko case where 6s 0.37 and 5d 0.52 were obtained. However these differences can be attributed to the change in the pseudopotential used by the lanthanum atom), therefore the theoretical study of this triplet state was carried out.

Surprisingly, the ground state and the triplet state are very similar in energy (the difference is ∼1.87 eV favoring the ground state), indicating that the triplet state should be easy to reach, a factor which reinforces the EPR results cited above. The important facts are the electronic behavior of the triplet state; fig. 6 shows a comparison of the frontier molecular orbital diagrams for both configurations.

The HOMO of the triplet state is folded into two SOMÓs where the upper has practically the same value as the corresponding HOMO of the ground state; likewise the LUMO of the triplet state is more or less 0.3 eV more stable than that corresponding to the ground state, therefore the energy gap for the triplet state is narrow in comparison with the value reported above (1.6 eV), this fact suggests that electronic promotion is easier in the triplet state. This electronic promotion is very important when discussing the nature of the extra stabilization of this species, because the proximity between the frontier molecular orbitals causes a real current drive along all the bulk of the molecule, a feature which conforms to the shape of the corresponding molecular orbitals (Fig. 7).

Electronic flow goes from the HOMO that in this case is an eigenfunction covering the entire surface of the molecule, to the LUMO that is concentrated at the center where both the lanthanum atoms and the benzene ring are united, a distribution which is very different to those pertaining to the ground state discussed above.

4. Conclusions

Two kinds of lanthanum organometallic complexes with different oxidation state were compared in order to establish their relative thermodynamic stabilities; those containing only cyclopentadienyl ligands and those which can be joined to both cyclopentadienyl ligands and a benzene ring. The energy study focusing on the homodesmotic and isodesmic reactions indicates more relative stability in the case of the compound containing a benzene ring. The source of this extra stability is discussed on the basis of the nature of the corresponding frontier molecular orbitals. The LUMO of the molecule containing lanthanum with oxidation state +2 shows strong back-bonding behavior and allows electronic flow from the two electrons derived from lanthanum, as well as the stabilization of a triplet state.

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