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DFT studies of some structures and reactions of lanthanides complexes

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Abstract

An account of our own DFT calculations on structures and reactions of some lanthanides complexes is given. For each of the Ln complexes the entire family, La to Lu, has been studied. Comparison between calculations with 4f electrons in the valence shell and in the core confirm the current belief that the 4f electrons are uninvolved in bonding so that 4f electrons can be included in the core. The calculations show that special care with the modeling of ligands is necessary, since oversimplification of the ligands can lead to structural artefacts. The artefacts are probably due to the large size of the lanthanide ions which favors interactions that do not necessarily represent the situation in experimental complexes. For instance agostic interactions and distortion of the coordination sphere that do not exist in the real systems are obtained when N-$(SiMe_3)_2$ is modeled by N-$(SiH_3)_2$. However, if caution is used, calculated structures agree nicely with experiment (for example, $CeCl(NR_2)_3)$, $R = SiMe_3$). The hydrogen exchange reaction, $Cp_2Ln–H^* + H–H \rightarrow Cp_2Ln–H + H^*–H$, shows that in agreement with the experimental evidence, this reaction is facile for most lanthanides. Some dependence on the nature of the lanthanide metal is obtained. While currently described as a σ-bond metathesis, the reaction can also be viewed as a nucleophilic addition of H^- to H_2 in the field of a lanthanide ion. Calculations of structural and reactivity properties of large size lanthanides complexes for any Ln element are feasible within certain limitations that are discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: DFT; Lanthanide; Molecules; Orbital; Ligand modeling

1. Introduction

The chemistry of lanthanides has developed into an important area in organometallic chemistry. This activity reflects the growing realization that these elements have an important role to play in chemistry. However, only a few lanthanides are currently used because of their relative abundancy and therefore the properties and reactivities of several centers remain essentially unexplored. In addition, it is implicitly thought that all members of the lanthanide family will show similar reactivity. As a consequence, the incentive to carry out experiments on low abundance rare earth elements is inhibited. Theoretical studies can provide a useful and relatively inexpensive approach to this unexplored territory. While the power of theory is now well established for understanding structures and mechanisms in organic chemistry and in organometallic chemistry of d-transition metal elements [1–3], the theoretical studies of 4f elements have been considered difficult due to the presence of open shell 4f electrons. Calculations treating explicitly the f electrons have been limited to very small systems of usually spectroscopic interest [4]. Only a limited number of calculations that include the 4f electrons in the core have been carried on large systems of chemical interest. Calculations have been most often carried out on selected lanthanides like La, Sm, Eu, Gd, Yb, Lu [5–21]. The computational difficulty is sometimes circumvened by using yttrium as a model for lanthanides (see for instance [22]). While Y and Ln have often similar chemistry, a more quantitative understanding of how the physical and chemical properties change across the row is lacking. The halides complexes have been the focus of a large number calculations and controversies [22–32]. Some force field

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and semi-empirical calculations have been carried out [33,34]. Fundamental theoretical studies of the lanthanides elements and di- or triatomic complexes have been carried out but are not cited in this work. A review on the particularities of the calculations of heavy elements has been published [35].

Another difficulty in the computational study of lanthanides complexes is related to their high coordination number (up to 8 or 9) and the sterically bulky ligands used in the experimental studies. In the domain of d-transition metal complexes, modeling large ligands by small ones (PR_3 replaced by the universal PH_3) is a satisfactory practice although some limitations are now being discovered [36]. As it will be shown below, similar simplification may be more questionable for lanthanides complexes. The problem of ligand modeling is especially important for the study of catalysis. A vast proportion of lanthanide complexes of interest in catalysis have one or two substituted cyclopentadienyl ligands. Modern computational techniques like DFT and QM/MM methods as well as fast computers have resulted in immense progresses and large systems are within the realm of computational studies. Despite these advances, studies of lanthanides complexes are still at the limit of computational feasibility. For this reason, it is of great interest to develop a calculation level which allows computational studies of large size systems for the entire lanthanide family. In this review we give an account of our work in this domain. We will first briefly describe the calculation level that we have used and how we have validated the method through comparison with experiments. We will then describe our initial studies on reactivity.

2. Validating the computational method on the structural properties of triamido complexes

2.1. Are the 4f electrons involved in bonding?

The triamido complexes $Ln(N(SiMe_3)_2)_3$ are known for almost all the lanthanide family and they are thus an ideal system for testing how the level of calculations agrees with the experimental facts. In a first set of calculations, we had to ascertain if the 4f electrons needed to be in the valence shell (the core is thus [Xe]) or if they could be added to the core. Although, it is currently considered that 4f electrons of lanthanides are relatively uninvolved in bonding, a systematic and quantitative evaluation was necessary. Calculations with 4f electrons in the valence (small core calculations) are computationally highly demanding and the comparison of the calculations with 4f electrons in the core (large core calculations) can only be carried out on small systems. The simplest tris-amido complex, $Ln(NH_2)_3$, was chosen initially. Comparison with experiments, on $Ln(N(SiMe_3)_2)_3$ does not give meaningful results since the Ln–N distance is very sensitive to the substituent on nitrogen. We thus focused on the comparison between the small and large core calculations. The small core calculations clearly show that the 4f electrons do not participate to bonding. Hund's rule is obeyed for all complexes and the ground state configuration corresponds to the highest spin number. Charge analysis shows that the number of 4f electrons is equal to that of the isolated atom. The non-participation of the 4f electrons in bonding seems quantitatively valid and good results should be expected when the 4f electrons are incorporated in the effective core potential. The large core potential was chosen according to the formal oxidation state of Ln; three for all elements except that of four for Ce for and two for Eu and Yb. The comparison between the small and large core calculations on $Ln(NH_2)_3$ (Ln = La to Lu) is rewarding since they give very similar structural results. The Ln–N bond is longer by only 0.04 Å with the large core calculations (Fig. 1). The coordination is essentially trigonal planar for the whole series for the two levels of calculation. There is a tendancy for very slightly smaller N–Ln–N angle (118°) for the earlier lanthanides. The lanthanide contraction (0.179 Å) is very well reproduced with the large core potential at the DFT level (0.179 with B3PW91). Other levels of calculations (HF, MP2, B3LYP) give similar results and the best agreement is obtained with B3PW91 functional.

2.2. Comparing experimental and calculated structures. The problem of model in lanthanide complexes

In the next set of calculations we introduced the silyl group in order to compare the metrical parameters for

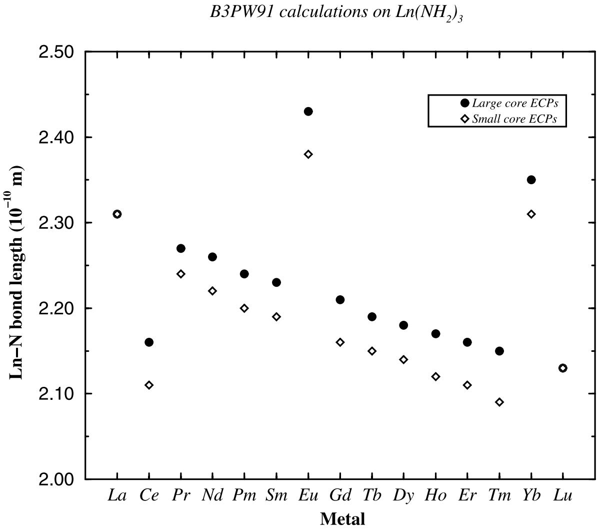
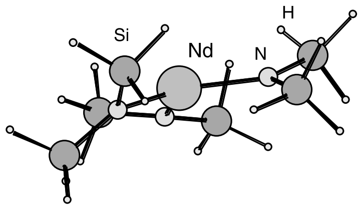


Fig. 1. Ln–N bond lengths (Å) for $Ln(NH_2)_3$ complexes at the B3PW91 level (taken from Ref. [37]).

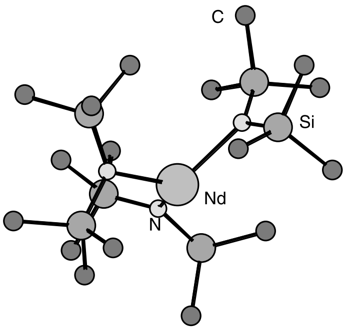
the calculated systems with those in the experimental $Ln(N(SiMe_3)_2)_3$ complexes. The experimental $SiMe_3$ group was modeled by SiH_3 as currently done in theoretical studies where the replacement of many alkyl or even aryl spectator groups by H does not lead to artefacts. To our big surprise this approach is not applicable in the case of $Ln(N(SiH_3)_2)_3$. The DFT calculations reveal also an unusual dependence of the structure with the level of calculations. In a first set of calculations, the geometry optimization was carried out without including any d-polarization function on the silicon center. The calculated Ln–N bond was significantly elongated with respect to the values found for $Ln(NH_2)_3$ when the d-polarization function was not included. This is in line with partial electron delocalization of the nitrogen lone pair to the SiH_3 group. The Ln–N bonds are found to be too short and the N–Si bond too long when compared to the experimental values (Table 1). The two bond lengths differ from the experimental values by around 0.06 Å. However, the overall experimentally observed propeller shape (also called helicoidal) made by the three $N(SiMe_3)_2$ ligands is well reproduced as illustrated for the neodymium complexes (Fig. 2). In particular the calculations show the absence of agostic bonds ([38]) in agreement with the experimental structures. At this stage, we naturally thought that improving the quality of the calculations by a better representation of the silicon atom would improve the bond lengths without affecting the overall structure of the complexes. It is indeed well known in the theoretical community that d-polarization functions are necessary for the correct representation of silicon.

Table 1
DFT(B3PW91) optimized geometrical parameters (Å) for $Ln(N(SiH_3)_2)_3$ without d-polarization functions on Si and experimental (X-ray) values (taken from Ref. [39])

Metal	Experiment		$Ln(N(SiH_3)_2)_3$	
	Ln–N	N–Si	Ln–N	N–Si
La	2.40	1.70	2.36	1.76
Ce	–	–	2.21	1.76
Pr	–	–	2.32	1.76
Nd	2.36	1.70	2.28	1.76
Pm	–	–	2.28	1.76
Sm	–	–	2.27	1.76
Eu	2.53	1.70	2.48	1.76
Gd	–	–	2.24	1.76
Tb	2.26	1.70	2.23	1.76
Dy	2.22	1.70	2.21	1.76
Ho	–	–	2.20	1.76
Er	2.21	1.70	2.19	1.76
Tm	–	–	2.19	1.76
Yb	2.44	1.70	2.39	1.76
Lu	2.23	1.70	2.18	1.76



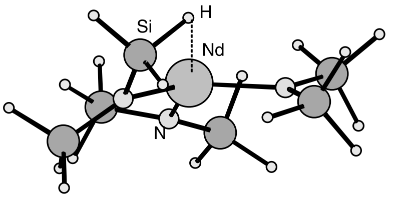
Helicoidal Structure



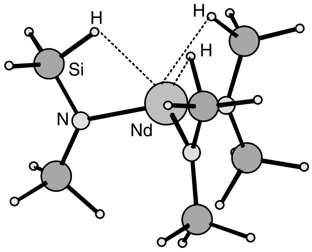
Experimental Structure

Fig. 2. DFT(B3PW91) optimized structure (no d-polarization functions on Si) for $Nd(N(SiH_3)_2)_3$ and experimental (X-ray) structure for $Nd(N(SiMe_3)_2)_3$ (taken from Ref. [39]).

The calculations of $Ln(N(SiH_3)_2)_3$ with d-polarization functions on Si lead to the occurrence of two minima. For the two minima, the Ln–N bond lengths were less than 0.02 Å shorter than the experimental values and the N–Si bonds were quantitatively reproduced (1.70 Å regardless of identity of the lanthanide metal for all structurally characterized tris-amido complexes). While the bond lengths are successfully reproduced the occurrence of two minima and their overall shape raise some concern. The calculated propeller minimum, whose shape is similar to the experimental structure has one β-agostic Si–H bond while no short Ln···H interactions are observed in the experimental system (Fig. 3). However, a corolla structure with three agostic Si–H bonds (Fig. 3) is found 10 kcal mol^{-1} more stable than the propeller structutre. This corolla structure does not correspond to any known experimental system and is significantly different from the propeller geometry. This result is somewhat disappointing since it shows a significant limitation in modeling ligands for lanthanide complexes. However, the artefact is understandable. The d-polarization functions on Si makes SiH_3 more efficient in delocalizing the amido nitrogen lone pair as supported by a charge analysis. This shortens the Si–N bond and as consequence lenghtens the Ln–N bond. The accumulation of electron density in the Si–H bonds makes them better candidates for an agostic interaction. Our calculations suggest that a β lanthanide···Si–H agostic interaction can be estimated to 5 kcal mol^{-1}. The experimental structure which has C–H bonds (not as good candidate for agostic interaction as Si–H) at a γ position (not as favorable as a β position) has no agostic interactions.



Helicoidal structure



Corolla Structure

Fig. 3. DFT(B3PW91) propeller (also called helicoidal) and corolla structures for $Nd(N(SiH_3)_2)_3$ (d-polarization functions on Si) (taken from Ref. [39]).

The calculations illustrate the importance of agostic interactions in lanthanide complexes. These interactions are favored by the large metal radius and the high oxidation state of the lanthanide. In fact γ-C–H agostic interactions have been found in $Ln(CH(SiMe_3)_2)_3$ (Ln = La, Sm), a system we are currently studying [40]. Alternative interpretations of related systems, (dmpe)-$Yb(N(SiMe_3)_2)_2$ [41] and $(C_5Me_5)La(CH(SiMe_3)_2)_2$ have been published. For the Yb complex, a Yb···Me interaction was proposed. For the La complex, a neutron diffraction study and DFT calculations suggest the presence of a β-agostic Si–C interaction [17] whose existence was suggested previously [42]. Our results on the trialkyl complexes are similar. It remains to be understood why bis-silylalkyl complexes have agostic Si–C bonds while bis-silylamido complexes do not.

Another interesting outcome of the computational studies is the sensitivity of the Ln–N and N–Si bond lengths to the model and level of calculations. This sensitivity is fully supported by experimental evidence. Thus, the X-ray structure of the recently synthesized complex $CeCl(N(SiMe_3)_2)_3$ shows Ce–N 2.217 and N–Si 1.75 Å [43]. While the calculated Ce–N (2.21 Å) in the cerium(IV) cation, $Ce(N(SiH_3)_2)_3^+$, is in excellent agreement with that found in $CeCl(N(SiMe_3)_2)_3$, the difference in the N–Si bond length is significant. The experimental N–Si bond length is also significantly longer than in other NR_2 ($R = SiMe_3$) Ln complexes. The calculation of $CeCl(N(SiH_3)_2)_3$ shows an overall structure in full agreement with the experimental structure (Ce–Cl as a C_3 axis) and metric parameters in good agreement with the X-ray structure [43]. The Ce–Cl bond is almost quantitatively reproduced (2.589 Å calculated vs. 2.598 Å experimental), but the metrical Ce–N distance is slightly too long (2.246 Å calculated vs. 2.217 Å experimental). The N–Si bond length is very well reproduced (1.762 Å calculated vs. 1.75 Å experimental) and is indeed found to be significantly longer than in the Ln(III) compounds, $Ln(N(SiMe_3)_2)_3$. In this case no agostic bond was found in agreement with the experimental observation.

2.3. *Perspective and limitations for the calculations of the structures of lanthanides complexes*

The few computational studies of lanthanides complexes described above show promising potential for DFT calculations to help understand the structures of large lanthanide complexes at a reasonable computational time since the 4f electrons can be added to the core. However, precautions are necessary, as oversimplification of the ligands can lead to structural artefacts. This is not surprising for ions of large ionic size and high coordination numbers. The dominance of ionic bonding, the weakness of orbital interactions, the lack of a strong ligand field lead to very flexible geometries which is challenging for calculations (soft potential energy surface). Meaningful models of the experimental systems are crucial. Introducing all of the ligands or molecules such as coordinated solvent molecules of the first coordination sphere in the calculated system is probably very important. This contrasts with the transition metal systems where loss of a ligand is not necessarily associated with a coordination sphere re-organization. As an example, $M(CO)_6$ is an octahedron and $M(CO)_5$ is square based pyramid for M = Group VI [44]. The calculations reproduce very well the changes in the metric parameters in closely related systems. The lanthanide contraction is quantitatively reproduced offering possibility to study trends within the lanthanide family. The influence of small changes, like the presence of Cl, in the Cerium tris-amido complex seems to be adequately modeled. Although there is still much to learn from calculations of other lanthanides complexes, it already appears that DFT calculations can be reliably used for modeling structural determination when all of the ligands in the first coordination sphere are known. When the number of atoms become unmanageable for DFT calculations, the pouplar QM/MM methods [45,46] offer expanded possibilities. They have been used successfully in transition metal organometallic chemistry [36] in particular for the study of change in coordination sphere [47] of agostic bonding [48,49] and even for the study of reactivity. For some recent examples in different domains see [50–52]. QM/MM calculations should be as useful for the lanthanide complexes.

3. Validating the calculations for reactivity of lanthanide complexes

Lanthanide complexes are catalysts for some important chemical transformations as shown in some key references [53–57]. In contrast, theoretical studies of reactivity pattern are still scarce. DFT calculations of the activation of H_2 by $Cl_2La–H$ and $Cl_2Lu–H$ [58] and that of H_2 and CH_4 by $Cl_2Lu–Z$ ($Z = H$, Me) [59,60] have been reported. Most computational studies have been carried out for transition metal elements with a d^0 shell like Zr(IV), Y(III) and Sc(III) [61]. While all elements of Groups III and IV with their empty d shells have related reactivities, there is a clear need for a quantitative understanding of how the electronic structure of the f-block elements influence the reactivity relative to that of the f^0 d^0 elements.

The discovery by Watson that Cp_2LuMe activates CH_4 has attracted considerable attention (Eq. (1)) [62]. A number of C–H bonds from various hydrocarbons have been activated by late transition metal systems (for selected reviews and papers [63–67] and references therein) and a number of mechanistic routes have been described by computational studies [2,68,69]. In the case of lanthanide complexes the absence of 5d electrons and the chemical interness of the 4f electrons limit the mechanistic possibilities to a σ-bond metathesis process

$$(C_5Me_5)_2LuMe + H - CH_3^* \rightarrow (C_5Me_5)_2LuMe^* + H - CH_3 \quad (1)$$

Before carrying out calculations on Eq. (1) [70], we must understand the main features of a σ-bond metathesis for the entire Ln family on a computational simple model system. The H exchange shown in Eq. (2), which has been also observed experimentally [62], was chosen.

$$Cp_2^*LuH + D_2 \rightarrow Cp_2LuD + HD \quad (2)$$

A study of the H exchange as shown in Eq. (3) for the entire Ln family (Ln = La to Lu) was carried out [71] using the usual replacement of C_5Me_5 by C_5H_5 (Cp). Despite the smaller size of C_5H_5 and the lower electron donating ability compared to C_5Me_5, no modeling problem was expected. Cyclopentadienyl has often been modeled by Cl with transition metal and selected lanthanide centers. The H exchange reaction of Eq. (3) and the CH_4 activation of Eq. (1) have been calculated using Cp_2ScZ, $Cl_2Sc–Z$ [72] and $Cl_2Lu–Z$ ($Z = H$, CH_3) [59,60], $Cl_2M–H$ (M = Sc, Y, La, Lu, Zr^+, B and Al) [58].

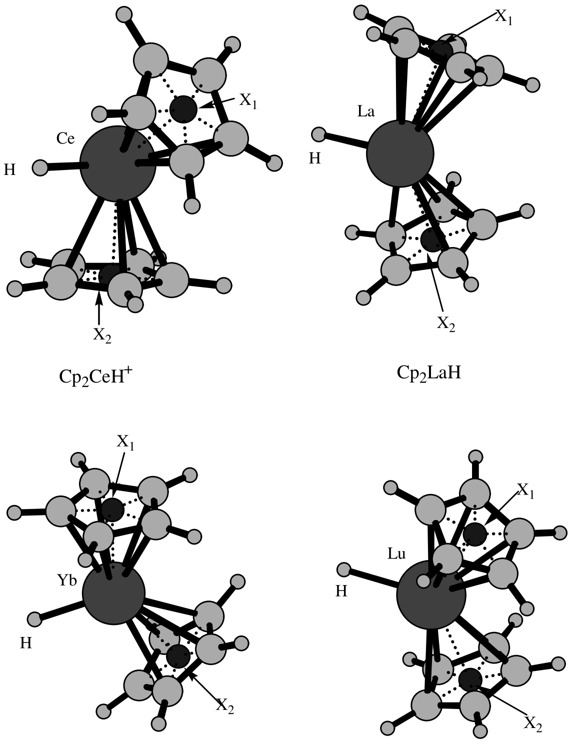
$$Cp_2Ln - H^* + H - H \rightarrow Cp_2Ln - H + H^* - H \quad (3)$$

Using the method of calculations previously established (4f electrons in the core) we have determined the structure of reactants, transition structures and energy profile for the entire lanthanide series, La to Lu. Although, lanthanide hydride complexes are known as oligomers [73] the reactive species is assumed to be a monomer. The monomeric $Cp_2Ln–H$ is thus considered to be the reactant. The structure of $Cp_2Ln–H$ is very similar to that found for d^0 transition metal $Cp_2M–R$ complexes [74] for analogous reasons. The hydride is in the equatorial plane but off the C_2 axis of Cp–Ln–Cp for early lanthanides. For later lanthanides, Eu to Lu, the lanthanide has a trigonal planar geometry as shown by the sum α of the Ligand–Ln–Ligand angles (Table 2). Thus, in $Cp_2Ln–H$, like in LnX_3, Ln has a non-planar trigonal coordination for selected lanthanides (Fig. 4 and Table 2).

Despite the presence of an empty coordination site at the lanthanide, no $Cp_2LnH(H_2)$ could be located as a minimum on the potential energy surface for any Ln. Probably H_2 is too weak a base and Ln is too weak an acid to make the donor–acceptor interaction energy sufficiently large to stabilize the H_2 adduct. The absence of any electrons on Ln to back-donate into $\sigma^*(H_2)$ also contributes to decreasing the stability of any adduct. It is of interest to note that $Cl_2Ln–H$ makes an H_2 adduct with a binding energy of 1.2 kcal mol^{-1}. The Cp ligand is more of an electron donor than Cl. This makes Ln a weaker Lewis acid with Cp than Cl which energetically disfavors the dihydrogen adduct. This shows some limitations of the isolobal analogy [75]. Cl and Cp are isolobal since they both use occupied orbitals of similar symmetry to bind to the metal (an a and an e set). However, the difference in the electronegativity of the two groups results in different binding properties of $Cp_2Ln–H$ and $Cl_2Ln–H$ especially toward a weak base like H_2.

Table 2
Geometrical parameters, r_e (Å) and X_1–Ln–X_2 angle (X_1 and X_2 are the centers of the C_5H_5 rings (°)), and pyramidalization ($\alpha = \Sigma$ (Ligand–Ln–Ligand angles) (°)) for Cp_2LnH at the B3PW91 level (taken from Ref. [71])

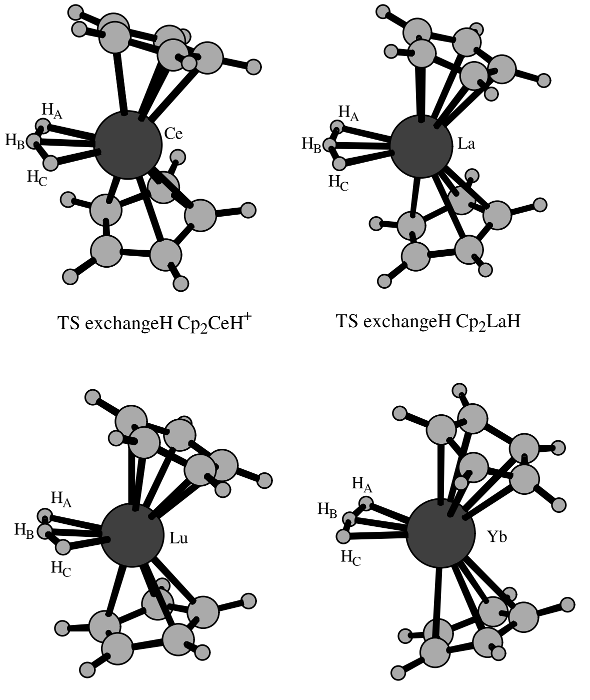
Metal	Oxidation state	α	r_e(M–H)	X_1–Ln–X_2
La	3	336.8	2.142	134.3
Ce	4	317.8	1.959	130.0
Pr	3	343.3	2.112	136.9
Nd	3	346.1	2.099	137.9
Pm	3	349.9	2.088	138.9
Sm	3	353.0	2.078	139.6
Eu	2	360.0	2.331	131.3
Gd	3	359.9	2.059	141.1
Tb	3	360.0	2.045	140.9
Dy	3	360.0	2.031	140.7
Ho	3	360.0	2.018	140.6
Er	3	360.0	2.005	140.4
Tm	3	360.0	1.994	140.2
Yb	2	360.0	2.225	131.6
Lu	3	360.0	1.972	140.1



Cp_2CeH^+ Cp_2LaH

Cp_2YbH^- Cp_2LuH

Fig. 4. DFT(B3PW91) optimized geometry for Cp_2LnH for Ln = La, Ce, Yb and Lu (X_1 and X_2 are the centers of the C_5H_5 rings (taken from Ref. [71]).



TS exchangeH Cp_2CeH^+ TS exchangeH Cp_2LaH

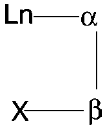
TS exchangeH Cp_2LuH TS exchangeH Cp_2YbH^-

Fig. 5. DFT(B3PW91) optimized geometry of the transition state for hydrogen exchange for Ln = La, Ce, Yb and Lu (taken from Ref. [71]).

With the exception of Ce, the transition state has a diamond shape compressed along the Ln···H_B direction (H_A–Ln–H_C average 56°, H_A–H_B–H_C average 156°) with a shorter central Ln–H_B distance and longer wingtip Ln–H_A and Ln–H_C distances (Fig. 5).

The transition state has C_{2v} symmetry although a very slight distortion is obtained for La and Pr. The distance between two adjacent H is remarkably short (around 1.03 Å) and just a little longer for the anionic Eu and Yb systems (1.05 Å). The charge distribution shows accumulation of electron density on the wingtip H_A and H_C. A bond analysis shows the existence of two wingtip Ln–H_A(H_C) bonds and the absence of a Ln–H_B central bond for any lanthanide. This description suggests that the transition state should be viewed as an H_3^- ligand bonded to the metal through the wingtip hydrogen centers. The large H_A–H_B–H_C angle is also consistent with the structure of an anion H_3^-. In other words, this σ-bond metathesis which used the two electrons of the Ln–H bond and the two electrons of the dihydrogen can alternatively be viewed as a nucleophile addition of an hydride to H_2 in the field of a large lanthanide ion.

The trend in activation energy calculated as the difference in energy between the separated reactants and the transition state follows a non-monotonic behavior. With the exception of Ce, Eu and Yb, the activation energy decreases from 1.4(La) to 0.7 kcal mol^{-1} around Pm and Sm before increasing to 3.1 kcal mol^{-1} (Lu). These values are similar to that for Cl_2Sc–H [59] but significantly smaller than for Cl_2Lu–H [60]. The larger calculated activation energy for Cl_2Lu–H compared to that for Cp_2Lu–H can be due, in part, to the different DFT methodologies. It is also consistent with the fact that a more electron donating ligand (Cp) increases the electron density on the hydride which donates electrons more easily to the incoming H_2. The highest barriers have been calculated for $Cp_2CeH_3^+$ (5.05 kcal mol^{-1}), $Cp_2EuH_3^-$ (5.03 kcal mol^{-1}) and $Cp_2YbH_3^-$ (7.20 kcal mol^{-1}). The energy barrier is thus small or very small for all lanthanides. The metal center stabilizes the anionic H_3^- ligand at the transition state and thus makes the exchange energetically facile. Why is the activation energy therefore dependent on the nature of the metal even though the 4f electrons of Ln play no role in the Ln–ligand interaction? We suggest that the electronegativity of the lanthanide metal plays two opposite roles in this reaction. As mentioned earlier, the electrons of the Ln–H bond are key to the reaction. It is likely that reactants in which the Ln–H bond is more polarized toward the hydride would be more reactive. The lanthanide contraction gives some useful insight into this process. The longer La–H distance (in comparison to Lu–H) suggests that the electrons of the La–H bond are more available for the metathesis reaction. However, at the



Scheme 1.

transition state, the metal also needs to stabilize an anionic ligand (H_3^-) mainly through its empty 5d-orbitals. Thus, electronegative Ln with 5d orbitals of lower energy would be more efficient in stabilizing the transition state. These opposing effects can be the reasons for the non-monotonic behavior and for the lowest activation energy occurring around Pm and Sm.

The same explanation accounts for the singularities with $Cp_2Ce–H^+$, $Cp_2Eu–H^-$ and $Cp_2Yb–H^-$. The electrons of the Ce–H bond in cationic $Cp_2Ce–H^+$ are poorly available for reaction while the anionic Cp_2EuH^- and Cp_2YbH^- are not efficient at stabilizing the transition state since the negative charge raises the energy of the empty 5d orbitals of the lanthanide.

This study illustrates the importance of carrying out calculations for the entire Ln family since the reactivity may depend on Ln. We are presently exploring the reactivity with CH_4 [70], and SiH_4 [76]. We are also in the process of comparing the reactivity of a C–H and a C–F bond.

4. Perspectives and limitations

Theoretical studies of lanthanide complexes are still scarce and numerous difficulties and pitfalls no doubt lie in wait for us in future. Nevertheless, some points are already becoming clear. From the literature and our experience, it appears that 4f electrons do not need to be included in the valence shell but can be treated as part of the core. While this approximation saves considerable computational time it also introduces some important limitations. A given core is only valid for a given formal oxidation state of the lanthanide. It is therefore not possible to calculate any process associated with a change of formal oxidation state of the lanthanide. This creates an important limitation for theoretical studies of reactivity. Calculations of spectroscopic properties of lanthanide complexes are also most probably poorly represented within the large core approximation. These limitations are thus somewhat analogous to those met in calculations of first row transition metals. Apart from these exceptions, calculations are very satisfactory. Structural changes associated with changes in ligands are well represented and the relativistic effective core potential describes the relativistic contraction well. Another precaution concerns the modeling of ligands. The lanthanide center can attain a very high coordination number owing to the large metal radius. If a lanthanide quantum model structure has only a small number of ligands, interactions can occur that do not necessarily represent the situation in experimental complexes. In particular, the β-group, X, of any ligand can fold into a four membered ring formation of the type Ln-α-β-X (Scheme 1). It is important to ensure that X well represents the experimental chemical group.

The calculations for reactivity are even rarer and to our knowledge the only exploration for the entire Ln family has only been carried out by us and only for the H exchange reaction. We have found that the currently accepted idea that all lanthanides show a monotonic reactivity trend may not be completely true, so there is much to learn by studying the full lanthanide series. We have also found a significant dependence of the activation energy on the nature of the ancillary ligands ($Cp_2Ln–H$ vs. $Cl_2–Ln–H$) but additional comparative computational studies are necessary. To be safe, it is probably wise to use models of ligands that are as close to reality as possible. These precautions should not hamper further calculations and studies of large lanthanides complexes of chemical importance. The use of both DFT and of DFT QM/MM methods should permit calculations of complexes to provide data very close to the experimental reality. Both structural and reactivity aspects are now computationally accessible for a large number of these systems.

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