

## Chapter 7

# Lanthanide complexes: electronic structure and H-H, C-H and Si-H bond activation from a DFT perspective

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This paper discusses some relationships between the electronic structure and the reactivity of lanthanide complexes. The electronic structures of some representative lanthanide complexes are described. The *4f* electrons do not participate in the Ln-X bond and a comparison between lanthanide and  $d^0$  transition metal complexes from Groups 3 and 4 highlights the dominant ionic character in the bonding to lanthanide centers. However some covalent character cannot be excluded and this covalent character rationalizes the geometry of the complexes such as the non-planar structure of  $\text{LaX}_3$  ( $X = \text{H, Me, F}$ ). The consequences of the nature of the bonding on the  $\beta$  Si-C agostic interaction in  $\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_3$  is presented. The unusual O-bonding mode of CO to  $\text{Cp}^*_2\text{Yb}$  is briefly summarized. The reactivity of  $\text{X}_2\text{Ln-Z}$  ( $X = \text{Cp, H, Cl}$ , effective group potential;  $Z = \text{H, Me}$ ) with simple molecules like  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{SiH}_4$  is compared. It is shown that the strong ionic character of the lanthanide bonding is key to rationalizing the selectivity of the  $\sigma$ -bond metathesis with alkane and to the lack of it in the case of silane. In particular, the position  $\beta$  to the metal center in the diamond shape *4c-4e*-transition state is not allowed for a methyl group (transition state of very high energy) whereas it is permitted to a silyl group. This is shown to be related to the relative ability of carbon and silicon to be hypervalent.

The activation of inert bonds has long been a key concern of organometallic chemists. Oxidative addition has been recognized as an efficient route for inert bond activation and considerable effort has been spent analyzing the reactivity with a wide variety of transition metal fragments in which the metal can be oxidized.(1) Sigma-bond metathesis, which occurs without change of oxidation state at the metal center, has also been used especially in relation to efficient catalysts for polymerization.(2) These two types of reactions have both attracted the attention of computational chemists.(3) It is not our intention to present an overview of this very rich field. We focus on the theoretical approach of the reactivity of lanthanocene derivatives with H<sub>2</sub>, CH<sub>4</sub> and SiH<sub>4</sub>.

Bond activation by lanthanide complexes has attracted less attention despite the key discovery by Watson of CH<sub>4</sub> activation by Cp\*<sub>2</sub>Lu-CH<sub>3</sub> (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>). (4) Organometallic chemistry of lanthanide complexes is the concern of a relatively small number of groups in the world despite the well known ability of lanthanide complexes to be involved in important catalytic processes including polymerization.(2,5) In addition, only a few members of the series of lanthanide elements have been experimentally studied because of stability problems.

Computational studies of lanthanide species are still few (6-37) (a non-comprehensive list is given) in comparison to the increasing flow of calculations on *d* transition metals. Only recent reviews on the theoretical treatment of reactivity are cited here.(3) A number of studies have been carried out on relatively small systems like the halide complexes.(14-17) Some studies on *4f* element complexes have been focused on the coordination of lanthanide ions(10,11) in connection to extraction and separation of nuclear waste. Calculations of the organometallic molecular compounds and reactivity of lanthanide complexes are scarce.(21-25,28,29,32,33) especially when one takes into account the fact that, in many cases, lanthanide centers have been represented by isoelectronic group 3 metal centers such as scandium and yttrium.(12,22,23) Several factors have probably discouraged computational studies of lanthanide complexes. One major difficulty is the presence of open *4f* shells. Calculations treating explicitly the *4f* electrons by use of a small-core quasi-relativistic effective core potential (ECP) have been limited to small systems, usually of spectroscopic interest,(13) due to the large number of electrons (42 electrons for Yb). It has been accepted that *4f* electrons do not participate in the lanthanide-ligand bond. Therefore, most calculations have been carried out by using large-core quasi-relativistic ECP in which the *4f* electrons are included in the core leading to pseudo-closed systems. Another difficulty is associated with relativistic effects.(6) The scalar relativistic effect is included in the small and large-core ECP's but the spin-orbit coupling is not treated. It is also currently recognized that spin-orbit coupling has no drastic influence on the structure of *4f* complexes because the *4f* electrons do not participate in bonding, unlike what has been shown for actinides.(6)

The next important difficulty in the calculations of lanthanide complexes is the size of the ligands in the coordination sphere of the metal. The lanthanide ion has a large ionic radius and thus can accommodate either a large number (up to 12) of small- to medium-size ligands or a smaller number of very bulky ligands.<sup>(5)</sup> This introduces in the calculations, an important number of atoms and therefore a large number of degrees of freedom which makes the geometry optimization a time-consuming process. Furthermore, bulky ligands can have a large number of conformers, and there is no simple procedure to locate an absolute minimum on a potential energy surface that may have many secondary minima close in energy. Reducing the number of atoms in the ligand is a current technique among computational chemists and in many cases presents no difficulties. For instance  $C_5Me_5$  has usually been modeled by  $C_5H_5$  but also by Cl or H with relative success.<sup>(22-24,38)</sup> However, the use of other models, like  $SiH_3$  for  $SiMe_3$ , has led to artifacts and structures that cannot be compared to the experimental species.<sup>(30)</sup> Special caution is thus needed in the modeling of ligands of lanthanide complexes. The necessity to take into consideration the full nature of ligands for the study of weak interactions, such as the agostic interaction, has been noted for *d*-metal transition systems.<sup>(39)</sup> This should be a key concern for lanthanide complexes. For this reason, the hybrid QM/MM method has been extremely useful for the study of large size complexes.<sup>(40)</sup>

Here, we analyze first the participation of the *4f* electrons in lanthanide-ligand bonds. Computations suggest that *4f* electrons can be put in the core of the ECP. This allows the calculations of large systems with manageable computational effort. The strong ionic character of the lanthanide-ligand bond is discussed and some consequences on structures are presented. The reactivity of models of  $Cp_2Ln$  with  $H_2$ ,  $CH_4$  and  $SiH_4$  is discussed. The trends can be rationalized using the strong ionic character of the lanthanide-ligand bonds.

## The electronic structure of the Ln-X bond

### Non-participation of the *4f* electrons of the Ln center in the Ln-X bonds

It has been widely accepted within the “lanthanide” community that, unlike the *5f* electrons for actinides, the *4f* electrons on the lanthanide centers do not participate in bonding to the coordinated ligand. This qualitative statement needed some quantitative evaluation by theory. Earlier studies, carried out on few systems and lanthanide elements, have shown that the *4f* electrons do not participate in the lanthanide ligand bonding.<sup>(13)</sup> We have carried out a systematic study of  $LnX_3$  ( $X = NH_2$ ) for the entire series of lanthanide elements, in which we have compared the results of calculations with explicit participation

of the  $4f$  electrons (small-core ECP) with calculations in which the  $4f$  electrons are part of the core (large-core ECP).<sup>(27)</sup> The results of calculations show the non-involvement of the  $4f$  electrons. The Ln-N bond distance is shorter by only 0.04 Å with a small-core ECP than with a large-core ECP for any lanthanide center. This difference has been attributed to the lack of core-valence correlation with a large-core ECP and not to the participation of the  $4f$  electrons. The lack of participation of the  $4f$  electrons in bonding is also evidenced by the calculated  $4f$  orbital occupancy. The total number of  $4f$  electrons, as calculated by an NBO analysis, is equal to that in the isolated atom and determines the total spin of the molecule as indicated by its electronic configuration. In each case, the most stable spin state is that predicted by Hund's rule. The non-participation of the  $4f$  electrons in bonding with a ligand behaving as both  $\sigma$ - and  $\pi$ -electron-donor ( $\text{NH}_2$ ) has also been established in the case of a  $\pi$ -accepting ligand such as CO. Calculations of  $\text{H}_2\text{Yb}(\text{CO})_{1,2}$ , models for  $(\text{C}_5\text{Me}_5)_2\text{Yb}(\text{CO})_{1,2}$  show the absence of back-donation from the  $4f$  electrons of the  $\text{Yb}^{\text{II}}$  center to the CO ligand. The level of calculation has been validated by comparing the calculated geometry and  $\nu_{\text{CN}}$  stretching frequency of  $\text{Cp}_2\text{Yb}(\text{CNMe})_2$  with the corresponding experimental data on  $\text{Cp}^*_2\text{Yb}(\text{CN}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_2$ .<sup>(31)</sup> Calculations of  $\text{Cp}_2\text{Yb}(\text{CO})_{1,2}$  have been carried out with a large-core ECP for Yb. The observed  $\nu_{\text{CO}}$  stretching frequencies which are lower than that of free CO, have been interpreted as coordination of CO to Yb via the oxygen atom.<sup>(31)</sup> Therefore, the  $4f$  electrons can probably be safely included in the core ECP for all types of lanthanide complexes. The lanthanide contraction (the difference between the Lu-X and La-X bond lengths) is well represented by use of the averaged relativistic electron core potential (AREP). The calculations give values varying between 0.165 and 0.185 Å depending on X.<sup>(36)</sup>

One should highlight the limitations associated with the use of the large-core ECP in the calculations. Each large-core ECP is specific not only of a lanthanide element but to its oxidation state. Therefore, it is not possible to compare complexes with a lanthanide in different oxidation states because the total energies with different core ECP's cannot be compared. It is thus also not possible to carry out a computational study of a reaction involving a change of oxidation state at the lanthanide center in the way done currently with  $d$  transition metal complexes. Luckily, the  $\sigma$ -bond metathesis reactions, predominant in lanthanide chemistry, can be studied with this methodology.

### Strong Ionic Nature of the Ln-X Bond

The nature of the Ln-X bonding has been the subject of several papers.<sup>(15-17,36)</sup> The lanthanide elements are electropositive centers resulting in ionic Ln-X bonding. However the covalent bonding cannot be totally excluded. It plays a key role in the non-planarity of  $\text{LnF}_3$  which has interested the theoretical community for many years.<sup>(14-16,41)</sup> We have carried out a calculation of

several sets of  $\text{MX}_3$  ( $\text{M} = \text{Ln}, \text{Sc}, \text{Y}, \text{Ti}^+, \text{Zr}^+, \text{Hf}^+$ ;  $\text{X} = \text{H}, \text{Me}, \text{Hal}, \text{NH}_2$ ). Non-planar geometries have been obtained for  $\text{X} = \text{H}, \text{Me}$  and  $\text{F}$  for earlier lanthanide and group 4 cationic complexes. Late lanthanide centers and group 3 metal complexes as well as  $\text{Cl}, \text{Br}, \text{I}$  and  $\text{NH}_2$  favor a nearly planar or totally planar geometry. An NBO analysis of these complexes has shown a significant  $5d$  participation in the Ln-X bonding which is known to favor pyramidalization for  $d^0$   $\text{MX}_3$  complexes.(42) Comparison with  $\text{ScX}_3, \text{YX}_3, \text{TiX}_3^+,$  and  $\text{HfX}_3^+$  shows that the participation of the valence  $d$  orbitals is considerably smaller for all lanthanide complexes than for the group 3 and 4 complexes. The  $6s$  participation is not negligible either but also smaller than for group 3 and 4 elements while the  $6p$  participation is almost null. The total charges remain close to the charges given by the formal oxidation number in the case of all lanthanide elements and are considerably smaller in the case of the group 3 and 4 transition metal centers. This illustrates the predominant ionic character in an Ln-X bond but shows how the small amount of covalent contribution is fundamental to rationalizing the geometry of lanthanide complexes. Similar conclusions have been reached in a study of  $\text{Ln}\{(\text{CH}(\text{SiMe}_3)_2)_3\}_3$ .(35,37)

### The ionic character of the Ln-X bond and the agostic interaction

The C-H agostic interaction manifests itself by a short distance between a metal center and a C-H bond, traditionally part of a ligand coordinated to the metal center. It is also manifested by an elongation of the agostic C-H bond as shown by spectroscopic or solid-state data.(43) This interaction, which occurs when the metal is electron-deficient, has been first interpreted as the donation of electron density of the C-H bond to an empty coordination site of the metal. This interaction is weak because the C-H bond is a very poor Lewis base even if the electron deficient metal center is a reasonably powerful Lewis acid. Furthermore, this weak interaction needs some through-space overlap between the metal center and the C-H bond. This is why a C-H bond is a better candidate for an agostic bond than any C-C bond of an alkyl chain. The C-H bonds shield the C-C bond from access to the metal center which explains why there are no reported agostic C-C bonds except under some specific constraints.(44) However, this is in contradiction with the report of agostic  $\beta$  Si-C bonds, suggested by the much longer Si-C distance compared to other Si-C bonds within the same molecule. Several lanthanide complexes with an elongated Si-C bond part of  $\text{CH}(\text{SiMe}_3)_2$  or  $\text{N}(\text{SiMe}_3)_2$  ligand have been reported.(19,37,45,46) The absence of a  $\gamma$ -C-H agostic bond in these complexes is surprising because  $\gamma$ -agostic bonds have been reported,(47) and because the metal center could easily access the electron density of a C-H bond from a Me group of  $\text{CH}(\text{SiMe}_3)_2$  or  $\text{N}(\text{SiMe}_3)_2$ .

Calculations of complexes with reported elongated Si-C bonds in the solid state structure have been carried out.(19,35,37) The QM/MM calculations reproduce well the experimental geometrical features as shown for  $\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_3$  in Figure 1 (1 and 2).(35) Calculations show an elongation of a single  $\beta$  Si-C bond and the absence of any long C-H bond in the  $\alpha$  and  $\gamma$  positions. The traditional interpretation of the agostic interaction cannot be satisfactory. In a study of  $\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_3$  and  $\text{La}\{\text{N}(\text{SiMe}_3)_2\}_3$ , we have suggested that the elongation of the  $\beta$  Si-C bond is due, in part, to a delocalization of the lone pair used for Ln-R bonding for  $\text{R} = \text{CH}(\text{SiMe}_3)_2$  and  $\text{N}(\text{SiMe}_3)_2$  within the ligand.(35,36) This interpretation is not new in the literature.(48) In key theoretical studies of  $\text{Cl}_3\text{Ti-CH}_2\text{-CH}_3$ , it has been suggested that the  $\beta$ -agostic C-H in  $\text{Cl}_3\text{Ti-CH}_2\text{-CH}_3$  is due to a delocalization of the electron density of the Ti-C bond within the ethyl ligand.(48b) Similar analysis has been reported for  $\text{Li-CH}_2\text{-CH}_3$ .(48c) A similar interpretation was suggested for an Yb complex prior to computational support.(48a) What was suggested for early  $d$  transition metal complexes is enhanced for lanthanides complexes. The much greater ionic character of the Ln-C bond, compared to that of a Ti-C bond, makes the electron density of the Ln-C bond even more localized on C. The delocalization by negative hyperconjugation (delocalization into the  $\sigma^*$  orbital of the adjacent bonds), well established in numerous anions, elongates all  $\sigma$  bonds that are vicinal to the carbanionic lone pair. This delocalization is magnified with 3<sup>rd</sup> row elements like silicon, because  $\sigma^*_{\text{Si-C}}$  is at lower energy than  $\sigma^*_{\text{C-C}}$ . However the lanthanide ion plays a role. If negative hyperconjugation was the only cause for elongations of bonds, all Si-C bonds of the  $\text{SiMe}_3$  groups in  $\text{CH}(\text{SiMe}_3)_2$  would be long. This is not the case and only the  $\beta$  bond pointing towards the metal is elongated. The strong electrostatic field of the metal polarizes the electron density in the ligands, the  $\sigma^*_{\text{Si-C}}$  of the bond closest to the metal receives more density which in turn further elongates this bond. An immediate consequence of this interpretation is that the elongation of the Si-C bond in a  $\text{N}(\text{SiMe}_3)_2$  ligand should not be as large as in  $\text{CH}(\text{SiMe}_3)_2$  because a nitrogen lone pair would delocalize less than a carbanionic lone pair. This is supported by the available experimental data on the amido complexes.(46) It should be pointed out that the traditional interpretation (donation of the electron density of the  $\sigma$  bond to the metal center) and the interpretation by negative hyperconjugation are interconnected and are not easy to separate. This is why the donation of the Si-C bond to the metal center has been considered as the major effect in another study of  $\text{Ln}\{\text{CH}(\text{SiMe}_3)_2\}_3$  ( $\text{Ln} = \text{La, Sm}$ ). (37)

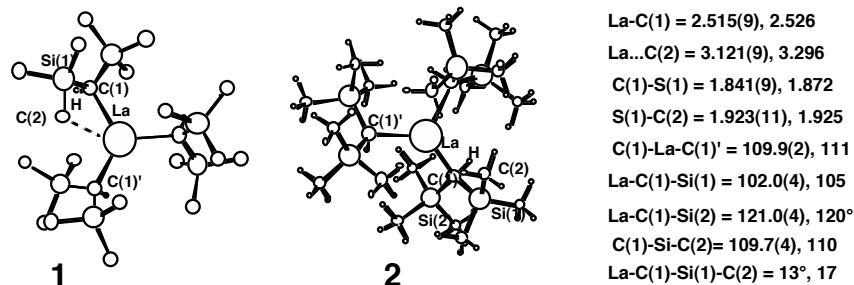
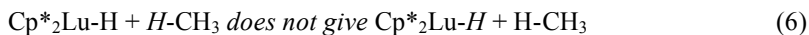
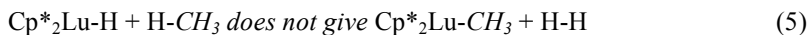
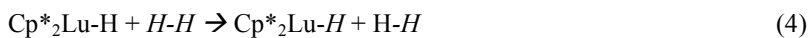
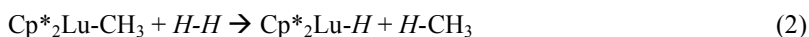
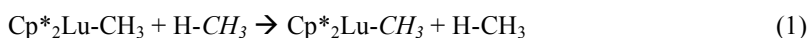


Figure 1. Experimental,(45) **1**, and QM/MM,(35) **2**, structures of  $\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_3$ . Distances (experimental, calculated) in Å, Angles in degrees.

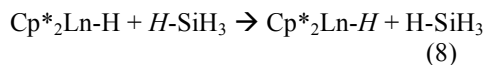
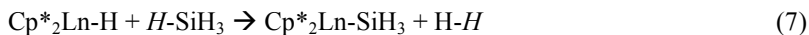
## Sigma Bond Activation

The discovery that  $\text{Cp}^*_2\text{Lu-CH}_3$  ( $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ) activates  $\text{CH}_4$  (eq 1) has been a landmark in the search for new catalysts able to activate inert bonds especially those in alkanes.(4) The  $\text{Cp}^*_2\text{Lu-CH}_3$  complex also reacts with  $\text{H}_2$  to give  $\text{Cp}^*_2\text{Lu-H}$  and  $\text{CH}_4$  (eq 2), but it does not give the hydride complex and a product resulting from the formation of a C-C bond when reacting with  $\text{CH}_4$  (eq 3). The hydride complex  $\text{Cp}^*_2\text{Lu-H}$  exchanges H with  $\text{H}_2$  as proven by isotope labeling (eq 4).  $\text{Cp}^*_2\text{Lu-H}$  does not react with  $\text{CH}_4$  to give back the methyl complex (eq 5) and it does not undergo H/H exchange with  $\text{CH}_4$  (eq 6).

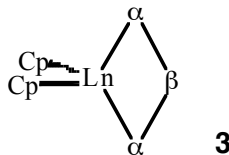


Several examples of reactions with a Si-Y bond (Y = H, R) and different lanthanide elements are known: synthesis of organolanthanide silyl complexes, hydrido complexes, hydrosilylation of alkenes and dehydropolymerization of silane.(49,50) In these reactions, one key issue is the comparison between the

silylation reaction represented with  $\text{SiH}_4$  as a model silane by eq 7 and the H/H exchange reaction represented by eq 8.



These reactions need to occur by  $\sigma$ -bond metathesis via a  $4c-4e$ -transition state **3**, because there is no available  $d$  electron on the metal center and because the  $4f$  electrons are too deep in energy to be involved in redox processes. Eqs 2 and 5 suggest that formation of the hydride lanthanide complex from the alkyl complex is exothermic. The regioselectivity indicated by eqs 1 and 3 as well as eq 6 suggests that, in the  $4c-4e$ -transition state, the position opposite to the metal center (position  $\beta$ ) cannot be occupied by an alkyl group but only by H. In contrast, no equivalent regioselectivity is mentioned for silane derivatives where the silicon center can occupy the  $\alpha$  or  $\beta$  positions in the  $4c-4e$ -transition state.



The reaction of eq 4 occurs at low temperature whereas the reaction of eq 1 occurs at room temperature, suggesting a higher barrier for the latter.<sup>(4)</sup> These reactions have been run with selected lanthanide elements and there is no information on the influence of the lanthanide on these reactions. The non-implication of the  $4f$  electrons in Ln-X bonding suggests that all lanthanide elements could have similar reactivity. However the change in the Ln atomic radius, the related lanthanide contraction, as well as the variation in electronegativity can influence the reactivity. We thus have looked at the energy profile of eq 1 to 8 for any Ln element.

### Reaction of $\text{Cp}_2\text{Ln-H}$ with $\text{H}_2$

This reaction has been thoroughly studied.<sup>(21-24,28)</sup> The  $\text{Cp}^*_2\text{Ln-H}$  species, never isolated as a monomer, forms dimers or oligomers with bridging hydrides.<sup>(51)</sup> It has been accepted that the monomer is the reactive species and has thus been considered in all computational studies. Modeling  $\text{C}_5\text{Me}_5$  has been needed for saving computational time.  $\text{C}_5\text{H}_5$  is a current model but models like H, Cl and effective group potentials (EGP) have also been used.<sup>(23,24,29,50)</sup> DFT (B3PW91) calculations with the large core ECP from the Stuttgart-Dresden groups were carried out for all Ln.<sup>(28)</sup> The usual oxidation state III has been considered by having neutral  $\text{X}_2\text{Ln-H}$ . However oxidation state IV is accessible

for Ce and oxidation state II is accessible for Eu and Yb. For this reason,  $\text{Cp}_2\text{Ce-H}^+$ ,  $\text{Cp}_2\text{Eu-H}^-$ ,  $\text{Cp}_2\text{Yb-H}^-$  were considered to estimate the influence of the oxidation state of Ln. This leads to some singularities, left aside here.(28,32,33)

The Ln-H bond in  $\text{Cp}_2\text{Ln-H}$  is not along the  $C_2$  axis of  $\text{Cp}_2\text{Ln}$ , which indicates a preference for a pyramidal lanthanide as found for  $\text{LnX}_3$ . The  $\text{H}_2$  molecule does not form a stable adduct with  $\text{Cp}_2\text{Ln-H}$  with the method of calculation used. The two cyclopentadienyl and the hydride ligands are probably sufficiently electron-donating to decrease significantly the Lewis acidity of the lanthanide center. The H/H exchange of eq 4 has a very low energy barrier, which varies between 0.67 to 3.1 kcal/mol depending on the  $\text{Ln}^{\text{III}}$  element. The smallest barrier occurs around Pm and Sm namely near the middle of the lanthanide series. Significantly higher barriers from 5 to 8 kcal/mol have been obtained for  $\text{Ce}^{\text{IV}}$ ,  $\text{Eu}^{\text{II}}$  and  $\text{Yb}^{\text{II}}$  complexes. The very low barriers for  $\text{Ln}^{\text{III}}$  complexes represent properly a reaction observed at low temperature.

The  $4c-4e$ -transition state has the geometry of a diamond compressed along the Ln-H $\beta$  direction as schematically represented in 4. The  $\text{H}\alpha\text{-H}\beta\text{-H}\alpha'$  angle is around  $156^\circ$  for any  $\text{Ln}^{\text{III}}$  element. This leads to a short distance between Ln and H $\beta$ . A charge analysis indicates that H $\alpha$  and H $\alpha'$  are negatively charged, H $\beta$  positively charged and that there is no bond between Ln and H $\beta$ . This description suggests that the transition state should be viewed as an  $\text{H}_3^-$  ligand bonded to the metal center through the wingtip H $\alpha$  and H $\alpha'$  centers. This interpretation is also consistent with the obtuse  $\text{H}\alpha\text{-H}\beta\text{-H}\alpha'$  angle, not too far from the  $180^\circ$  angle in isolated  $\text{H}_3^-$ . The short Ln-H $\beta$  distance is the result of the short H $\alpha$ -H $\beta$  distances in the  $\text{H}_3^-$  moiety but not that of an interaction with Ln.

There is only a small influence of the lanthanide center (taken in oxidation state III). For this reason, we show the energy profile for La in Figure 2. There is no clear reason for the energy barrier to be the smallest near the middle of the lanthanide series, but this pattern has been found for reactions of eqs 1 to 8.

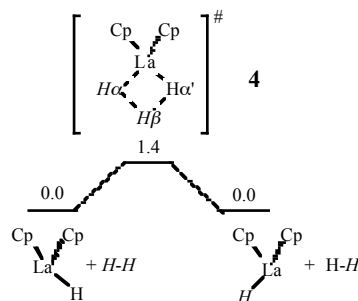


Figure 2. Potential energy profile (kcal/mol) for the reaction of eq 4.(28)

Although calculations with the explicit  $\text{C}_5\text{H}_5$  ligand can be carried out at reasonable computational time, there is interest in comparing results with

models of  $C_5H_5$ . Folga and Ziegler have considered  $Cl_2Lu-H$  with a functional different from ours.<sup>(24)</sup> They have found that  $H_2$  coordinates to Lu to form a dihydrogen adduct, only 1 kcal/mol more stable than the isolated reactants, before the H/H reaction takes place. Their calculated barrier is also considerably higher (10.6 kcal/mol above the isolated reactants). Is this due to the difference in the functional or in the modeling of the reagent? The questions have been answered via a comparison of the H/H exchange reaction with  $X_2Ln-H$  ( $X = H, Cl$  and an EGP) using the same level of calculations as for  $X = C_5H_5$ .<sup>(29)</sup>

No search for an  $H_2$  adduct was carried out; the comparison has been focused on the height of the energy barrier and the geometry of the transition state. The energy barriers for the  $X_2Ln^{III}-H$  complexes vary between 1.8 and 4.5 kcal/mol for  $X = H$ , between 1.9 and 8.4 kcal/mol for  $X = Cl$  for the entire lanthanide family. The energy barriers are almost equal with the explicit  $C_5H_5$  and the EGP representing this ligand. This shows that the high barrier found by Folga and Ziegler is associated, in great part, with the modeling of Cp by Cl (in the case of Lu the energy barrier is 10.6 kcal/mol for Folga and Ziegler and 8.4 kcal/mol in our work). Although the energy barrier is higher than that found with the Cp ligand, all calculations give an energy barrier characteristic of a kinetically facile reaction. Remarkably, Cl is the poorest model for Cp because it is a poor electron donor despite the presence of Cl lone pairs which can act like the degenerate  $e$  orbitals of Cp and make Cl and Cp formally isolobal. The more electron-donating hydride ligand gives numerical results closer to that with explicit  $C_5H_5$ . Furthermore the variation of the barrier within the lanthanide series is slightly different for explicit Cp and H and Cl. In particular, the lower barrier near the middle of the lanthanide series is not obtained with  $X = H$  and Cl for eq 4. The geometrical shape of the transition states is reasonably well reproduced by all models with systematic shifts in distances.

These comparisons show that modeling Cp by Cl and H is acceptable for obtaining gross features but not subtle effects. The relative energy barriers for Cp and Cl supports the interpretation of the H/H exchange as a nucleophilic substitution of  $H^-$  at  $H_2$  in the coordination sphere of Ln. A more electron-donating ligand (Cp vs Cl) makes H more hydridic in  $Cp_2Ln-H$  than in  $Cl_2Ln-H$ . The energy barrier for H/H exchange is thus lower with the Cp ligand.

#### Reactions of $X_2Ln-CH_3$ with $H_2$ or $X_2Ln-H$ with $CH_4$

The reaction of eq 2 is exothermic with a calculated energy of reaction of around 13.3 kcal/mol for all  $Cp_2Ln^{III}$  complexes. With Cl in place of Cp, the calculated energy of reaction is around 7.8 kcal/mol which is similar to the value reported by Folga and Ziegler.<sup>(24)</sup> The energies of reaction of eq 2 are reasonably close for Cp and Cl ligands and for computational time-saving reasons, the full energy profiles for the entire series of lanthanide elements and for eqs 1, 2, 3, 5 and 6 were calculated with Cl in place of Cp. The calculations

done for eq 4 with X = H, Cl and Cp, have given a higher energy barrier for Cl than for Cp. Similar trends are expected for the other reactions. The energy barrier does not vary much with the lanthanide element. A calculation with Cp was thus carried out only for La for eqs 2 and 5 (Figure 3).

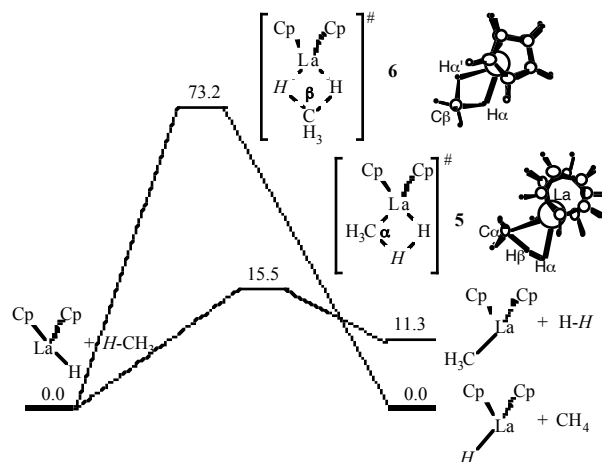


Figure 3. Potential energy profile (kcal/mol) for reactions of eqs 2 and 6.(32)

The  $X_2Ln-CH_3$  complexes react with  $H_2$  to form  $X_2Ln-H$  and  $CH_4$  (eq 2) but the  $X_2Ln-H$  complexes do not undergo H/H exchange in presence of  $CH_4$  (eq 6). The activation barrier for eq 2 varies depending on the  $Ln^{III}$  element between 5.5 kcal/mol and 9.2 kcal/mol above separated  $Cl_2Ln-CH_3$  and  $H_2$  with a minimum of 5.1 kcal/mol around Pm and Sm and the highest value for Lu. The activation barrier for eq 6, which is over 70 kcal/mol for any  $Ln^{III}$  element, shows that the H/H exchange is a kinetically forbidden reaction. The energy values for  $Cp_2La$  and  $Cl_2La$  are similar.

The two transition states, for eqs 2 and 6, differ by the position of the  $CH_3$  in the  $4c-4e$ -transition states. The Me group is in the  $\alpha$  position,  $\square$ , for eq 2 and in the  $\beta$  position for eq 6. It has been shown that the  $\beta$  position in  $4c-4e$ -transition state is unfavorable for a  $CH_3$  group.(22,52) In the case of eq 2,  $H\alpha$ ,  $H\beta$  and C of  $CH_3$  are almost aligned (5) and a  $CH_3^{\delta-}$  group abstracts  $H^+$  from a strongly polarized  $H^{\delta-}-H^{\delta+}$  species. This occurs in the coordination sphere of Ln. In the transition state for eq 6, a  $CH_5^-$  anion is formed (6) as shown by the square base pyramid geometry at C. It is currently accepted that  $CH_5^-$  species is an unfavorable species, especially in the absence of electronegative substituents to stabilize the hypervalent carbon. Groups favoring hypervalent anionic pentacoordination makes this transition state energetically accessible (see  $SiH_4$ ).

### Reactions of $X_2Ln-CH_3$ with $CH_4$

The only possible reaction between  $X_2Ln-CH_3$  and  $CH_4$  should be the exchange of the methyl groups (eq 1) because the Me group should not go at the  $\beta$  position in the  $4c-4e$ -transition state. This prevents the formation of  $X_2Ln-H$  and  $C_2H_6$  (eq 3) for which an energy barrier of at least 70 kcal/mol is expected. In addition, this latter reaction is calculated to be endothermic by around 5.70 kcal/mol for  $X = Cl$  and by around 11 kcal/mol for  $X = Cp$  for any  $Ln^{III}$  elements. The energy profile for  $Cp_2La$  is shown in Figure 4 for eq 1.

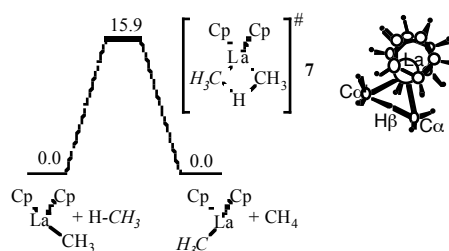


Figure 4. Potential energy profile (kcal/mol) for the reaction of eq 1.(32)

The geometry of the transition state corresponding to the methyl exchange reaction (eq 1) as observed by Watson is shown in 7. There is essentially full alignment between the two carbons and the central hydrogen that transfers between the two methyl groups. This reaction should better be viewed as a proton transfer between two methyl anions in the coordination sphere of the lanthanide center. The activation energy for reaching this transition state varies between 15.9 and 17.3 kcal/mol with the minimum around Pm and Sm with Cl ligand. This relatively low activation energy is consistent with the experimental data. The calculated value is significantly lower than the one calculated with the same model but with another functional (26 kcal/mol) by Folga and Ziegler.(24) The values calculated with  $Cl_2Ln$  and  $Cp_2Ln$  are close.

### Reactions of $Cp_2Ln-H$ with $SiH_4$

The energy patterns of the two reactions of  $Cp_2Ln-H$  with  $SiH_4$ , as represented by eq 7 and 8, are shown in Figure 5. The energy profiles of the H/H exchange reaction (eq 8) are drastically different from that with  $CH_4$  (eq 6). In the case of the silane, the reaction starts by the formation of an  $SiH_4$  adduct. The bond dissociation energy of  $SiH_4$  varies between 4 and 6 kcal/mol which indicates only weak bonding of  $SiH_4$ . The most important change compared to  $CH_4$  lies in the energy barriers. The energy barrier for H/H exchange is only

between 1.7 and 1.9 kcal/mol above this adduct. This strongly contrasts with the case of  $\text{CH}_4$  where the H/H exchange is associated with a barrier of 70 kcal/mol. The H/H exchange reaction forbidden for  $\text{CH}_4$  is very facile for  $\text{SiH}_4$ . The geometry of the transition state (**8**) shows that the  $\text{SiH}_5^-$  moiety has the geometry of a square pyramid with the two exchanging H at the basal sites. The difference between  $\text{CH}_4$  and  $\text{SiH}_4$  appears to be in the relative stability of  $\text{CH}_5^-$  and  $\text{SiH}_5^-$  and not in a change in the geometry of the transition states.

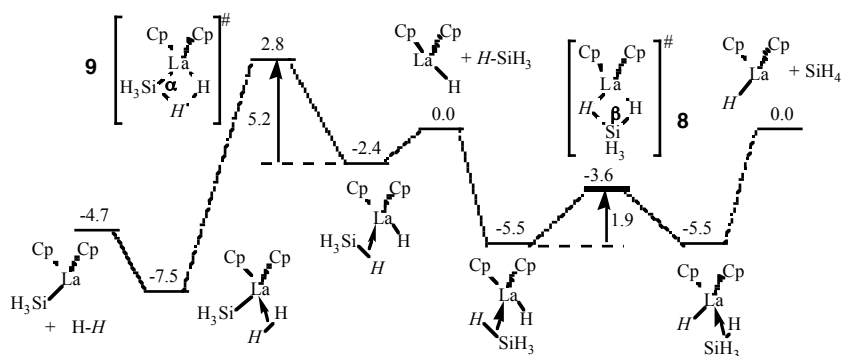
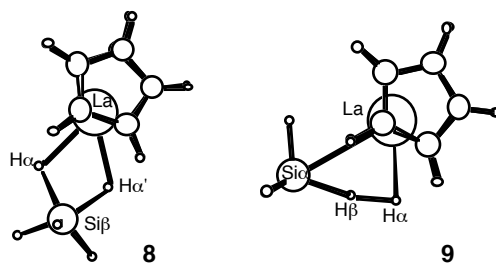


Figure 5. Potential energy profile (kcal/mol) for eqs 7 and 8.(33)



The silylation reaction (eq 7) is calculated to be energetically favorable. The reaction energy varies between 3 and 4.7 kcal/mol for all  $\text{Ln}^{\text{III}}$  centers. As shown in Figure 5, the reaction starts with the formation of a weak silane adduct (BDE around 2 kcal/mol); a transition state, 5.2 kcal/mol above the  $\text{SiH}_4$  adduct, leads to an  $\text{H}_2$  complex, 5 kcal/mol lower than the silane adduct. This reaction also has a low energy barrier, but it is slightly higher than the barrier for H/H exchange. The geometry of the transition state (**9**) is also a distorted diamond with a  $\text{Si}\alpha\text{-H}\beta\text{-H}\alpha$  angle between  $164^\circ$  and  $168^\circ$  depending on the  $\text{Ln}^{\text{III}}$  element.

### Comparison of activation of H<sub>2</sub>, CH<sub>4</sub> and SiH<sub>4</sub>

The results above show no significant influence of the lanthanide element for any of the reactions and a moderate influence of the model used for cyclopentadienyl. Consequently, we can compare the calculations done with Cp<sub>2</sub>La which are shown in Figures 2-5.

Activation of H<sub>2</sub> by Cp<sub>2</sub>La-H (eq 4) entails almost no energy barrier. Reaction of H<sub>2</sub> with Cp<sub>2</sub>La-CH<sub>3</sub> requires a slightly higher barrier but the value of 4.2 kcal/mol is still characteristic of a kinetically facile reaction. There is a thermodynamic drive to form the hydride complex. The increase in the energy barrier when H is substituted by a Me group has been documented in the reductive elimination.<sup>(53)</sup> A Me group has directional bonding preference whereas the spherical *1s* orbital of H allows bonding in all directions. In agreement with this fact is the higher but still accessible energy barrier (15.9 kcal/mol) for the methyl exchange process of eq 1. The higher energy barriers are in agreement with the higher temperature at which this reaction has been observed.

The reactivity of CH<sub>4</sub> and SiH<sub>4</sub> is quite different. The greater difference concerns the H/H exchange reaction. The energy barrier is inaccessibly high (73.2 kcal/mol) for CH<sub>4</sub> and very low (1.9 kcal/mol) for SiH<sub>4</sub>. The reaction is best described as a nucleophilic substitution of H at either C or Si in the coordination sphere of Ln. The transition state is a pentacoordinated anionic species CH<sub>5</sub><sup>-</sup> or SiH<sub>5</sub><sup>-</sup> which is energetically highly unfavorable for C and much more favorable for Si. A carbon center cannot be at the β position in the *4c-4e*-transition state but the energy barrier is lowered with electronegative substituents (F), known to stabilize a hypervalent species (in progress). We have also verified vinyl and phenyl groups do not favor either the β position.

The reactions of the lanthanide-hydride complex with CH<sub>4</sub> and SiH<sub>4</sub> to form the lanthanide-methyl and lanthanide-silyl complexes also show differences. Formation of the methyl complex from the hydride complex is energetically disfavored (the reaction energy is 11.3 kcal/mol for eq 5) whereas formation of the silyl complex is energetically favored (the reaction energy for eq 7 is -4.7 kcal/mol). The endothermicity associated with eq 5 suggests that the La-H bond is stronger than the La-Me bond because the H-H and C-H bond energies are similar. No simple conclusion can be drawn from the exothermicity of eq 7. The Si-H bond in SiH<sub>4</sub> is weaker than the C-H bond in CH<sub>4</sub>, which can explain the reaction exothermicity of eq 7. The calculations suggest that the Ln-silyl bond is not weak. Reactions of organosilanes with lanthanide hydride complexes can thus occur *via* reactions of eqs 7 and 8. Multiple step reactions can lead to a high variety of products observed experimentally.<sup>(49)</sup>

### Conclusions and perspectives

The theoretical studies of some complexes and reactions involving lanthanide complexes allow to draw the following conclusions:

- The  $4f$  electrons do not participate in lanthanide-ligand bonding. This allows to carry out calculations with large-core ECP. Because of the dependence of the large-core ECP on the oxidation state of the lanthanide, only reactions involving no redox process at the metal center can be studied.
- The Ln-X bond has a strong ionic component, which is much larger than for isoelectronic group 3 and 4 complexes. Therefore modeling lanthanide elements by group 3 or 4 metals may not be appropriate. Despite the predominantly ionic character in Ln-X bonding, the covalent part involving a participation of the Ln  $5d$  orbitals is key to rationalizing the geometry of lanthanide complexes such as the non-planar geometry of  $\text{LnX}_3$  for  $X = \text{H}$ , alkyl and F.
- The strong ionic character of the Ln-X bond suggests that the  $\beta$  agostic Si-C bond observed in complexes with  $\text{CH}(\text{SiMe}_3)_2$  and  $\text{N}(\text{SiMe}_3)_2$  ligands is in part due to a delocalization of the C or N lone pair involved in bonding with Ln in the  $\beta$  Si-C bond closer to the metal. The delocalization is stronger for  $\text{CH}(\text{SiMe}_3)_2$  than for  $\text{N}(\text{SiMe}_3)_2$ , consistent with a greater Si-C elongation in the former ligand.
- The strong ionic character of the Ln-X bond brings a new perspective to the  $\sigma$ -bond metathesis reactions. The reaction of  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{SiH}_4$  with  $\text{Cp}_2\text{Ln-H}$  or  $\text{Cp}_2\text{Ln-CH}_3$  are best viewed as nucleophilic substitution by  $\text{H}^-$  or  $\text{CH}_3^-$  at  $\text{H}_2$ ,  $\text{CH}_4$  or  $\text{SiH}_4$  in the coordination sphere of the lanthanide cation. This leads to a very low energy barrier for H/H exchange in the reaction of  $\text{Cp}_2\text{Ln-H}$  with  $\text{H}_2$  and  $\text{SiH}_4$  but to a forbidden H/H exchange in the reaction of  $\text{Cp}_2\text{Ln-H}$  with  $\text{CH}_4$ . The different behavior for  $\text{CH}_4$  and  $\text{SiH}_4$  is due to the formation, at the transition state, of  $\text{CH}_5^-$  and  $\text{SiH}_5^-$  respectively. Hypervalency is unfavorable for C and more favorable for Si. The reactions with alkanes are thus very selective. Only H can take the position  $\beta$  to the metal in the  $4c-4e$ -transition state. Preliminary calculations with other reactants like alkenes and arene give similar results. No such selectivity occurs with silane derivatives because the silyl group can take the positions  $\alpha$  and  $\beta$  to the metal center in the  $4c-4e$ -transition state.
- There is no calculated significant influence of the lanthanide element for a given oxidation state (here  $\text{Ln}^{\text{III}}$ ) on the energy of reaction and energy barrier for all studied reactions. One should not exclude effects that are not present here like the steric bulk of ligands, which can influence the accessibility to the metal center in the case of the late lanthanides, which have a smaller ionic radius.

To what extent are these results characteristic of lanthanide complexes? Alkali and alkali-earth elements also give ionic bonding but no similar reactivity has been reported. Is this difference in reactivity associated with the difference in ionic radius, the small covalent character in the lanthanide elements, or with other factors? Clarifying these points would help to rationalize the uniqueness of lanthanide complexes in activating inert bonds.

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