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DFT Study of H−H Activation by Cp_2 LnH d^0 Complexes

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Abstract: The energy required to activate the H−H bond in the entire series of Cp_2LnH complexes has been calculated by DFT (B3PW91) methods. The activation energies have been calculated to vary from 0.5 to 8.0 kcal·mol^{-1}, indicating an overall facile reaction. The electronegativity of the lanthanide in its most stable oxidation state is suggested to be a leading factor for interpreting the trends in activation energy. The geometry of the transition state is best viewed as an almost linear H_3^- ligand with short H−H distances and strong M−H interaction, through the wingtip H centers, with Ln. The exchange reaction is thus established to be a σ bond metathesis reaction.

Introduction

The activation of an inert X−Y bond usually occurs through an oxidative addition process in which electrons from the metal are transferred into the antibonding orbital of the X−Y bond. For this reason, d^0 centers cannot be a candidate for bond activation by oxidative addition. In this sense, the discovery that $Cp^*{}_2Lu{-}R$ (R = H, Me) could activate H−H or CH_4 (eq s1−2) was thus a landmark in mechanistic understanding as well as leading to new catalysts.[1]

$$Cp^*{}_2LuH + D_2 \rightarrow Cp_2LuD + HD \tag{1}$$

$$Cp^*{}_2Lu(Me) + CH_4 \rightarrow Cp_2Lu(CH_3) + Me - H \tag{2}$$

Since no electrons are available on the metal, the activation of the inert H−H or C−H bonds must necessarily occur without change of oxidation state at the metal. An alternative mechanism involves a σ bond metathesis involving the electrons of the Ln−R and H−H or C−H bonds. Since the electrons of the M−R bond as well as those of the H−H or C−H bond are in relatively low-lying occupied orbitals, it seems surprising that the reaction occurs with very little activation energy.

Theoretical methods have been used with great success to understand the activation of inert bonds.[2,3] In most cases that have been studied by theoretical methods, activation has been initiated by an oxidative cleavage of the bond. Theoretical studies of metathesis reactions have also been reviewed.[4] EHT studies of activation of H−H and C−H bonds by d^0 complexes suggest that the activation is feasible.[5] Metathesis reactions involving late transition metals in high oxidation states and hydrogenolysis reactions have also been calculated.[2] DFT calculations of R−H (R = H, C, Si) bond activation by Cp_2ScZ, Cl_2ScZ,[6] and Cl_2LuZ (Z = H, CH_3)[7,8] have shown that the initial step is the formation of an R−H adduct that passes through a four-center transition state and leads to the exchanged Z−H adduct. The activation energy has been found to depend strongly on the nature of the R−H bond. Recently, the σ bond metathesis of acetylene with Cl_2ZrH^+ and $Cl_2ZrCH_3^+$ was studied with all-electron HF and MP2 ab initio calculations.[9] From the available studies, it appears that metathesis is easier for Sc than for Lu but the influence of the nature of lanthanide has not been understood.

In this study, we have thus used DFT calculations to study the reaction shown in eq 1 for the entire series of lanthanide elements. We have considered that H_2 reacts with the monomeric biscyclopentadienyl hydride species even if this is not the usual structure of the reactant.[10] In agreement with experimental evidence, the H−H exchange process has been found to have a low activation energy. However, differences between the various lanthanides have emerged from the calculations. A discussion of the results permits a better understanding of the factors that control metathesis reactions with d^0 lanthanide centers.

Computational Details

In previous studies,[11,12] we have shown that Large core Relativistic Effective Core Potentials (RECPs) optimized by the Stuttgart−Dresden Group[13−15] are well adapted to the calculation of the geometries of lanthanide complexes since 4f electrons do not participate in Ln−X bonding. The basis sets adapted to the different RECPs augmented by a polarization function (f function for the lanthanide) were used. Carbon and hydrogen have been treated with an all-electron 6-31G** basis set. Calculations were carried out at the DFT level by using the hybrid functional B3PW91[16,17] with the Gaussian 98 suite of programs.[18] Geometry optimization was carried out without any symmetry restric-

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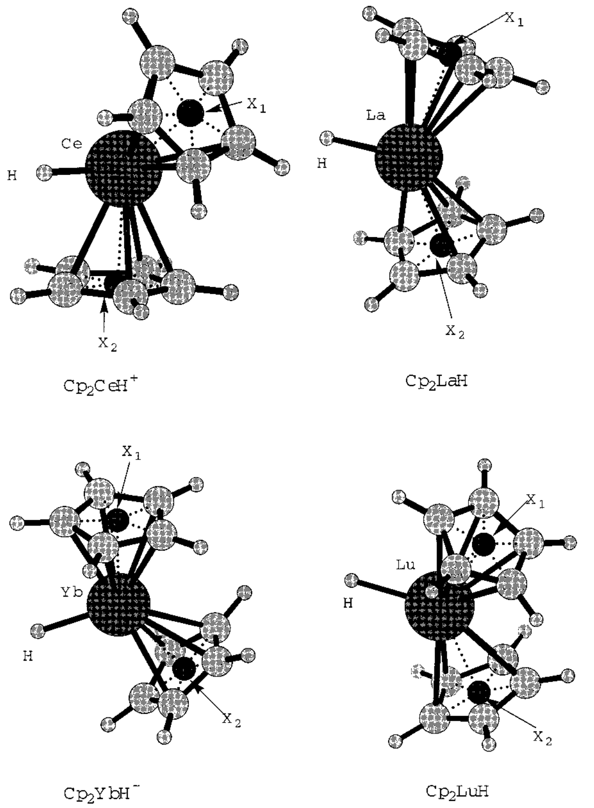

Figure 1. DFT(B3PW91) optimized geometry for Cp_2LnH for Ln = La, Ce, Yb, and Lu.

tions. The nature of the extrema (minimum or transition structure) was verified with analytical frequency calculations.

Results

Structure of Cp_2LnH. These complexes do not exist in general as monomers.[10] However, the structure of the monomeric species is on its own right. For the lighter lanthanides, Cp_2LnH has a C_s structure in which the Ln−H direction is not along the C_2 axis of the Cp−Ln−Cp moiety (Figure 1). The plane that is defined by the centroids X_1 and X_2 of the two cyclopentadienyl ligands and the hydride center does not contain the metal center. Thus Ln, X_1, X_2, and H define a pyramidal geometry at the metal center, as illustrated by the fact that the sum α of the three bond angles is less than 360° (Table 1). The value of α, which is the smallest for Ce, otherwise increases from La to Eu (360°). Thus the pyramidalization is largest for Ce and a trigonal planar geometry is preferred for Eu as well as for the heavier lanthanides.

Table 1. Geometrical Parameters, r_e (Å) and X_1−Ln−X_2 Angle (see text, deg), and Pyramidalization (α, deg; see text) for Cp_2LnH at the B3PW91 Level

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

Even when the lanthanide center has a preference for a nonplanar structure, the potential energy surface for the inversion at the metal has been found to be very soft and thus the hydride moves without any noticeable energy cost into the bisector plane of the Cp−Ln−Cp group (1.26 kcal·mol^{-1} for La to 0.26 kcal·mol^{-1} for Lu). The above results highlight some similarities between Cp_2LnH and LnX_3 (X = H, CH_3, F, Cl),[12] where Ln prefers a pyramidal geometry. For any of these systems, Ce, Eu, and Yb tend to deviate significantly from the trends show by the other lanthanides. The extend value of pyramidalization has however been calculated to be larger for X = H, CH_3 , and F than in Cp_2LnH. From this work, it seems that Cl best represents the geometrical pattern of biscyclopentadienyl complexes[19,20] and we are in the process of comparing further the Cp and Cl as ligands in lanthanide complexes.[21] The molecular orbital interpretations of the geometries of d^0 Cp_2MR (M = transition metal complex)[22] and of LnX_3 lanthanide[12] are in fact similar. A pyramidal structure at the lanthanide makes better use of the d orbitals for Ln−ligand bonds.

The Cp−Ln−Cp angle is an important factor in the behavior of biscyclopentadienyl complexes. This angle varies from 134.3° for La to 140.1° for Lu but has a minimum value of 130.0° for Ce. In this case, this angle is in part determined by the steric hindrance of the two Cp ligands and thus cannot be compared to the angles with substitued cyclopentadienyl groups. The Ln−Cp distances are also well reproduced quantitatively. Thus the average Ln−Cp distance is close to the average value determined experimentally for the Yb and Lu complexes (calcd 2.587 Å vs exptl 2.505 Å for Yb and calcd 2.325 Å vs exp 2.383 Å for Lu).[23] The Ln−H distance cannot be compared directly to any experimental value. An appropriate test for the validity of the method of calculations is the lanthanide contraction (r_e(Lu−H) − r_e(La−H)), which is equal to 0.170 Å in close agreement with the accepted value of 0.179 Å. As has been previously obtained for LnH_3, the Ln−H ligand is especially short for Cp_2CeH^+ and long for Cp_2EuH^- and Cp_2YbH^-. On the basis of these results, the calculations with large core RECPs' therefore seem appropriate for these systems.

Path for H−H Exchange. No H_2 adduct could be located on the potential energy surface for any Cp_2LnH complex. 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 an

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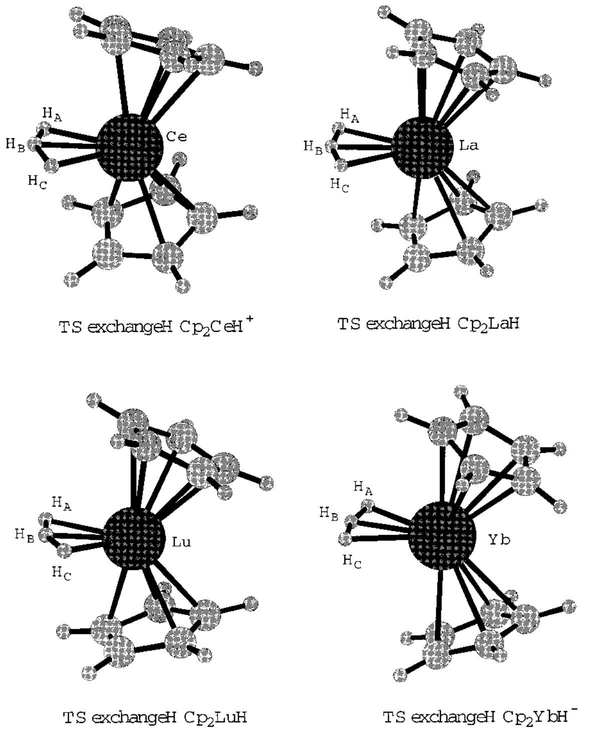
Table 2. DFT Optimized Geometrical Parameters, r_e (Å) and Angles (deg), for the Hydrogen Exchange Transition State, $Cp_2Ln(H_3)$

metal	$r_e(M-H_A)$	$r_e(M-H_B)$	$r_e(M-H_C)$	$r_e(H_A-H_B)$	$r_e(H_B-H_C)$	$H_A-H_B-H_C$	X_1-Ln-X_2
La	2.276	2.262	2.294	1.015	1.043	156.2	141.1
Ce	2.149	2.148	2.099	0.897	1.214	149.1	138.3
Pr	2.239	2.220	2.254	1.023	1.035	156.2	141.6
Nd	2.229	2.202	2.230	1.028	1.030	156.1	141.8
Pm	2.212	2.183	2.213	1.029	1.031	156.1	141.8
Sm	2.196	2.166	2.197	1.029	1.031	156.0	141.8
Eu	2.427	2.327	2.427	1.047	1.047	165.3	133.7
Gd	2.169	2.134	2.170	1.030	1.031	156.0	141.8
Tb	2.153	2.117	2.154	1.031	1.031	156.0	141.8
Dy	2.140	2.102	2.141	1.031	1.032	156.0	141.8
Ho	2.127	2.087	2.128	1.031	1.032	156.0	141.8
Er	2.114	2.073	2.115	1.032	1.032	156.0	141.8
Tm	2.103	2.060	2.104	1.032	1.032	156.0	141.8
Yb	2.350	2.237	2.350	1.049	1.050	165.7	134.2
Lu	2.083	2.037	2.084	1.033	1.033	156.0	141.9



TS exchangeH Cp_2CeH^+ TS exchangeH Cp_2LaH

TS exchangeH Cp_2LuH TS exchangeH Cp_2YbH^-

Figure 2. DFT(B3PW91) optimized geometry of the transition state for hydrogen exchange for Ln = La, Ce, Yb, and Lu.

Table 3. DFT Calculated Activation Barrier (ΔE, kcal·mol^{-1}) for the Hydrogen Exchange Reaction

metal	oxidation state	ΔE	metal	oxidation state	ΔE
La	3	1.41	Tb	3	1.28
Ce	4	5.05	Dy	3	1.54
Pr	3	0.96	Ho	3	1.81
Nd	3	0.85	Er	3	2.09
Pm	3	0.67	Tm	3	2.45
Sm	3	0.69	Yb	2	7.20
Eu	2	5.03	Lu	3	3.06
Gd	3	1.21			

adduct. The absence of any electrons on Ln to back-donate into σ^* (H_2) also contributes to decreasing the stability of any adduct. This result contrasts with that of Folga et al., where an adduct of H_2 was obtained.[8] The use of a different functional and of Cl in place of Cp are two factors that could contribute to the different results. Transition states for H−H exchange have been located for each Ln center. The vector associated with the negative eigenvalue of the Hessian (around 800 cm^{-1} for all Ln) is associated with the central H moving toward one of the two wingtip hydrides. With the exception of Ce (to be discussed later), 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 (Figure 2). The Cp−Ln−Cp angle is constant for the whole series (141°) and thus differs from that in the reactents (Table 2). For early Ln centers (La and Pr), $Ln-H_A$ is slightly different from $Ln-H_B$. A C_{2v} structure is obtained for heavier lanthanides. The Ln−H distances decrease from La to Lu with the exception of Eu and Yb where the total negative charge on the complex causes the expected elongation of the Ln−H distances. The two H−H distances are remarkably short for most lanthanides (around 1.03 Å) and hardly longer than 1.05 Å for the anionic Eu and Yb systems. All the Ln−H distances are short and remarkably the shortest is the central $Ln-H_B$ distance ($r_e(Ln-H_A) - r_e(Ln-H_B)$ reaches 0.1 Å for Eu and Yb). This could suggest the formation of a $Ln-H_B$ bond. Due to the highly ionic character of the lanthanide−ligand interaction, the formation of a Ln−H bond would mean that the three hydrogens would have hydridic character. However, a charge analysis shows that this is not the case. According to a Mulliken charge distribution, H_A and H_C have equivalent hydridic character, with an atomic charge of −0.15 for the whole series of lanthanide complexes, whereas H_B is sightly electron deficient, with an atomic charge of +0.03. Moreover, the Mulliken overlap populations also support the existence of two wingtip $Ln-H_A$ (H_C) bonds (0.13 for any Ln) and the absence of a $Ln-H_B$ central bond (0.04). Although the absolute Mulliken overlap population values should be considered with caution, relative values are known to be reliable. 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 short $Ln-H_B$ distance is a result of the short H_A-H_B and H_B-H_C distances but not of an interaction with Ln.

The transition state for $Cp_2CeH_3^+$ is very different from those of the other lanthanides. Its geometry is that of an H_2 ligand attacking the Ce−H bond. At the transition structure, the H_A-H_B distance of the attacking H_2 is only 0.897 Å and the $H_B\cdots H_C$ distance is the longest of all calculated systems (1.214 Å) in this work.

The trend in activation energy, calculated as the difference in energy between the separated reactants and the transition state, follows a nonmonotonic behavior (Table 3). With the exception of Ce, Eu, and Yb, the activation energy decreases from 1.4 to 0.7 kcal/mol before increasing to 3.06 kcal/mol (Lu). These values are thus of the same order of magnitude as that for Cl_2ScH (5.5 kcal/mol).[7] The highest barriers have been calculated for $Cp_2CeH_3^+$ (5.05 kcal/mol), $Cp_2EuH_3^-$ (5.03 kcal/mol), and $Cp_2YbH_3^-$ (7.20 kcal/mol). For any lanthanide, the barrier is thus either small or very small and H exchange should occur easily or even very easily.

The H−H exchange reaction is a metathesis involving the 4 electrons of the Ln−H and H−H bonds. At the transition state the 4 electrons are mostly located on the wingtip H centers of the H_3^- ligand. The metal center stabilizes this anionic ligand at the TS and thus makes the exchange energetically facile. Why is the activation energy therefore dependent on the nature of the metal even though the f electrons of Ln play no role in the Ln−ligand interaction[11] and all these complexes are calculated as isoelectronic? We suggest that the electronegativity of the lanthanide plays two opposite roles in this reaction. As mentioned earlier, a metathesis reaction uses the electrons of the Ln−H bond for the reactivity. It is most likely that reactants (Cp_2LnH) in which the Ln−H bond is more polarized toward the hydride would be reactive toward metathesis. In the present systems, the lanthanide contraction can give some information. The longer La−H bond (in comparison to Lu) suggests that the electrons of the La−H bond may be more involved in a metathesis reaction that these of Lu−H. However, at the transition state, the metal also needs to stabilize an anionic ligand (H_3^-) mainly through its d orbitals. Thus, electronegative Ln centers, which have lower d orbitals, would be more efficient in lowering the energy of the transition state. These two opposite effects of the metal center could explain why the activation energy goes in a nonmonotonic manner and why the calculations indicate the lowest activation energy occurs with Sm.

A similar analysis explains the different results obtained with Ce, Eu, and Yb. The cationic Cp_2CeH^+ would have the electrons of the Ce−H bond least available for reactivity. The lack of availability of the electrons of the Ce−H bond also results in the different structure of the TS: the incoming H_2 remains an intact dihydrogen ligand. The higher activation barriers for the anionic Eu and Yb complexes cannot be due to the lack of hydridic character in the reactant (always higher for an anionic system) but to the associated high energy level of the d block of Ln caused by the same negative charge that is less efficient in stabilizing H_3^-. The same negative total charge is responsible for the longer H_A-H_B and H_B-H_C distances in the transition states.

There has been much interest in the directionality of approach of the substrate to a Cp_2M-R system.[2] In the present case, the extreme softness of the potential energy surface for motions of atoms in the bisector plane of Cp−Ln−Cp prevents any discussion of this point. The bond metathesis involved in the H−H exchange process is thus a facile process in these species due to the presence of a hydridic ligand and to low-lying d orbitals available to stabilize the H_3^- ligand. These combined properties are characteristic of d^0 early transition metal complexes and also of the lanthanide series.

Conclusions

This study shows that it is possible to study the structure and reactivity of lanthanide complexes containing cyclopentadienyl ligands with large core ECP and DFT calculations. The calculations reproduce in a qualitative way the main characteristic of the reactants as well as the lanthanide contraction for the Ln−H bond distance. The calculations also highlight that the geometries of Cp_2LnH and LnX_3 ($X = H, CH_3$, halides) have some strong similarities. In both systems, there is a preference for a non-trigonal-planar coordination at the metal center, especially in the case of early lanthanide members. The chlorine ligand is probably a reasonable model for Cp for the geometrical aspects of the complexes. It remains to be demonstrated whether Cl is also a good model of Cp for representing energy changes associated with reactivity.

H−H activation by Cp_2LnH has been found to be a facile reaction for all lanthanides. The reaction involves a tightly bonded H_3^- ligand with short H−H distances characteristic of a bond metathesis reaction. The activation energy depends on the lanthanide center in a subtle way. Electropositive (early) lanthanides make the electron density of the metal hydride more available for reactivity but are also less efficient at stabilizing an anionic H_3^- ligand in the TS.

The lanthanide contraction suggests that the electron of the Ln−H bond is less available for σ bond metathesis reaction for late lanthanide centers but may better stabilize the H_3^- ligand in the TS. These opposite effects result in the lowest activation energy for lanthanides occurring near the middle of the series (Nd, Pm, or Sm) for which there is probably a good compromise between the ability for the hydride to donate electrons and for the metal to stabilize the anionic H_3^- ligand. Other reactions such as that shown in eq 2 should occur through the same process. This present study suggests that lanthanide centers can activate inert bonds. It is known that C−H bond activation is intrinsically more difficult than that of H−H.[2] It is thus of great interest to determine the ability of the various lanthanide complexess to activate the C−H bond. This study is in progress.

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