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DFT study of CH_4 activation by d^0 Cl_2LnZ (Z = H, CH_3) complexes

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DFT(B3PW91) calculations of the activation of CH_4 by models (Cl_2LnZ) of Cp^*_2LnZ (Z = H, Me) have been carried out for the entire lanthanide series. Cl_2LnZ appears to be a good model for Cp^*_2LnZ. It reproduces well the coordination around the lanthanide. The energetics of the transformation $X_2LnH + CH_4 \longrightarrow X_2LnCH_3 + H_2$ are fairly close for X = Cl and Cp and the difference in behavior can be attributed to the stronger electron donating ability of Cp. Formation of the lanthanide hydride complex is calculated to be exothermic in agreement with experimental evidence. The energy profiles of the reactions $Cl_2LnH + CH_4 \longrightarrow Cl_2LnCH_3 + H_2$; $Cl_2LnH^* + CH_4 \longrightarrow Cl_2LnH + H^*CH_3$; $Cl_2LnCH^*_3 + CH_4 \longrightarrow Cl_2LnCH_3 + H\text{–}CH^*_3$ have been calculated. The transition states for the first and third transformations are energetically accessible, in good agreement with the known experimental data. The second reaction has a transition state of very high energy indicating an unfeasible reaction. The geometry of the transition stuctures are suggestive of a proton transfer between two anionic species (Z and CH_3^-; Z = H^- and CH_3^-) in the field of the lanthanide fragment.

Introduction

The discovery that $Cp^*_2Lu\text{–}CH_3$ ($Cp^* = C_5Me_5$) activates CH_4 (eqn. (1))[1] has been a landmark in the search for new catalysts able to activate inert bonds especially those in alkanes.[2–13]

$$Cp^*_2Ln\text{–}CH_3 + H\text{–}CH_3 \longrightarrow Cp^*_2Ln\text{–}CH_3 + H\text{–}CH_3 \quad (1)$$

$$Cp^*_2Ln\text{–}CH_3 + H\text{–}H \longrightarrow Cp^*_2Ln\text{–}H + H\text{–}CH_3 \quad (2)$$

$$Cp^*_2Ln\text{–}H + H\text{–}CH_3 \longrightarrow Cp^*_2Ln\text{–}H + H\text{–}CH_3 \quad (3)$$

$$Cp^*_2Ln\text{–}H + H\text{–}H \longrightarrow Cp^*_2Ln\text{–}H + H\text{–}H \quad (4)$$

Since no electrons are available on the lanthanide, the activation of the C–H bond must necessarily occur without change of oxidation state at the metal center. In a related reaction, $Cp^*_2Ln\text{–}H$ exchanges H in the presence of H_2. An early MO analysis suggested the exchange of hydrogen occurs *via* a σ-bond metathesis between the Ln–H and H–H bonds.[14] DFT calculations of this reaction have shown it to be energetically very easy and to occur *via* a 4-center (4-c) transition state representative of a bond metathesis process.[15] The energy of activation has been found to depend on the nature of the lanthanide although it remains low for the entire Ln series. The activation of CH_4 should follow a similar pattern. However it is known that C–H is more difficult to activate than H–H mainly because of the spherical nature of the 1s H orbital and the directional nature of the Me sp^3 hydrid.[16–18] For similar reasons, a σ-bond metathesis involving metal–H and H–H bonds is expected to be kinetically more facile than that involving M–Me and C–H bonds. Experimental results support this trend: eqn. (1) requires heating at 70 °C whereas eqn. (2) occurs at room temperature. Remarkably $Cp^*_2Lu\text{–}H$ does not react with CH_4 to exchange hydrogens (eqn. (3)) or to make $Cp^*_2Lu\text{–}Me$ (reverse of eqn. (2)). Furthermore these three reactions should have higher activation energies than the hydrogen exchange in eqn. (4). An interesting side question is thus to determine if the lanthanides associated with the highest activation energy in the case of eqn. (4) could make eqn. (1) energetically unfeasible. This would be informative of the ability of different lanthanides to activate CH_4.

Theoretical calculations have been used to understand the activation of inert bonds with considerable success.[19,20] In most studies, C–H activation has been initiated by an oxidative cleavage of the C–H bond; theoretical studies of metathesis reactions have also been reviewed.[21] EHT studies of the activation of H–H and C–H bonds by d^0 complexes suggest that the activation is feasible.[14] Metathesis reactions involving late transition metals in high oxidation states and hydrogenolysis reactions have also been calculated.[19] DFT calculations of R–H (R = H, CH_3, SiH_3) bond activation by $Cp_2Sc\text{–}Z$,[22,23] $Cl_2Sc\text{–}Z$[22,24] and $Cl_2Lu\text{–}Z$ (Z = H, CH_3)[23,25] have shown that the initial step of the reaction is the formation of an R–H adduct which leads to a Z–H adduct through a 4-c-transition state. In contrast, the recent DFT calculations of H–H bond activation by $Cp_2Ln\text{–}H$ suggest the absence of an initial adduct. The easily energetically accessible 4-c-transition state connects to separated $Cp_2Ln\text{–}H$ and H_2.[15]

In this paper, DFT calculations have been carried out to study the reactions shown in eqn. (1)–(3) for the entire series of the lanthanide elements. To save computational time, the cyclopentadienyl ligand was not explicitly represented but was modeled by a Cl ligand. The Cl model for Cp or Cp* has been extensively used in the past[23–27] and has led to some controversy in the case of non d^0 species.[28,29] In the case of a d^0 metal center and for problems similar to this work, the modeling seems appropriate and trends (activation energy for activating R–H) are reproduced appropriately.[23,25] The σ-bond metathesis of acetylene with $Cl_2Zr\text{–}H^+$ and $Cl_2Zr\text{–}Me^+$ has been studied with all electron HF and MP2 calculations.[27] The activation energy has been calculated to be lower for Sc than Lu but the influence of the lanthanide center within its series remains unknown.[22,23,25] DFT calculations on the reaction described in

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eqn. (4) have shown that the activation energy is lower for early lanthanides like neodynium, promethium or samarium than for late elements like lutetium. Will similar trends apply to activation of CH_4?

Ce, Eu and Yb have two accessible oxidation states, III and IV for Ce, III and II for Eu and Yb. This provides the opportunity for studying the influence of the lanthanide oxidation state on the activation of CH_4. It should be emphasized that the oxidation state of the lanthanide metal does not vary during the σ-bond metathesis reaction. Test calculations have shown that Ce(III), Eu(III), and Yb(III) behave very similarly to the other Ln(III) elements. For this reason, a complete study was carried out for Ce(IV), Eu(II), Yb(II) in order to have a better vision of the influence of the oxidation state. Only the most relevant systems were calculated for Ce(III), Eu(III) and Yb(III) for analysing the role of the oxidation state on the reactivity.

Computational details

In previous studies[30,31] we have shown that large core relativistic effective core potentials (RECPs) optimized by the Stuttgart–Dresden Group[32–34] are well adapted to the calculation of the geometries of lanthanide complexes as 4f electrons do not participate in Ln–X bonding. Basis sets adapted to the different RECPs augmented by a polarisation function (f function for the lanthanide) were used. Chlorine atoms were also treated with a RECP in combination with the adapted basis set, augmented by a d function for polarisation. Carbon and hydrogen have been treated with an all-electron 6-31G** basis set. Calculations were carried out at the DFT level using the hybrid functional B3PW91[35,36] with the Gaussian 98 suite of programs.[37] Geometry optimizations were carried out without any symmetry restrictions. The nature of the extrema (minimum or transition structures, TS) was verified with analytical frequency calculations. ZPE and entropic contributions were calculated from the approximation of harmonic frequencies. The free Gibbs energies G are given for $T = 298.15$ K.

Results and discussion

Cl as a model for Cp

All lanthanide hydride complexes are dimeric or oligomeric.[38] This aspect has not been included since the monomeric species are the reactive species. The lanthanide complexes in this work have an empty valence d shell. Our own calculations have shown that the coordination at the lanthanide center is essentially identical for $Cl_2Ln–H$ and $Cp_2Ln–H$.[39] The Ln–H bond is slightly longer than Cp (average 0.03 Å), in agreement with the higher electron donating power of Cp. The only strong discrepancy appears for a cationic cerium complex. As expected from the presence of a cationic charge, Ce–H is the shortest of the Ln–H bonds in $Cp_2Ln–H$; however this is not the case for $Cl_2Ce–H^+$ in the $Cl_2Ln–H$ series. Therefore the results for $Cl_2Ce–H^+$ and most probably those for $Cl_2Ce–CH_3^+$ should be taken with considerable caution. It is not suprising that a more accurate representation of the donating ability of a ligand may be especially needed for a proper representation of a cationic system.

A key point for our study is also a proper representation of the energy of reaction. The reaction shown in eqn. (2) produces a metal hydride from methyl complexes. We have thus calculated the energy of reaction for eqn. (2) for the entire lanthanide series with Cp and Cl ligands (Table 1). Eqn. (2) is exothermic for all lanthanide elements (with the exception of Ce in the case of Cl ligand) although less so for Cl than Cp. Thus, formation of a monomeric lanthanide hydride is calculated to be exothermic. Formation of oligomeric species should make the reaction more exothermic. With the exception of charged species (Ce, Eu, Yb), the exothermicity is about 8 kcal mol^{-1} for Cl and 13 kcal mol^{-1} for Cp. The reaction energies, then are significantly different as could be expected from the difference in electron donating ability of Cp *vs.* Cl. The lanthanide center is more electrophilic with electron accepting Cl than electron donating Cp. As a consequence, the energy preference for $Ln–CH_3$ over Ln–H is stronger for X = Cl than for Cp as H is less electron donating than Me. The trend, however, is similar for Cl and Cp and thus it is possible to use Cl as a model of Cp (Table 1). One should, however, consider that Cl may not be an appropriate model for Cp in the cerium complex since the thermochemistry for eqn. (2) is not properly reproduced. In a separate study where several models for cyclopentadienyl are compared, the activation energy for H exchange (eqn. (4)) is slightly higher for Cl than Cp.[39] This is also consistent with Cl giving less electron density to the lanthanide, which in turns requires more electron density from the hydride. The activation energy of eqn. (4) decreases with increasing hydridic character in the Ln–H bond, as was shown previously.[15] Thus, the activation energy for bond metathesis calculated with $Cl_2Ln–Z$ is an upper limit of the value which would be obtained with $Cp_2Ln–Z$. In order to validate this hypothesis, a comparison of the activation barriers has been performed for Cl_2LaH and Cp_2LaH. The calculated energy barrier for the reaction going from the hydride to the methyl complex (reverse of eqn. (2)) is 12.3 kcal mol^{-1} for Cp and 13.3 kcal mol^{-1} for Cl. For the reaction shown in eqn. (3), the energy barriers are also comparable: 65.3 kcal mol^{-1} for Cp and 71.2 kcal mol^{-1} for Cl. These test calculations show that Cl is an appropriate model for Cp in these systems. However, we should still keep in mind that the activation energies calculated for $Cl_2Ce–Z^+$ may be very different from that which would have been obtained with $Cp_2Ce–Z$. Having established this and recognized the limitations, we now use Cl exclusively as ligand in the following calculations.

Table 1 DFT calculated reaction energy (ΔG^0 kcal mol^{-1}) for $X_2LnH + CH_4 \longrightarrow X_2LnCH_3 + H_2$ with X = Cl, Cp (reverse of eqn. (2))

Ln	Oxidation state	ΔG^0 (Cl)	ΔG^0 (Cp)
La	3	8.01	13.30
Ce	4	−1.88	13.50
Pr	3	7.84	13.20
Nd	3	7.73	13.20
Pm	3	7.77	13.30
Sm	3	7.70	13.20
Eu	2	17.37	19.70
Gd	3	7.57	13.10
Tb	3	7.68	13.30
Dy	3	7.63	13.30
Ho	3	7.57	13.30
Er	3	7.49	13.20
Tm	3	7.61	13.30
Yb	2	15.23	18.70
Lu	3	7.82	13.10

The reactants $Cl_2Ln–Z$; Z = H, Me

The structure of $Cl_2Ln–Z$ is remarkably independent of the nature of Z (Tables 2 and 3). The Cl–Ln–Cl angle is only on average 2° smaller for Z = H. The pyramidalization at Ln, measured by the sum of the angles between the ligands, is equal for the two systems (average difference of 1°). The lanthanide contraction of Ln–H and Ln–C respectively are equal to 0.160 Å and 0.165 Å. There are no α-agostic C–H bonds in $Cl_2Ln–CH_3$. Similarly, no α-agostic bonds have been reported in calculations on $Cp_2Sc–CH_3$ or $Cl_2Lu–CH_3$.[23–25] A common concern in studies of bimolecular reactions is establishing the existence of an adduct between the reactants. In the present system, such an adduct would lie in a shallow energy well since it would result from the interaction of a very weak Lewis base (C–H bond) with an electropositive center unable to participate

Table 2 Geometrical parameters, r_e (Å) and Cl–Ln–Cl angle (°) for Cl_2LnH at the B3PW91 level

Ln	Oxidation state	r_e(Ln–H)	Cl–Ln–Cl
La	3	2.100	118.3
Ce	4	1.947	103.6
Pr	3	2.067	118.9
Nd	3	2.052	117.5
Pm	3	2.038	119.7
Sm	3	2.025	120.0
Eu	2	2.269	123.7
Gd	3	2.003	121.3
Tb	3	1.992	121.9
Dy	3	1.982	122.5
Ho	3	1.972	123.2
Er	3	1.962	124.0
Tm	3	1.958	126.2
Yb	2	2.180	123.1
Lu	3	1.940	125.3

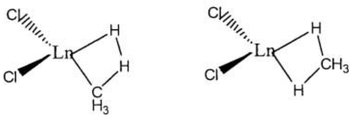
Table 3 Geometrical parameters, r_e (Å) and Cl–Ln–Cl angle (°) for Cl_2LnCH_3 at the B3PW91 level

Ln	Oxidation state	r_e(Ln–C)	r_e(C–H)	Cl–Ln–Cl
La	3	2.449	1.103	119.7
Ce	4	2.303	1.099	105.2
Pr	3	2.415	1.103	120.2
Nd	3	2.400	1.099	120.4
Pm	3	2.386	1.103	120.9
Sm	3	2.373	1.103	121.3
Eu	2	2.596	1.106	128.3
Gd	3	2.351	1.103	122.4
Tb	3	2.339	1.102	123.1
Dy	3	2.328	1.102	123.9
Ho	3	2.318	1.101	125.9
Er	3	2.308	1.100	126.9
Tm	3	2.301	1.101	127.5
Yb	2	2.520	1.105	126.4
Lu	3	2.284	1.101	128.5

in backdonation. Not suprisingly, the existence of the adduct appears to depend on the precise nature of the two partners and, unfortunately also on the model chosen for the calculations. Thus, adducts between H_2 or CH_4 and Cl_2Lu–Z (Z = H, Me) have been obtained with bond energies varying between 0.4 and 10 kcal mol^{-1}.[25] Replacing the model Cl ligand by the full Cp ligand has resulted in the absence of an adduct between H_2 and Cp_2Ln–H for any lanthanide element.[15] This is again consistent with Cp donating more electron density to the lanthanide center which in turn is less electrophilic and does not stabilize as well the very weak incoming Lewis base. Since CH_4 and H_2 are both poor Lewis bases, the presence of an adduct between CH_4 and Cp_2Ln–H would be at best in an extremely shallow well if it existed at all. To avoid any artefact linked to the model, no further searches of any adduct were carried out, and the activation energies for reactions (1)–(3) are considered as the differences in energy between the 4-c-transition state and the separated reactants.

Activation of CH_4 by Cl_2LnH

For the sake of simplicity the reactions which are discussed correspond to the reaction of CH_4 with a lanthanide complex (the reverse of eqn. (2), eqn. (−2), and eqn. (3)). In these two reactions, CH_4 reacts with the lanthanide hydride, with a different chemio-selectivity. In the reaction shown by eqn. (−2), the C–H bond approaches the Ln–H bond with CH_3 closer to the metal. The 4-c-transition state has the methyl group in an α-position (**1** in Chart 1). In the reaction of eqn. (3), the C–H bond has H nearer the lanthanide and CH_3 is at the β-position (**2** in Chart 1).



1 **2**

Chart 1

The β-position is usually considered as disfavored[24,40,41] but no systematic investigation has been carried out. The transition states were located for the two directions of approach of H–CH_3 and the geometrical parameters are given in Tables 4 and 5. Transition states for α-CH_3 are around 14 kcal mol^{-1} above the separated reactants, Cl_2Ln–H + CH_4, while the transition state for β-CH_3 is around 73 kcal mol^{-1} above the separated reactants (Table 6). Reaction (3) is clearly not feasible. In contrast, the reaction with CH_3 at the α-position is calculated to have a low activation energy (4–5 kcal mol^{-1} above separated reactants Cl_2Ln–CH_3 + H_2) (eqn. (2)). The energy barrier with Cp should be even lower. Thus, the activation of H_2 by Cp_2Ln–CH_3 is only marginally more difficult than with Cp_2Ln–H. Our results can be compared with the previous study of Cl_2Lu–CH_3 done with a frozen core approximation and a non-hybrid functional.[25] Both studies agree on the thermodynamic preference for making Ln–H complexes. Our study gives an activation energy closer in agreement with the experimental conditions (room temperature reaction)[42,43] since our activation energy (9.30 kcal mol^{-1}) is significantly lower than their value (19.6 kcal mol^{-1}) above Cl_2Ln–CH_3 + H_2.

With the exception of the charged species (Ce, Eu and Yb) our calculations show only a marginal influence of the lanthanide on the activation energy (averaging 13 kcal mol^{-1}) showing the reaction to be equally as feasible for almost all lanthanide centers. The significantly lower value calculated for Ce is probably an artefact of the use of Cl as a model for Cp while the high activation energies (> 20 kcal mol^{-1}) for anionic Cl_2Eu–$(CH_3)^-$ and Cl_2Yb–$(CH_3)^{4-}$ are in full agreement with the high activation energy calculated previously in the case of H exchange (eqn. (4) and Cp ligand).[15] Our results even suggest that $Cp^*{}_2Eu$–$(CH_3)^-$ and $Cp^*{}_2Yb$–$(CH_3)^-$, two anionic methyl complexes, could be stable in the presence of H_2 at least at low temperatures. While the influence of the lanthanide on the activation energy seems marginal, calculations for H exchange (eqn. (4)) and the present study both agree that σ-bond metathesis is energetically easier for some early lanthanides like Nd, Pm or Sm than for late lanthanides like Tm or Lu.

The structure of the 4-c-transition state is similar for all lanthanides (with the exception of Ce, which will not be discussed further). It is shown here for La (Fig. 1a). The reaction occurs in the mirror plane of Cl_2La, and the geometry of the TS resembles the reactants in agreement with the Hammond principle. The coordination around La has not been modified in any significant manner from free Cl_2La–CH_3. The elongation of the two σ bonds in the transition state is not very large: the La–C bond is elongated by only 0.13 Å and the H–H distance (0.95 Å) is typical of that found in "stretched dihydrogen" complexes.[44] The two H centers have a short bond distance to La with the hydrogen H_β closer to CH_3 having the shorter La–H distance (La–H_α = 2.276 Å, La–H_β = 2.222 Å). The most striking feature of the transition state is the near aligment of CH_3 with the H–H vector (H_α–H_β–C = 165° for La). The C_3 axis of CH_3 is no longer directed toward La as in the starting reactant structure. The C_3 axis of the CH_3 group makes an angle of 33° with the C–La direction and of 27° with the C–H_β direction; therefore, the sp^3 hybrid orbital of CH_3 does not point towards La but tilts towards the approaching H. The carbon is best viewed as being at the center of a distorted trigonal bipyramid in which La occupies an apical site and the transfering hydrogen, H_β, occupies an equatorial site. This transition state is indicative of a proton transfering from H_2 to

Table 4 DFT optimized geometrical parameters, r_e (Å) and angles (°), for the C–H activation transition state (reverse of reaction (2)), as shown in **1**

Ln	r_e(Ln–H$_\alpha$)	r_e(Ln–H$_\beta$)	r_e(Ln–C$_\alpha$)	r_e(H$_\alpha$–H$_\beta$)	r_e(H$_\beta$–C$_\alpha$)	H$_\alpha$–H$_\beta$–C$_\alpha$	Cl–Ln–Cl
La	2.276	2.222	2.575	0.953	1.550	164.9	123.6
Ce	2.126	2.121	2.451	0.981	1.509	159.3	121.1
Pr	2.239	2.184	2.532	0.952	1.554	164.2	123.6
Nd	2.223	2.167	2.512	0.951	1.556	163.9	123.7
Pm	2.208	2.151	2.493	0.951	1.558	163.6	123.7
Sm	2.194	2.135	2.475	0.950	1.561	163.3	123.7
Eu	2.432	2.284	2.661	0.919	1.641	171.7	123.6
Gd	2.167	2.107	2.445	0.950	1.563	162.9	123.8
Tb	2.156	2.093	2.427	0.950	1.565	162.5	123.8
Dy	2.141	2.078	2.415	0.950	1.567	162.3	123.7
Ho	2.128	2.065	2.401	0.951	1.569	162.1	123.6
Er	2.116	2.052	2.387	0.951	1.569	161.9	123.5
Tm	2.106	2.041	2.377	0.951	1.571	161.7	123.4
Yb	2.352	2.195	2.586	0.934	1.622	171.6	122.8
Lu	2.093	2.033	2.367	0.951	1.574	161.7	123.5

Table 5 DFT optimized geometrical parameters, r_e (Å) and angles (°), for the hydrogen exchange transition state (reaction (3)), as shown in **2**

Ln	r_e(Ln–H$_\alpha$)	r_e(Ln–H$'_\alpha$)	r_e(Ln–C$_\beta$)	r_e(H$_\alpha$–C$_\beta$)	r_e(H$'_\alpha$–C$_\beta$)	H$_\alpha$–C$_\beta$–H$'_\alpha$	Cl–Ln–Cl
La	2.166	3.015	2.564	1.838	1.307	153.0	123.4
Ce	2.014	2.949	2.407	1.745	1.412	152.9	115.3
Pr	2.139	2.987	2.534	1.842	1.310	153.1	123.6
Nd	2.119	2.976	2.505	1.847	1.313	153.3	123.9
Pm	2.106	2.974	2.491	1.853	1.314	153.7	124.3
Sm	2.093	2.969	2.476	1.847	1.317	153.9	124.6
Eu	2.343	3.197	2.778	1.879	1.365	165.3	123.7
Gd	2.069	2.966	2.451	1.866	1.321	154.6	125.0
Tb	2.057	2.962	2.439	1.869	1.323	155.0	125.0
Dy	2.045	2.959	2.424	1.875	1.325	155.1	125.2
Ho	2.034	2.954	2.410	1.879	1.328	155.3	125.1
Er	2.024	2.950	2.396	1.883	1.331	155.6	125.1
Tm	2.014	2.948	2.386	1.887	1.333	155.8	125.0
Yb	2.257	3.099	2.645	1.862	1.352	165.4	122.8
Lu	2.005	2.944	2.373	1.891	1.337	156.0	125.2

Table 6 DFT calculated reaction energies (ΔG^0 kcal mol^{-1}) and activation barriers (ΔG kcal mol^{-1}) for reverse of reaction (2) and reaction (3) with the Cl ligand

Ln	Oxidation state	ΔG_2^0	ΔG_3^0	ΔG_2	ΔG_3
La	3	8.01	0.00	13.46	71.25
Ce	4	−1.88	0.00	7.11	49.96
Pr	3	7.84	0.00	13.12	70.64
Nd	3	7.73	0.00	13.01	70.34
Pm	3	7.77	0.00	12.86	70.11
Sm	3	7.70	0.00	12.81	69.84
Eu	2	17.37	0.00	21.14	70.57
Gd	3	7.57	0.00	13.05	79.16
Tb	3	7.68	0.00	13.04	79.53
Dy	3	7.63	0.00	13.18	79.88
Ho	3	7.57	0.00	13.33	80.25
Er	3	7.49	0.00	13.54	80.67
Tm	3	7.61	0.00	13.97	81.28
Yb	2	15.23	0.00	24.33	65.78
Lu	3	7.82	0.00	17.12	82.47

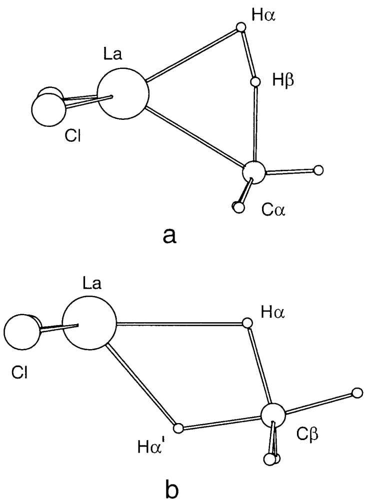


Fig. 1 Optimized geometries for the transition states of reactions (−2) (a) and (3) (b) for La and Cl as a model for Cp

the methyl anion, leaving behind a hydrid which is stabilized by the La cation. While this reaction may be regarded as a σ-bond metathesis, it can also be viewed as another exemple of the heterolytic cleavage of an H_2 coordinated to a Lewis acid with the CH_3 group acting as a Lewis base.[45]

Since the CH_3^- anion is interacting with the approaching H_β^+ and the cationic Cl_2Ln^+ center, it is possible to consider that a formal $LnCH_4^+$ is being formed in the TS. The extreme fluxionality of this species is well known; a distorted trigonal bipyramid structure is therefore appropriate. Furthermore, penta-coordination with an overall positive charge is energetically accessible for a carbon center.

The very high energy of the transition state with CH_3 at the β-position (Fig. 1b, Tables 5 and 6) can be easily understood from the conclusions of the preceeding discussion. The CH_3^+ group is bound to two hydrides that are themselves in close proximity to the Cl_2La fragment. The transition state can then be best viewed as a CH_5^- group which is η^2 bound to Cl_2La^+. The carbon is at the center of a trigonal bipyramid in which La is closer to the axial hydride (C–H$_\alpha$ = 1.838 Å, La–H$_\alpha$ = 2.166 Å) than to the equatorial hydride (C–H$_\alpha'$ = 1.307 Å, La–H$_\alpha'$ = 3.015 Å), in agreement with the higher electron density carried by the apical ligand in a hypervalent CH_5^- system. This transition state with CH_3 at the β position is particularly high in energy as carbon cannot stabilize a hypervalent anionic system.

Activation of CH_4 by Cl_2LnCH_3

$Cp^*_2Lu–CH_3$ activates CH_4, resulting in the exchange of methyl groups and formation of a molecule of methane (eqn. (1)); no ethane or $Cp^*_2Ln–H$ is observed. Using Cl as a model of Cp, the thermodynamic preference of the reaction was examined. The formation of ethane and a $Cl_2Ln–H$ bond is thermodynamically endothermic (Table 7) with an average value of 11.3 kcal mol^{-1} for Cl and 5.7 kcal mol^{-1} for Cp. The anionic species $Cp_2Eu–CH_3^-$ and $Cp_2Yb–CH_3^-$ would give an athermic reaction with an even greater preference for forming the Ln–H bond than the other lanthanide elements. Formation of ethane is thus thermodynamically unfavourable, as expected from the weaker energy of an C(sp^3)–C(sp^3) bond in comparison to C(sp^3)–H. The need to introduce a CH_3 group at the β-position in the transition state would also make the formation of ethane kinetically unfavourable. Because of this, the reaction of eqn. (1) has been studied further (Tables 8 and 9). The energy of the transition state is between 15.6 and 19.7 kcal mol^{-1} above the separated reactants. The slightly lower energy calculated for Ce cannot be trusted. Reaction (1) is thus more difficult than the reverse of eqn. (2) as is expected because of the additional presence of a CH_3 group as a part of the 4-c-transition state. This is in agreement with the experimental observation that heating was required for the reaction to proceed in the case of Lu.[1] The nature of the lanthanide does not influence the activation energy to a great degree. In particular, the activation energies for anionic Cl_2Eu^- and Cl_2Yb^- are only slightly higher than for the neutral species. It is also remarkable that the trend obtained for the H exchange reaction (eqn. (4)) or for the activation of H_2 by $Cl_2Ln–CH_3$ (eqn. (2)) which both shows an increase of the activation energy with later lanthanides is not apparent for eqn. (1). However, confirmation of this result with full Cp ligands in the calculations is needed.

Table 7 DFT calculated reaction energies (ΔG^0 kcal mol^{-1}) for $X_2LnCH_3 + CH_4 \longrightarrow X_2LnH + C_2H_6$ with X = Cl, Cp

Ln	Oxidation state	ΔG^0 (Cl)	ΔG^0 (Cp)
La	3	10.97	5.70
Ce	4	20.87	5.50
Pr	3	7.71	5.70
Nd	3	11.25	5.80
Pm	3	11.21	5.70
Sm	3	11.28	5.70
Eu	2	1.60	−0.70
Gd	3	11.40	5.90
Tb	3	11.30	5.70
Dy	3	11.34	5.70
Ho	3	11.41	5.70
Er	3	11.49	5.80
Tm	3	11.37	5.70
Yb	2	2.60	0.30
Lu	3	11.40	5.90

The structures of the transition states are also very similar for all lanthanide elements; The TS for La is shown in Fig. 2.

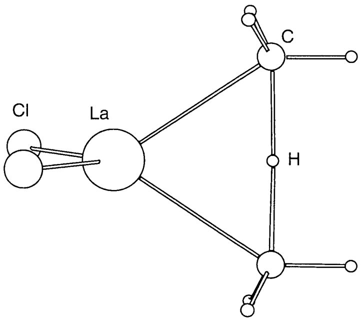


Fig. 2 Optimized geometry for the transition state of reaction (1) for La and Cl as a model for Cp.

The two La–C distances are equal at the TS. The La–C bond has been elongated from 2.449 Å in the reactant to 2.604 Å in the transition state. The transfering H is equidistant from the two carbon centers (1.448 Å in the case of La). The C–H–C angle is equal to 177.7° resulting in short La–H distances, 2.192 Å. As a consequence, the C–La–C angle is 67.6°. The C_3 axis of the two CH_3 groups is strongly tilted away from La as shown by the angle of 60° between the C_3 axis of CH_3 and the C–La vector. The C_3 axis of the CH_3 group is much more tilted toward the transferring H (angle of 24° in case of La). This reaction is thus best viewed as a proton transfering between two CH_3^- groups in the vicinity of a La cation. Since the role of the lanthanide in the transition state is mostly to stabilize the negative charge on the anionic methyl groups, the highest energy of the transition state is obtained for the anionic fragments like Cl_2Eu^- and Cl_2Yb^-.

Influence of the oxidation state

The reactivity of all lanthanides metal was calculated to be very similar with the exception of $Cl_2Ce(R)^+$, $Cl_2Eu(R)^-$, $Cl_2Yb(R)^-$ (R = H, CH_3). To confirm this, the neutral analogues for which the oxidation state of the lanthanide center is III were considered. They behave very similarly to the other Ln(III) complexes. Thus the activation energy for eqn. (−2) is 13.23 kcal mol^{-1} for $Cl_2Ce(H)$, 12.81 kcal mol^{-1} for $Cl_2Eu(H)$, and 14.21 kcal mol^{-1} for $Cl_2Yb(H)$. For the reaction of eqn. (1) the corresponding values are 16.87 kcal mol^{-1} $Cl_2Ce(CH_3)$, 15.79 kcal mol^{-1} $Cl_2Eu(CH_3)$, 16.21 kcal mol^{-1} ($Cl_2Yb(CH_3)$). The role of the charge has already been discussed in the study on the activation of H_2.[15] The positive charge decreases the nucleophilicity of R while the negative charge makes the lanthanide center

Table 8 DFT optimized geometrical parameters, r_e (Å) and angles (°), for the C–H activation transition state (reaction (1))

Ln	r_e(Ln–C$_\alpha$)	r_e(Ln–H$_\beta$)	r_e(Ln–C$'_\alpha$)	r_e(C$_\alpha$–H$_\beta$)	r_e(H$_\beta$–C$'_\alpha$)	C$'_\alpha$–H$_\beta$–C$_\alpha$	C$'_\alpha$–Ln–C$_\alpha$
La	2.604	2.192	2.604	1.449	1.449	177.7	67.6
Ce	2.465	2.100	2.465	1.458	1.458	171.4	72.2
Pr	2.561	2.154	2.561	1.449	1.449	176.7	68.9
Nd	2.541	2.137	2.541	1.450	1.450	176.0	69.5
Pm	2.522	2.121	2.522	1.450	1.450	175.6	70.0
Sm	2.505	2.105	2.505	1.451	1.451	175.0	70.7
Eu	2.696	2.251	2.696	1.455	1.455	178.5	65.3
Gd	2.475	2.078	2.475	1.451	1.451	174.3	71.7
Tb	2.458	2.064	2.458	1.452	1.452	173.8	72.3
Dy	2.444	2.051	2.444	1.453	1.453	173.4	72.8
Ho	2.429	2.038	2.429	1.453	1.453	172.9	73.3
Er	2.415	2.026	2.415	1.454	1.454	172.6	73.8
Tm	2.405	2.015	2.405	1.455	1.455	172.3	74.2
Yb	2.612	2.167	2.612	1.458	1.458	180.0	67.8
Lu	2.384	1.995	2.384	1.456	1.456	171.8	75.0

Table 9 DFT calculated reaction energies (ΔG^0 kcal mol^{-1}) and activation barriers (ΔG kcal mol^{-1}) for reaction (1)

Ln	Oxidation state	ΔG_1^0	ΔG_1
La	3	0.00	17.26
Ce	4	0.00	14.38
Pr	3	0.00	16.65
Nd	3	0.00	16.44
Pm	3	0.00	16.11
Sm	3	0.00	15.92
Eu	2	0.00	17.36
Gd	3	0.00	15.81
Tb	3	0.00	15.62
Dy	3	0.00	15.62
Ho	3	0.00	15.66
Er	3	0.00	15.77
Tm	3	0.00	15.97
Yb	2	0.00	19.71
Lu	3	0.00	16.42

much less able to stabilize the strong negative charge in the $[R \cdots H \cdots R']$ fragment ($R, R' = H$ or CH_3) at the transition state. Thus while the f electrons play no active chemical role, the charge strongly influences the reaction and deactivates the complex in the metathesis reaction.

Conclusions

Calculations show the reactions described in eqn. (1) and (−2) to be kinetically accessible. While overall the reaction is a σ-bond metathesis with a 4-c–4-el transition state, the study with CH_3 brings new information that was not apparent in the case of the H exchange process (eqn. (4)). The reactions are in fact best viewed as a transfer of a proton between two anionic groups in the proximity of a lanthanide center. It is remarkable that the lanthanide is able to carry out reactions that are not seen with Grignard reagents or alkyllithiums in which an anionic alkyl group is in the vicinity of a cationic metal center. The larger size of the lanthanide ion may be one factor which makes eqn. (1) possible. A smaller cation is probably not able to stabilize the two R^- groups during the transfer of H^+. However, the lanthanide center is unable to stabilize the CH_5^- anion which is formed in the transition state of the reaction in eqn. (3). Substitution at the carbon or replacement of CH_3 by groups like SiR_3 or a phenyl group which better stabilize a more hypervalent anion[46] could make H exchange in eqn. (3) accessible. This is under study in our group.

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