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A DFT Study of SiH_4 Activation by Cp_2LnH

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A theoretical study of SiH_4 activation by Cp_2LnH complexes for the entire series of lanthanides has been carried out at the DFT-B3PW91 level of theory. The reaction paths corresponding to H/H exchange and silylation, formation of $Cp_2Ln(SiH_3)$, have been computed. They both occur via a single-step σ-bond metathesis mechanism. For the athermal H/H exchange reaction, the calculated activation barrier averages 1.8 kcal·mol^{-1} relative to the precursor adduct $Cp_2LnH(\eta^2\text{-}SiH_4)$ for all lanthanide elements. The silylation path is slightly exogenic ($\Delta E \sim -6.5$ kcal·mol^{-1}) with an activation barrier averaging 5.2 kcal·mol^{-1} relative to the precursor adduct where SiH_4 is bonded by two Si–H bonds. Both pathways are therefore thermally accessible. The H/H exchange path is calculated to be kinetically more favorable whereas the silylation reaction is thermodynamically preferred. The reactivity of this familly of lanthanide complexes with SiH_4 contrasts strongly with that obtained previously with CH_4. The considerably lower activation barrier for silylation relative to methylation is attributed to the ability of Si to become hypervalent.

Introduction

Organometallic lanthanide complexes of the type Cp_2LnH and Cp_2LnR are able to activate inert bonds such as H−H,[1−3] C−H,[1,4,5] Si−H, Si−C,[6−13] and C−F.[14] Since the Ln(III) centers in Cp_2LnX complexes have an empty 5d-shell and a strongly stabilized 4f-shell, the activation of a Y−Z σ-bond cannot proceed by oxidative addition. It has been experimentally and theoretically shown that σ-bond activation occurs via 4-center σ-bond metathesis (see ref 15 and references therein).[2,3,9]

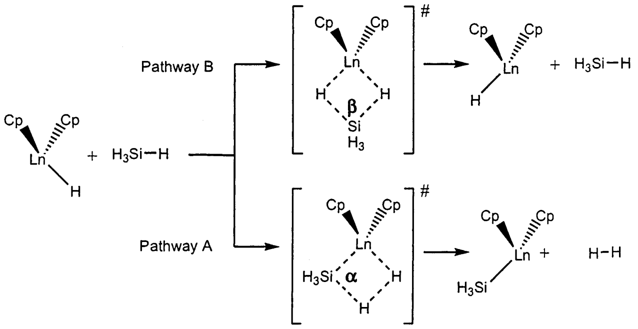

Figure 1. Possible reactions between Cp_2LnH and SiH_4.

Several exemples of reactions with a Si−Y bond (Y = H, R) are known: synthesis of organolanthanide silyl complexes,[10−13] hydrido and deuterio complexes,[6] hydrosilylation of alkenes,[7] and dehydropolymerization of silane.[16] In these reactions, one issue is the comparison between the silylation reaction (path A, Figure 1) and the H/H exchange

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reaction (path B, Figure 1), which could both occur when a Si−H bond reacts with a lanthanide hydride complex. A similar issue concernes the reactivity of the Si−C bond. The comparison of paths A and B for the Si−H bond is the focus of this work. Studies of the reaction of Cp_2LnX derivatives with $R^1R^2R^3SiH$ have shown that the products of reactions can be influenced by minor modifications of the chemical environment of the active site of the catalyst (substitution on the Cp rings, nature of X and of R^1, R^2, and R^3). It has been shown that Cp_2LnX-type complexes with bulky X ligands drive the reaction toward the formation of a Ln−Si bond, and conversely, complexes with less hindered X ligands prefer an H/H exchange reaction.[6,11,13] However, there is no experimental proof that the final products originate from a single metathesis reaction,[12,13] and in many cases, mechanisms with succesive metathesis reactions have been postulated.

Theoretical studies of Si−H bond activation as shown in paths A and B (Figure 1) are still scarce. ZINDO/1 calculations[6] of the Si−H activation by Cp_2YH indicate that both patways are thermally accessible. However, path A should be the uniquely followed route since it is associated with a lower activation barrier (8 kcal·mol^{-1}) and a drastically preferred energy of reaction (85 kcal·mol^{-1}) relative to path B, which is an athermic reaction. This difference in energy profile should lead to only one product, which does not agree with the experimental observations. DFT calculations[9] of SiH_4 activation by Cl_2ScH find that pathway A is endothermic by 0.8 kcal·mol^{-1} with respect to an adduct $Cl_2ScH(SiH_4)$ with an activation barrier of 9.3 kcal·mol^{-1}. Path B was not studied in this latter work.

In the present work, DFT calculations have been used to gain insight into the reaction of Cp_2LnH with SiH_4. Pathways A and B have been computed. The calculations have been carried out for the entire series of lanthanide elements to assess the influence of the metal center on the reaction profile. It has been assumed that SiH_4 reacts with the monomeric hydride species, even though Cp_2LnH is stable in a dimeric form.[17,18] The differences between the computational results obtained for activation of CH_4[19] and SiH_4 are discussed.

Computational Details

In previous studies,[20,21] we have shown that large core relativistic effective core potentials (RECPs) optimized by the Stuttgart−Dresden group[22−24] are well-adapted to the calculation of the geometries of lanthanide complexes as 4*f* electrons do not participate in Ln−X bonding. Consequently they were also used in the present study. Basis sets adapted to the different RECPs augmented by a polarization function (f − 1.000) were used. Silicon atoms were also treated with a large core RECP[25] in combination with the adapted basis set, augmented by a polarization function (d − 0.284). Carbon and hydrogen have been described with an all-electron 6-31G(d,p) double-ζ basis set.[26] Calculations were carried out at the DFT level of theory with the hybrid functional B3PW91,[27,28] previously tested on related systems,[20] with the Gaussian 98 suite of programs.[29] Geometry optimizations were carried out without any symmetry restrictions. The nature of the extrema (minimum or transition structures) was verified with analytical frequency calculations. Only ΔE are reported for a better discussion of the bonding properties of lanthanides complexes. It was verified that ΔG would not change the activation barrier. Entropy disfavors species which are weakly bonded and this is pointed out in due time. Ce, Eu, and Yb have two accessible oxidation states (III or IV for Ce, II and III for Eu and Yb). We choose to calculate the reactivity of Cp_2CeH^+, Cp_2EuH^-, and Cp_2YbH^- in order to have an estimate of the influence of the oxidation state. We have verified in an earlier work[19] that the usual oxidation state III gives a result similar to other lanthanides (III) for these elements.

Computational Model

To construct a maneagable but realistic model system, we have employed the following restrictions:

(1) The solvent effect has been neglected: Silanes react with organolanthanide complexes in aprotic and apolar solvents[6,12] and neglecting the solvent in the computational model should be an acceptable approximation.

(2) The monomeric Ln−H complex is the reactive species: The capability of the f-element to have high coordination number (between 7 and 9, depending on the size of metallic cation) favors the formation of dimers or oligomers. However, only the monomer has the empty coordination site at Ln necessary for reactivity. For this reason, only monomeric lanthanide hydride complexes have been considered. The dissociation reaction of the oligomer or dimer into monomer has not been considered.

(3) The cyclopentadienyl-type ligands are represented by C_5H_5: Pentamethylcyclopentadienyl (Cp*) is a currently used ligand that increases the solublility and disfavors the oligomeric form. C_5H_5, usually considered as an acceptable computational model for C_5Me_5, is used in this study. The explicit use of C_5H_5 is preferable although some alternative

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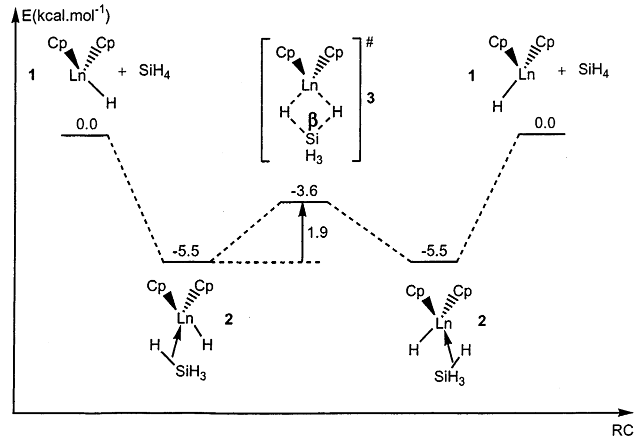

Figure 2. Computed energy profile for the H/H exchange reaction: pathway B, for Ln = La.

models are under study.[30] We note that the further replacement of C_5H_5 by H or Cl in some cases has led to difficulties.[31]

Results

A notation has been introduced for clarity. The position of any atom or group in the direct vicinity of the Ln center is called α. The next two positions are called β and γ. All Ln(III) have similar geometrical and energy patterns. Unless otherwise specified, detailed numerical results are given for La. Trend and average values for the other Ln(III) complexes are reported when significant. Ce(IV), Eu(II), and Yb(II) complexes are discussed separately.

Hydrogen Exchange Reaction. Figure 2 presents the calculated energy profile of the thermoneutral H/H exchange reaction for La. Two stationary structures corresponding to an adduct **2** of SiH_4 to Cp_2LaH and to a transition state **3** have been located on the potential energy surface (PES). Intrinsic reaction coordinate (IRC) calculations show that the transition state **3** connects to the two equivalent adducts **2**. The binding dissociation energy Δ*E* of **2** into SiH_4 and Cp_2LaH is equal to 5.5 kcal·mol^{-1}, which indicates only a very moderate stability for **2**. It should be borderline to nonbonding with inclusion of entropy. In the adduct **2** SiH_4 and Cp_2LaH make a 4-center/4-electron bond (Si−H$^{\alpha'}$ and La−H$^{\alpha}$). The silicon center (Figure 3) has a trigonal bipyramidal environment representative of the formation of a SiH_5^- moiety. The adduct can be viewed as coming from the addition of a hydride to SiH_4. The apical positions of the trigonal bipyramid are occupied by the hydride H$^{\alpha}$ and H$^{\gamma}$ (Table 3: *trans*-H$^{\gamma}$−Si−H$^{\alpha}$ around 180° and *cis*-H$^{\gamma}$−Si−H^{i} averages 98°). The Si−H$^{\alpha'}$ bond is elongated by 0.09 Å relative to free SiH_4 (Si−H = 1.492 Å). Similarly, the Ln−H$^{\alpha}$ bond is lengthened by 0.036 Å compared to that in isolated Cp_2LaH.[3]

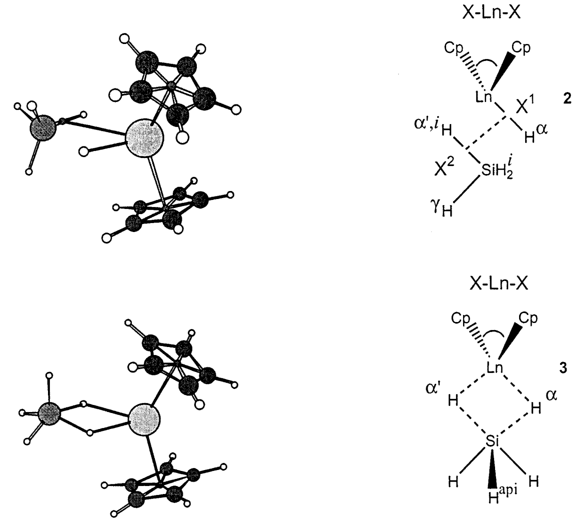

Figure 3. 3D structure and schematic representation of silane adduct (**2**) and transition state (**3**) for Ln = La; X and X^{i} are respectivelly defined as the geometrical center of a Cp ring and the middle of an X−Y bond.

Table 1. Geometrical Parameters of Precursor Adduct **2** ($Cp_2LnH(\eta^2\text{-}Si^{\beta}H_4)$)[a]

Ln	Ln−H$^{\alpha}$	Si−H$^{\alpha'}$	Ln−X^2	X^1−X^2	X−Ln−X	H^i−Si−H$^{\gamma}$
La	2.177	1.575	2.797	2.132	136.4	98.1
Ce	1.971	1.542	2.953	2.594	131.2	108.9
Pr	2.148	1.577	2.744	2.102	138.1	98.0
Nd	2.134	1.578	2.721	2.090	138.8	97.9
Pm	2.123	1.579	2.698	2.078	139.4	97.9
Sm	2.110	1.580	2.679	2.069	139.7	97.8
Eu	2.362	1.571	2.867	2.098	134.2	93.4
Gd	2.086	1.579	2.646	2.056	139.9	97.9
Tb	2.073	1.579	2.627	2.048	140.0	97.9
Dy	2.061	1.578	2.612	2.043	139.9	97.9
Ho	2.049	1.577	2.597	2.039	139.9	97.9
Er	2.036	1.576	2.584	2.035	139.9	98.0
Tm	2.025	1.575	2.573	2.033	139.8	98.1
Yb	2.266	1.565	2.779	2.070	135.7	93.6
Lu	2.006	1.571	2.556	2.034	139.5	98.3

[a] H$^{\gamma}$−Si−H$^{\alpha}$−Ln ∼ 180°; X is the geometrical center of a Cp ring, X^1 is the middle of the Ln−H$^{\alpha}$ bond, X^2 is the middle of the Si−H$^{\alpha'}$ bond. Distances are given in Å and angles in deg.

The transition state **3** (Figure 3) has a four-member ring representative of a σ-bond metathesis reaction. Ln−H$^{\alpha}$ and Ln−H$^{\alpha'}$ have approximatively the same bond length (Table 2) for all Ln elements. These two bonds are elongated by 0.11 Å relative to that in Cp_2LaH. A similar behavior is found for the Si−H$^{\alpha}$ and Si−H$^{\alpha'}$ bonds, with an elongation of 0.18 Å relative to free SiH_4.

The other Ln(III) elements give values close to that for La. The average lenthening of Ln−H$^{\alpha}$ is 0.032 and 0.091 Å in the adduct **2** and in the transition state **3**, respectively. Similarly the Si−H$^{\alpha'}$ bond is elongated by an average of 0.085 Å in **2** and 0.197 Å in **3**.

The silicon atom is pentacoordinated in **2** and in **3**. A Mulliken charge analysis shows that the charges are not much changed between **2** and **3**: La (0.85 in **2**; 0.86 in **3**), Si (0.07 in **2**; 0.06 in **3**), H$^{\alpha}$ (−0.14 in **2**; −0.18 in **3**), and H$^{\alpha'}$ (−0.23 in **2**; −0.17 in **3**). The silicon center is thus hypervalent as in a SiH_5^- in **2** and **3**. As mentionned earlier Si is in a trigonal-bipyramidal geometry in **2** but is in a square based pyramidal geometry in **3**. The transformation from **2** to **3** corresponds thus to a "turn-style" type rotation of the SiH_3 fragment with respect to Si−H$^{\alpha}$ and Si−H$^{\alpha'}$. In agreement

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Table 2. DFT Optimized Geometrical Parameters for the $Cp_2LnSi^{\beta}H_5$ Transition State (**3**)[a]

Ln	$Ln-H^{\alpha}$	Ln−Si	$Ln-H^{\alpha'}$	$Si-H^{\alpha}$	$Si-H^{\alpha'}$	$H^{\alpha}-Si-H^{\alpha'}$	X−Ln−X	$H^{api}-Si-H^{\alpha}-Ln$
La	2.265	3.282	2.246	1.696	1.683	78.8	138.8	89.0
Ce	−	−	−	−	−	−	−	−
Pr	2.222	3.241	2.212	1.694	1.686	78.8	139.5	91.0
Nd	2.203	3.222	2.195	1.693	1.687	78.8	139.7	91.9
Pm	2.185	3.203	2.180	1.693	1.688	78.8	139.8	92.7
Sm	2.169	3.186	2.165	1.693	1.689	78.9	139.9	93.4
Eu	2.400	3.351	2.401	1.641	1.641	83.8	133.9	93.4
Gd	2.140	3.153	2.138	1.693	1.690	79.0	140.0	94.6
Tb	2.125	3.135	2.123	1.693	1.691	79.0	139.9	95.2
Dy	2.112	3.119	2.111	1.694	1.691	79.1	140.0	95.8
Ho	2.098	3.104	2.097	1.693	1.691	79.1	140.0	96.2
Er	2.085	3.089	2.084	1.693	1.691	79.1	140.0	96.7
Tm	2.074	3.075	2.073	1.693	1.692	79.2	140.0	97.1
Yb	2.312	3.251	2.313	1.641	1.641	84.2	135.8	97.2
Lu	2.053	3.050	2.053	1.693	1.692	79.2	140.0	97.9

[a] X is the geometrical center of a Cp ring. Distances given in Å and angles in deg.

Table 3. DFT Calculated Reaction Energies (ΔE_B, kcal·mol^{-1}) and Activation Barriers ($\Delta E_B^{\ddagger}$, kcal·mol^{-1}) for the H/H Exchange Reaction: Pathway B (reaction energy = 0)

Ln	oxidation state	ΔE_B(**2**)	$\Delta E_B^{\ddagger}$ (**3**)[a]
La	III	−5.5	1.9
Ce	IV	−8.3	*b*
Pr	III	−5.8	1.7
Nd	III	−5.8	1.7
Pm	III	−5.8	1.7
Sm	III	−5.9	1.7
Eu	II	−9.6	1.3
Gd	III	−5.5	1.7
Tb	III	−5.4	1.7
Dy	III	−5.2	1.7
Ho	III	−5.0	1.7
Er	III	−4.8	1.8
Tm	III	−4.5	1.8
Yb	II	−8.2	1.6
Lu	III	−4.0	1.9

[a] Activation barrier given relative to complex **2**. [b] No TS for σ-bond metathesis could be located on the PES.

with the rich literature on hypervalent silicon and the well-known fluxionality of pentacoordinated Si (ref 32 and references therein), calculations with the present method and level give a bipyramidal geometry for SiH_5^- and a "turn-style" transition state for pseudorotation only (1.9 kcal·mol^{-1}) above the ground state. The H/H exchange activation barrier in the presence of Cp_2La has an equivalent activation barrier. The primary role of Cp_2La is thus to stabilize the SiH_5^- moiety without slowing down its fluxionality. The H/H exchange reaction can thus be alternatively seen as a nuclephilic substitution of an hydride by another hydride occurring at Si with retention of configuration.

The energy profile has been computed for the entire series of lanthanides (Table 3). The charged complexes (Ce(IV), Eu(II), and Yb(II)) show a different reactivity that will be discussed later. The other lanthanide(III) complexes show similar reactivities. The computed activation barriers vary from 1.7 to 1.9 kcal·mol^{-1} with a minimum around the middle of the lanthanide series (Pm, Sm). The same behavior has previously been reported in the case of H−H and C−H activation.[3,19]

The cationic charge and higher oxidation state of the metal center should make Cp_2CeH^+ different from the previously discussed $Cp_2Ln^{III}H$ complexes. The $Ce-H^{\alpha}$ bond is significantly shorter (1.971 Å) in Cp_2CeH^+ than the Ln−H bond in $Cp_2Ln^{III}H$ (average 2.06 Å). The hydridic character is diminished as indicated by the Mulliken charge on H^{α} (−0.10 in adduct **2** compared to an average of −0.22 in the related system for all other Ln(III) centers). The binding dissociation energy (BDE) of SiH_4 in **2** is thus stronger for Ce(IV) (8.5 kcal·mol^{-1}) than for other Ln(III) (average 5.5 kcal·mol^{-1}). The geometry of the adduct in the case of Ce(IV) is however different from that for Ln(III) (Table 1). The geometry of the SiH_4 moiety is still very close to that of isolated SiH_4 with no elongated Si−H bond and tetrahedral bond angles around Si. Clearly in this adduct there is no indication of the hydride acting as a nucleophile to SiH_4. Consistent with these specificities, no transition state for the H/H exchange reaction could be located on the potential energy surface.

For anionic Cp_2EuH^- and Cp_2YbH^-, there is also a strong interaction with SiH_4 with BDE equal to 9.6 kcal·mol^{-1} for Eu and 8.2 kcal·mol^{-1} for Yb (Table 3). As expected from the anionic charge on the complexes, a large hydridic charge is found on H^{α} in the adduct **2** (−0.25 for Eu, −0.25 for Yb). The silane has a strong interaction with H^{α} and adducts **2** are best viewed as SiH_5^- (trigonal bipyramid) interacting with Cp_2Ln. This is supported by the metric of the complexes: an in particular by the short $Si-H^{\alpha}$ distance 1.73 Å (1.90 Å for the other lanthanide metals) and the long $Ln-H^{\alpha}$ distance (2.362 Å for Eu and 2.266 Å for Yb compared to an upper value of 2.15 Å for Ln(III)). A turn style type transition state for pseudorotation that exchanges short and long $Si-H^{\alpha}$ bonds in these adducts has been located 1.3 (Eu) and 1.6 (Yb) kcal·mol^{-1} above the adducts **2**. This reaction is thus best viewed as a structural rearrangement rather than a σ-bond metathesis.

Silylation Reaction. As previously, the case for the neutral Ln(III) complexes is discussed first. Figure 4 shows the computed energy profile for the silylation reaction (pathway A) for La. The reaction from Cp_2LaH plus SiH_4 to $Cp_2La(SiH_3)$ plus H_2 is exogenic by −4.7 kcal·mol^{-1} probably mainly because of the formation of the strong H−H bond.

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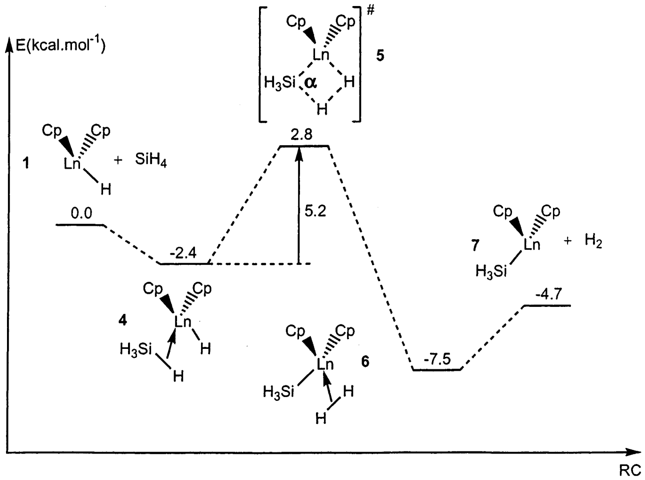

Figure 4. Computed energy profile for the silylation reaction: pathway A, for Ln = La.

Two adducts (**4**, **6**) and a transition state **5** have been located on the potential energy surface. The La−silyl−dihydrogen complex **6** is −5.1 kcal·mol^{-1} more stable than the La−hydride−silane complex **4** also because of the strong H−H bond. Similar results are obtained for the other Ln(III) complexes whereby complex **6** is on average −4.8 kcal·mol^{-1} more stable than **4**. Complex **4** is 3.1 kcal·mol^{-1} less stable than **2**. These two complexes differ by the relative orientations of the Si−H bond and La−H bonds. The charge alternation (La 0.847, H$^{\alpha}$ −0.230, Si 0.067, H$^{\alpha'}$ −0.136) in the four-member ring formed by the La−H and Si−H bonds is clearly in favor of **2** whereas the proximity of La and Si which are both positively charged (La 0.682, Si 0,021) disfavors **4**. For the other Ln(III) complex **4** is on average 3.2 kcal·mol^{-1} more stable than **2**.

For all Ln(III) elements but Lu, SiH_4 is bonded to the metal center with two Si−H bonds, the La−H$^{\alpha}$, Si−H$^{\beta}$, and Si−H^{ago} being all in the mirror plane of Cp−La−Cp (Figure 5). The two Si−H bonds are of almost equal lengths, elongated by only 0.015 Å from Si−H in free SiH_4 (Table 4). SiH_4 thus can be be viewed as side bonded to La(η^2-SiH_4) with an additional agostic Si−H bond or alternatively as η^3-bonded via the two Si−H bonds. Despite these double interactions with La, the binding dissociating energy of SiH_4 in **4** is only 2.4 kcal·mol^{-1}. Entropy would disfavor such minima.

The coordination of SiH_4 is different in the case of Lu. The smaller ionic radius disfavors high coordination number and SiH_4 is bonded in a side-way η^2 manner via a single Si−H$^{\beta}$ bond. The binding dissociation energy (0.7 kcal·mol^{-1}) is also significantly smaller than with the other lanthanide(III) centers. Considering all Ln(III) complexes, it is thus probably more appropriate to consider that SiH_4 is η^2-bonded via a single Si−H bond with an additional Si−H agostic interaction to the lanthanide center when it is permitted by the ionic radius of the lanthanide element. This point of view will also be more appropriate with the description of the structures along the reaction path (see after).

At the transition **5** state the Si−H$^{\beta}$ directly involved in the reaction is elongated by 0.24 Å whereas the other Si−H^{ago} bond, not involved in the σ-bond metathesis, is only elongated by 0.02 Å compared to the respective Si−H bonds in **4** (Tables 4 and 5). The H$^{\alpha}$−H$^{\beta}$ bond is clearly well-formed (1.213 Å) at the transition state. Only negatively charged atoms (H^{ago}, Si, and H$^{\beta}$) can really have a bonding interaction with La.

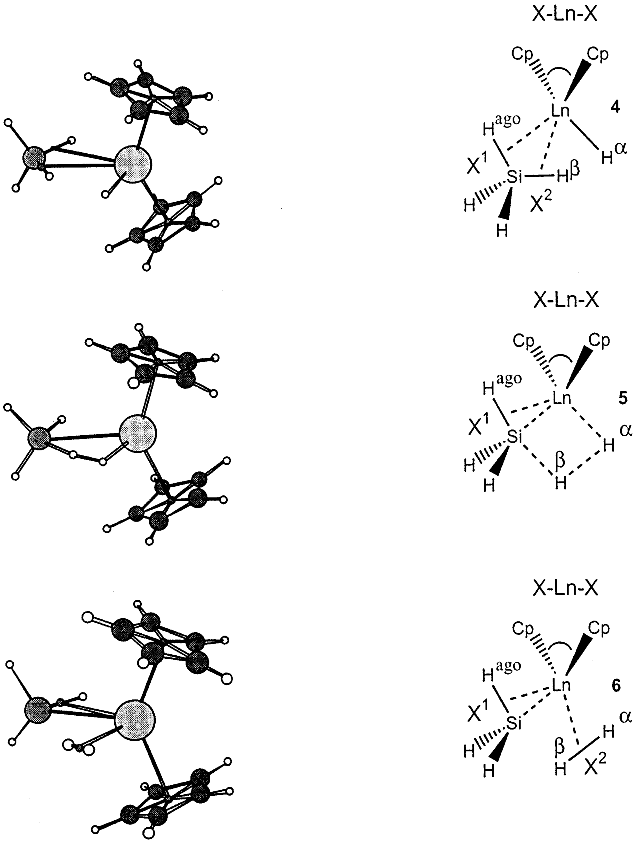

Figure 5. 3D structure and schematic representation of silane adduct (**4**), transition state (**5**), and molecular dihydrogen adduct (**6**) for Ln = La; X and X^{i} are respectivelly defined as the geometrical center of a Cp ring and the middle of an X−Y bond.

No transition state in which only Si, H$^{\alpha}$, and H$^{\beta}$ are bonded to Ln could be located even for Lu. Thus an agostic Si−H bond is maintained during the silylation reaction for all Ln(III) elements.

At the transition state **5**, Si is in a pentagonal bipyramidal coordination with La at an equatorial site and H$^{\beta}$ and H^{ago} at the apical sites (H^{ago}−Si−H$^{\beta}$ = 165°) (Table 5). An electropositive group such as the Cp_2La fragment is an unfavorable factor as a ligand in a pentacoordinated silicon species which is best stabilized by electronegative ligands at either the apical or axial sites. For this reason, the transition state **5** for silylation is 6.8 kcal·mol^{-1} higher in energy than the transition **3** for H/H exchange. Not only is the transition state **5** higher than the transition **3** but also the activation barrier is higher for the silylation reaction (5.2 kcal·mol^{-1} in the case of La, reaction path A) than for the H/H exchange (1.9 kcal·mol^{-1} for La, reaction path B). The closer proximity of the two electropositive centers, La and Si, in the transition state **5** is responsible for this result. Values for the other Ln(III) elements are qualitatively similar with barriers varying between 5.0 and 5.8 kcal·mol^{-1}. As in the H/H

Table 4. Geometrical Parameters of Precursor Adduct **4**[a]

Ln	$Ln-H^{\alpha}$	$Ln-X^1$	$Ln-X^2$	$Si-H^{\beta}$	$Si-H^{ago}$	$X-Ln-X$	$Si-H^{\beta}-H^{\alpha}$
La	2.147	3.128	3.104	1.504	1.509	136.5	149.7
Ce	1.971	2.808	2.804	1.523	1.528	132.6	148.4
Pr	2.114	3.048	3.025	1.506	1.509	137.5	149.5
Nd	2.099	3.015	2.992	1.506	1.509	137.9	149.4
Pm	2.085	2.985	2.961	1.507	1.509	138.2	149.4
Sm	2.072	2.962	2.936	1.508	1.509	138.4	149.5
Eu	–	–	–	–	–	–	–
Gd	2.048	2.936	2.899	1.508	1.508	138.5	149.9
Tb	2.034	2.921	2.880	1.509	1.508	138.5	150.1
Dy	2.021	2.916	2.866	1.509	1.508	138.5	150.4
Ho	2.009	2.914	2.854	1.509	1.507	138.5	150.8
Er	1.997	2.918	2.844	1.510	1.506	138.5	151.4
Tm	1.986	2.949	2.839	1.510	1.504	138.7	153.2
Yb	–	–	–	–	–	–	–
Lu	1.969	3.462	2.967	1.508	1.492	138.7	174.2

[a] X is the geometrical center of a Cp ring, X^1 is the middle of the $Si-H^{ago}$ bond, X^2 is the middle of the $Si-H^{\beta}$ bond. Distances given in Å and angles in deg.

Table 5. DFT Optimized Geometrical Parameters of the $Cp_2LnSi^{\alpha}H_5$ Transition States (**5**)[a]

Ln	$Ln-Si$	$Ln-H^{\beta}$	$Ln-H^{\alpha}$	$Si-H^{\beta}$	$H^{\alpha}-H^{\beta}$	$Ln-X^1$	$Si-H^{ago}$	$X-Ln-X$	$Si-H^{\beta}-H^{\alpha}$	$H^{ago}-Si-H^{\beta}$
La	3.138	2.339	2.197	1.748	1.213	2.919	1.530	140.3	167.4	112.0
Ce	2.900	2.161	2.055	1.881	1.072	2.596	1.555	138.6	161.3	109.4
Pr	3.083	2.296	2.162	1.748	1.216	2.846	1.531	141.0	166.5	112.0
Nd	3.058	2.277	2.146	1.749	1.217	2.814	1.532	141.2	166.1	111.9
Pm	3.036	2.259	2.132	1.750	1.218	2.784	1.533	141.3	165.8	111.9
Sm	3.015	2.243	2.119	1.750	1.218	2.757	1.534	141.3	165.5	111.9
Eu	3.557	2.545	2.349	1.680	1.359	3.477	1.515	135.2	179.0	113.9
Gd	2.981	2.214	2.095	1.754	1.215	2.713	1.535	141.4	165.0	111.9
Tb	2.964	2.198	2.081	1.755	1.215	2.689	1.535	141.3	164.7	111.9
Dy	2.949	2.184	2.069	1.757	1.214	2.670	1.536	141.3	164.5	111.9
Ho	2.934	2.171	2.058	1.759	1.212	2.650	1.536	141.3	164.3	111.9
Er	2.920	2.158	2.046	1.761	1.211	2.632	1.537	141.2	164.0	111.9
Tm	2.909	2.146	2.036	1.763	1.209	2.616	1.537	141.1	163.9	111.9
Yb	3.501	2.444	2.256	1.705	1.309	3.458	1.515	136.8	179.8	114.3
Lu	2.889	2.124	2.018	1.766	1.205	2.593	1.537	141.1	163.7	111.9

[a] X is the geometrical center of a Cp ring, X^1 is the middle of the $Si-H^{ago}$ bond. Distances are given in Å and angles in deg.

exchange reaction, the lower barrier is around the middle of the lanthanide series (Nd, Pm, Sm) and the maximum for Lu.

The $Si-H^{\beta}-H^{\alpha}$ angle is equal to 150° (La). Similar values are obtained for the other Ln(III) elements (Table 5). This wide angle was also obtained for H−H−C in the case of the methylation reaction between CH_4 and Cp_2LnH.[19] Therefore in the case of the silylation reaction, it is also possible to view the reaction as an intramolecular deprotonation (H^{β}) of SiH_4 by a hydride H^{α} in the coordination sphere of Ln.

The transition state **5** connects to an H_2 adduct $Cp_2LaSiH_3(\eta^2\text{-}H_2)$ (**6**, Figure 5). The absence of back-donation from La to H_2 results in a short H−H distance (0.76 Å) and a small binding dissociation energy of H_2 (2.8 kcal·mol^{-1}). Entropy would thus favor the formation of separated H_2 and Cp_2LaSiH_3. Complex **6** also has an agostic SiH_3 group with one Si−H bond elongated by 0.10 Å compared to the Si−H bond distance in free SiH_4. The Si−H α-agostic interaction is also present in $Cp_2La(SiH_3)$ with a Si−H elongated by 0.10 Å with respect to that in free SiH_4. However, another minimum without Si−H agostic interaction was found for $Cp_2La(SiH_3)$ only 0.7 kcal·mol^{-1} higher in energy. The stabilization associated with the agostic interaction is thus very small despite the low coordination number of La. The Si−H agostic bond is poorly oriented in $Cp_2La(SiH_3)$ with respect to the empty site of La to make any energetically efficient interaction. Similar results have been obtained with the other Ln(III) elements (Table 7). The binding dissociation energy of H_2 varies between 1.5 kcal·mol^{-1} for Lu and 3.8 kcal·mol^{-1} for Pm and Sm. The agostic SiH bond is present for all Ln(III) systems.

Table 6. Geometrical Parameters of the Dihydrogen Adduct **6** ($Cp_2LnSiH_3(\eta^2\text{-}H_2)$)[a]

Ln	$Ln-Si$	$Si-H^{ago}$	$H^{\alpha}-H^{\beta}$	$Ln-X^1$	$Ln-X^2$	$X-Ln-X$
La	2.973	1.588	0.762	2.641	2.620	139.0
Ce	2.807	1.613	0.787	2.421	2.297	141.2
Pr	2.932	1.590	0.763	2.594	2.561	138.6
Nd	2.914	1.590	0.763	2.573	2.534	138.5
Pm	2.896	1.591	0.764	2.552	2.503	138.5
Sm	2.880	1.591	0.765	2.534	2.481	138.4
Eu	–	–	–	–	–	–
Gd	2.851	1.592	0.765	2.503	2.447	138.3
Tb	2.835	1.592	0.766	2.484	2.419	138.2
Dy	2.822	1.592	0.767	2.470	2.401	138.2
Ho	2.808	1.592	0.767	2.455	2.384	138.1
Er	2.795	1.592	0.768	2.442	2.368	138.1
Tm	2.784	1.592	0.768	2.430	2.353	138.1
Yb	–	–	–	–	–	–
Lu	2.762	1.592	0.769	2.408	2.332	138.1

[a] X is the geometrical center of a Cp ring, X^1 is the middle of the $Si-H^{ago}$ bond, X^2 is the middle of the $H^{\alpha}-H^{\beta}$ bond. Distances are given in Å and angles in deg.

For the Ce(IV) complex, the reaction energy for the silylation reaction is different from that of the Ln(III)

Table 7. DFT Calculated Reaction Energies (ΔE_A, kcal·mol^{-1}) and Activation Barriers ($\Delta E_A^{\ddagger}$, kcal·mol^{-1}) for the Silylation Reaction: Pathway A

Ln	oxidation state	ΔE_A	$\Delta E_A(\mathbf{4})$	$\Delta E_A^{\ddagger}(\mathbf{5})$[a]	$\Delta E_A(\mathbf{6})$
La	III	−4.7	−2.4	5.3	−7.5
Ce	IV	1.6	−10.1	9.5	−5.1
Pr	III	−4.4	−2.7	5.1	−7.8
Nd	III	−4.3	−2.8	5.0	−7.9
Pm	III	−4.2	−2.8	5.0	−8.0
Sm	III	−4.1	−2.8	5.0	−7.9
Eu	II	−2.8	[b]	3.7[c]	[b]
Gd	III	−3.9	−2.3	5.1	−7.3
Tb	III	−3.7	−2.1	5.1	−7.0
Dy	III	−3.6	−1.9	5.1	−6.7
Ho	III	−3.4	−1.6	5.2	−6.3
Er	III	−3.3	−1.3	5.3	−5.9
Tm	III	−3.2	−1.0	5.4	−5.4
Yb	II	−15.3	[b]	5.2[c]	[b]
Lu	III	−3.0	−0.7	5.8	−4.5

[a] Activation energy given relative to complex **4**. [b] No adduct of silane or molecular hydrogen could be located on the PES. [c] Activation energy given relative to the separate reactants.

complexes. The SiH_4 adduct **4** is more stable for Ce(IV) (BDE = 10.1 kcal·mol^{-1}) than for the other Ln(III) metals (average BDE = 2.0 kcal·mol^{-1}). This is the unique case where adduct **4** becomes more stable than the adduct **2**. As seen in the case of **2** also, the greater stability of the adduct for Ce(IV) originates from the larger Lewis acidity of the metal in $[Cp_2CeH]^+$. Due to this stabilization, the activation barrier is higher (9.5 kcal·mol^{-1} vs an averaged value of 5.1 kcal·mol^{-1}). The geometrical features of the transition state are however similar for Ce(IV) and the other lanthanide(III) elements. The main difference lies in the strength of the agostic interaction. The elongation of the Si−H bond is greater by 0.025 Å in the case of transition state for Ce(IV) than for all Ln(III) analogues, indicating a stronger agostic interaction in the Ce(IV) case. This is again in good agreement with the higher Lewis acidity of this complex.

In the case of anionic $[Cp_2EuH]^-$ and $[Cp_2YbH]^-$, no adducts of SiH_4 or H_2 have been located on the PES. The electrostatic repulsion between the anionic $[Cp_2EuH]^-$ or $[Cp_2YbH]^-$ and the free silane or H_2 disfavors the formation of adducts. However, the transition states for the silylation reaction have been located. The calculated activation barriers do not differ much from these found for the other lanthanides. The transition states determined in the case of Eu and Yb connect thus directly to separate SiH_4 and hydride complex or H_2 and lanthanide silyl complex.

Discussion

SiH_4 makes adducts to all Cp_2Ln(III)H as well as to $[Cp_2CeH]^+$. However, the binding dissociation energy is small (from around 2 to 10 kcal·mol^{-1}) and entropy should favor dissociation. Agostic Si−H interaction is also present showing the preference of lanthanide for high coordination number. Silane complexes are well reported from either experimental or theoretical studies for transition metal complexes capable of back-donation as mentionned among others in selected references.[33−38] No stable silane complexes have been reported for d^0 metal centers but a number of agostic Si−H interactions have been reported and also studied with quantum methods notably in groups 3 and 4 or lanthanide complexes.[39−46] Si−H is clearly a good candidate for agostic interactions even in the absence of back-donation from the metal. No direct computational comparison can be done between the binding of Si−H and C−H bonds since different computational models were used.[19] Adducts between SiH_4 and $Cp_2Ln^{III}H$ have been located as minima on the potential energy surface, which was not the case with H_2.[3] Even though stable adducts of silane and the biscyclopentadienyllanthanide hydride complex are unlikely to be isolated because entropy would favor dissociation of the silane and the lanthanide hydride complex, the calculations suggest that SiH_4 acts as a more powerful Lewis base to the electron poor lanthanide center than H_2. The reaction energy is zero for the H/H exchange whereas the silylation process is slightly exogenic. The silylation reaction should thus be the energetically favored pathway based on the energy of products. However, the activation barrier is smaller for the H/H exchange than for the silylation by approximatively 3.5 kcal·mol^{-1}. The H/H exchange reaction is thus kinetically favored. Nonetheless, the two activation barriers are similar and the two paths could both occur. It should be kept in mind that this small difference in activation barriers still leads to a relative rates of $k_B/k_A = 370$ in favor of path B.

The low activation barrier found in the calculations is in agreement with the fact that the Si−H activation reaction is too fast to be monitored by NMR even at −78 °C.[12] Moreover, the small difference in activation energies between the two pathways does not allow one of the two paths which have been suggested in the literature to be excluded.[6−13] Varying the reaction conditions (solvent, ligand, temperature) gives access to H/H exchange or silylation products.[6]

The key to the low-energy barriers for the two reactions is the ability of Si to stabilize pentacoordination with an overall negative charge. Such a bonding situation has been found in the solid-state structures of several systems,[47−56]

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which suggests that it can also correspond to a low transition state in the appropriate case. The stabilization of the transition state is more important when the hypervalent Si species is more stable. Hypervalent complexes are more stable when the electropositive hypervalent center is surrounded by electronegative atoms or groups. This is why the transition for H/H exchange is lower than that for silylation. This contrasts drastically with the reaction of CH_4 with Cp_2LnH. Hypervalent carbon is heavily disfavored especially with poorly electronegative ligands. Although comparison of the numerical values should be done with caution because of the difference in the model ligands used in the calculations, the activation barrier for H/H exchange with CH_4 was found to be around 73.2 kcal·mol^{-1} for H/H exchange and around 15.5 kcal·mol^{-1} for methylation. It is around 2 and 5 kcal·mol^{-1} with SiH_4 for the corresponding reactions. The more drastic influence is on the H/H exchange reaction where the pentacoordinated SiH_5^- is best stabilized. The low activation barrier for the silane agrees with the experimental data[6] according to which the H/H exchange and silylation reactions are kinetically accessible reactions. The replacement of CH_4 by SiH_4 also reverses the thermodynamics of the reactions. With alkane, the reaction goes preferencially toward formation of the Ln−H complex,[19] whereas with silane, formation of the silyl complex is energetically favored.

Conclusions

The present paper presents a systematic study of Si−H activation of SiH_4 by Cp_2LnH complexes. The reactions proceed through a σ-bond metathesis mechanism. The reaction yields two different products resulting from either H/H exchange or silylation. Both paths are found to be kinetically accessible for SiH_4, which contrasts with the results obtained for CH_4.[19] The activation barrier goes through a minimum for the middle of the lanthanide series (Nd−Dy) for the two reactions, a tendancy already found in the reaction with CH_4. The coordination aptitude of Si to stabilize a hypervalent coordination makes the two reactions accessible in energy. The H/H scrambling reaction is found to be the kinetically favored route whereas the silylation reaction is preferred thermodynamically. However, the difference in the activation energies between these two reactions is very small and both should occur. This finding is in agreement with the fact that the reaction can be easily oriented by changing the reaction conditions.

This is a first step in the study of Si−X activation catalyzed by lanthanide complexes. We are presently investigating a catalytic cycle involving Si−C activation. This study is also part of a systematic study of σ-bond activation by lanthanide complexes. Work is in progress on C−F activation.

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