# Chemoselectivity in σ bond activation by lanthanocene complexes from a DFT perspective: reactions of $Cp_2LnR$ (R = $CH_3$, H, $SiH_3$) with $SiH_4$ and $CH_3$–$SiH_3$†‡

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The pathways for the σ bond metathesis reactions between $Cp_2LnCH_3$ and $SiH_4$ to give either $Cp_2LnSiH_3$ and $CH_4$ ($CH_3$/$SiH_3$ exchange) or $Cp_2LnH$ and $H_3C$–$SiH_3$ (Si–C coupling) have been studied using DFT(B3PW91) calculations. It is shown that the nature of the lanthanide atom has essentially no influence on the free enthalpy profile. All reactions that could occur between $H_3C$–$SiH_3$, formed from the reaction between the initial reagents ($Cp_2LnCH_3$ and $SiH_4$), and the lanthanocene complexes ($Cp_2LnH$ or $Cp_2LnSiH_3$), have been then studied for La only. The activation of the Si–H bond is preferred over that of Si–C or C–H bonds. In addition, in the reaction of $Cp_2LaH$ with $SiH_3CH_3$, the silyl group favours the formation of the C-bonded alkylsilyl complex. The activation of the Si–H bond is not selective, *i.e.* Si can be at either the α or β sites, with respect to the metal center, in the 4-center transition state. The reaction between $Cp_2LaSiH_3$ and $SiH_4$ is preferentially the exchange of $SiH_3$ groups over the Si–Si coupling, mostly for thermodynamic reasons. The Si–Si coupling is however not strongly disfavoured by thermodynamics and has an accessible activation energy.

## Introduction

Since the discovery in the 1980's by Watson *et al.*[1,2] that $Cp^*_2LuCH_3$ ($Cp^* = \eta^5$-$C_5Me_5$) activates inert σ bonds such as the methane C–H bond, organolanthanide complexes have gained attention in the chemical community.[3] Experimental work has shown that various lanthanocene derivatives can activate not only C–H[1,4–7] in alkanes and arenes but also the C–F bond[8,9] in fluoroalkanes and fluoroarenes, as well as the Si–H bonds in alkyl- and arylsilanes.[10–17] However, these complexes rarely lead to homocoupling products *via* C–C, Si–Si or cross coupling products *via* Si–C bond formation.[16,17] Formation of C–C bonds is observed because the lanthanide complexes are also Ziegler–Natta type polymerization catalysts.[18] However, examples of Si–C and Si–Si coupling/decoupling reactions are known. Silane dehydropolymerization has been proposed to occur *via* σ bond metathesis.[13,14,16] This reaction, which has been found for early transition metal and lanthanide complexes, is supposed to occur by successive Si–H bond activations. In the reaction of $C_6H_5$–$SiH_3$ with $Cp^*_2SmH$, the trimer of $Cp^*_2Sm$–$SiH_3$ is the main product formed together with redistribution products, such as $C_6H_6$, $Ph_2SiH_2$, $Ph_3SiH$ or $SiH_4$, as well as some Si–Si coupling products. In this case, the redistribution products originate from a Si–C coupling reaction.[16]

Considerable amounts of information on the chemistry of silanes with various metals, including lanthanides, can be found in the review of Corey and Braddock-Wilking.[19] However, the factors which control the reactivity preferences (selectivity) with lanthanide complexes are still unclear and a theoretical study is then the method of choice to investigate the elementary steps that are needed to account for the variety of products. Several reactions implying C–H bond activations have been studied computationally.[20–22] In the case of silane, computational works have shown that the reaction of $Cp_2LnH$ with $SiH_4$ to give $Cp_2LnSiH_3$ and $H_2$ has a low energy barrier and is thermodynamically accessible. The thermodynamically neutral reaction that exchanges the hydrogen atoms of the lanthanide complex and the silane has also a low energy barrier.[23] Calculations by Ziegler and Folga using the ADF program have shown that the reaction of $Cl_2ScSiH_3$ with $SiH_4$ could lead to the formation of $SiH_3$–$SiH_3$ with an accessible energy barrier.[24] In no case was the cross coupling reaction involving the formation and cleavage of an Si–C bond studied.

In this paper, we have used DFT calculations to determine the energy profiles for the reactions between $Cp_2LnCH_3$ and $SiH_4$ to form $Cp_2LnSiH_3$ and $CH_4$ (termed the $CH_3$/$SiH_3$ exchange) and to form $Cp_2LnH$ and $CH_3$–$SiH_3$ (termed the

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† Electronic supplementary information (ESI) available: Tables S1 to S6 of structural information for the reactions of eqns (1) and (2) for Ln = La to Lu. List of coordinates, energies and free enthalpies for all structures with La. See DOI: 10.1039/b617425f

‡ The HTML version of this article has been enhanced with colour images.

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C–Si coupling). The influence of the nature of the lanthanide metal on the energy profiles has been also studied. Since the influence of the metal has been found to be small, reactions that could occur between $Cp_2LnH$ and the products obtained from the first set of reactions have been studied for La only. These reactions include the activations of the C–H, Si–H and C–Si bonds from $CH_3–SiH_3$. In addition, the calculation of the energy profile for the reaction of $Cp_2Ln–SiH_3$ with $SiH_4$ allows discussion of some aspects of the dehydropolymerization of silanes. All reactions considered are shown in eqns (1)–(10). The reaction of $Cp_2LnH$ with $SiH_4$, which has been previously published, will be also mentioned.[23]

$$Cp_2Ln–CH_3 + H–SiH_3 \rightarrow Cp_2Ln–SiH_3 + H–CH_3 \quad (1)$$

$$Cp_2Ln–CH_3 + H–SiH_3 \rightarrow Cp_2Ln–H + CH_3–SiH_3 \quad (2)$$

$$Cp_2Ln–H + H–SiH_2CH_3 \rightarrow Cp_2Ln–H + H–SiH_2CH_3 \quad (3)$$

$$Cp_2Ln–H + H–SiH_2CH_3 \rightarrow Cp_2Ln–SiH_2CH_3 + H–H \quad (4)$$

$$Cp_2Ln–H + H–CH_2SiH_3 \rightarrow Cp_2Ln–H + H–CH_2SiH_3 \quad (5)$$

$$Cp_2Ln–H + H–CH_2SiH_3 \rightarrow Cp_2Ln–CH_2SiH_3 + H–H \quad (6)$$

$$Cp_2Ln–H + H_3Si–CH_3 \rightarrow Cp_2Ln–SiH_3 + H–CH_3 \quad (7)$$

$$Cp_2Ln–H + H_3Si–CH_3 \rightarrow Cp_2Ln–CH_3 + H–SiH_3 \quad (8)$$

$$Cp_2Ln–SiH_3 + H–SiH_3 \rightarrow Cp_2Ln–H + H_3Si–SiH_3 \quad (9)$$

$$Cp_2Ln–SiH_3 + H–SiH_3 \rightarrow Cp_2Ln–SiH_3 + H–SiH_3 \quad (10)$$

### Computational details

The lanthanide metal centers have been represented with the large core pseudo-relativistic effective core potential (RECP) from the Stuttgart group[25–28] and the basis set associated with these RECPs has been augmented by an f polarization function. The carbon and hydrogen atoms are treated with an all-electron double-$\zeta$, 6-31G(d,p), basis set.[29] Silicon atom has been treated with an RECP with the adapted basis set,[30] augmented by a d polarization function. All the calculations have been carried out with the Gaussian 98 suite of programs[31] at the DFT level using the B3PW91 hybrid functional.[32,33] The geometry optimizations have been performed without any symmetry constraints. The nature of all extrema has been verified by analytic determination of frequencies and the connections between transition states and minima have been established by an optimization of the structures distorted along the intrinsic reaction coordinate (IRC). The Gibbs energies (free enthalpies) have been calculated at 298.15 K within the harmonic approximation for frequencies. The coordinates, energy and free enthalpies of all calculated species in the case of La are given in the ESI.†

## Results and discussion

### Reactions of $Cp_2LaCH_3$ with $SiH_4$

For convenience, [M] represents $Cp_2M$. The variation of Gibbs energies, $\Delta G$, relative to the separate reagents, is used for discussing the reaction profiles. It has been verified that using the variation of potential energies $\Delta E$ in place of $\Delta G$ does not modify the relative positions of transition states and minima for the reactions studied and thus leads to the same interpretation of the results. The entropic term has its main effect in reactions involving change of molecularity (formation of complexes from separate reactants and associated reverse reactions).

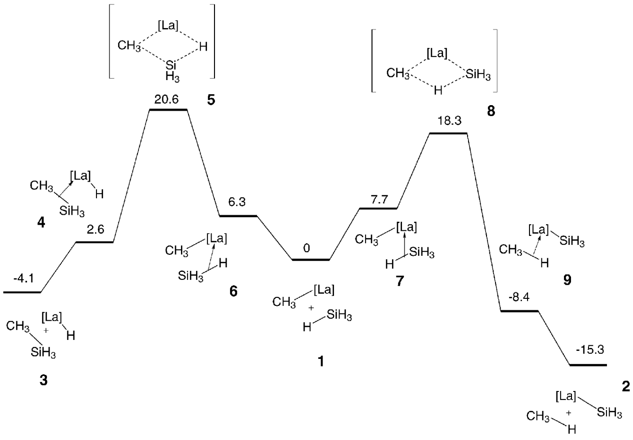

**Fig. 1** Free enthalpy profiles (kcal $mol^{-1}$) for the $CH_3/SiH_3$ exchange reaction (eqn (1)) and formation of $CH_3–SiH_3$ (eqn (2)).

The calculated Gibbs energy profiles for reactions shown in eqn (1) and eqn (2) are presented in Fig. 1 and the structures of the extrema are shown in Fig. 2. The $CH_3/SiH_3$ exchange reaction (right-hand side of Fig. 1) yields [La]–$SiH_3$ and $CH_4$, **2**, after formation of the first adduct ([La]–$CH_3$)($SiH_4$), **7**, passage through transition state **8** and decomposition of the adduct ([La]–$SiH_3$)($CH_4$) **9**. It should be noted that the relative potential energies ($\Delta E$) of the adducts are lower than that of the separate reactants but that their relative Gibbs energies are higher due to the entropic factor associated with the change of molecularity resulting from the formation of one complex from two molecules. From the literature, it appears that the translational part of the entropic factor, which contributes most to the variation in entropy, may be exaggerated so that the free enthalpy of the adducts and transition state may be closer in energy to the separate reactants than indicated by the calculated $\Delta G$.[34] This leads to no modification of the results in this work. The $SiH_3–CH_3$ coupling reaction (left-hand side of Fig. 1) yields [La]–H and $H_3C–SiH_3$ (**3**) *via* the adduct **6**, the transition state **5** and the adduct **4**. The two reactions are exoergic, the larger free enthalpy of reaction being for the formation of [La]–$SiH_3$ and $CH_4$. The thermodynamic preference for formation of the silyl complex and methane over the hydride complex and methylsilane is in line with previous studies: the reaction of [La]–H with $CH_4$ to form [La]–$CH_3$ and $H_2$ is endoergic while that of [La]–H with $SiH_4$ to form [La]–$SiH_3$ and $H_2$ is exoergic.[20,23,35] These thermodynamic features are associated with the variation in bond strength in the metallic complex and the non-metallic species. Due to the difficulty in calculating a homolytic Ln–X bond dissociation energy when using large core ECP, we only calculated the bond free energies (Si–H, C–H and Si–C) in $SiH_4$, $CH_4$ and $SiH_3–CH_3$. Previous studies on bond dissociation energies

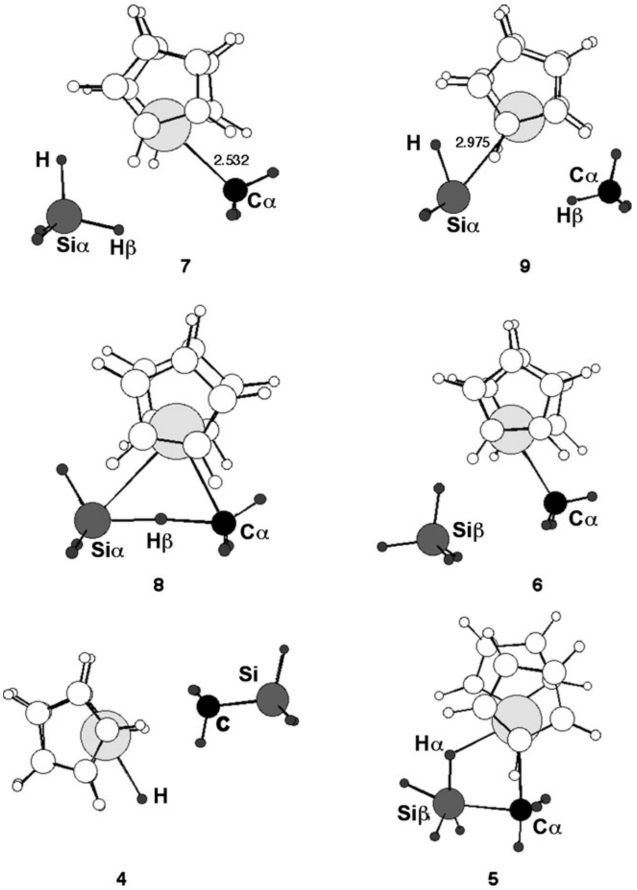

**Fig. 2** Optimized structures of the extrema for the reactions of eqns (1) and (2). The distances are given in Å.

have shown that DFT performs correctly on relative bond dissociation energies even though some detailed substituent effects are more difficult to represent.[36] The calculated bond dissociation free enthalpies BDG, and associated bond dissociation energies, BDE, are: BDG 78.8, BDE 91.8 for Si–H in $SiH_4$, BDG 96.0, BDE 112.3 for C–H in $CH_4$, and BDG = 69.6, BDE 86.4 kcal $mol^{-1}$ for Si–C in $CH_3$–$SiH_3$. The energy of reaction of eqn (1) is therefore in large part determined by the difference of $-17.2$ kcal $mol^{-1}$ in energy between the weaker Si–H and the stronger C–H bonds suggesting that the La–Si and La–C bond strengths are of similar magnitude since the energy of the bond metathesis reaction is $-15.2$ kcal $mol^{-1}$. In contrast, for eqn (2), the variation in free energy of $+9.2$ kcal $mol^{-1}$ associated with the loss of the Si–H bond and the formation of the Si–C bond would give an endoergic reaction. This is thus compensated by the variation in free energies in the lanthanide complexes and confirms that the La–H bond energy is stronger than the La–C(alkyl) bond energy. This analysis thus suggests that the La–H is stronger than the La–C and La–Si bonds, which are of similar strength.

We describe qualitatively the geometries of the intermediates and transition state of the $CH_3$/$SiH_3$ exchange reaction (eqn (1)) because none of the values is remarkable. Quantitative geometrical features are given in the ESI.† The reaction starts with the formation of a σ-adduct of $SiH_4$ **7**. In **7**, two H of $SiH_4$ are close to La, which indicates that $SiH_4$ is $\eta^3$-coordinated to La. $SiH_4$ coordination is endoergic by 7 kcal $mol^{-1}$, which is due, as mentioned earlier, to the loss of the translational entropy. The adduct **7** leads to a σ-bond metathesis transition state, **8**, in which $SiH_3$ and H are at the α and β positions, respectively of the 4-center transition state (Fig. 2). At the transition state **8**, the carbon atom, the transferring H and the silicon atom are almost aligned. Similar situations have been obtained for the reactions of [Ln]–H or [Ln]–$CH_3$ with $H_2$, $CH_4$ and $SiH_4$.[20–23,37] The alignment of C, H and Si clearly suggests that this elementary step is a proton transfer between the negatively charged groups, $SiH_3$ and $CH_3$, in the stabilizing field of the positively charged lanthanide atom. The calculated activation energy of 18.3 kcal $mol^{-1}$ is relatively low, which suggests that this elementary step is energetically accessible. The activation energy is calculated to be significantly lower than that for $CH_4$ activation by [La]–$CH_3$, for which a value of 28.5 kcal $mol^{-1}$ was found at the same level of methodology.[22] The transition state **8** leads to a complex between [La]–$SiH_3$ and $CH_4$, **9**, where the methane is $\eta^3$-bonded to La. Even if $CH_4$ is bonded to La with two C–H bonds, the $SiH_3$ group distorts to establish one α-agostic Si–H bond. This contrasts with the structure of the $SiH_4$ adduct **7** where the methyl group is not α-agostic. The Si–H bond has a greater propensity to become agostic than C–H bond due to the more hydridic character of the silicon hydride.[38]

The $CH_3$–$SiH_3$ coupling reaction (Fig. 1 left) is initiated by the formation of a silane adduct **6**, which differs from **7** in the orientation of the Si–H bond relative to the La–C bond but has almost the same free enthalpy (6.3 kcal $mol^{-1}$). In **6**, $SiH_4$ is $\eta^1$-coordinated to La. This coordination mode, which is less rotationally restrained, has thus a lower free enthalpy than **7**. Species **6** leads to the transition state **5**, in which $SiH_3$ is at the β position and H at the α position of the 4-center transition state **5** (Fig. 2). In **5**, the silicon has a square pyramidal geometry as previously obtained in the reaction of [La]–H with $SiH_4$.[23] The transition state **5**, which is 20.6 kcal $mol^{-1}$ above the separated reactants, leads to a $CH_3$–$SiH_3$ adduct **4**, in which $CH_3$ is close to the metal. This adduct is almost at the same free enthalpy ($\Delta G$ = 2.6 kcal $mol^{-1}$) as the separate reactants so that decoordination of the methylsilane further lowers the free enthalpy by 6.7 kcal $mol^{-1}$.

The reactions of eqns (1) and (2) have comparable activation energies and therefore the two reactions should both be observed. This is due to the ability of the $SiH_3$ group to occupy the α or the β positions of the 4-center transition state of a σ bond metathesis transition state with almost equal energies as noted previously for the reactions of $Cp_2LnH$ with $SiH_4$.[23] Formation of the metal hydride as well as of the metal silyl is thus expected. These two complexes can themselves react with the reactant or with the products obtained from these two reactions. *A priori*, one should study the reactions of the hydride and the silyl complexes with the C–H, Si–H and Si–C bonds of the various possible reactants. However, it now appears that the energy profiles of the reactions are qualitatively similar for the hydride and for the silyl complex; consequently, we have focused on the reactions of the various reactants with the hydride complex. Nevertheless, the reaction of the silyl complex with $SiH_4$ will also be discussed because it can give information on the silane dehydropolymerization mechanism.

### Influence of the metal centre

As shown in previous work, the nature of the lanthanide has little influence on the energy profile of the reaction[20–23,37] We verified that this was also the case for these two reactions because they have similar activation barriers. The free enthalpy profiles were calculated for all lanthanide metals and the results are given in the ESI.† The activation energies vary from 18.3 to 23.0 kcal mol$^{-1}$ for $CH_3/SiH_3$ exchange reaction (eqn (1)) and from 20.6 to 23.4 kcal mol$^{-1}$ for the $SiH_3$–$CH_3$ coupling reaction (eqn (2)). Free enthalpies of reaction have a narrower energy range ($\leq$2 kcal mol$^{-1}$). The main results found for La apply to all the lanthanides: the activation energy for the $CH_3/SiH_3$ exchange reaction is marginally lower than for the $CH_3$–$SiH_3$ coupling reaction, the first reaction being more exoergic. There is a slight tendency for the activation energies to increase from La to Lu and for the reactions to become slightly less exoergic. However the variations are too small to be significant and it can be concluded that the results found for La apply to all Ln(III) metals. For this reason, all the following calculations have been carried out for La only.

### Reactions of $Cp_2LaH$ with $SiH_3$–$CH_3$

The free enthalpy profiles for the σ bond metathesis reactions described by eqns (3) to (8) are shown in Fig. 3, 4 and 5.

### Si–H activation

The results for the reactions of eqn (3) (H/H exchange) and eqn (4) (formation of the $SiH_2CH_3$ complex and $H_2$, termed H/Si exchange or silylation) are shown in Fig. 3 on the left and right hand sides, respectively. The free enthalpy profiles resemble those for eqns (1) and (2) and that obtained for the reaction of [La]–H with $SiH_4$.[23] The geometrical features are almost identical to what described before and thus attention will be focused on the energetic data.

The H/H exchange is by definition an isoergic process whereas the H/Si exchange is calculated to be slightly endoergic (2.9 kcal mol$^{-1}$). Considering the accuracy of the modelling these two reactions should be both considered as essentially isoergic. The activation energies are however somewhat different; the H/H exchange has a low activation energy of 10 kcal mol$^{-1}$ while the silylation of the metal has a higher activation energy of 16.4 kcal mol$^{-1}$. Similar trends were found in the reaction of [La]–H with $SiH_4$, suggesting that the substituent on the silyl group does not have significant influence on the electronic aspects of the Si–H activation. To be sure, steric effects, which are not incorporated in these calculations (use of $C_5H_5$ ligand and of a small silylalkane) may play a role. At the present level of modelling, reactions (3) and (4), which both have low activation energies and comparable energy of reaction, should both occur. Thus, the Si–H bond can be activated either for non-productive bond metathesis or to form a silyl complex.

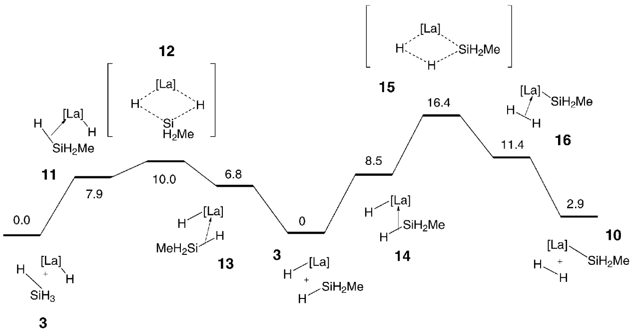

**Fig. 3** Free enthalpy profiles (kcal mol$^{-1}$) for the H/H exchange reaction (eqn (3)) and the silylation reaction (eqn (4)).

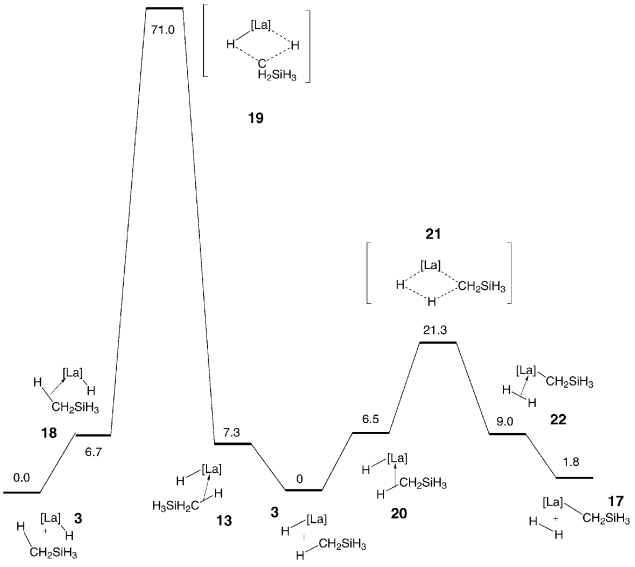

**Fig. 4** Free enthalpy profiles (kcal mol$^{-1}$) for the H/H exchange reaction (eqn (5)) and the alkylation reaction (eqn (6)).

### C–H activation

The relevant reactions are described in eqn (5) (H/H exchange) and eqn (6) (alkylation of the metal with associated formation of $H_2$). The free enthalpy profiles are shown in Fig. 4.

The H/H exchange is isoergic whereas the methylation of the metal is endoergic by only 1.8 kcal mol$^{-1}$. This value is small showing that alkylation of the metal by an alkylsilane is not disfavoured by thermodynamics. This is a significant difference from the results obtained for the reaction of [La]–H with $CH_4$ to yield [La]–$CH_3$ and $H_2$, where the methylation of the lanthanide was endoergic by about 13 kcal mol$^{-1}$. Considering that all groups coordinated to a lanthanide are strongly negatively charged, a silyl group, which stabilizes negative charge through delocalization into its $\sigma^*_{SiH}$ bonds, significantly stabilizes the alkyl group next to the lanthanide. Previous studies have shown that Si–C bonds can also stabilize a negative charge so that this stabilizing effect should not be limited to the $SiH_3$ group but should be present for all $SiR_3$ groups.[39,40]

The activation energy (over 70 kcal mol$^{-1}$) shows that the H/H exchange reaction is not accessible while that for alkylation of the metal is considerably lower (21.3 kcal mol$^{-1}$). Only the latter reaction is thus kinetically accessible. The activation energy for reaction 4 is lower by 4 kcal mol$^{-1}$ compared with the methylation reaction with $CH_4$, which indicates that the stabilizing influence of the silyl group, already noted for the free enthalpy of reaction, also occurs at the transition state. This is due to the strong charges developed in the transition state on the groups in the vicinity of the metal, which induces the stabilizing effect of the silyl substituent to the alkyl group.

### Comparison of Si–H and C–H activation

All reactions are permitted by thermodynamics and thus only the activation energies need be considered to access their feasibility. The main difference between Si–H and C–H activation is that the H/H exchange is not energetically accessible when the two H are bonded to a carbon while it is very accessible when they are bonded to Si. The activation energy of the Si–H bond to give a silyl complex is lower than that of the C–H bond to give a C-bonded alkylsilyl complex. Thus, over all, the activation of the Si–H bond should occur preferentially to that of a C–H bond in an alkylsilane. This is not surprising since it is well recognized that the Si–H bond is more reactive than a C–H bond because it is weaker and more polarizable. The interesting point is that the presence of a silyl group in the alkylsilane makes the C–H bond more reactive by stabilizing the C-bonded alkylsilyl complex and lowering the activation energy for C–H activation. In contrast, the methyl group has no significant influence on the energy barrier and energy of reaction for the Si–H activation, although, to be sure, steric factors could disfavour reactions at hindered bonds.

### Si–C activation

The free enthalpy profiles of the reactions corresponding to the activation of the Si–C bond are shown in Fig. 5. In these two reactions, the Si–C bond is cleaved to give either a silyl complex and an alkane (eqn (7)) or an alkyl complex and a silane (eqn 8). The formation of a silyl complex and an alkane (Fig. 5 left) is thermodynamically preferred to that of an alkyl complex and a silane (Fig. 5 right), because of the formation of the stronger alkane C–H bond in the former. Similar factors have explained the free energy of reaction for the reaction of eqn (1). However, the very high activation energy associated with the presence of a carbon at the β position of the 4-center transition state prevents this reaction from occurring. The same features have been found for eqn (5) (Fig. 4 left). Thus despite the thermodynamic driving force for the reaction, the transition state is energetically inaccessible. In contrast, the reaction which forms the methyl complex and the silane is slightly endoergic but has an energetically accessible transition state. It should be noted that the reaction is significantly more favoured thermodynamically than the reaction between [La]–H and $CH_4$ to give [La]–$CH_3$ and $H_2$ because the cleaved Si–C bond is significantly weaker than a C–H bond (see BDEs reported earlier).

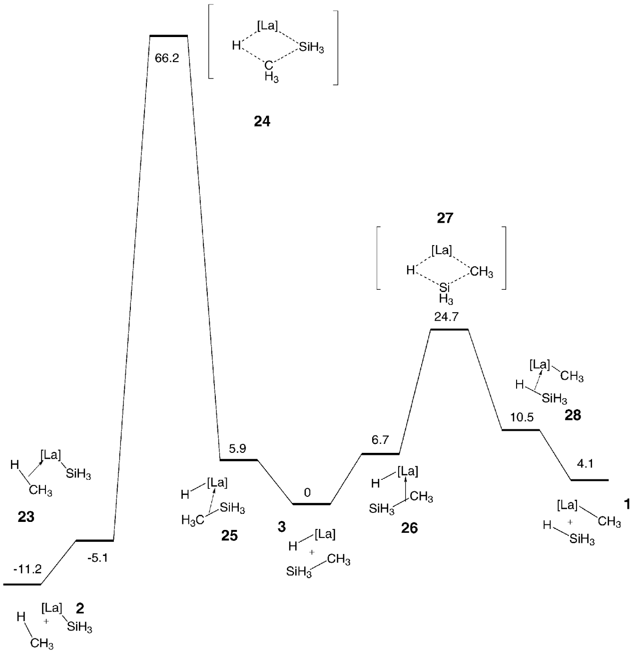

**Fig. 5** Free enthalpy profiles (kcal $mol^{-1}$) for the activation of $CH_3$–$SiH_3$ to give the silylation complex (eqn (7)) and the alkyl complex (eqn (8)).

The most favourable reactions of [La]–H with $CH_3$–$SiH_3$ are thus the two reactions involving the activation of the Si–H bond (eqns (3) and (4)). The transition states for these two reactions are lower than those associated with the activations of the Si–C and C–H bonds and the thermodynamics are essentially neutral for the two reactions. The next most preferred reaction, *i.e.* that of the C–H bond to form the alkylsilyl complex, has a moderately higher activation energy and is essentially thermoneutral. The direct σ bond metathesis of the Si–C bond to give the alkyl complex and silane requires a higher activation energy. However, the calculated value of 24 kcal $mol^{-1}$ and the moderate endoergicity suggest that the reaction is accessible. These reactions have been mentioned to account for the formation of the products seen in the reaction of Ph–$SiH_3$ with $Cp^*_2Sm$–H.[16] A computational study of the reaction between these two specific species accounts for the large number of redistribution products and will be published separately.

### Si–Si coupling: reactions of $Cp_2LaSiH_3$ with $SiH_4$

The free enthalpy profiles, calculated for eqn (9) ($SiH_3/SiH_3$ exchange *via* Si–H activation) and eqn (10) ($SiH_3$–$SiH_3$ coupling) are shown in Fig. 6. The first reaction is isoergic with a low activation energy (17.7 kcal $mol^{-1}$) (**34**), even slightly lower than the $CH_3/SiH_3$ exchange (eqn (1)); the transition state is reached from an $SiH_4$ adduct **33**, which is 6.9 kcal

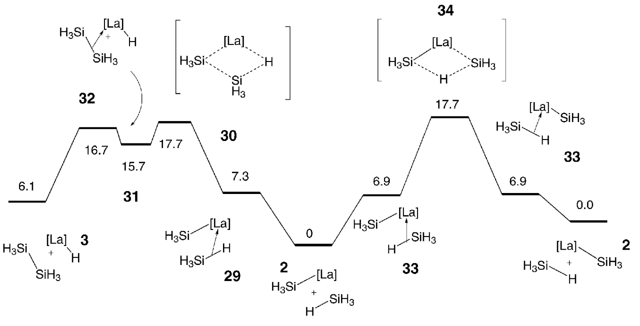

**Fig. 6** Free enthalpy profiles (kcal $mol^{-1}$) for the formation of the Si–Si bond (eqn (9)) and the Si/Si exchange (eqn (10)).

$mol^{-1}$ above the separate reactants. As was the case for the reaction of eqn (1), the pathway of this reaction is best viewed as a proton transfer of the two silyl groups in the field of the positively charged lanthanide atom. The coupling of the two silyl groups corresponds to a reaction that has not been studied previously and the nature of the intermediates and transition states is discussed in more detail. The reaction starts with the formation of an $SiH_4$ adduct **29** (Fig. 6), lying 7.3 kcal $mol^{-1}$ above the separate reactants, to reach a transition state **30** with an activation energy of 17.7 kcal $mol^{-1}$. This transition state leads to an $SiH_3$–$SiH_3$ adduct **31**, 15.7 kcal $mol^{-1}$ above the separated reactants which itself leads to another transition state **32** with a free enthalpy of 16.7 kcal $mol^{-1}$. This latter transition state yields the final products [La]–H and $SiH_3$–$SiH_3$, **3**. The reaction is endoergic by 6.1 kcal $mol^{-1}$ in the direction of the formation of the Si–Si bond. The reactions described in eqns (9) and (10) thus have similar activation energies and differ only slightly in their energy of reaction.

The geometry corresponding to the stationary points is presented in Fig. 7. The structure of **29**, which is a $SiH_4$ adduct to [La]–$SiH_3$, shows that the $SiH_3$ group is α-agostic while $SiH_4$ is $\eta^2$-bonded. This illustrates how the group with the highest negative charge ($SiH_3$) maximizes its interaction with the electropositive metal. The α-agostic structure of the $SiH_3$ group modifies the direction of the Si $sp^3$ lone pair, which does not point toward the metal but towards the other Si atom. Thus, despite the long distance between the two Si in this adduct, 3.9 Å, the adduct is well prepared for establishing a new Si–Si bond. The geometry of the transition state **30** resembles that previously obtained for the reaction of [La]–H with $SiH_4$. The β Si atom has square pyramidal geometry, with one apical H, typical for a hypervalent Si atom. The high-lying intermediate **31**, which leads to **30**, has a geometry close to that of **30** but with a shorter Si–Si distance and $Si_\beta$ in a geometry close to a trigonal bipyramid. It leads to the other transition state **32**, where $Si_\beta$ also has a trigonal pyramidal geometry and which differs from **31** mostly by having a significantly lengthened $Si_\beta$–$H_\alpha$ bond. From **30** to **32**, the main change has thus been a pseudorotation of the pentacoordinated $Si_\beta$ associated with variations in the lengths of the bonds to be made and cleaved (Si–Si and Si–H). It is not surprising that these structures are close in energy. This reaction occurs with the hydrogens having interactions with both the metal and Si, during Si–H activation. This situation has been established experimentally and has been termed SiSHA (silicon secondary hydrogen attraction) by the group of Chaudret and Sabo-Etienne[41] and IHI (interligand hypervalent interaction) by Nikonov.[42]

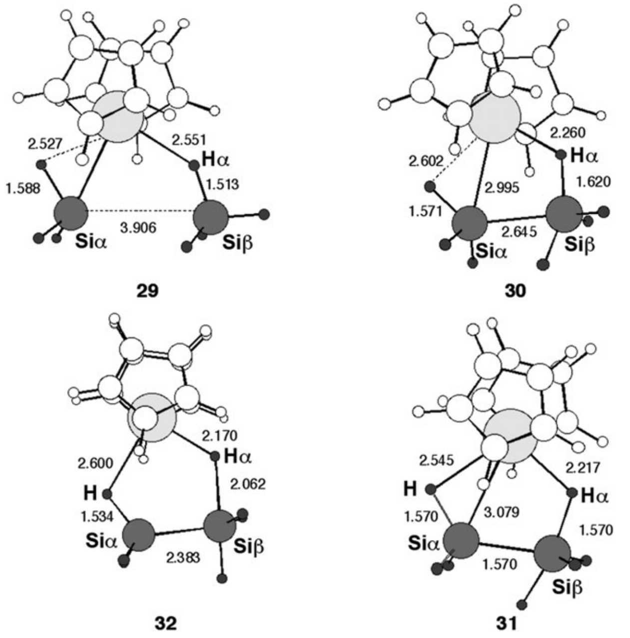

**Fig. 7** Optimized structures of the extrema for the reaction in eqn (9). The distances are in Å.

The coupling reaction of the two silyl groups has an accessible activation energy but is slightly endoergic. The dehydropolymerization reaction is thus slightly disfavoured by thermodynamics. However, substituent effects may easily modify the energy of reaction which could then become feasible. Computational studies on Ph–$SiH_3$ in a forthcoming paper will illustrate this point.[43]

## Conclusions

DFT studies of the free enthalpy profiles of the σ bond metathesis reaction of [La]–R (R = $CH_3$, H and $SiH_3$) with $SiH_4$ and $SiH_3$–$CH_3$ allow a better understanding the factors that control the reactivity in σ-bond metathesis processes. The Si–H bond can be activated by alkyl and hydride lanthanocene complexes to form either silyl or hydride derivatives and the associated products (alkane, silylalkane or $H_2$). There is no significant preference for the reactions to go *via* a transition state with the silyl group at either the α or β positions. Consequently, a silyl complex can be formed from the hydride complexes. Substitution of the silane by an alkyl group does not modify the reactivity of the Si–H bond, though to be sure large steric effects have not been included. The activation of the Si–H bond is also kinetically accessible with a silyl complex but in this case there is a thermodynamic preference for the silyl exchange reaction over the formation of a new Si–Si bond. Dehydropolymerization does not require a high activation energy but is slightly unfavourable thermodynamically. However the cleavage of an Si–Si bond by a lanthanocene hydride is thermodynamically accessible.

The cleavage of an Si–C bond by a hydride complex requires a higher activation energy than the cleavage of the Si–H bond. Furthermore, in the elementary step directly cleaving the Si–C bond, the only reaction which has an accessible barrier and is not too disfavoured thermodynamically is the one which forms the alkyl complex and the free silane. The reaction which forms a silyl complex and the free alkane is strongly disfavoured because of the presence of an alkyl group at the highly unfavourable β position in the transition state. Overall, alkylsilanes prefer to react *via* the Si–H bond than *via* the Si–C bond. The activation of the C–H bond of alkylsilane obeys the rules already established for alkane activation. The reactions that would put the $CH_3$ group at the β position in the transition state have very high activation energies so that the only possible products have the C-bonded alkylsilyl at the α position. It is remarkable that the silyl group lowers the activation energy and thermodynamically favours the formation of the alkyl complex from the reaction of the hydride lanthanocene and silylalkane. This reaction, which is significantly disfavoured in the case of non-substituted alkanes, benefits from the ability of the silyl group to stabilize the negatively charged alkyl group in a C-bonded alkylsilyl complex. The nature of the metal has been shown to have little influence on the energy profiles but one should remember that steric effects must also play a role.[44] In addition, results obtained for alkylsilanes should not be extended to arylsilanes without caution because the small differences in the activation energies and energies of reaction which differentiate some of the reactions from this work can be influenced by the phenyl group. Therefore the study of the reaction between $PhSiH_3$ and $Cp_2Sm$–H will be published separately.[43]

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