

Articles

DFT Investigation of the Catalytic Hydromethylation of α -Olefins by Metallocenes. 1. Differences between Scandium and Lutetium in Propene Hydromethylation

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A DFT study of the catalytic properties of Cp_2ScCH_3 and Cp_2LuCH_3 in the hydromethylation of propene has been performed. The catalytic behavior of Cp_2ScCH_3 is confirmed, and the formation of secondary products is rationalized. It is shown that Cp_2LuCH_3 cannot exhibit catalytic behavior and that only stoichiometric conversion of propene to isobutane could be observed. The difference in reactivities between the two metallocenes has been investigated, and an electronic explanation is given based on differences in the coordination of propene. However, the intrinsic reactivities of the two metallocenes is proposed to be driven by both electronic and steric effects.

Introduction

The problem of functionalizing olefins via selective reactions with saturated hydrocarbons is still an important research area.^{1–12} Some stoichiometric reactions have been proposed, but the number of catalytic processes are rather limited.^{5–12} Recently, a study by Sadow and Tilley¹³ reported the possibility of the catalytic hydromethylation of propene by a permethylscandocene methyl complex. Indeed, at room temperature and after 3 days of reaction, a mixture of propene and methane (9 and 10 equiv, respectively) was transformed to isobutane in the presence of $\text{Cp}^*_2\text{ScCH}_3$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$). The yield was 3 equiv

of isobutane for 1 equiv of catalyst. However, a part of the catalyst was transformed into $[\text{Sc}]\text{-CH}_2\text{CHMe}_2$ (isobutyl complex; $[\text{Sc}] = \text{Cp}^*_2\text{Sc}$) and $[\text{Sc}]\text{-CH=CHMe}$ (vinyl complex). Heating the mixture led to decomposition of the catalyst to unknown products and a yield of 4 equiv of isobutane. Moreover, the authors found that there is no evidence for Cp^*_2ScH formation and, thus, have concluded that the methyl complex is the active species. In addition, the lack of detected isobutene implies that β -hydride elimination does not represent a major decomposition pathway. Thus, the catalytic cycle given in Figure 1 is favored. However, experimental observations suggested the occurrence of several secondary processes that are competitive with this cycle, including degradation of the catalyst.

The permethylscandocene methyl complex was previously used by Thompson et al.¹⁴ for a stoichiometric reaction with propene. The main products of reaction were isobutane and the vinyl complex, also observed by Sadow and Tilley.¹³ Since the lanthanide complexes are very often observed to exhibit the same reactivity as the corresponding group III complexes, a related study by Watson and Parshall should be mentioned.¹⁵ In a study of propene polymerization in the presence of the lutetium complex $\text{Cp}^*_2\text{LuCH}_3$, the authors speculated on the possibility of observing the allylic and vinylic activation of propene. Thus, it seems that a difference in reactivity between scandocene and lutetocene might be expected.

In the last few years, theoretical investigations of chemical reactivity involving lanthanide centers have been of increasing interest. Indeed, the use of relativistic effective core potentials

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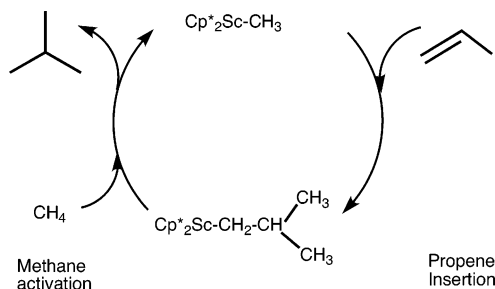


Figure 1. Experimentally postulated mechanism for the hydromethylation of propene.

(RECPs) that include the 4f electrons in the core¹⁶ allowed systematic studies of bond activations^{17–20} and bond insertions.²¹ Investigation of catalytic hydromethylation by theoretical methods appears to be an interesting problem since a number of competitive reactions should be considered and compared. Moreover, on the basis of analysis of electron densities, such as with the natural bonding orbital (NBO) analysis,²² the origin of the difference between scandium and lutetium can be addressed. Differences in reactivities between complexes of scandium and lutetium are usually attributed to steric effects stemming from the difference in ionic radius between these two metals.

In this paper, the productive and competing reactions of the proposed catalytic cycle have been investigated by DFT methods, for both Cp_2ScCH_3 and Cp_2LuCH_3 ($\text{Cp} = \text{C}_5\text{H}_5$). In particular, the potential catalytic behavior of Cp_2ScCH_3 is predicted, and the formation of side products is rationalized. In the case of Cp_2LuCH_3 , it will be argued that hydromethylation cannot be catalytic and that the reaction can only release 1 equiv of isobutane per equiv of catalyst. The formation of allyl and vinyl complexes appears to be the most likely competing reactions. Moreover, the differences in reactivities between Sc and Lu will be addressed.

Computational Details

In previous studies^{16–18} we have shown that large core relativistic effective core potentials (RECPs) optimized by the Stuttgart–Dresden group^{23–25} are well adapted to the calculation of geometries of lanthanide complexes, as 4f electrons do not participate in a lanthanide–ligand bond. A basis set adapted to the RECP augmented by a polarization f function was used for lutetium. Similarly, the scandium atom has been treated with a RECP optimized by the Stuttgart group²³ and the corresponding optimized basis set, augmented by a set of f polarization functions. Carbon and hydrogen have been treated with an all-electron 6-31G(d,p) basis set.²⁶ Calculations were carried out at the DFT level using the hybrid functional B3PW91^{27,28} with the Gaussian 98 suite of programs.²⁹

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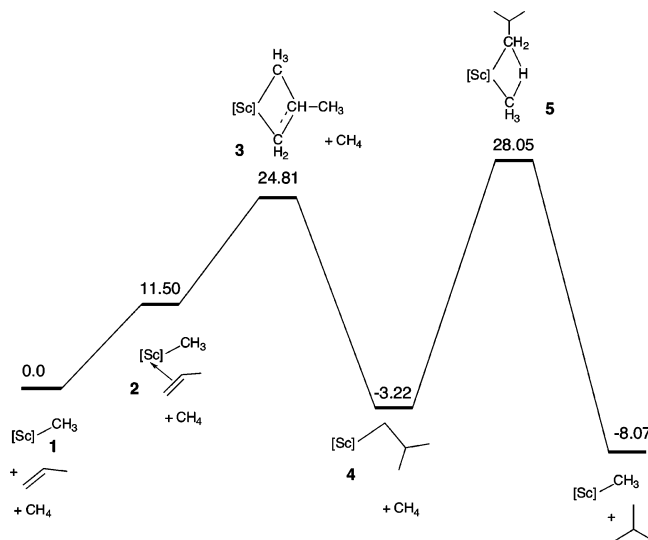


Figure 2. Free energy profile (ΔG) in kcal mol^{-1} for the hydromethylation of propene with $\text{Cp}_2\text{Sc}-\text{CH}_3$; [Sc] = Cp_2Sc .

Geometry optimizations were carried out without any symmetry restrictions. The nature of the extrema (minimum or transition state) was verified with analytical frequency calculations. ZPE and entropic contributions were calculated using the approximation of harmonic frequencies. The free energies G are given for $T = 298.15$ K. All of the calculations have been carried out with the Cp (C_5H_5) ligands.

Results and Discussion

Validation of the Experimentally Proposed Mechanism.

(a) Energetic Profile. The experimentally proposed mechanism for propene hydromethylation was first investigated for the scandium-based compound Cp_2ScCH_3 . The assumed mechanism consists of two elementary reactions. In the first one, the propene inserts into the Sc–C bond of Cp_2ScCH_3 , to give the isobutyl complex $\text{Cp}_2\text{ScCH}_2\text{CH}(\text{CH}_3)_2$. The second step is the activation of methane by σ -bond metathesis with the isobutyl complex, to regenerate Cp_2ScCH_3 and release isobutane. The computed free energy profile (ΔG), relative to the separated reactants Cp_2ScCH_3 and propene, is shown in Figure 2.

Propene insertion is exergonic ($\Delta G^0 = -3.22 \text{ kcal mol}^{-1}$). It begins with the formation of a π -bonded adduct of propene with the scandium center **2**. This adduct has a free energy of formation of $11.50 \text{ kcal mol}^{-1}$, which is principally caused by the loss of entropy associated with coordination of free propene. The adduct then proceeds to a four-membered transition state for insertion, **3**. The latter is $13.31 \text{ kcal mol}^{-1}$ above the adduct. The activation energy for insertion is calculated to be $24.81 \text{ kcal mol}^{-1}$ above the separated reactants, which corresponds to a kinetically accessible process.

The second step in the catalytic cycle (methane activation) is exergonic with a free energy of reaction of $-4.85 \text{ kcal mol}^{-1}$

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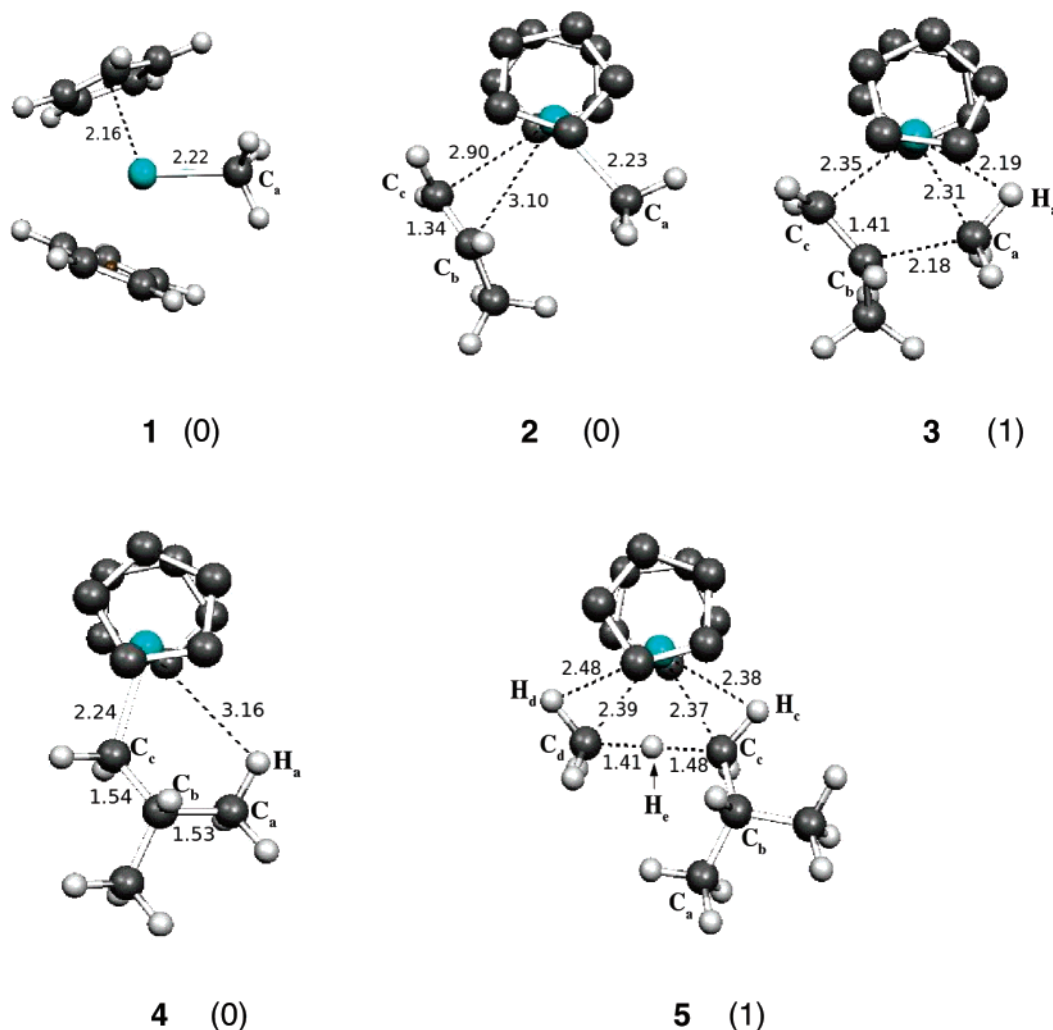


Figure 3. Optimized geometries (distances in \AA) of the extrema for the hydromethylation of propene with $\text{Cp}_2\text{Sc}-\text{CH}_3$. The number of imaginary frequencies is given in parenthesis (0 for a minimum and 1 for a transition state). The hydrogen atoms have been omitted from the C_5H_5 ligands for all structures except **1**.

with respect to the separated isobutyl complex and methane. Despite a considerable computational search, no CH_4 adduct was located as a minimum on the potential energy surface. The transition state **5** leads directly to Cp_2ScCH_3 and isobutane. No isobutane adduct was located as a minimum. Since the activation energy, relative to the separated isobutyl complex **4** and methane, for this reaction is $31.27 \text{ kcal mol}^{-1}$, this process is also kinetically accessible. The σ -bond metathesis process appears to be the rate-determining step. The two-step mechanism proposed for the hydromethylation of propene with Cp_2ScCH_3 catalyst is therefore calculated to have accessible transition states and could be catalytic since the initial complex is regenerated. However these activation energies are not negligible and other reactions can compete with any of these two elementary steps. Thus, the possibility of competing reactions should be investigated for both steps in the catalytic cycle.

(b) Geometries. The geometries of the minima and transition states are presented in Figure 3. For the catalyst **1**, the $\text{Sc}-\text{C}$ distance is 2.22 \AA . The C_3 axis of the methyl group, corresponding to the direction of the sp^3 orbital involved in bonding to the metal, points toward the metal center. The $\text{C}=\text{C}$ double bond distance is equal to 1.33 \AA for free propene.

In the precursor adduct **2**, the π orbital of the propene is oriented toward the scandium center. The $\text{Sc}-\text{C}_c$ distance (2.90 \AA) is shorter than the $\text{Sc}-\text{C}_b$ distance (3.10 \AA), which is due to

a slight charge difference between the two carbons (a NBO analysis gives charges of -0.03 on C_cH_2 and $+0.07$ on $\text{C}_b\text{H}(\text{CH}_3)$). However, the propene molecule is little affected by the coordination: the $\text{C}=\text{C}$ double bond distance is hardly modified (C_c-C_b length = 1.34 \AA) and no pyramidalization is observed at C_c or C_b . In the same way, the methyl group coordinated to Sc is not distorted. The $\text{Sc}-\text{methyl}$ distance is equal to 2.23 \AA , and the C_3 axis is still pointing toward scandium. In the adduct **2**, the geometry of the metal moieties and of the coordinated propene is essentially that of the separated reactants, and the geometry of **2** is therefore far from that of the transition state. In other words, the coordination of the propene to Sc does not prepare the two species to cross the transition state. The higher energy of the adduct compared to the separated reactant is essentially associated with the loss of entropy upon the formation of one molecule from the union of two molecules.

Adduct **2** leads to the transition state **3**, in which the scandium and the three carbon atoms are coplanar in a four-membered-ring transition state. The $\text{Sc}-\text{C}_c$ distance is equal to 2.35 \AA , and the double bond of propene is elongated to 1.41 \AA . Both olefinic carbons are slightly pyramidalized. The $\text{Sc}-\text{C}_a$ bond, which is to be cleaved, is equal to 2.31 \AA (0.09 \AA longer than in the reactant **1**). The methyl group, now interacting with the propene, has tilted so that its C_3 axis (and thus its sp^3 orbital) is oriented toward C_b . The distance between C_b (propene) and

Table 1. Geometric Data for the Transition State 5^a

[Sc]CH ₂ CH(CH ₃) ₂ part		[Sc]CH ₃ part	
Sc–C _c	2.37	Sc–C _d	2.39
C _c –H _e	1.48	C _d –H _e	1.41
Sc–H _c	2.38	Sc–H _d	2.48
C _c –H _c	1.10	C _d –H _d	1.10
Sc–C _c –H _e	76.6	Sc–C _d –H _e	81.5

^a Distances are in Å and angles in deg. The [Sc]CH₂CH(CH₃)₂ and [Sc]CH₃ parts refer to the right- and left-hand sides of species **5**, respectively, as shown in Figure 3, where the atomic labels are given.

C_a (methyl) is 2.18 Å. A consequence of the tilt of the methyl group is that one of its hydrogens is closer to the metal (2.19 Å) and the Sc–C_a–H_a angle is close to 70°. The slight elongation of C_a–H_a indicates a weak agostic interaction. The NBO analysis of **3** showed that H_a carries the same charge as the other hydrogen atoms of the methyl group. However, at the level of second-order perturbation theory, there is a charge delocalization between the σ_{CH} bond and an empty d orbital of the metal center, which indicates a stabilizing interaction. To go from the propene adduct **2** to the transition state **3**, it is necessary to pyramidalize the propene carbons and change the orientation of the methyl group's C₃ axis. These two distortions are energy-demanding, which explains the high activation energy from **2** to **3**.

The transition state **3** gives the isobutyl compound Cp₂ScCH₂CH(CH₃)₂, **4**, in which the C_b–C_a bond distance is equal to 1.53 Å. The Sc–C_c distance is 2.26 Å (0.04 Å longer than the Sc–C_a bond) in reactant **1**, and the Sc–C_c–C_b angle is about 127°. The hydrogen H_a is far from scandium, the Sc–C_a–H_a angle is equal to 103°, and there is no evidence for a γ-agostic interaction, which is consistent with the absence of α-agostic assistance in the transition state.

In the second step of the catalytic cycle, the C_d–H_e bond of methane is broken in a σ-bond metathesis process. The transition state **5** has the four-membered-ring geometry formed by Sc, C_c, H_e, and C_d, with the three atoms C_c–H_e–C_d nearly collinear (C_c–H_e–C_d = 179.1°). Similar geometrical features have been found in many σ-bond metathesis reactions with early and lanthanide metals.^{17,18} This transition state, with a Sc–H_e distance of 1.88 Å, can be viewed as involving a proton transfer between the methyl and isobutyl groups, as it was found for related σ-bond metathesis reactions with lanthanide metals.^{17,18} Other geometric features are summarized in Table 1. The C₃ axes of both alkyl groups are directed toward H_e, so that H_c and H_d are close to scandium. The C_c–H_c and C_d–H_d bonds are not significantly elongated and the NBO charges of the hydrogens on C_c and C_b are not significantly modified, although second-order perturbation theory indicates some charge delocalization between the two σ CH bonds and empty Sc d orbitals. This is indicative of weak α-agostic interactions. Comparing **5** with the perfectly symmetric transition state for Watson's methyl-exchange reaction,³⁰ it appears that **5** is similar to the latter but is slightly less symmetric due to the difference in the nature of the two organic groups involved in the proton transfer reactions.

During the reaction, the distance between the metal and the centroids of the Cp groups (X) is little affected (ranging from 2.17 to 2.20 Å). The X–Sc–X angle decreases slightly from the reactant **1** (137.4°) to the more crowded isobutyl compound **4** (134.7°). This could be explained by either electronic or steric effects. Indeed, the decrease of the X–Sc–X angle would increase the permanent dipole moment of the Cp₂Sc⁺ fragment

and provide a stronger interaction with the alkyl group. However, an NBO analysis indicated that the ionic character of the Sc–C bond remains constant. Thus, the variation in X–Sc–X angles for the two alkyl complexes is principally caused by the steric hindrance of the alkyl group.

Investigation of Possible Competing Reactions. Apart from the productive steps described in the previous section, a number of competing secondary reactions may occur for the species involved in the catalytic cycle of Figure 1. The aim of this section is to determine which of these might compete with the catalytic process and potentially prevent the formation of isobutane and/or lead to the experimentally observed secondary products. In the following, two thermodynamically favored reactions will be considered to be kinetically competitive if the difference between their activation energies is less than 5 kcal mol⁻¹. This corresponds to the precision of the computing method.

Among all possible reactions, some can be easily eliminated, such as activation of the σ_{C–C} bond of propene, which is unlikely to occur for steric reasons. Consequently, this reaction has not been considered. The σ-bond metathesis reactions that would involve a four-electron, four-center transition state with carbon at the β-position are known to have a high activation energy.³⁰ This has been confirmed in the case of methane activation by Cp₂ScCH₃ (forming Cp₂ScH and releasing ethane); the calculated activation energy is over 90 kcal mol⁻¹. These types of reactions have therefore not been considered. Finally, β-hydrogen elimination has been experimentally and theoretically found to be strongly disfavored as a termination process in polymerization (energy barriers around 70 kcal mol⁻¹),³¹ which is consistent with the observation by Sadow and Tilley¹³ that neither Cp*₂ScH nor isobutene was observed during hydro-methylation. The β-hydrogen elimination from the isobutyl complex was, however, calculated as a benchmark test for the calculations. An endergonic formation of Cp₂Sc–H and isobutene definitely rules out this reaction, which will not be considered further in the following discussion.

Reactions that may compete with the first catalytic step (propene insertion) include activations of the vinylic or allylic C–H bonds of propene and the 2,1-insertion of propene into the M–C bond of **1**. Figure 4 provides a schematic representation of these reactions. Reactions that may compete with the second catalytic step (σ-bond metathesis between methane and **4**) also include activations of vinylic or allylic C–H bonds of propene as well as 1,2- and 2,1-insertions of propene, and β-hydrogen and β-methyl transfers (see Figure 6). In addition, methyl exchange between Cp₂ScCH₃ and CH₄ (methane activation) was also studied.

As the geometries are very similar to those described in the previous section, we will focus on the energetics of the reactions. For all reactions, the entire pathways have been computed. However, to simplify the analysis, only the free energy of reaction (ΔG⁰) and the activation energies (ΔG[‡]), using the separated Cp₂ScCH₃ and propene as reference, are presented for each reaction considered. The results are summarized in Tables 2 and 3.

All reactions are nearly thermoneutral except for the allylic activation of propene, which is significantly exergonic. This reaction leads to a π-allyl compound, which is very stable because of electronic delocalization (cf. Figure 5). Since all reactions are thermodynamically favorable or almost thermoneutral (2,1 propene insertion), the selectivities must be under kinetic control. The 1,2 propene insertion has the lowest barrier,

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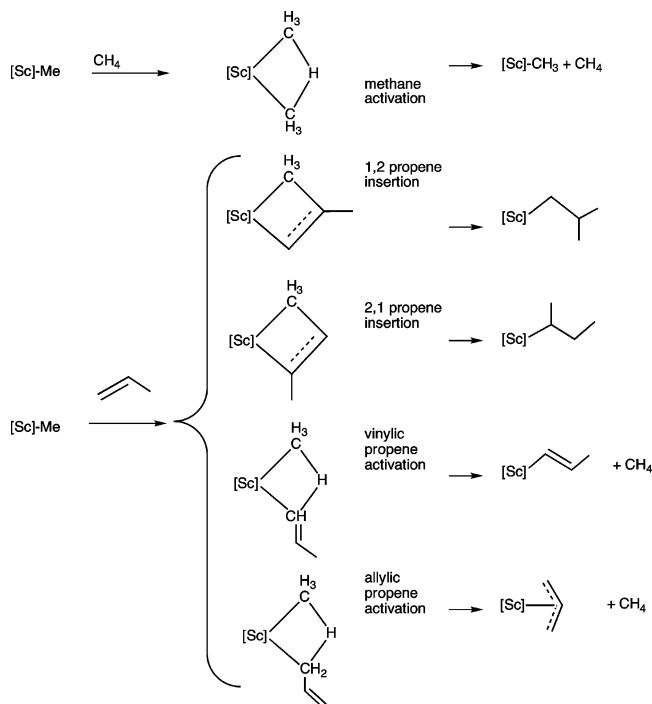


Figure 4. Reactions competing with propene insertion with a schematic representation of the transition states; [Sc] = Cp_2Sc .

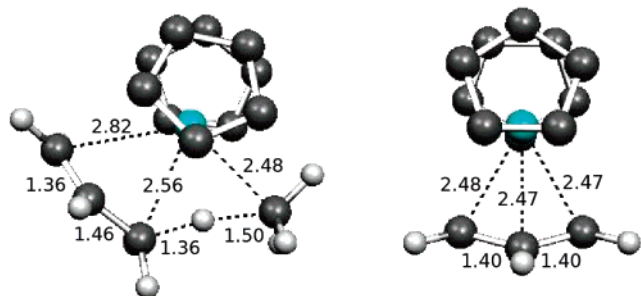


Figure 5. Optimized geometries (distances in Å) of the transition state (left) for allylic propene activation with Cp_2ScCH_3 and the corresponding π -allyl complex (right). The hydrogen atoms have been omitted from the C_5H_5 ligands.

but the vinylic activation of propene is also competitive with an activation energy of $27.94 \text{ kcal mol}^{-1}$. Insertion errors could also occur, as the 2,1-insertion activation energy is only $28.81 \text{ kcal mol}^{-1}$. Other reactions, i.e., the allylic activation of propene and methane activation, have higher activation energies and are less likely to occur. In the case of the allylic activation, the geometry of the transition state is presented in Figure 5. The π -allyl group is nearly formed, corresponding to a late transition state. However the activation energy is rather high, which may be due to the considerable geometrical and electronic reorganization from reactants to transition state. Thus, according to the calculations, the isobutyl complex is the major product of the reaction of **1** with propene. This is in agreement with the experimental data for the Cp^*_2Sc system.¹³ However, two minor products may be formed with comparable activation energies, namely, the propenyl complex, resulting from vinylic activation, and the 1-methylpropyl complex, resulting from 2,1-insertion.

For the processes competing with the second catalytic step (methane activation), only reactions starting from the isobutyl complex, which is the major product of the reaction of **1** with propene, have been investigated. These are listed in Table 3, along with values for the reaction of methane with the isobutyl

complex for comparison. All energy values are given relative to the separated $\text{Cp}_2\text{ScCH}_2\text{CH}(\text{CH}_3)_2$ and organic molecules.

All reactions are exergonic. The vinylic activation is the most kinetically favored, with an activation energy of only $26.50 \text{ kcal mol}^{-1}$. The productive methane activation is nevertheless competitive ($\Delta G^\ddagger = 31.26 \text{ kcal mol}^{-1}$). Consequently, the hydromethylation of propene is among the most favorable pathways with the postulated catalytic mechanism. It is important to note that, if both competing reactions release isobutane, only the methane activation regenerates the catalyst. Indeed, the vinylic activation destroys the catalyst, as the latter cannot be regenerated by C–H activation of methane, since this reaction is found to be endergonic by $3.72 \text{ kcal mol}^{-1}$ with an activation energy of $32.02 \text{ kcal mol}^{-1}$. This result may explain the relatively low turnover that is experimentally observed.

It should also be noted that on the basis of these calculations, insertion reactions involving the isopropyl complex are not competitive. This is also in agreement with the fact that group III metallocene complexes do not efficiently polymerize propene; the main secondary products were vinyl and allyl complexes, and poly(propene)s were not observed.¹³ Our calculations agree with this observation. Moreover, the theoretical data are in line with experimental observations of Thompson et al.,¹⁴ that, in the absence of methane, the vinylic product $\text{Cp}^*_2\text{ScCH}=\text{CH}-\text{CH}_3$ is preferentially formed from reaction of the isobutyl complex with propene.

Results with the Lutetium Complex Cp_2LuCH_3 . (a) **Energetic Profile.** A similar theoretical study was carried out with the lutetium-based catalyst Cp_2LuCH_3 , **6**. The free energy profile of the catalytic cycle, which could form isobutane, is given in Figure 7. Propene insertion is slightly exergonic ($\Delta G^0 = -3.84 \text{ kcal mol}^{-1}$). This reaction begins with the coordination of propene to form a π -adduct of propene, **7**. Structure **7** is calculated to be $7.05 \text{ kcal mol}^{-1}$ above the separated reactants, which is roughly 4 kcal mol^{-1} less than for Sc. As the loss of entropy is similar, it means that propene interacts more strongly with Lu than with Sc. The subsequent propene insertion has an activation energy of $22.66 \text{ kcal mol}^{-1}$ (transition state **8**) with respect to the separated reactants. Thus, this reaction, **6** to **9** via **8**, has an accessible activation energy. As for Sc, the π -adduct does not adequately prepare the transition state, and the activation energy relative to the propene adducts is found to be similar for Sc and Lu (around $13.5 \text{ kcal mol}^{-1}$).

The second catalytic step (methane activation) is exergonic ($\Delta G^0 = -4.22 \text{ kcal mol}^{-1}$). In contrast to scandium, this process begins by coordination of methane to the lutetium center. The free energy of formation of the resulting σ -adduct, **10**, is $12.13 \text{ kcal mol}^{-1}$ above the separated isobutyl complex and methane. It is followed by the four-membered-ring transition state **11**, which is $19.01 \text{ kcal mol}^{-1}$ above the adduct. The total activation energy for the reaction from **9** to **11** is thus $31.14 \text{ kcal mol}^{-1}$. The released isobutane then stays in the coordination sphere of the metal to form the σ -adduct **12**, which is $7.49 \text{ kcal mol}^{-1}$ (in free energy) above the separated isobutyl complex and methane. This is also a difference between the Lu and Sc systems, since no alkane adducts were identified for the Sc reactions.

(b) **Geometries.** The geometries of Cp_2ScCH_3 and Cp_2LuCH_3 are very similar. In the latter, the Lu–C bond distance is 2.35 Å , which is 0.13 Å longer than that in the scandium compound. This difference is comparable to the difference of ionic radii between the two metals (0.11 Å). The same conclusion can be drawn for the distance between the lutetium and the centroids

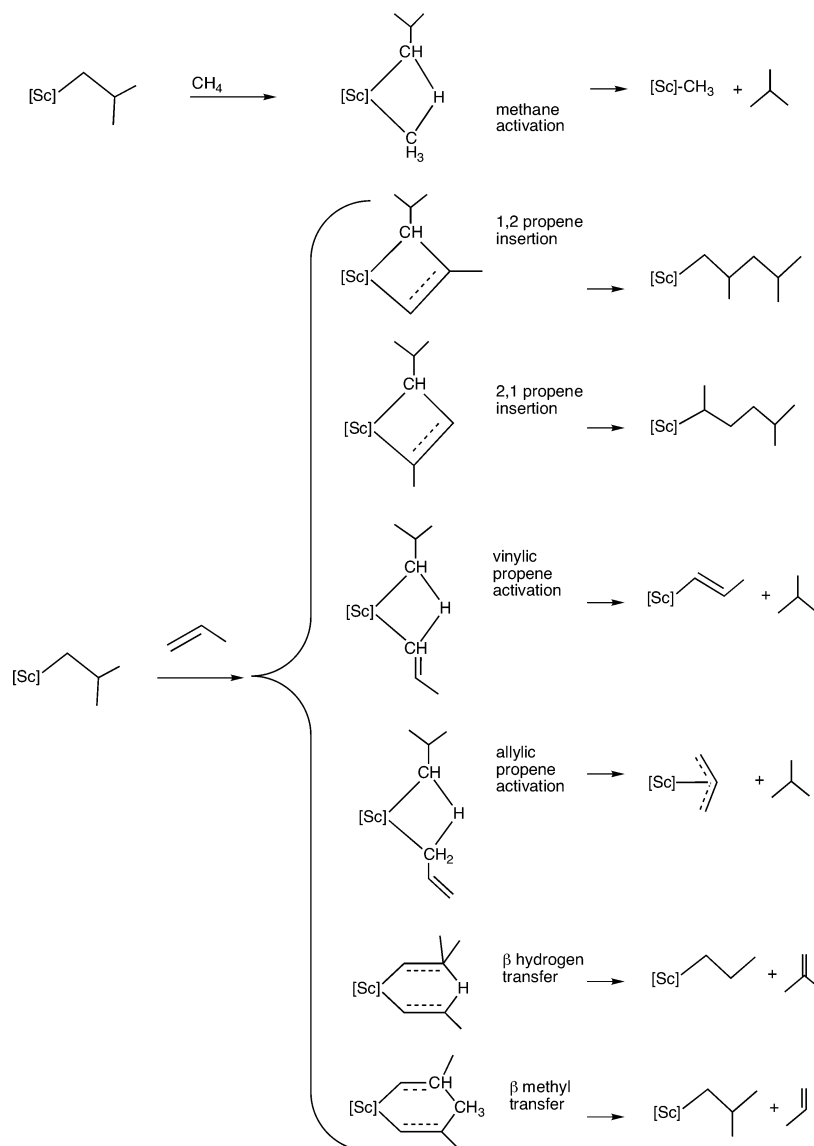


Figure 6. Representation of the reactions competing with methane activation with schematic representation of the transition states; [Sc] = Cp₂Sc.

Table 2. Free Energies (in kcal mol⁻¹) for Reactions with Cp₂ScCH₃ Described in Figure 4^a

reaction	ΔG^0	ΔG^\ddagger
1,2 propene insertion	-3.22	24.81
2,1 propene insertion	3.64	28.81
methane activation	0.00	32.49
vinylic propene activation	-3.72	27.94
allylic propene activation	-12.72	31.69

^a All energies are given relative to the separated Cp₂ScCH₃ and propene.

X of the Cp rings (2.35 Å), which is about 0.15 Å longer than for the scandium compound. The X–Lu–X angle is equal to 136.2°.

In the propene π -adduct **7**, the Lu–C_c and Lu–C_b distances are equal to 2.93 and 3.10 Å, respectively, which are similar to corresponding distances for the scandium adduct. As in the case of Sc, the metal–C(propene) bond distance is shorter with the methylene carbon, which has the higher negative charge (NBO charges are equal to -0.04 on C_cH₂ and equal to +0.06 on C_bHCH₃). The larger ionic radius for Lu compared to Sc should have led to longer metal–propene distances in the case of Cp₂-LuCH₃(η^2 -CH₃CH=CH₂). As this is not the case, this suggests that lutetium interacts more strongly with propene. This is in

Table 3. Free Energies (kcal mol⁻¹) for Reactions with Cp₂ScCH₂CH(CH₃)₂ Described in Figure 6^a

reaction	ΔG^0	ΔG^\ddagger
methane activation	-4.85	31.26
1,2 propene insertion	-6.50	35.59
2,1 propene insertion	-4.67	40.69
vinylic propene activation	-8.57	26.50
allylic propene activation	-17.57	32.51
β -hydrogen transfer	-1.61	43.26
β -methyl transfer	0.00	88.32

^a All energies are given relative to the separated Cp₂ScCH₂CH(CH₃)₂ and organic molecules.

agreement with the lower free energy of the π -adduct for Lu vs Sc (by roughly 4 kcal mol⁻¹) compared to corresponding separated reactants. This stronger interaction is also confirmed by an NBO analysis. The interaction between the π -system of propene and the lowest vacant orbital of the metal (mainly d), evaluated by second-order perturbation theory, is stronger by 2.5 kcal mol⁻¹ for Lu. However, this stronger interaction does not significantly modify the geometry of the propene, which is planar with a C–C double bond equal to 1.34 Å in Cp₂-LuCH₃(η^2 -CH₃CH=CH₂).

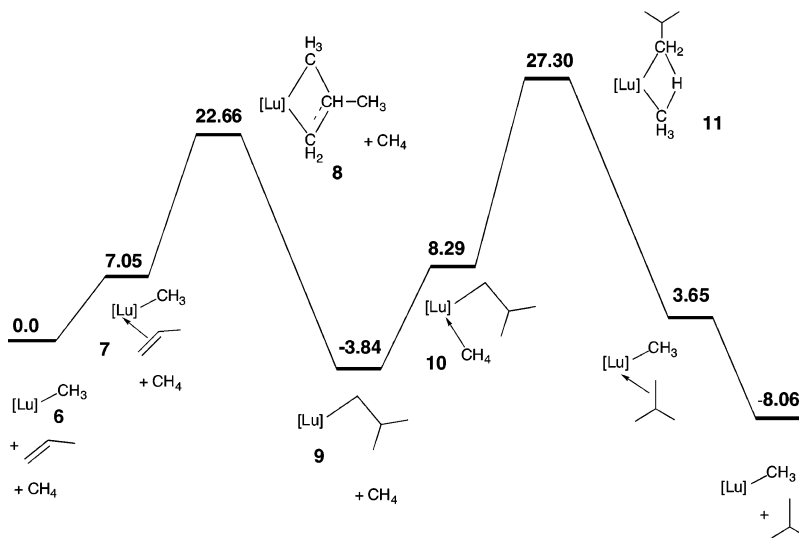


Figure 7. Free energy profile (ΔG), in kcal mol⁻¹, for the hydromethylation of propene with Cp₂LuCH₃; [Lu] = Cp₂Lu.

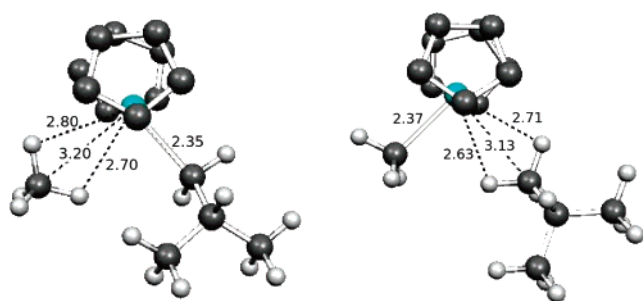


Figure 8. Optimized geometries (distances in Å) of the Cp₂Lu-isobutyl-methane complex (left) and the Cp₂Lu-methyl-isobutane complex (right). The hydrogen atoms have been omitted from the C₅H₅ ligands.

The geometries of the transition state for 1,2 propene insertion (**8**) to yield the isobutyl compound **9** and of the transition state for methane metathesis (**11**) are essentially equal for scandium and lutetium. The Lu–C and Lu–H distances are about 0.12 Å longer than the corresponding Sc–C and Sc–H distances, and the C–C and C–H distances are very similar. The difference in stabilization energies for the π -adducts for Sc (**2**) and Lu (**7**) is translated to the transition states **3** vs **8**. The transition state **8** is calculated to be more stable for Lu than for Sc by approximately 2.5 kcal mol⁻¹, showing that the interaction between the metal and propene is stronger for Lu than for Sc. Consequently, as the free energy necessary to go from the π -adduct to the transition state is the same for both metals, the more stable adduct leads to a lower activation energy for the propene insertion step.

For the activation of CH₄, going through transition state **11**, the activation energies relative to the isobutyl compound are similar for Sc (27.93 kcal mol⁻¹) and Lu (28.61 kcal mol⁻¹). The presence of a σ -adduct between Cp₂M(CH₂-CH(CH₃)₂) and CH₄, in the case of Lu only, does not lower the activation energy because the bonding interaction between the Lu fragment and methane is weak, as evidenced by the high free energy of the methane σ -adduct, which is 12 kcal mol⁻¹ above the separated reactants. The bonding energy between these two species being small, the free energy of the CH₄ adduct is mostly controlled by the entropy. In other words, the energy of the σ -adduct is not low enough to pull down the energy of the transition state.

In the adducts of Cp₂Lu(CH₂-CH(CH₃)₂) with methane (**10**) and isobutane (**12**), the Lu–C distances are 3.20 and 3.13 Å,

Table 4. Energetics for Reactions of the Lu-Based Catalyst^a

Lu reactant	reaction	ΔG^0	ΔG^\ddagger
Cp ₂ LuCH ₃	1,2 propene insertion	-3.84	22.66
	2,1 propene insertion	0.58	26.16
	methane activation	0.00	33.11
	vinylc propene activation	-4.67	26.21
	allylic propene activation	-15.82	24.07
Cp ₂ LuCH ₂ CH(CH ₃) ₂	methane activation	-4.22	31.14
	1,2 propene insertion	-4.42	29.41
	vinylc propene activation	-8.01	24.98
	allylic propene activation	-19.80	25.39
	β -hydrogen transfer	-2.17	34.72

^a Free energies (kcal mol⁻¹) are given relative to the separated reactants. See Figures 4 and 6 for definition of the reactions.

respectively. In both cases, two hydrogens of the coordinated alkane are oriented toward the metal, such that the Lu \cdots H distances are around 2.70 Å. The relatively short Lu \cdots H distances do not result in elongated C–H bonds. To determine the nature of these adducts, NBO analyses were performed. The interacting carbon is negatively charged (-0.96), whereas the hydrogens are positively charged (+0.23 to +0.26). Therefore, in these adducts, the lutetium interacts only with the carbon.

(c) Competing Reactions. The calculations show that the hydromethylation of propene is thermodynamically accessible because the free energies of the products (Cp₂Lu–CH₃ + isobutane) are lower than those of the reactants (Cp₂Lu–CH₃ + propene + CH₄) by 8 kcal mol⁻¹, and the activation energies along the postulated pathways are not too high. However, to determine if this reaction may occur, it is necessary to compare the energy profiles of competing reactions to that of the hydromethylation of propene. The reactions that have been considered for scandium have also been considered for Lu. Only the β -methyl transfer, which has been shown to have a very high activation energy, has been ignored. The free energies of reaction and the activation energies are shown in Table 4.

For Cp₂LuCH₃, all reactions are nearly thermoneutral or exergonic. The vinylc and allylic activations of propene have similar activation energies (26.21 and 24.07 kcal mol⁻¹, respectively) and are therefore competitive. The 2,1-insertion of propene has an activation energy of 26.16 kcal mol⁻¹. The 1,2-insertion of propene, which has the lowest activation energy (22.66 kcal mol⁻¹), still corresponds to the favored path. All of the reactions involving propene are competitive. The calculations show that the π -propene adduct **7** is the starting reactant for all reactions (the 1,2 and 2,1 propene insertions, the vinylc and

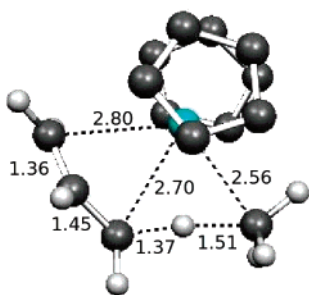


Figure 9. Optimized geometry (distances in Å) of the transition state for allylic activation with Cp_2LuCH_3 . The hydrogen atoms have been omitted from the C_5H_5 ligands.

the allylic propene activations) and that all reactions involving propene have lower activation energies for Lu than for Sc. In particular, the more stable π -propene adduct in the case of Lu lowers the activation energies associated with propene reactions. The interaction of the metal center with the π -system of the olefin is thus a key factor for determining the reactivity of the lutetium complex. Other reactions such as methane activation (Table 4) are less favorable.

The transition state for allylic propene activation is shown in Figure 9. Its geometry is very close to that found for the Sc case. Thus, the difference in activation energies between Sc and Lu (7 kcal mol⁻¹ lower for Lu) is in large part due to the difference in energy of the precursor π -adducts (4 kcal mol⁻¹ lower for Lu). As in the Sc case, the isobutyl complex is the major product of the interaction of Cp_2LuCH_3 with propene, since it is associated with a lower activation energy. However, three minor products should also be observed, namely, the propenyl, the π -allyl, and the 1-methylpropyl complexes.

Similar reactions involving $\text{Cp}_2\text{LuCH}_2\text{CH}(\text{CH}_3)_2$ in place of Cp_2LuCH_3 have been considered. All reactions are exergonic (Table 4). The two reactions with the lowest activation energies are the vinylic ($\Delta G^\ddagger = 24.98$ kcal mol⁻¹) and allylic ($\Delta G^\ddagger = 25.39$ kcal mol⁻¹) activations of propene. Both reactions yield isobutane but destroy the catalyst by forming $\text{CpLuCH}=\text{CHCH}_3$ and the π -allyl complex, respectively. The methane activation has a higher activation energy ($\Delta G^\ddagger = 31.14$ kcal mol⁻¹). Thus, as in the reactions with Cp_2LuCH_3 , processes initiated by formation of a propene adduct have lower activation energies. As a consequence, the favored first step for reaction of Cp_2LuCH_3 in the presence of a mixture of propene and CH_4 is the insertion of propene. This yields the isobutyl complex, which also prefers to react with propene. The catalyst Cp_2LuCH_3 cannot be regenerated and, consequently, the hydromethylation reaction cannot be a catalytic reaction with the lutetium complexes. In contrast, it can produce a stoichiometric amount of isobutane from the reaction of Cp_2LuCH_3 and one molecule of propene.

Influence of the Nature of the Cyclopentadienyl Ligand.

A few comments should be made concerning use of the Cp ligand (Cp = C_5H_5) as a model for the Cp^* ligand ($\text{Cp}^* = \text{C}_5\text{Me}_5$), which was employed in the experimental studies on the hydromethylation reaction. This is particularly relevant given the small differences in activation energies (ca. 5 kcal mol⁻¹) for competitive reactions examined in this study (e.g., methane, vinylic, and allylic activations). Calculations with Cp^* ligands are computationally demanding, and only a few examples can be found in the literature.^{19,31–34} Indeed, the influence of modeling Cp^* with Cp has been considered for the activation

of methane by $\text{Cp}^*_2\text{MCH}_3$ complexes^{19,32} and for the polymerization of ethylene by $\text{Cp}^*_2\text{NdCH}_2\text{CH}_3$.²¹ Calculations show that methane activation has a higher activation energy with Cp^* (vs Cp) ligands,^{19,32} but the replacement of Cp by Cp^* increases the activation energy for Sc (4 kcal mol⁻¹) more than for Lu (~1.5–2 kcal mol⁻¹), since a reaction at the smaller Sc atom is more sensitive to the steric influence. Related results obtained by Perrin et al. reveal that the increase in the activation energy to ethylene insertion into the Nd– CH_2CH_3 bond is attributed to the steric influence of the cyclopentadienyl methyl groups and not to an electronic factor.²¹ On the basis of these results, it is expected that all the activation energies calculated in this study should be higher with Cp^* than with Cp. In the case of Lu, the methyl cyclopentadienyl groups should have only moderate influence because of the large ionic radius of the metal and the relative activation energies of all reactions should be similar for Cp and Cp^* . For the scandium systems, the replacement of Cp by Cp^* should increase relatively more the activation energies for the reaction involving the propene compared to those involving the small CH_4 molecule. Notably, the vinylic activation of propene should still be competitive with methane activations because the activation energies involving Cp complexes are lower by around 5 kcal mol⁻¹. Therefore, all activation energies should be higher with Cp^* (vs Cp), but the relative results found for propene and methane should be similar for these two cases. We believe that the trend calculated with the Cp ligand should also apply in the case of Cp^* .

Comparison of Reactivities for Scandium and Lutetium Complexes. The activation energies for the C–H bond activation of several alkanes (methane, propane, isobutane) by σ -bond metathesis with Cp_2ScCH_3 and Cp_2LuCH_3 are shown in Figure 10. The vinylic and allylic activations for propene are included for comparison. The lutetium catalyst favors the activation of a C–H bond of propene over that of any alkane since the activation energies with propene are lower by at least 6 kcal mol⁻¹. On the contrary, for Cp_2ScCH_3 , the preference for activation of a C–H bond of propene is less pronounced since this difference in activation energy is smaller than 4 kcal mol⁻¹. We also note that the activation energies increase for a given metal with the size of the alkane and that the activation energies for a given alkane are close for Sc and Lu. We discuss first the relative activation energies for alkanes, and second, we discuss the propene.

(a) Influence of the Alkane. As can be seen from Figure 10, for a given metal, the activation energies for alkyl group exchange between Cp_2MCH_3 and HR to give Cp_2MR and CH_4 depend on the size of the alkane. Larger alkanes give higher activation energies. It has been shown that the activation energies of these σ -bond metathesis reactions can be related to the charge redistribution that occurs from reactant to product.³² Two parameters have been used: Δq (charge difference for the metallic fragment between the reactant and the TS) and “pol” (the polarization of the incoming alkane molecule). The values for these parameters are identical for propane and isobutane for a given metal fragment (Table 5). Therefore, the higher activation energies for isobutane relative to propane (Table 5) do not originate from different charge redistributions during the reaction. The larger size of the isobutane is most likely responsible for the higher activation energies.

The activation energies for alkyl group exchange in the reaction of propene with Cp_2ScCH_3 and Cp_2LuCH_3 are similar

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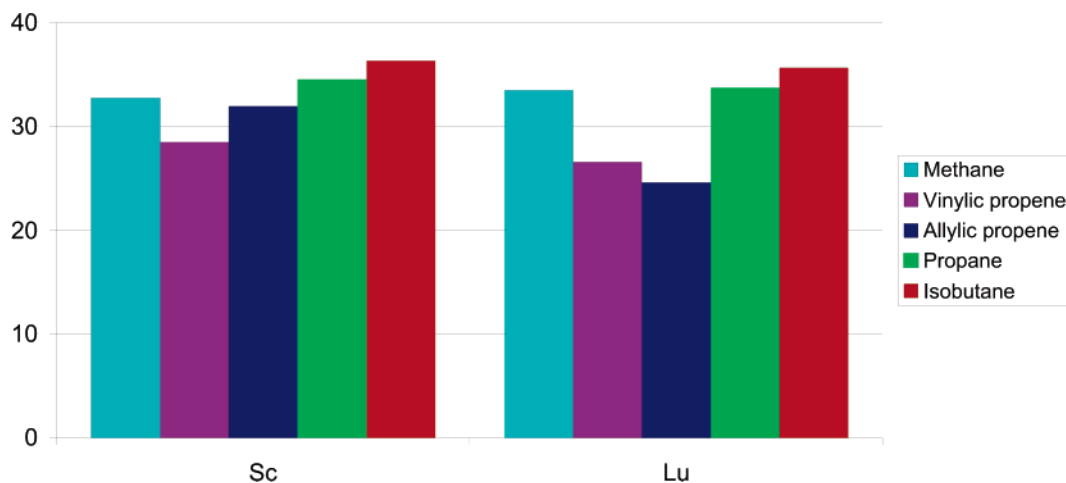


Figure 10. Activation energies (ΔG), in kcal mol⁻¹, for the C–H activation of alkanes and alkenes with Cp₂MCH₃ (M = Sc, Lu).

Table 5. Calculated Activation Energies and Parameters Δq and “pol” for Alkane Activation in the Reaction Cp₂M–CH₃ + HR to Give Cp₂MR + CH₄^a

reaction		ΔG^\ddagger	Δq	“pol”
Cp ₂ ScCH ₃	propane activation	34.35	-0.20	-0.06
	isobutane activation	36.12	-0.21	-0.05
Cp ₂ LuCH ₃	propane activation	33.38	-0.09	-0.17
	isobutane activation	35.36	-0.10	-0.19

^a See ref 32 for definitions.

(34.35 kcal mol⁻¹ for scandium and 33.38 kcal mol⁻¹ for lutetium), as shown in Figure 10. Earlier studies have shown that the smaller ionic radius of Sc (75 pm) compared to Lu (86 pm) makes a reaction at Sc more sensitive to steric effects.³² Therefore the activation energies will increase more for Sc (vs Lu) with the Cp-to-Cp* replacement. The relative activation energy for the alkyl exchange reaction between the scandocene reactant and HR' is therefore under significant steric control. The reaction is hampered for large alkanes and probably more for Sc than Lu.

(b) Reactions with Propene. The main difference between Sc and Lu is the stability of the π -adduct of propene. The π -complex is more stable with Lu, although it has not been isolated. In the absence of back-donation, the alkene ligand is only weakly bonded to the metal and the interaction between the metal and the propene is essentially electrostatic, as shown by the NBO analysis in the case of Cp₂LuCH₃(η^2 -CH₂=HCH₃), **7**. The electrostatic interaction between the metal and propene is most conveniently analyzed in terms of the charge on the entire metallocene fragment. The charge on the Cp₂Lu fragment in Cp₂LuCH₃ is equal to +0.69. In Cp₂ScCH₃, the bonds between Sc and the ligand have a stronger covalent character, which decreases the positive charge on the metal; the charge on the Cp₂Sc fragment is equal to +0.56. In Cp₂YCH₃, the charge on the Cp₂Y fragment is +0.68 and the ionic radius is larger than that of Lu (1.019 vs 0.977).³² This is consistent with the alkene adducts observed for Cp*₂YR (R = primary alkyl)³⁵ and the absence of an observable propene adduct in the case of Cp₂ScCH₃. The propene adduct should be even less favored in Cp*₂ScCH₃ because of the larger steric hindrance between the metal fragment and the olefin.

Although the geometry of the propene is hardly modified by coordination to the metal, the π -electron density is slightly

stabilized by the electron-deficient metal center, as shown by the second-order perturbation theory in the NBO analysis. This stabilizing interaction does not exist with an alkane because the electron density of a C–H bond is significantly less perturbed by the metal even in an agostic interaction. There is therefore no methane adduct for Sc and no significant ones for Lu. Thus, in the case of Cp₂ScR, there is no preference for the propene (vs methane) to interact with the metal. In contrast, Cp₂LuR prefers to interact with propene when R is either methyl or isobutyl. These stabilizing interactions between the Lu fragment and the propene are maintained in the transition states, which results in Cp₂LuR having lower activation energies for all reactions involving propene. Therefore, Cp₂LuR reacts preferentially with alkene over alkane. It also accounts for the lower activation energy for the allylic propene activation compared to the vinylic activation because the interaction between the π orbital of propene and Lu is more efficiently maintained at the transition state for the former. Thus, the successive reactions of propene and alkane in the hydromethylation of the propene are possible for Sc but less favored for Lu. The reactivities of Cp₂ScR and Cp₂LuR are determined by the relative coordination energies of σ - and π -bonded substrates, which are partly determined by electronic factors reinforced by steric effects.

Conclusion and Perspectives

In this paper, it has been possible to rationalize some experimental observations on the catalytic properties of a scandocene complex. In particular, in agreement with the observations of Sadow and Tilley¹³ and Thompson et al.,¹⁴ it has been possible to demonstrate that, in the presence of scandocene, propene can be converted into isobutane, with a relatively good yield, in the presence of CH₄. Moreover, it has been shown that, mainly for the second step of the catalytic cycle, vinylic and allylic activations of propene become competitive, which accounts for the secondary products. These reactions, although releasing isobutane, destroy the catalyst since no regeneration, from C–H activation of methane, is possible.

In the case of the lutenocene catalyst, even though propene insertion is the major reaction for the methyl complex, all reactions involving propene are possible, which is unfavorable for selectivity. The reactivity pattern is even less favorable for the second catalytic step, since methane activation is not competitive with the vinylic and allylic activation of propene. Thus, the reaction cannot be catalytic and the highest possible

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yield of isobutane would correspond to one molecule of isobutene for one molecule of catalyst.

The difference in reactivity between the scandocene and lutenocene complexes has been investigated. Rather than the classical steric explanation, based on the differences in sizes of the two metals, we have proposed an electronic argument. This is based on a difference in the stabilities of propene π -adducts for the two metals. This difference, which is found to be around 4 kcal mol⁻¹ in favor of lutenocene, is also observed in the activation energies. This stronger interaction with the π -system is more stabilizing for the more electron-deficient Lu center. Thus, the lutenocene favors all reactions with propene over reactions with alkanes, since σ -adducts of alkane are not so stabilizing. Steric factors cannot be neglected, however, and it was found that they mostly influence the relative reactivity of alkanes. In order to gain more insight into the influence of electronic and steric factors, similar studies with the *ansa*-(silylene)metallocenes are being carried out. In this system, both

electronic and steric effects change relative to the Cp*₂MCH₃ analogues. Indeed, the metal should be more electron deficient and the coordination site less crowded than in Cp₂MCH₃. These effects have in fact been observed in recent studies of [Me₂Si-(C₅Me₄)₂]ScR *ansa* complexes.³⁷

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Supporting Information Available: The Cartesian coordinates, the electronic energy, and free energies of all the optimized structures are available free of charge via the Internet at <http://pubs.acs.org>.

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