DFT Investigation of the Catalytic Hydromethylation of Olefins by Scandocenes. 2. Influence of the Ansa Ligand on Propene and Isobutene Hydromethylation

Noémi Barros,[†,‡,§] Odile Eisenstein,[*,‡] Laurent Maron,[*,†] and T. Don Tilley[*,∥]

LPCNO, Université de Toulouse, INSA, UPS, LPCNO, 135 avenue de Rangueil, F-31077 Toulouse, France, and CNRS, LPCNO, F-31077 Toulouse, France, Institut Charles Gerhardt, UMR 5253 CNRS-UM2-ENSCM-UM1, cc 1501, Université Montpellier 2, Place E. Bataillon, 34095 Montpellier Cedex 05, France, ICSM, UMR 5257 CEA-CNRS-UM2, Site de Marcoule, BP 17171, 30207 Bagnols sur Cèze Cedex, France, and Department of Chemistry, University of California, Berkeley, California 94720-1460

Received December 19, 2007

Density functional theory (B3PW91) calculations have been carried out for the hydromethylation of propene and isobutene catalyzed by *ansa*-$Me_2Si(C_5Me_4)_2ScCH$, as modeled by $H_2Si(C_5H_4)_2ScCH_3$. The calculations show that the hydromethylation of isobutene, but not propene, could be catalytic, and the difference may be attributed to a combination of electronic and steric factors. Several side reactions have also been considered. The catalytic cycle is completed only for cases in which both the olefin and methane can interact with the Lewis acidic metal center in separate steps. Olefins have greater coordination strengths than methane unless steric factors dominate. In the case of the ansa complex, which is more Lewis acidic and slightly more open than a nonansa complex, calculations show that the strong binding of propene blocks the catalytic cycle. This is not the case for the more bulky isobutene, which is a poorer ligand and thus allows competitive access of methane to the metal center.

Introduction

The functionalization of single bonds, and in particular C−H bonds, has been a long-term goal in the context of selective synthetic routes to fine chemicals. Intense interest in this topic has led to important advances including the discovery of several mechanisms by which transition-metal species react with unactivated C−H bonds.[1] A primary goal of research in this area is the discovery of catalysts for the addition of C−H bonds across the double bond of an olefin. In this context, certain complexes of the lanthanides and related metals are attractive because they are known to facilitate the addition of Si−H and N−H bonds across an olefin.[2,3] The ability of similar complexes to activate C−H bonds suggests that it may be possible to find catalysts for the addition of hydrocarbons (such as methane) across an olefin.[4,5]

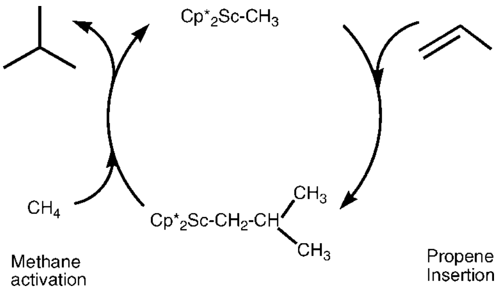

Figure 1. Postulated mechanism for the hydromethylation of propene.

We have been interested in the hydromethylation of olefins catalyzed by $(C_5Me_5)_2ScCH_3$ (or $Cp^*{}_2ScCH_3$). Experimental results suggest that hydromethylation may occur by insertion of the olefin into a Sc−Me bond, followed by the activation of methane in a concerted σ-bond metathesis step (Figure 1). This last step regenerates the catalyst $Cp^*{}_2ScCH_3$ and releases the product of the addition of methane across the olefin.[4] The challenge in this reaction is to avoid unwanted side reactions, and in particular olefin polymerization. Previous results have shown that the ansa complex $Me_2Si(C_5Me_4)_2ScMe$ (**1**) is twice as reactive as $Cp^*{}_2ScCH_3$ (**2**) toward methane, and it is an efficient catalyst for the addition of methane across the double bond of 1,1-disubstituted olefins.[5] However, this catalyst is inefficient for the hydromethylation of olefins such as propene. In contrast, complex **2** is more efficient in the hydromethylation

---

[*] To whom correspondence should be addressed. E-mail: odile.eisenstein@univ-montp2.fr (O.E.), laurent.maron@irsamc.ups-tlse.fr (L.M.), tdtilley@berkeley.edu (T.D.T.).

[†] LPCNO, Université de Toulouse.

[‡] Université Montpellier 2.

[§] ICSM, Marcoule.

[∥] University of California.

(1) For reviews, see for instance: Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. Davies J. A.; Watson, P. L.; Greenberg, A.; Liebman, J. F. *Selective Hydrocarbon Activation*; VCH Publishers: New York, 1990. Arndtsen, B. A.; Bergman, R. G.; Mobley, T. A.; Peterson, T. H. *Acc. Chem. Res.* **1995**, *28*, 154. Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259. Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. Guari, Y.; Sabo-Etienne, S.; Chaudret, B. *Eur. J. Inorg. Chem.* **1999**, 1047. Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507.

(2) Molander, G. A.; Romero, J. A. C. *Chem. Rev.* **2002**, *102*, 2161.

(3) For recent papers on hydrosilylation, see for instance: Horino, Y.; Livinghouse, T. *Organometallics* **2004**, *23*, 12. Robert, D.; Trifonov, A. A; Voth, P.; Okuda, J. *J. Organomet. Chem.* **2006**, *691*, 4393. Buch, F.; Brettar, H.; Harder, S. *Angew. Chem., Int. Ed.* **2006**, *45*, 2741. For hydroboration, see for instance: Harrison, K. N.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 9220. For hydroamination, see for instance: Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 4108. Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673.

(4) Sadow, A. D.; Tilley, T. D. *J. Am. Chem. Soc.* **2003**, *125*, 7971.

(5) Fontaine, F. G.; Tilley, T. D. *Organometallics* **2005**, *24*, 4340.

10.1021/om701270w CCC: $40.75

of propene (vs isobutene).[4] Furthermore, it has been shown that propene inserts into the Sc−Me bond of **1** to produce the isobutyl complex, but further reaction with methane does not occur.[5]

Computational studies can be useful to gain further insight into these questions. Earlier studies on closely related complexes have shown that the energy profiles for the hydromethylation of propene by Cp_2ScCH_3 and Cp_2LuCH_3 (Cp = C_5H_5) are sensitive to subtle balances between the Lewis acidity of the metal fragment and steric factors.[6] Lewis acidity at the metal center favors coordination of the olefin, which is superior to methane as a Lewis base. However, a steric factor, directly related to the ionic radius of the metal, disfavors coordination of the olefin for smaller metals and thus favors the hydromethylation reaction. Herein we describe extension of these studies to analogous ansa complexes for which the observed hydromethylation chemistry is distinctly different. Related computational studies have demonstrated the importance of steric factors and the role of the ansa ligand on σ-bond metathesis.[7] The influence of the ansa bridge in zirconocene complexes has been probed by a combination of IR spectroscopy, electrochemistry, and computational studies.[8]

Density functional theory (DFT) calculations have been used to analyze the energy profiles for hydromethylations of olefins (propene and isobutene) with the ansa complex, modeled by $H_2Si(C_5H_4)ScCH_3$ ($OpScCH_3$, $\mathbf{1_H}$). These results are compared to those previously obtained for Cp_2ScCH_3, for a better understanding of the role of the ansa ligand.

Computational Details

Calculations were carried out at the DFT level using the hybrid functional B3PW91[8] with the *Gaussian 98* suite of programs.[9] Scandium has been treated with a relativistic effective-core potential (RECP) from the Stuttgart group[10] and the corresponding optimized basis set, augmented by an f polarization function. Silicon was also treated with a large-core RECP in combination with the adapted basis set, augmented by a polarization d function (exp = 0.284). An all-electron 6-31G(d,p) basis set is used for C and H.[11] Geometry optimizations were carried out without any symmetry restriction. The nature of the extrema (minimum or transition state) was verified with analytical frequency calculations. Zero-point-energy (ZPE) and entropic contributions were calculated using the approximation of harmonic frequencies. The results are discussed in term of Gibbs free energies *G*, calculated for *T* = 298.15 K, but it has been verified that using *G*, *E*, and *E* + ZPE gives similar results. The population analysis was carried out using the natural-bond-order (NBO) method.[12]

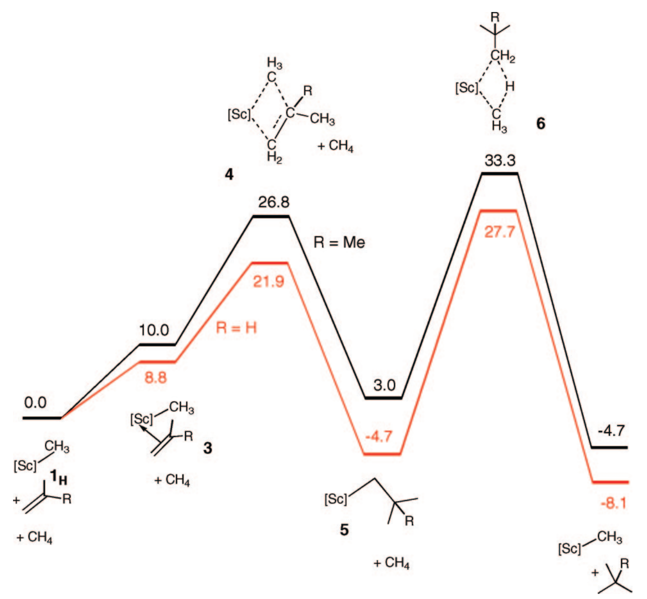

Figure 2. Gibbs free-energy profiles (kcal mol^{-1}) for the hydromethylation of propene (red) and isobutene (black) with $OpScCH_3$. [Sc] = OpSc.

Results

Hydromethylation of Propene by $OpScCH_3$. (a) Hydromethylation Pathway. The Gibbs free-energy profile of the two-step reaction presented in Figure 2 is similar to that found for the reaction with $Cp_2Sc\text{-}CH_3$, and only a brief description is necessary.[6] The propene binds only weakly to Sc via its π bond to form **3**, because of the lack of any back-bonding interaction. The Gibbs free energy for the coordination of propene is therefore dominated by the entropic term, and the coordination of propene is endergonic by 8.8 kcal mol^{-1}. The insertion of the propene occurs via a four-center transition state, **4**, with an activation free energy that is 13.1 kcal mol^{-1} above that of the propene adduct. The overall activation free energy for the propene insertion is 21.9 kcal mol^{-1}, and the resulting isobutyl complex $OpScCH_2CH(CH_3)_2$ (**5**) is formed in an exergonic manner ($\Delta G_0 = -4.7$ kcal mol^{-1}).

The reaction of methane with the isobutyl complex releases isobutane and regenerates the catalyst. This step is also exergonic with a ΔG_0 of −3.4 kcal mol^{-1} relative to the isobutyl compound and −8.1 kcal mol^{-1} relative to the separated reactants, $OpScCH_3$ and propene. No methane adduct is found as an intermediate before the four-center transition state for the σ-bond metathesis (**6**). The activation free energy for this elementary step is 32.4 kcal mol^{-1} (27.7 kcal mol^{-1} above the separated reactants). The transition state directly yields the separated $OpScCH_3$ and isobutane.

The optimized geometries of the minima and transition states are shown in Figure 3. In $OpScCH_3$, the Sc−C bond length is 2.21 Å and the absence of an agostic interaction is indicated by the direction of the C_3 axis of the methyl group, which is aligned with the Sc−C axis. The Sc−Cp_{ct} (ct = cyclopentadi-

---

(6) Barros, N.; Maron, L.; Eisenstein, O.; Tilley, T. D. *Organometallics* **2006**, *25*, 5699.

(7) Woodrum, N. L.; Cramer, C. J. *Organometallics* **2006**, *25*, 68. Lewin, J. L.; Woodrum, N. L.; Cramer, C. J. *Organometallics* **2006**, *25*, 5906.

(8) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercaw, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Perdew, J. P.; Wang, W. *Phys. Rev. B* **1992**, *45*, 13244.

(9) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, G.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

(10) Dolg, M.; Stoll, H.; Savin, A.; Preuss, H. *Theor. Chim. Acta* **1989**, *75*, 173.

(11) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(12) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

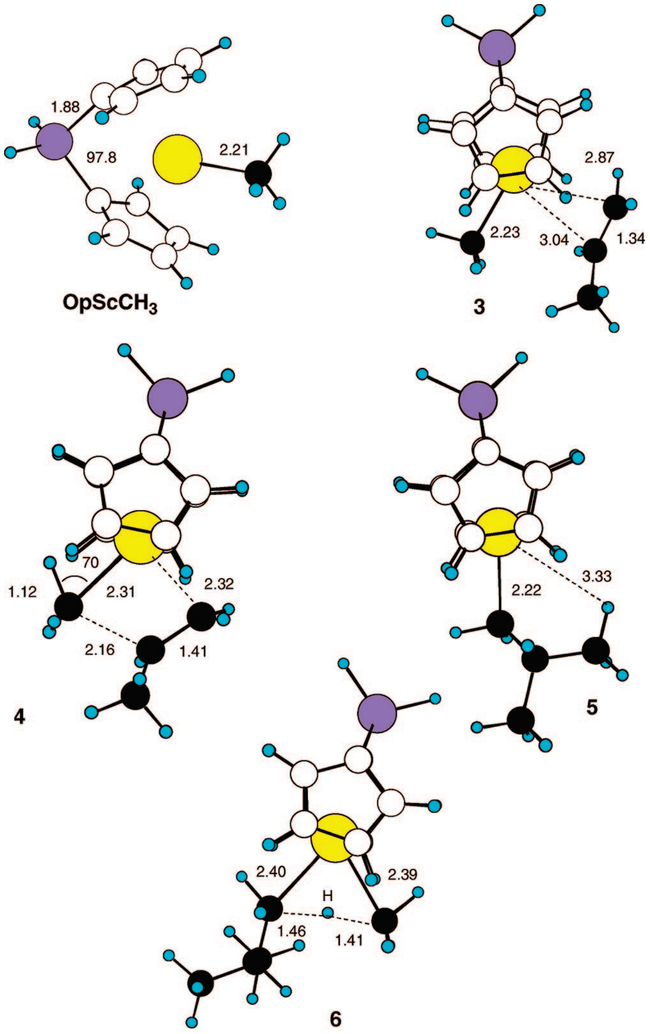

Figure 3. Optimized structures (distances in angstroms and angles in degrees) of the extrema for the hydromethylation of propene by $OpScCH_3$.

enyl center) distance is 2.17 Å, and the angle between the two Sc−Cp$_{ct}$ directions is 130°, which is 7° less than that in $OpScCH_3$.

In the adduct **3**, the propene is almost planar with a C=C distance equal to that of free propene (1.34 Å). The propene is η^2-bonded with a slight shift of Sc toward the less substituted C (2.87 vs 3.04 Å for the substituted C), and this is associated with a higher electron density on the less substituted propene C. The main change in the geometry of the metal fragment is the position of the methyl group. In $OpScCH_3$, the Sc lies in the plane defined by the centers of the cyclopentadienyl rings and the C of the methyl group, while in the propene complex, the metal is in a pseudotetrahedral environment defined by the cyclopentadienyl rings, the C=C midpoint, and the methyl group. It should be noted that moving the methyl group in or out of the mirror plane defined by the Cp centroids and a d^0 group III or lanthanide metal requires very little energy.[13] Bond distances are hardly changed upon propene coordination to $OpScCH_3$, as shown by the Sc−C(Me) bond length, which increases by only 0.02 Å. The bonding interaction between propene and $OpScCH_3$ is weak, and the formation of the propene complex is endergonic.

The transition state **4**, for the insertion of propene into the Sc−Me bond, has a planar four-center ring formed by Sc, the C of the methyl group, and the two C atoms of the propene π bond. The two Sc−C bond lengths are essentially equal (2.31 and 2.32 Å), and the C−C distance is equal to 1.41 Å. The C_3 axis of the methyl group points toward the closer olefinic C of propene. As a result, one of the H atoms of the methyl group is pushed toward Sc. This lengthens the corresponding C−H bond to 1.12 Å, indicating the formation of an agostic interaction. This is further supported by the second-order pertubation analysis from the NBO analysis, which confirms that the σ_{C-H} orbital interacts with an empty Sc d orbital.

The isobutyl complex $OpScCH_2CH(CH_3)_2$ (**5**), resulting from insertion of propene into the Sc−Me bond, has no remarkable structural features. The Sc−C bond length is equal to that in the methyl complex, and all H atoms are far from the metal, indicating the absence of any agostic interaction. The transition state **6**, for reaction of the isobutyl complex with CH_4 to form $OpScCH_3$ and isobutane, has the geometric features previously noted for σ-bond metathesis reactions.[6] The squashed Sc−C−H−C rhombus, with a C−H−C angle of 180°, is characteristic of a proton transfer between the two alkyl groups (the NBO charge of the transferring H is +0.26). The proton is closer to the methyl C (1.41 Å) than to the isobutyl C (1.46 Å), in agreement with the Hammond postulate. At the transition state, sp^3 electron pairs of the C atoms nearer to the metal are significantly oriented toward the transferring proton, in order to optimize interaction with the latter. The loss of interaction between the alkyl groups and the Sc is partially compensated for by agostic interactions of the α-C atoms of the methyl and isobutyl groups. These features (free-energy profiles and geometries of extrema) are very similar to those found in the study of the hydromethylation of propene with Cp_2ScCH_3, and subtle differences will be discussed later.

(b) Side Reactions. The main reaction path, which gives the isobutane product, has two individual steps with relatively large activation free energies. Other reactions could lead to byproducts and/or prevent the regeneration of the catalyst. In the following, the free energies of reactions, and the activation free energies of several plausible reactions described in Figure 4, are shown in Table 1. The nonproductive methyl group exchange between $OpScCH_3$ and CH_3−H is also given for reference. Exergonic reactions whose activation free energies differ by less than 5 kcal mol^{-1} will be considered capable of producing side products, in competition with the main hydromethylation reaction (this value stems from the currently recognized accuracy of computations).

In our previous study of the hydromethylation of propene with Cp_2ScCH_3,[6] it was established that only the reactions shown in Figure 4 had activation free energies sufficiently close to those involved in the hydromethylation process to yield side products. Because one should not expect major changes in reactivity patterns between the nonansa and ansa species, we have considered the same reactions. In addition, it should be noted that β-H transfer from the isobutyl group to the coordinated propene (a type of reaction often considered as mainly responsible for polymerization termination) has been found to have a high activation free energy (over 40 kcal mol^{-1}) in our study of hydromethylation with Cp_2ScCH_3.[6] This is in agreement with the computational studies of Ziegler et al.[14] There is no need to study the reaction involving a β-H because the aim of this study is to compare the reactions with propene and isobutene

---

(13) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. Perrin, L.; Maron, L.; Eisenstein, O. *Faraday Discuss.* **2003**, *124*, 25.

(14) Margl, P.; Deng, L.; Ziegler, T. *J. Am. Chem. Soc.* **1999**, *121*, 154.

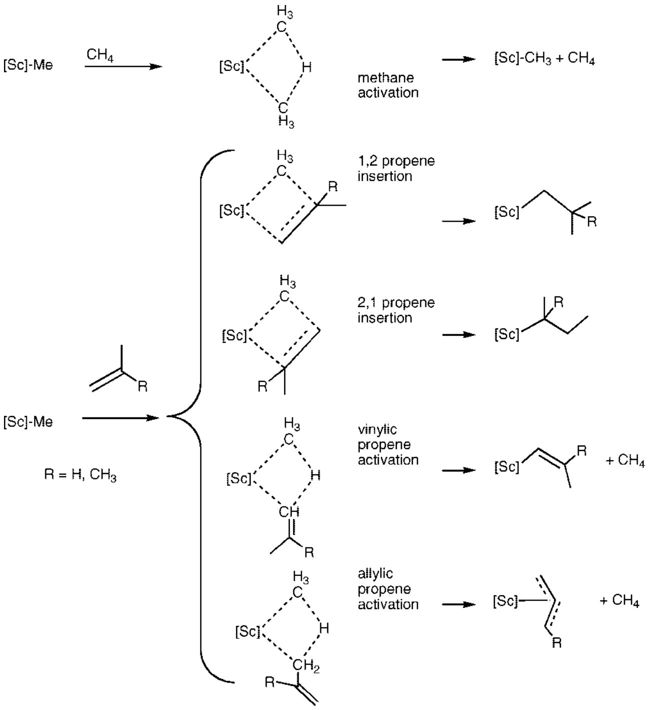

Figure 4. Schematic representation of possible reactions forming an alkane derivative between $OpScCH_3$, CH_4, and propene, [Sc] = OpSc.

Table 1. Energetics for Reactions Involving Propene or Methane with $OpScCH_3$ or $OpScCH_2CH(CH_3)_2$[a]

reactant	reaction	$\Delta G°$	$\Delta G^{\ddagger}$
	1,2 propene insertion	−4.7	21.9
	2,1 propene insertion	2.2	26.2
$OpScCH_3$	methane activation	0.0	30.6
	allylic propene activation	−15.3	28.5
	vinylic propene activation	−4.5	26.6
$OpScCH_2CH(CH_3)_2$	1,2 propene insertion	−4.8	32.3
	methane activation	−3.4	32.4
	allylic propene activation	−18.7	30.7
	vinylic propene activation	−7.9	26.1

[a] Gibbs free energies, ΔG, are given in kcal mol^{-1} relative to the associated reactants. See Figure 4 for definitions of the reactions.

and there is no β-H in the neopentyl complex formed by insertion of isobutene into the Sc−Me bond (see the next section). In addition, as shown below, the hydromethylation of propene is not the preferred reaction between $OpScCH_3$, propene, and CH_4. Thus, additional side reactions such as β-H transfer and β-H elimination have limited relevance to this study.

The reactions that have been considered are the insertion of propene along two possible orientations and C−H activation of the propene. The starting metal complex can be $OpScCH_3$ or the isobutyl intermediate $OpScCH_2CH(CH_3)_2$. Table 1 shows that the propene 2,1 insertion in $OpScCH_3$ is endergonic, with a barrier higher than that for the 1,2 insertion of propene. It was not considered further because it is not an exergonic reaction.

The preferred insertion reaction of $OpScCH_3$ forms the isobutyl complex. Only the allylic activation of propene would give a significantly more stable product, but the associated activation free energy is higher by almost 7 kcal mol^{-1}. This difference in activation free energy could be sufficient enough to make the 1,2 insertion the only feasible reaction in the case of $OpScCH_3$. All activation free energies are higher with the $OpScCH_2CH(CH_3)_2$ intermediate, as expected from the increased size of the alkyl group. Two reactions, vinyl and allylic C−H activation, have barriers lower than that of the C−H activation of CH_4. These two reactions also yield isobutane but do not regenerate the catalyst. The formation of the allylic complex, which is very thermodynamically favored (optimized structure shown in Figure 5), would be particularly efficient in destroying the catalyst. These results agree with the experimental observations that isobutane is formed in the reaction of $Me_2Si(C_5Me_4)_2ScCH_3$ with propene, even in the absence of methane, and that the reaction is not catalytic. The reasons for these preferences will be discussed later.

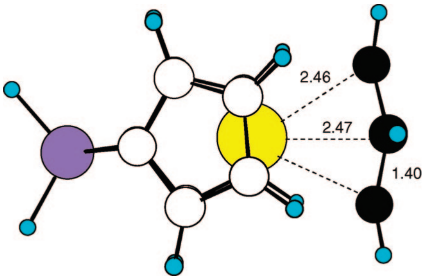

Figure 5. Optimized structure (distances in angstroms) of $OpSc(\eta^3\text{-}CH_2CHCH_2)$.

Table 2. Energetics for Reactions Involving Isobutene with $OpScCH_3$ and $OpScCH_2CH(CH_3)_2$[a]

reactant	reaction	$\Delta G°$	$\Delta G^{\ddagger}$
	1,2 isobutene insertion	3.0	26.8
	2,1 isobutene insertion	7.9	37.0
$OpScCH_3$	methane activation	0.0	30.6
	vinylic isobutene activation	−2.7	29.6
	allylic isobutene activation	−12.6	31.3
$OpScCH_2CH(CH_3)_2$	1,2 isobutene insertion	5.2	37.6
	methane activation	−7.6	30.3
	vinylic isobutene activation	−10.4	30.9
	allylic isobutene activation	−20.2	35.7

[a] Gibbs free energies, ΔG (kcal mol^{-1}), are given relative the corresponding reactants. See Figure 4 for definitions of the reactions.

Hydromethylation of Isobutene by $OpScCH_3$. The reaction pathway for the hydromethylation of isobutene by the ansa complex $OpScCH_3$ was calculated. The overall features of the extrema are similar to those found for propene: while the distance between Sc and isobutene is larger than for propene (average 0.2 Å longer), the geometries of the two transition states are very similar. The free-energy profile from Figure 2 shows that all extrema (intermediates as well as transition states) are at higher energies (4−5 kcal mol^{-1}) relative to separated reactants than in the case of propene, but the formation of neopentane is still exergonic.

The activation free energies for the side reactions of Figure 4 are given in Table 2. The reaction of $OpScCH_3$ with the lowest activation free energy is the 1,2 isobutene insertion; it forms an intermediate, $OpScCH_2C(CH_3)_3$, which is less stable than the separated reactants such that the reverse reaction, the β-Me elimination, has a lower activation free energy (23.8 kcal mol^{-1}) and is entropically favored. The vinylic activation of isobutene has an activation free energy only 3 kcal mol^{-1} higher than the 1,2 insertion reaction and leads to more stable products. Thus, this process could efficiently yield observable species. The allylic activation of isobutene has a high activation free energy and should not occur even if it would lead to a stable allylic complex. The 2,1 isobutene insertion has a significantly higher activation free energy; hence, the isopentyl complex (and any isopentane derived therefrom) should be formed in negligible quantities. Thus, the steric bulk of the isobutene raises the

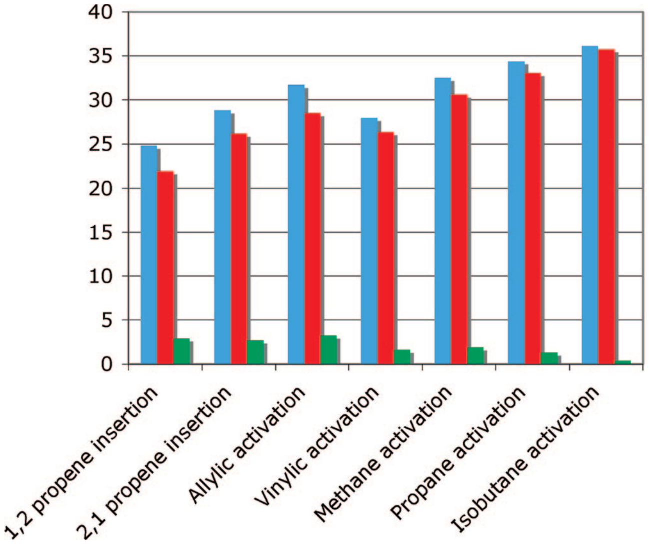

Figure 6. Activation free energies ($\Delta G^{\ddagger}$ in kcal mol^{-1}) with Cp_2ScCH_3 (blue), $OpScCH_3$ (red), and the difference between the two values (green). See Figure 4 for definitions of reactions.

activation free energies of the reactions because the two methyl groups have to be near the cyclopentadienyl rings at the transition states. The transition state for the vinylic activation of isobutene is less influenced by these steric interactions because the two methyl groups remain far from the cyclopentadienyl rings.

These results are in agreement with the experimental observations. The product of vinylic activation of isobutene, $Me_2Si(C_5Me_4)_2ScCH{=}C(CH_3)_2$, is observed but is slowly consumed during the reaction. The intermediate $Me_2Si(C_5Me_4)_2ScCH_2C(CH_3)_3$, resulting from the 1,2 insertion of isobutene, has not been isolated but has been identified as a likely product via labeling studies with $^{13}CH_4$.[5] The experiments indicate that $Me_2Si(C_5Me_4)_2ScCH_2C(CH_3)_3$ forms by the insertion of isobutene into the Sc−Me bond but readily degrades via β-Me elimination/deinsertion. This is consistent with an endergonic formation of $Me_2Si(C_5Me_4)_2ScCH_2C(CH_3)_3$.

In the case of $OpScCH_2CH(CH_3)_2$, the reaction with the lowest activation free energy is the C−H activation with methane, which yields the desired neopentane and reforms the catalyst $OpScCH_3$. The vinylic activation of isobutene has almost the same activation free energy. The other reactions have significantly higher activation free energies. These computational results are qualitatively in agreement with the experimental results. It was shown that the formation of neopentane requires methane and that the reaction is catalytic. No neopentane is formed in the absence of CH_4, which suggests that the activation free energy for the vinylic activation of isobutene by $OpScCH_2C(CH_3)_2$ has been underestimated. This is probably due to the lack of methyl groups on the cyclopentadienyl ligands of the model complex.

Discussion

Comparison between Cp_2ScCH_3 and $OpScCH_3$ and between Propene and Isobutene. The activation free energies for the reactions studied in this work are given in Figure 6 for Cp_2ScCH_3[6] and $OpScCH_3$. For the sake of discussion, the activation free energies for the cleavage of a primary C−H bond in propane ($\Delta G^{\ddagger} = 34.6$ and 33.1 kcal mol^{-1} for Cp_2ScCH_3 and $OpScCH_3$, respectively) and isobutane ($\Delta G^{\ddagger} = 36.1$ and 35.8 kcal mol^{-1} for Cp_2ScCH_3 and $OpScCH_3$, respectively) have been added.

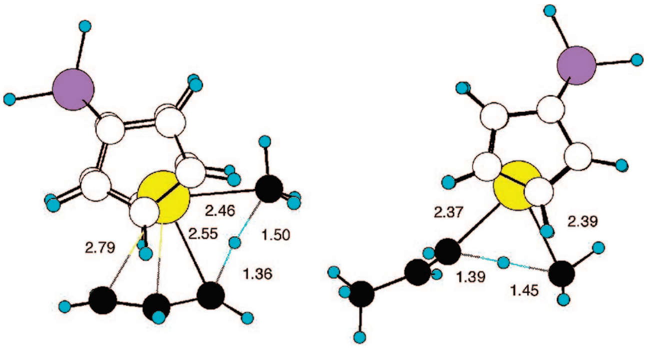

Figure 7. Optimized geometries (distance in angstroms) of the transition states for allylic (left) and vinylic (right) activation of propene by $OpScCH_3$.

The activation free energies are systematically lower for the $OpScCH_3$ complex, with the difference being larger for reactions involving interaction of the propene π system with the metal center (insertion and allylic activation) but smaller for reactions involving the vinylic C−H bond. The activation free energies for reactions with alkanes are similar for Cp_2ScCH_3 and $OpScH_3$, and the difference in activation free energies decreases with the alkane size. There is no marked geometric difference between the geometries of the transition states involving Cp_2ScCH_3 and $OpScCH_3$, and in particular the metal–ligand distances are essentially equal. A purely steric interpretation of the differences in activation free energies is therefore not sufficient. All reactions with the propene start from the π adduct of propene with the metal. The activation free energies $\Delta G^{\ddagger}$ were thus decomposed into two components: the free energy for coordination of the olefin (ΔG^{c}) and the difference in the free energy between the transition state and the π adduct (ΔG^{a}). These values are given for the four reactions studied here between propene and Cp_2ScCH_3 or $OpScCH_3$.

This analysis shows that the ΔG^{a} values are similar for Cp_2ScCH_3 and $OpScCH_3$ and that the lower activation free energies for $OpScCH_3$ originate from a systematically lower (less positive) ΔG^{c}, indicating a stronger interaction between the olefinic π bond and Sc.

The geometries of the transition states show that π interactions are maintained into the transition states (Figure 7). In the case of allylic activation, the propene π bond points toward Sc and the allyl ligand is almost formed (Sc−C distances are from 2.8 to 2.55 Å for the two outsides C atoms). Note that the transferring proton is closer to the allylic group than to the methyl ligand. In the case of vinylic activation, the propene π bond interacts with the metal via one C atom, 2.38 Å from Sc. An NBO analysis confirms this, and the second-order pertubation term shows that the occupied π orbital of propene interacts with an empty Sc d orbital.

The stronger interaction of the π orbitals of propene with $OpScCH_3$ (vs Cp_2ScCH_3) is due to the smaller $Cp_{ct}{-}Sc{-}Cp_{ct}$ angle enforced by the ansa group. This smaller angle increases the dipole moment of $OpScCH_3$ relative to Cp_2ScCH_3. Propene acts as a better coordinating ligand than an alkane, which is a very poor Lewis base. As a consequence, the coordination and subsequent reactions with propene are preferred over reactions with CH_4. Thus, after propene has inserted into the Sc−Me bond (the most favorable reaction for $OpScCH_3$), the following step preferentially involves propene. This reactivity trend, established

Table 3. Decomposition of the Activation Free Energies (kcal mol^{-1}) for the Reaction of Propene with Cp_2ScCH_3 and $OpScCH_3$[a]

	Cp_2ScCH_3			$OpScCH_3$		
reaction	ΔG^c	ΔG^a	$\Delta G^{\ddagger}$	ΔG^c	ΔG^a	$\Delta G^{\ddagger}$
1,2 propene insertion	11.5	13.3	24.8	8.8	13.1	21.9
2,1 propene insertion	11.6	17.6	28.8	7.7	18.4	26.2
allylic activation	11.3	20.4	31.7	9.0	19.5	28.5
vinylic activation	11.5	16.5	27.9	9.7	16.6	26.35

[a] See the text for definitions of terms.

Table 4. Decomposition of the Activation Free Energies (kcal mol^{-1}) for the Reaction of Isobutene with $OpScCH_3$[a]

reaction	ΔG^c	ΔG^a	$\Delta G^{\ddagger}$
1,2 isobutene insertion	10.0	16.8	26.8
2,1 isobutene insertion	10.5	26.5	37.0
allylic activation	9.3	21.9	29.6
vinylic activation	10.0	19.7	31.3

[a] See the text for notations.

in the case of the Sc−Me bond, also holds for the Sc−$CH_2CH(CH_3)_2$ bond, but the steric effects increase the energies of all intermediates and transition states.

To allow CH_4 to react with the product of olefin insertion, olefin coordination should be prevented. This can be done by increasing the steric bulk of the olefin, as in replacing propene with a secondary terminal olefin such as isobutene. To analyze further the effect of the replacement of propene by isobutene, we have carried the energy decomposition scheme as was done in the case of propene. The total activation free energies were decomposed into free energies for coordination of the olefin (ΔG^c), and the remaining ΔG^a, in the case of reactions with $OpScCH_3$.

Comparison of the values of Tables 3 and 4 shows that the coordination energies are weaker for isobutene (higher free energies of coordination) by as much as 2 kcal mol^{-1}. This has mostly a steric origin because isobutene is more electron-rich than propene. However, the main origin of the higher activation free energies for the reactions involving isobutene compared to propene is the other term, ΔG^a. Increasing the bulk in the olefin and the alkyl group raises the free energy of these transition states. The steric effect is maximized for the allylic activation because of the repulsive interactions involving the methyl groups of the olefin, which point toward the cyclopentadienyl rings. It is much smaller for vinylic activation because the two methyl groups remain far from the cyclopentadienyl rings. In summary, the reaction of isobutene is significantly hampered, allowing the methane group to preferentially react with $OpScCH_2C(CH_3)_3$. This favors catalytic hydromethylation.

Conclusion

The analysis presented here demonstrates the interplay of steric and electronic factors in determining the catalytic properties of metallocene complexes. In particular, it is seen that the Lewis acidity of the metal center and the Lewis basicity of the organic fragments must be manipulated by appropriate steric factors that reverse the usual preference for the metal to bind olefins over methane. The same argument has been developed in the comparison of Cp_2ScCH_3 and Cp_2LuCH_3. The latter is a stronger Lewis acid, and this prevents catalytic hydromethylation.[6] In the present case, the presence of the ansa bridge increases the Lewis acidity of the metal fragment, which, in turn, disfavors the catalytic process. The calculations show that the activation free energies of all reactions involving the olefin, including the CH vinylic activation, are lowered by the interaction between the π bond and the metal center. This accounts in particular for the presence of intermediates like $Me_2Si(C_5Me_4)_2ScCH{=}(CH_3)_2$. These studies also illustrate the sensitivity of the catalytic activity to small modifications of the reactants.

Acknowledgment. The French authors thank CALMIP for a generous donation of computational time. N.B. thanks the CEA for a Ph.D. fellowship. L.M. thanks the Institut Universitaire de France for funding his junior member position. The French authors thank the CNRS and the Ministère de l'Enseignement Supérieur et de la Recherche for funding. They also thank the CNRS for specific financial support of the collaboration with the University of California Berkeley via PICS 3442. T.D.T. acknowledges support from the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

Supporting Information Available: List of coordinates, energies (E), and free energies (G) of all calculated species. This material is available free of charge via the Internet at http://pubs.acs.org.

OM701270W