

A DFT Study of the Simmons–Smith Cyclopropanation Reaction

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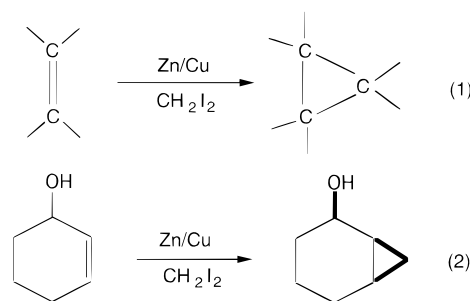
Abstract: In this paper we have used a DFT (B3LYP) approach to investigate the potential energy surface for the reaction between ethylene and (chloromethyl)zinc chloride (ClCH_2ZnCl), which represent a model system for the Simmons–Smith cyclopropanation reaction. Two reaction channels have been found: one leads to the cyclopropane product (addition channel) and the other to the propene product (insertion channel). The addition reaction has an activation energy of $24.7 \text{ kcal mol}^{-1}$ and, as experimentally found, is favored with respect to the insertion, which is characterized by a larger activation energy ($36.0 \text{ kcal mol}^{-1}$). The addition transition state corresponds to a three-centered structure which explains the stereochemical features which have been experimentally observed for this reaction. A simple diabatic model is used to rationalize the reactivity pattern that characterizes the Simmons–Smith cyclopropanation and the different behavior observed for the reaction between singlet methylene $^1\text{CH}_2$ and olefins.

Introduction

The Simmons–Smith cyclopropanation of olefins (eq 1 in Scheme 1) represents one of the most important applications of organozinc reagents in organic chemistry.^{1,2} The synthetic utility of this reaction arises from the following features: (i) it is stereospecific (a strict retention of the olefin geometry is observed), (ii) it is general with regard to the olefin structure, (iii) insertion into the vinylic C–H bond has never been observed, and (iv) it shows an activating and *syn* directing effect of hydroxyl and other functions (for instance 2-cyclohexen-1-ol and its derived methyl ether are reported to give the *syn* alcohol product exclusively; see eq 2 of Scheme 1).³

During the last three decades a variety of methods to generate Simmons–Smith reagents have been proposed. These methods can be classified into three general classes: (a) the original Simmons–Smith procedure, where an ethereal suspension of a zinc/copper couple with diiodomethane (as reported in eqs 1 and 2 of Scheme 1) is used to generate an organometallic reagent capable of transforming olefins into cyclopropanes;^{1a,b} (b) the Furukawa procedure, where an alkylzinc and a 1,1-dihaloalkane serve to generate cyclopropanating reagents;⁴ and (c) the method reported by Wittig and co-workers,⁵ which is based on the reaction between a zinc(II) salt and a diazoalkane. Many

Scheme 1



modifications of these three main reaction schemes have been subsequently proposed by different authors.⁶ Variations of the original Simmons–Smith method include the use of $\text{Zn/CuCl/CH}_2\text{I}_2$,^{6a} $\text{Zn–Ag couple/CH}_2\text{I}_2$,^{6b} $\text{Zn/TiCl}_4/\text{CH}_2\text{Br}_2$,^{6c} and $\text{Zn/AcCl/CuCl/CH}_2\text{Br}_2$.^{6d} In the Furukawa scheme the treatment of Et_2Zn with substituted diiodides, such as benzylidene and ethylene iodide, also produces active cyclopropanating reagents.^{4c}

Despite the synthetic importance of this reaction, a detailed understanding of the mechanism and a knowledge of the structure of the active species are still lacking even if various studies have pointed out that a (halomethyl)zinc “ XCH_2Zn ” moiety could be involved. Early studies by Simmons, for example, provided indirect evidence for the existence of IZnCH_2I species which were indicated as the active cyclopropanating reagent, and a three-centered transition state was proposed to account for the observed stereoselectivities (see Scheme 2).^{1d} Wittig came to similar conclusions investigating the reagents obtained from ZnX_2 ($\text{X} = \text{Cl, I}$) and ethereal CH_2N_2 . He was the first to examine the reactivity of (chloromethyl)zinc chloride (ClCH_2ZnCl) and bis(chloromethyl)zinc

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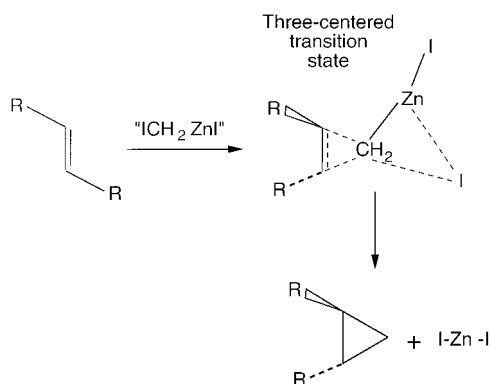
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Scheme 2



((ClCH₂)₂Zn), which were found to behave similarly to ICH₂ZnI and (ICH₂)₂Zn.^{5b} More recently Denmark obtained important structural information on the zinc carbenoids by X-ray crystallography^{2a} and showed that bis(chloromethyl)zinc is more reactive than bis(iodomethyl)zinc.^{2b}

In this paper we present the results of a theoretical study, carried out at the density functional theory (DFT)⁷ level, of the Simmons–Smith cyclopropanation reaction which, to our knowledge, has never been investigated with theoretical methods. It is our goal to apply the DFT theory to shed light on the mechanistic details (energetics and kinetics) of this important transition metal-mediated reaction. The model system that we have considered is formed by one ethylene molecule and (chloromethyl)zinc chloride (ClCH₂ZnCl) that we assume to represent the active form of the cyclopropanating reagent.

Computational Method

All the DFT computations reported here were performed with the Gaussian 94⁸ series of programs, using the hybrid Becke's three-parameter exchange functional^{9a,b} denoted here as B3LYP. Following the Gaussian 94 formalism this functional can be written in the following form:

$$0.80E(S)_x + 0.20E(\text{HF})_x + 0.72E(\text{B88})_x + 0.19E(\text{LOCAL})_c + 0.81E(\text{NON-LOCAL})_c$$

where $E(S)_x$ is the Slater exchange,^{9a,b} $E(\text{HF})_x$ is the Hartree–Fock exchange, $E(\text{B88})_x$ represents the Becke's 1988 non-local exchange functional corrections,^{9d} $E(\text{LOCAL})_c$ corresponds to the Vosko, Wilk, and Nusair local correlation functional,^{9c} and $E(\text{NON-LOCAL})_c$ corresponds to the correlation functional of Lee, Yang, and Parr ($E(\text{LYP})_c$),^{9e,f} which includes both local and nonlocal terms.

Two different basis sets were used. The simpler one corresponds to a Local Spin Density (LSD)-optimized basis set of double- ζ quality in the valence shell plus polarization functions (DZVP).¹⁰ The more accurate basis set is the 6-311G** basis¹¹ provided by Gaussian 94. This basis corresponds to the MacLean–Chandler basis for second-

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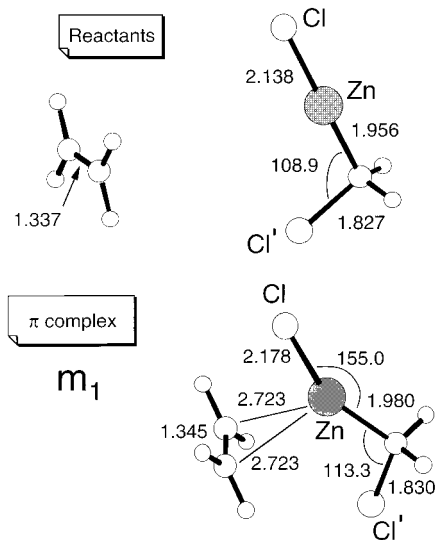


Figure 1. Schematic structures of reactants and the intermediate π complex m_1 (bond lengths are in angstroms and angles in degrees).

row atoms^{11b} and to the Wachters–Hay basis,¹² augmented with f functions, for first-row transition metals. In all cases the geometries of the various critical points were fully optimized with the gradient method available in Gaussian 94, using the DZVP basis set, and the nature of each critical point was characterized by computing the harmonic vibrational frequencies. To obtain more accurate energetics single point computations were performed with the 6-311G** basis set on the DZVP optimized geometries.

Results and Discussion

A. Structures and Energetics. In this section we discuss the singlet potential surface associated with the reaction between one ethylene molecule and the (chloromethyl)zinc chloride (ClCH₂ZnCl). In addition to reactants and products we have located four critical points: a π -complex, denoted as m_1 , involving ethylene and the metal atom, two transition states (TS₁ and TS₂), and an addition product complex denoted as m_2 . The corresponding molecular structures are schematically represented in Figures 1–3 together with the values of the most relevant geometrical parameters. The corresponding energy values are reported in Table 1. In this Table we have also collected the activation energies (E_a) and the reaction enthalpies (ΔH) which include the zero-point vibrational energy corrections (ZPVE) scaled by a 0.9806 factor as recommended by Scott and Radom.¹³ Inspection of Figure 1 shows that the active species ClCH₂ZnCl is characterized by a collinear arrangement of the chlorine, zinc, and carbon atoms ($\angle \text{ClZnC} = 180^\circ$). A π -complex (m_1) between ClCH₂ZnCl and ethylene can form without any barrier. The formation of this complex, which has C_s symmetry and is characterized by a C–Zn distance of 2.723 Å between the olefin carbon atoms and the Zn atom, causes a significant decrease of the $\angle \text{ClZnC}$ angle, which becomes 155° . The interaction of the ClCH₂ZnCl moiety with the π olefin orbitals is also responsible for a slight lengthening of the Zn–Cl, Zn–C, and C–C olefin bonds, which become 2.178, 1.980, and 1.345 Å, respectively. As shown by the frequency

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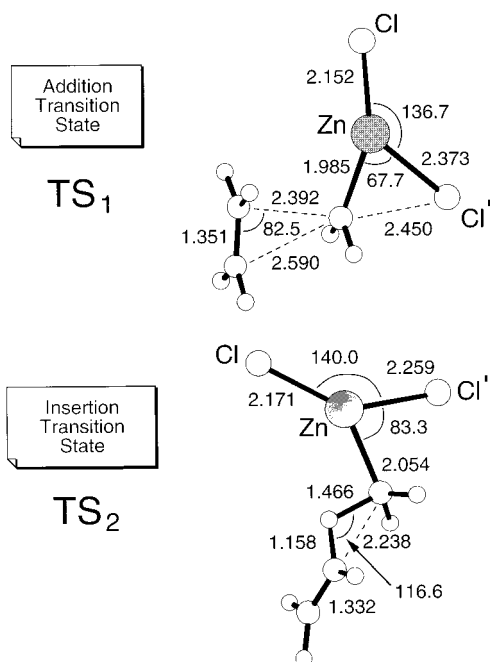


Figure 2. Schematic structures of the addition transition state TS₁ and of the insertion transition state TS₂ (bond lengths are in angstroms and angles in degrees).

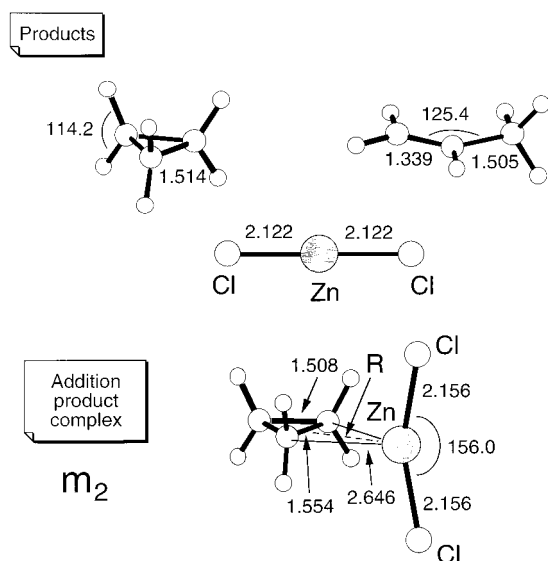


Figure 3. Schematic structures of the addition product complex m_2 and of the final products of the reaction (bond lengths are in angstroms and angles in degrees).

computation, TS₁ (see Figure 2) is a transition state associated with the addition of the methylene fragment to the C–C double bond. In this structure, which has C_s symmetry, the C–C olefin bond is only slightly longer (1.351 Å) than in free ethylene and the two new forming C–C bonds are still quite long (2.392 and 2.590 Å). A strong structural change is observed in the ClCH₂ZnCl moiety where the chlorine atom is moving away from the methylenic carbon (C–Cl' = 2.450 Å) and is approaching the metal atom (the Zn–Cl' distance is 2.373 Å). This transition state is a three-centered structure quite similar to that proposed by Simmons to explain the stereochemical features of this reaction. The second transition state TS₂ corresponds to the attack of the methylene fragment on the vinylic C–H bond. The geometrical features of this transition structure and the analysis of the transition vector corresponding to the imaginary frequency indicates that TS₂ leads to the

Table 1. Energy Values (E),^a Zero-Point Vibrational Energies (ZPVE),^b Activation Energies (E_a)^b or Reaction Enthalpies (ΔH)^b Computed for the Various Critical Points with the DZVP and the 6-311G** Basis Sets

	DZVP		6-311G**		
	E	ZPVE	E_a or ΔH	E_a or ΔH	
reactants	–2817.39048	49.10		–2817.74033	
m_1	–2817.39891	50.15	–4.24	–2817.74841	–4.02
TS ₁	–2817.35994	49.25	19.10	–2817.70113	24.75
TS ₂	–2817.33887	47.74	31.02	–2817.68077	36.01
m_2	–2817.45138	52.26	–35.06	–2817.78796	–26.73
products I ^c	–2817.44234	51.27	–30.38	–2817.77456	–19.31
products II ^c	–2817.45626	50.30	–40.08	–2817.78863	–29.11

^a Atomic units. ^b kcal mol^{–1}. ^c Products I: cyclopropane + ZnCl₂, products II: propene + ZnCl₂.

insertion of CH₂ into the C–H bond. The three atoms involved in the process are arranged in a three-centered structure, characterized by a $\angle\text{CHC}$ angle of 116.6°, where the C–H olefin bond is breaking and two new bonds are simultaneously forming: one between the hydrogen atom and the methylene carbon (1.466 Å) and the other between the olefin carbon atom and the methylene carbon atom (2.238 Å). The insertion process is again responsible for strong structural changes in the active reagent. These changes are similar to those observed in TS₁: the chlorine atom Cl' is moving away from the methylene carbon atom (C–Cl' = 2.871 Å) to form a new bond with the metal atom (Zn–Cl' = 2.259 Å); this motion involves a simultaneous lengthening of the C–Zn bond which becomes 2.054 Å.

The critical point m_2 (see Figure 3) corresponds to a complex between the cyclopropane product and the ZnCl₂ molecule. In this complex the cyclopropane ring is slightly distorted, being characterized by C_{2v} symmetry and not by C_3 symmetry. The two equivalent C–C bonds are slightly shorter (1.508 Å) than the C–C bonds in an isolated cyclopropane molecule (1.514 Å), while the C–C bond interacting with the metal atom is longer (1.554 Å). The ZnCl₂ moiety is significantly bent in the opposite direction to the ring ($\angle\text{ClZnCl} = 156^\circ$) with the ClZnCl plane orthogonal to the cyclopropane plane.

A computation of the intrinsic reaction coordinate (IRC)¹⁴ starting from the two transition states TS₁ and TS₂ in both reactant and product directions shows that both transition states lead directly to the final products (cyclopropane and ZnCl₂ in the former case and propene and ZnCl₂ in the latter). These computations also show that both complexes m_2 and m_1 are not involved either in the addition or in the insertion path.

We discuss now the energetics of the reaction using the values obtained with the 6-311G** basis set. The activation energy for the addition process (24.75 kcal mol^{–1}) is much lower than the activation energy for the insertion process (36.01 kcal mol^{–1}); this indicates that, under mild conditions such as those used to carry out the reaction, the main process is the addition and the insertion cannot significantly compete. All these results are summarized in Figure 4. From this figure it is evident that both reaction channels are exothermic and that the insertion reaction is more exothermic (29.11 kcal mol^{–1}) than the addition reaction (19.31 kcal mol^{–1}).

Additional computations carried out on cyclopropane and ZnCl₂ at different values of the distance R between the middle point of the C–C bond and the metal atom have pointed out that the m_2 complex can form without any barrier from the two product molecules (cyclopropane and ZnCl₂). Along the path

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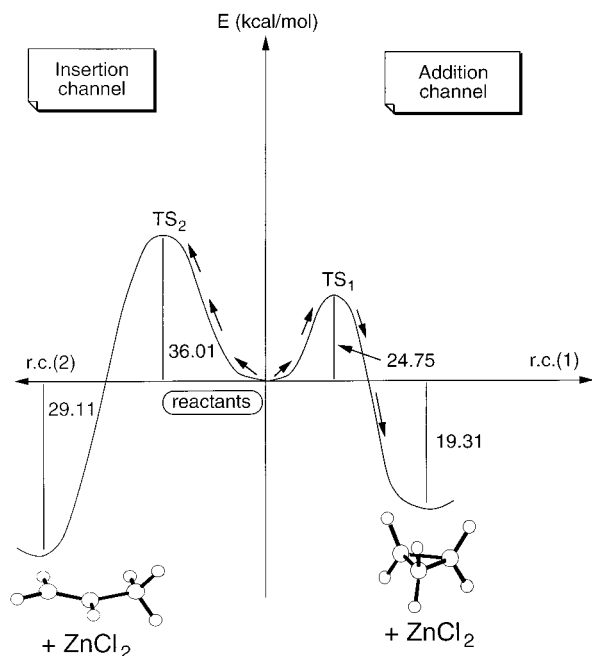


Figure 4. Schematic representation of the potential surface associated with the reaction between ethylene and ClCH_2ZnCl (r.c.(1): reaction coordinate for addition; r.c.(2): reaction coordinate for insertion).

connecting the two critical points (separated molecules and m_2) the reaction surface is initially very flat, then the energy decreases to reach the complex m_2 , which is $8.41 \text{ kcal mol}^{-1}$ below the asymptotic limit. However, it is important to point out that the existence of the m_2 product complex (and similarly m_1) is probably a shortcoming of the theoretical model that we have used and which neglects the solvent effect. These reactions are usually carried out in polar solvents (an ethereal solution is used in the original Simmons–Smith procedure and represents one of the most common environments where cyclopropanations are carried out) and in such a situation ZnCl_2 , as a Lewis acid, is most likely coordinated with solvent molecules. To roughly estimate the energetic effect of this coordination we have computed the energy of the complex that forms between ZnCl_2 and dimethyl ether. At the B3LYP/6-311G** level this complex, which is shown in Figure 5, is $19.34 \text{ kcal mol}^{-1}$ more stable than the separated molecules. In the same figure we have schematically compared the stabilization energies associated with the formation of both complexes, i.e. the complex between ZnCl_2 and $\text{O}(\text{CH}_3)_2$ and that between ZnCl_2 and cyclopropane (m_2). Since this stabilization is significantly larger in the former case, it is reasonable to assume that in a polar solvent ZnCl_2 preferentially coordinates a dimethyl ether molecule instead of a cyclopropane molecule.

B. Diabatic Model. The trend of the activation barriers in the comparison between the addition and insertion processes (larger activation energy found in the latter case) can be easily understood by means of a simple diabatic model based upon spin recoupling in VB theory.¹⁵ Within this model, at any point along the reaction coordinate, the total wave function can be represented to a good approximation (see eq 1) as a linear combination of two configurations Φ_R and Φ_P , which describe the electron coupling of reactants and products, respectively.

$$\Psi = a\Phi_R + b\Phi_P \quad (1)$$

At the beginning of the reaction, where Φ_R is much lower in

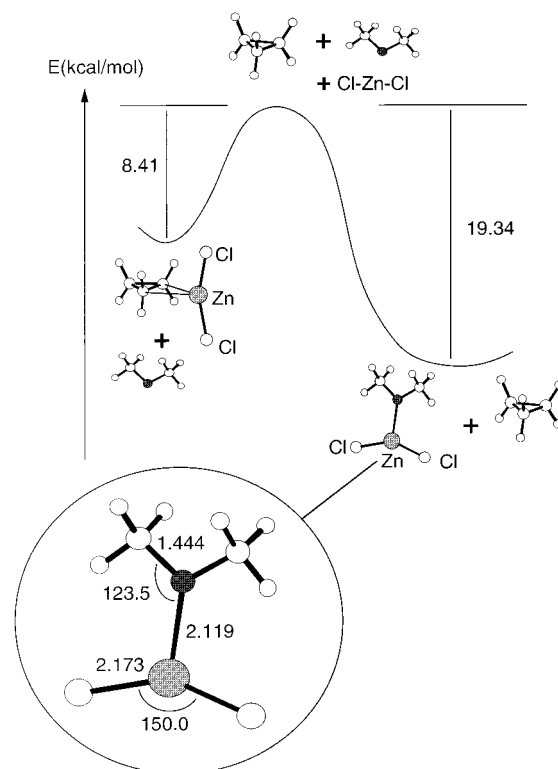


Figure 5. Schematic representation of the stabilization processes corresponding to the formation of the two complexes: cyclopropane– ZnCl_2 and $(\text{CH}_3)_2\text{O}-\text{ZnCl}_2$ (bond lengths are in angstroms and angles in degrees).

energy than Φ_P , Φ_R dominates ($a \gg b$). On going from reactants to products the energy gap between the two configurations decreases and in the transition state region the two configurations are almost degenerate: consequently the importance of Φ_R decreases and that of Φ_P increases. After the transition state region, as the reaction proceeds toward completion, Φ_P becomes lower in energy than Φ_R and dominates ($b \gg a$). Thus the variation of the relative importance of Φ_R and Φ_P describes the process of breaking covalent bonds and forming new bonds, which occurs in most organic reactions, and the change of the coupling scheme of the electrons involved in the bonds.

This process can be easily represented in a diagram where we report the energy of the reacting system versus the reaction coordinate. In this diagram the total energy profile is decomposed into two component curves: one, which is indicated as *reactant diabatic*, describes the energy behavior of the reactant configuration Φ_R (reactant spin coupling = reactant bonding situation) along the reaction coordinate; the other is denoted as *product diabatic* and describes the energy trend of the product configuration Φ_P (product spin coupling = product bonding situation). The reactant diabatic, on passing from reactants to products, is repulsive while the product diabatic is attractive. The crossing between the two diabatics determines the position of the transition state and the magnitude of the activation energy.

In Figure 6 we have represented the qualitative behavior of the two diabatics for the addition and insertion reactions. For the addition reaction the reactant diabatic corresponds to a situation where the two π electrons of the olefin bond are coupled to a singlet and the same happens for the two electrons of the C–Cl bond and the two electrons of the Zn–C bond (reactant configuration Φ_R). In the product diabatic each electron of the olefin π bond is singlet spin coupled with one of the two electrons of the CH_2 fragment to form the two C–C bonds of the cyclopropane product; furthermore, the two

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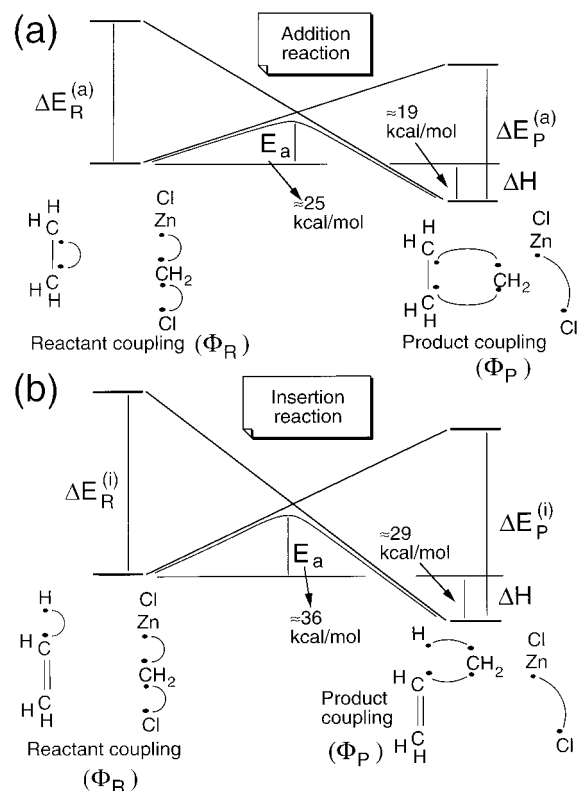


Figure 6. Correlation diagrams for addition (a) and insertion (b) in the reaction $\text{ClCH}_2\text{ZnCl} + \text{H}_2\text{C}=\text{CH}_2$.

electrons centered on the chlorine and metal atoms are coupled to a singlet to form a Zn–Cl bond in the ZnCl_2 fragment (product configuration Φ_P). The reactant and product configurations are schematically represented in the two coupling schemes reported at the bottom of Figure 6a. The insertion reaction is characterized by a similar coupling scheme where, instead of the two olefin π electrons, we must consider the two σ electrons associated with one of the C–H vinylic bonds (see the two coupling schemes reported at the bottom of Figure 6b).

In this type of diagram the position of the crossing, and consequently the size of the barrier, is determined by three factors: (i) the energy difference between the product diabatic at the product geometry and the reactant diabatic at the reactant geometry, which corresponds approximately to the reaction enthalpy (ΔH); (ii) the energy difference between the reactant and product diabatic at the reactant geometry (ΔE_R on the left side of the diagram); and (iii) the energy difference between the reactant and product diabatic at the product geometry (ΔE_P on the right side of the diagram).

ΔH can be estimated on the basis of the computed quantum-mechanical energy values of reactants and products: from Table 1 it is evident that this term is larger for insertion (29.11 kcal mol⁻¹) than for addition (19.31 kcal mol⁻¹). The evaluation of ΔE_R and ΔE_P is less obvious. ΔE_R represents the energy required for decoupling the three electron pairs associated with the Zn–C bond, the C–Cl bond, and the olefin π bond (addition) or, alternatively, the C–H σ bond (insertion) and can be evaluated to a good approximation from the energies of these breaking bonds. Since the contribution to ΔE_R arising from the ClCH_2ZnCl fragment is the same for the two reactions, the variation of ΔE_R on going from addition ($\Delta E_R^{(a)}$) to insertion ($\Delta E_R^{(i)}$) is determined by the difference between the energy of the olefin π bond and that of a vinylic C–H bond: since the former (about 60 kcal mol⁻¹)¹⁶ is much smaller than the latter

(about 108 kcal mol⁻¹),¹⁷ $\Delta E_R^{(i)}$ is larger than $\Delta E_R^{(a)}$. In a similar way we can evaluate the relative magnitude of $\Delta E_P^{(a)}$ and $\Delta E_P^{(i)}$, which represent the energy required for decoupling the electron-pair of the Zn–Cl bond in ZnCl_2 and the two electron-pairs of the two new C–C bonds in cyclopropane (addition) or the two new C–C and C–H bonds in propene (insertion). In the comparison between $\Delta E_P^{(a)}$ and $\Delta E_P^{(i)}$ we can again neglect the contribution arising from the Zn–Cl bond in ZnCl_2 since it is the same for addition and insertion. Thus to determine the trend of ΔE_P we can compare the energies of the two new C–C bonds in cyclopropane (about 54 kcal mol⁻¹)¹⁸ to the energies of the new C–C and C–H bonds in propene (97 and 98 kcal mol⁻¹, respectively)¹⁷. These values indicate that ΔE_P must increase significantly on going from addition to insertion ($\Delta E_P^{(i)} > \Delta E_P^{(a)}$).

While the effect of the change of ΔH on going from addition to insertion is that of decreasing the energy barrier, the effect of the variation of both ΔE_R and ΔE_P is opposite and dominant: the final overall effect of the simultaneous variation of ΔH , ΔE_R , and ΔE_P is a smaller energy barrier, which characterizes the addition process. It is interesting to point out that the preference for addition with respect to insertion cannot be easily rationalized in terms of the Hammond postulate since the former reaction is significantly less exothermic than the latter. This represents a further example of the better performance of the diabatic model where not only the reaction enthalpies but also other factors such as the energies of the forming and breaking bonds (ΔE_R and ΔE_P) are taken into account to determine the position of the transition state and the entity of the barrier.

Another interesting aspect concerning this class of reactions is the comparison between the Simmons–Smith cyclopropanation and the reaction of singlet methylene ¹CH₂ with olefins. It is well-known that the insertion of singlet carbenes into vinylic C–H bonds can compete with the addition process, although the latter is faster.¹⁹ This competition has been theoretically explained by the fact that no energy barrier is found for the addition process while the insertion process is characterized by a small barrier that seems to disappear when the electron correlation is included in the computations.²⁰ We shall now demonstrate that the different reactivity pattern observed for singlet carbenes when compared to carbenoid species such as ClCH_2ZnCl can also be easily predicted on the basis of a diabatic model. To this purpose we have represented in Figure 7 the qualitative behavior of the reactant and product diabatals for the addition and insertion reactions for the model system formed by ethylene and singlet CH₂. The reactant diabatic is characterized by a singlet spin coupling between the two π electrons of the olefin bond and by a singlet coupling between the two electrons of the methylene moiety. In the case of addition in the product diabatic each electron of the olefin π bond is singlet spin-coupled with one of the two electrons of the CH₂ fragment to form the two new C–C bonds of cyclopropane. As pointed out for the Simmons–Smith reaction, the product coupling scheme for insertion is obtained by replacing the two olefin π electrons with the two σ electrons associated with one of the vinylic C–H bonds: the reactant and product configurations Φ_R and Φ_P for addition and insertion are schematically

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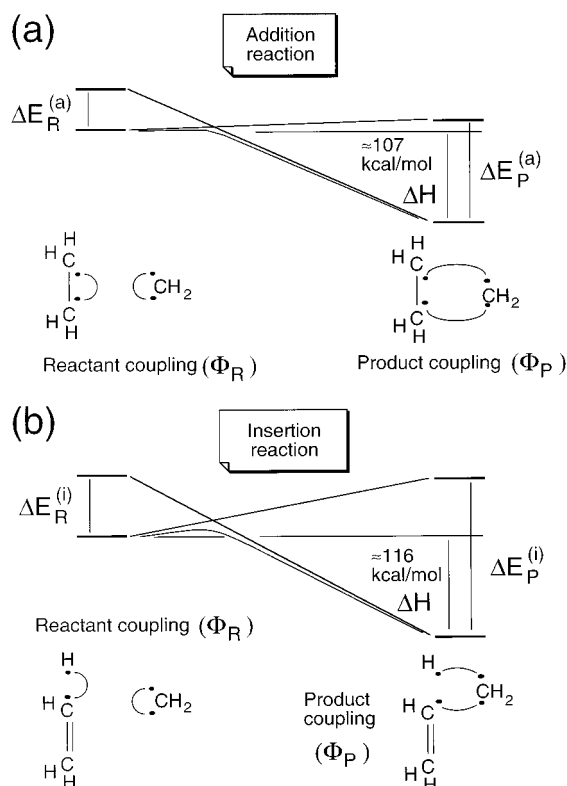


Figure 7. Correlation diagrams for addition (a) and insertion (b) in the reaction $^1\text{CH}_2 + \text{H}_2\text{C}=\text{CH}_2$.

represented by the two coupling schemes at the bottom of parts a and b of Figure 7, respectively. Also here we can estimate the trend of the two quantities ΔE_R and ΔE_P on going from addition to insertion on the basis of the energies of the breaking and forming bonds and ΔH from the total energies of reactants and products.

The most significant differences found in comparing the diabatic diagrams of Figure 7 with those previously discussed for the Simmons–Smith reaction (Figure 6) are the following: (i) ΔH becomes much larger (cyclopropane and propene are 107.7 and 116.5 kcal mol⁻¹ lower in energy than ethylene + singlet methylene respectively as obtained at the B3LYP/6-311G** level). (ii) ΔE_R and ΔE_P become smaller and less important, this being due to the fact that in the reaction between $^1\text{CH}_2$ and ethylene these quantities do not involve the breaking of the C–Cl, C–Zn, and Zn–Cl bonds. Furthermore, the small and negative contribution associated with the decoupling of the two electrons on methylene, which corresponds approximately to the singlet/triplet energy gap for this species, makes ΔE_R

even smaller (for CH_2 the triplet is the ground state, which is about 12 kcal mol⁻¹ lower in energy than the singlet²¹). Thus in this case the key factor that determines the overall trend is mainly the exothermicity of the reaction ΔH : this factor makes the barrier negligible in the case of addition and very small in the case of insertion.

Conclusion

In this paper we have studied, using a DFT (B3LYP) approach, the potential energy surface for the reaction between ethylene and (chloromethyl)zinc chloride which represents a model system for the Simmons–Smith cyclopropanation reaction. We have found that two reaction channels exist: one leading to the cyclopropane product (addition) and the other leading to the propene product (insertion). Since in the former case the energy barrier (24.75 kcal mol⁻¹) is significantly smaller than in the latter (36.01 kcal mol⁻¹), the addition process is favored and the competition of insertion is negligible as found experimentally. We have also demonstrated that the addition transition state corresponds to a three-centered structure similar to that originally suggested by Simmons. This cyclic structure explains the stereochemical features which have been experimentally observed for this reaction.

The two complexes m_1 and m_2 located on the reaction surface, and which form without any barrier, can be considered a shortcoming of our theoretical model, which neglects the presence of the solvent molecules. In a polar solvent (for example an ethereal solution) a Lewis acid such as ZnCl_2 will coordinate with one or more ether molecules which provide a larger stabilization energy (as shown by the calculations on the complex between ZnCl_2 and $\text{O}(\text{CH}_3)_2$).

We have also demonstrated that our results (addition favored versus insertion for the Simmons–Smith cyclopropanation) and the different reactivity pattern observed for the reaction of carbenes with olefins (competition between addition and insertion) can be easily rationalized by using a simple diabatic model. The diabatic analysis has pointed out that the variation of the energies of the bonds being broken and formed on passing from the addition (C–C π bond and C–C cyclopropane bonds) to the insertion (C–H bonds and C–C σ bond) and not the reaction enthalpies (ΔH) is the key factor that makes the addition much faster when carbenoid species are used as cyclopropanating reagents. In the case of the reaction involving $^1\text{CH}_2$ and ethylene the high exothermicities of both addition and insertion are mainly responsible for the very low or non-existent energy barriers of these reactions.

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