DFT Study of the Palladium-Catalyzed Cyclopropanation Reaction

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The palladium-catalyzed cyclopropanation of olefins has been investigated at the DFT-(B3LYP) computational level. The model system is formed by an ethylene molecule and the active catalytic species, which forms from a CH_2 fragment and the $Cl_2Pd(PH_3)_2$ complex. The results can be summarized as follows: (i) The active catalytic species is not a metal-carbene of the type $(PH_3)_2Cl_2Pd{=}CH_2$, as commonly assumed, but a carbenoid complex which can exist in two almost degenerate forms, $(PH_3)_2Pd(CH_2Cl)Cl$ and $(PH_3)Cl_2Pd(CH_2PH_3)$. (ii) The cyclopropanation can proceed either along concerted or multistep reaction pathways. (iii) The nonconcerted paths involve the formation of palladacyclobutane intermediates as indicated by the experimental evidence. (iv) The stereochemical outcome expected on the basis of the model system used here is in agreement with the experimental results (retention of the olefin configuration). (v) Sterically less hindered cyclopropane products should be favored when bulky groups are involved on the olefin and carbenoid moieties.

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Introduction

The cyclopropanation reaction catalyzed by transition metals, which can be formally defined as a [2+1] cycloaddition between a carbene-type species and an alkene, represents an important synthetic tool to obtain cyclopropane rings.[1] Since this three-membered cycle can be found in a variety of systems of chemical and biological interest, this reaction has stimulated various experimental studies with the purpose of understanding the mechanistic aspects and of developing new synthetic methods.[2,3]

The Simmons−Smith reaction, for instance, has been known for many years and represents a very useful and well-documented process to synthesize cyclopropane rings from simple alkyl-substituted olefins using diiodomethane in the presence of Cu/Zn.[1b,4] This reaction is proposed to proceed through a concerted transition state where a carbene unit is transferred to the alkene moiety from the carbenoid species (iodomethyl)zinc iodide, ICHR−ZnI, which represents the active catalytic species.

More recently, diazo compounds have been efficiently used in the presence of Cu, Pd, Ni, or Rh catalysts to generate transient organometallic species containing the carbene unit. Transfer of the carbene unit to an olefin bond affords the cyclopropane product. As pointed out in many reviews,[1,2] the reactivity of the carbenic carbon is significantly affected by the nature of the metal that determines the chemoselectivity of the active complex toward different classes of olefins.

The active species containing the carbene unit and obtained from the catalytic decomposition of diazo compounds by transition metal complexes is usually assumed to be a metal-carbene of the form

$$[L_nM{=}CR_2 \leftrightarrow L_nM^{-}{-}C^{+}R_2] \qquad (1)$$

This hypothesis is supported by some interesting, even not conclusive, experimental evidence such as carbene dimer formation and chirality transfer observed in cyclopropanation reactions.[1a] Furthermore various ruthenium alkylidene species of the type $(PR_3)_2Cl_2$-$Ru{=}CHR'$ have been isolated by Schwab and co-workers[5] and Grunwald and co-workers,[6] and some of these compounds have also been characterized by X-ray crystal structure analyses. However, other experimental results suggest that the active species could be a carbenoid derivative similar to that proposed for the

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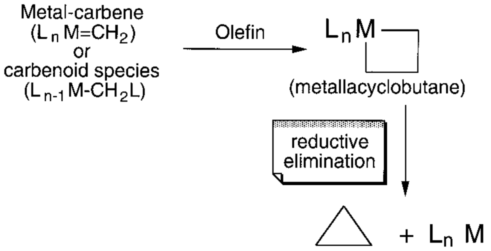
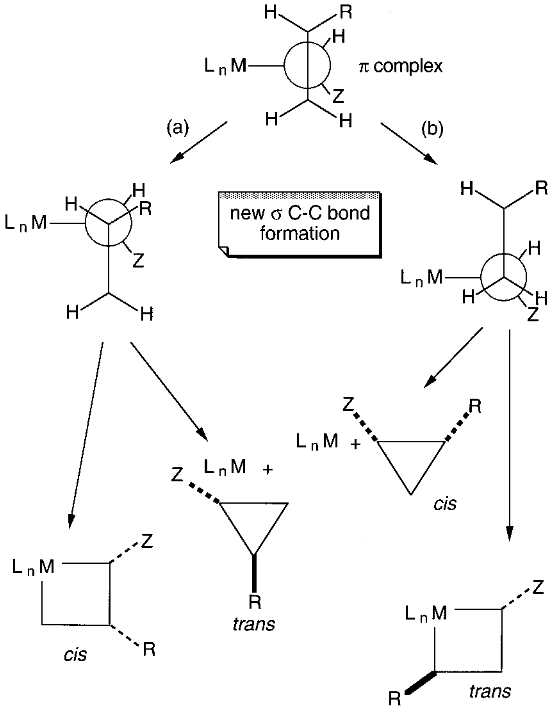
Scheme 1



Scheme 2



Simmons–Smith reaction. This carbenoid species can be considered to be the insertion product that is obtained by decomposition of diazocompounds in the presence of transition metal derivatives (eq 2).

$$L_n{-}M{-}X + RR'CN_2 \rightarrow L_n{-}M{-}CRR'{-}X + N_2 \; (L = \text{ligand}, X = \text{halogen}) \quad (2)$$

Insertion reactions of this type have been reported for M–H, M–N, and M–X (X = Cl, Br, I) bonds with simple diazocompounds, and quite recently McCrindle and coworkers have also isolated α-halogenomethyl derivatives of palladium and platinum and for the two complexes $(PPh_3)_2Pd(CH_2Cl)Cl$ and $(PPh_3)_2Pt(CH_2Cl)Cl$ they have studied in detail the X-ray structures.[7]

Different types of mechanisms have been proposed to explain the stereochemical outcome that depends on the metal used as a catalyst and on the size of substituents on both olefin and carbene. A mechanism involving the formation of metallacyclobutane as a reactive intermediate has been suggested in a number of papers.[2g,i] Following this hypothesis, the metallacyclobutane leads to the cyclopropane product by reductive elimination, which is expected to be a fast process (see Scheme 1). Even if this hypothesis, in a study of the cyclopropanation catalyzed by $(CO)_5WCHPh$, has been rejected by Casey[2b] as the sole explanation for the observed stereochemical preferences, quite recently Hoffman and coworkers[2i] prepared and isolated palladacyclobutane from (η^3-allyl)palladium complexes. These authors demonstrated the involvement of metallacycles in the cyclopropanation by a full characterization (NMR and crystal structure) of both palladacyclobutane and products.

A different mechanism was proposed by Doyle,[2e] who invoked an initial π complex between the olefin bond and the electrophilic carbene carbon followed by the formation of a new σ C–C bond (see Scheme 2). Displacement of the metal catalyst leads to cyclopropane formation. Within this model the stabilization of the developing electrophilic center by the electron-donating substituent R determines the motion of the alkene relative to the electrophilic carbon center of the reacting carbene (routes a and b in Scheme 2) and the stereochemistry of the products. Alternatively a metallacycle can be obtained. In this case the *trans*-cyclopropane isomer becomes the dominant product, as the steric hindrance of the R group increases. Other authors have suggested a concerted mechanism involving a multicentered transition state. This type of mechanistic explanation is particularly interesting in the case of Pd-catalysis, which is characterized by a stereochemical retention of the olefin fragment.[2a] Also, experimental studies of Pd-catalyzed cyclopropanations[2d] have shown that the increase of the steric bulk of the olefin substituents results in an enhancement of the relative amount of the sterically less hindered cyclopropane, which favors, at least for palladium, the metallacycle hypothesis.

Since the mechanistic scenario is rather confused and, to our knowledge, no detailed and accurate theoretical studies are available in the literature, we have carried out a theoretical investigation at the DFT level of the cyclopropanation reaction catalyzed by Pd complexes. Our study has two aims: to shed light on (i) the mechanistic details of this important reaction (concerted or stepwise reaction pathway and structure of the possible active intermediates such as π complexes or metallacycles) and (ii) the nature of the active form of the catalyst (metalcarbene, as commonly assumed, or carbenoid species such as that involved in the Simmons–Smith reaction). To this purpose, we have chosen as a model system an ethylene molecule reacting with the active species which forms from a $Cl_2Pd(PH_3)_2$ complex and the CH_2 fragment obtained after decomposition of diazomethane. $Cl_2Pd(PH_3)_2$ emulates the $Cl_2Pd(PPh_3)_2$ complex usually involved in the real experimental system.

Computational Procedure

All the DFT computations reported here have been performed with the Gaussian 98[8] series of programs using the nonlocal hybrid Becke's three-parameter exchange functional[9] denoted as B3LYP. The geometry of the various critical points on the reaction surface has been fully optimized with the gradient method available in Gaussian 98 using the DZVP basis set,[10] which is a local spin density (LSD)-optimized basis set of double-ζ quality in the valence shell plus polarization functions. A computation of the harmonic vibrational frequencies has been carried out to determine the nature of each critical point. To obtain more accurate energy values, single-

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point computations have been performed on the DZVP-optimized geometry using the 6-311G* basis set[11] on all atoms except palladium. The metal has been described by the energy-adjusted pseudopotential basis set proposed by Preuss and coworkers[12] (denoted as sdd pseudopotentials in the Gaussian 98 formalism). The zero-point energy (ZPE) values obtained from the frequency computations at the DZVP level have been included in the energy computations at the 6-311G* level.

To roughly evaluate the effect of the solvent, in some cases we carried out single-point computations on the gas-phase optimized structures using the polarized continuous model (PCM)[13] method available in Gaussian 98.

Results and Discussion

A. Structure of the Active Species. To investigate the nature of the active complex containing the carbene moiety (active form of the catalyst), we have compared the structure of the carbenoid species to that of the corresponding metal-carbenes (see also ref 14). This comparison has been carried out for three different situations, which differ in the number of phosphine ligands involved in the complex. The results (energies and structures) have been schematically reported in Figure 1. It is evident from the figure that, for a given number of phosphine ligands, the most stable species is always characterized by a carbenoid structure of the type [L]−Pd−CH_2−X, where [L] denotes the metal ligands and X = PH_3, Cl. The relative stability of the carbenoid-type complexes is also reported in the figure. The most stable species is a carbenoid involving two phosphines, one bonded to the metal and the other to the carbon (diphosphine carbenoid A). Another carbenoid species involving two phosphines (diphosphine carbenoid B) also exists. In this complex, which is slightly less stable than A (about 2.2 kcal mol^{-1} higher in energy), both phosphine ligands are bonded to the metal and a chlorine atom is bonded to the carbon atom. It is interesting to point out that both carbenoid species A and B are very similar to the carbenoid that has been demonstrated to be the active species in the Simmons−Smith cyclopropanation reaction.[4e]

The relevant structural features of the two carbenoids A and B are shown in Figure 1. Both complexes are square-planar and are characterized by a plane of symmetry (C_s symmetry). In A this plane contains the metal, the carbon, and the two phosphorus atoms, while in B the plane of symmetry is the plane defined by the metal, the methylene carbon, and the two chlorine atoms. The reliability of this model system, where the PH_3 groups are used to emulate the PR_3 ligands (R = Ph, *t*-Bu) of the real catalyst, has been checked elsewhere.[14] In that paper the authors have considered the complex $Cl_2(PMe_3)_2PdCH_2$, where the PMe_3 ligands better emulate the more cumbersome groups used in the experiment. It was demonstrated that the inclusion of the bulkier ligands leaves almost unchanged the thermodynamics of the carbene−carbenoid equilibrium (the difference between the two forms becomes 45.32 kcal mol^{-1}).

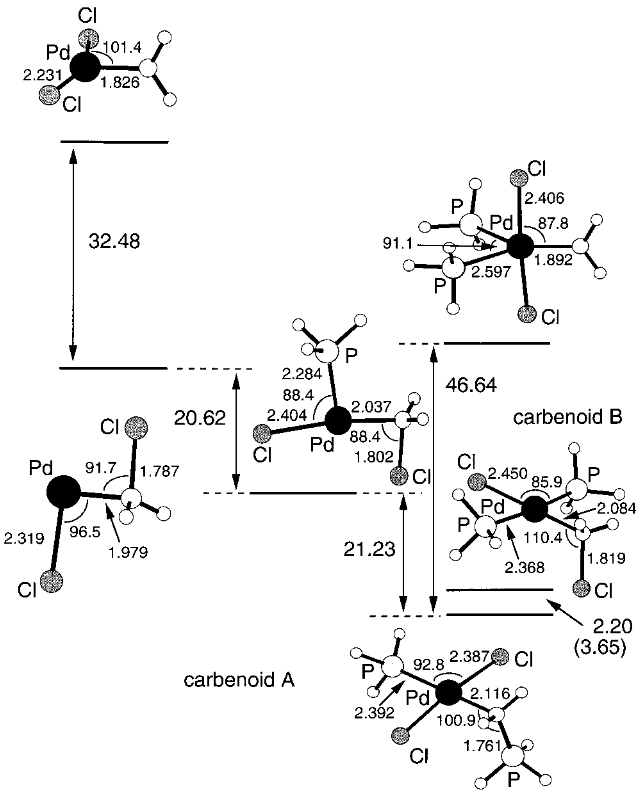

Figure 1. Schematic representation of the metal-carbene and carbenoid species for three different situations, which differ in the number of phosphine ligands (bond lengths are in Å and angles in deg). The relative energy values (kcal mol^{-1}) of the various species, computed with the 6-311G* basis (sdd on Pd), are reported. The value in parentheses includes the solvent effect ($\epsilon = 8.93$).

It is interesting to point out that, even if the structures of the two forms A and B are quite similar, the electronic situation and the origin of the various bonds in the two species are significantly different. In A two electrons on the metal are coupled with one electron on each chlorine atom to form two σ Pd−Cl bonds. The bond between the metal and the phosphorus atom can be described as a donation of the PH_3 lone-pair to the metal and a back-donation from the metal to the empty 3d orbitals of the ligand. The Pd−C bond is due to a donation of the σ electrons of the methylene moiety in the singlet state to the metal, while the C−P bond can be associated with a donation of the phosphorus lone-pair to the CH_2 empty orbital. In B two electrons on the metal are each coupled to one electron on the chlorine atom and to one electron on the CH_2 moiety to

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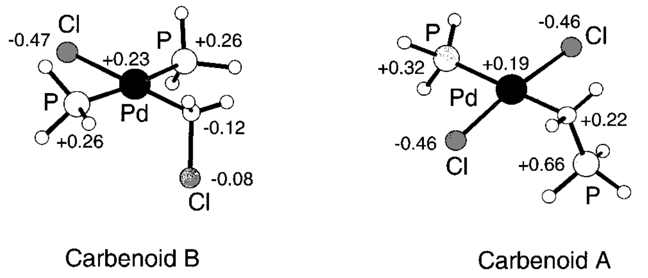
Scheme 3



form a σ Pd−Cl bond and a Pd−C bond, respectively. The CH$_2$ fragment is here in a triplet state, and the second of the two unpaired electrons is coupled to one electron on the other chlorine atom to create the C−Cl σ bond. Finally the two Pd−P bonds both originate from a donation of the PH$_3$ lone-pair to the metal and a back-donation from the metal to the empty orbitals of the ligand. The net charges of the various atoms and groups of the two species A and B, reported in Scheme 3, are in agreement with the bonding scheme previously described. In both A and B the PH$_3$ ligands bonded to the metal have similar positive charges (+0.32 and +0.26 in A and B, respectively); these values are consistent with the donation/back-donation mechanism which describes the Pd−P bond formation. The chlorine atoms bonded to the metal have in both cases a significant negative charge, in agreement with the polarization of the σ Pd−Cl bond. Also, it is interesting to observe that the charge of the CH$_2$ moiety is significantly different in the two species: +0.22 in A and −0.12 in B. The positive charge in the former case is a consequence of the donation of the σ electrons of the singlet CH$_2$ fragment to the metal, while the negative charge in the latter case is due to the polarization of the Pd−C bond.

The energy of the two carbenoids A and B has also been computed in the presence of the solvent effect. The solvent that has been emulated in the computations is CH$_2$Cl$_2$ (dielectric constant $\epsilon = 8.93$), which is the solvent commonly used in the experiment. The relative energies of the two species, reported in parentheses in Figure 1, show that in the presence of the solvent carbenoid A remains more stable than carbenoid B and the energy difference does not change significantly, becoming 3.65 kcal mol^{-1}.

The computed relative energies of the various metal-carbene and carbenoid complexes, obtained either in the gas phase or in the presence of the solvent, indicate that both A and B are possible active species for the cyclopropanation reaction. For this reason all reaction paths that originate from both complexes have been carefully investigated. The results are presented and discussed in the following section.

B. Cyclopropanation Reaction Paths: Concerted Direct Cyclopropanation or Multistep Reductive Elimination? In this section we discuss the singlet potential energy surface (PES) associated with the reaction between one ethylene molecule and the two possible active forms of the catalyst. For both carbenoids A and B we have found that a concerted reaction path exists leading to the cyclopropane product (path A1 and path B1). A schematic representation of the structures corresponding to the critical points located along the two paths, with the values of the relative energies, is given in Figure 2 (in the figure we have also indicated how the various structures are connected on the PES). In both cases the transition state (TS$_1$ along A1 and TS$_2$ along B1) describes the addition of the methylene fragment to the C−C double bond and corresponds to a three-centered structure very similar to that recently found in a theoretical study of the Simmons−Smith cyclopropanation reaction.[4f] In these structures the C−C olefin bond is only slightly longer (1.351 and 1.350 Å) than in free ethylene (1.337 Å) and the two new C−C bonds are far from being formed: 2.310 and 2.422 Å in TS$_1$ and 2.387 and 2.569 Å in TS$_2$. This indicates that both TS$_1$ and TS$_2$ are quite early transition states. Also, no significant lengthening of the Pd−C bond is observed on passing from the carbenoid reactant to the transition state. However, in both transition structures, as a consequence of the incoming ethylene, one of the two PH$_3$ ligands is moving away from the carbon and from the metal coordination sphere. In TS$_1$ the transfer of the methylene moiety to the ethylene molecule directly causes the breaking of the P−C bond and the removal of the corresponding PH$_3$ group. In TS$_2$ the loss of PH$_3$ is a consequence of the migration of the chlorine from the methylene carbon to the palladium atom. The first product encountered along both pathways is a complex (M$_1$) between the almost completely formed cyclopro-

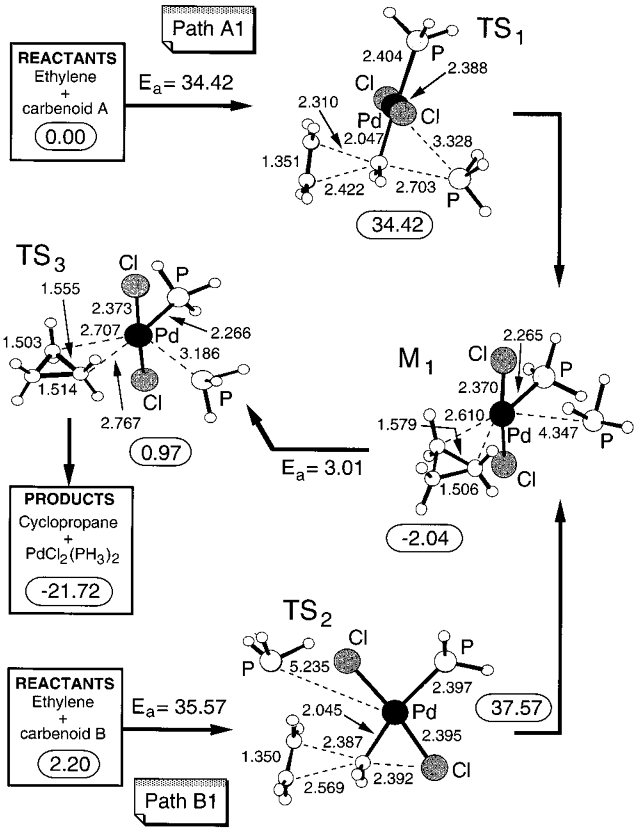


Figure 2. Schematic representation of the structures found along path A1 and path B1 (bond lengths are in Å and angles in deg). The energy values (kcal mol^{-1}) relative to reactants (carbenoid A + ethylene) and the activation energies E_a are reported. The absolute energy of reactants, computed with the 6-311G* basis (sdd on Pd), is −1852.72596 au. The corresponding ZPE correction is 85.47 kcal mol^{-1}.

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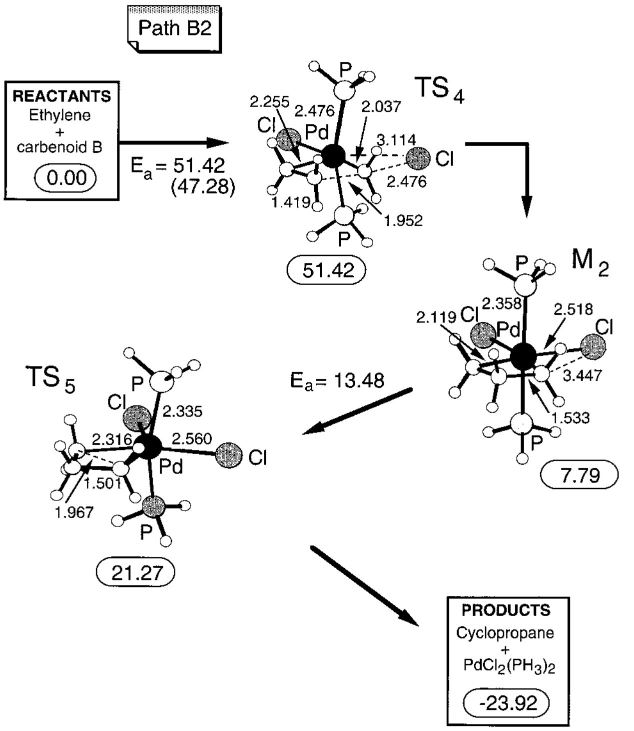

Figure 3. Schematic representation of the structures found along path B2 (bond lengths are in Å and angles in deg). The energy values (kcal mol^{-1}) relative to reactants (carbenoid B + ethylene) and the activation energies E_a are reported. The absolute energy of reactants, computed with the 6-311G* basis (sdd on Pd), is −1852.72164 au. The corresponding ZPE correction is 84.97 kcal mol^{-1}. The value in parentheses includes the solvent effect ($\epsilon = 8.93$).

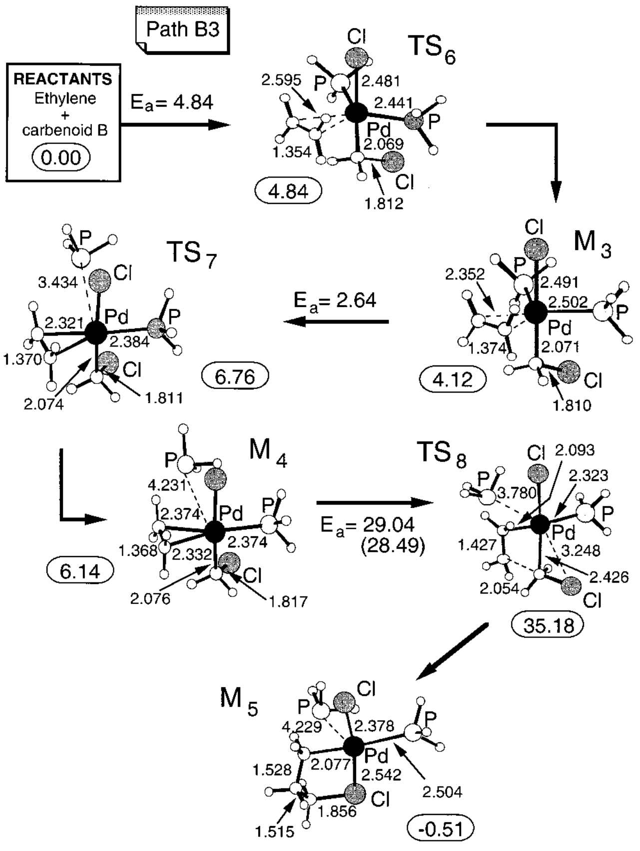

Figure 4. Schematic representation of the structures found along path B3: reactants → M_5 (bond lengths are in Å and angles in deg). The energy values (kcal mol^{-1}) relative to reactants (carbenoid B + ethylene) and the activation energies E_a are reported. The value in parentheses includes the solvent effect ($\epsilon = 8.93$).

pane molecule and the $PdCl_2(PH_3)_2$ fragment, where one PH_3 ligand is only weakly interacting with the metal (the Pd−P distance is 4.347 Å). However it is interesting to point out that in M_1 the Pd−P distance is becoming shorter (compare, for instance, 4.347 Å in M_1 to 5.235 Å in TS_2), suggesting that the phosphine group is now gradually increasing its interaction with the metal again. An additional transition state, TS_3, leads from M_1 to the final cyclopropane product. In TS_3 the Pd−P distance further decreases (3.186 Å) and the Pd−C distances further increase (2.767 and 2.707 Å) to afford the cyclopropane molecule and a $PdCl_2(PH_3)_2$ complex, which enters a new catalytic cycle. The two activation energies (E_a) computed for TS_1 and TS_2 are quite similar. In the former case (carbenoid A) a barrier of 34.42 kcal mol^{-1} must be overcome to afford the first product, M_1, which is 2.04 kcal mol^{-1} lower than reactants. In the latter case (carbenoid B) these two values become 35.57 and 4.24 kcal mol^{-1}, respectively. Finally a small barrier of 3.01 kcal mol^{-1} (TS_3) is required to reach the final product (cyclopropane + $PdCl_2(PH_3)_2$), which is 21.72 kcal mol^{-1} more stable than carbenoid A and 23.92 kcal mol^{-1} more stable than carbenoid B.

Two additional pathways leading to cyclopropane have been found for carbenoid B. These paths involve the formation of two different isomeric forms of the palladacyclobutane intermediate. Both isomers lead to cyclopropane through a reductive elimination process. The first path (path B2 schematically represented in Figure 3) corresponds to an attack of the ethylene molecule in the plane containing the two chlorine atoms, the palladium, and the carbon atom. In the corresponding transition state (TS_4) a new forming C−C bond between the methylene unit and one of the ethylene carbons can be detected (this new C−C bond is 1.952 Å). As a consequence of the incipient C−C single bond, the ethylene bond is losing its double bond character (it becomes 1.419 Å) and the chlorine atom is migrating from the methylene carbon to the metal atom. TS_4 leads to a palladacyclobutane intermediate M_2, characterized by C_{2v} symmetry, with the three carbon atoms, the metal, and the two chlorine ligands lying in the same plane. A second transition state (TS_5) leads from this intermediate to cyclopropane through the elimination of the $PdCl_2(PH_3)_2$ fragment (reductive elimination). In TS_5 the length of the two breaking C−Pd bonds is 2.316 Å, while the new forming C−C bond (required to complete the cyclic structure) is 1.967 Å. However, as reported in the figure, the activation energy of the rate-determining step for path B2 is very high (about 51.4 kcal mol^{-1}). Thus, even if the subsequent transformation from the palladacyclobutane to the products requires a much smaller energy (about 13.5 kcal mol^{-1}), the overall process is unlikely on energy grounds.

More interesting from the energetic point of view is the second reaction path found for carbenoid B (path B3 schematically represented in Figures 4 and 5), where the ethylene molecule approaches the carbenoid complex B along a direction that belongs to the P−Pd−P plane.

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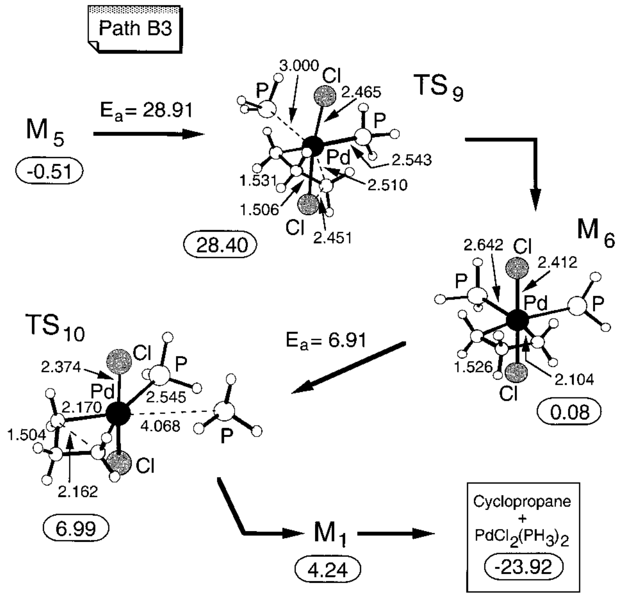

Figure 5. Schematic representation of the structures found along path B3: $M_5 \rightarrow$ cyclopropane (bond lengths are in Å and angles in deg). The energy values (kcal mol^{-1}) relative to reactants (carbenoid B + ethylene) and the activation energies E_a are reported.

In this case the formation of the palladacyclobutane intermediate is a more complex process involving four subsequent steps. A first step, characterized by an activation barrier of 4.84 kcal mol^{-1}, leads to the formation of a preliminary π complex (M_3), where the ethylene molecule weakly interacts with the metal atom. This interaction causes a lengthening of the Pd$-$P and Pd$-$Cl bonds with respect to the isolated carbenoid species (from 2.450 to 2.502 Å and from 2.387 to 2.491 Å, respectively). A stronger interaction between ethylene and palladium leads to the formation of a new complex, M_4, where one of the two phosphine ligands is being expelled from the metal coordination sphere (one of the Pd$-$P distances is now 4.231 Å, while the other Pd$-$P distance has become shorter, i.e., 2.374 Å). The barrier that must be overcome to pass from M_3 to M_4 is very small, i.e., only 2.64 kcal mol^{-1}. A much higher barrier (about 29 kcal mol^{-1}) is required to transform M_4 to a new intermediate M_5 that corresponds to a loose five-membered cycle with a bridged chlorine between the metal and the methylene group. This step can be considered as an insertion reaction of the ethylene molecule into the Pd$-$C bond. It is interesting to note that in M_5 the leaving phosophine ligand is still weakly interacting with the metal atom, the Pd$-$ P distance being 4.229 Å. A further rearrangement of the M_5 intermediate (breaking of the C$-$Cl bond and formation of a new Pd$-$C bond as described by transition state TS_9 represented in Figure 5) leads, after overcoming a barrier of 28.9 kcal mol^{-1}, to the formation of the palladacyclobutane intermediate M_6. M_6 is an isomer of the previously described palladacyclobutane M_2. It has C_{2v} symmetry, but the two chlorine atoms are now in axial positions. A reductive elimination with an activation energy of 6.91 kcal mol^{-1} leads to the formation of the final weak complex between cyclopropane and the $PdCl_2(PH_3)_2$ fragment (M_1 already discussed in Figure 2).

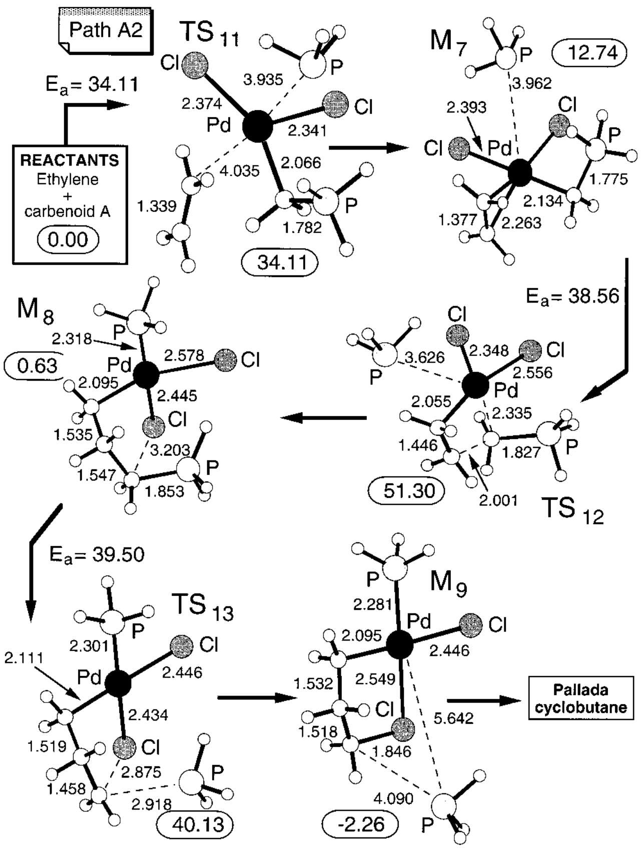

Figure 6. Schematic representation of the structures found along path A2 (bond lengths are in Å and angles in deg). The energy values (kcal mol^{-1}) relative to reactants (carbenoid A + ethylene) and the activation energies E_a are reported.

To obtain a more reliable estimate of the relative importance of the two paths B2 and B3, we have evaluated the effect of the solvent on the two activation energies associated with TS_4 (path B2) and TS_8 (path B3). The two barriers do not change significantly with respect to the gas-phase values, becoming 47.28 kcal mol^{-1} in the former case and 28.49 kcal mol^{-1} in the latter. Thus, even in the presence of the solvent, the reaction pathway involving TS_4 remains unlikely on energy ground.

A similar reaction pathway (path A2) has been determined for carbenoid A (see Figure 6). This path, however, does not involve a preliminary π complex, but leads directly to the formation of the complex M_7 (similar to complex M_4 located along path B3), where one of the two PH_3 ligands is replaced by the ethylene molecule. In M_7 also, as observed for M_4, the phosphine ligand that is expelled is still weakly interacting with the metal atom (P$-$Pd = 3.962 Å). However M_7 is significantly higher in energy than M_4 and, while M_4 forms easily, a quite large barrier (34.11 kcal mol^{-1}) must be overcome to obtain M_7 (transition state TS_{11}). To obtain more accurate information on this reaction channel, a computation of the intrinsic reaction coordinate (IRC), starting from TS_{11} in both the product and reactant directions, has been carried out. This computation has demonstrated that TS_{11} is connected directly to reactants (carbenoid A + ethylene) and to the intermediate M_7 and no π complex is involved. Two more barriers, one associated with transition state TS_{12} (38.56

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kcal mol^{-1}) and the other with transition state TS_{13} (39.50 kcal mol^{-1}), are required to reach complex M_9. This intermediate has a cyclic structure (resembling that of M_5, path B3), where a bridging chlorine atom is bonded simultaneously to a carbon atom and to the metal atom. The process that leads from M_7 to M_9 is more complex than the process connecting M_4 to M_5. Here, in the first step of the transformation ($M_7 \rightarrow TS_{12} \rightarrow M_8$), the methylene group migrates from the metal to one of the ethylene carbon atoms which moves away from the Pd atom. This new arrangement allows the weakly interacting PH_3 ligand to enter again the palladium coordination sphere (complex M_8). In the second step ($M_8 \rightarrow TS_{13} \rightarrow M_9$) the chlorine atom forms a new bond with the carbon to build the cycle and causes the removal of the second PH_3 group. A final transformation leads to a palladacyclobutane and to the final products by reductive elimination.

Two interesting points must be stressed. (i) The complex structural rearrangement needed to obtain M_9 from M_7 is a consequence of the initial position of the chlorine atom, which, first, must come closer to the methylene carbon and, then, replace the PH_3 group. Such a complicated structural modification is not required in the transformation $M_4 \rightarrow M_5$, since in M_4 the Cl atom is already bonded to the methylene carbon. (ii) A cyclic structure such as M_5 or M_9 can form because the chlorine ligand, unlike the PH_3 group, after having formed a σ bond with one atom (for instance the carbon of the methylene unit), can use one of the lone-pairs to interact with another atom (the metal). Thus a simultaneous interaction with two atomic centers (carbon and palladium) becomes possible. The different nature of the two ligands Cl and PH_3 explains why for carbenoid A we have not found a reaction path similar to path B2. This type of reaction path requires a ligand that can simultaneously interact with the methylene group and the metal (see transition state TS_4 and intermediate M_2): this is possible only if a chlorine atom, and not the PH_3 group, is originally bonded to the CH_2 fragment, as it occurs in carbenoid B.

All these results indicate that, at least for the small model system considered here, path A2 seems to be less interesting from an energetic point of view than path B3. In the latter case the two relevant activation energies are 29.04 and 28.91 kcal mol^{-1}, while in the former three significant barriers (34.11, 38.56, and 39.50 kcal mol^{-1}) must be overcome to reach the products.

The mechanistic scenario that springs from these computational results is somewhat different from that proposed by Doyle and co-workers.[2e] The preliminary π complex that we have located is due to the interaction between the olefin and the metal and does not involve the electrophilic methylene carbon as suggested by Doyle to explain the stereochemical outcome of these reactions. Furthermore this π complex transforms to a palladacyclobutane species that should give, as a predominant product, the sterically less hindered cyclopropane, when cumbersome substituents are bonded to the olefin carbons or to the methylene carbon, in agreement with the experimental evidence. Also, it is important to point out that all the reaction pathways discussed in the previous section are in agreement with the experimentally observed retention of olefin configuration. This is obvious for the two concerted channels found for both carbenoids A and B (paths A1 and B1), where the two new C−C bonds are formed simultaneously. However a retention of the olefin configuration should also result from the analysis of the other reaction pathways, where no intermediates have been found that make possible a rotation around the C−C olefin bond when this loses its double bond character.

Conclusion

In this paper we have studied at the DFT (B3LYP) level the potential energy surface for the palladium-catalyzed cyclopropanation of olefins. To this purpose we have chosen as a model system an ethylene molecule reacting with the active catalytic species which forms from a CH_2 fragment and the $Cl_2Pd(PH_3)_2$ complex. The results of our computations are relevant since they have elucidated the nature of the active species and have provided a complete mechanistic scenario for these processes. In particular these results can be summarized as follows.

(i) The active catalytic species is not a metal-carbene of the type $(PH_3)_2Cl_2Pd{=}CH_2$, as commonly assumed, but a carbenoid complex that can exist in two almost degenerate forms, i.e., $(PH_3)_2Pd(CH_2Cl)Cl$ (carbenoid A) and $(PH_3)Cl_2Pd(CH_2PH_3)$ (carbenoid B). A metal-carbene species $(PH_3)_2Cl_2Pd{=}CH_2$ also exists, but its energy is about 47 kcal mol^{-1} higher than the carbenoid complexes.

(ii) For both carbenoids A and B we have demonstrated the existence of either concerted or multistep reaction paths, all leading to the cyclopropane ring formation.

(iii) The most likely reaction channels for cyclopropanation are the two concerted paths determined for the two carbenoid species (path A1 and B1 with a barrier of 34.42 and 35.57 kcal mol^{-1}, respectively) and a multistep pathway that originates from carbenoid B. This path is characterized by two activation barriers of about 29.0 and 28.4 kcal mol^{-1} (path B3). We have found that this nonconcerted path involves a preliminary π complex between the olefin and the metal and a metallacyclobutane intermediate. This mechanism, however, is somewhat different from that suggested by Doyle,[2e] where the proposed key interaction was that between the electrophilic carbene carbon of a metal-carbene species and the π double bond system. It is important to point out that the existence of palladacyclobutane intermediates along the reaction path agrees with the experimental results of several authors who demonstrated the involvement of metallacycles in the cyclopropanation processes.[2i]

(iv) The stereochemical outcome that can be expected from the various reaction paths is in agreement with the experimental evidence; that is, the original configuration of the olefin double bond should be maintained in all cases during the process. Furthermore the sterically less hindered cyclopropane product should be favored when bulky substituents are involved on the olefin and carbenoid moiety.

(v) The solvent effect, which mimics CH_2Cl_2, does not affect significantly either the relative stability of the two carbenoids A and B (active species) or the activation barriers. This finding indicates that the simple gas-phase model system used here is reliable to describe this class of catalyzed reactions.

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