Mechanism of Olefin Cyclopropanation by Diazomethane Catalyzed by Palladium Dicarboxylates. A Density Functional Study

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Abstract: The reaction of diazomethane with ethylene in the presence of palladium diformate has been studied through density funcional calculations. Several mechanistic paths leading to the formation of cyclopropane have been studied. The results obtained show that the reaction of palladium diformate with diazomethane is more favorable than the reaction with ethylene. The reaction with diazomethane may lead to two different isomeric complexes: a methylene-inserted complex and a palladium−carbene complex. Insertion of methylene is the most favorable process, but the resulting complex is not suitable for cyclopropanation. The reaction with two additional diazomethane molecules makes the formation of the bismethylene-inserted palladium−carbene complex favorable. Attack of ethylene on this palladium−carbene complex leads to the formation of cyclopropane.

Introduction

The reaction between diazoalkanes and olefinic substrates assisted by transition metal complexes is one of the most important protocols for the cyclopropanation of electron-deficient and electron-rich double bonds.[1−6] The parent diazocompound, diazomethane, has been employed as a source of methylene due to its easy dediazotization in the presence of many metal compounds. Among them, copper and palladium derivatives are the most usual and efficient agents for the reliable methylenation of olefins by diazomethane.[7−9]

Cyclopropanation of olefins with diazomethane catalyzed by palladium(II) acetate is a widely used synthetic method. However, the mechanistic pathway and the nature of the intermediates are not completely understood. It is currently assumed that the mechanism involves the formation of a palladium−carbene complex, resulting from the reaction between palladium(II) acetate and diazomethane, but there is no direct experimental evidence for the formation of these complexes. Nevertheless, their participation in the reactions is sustained by the existence of stable carbene complexes of other transition metals.[8] Moreover, the formation of carbene complex intermediates has been recently reported for the cyclopropanation with ethyl diazoacetate of enol ethers catalyzed by Cr(0) complexes[10] and of styrene catalyzed by Ru(II) complexes.[11]

The formation of palladium−carbene complexes competes with the generation of methylene-insertion derivatives. Thus, for instance, (chloromethyl)palladium(II) complexes are relatively stable compounds obtained from reaction of diazomethane with palladium(II) dichloride complexes containing chelating ligands such as olefins or phosphines.[12] These products result from carbene insertion into the metal−halogen bond.

In a recent theoretical study[13] of the complexes arising from the interaction between palladium diformate and methylene we have shown that palladium−carbene complexes are unstable with respect to methylene insertion in one of the Pd−O bonds. So, the effective formation of palladium−carbene complexes might be dubious.

The ability of palladium to coordinate olefins has led to the postulation of an alternative mechanism in which diazomethane attacks a previously coordinated olefin.[7] Whether the first step involves the reaction with diazomethane or with the olefin, cyclopropane formation requires a methylene transfer to the olefin. This process may take place through the formation of a metallacyclobutane followed by cyclopropane reductive elimination. These species have been observed for platinum in olefin metathesis and cyclopropanation.[14] The crystal structure of a pallada(II)cyclobutane has also been reported.[15]

In this paper, we present a theoretical study of the cyclopropanation of ethylene by diazomethane in the presence of palladium(II) diformate. We have considered several mechanistic routes to address the following points: (i) Which is the substrate, diazomethane or olefin, that interacts first with palladium; (ii) what is the role played in the mechanism by mehylene inserted complexes; and (iii) what is the mechanism of methylene

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transfer to the olefin? The results obtained have led us to postulate a mechanism in which palladium diformate reacts with two diazomethane molecules to form a bis-methylene inserted complex that would be the catalytic species. The reaction of additional diazomethane molecules with this species leads to the formation of an unstable palladium−carbene complex that reacts very fast with ethylene to yield cyclopropane.

Computational Details

Molecular geometries have been fully optimized at the generalized gradient approximation (GGA) level of calculation using Becke's[16] exchange potential and the correlation potential of Perdew and Wang[17] (BPW91) implemented in the Gaussian-98 program.[18] In these calculations we have used the effective core potentials of Hay and Wadt[19] for Pd. For the remaining atoms, we have used the D95 basis set[20] supplemented with a set of 3d polarization functions for C, N, and O. Harmonic vibrational frequencies have been computed for all stationary points at this level of calculation to characterize them as energy minima (all frequencies are real) or transition states (only one imaginary frequency). In specific cases, where the examination of this imaginary frequency did not allow the assignation of the transition state to the corresponding reactants and products, the intrinsic reaction coordinate (IRC) has been computed.[21]

For all the structures we have recalculated energies with the ADF program[22] using a larger basis set and including relativistic effects through the Zeroth Order Regular Approach (ZORA).[23] The inner electrons of Pd (up to 3d shell), C, N, and O have been treated within the frozen core approximation.[24] For the valence space the basis set V of the ADF database has been used. This is a triple-ζ basis set of uncontracted Slater-type orbitals supplemented with a set of 4f (Pd) 3d and 4f (C, N, and O), and 2p and 3d (H) polarization functions. All calculations have been done without taking into account solvent effects, so that all reported energies and Gibbs energies are gas-phase magnitudes.

Scheme 1

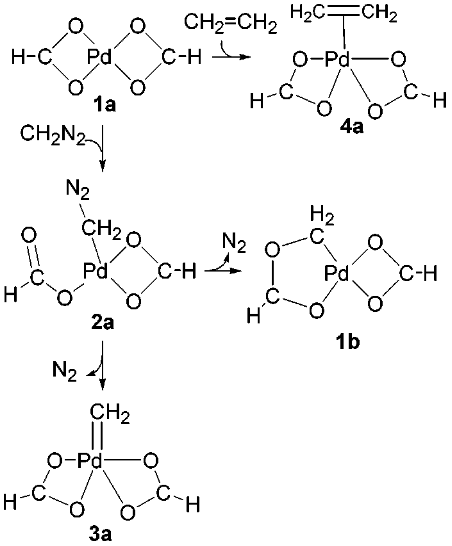

Table 1. Energies and Gibbs Energies[a] Relative to Reactants for the Stationary Points of the Reactions of **1a** with Diazomethane and Ethylene

stationary point[b]	ΔE	ΔG^0_{298}
1a + CH$_2$N$_2$		
TS(1a-2a)	0.8	10.0
2a	−17.2	−6.5
TS(2a-1b)	−10.4	−0.7
1b + N$_2$	−49.2	−46.9
TS(2a-3a)	−3.6	3.8
3a + N$_2$	−13.9	−14.5
1a + CH$_2$CH$_2$		
TS(1a-4a)	4.5	11.7
4a	−15.5	−3.7

[a] All values are given in kcal mol^{-1}. [b] See Scheme 1 and Figure 1.

Results and Discussion

We present in the first place the results corresponding to the competitive reactions of palladium diformate **1a** with diazomethane and ethylene (see Scheme 1). The geometries of the stationary points involved in these reactions are represented in Figure 1 and the corresponding relative energies and Gibbs energies are shown in Table 1.

Diazomethane coordinates to **1a** with a very small energy barrier to yield complex **2a**. At the transition state **TS(1a-2a)** diazomethane approaches **1a** perpendicularly to the Pd coordination plane. One of the Pd−O bonds breaks and diazomethane enters the vacant coordination site in the square-planar intermediate **2a**. This process is similar to the first step in the C−H bond activation of benzene and methane by palladium diformate recently studied by Biswas et al.[25] Intermediate **2a** is stabilized through a hydrogen bond involving the methylene group and the uncoordinated oxygen atom. A similar hydrogen bond has been recently observed in the crystal structure of a palladium(II) carboxylate complex.[26]

2a may eliminate nitrogen in two different ways. The first one leads to the formation of a complex in which the methylene group has inserted in one of the Pd−O bonds (**1b**) and involves a Gibbs activation energy of 5.8 kcal mol^{-1}. This process requires a rotation of the methylene group, which takes place

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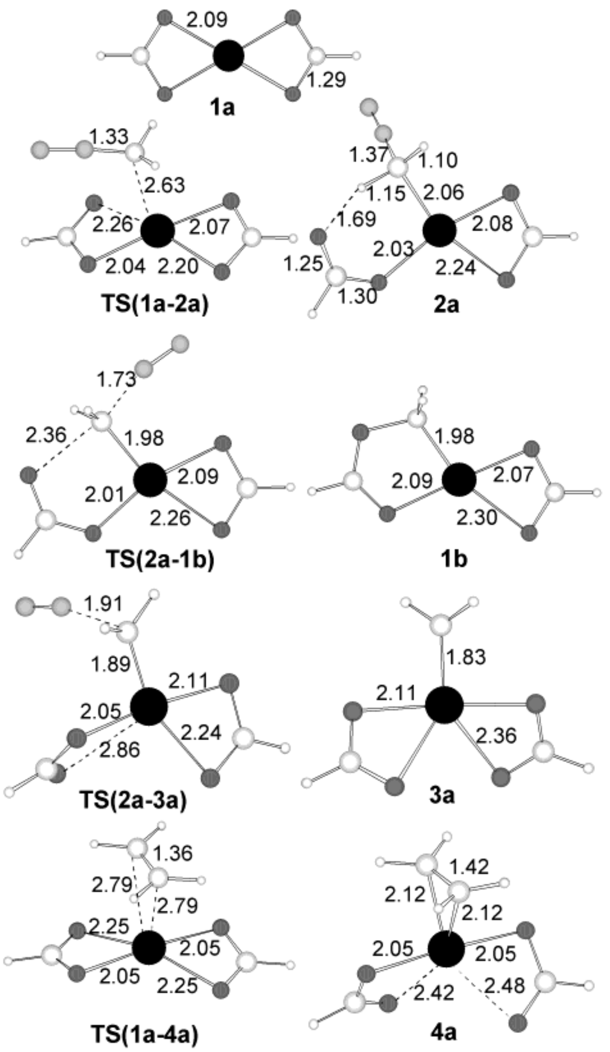


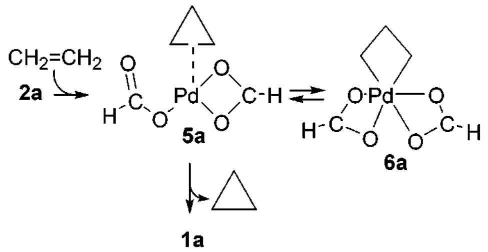
Figure 1. Geometries of the stationary points corresponding to the reactions of palladium diformate **1a** with diazomethane and ethylene. Selected interatomic distances are given in Å.

before the transition state **TS(2a-1b)**. The methylene-inserted complex **1b** presents a square-planar coordination around Pd and C_s symmetry. If we compare the values of the Pd−O bond lengths in **1b** with those corresponding to **1a**, we can observe a remarkable trans effect of the methylene group.

Nitrogen elimination in **2a** can also lead to the metal−carbene complex **3a**. In this case, the process does not involve the rotation around the Pd−C bond (see **TS(2a-3a)** in Figure 1). The final complex **3a** has a trigonal bipyramid structure with the methylene ligand in one of the equatorial positions. This process is endothermic and involves a Gibbs activation energy of 10.3 kcal mol^{-1}. We have also located a transition state connecting the two isomeric structures **1b** and **3a**. This structure is only 5.6 kcal mol^{-1} higher in energy than **3a** ($\Delta G^{\ddagger} = 4.6$ kcal mol^{-1}). From these results, we can conclude that the reaction between **1a** and diazomethane leads to the formation of the methylene inserted complex **1b**, whereas the formation of the carbene complex **3a** is not favorable.

Methylene insertion in Pd−Cl and Pt−Cl bonds of metal chloride complexes through reaction with diazomethane has been reported in the literature.[12,27] However, the proposed mechanism involves the formation of a palladium−carbene complex as intermediate,[27b] whereas our results indicate that this is not the case for palladium diformate.

Scheme 2



Let us now consider the reaction between **1a** and ethylene, which leads to the formation of **4a**. If we compare the energies involved in this process with those corresponding to the formation of **1b** (Table 1), we can observe that the reaction of **1a** with diazomethane is both thermodynamically and kinetically more favorable than the coordination of ethylene, thus confirming our previous assumption that cyclopropanation does not involve olefin coordination as the first step.[13]

If diazomethane reacts with palladium diformate in the first place, the next step in the cyclopropanation mechanism must involve the reaction with ethylene. We have studied the attack of ethylene on three different palladium complexes, **2a**, **1b**, and **3a**. These processes are summarized in Schemes 2, 3, and 4, respectively.

The attack of ethylene on **2a** (see Scheme 2 and Figure 2) leads to the formation of **5a**, which can be considered an edge-metalated cyclopropane, similar to complexes which have been proposed as intermediates in metallacyclobutane isomerizations.[28] **5a** is an energy minimum of the potential energy surface,

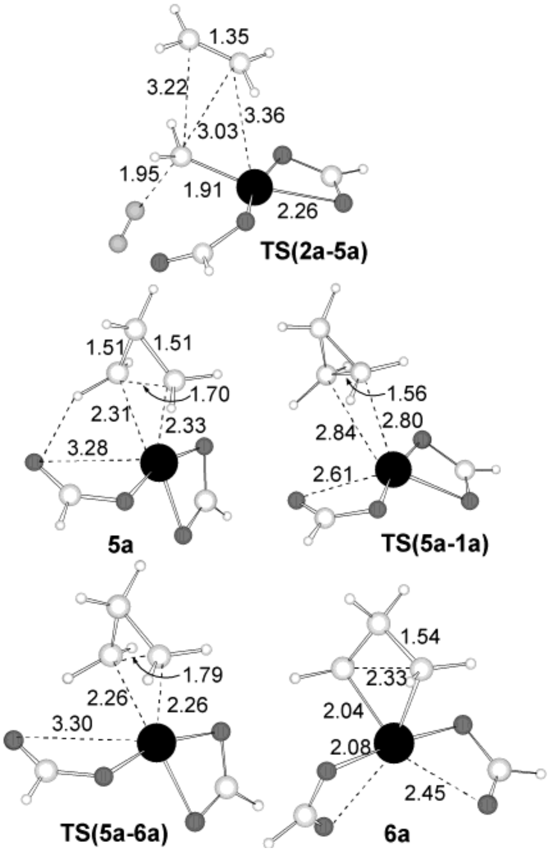


Figure 2. Geometries of the stationary points corresponding to the reaction between **2a** and ethylene. Selected interatomic distances are given in Å.

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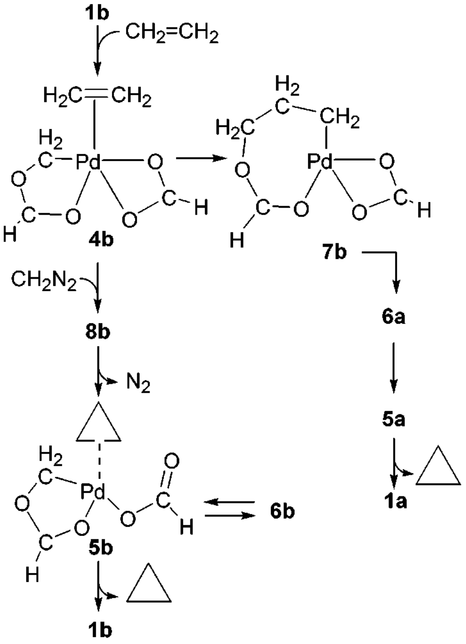
Table 2. Energies and Gibbs Energies[a] Relative to Reactants for the Stationary Points of the Reaction between **2a** and Ethylene

stationary point[b]	ΔE	ΔG^0_{298}
TS(2a-5a)	11.4	17.5
5a + N_2	−29.5	−26.9
TS(5a-1a)	−22.5	−20.4
1a + C_3H_6	−33.9	−40.9
TS(5a-6a)	−29.5	−26.5
6a	−41.9	−38.1

[a] All values are given in kcal mol^{-1}. [b] See Scheme 2 and Figure 2.

Scheme 3



but it evolves to palladacyclobutane **6a** with an energy barrier of only 0.05 kcal mol^{-1} when computed at the same level of calculation used in the geometry optimization. This barrier disappears when the energies are computed with the larger basis set, but the entropy contribution leads to a Gibbs activation energy of 0.4 kcal mol^{-1} (see Table 2). From these results it is not possible to assert whether **5a** is a real intermediate. However, this structure is also encountered along the reaction coordinate corresponding to reductive cyclopropane elimination from **6a**. This fact has been confirmed by computing the IRC connecting **TS(5a-6a)** with **5a** and **6a** (see Figure 2). The formation of palladacyclobutane **6a** from **5a** is energetically more favorable than cyclopropane elimination (see Table 2). However, when entropy is taken into account, the formation of cyclopropane becomes thermodynamically favorable.

From the values shown in Table 2, we can see that cyclopropane ring opening by **1a** is exothermic ($\Delta E = -8$ kcal mol^{-1}) and involves an energy barrier of 7 kcal mol^{-1}. Siegbahn and Blomberg[29] have reported that the formation of palladacyclobutane from a Pd atom and cyclopropane involves a reaction energy of −22.4 kcal mol^{-1} and it takes place with no energy barrier. The presence of a barrier and the lower exothermicity in the formation of **6a** from **1a** can be attributed to the important rearrangement of the formate ligands (see Figures 1 and 2). Cyclopropane ring opening by palladium dichloride has been reported to be very unfavorable.[30] However, in that study, important symmetry constrains were imposed to the palladacyclobutane complex, so that the stability of this structure could have been underestimated.

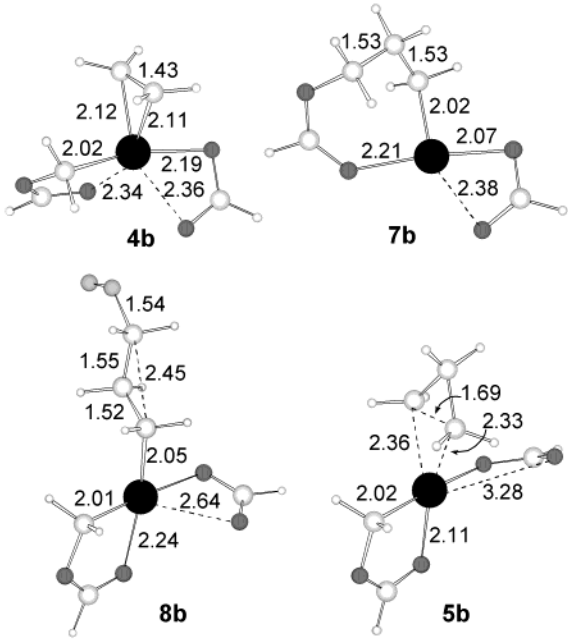


Figure 3. Geometries of the energy minima corresponding to the reactions shown in Scheme 3. Selected interatomic distances are given in Å.

Table 3. Energies and Gibbs Energies[a] Relative to Reactants for the Stationary Points of the Cyclopropanation Mechanism Starting from the Reaction of **1b** with Ethylene

stationary point[b]	ΔE	ΔG^0_{298}
	1b + CH_2CH_2	
TS(1b-4b)	8.4	17.7
4b	−10.7	1.8
TS(4b-7b)	18.0	29.4
7b	−14.3	0.8
TS(7b-6a)	17.6	29.4
6a	−10.0	2.2
	4b + CH_2N_2	
TS(4b-8b)	18.3	28.8
8b	10.7	21.9
TS(8b-5b)	10.6	20.9
5b + N_2	−27.0	−24.9
TS(5b-1b)	−21.7	−20.3
1b + C_3H_6	−40.4	−49.2
TS(5b-6b)	−26.5	−24.1
6b	−41.8	−38.3

[a] All values are given in kcal mol^{-1}. [b] See Scheme 3 and Figure 3.

The second cyclopropanation mechanism that we have considered corresponds to the attack of ethylene on **1b** (see Scheme 3). The geometries of the energy minima corresponding to this process are represented in Figure 3 and the relative energies and Gibbs energies of all the stationary points are shown in Table 3. The first step in Scheme 3 consists of the formation of the ethylene-coordinated complex **4b**. Coordination of ethylene to **1b** is less favorable than coordination to **1a** as we can see from the comparison between Tables 1 and 3.

Starting from **4b** we have considered two different reaction paths (see Scheme 3). In the first one, ethylene inserts into the

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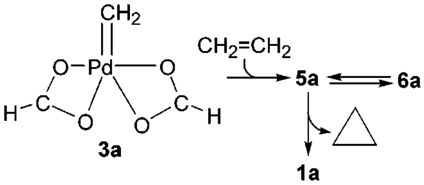
Scheme 4



$Pd-CH_2$ bond leading to the formation of **7b**. In a second step, this complex isomerizes into the palladacyclobutane **6a**. The formation of **6a** from **4b** can also take place in one step, but the corresponding energy barrier is notably larger (39.6 kcal mol^{-1}) than the ones involved in the two-step path. Cyclopropane can be formed through reductive elimination from **6a** according to the mechanism previously discussed (see Scheme 2).

The alternative mechanistic path involves the participation of an additional diazomethane molecule, which attacks the coordinated ethylene in **4b**. This process leads to the formation of intermediate **8b** with a Gibbs activation energy of 28.8 kcal mol^{-1}. In the transition state **TS(4b-8b)** the methylene group of diazomethane approaches one of the ethylene C atoms while the N_2 group is oriented outside with respect to ethylene. This orientation contrasts with the one corresponding to the attack on isolated ethylene which leads to the formation of a pyrazoline.[31]

8b is an energy minimum of the potential energy surface and its evolution to **5b** through nitrogen elimination involves an energy barrier of only 0.8 kcal mol^{-1} at the level of calculation used in the geometry optimization. When zero-point corrections are taken into account or when the energies are recalculated with the larger basis set, the barrier disappears, so that this structure cannot be considered as a real intermediate. Nitrogen elimination leads to **5b**, which is similar to **5a**. **5b** may evolve to palladacyclobutane **6b** or to **1b** and cyclopropane. The first process is energetically the most favorable one, but when entropy is taken into account the second one is the thermodynamically most favorable.

The third cyclopropanation mechanism (see Scheme 4) involves the attack of ethylene on the carbene complex **3a**. This process leads to **5a** with no energy barrier. Then, **5a** can evolve to palladacyclobutane **6a** or to **1a** and cyclopropane, as previously discussed.

From the results presented up to now, we can conclude that cyclopropane formation from the attack of ethylene on **1b** involves large activation Gibbs energies (27−29 kcal mol^{-1}), so that this process is not expected to be involved in the reaction mechanism. On the other hand, the activation Gibbs energy corresponding to the attack of ethylene on **2a** is not so high (17.5 kcal mol^{-1}), but it is still larger than those corresponding to the competitive nitrogen elimination reactions to form **1b** (5.8 kcal mol^{-1}) or **3a** (10.3 kcal mol^{-1}). Finally, reaction of ethylene with **3a** is expected to be very fast. However, the formation of **3a** is unfavorable with respect to that of **1b**. So, all results indicate that the formation of **1b** is very favorable, but that this species is not suitable for cyclopropanation.

We have seen that the reaction of **1a** with diazomethane to form the methylene-inserted complex **1b** involves very small energy barriers. For this reason, we have also studied reactions with additional diazomethane molecules leading to the formation of bis- or trismethylene-inserted complexes. For each case, we have also considered the competitive formation of the corresponding isomeric Pd−methylene complex (see Scheme 5). Table 4 presents the relative energies and Gibbs energies of the stationary points corresponding to these processes and the geometries of the energy minima are shown in Figure 4.

Scheme 5

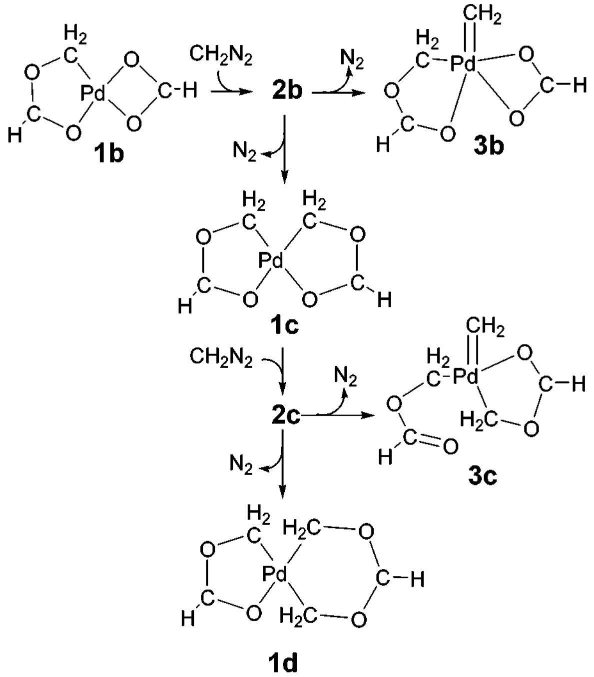


Table 4. Energies and Gibbs Energies[a] Relative to Reactants for the Stationary Points of the Reactions of Diazomethane with **1b** and **1c**

stationary point[b]	ΔE	ΔG^0_{298}
	1b + CH_2N_2	
TS(1b-2b)	6.3	16.7
2b	−11.5	−0.4
TS(2b-1c)	0.5	10.5
1c + N_2	−42.8	−39.3
TS(2b-3b)	5.6	14.8
3b + N_2	−6.4	−6.3
	1c + CH_2N_2	
TS(1c-2c)	7.9	18.0
2c	−1.1	9.4
TS(2c-1d)	17.2	26.7
1d + N_2	−1.8	0.2
TS(2c-3c)	16.1	23.7
3c + N_2	10.7	9.6

[a] All values are given in kcal mol^{-1} [b] See Scheme 5 and Figure 4.

Coordination of diazomethane to **1b** leads to the formation of **2b**. This process is both kinetically and thermodynamically less favorable than diazomethane coordination to **1a** (see Table 1), but it is more favorable than ethylene coordination to **1b** (see Table 3). Nitrogen elimination from **2b** can lead to the two isomeric complexes **1c** and **3b**. The formation of **1c**, in which there are two Pd−C bonds, is kinetically and thermodynamically more favorable than the formation of the Pd−methylene complex **3b**. **1c** is a cis square planar complex with C_{2v} symmetry. We have also optimized the geometry of the corresponding trans isomer, but it is 18.1 kcal mol^{-1} higher in energy than the cis isomer **1c**.

1c can react with a third diazomethane molecule to form **2c**. This complex can also eliminate nitrogen through two different paths. In this case, the most favorable one leads to the formation of the Pd−methylene complex **3c** with an activation Gibbs

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[31] Branchadell, V.; Muray, E.; Oliva, A.; Ortuño, R. M.; Rodríguez-García, C. *J. Phys. Chem. A* **1998**, *102*, 10106.

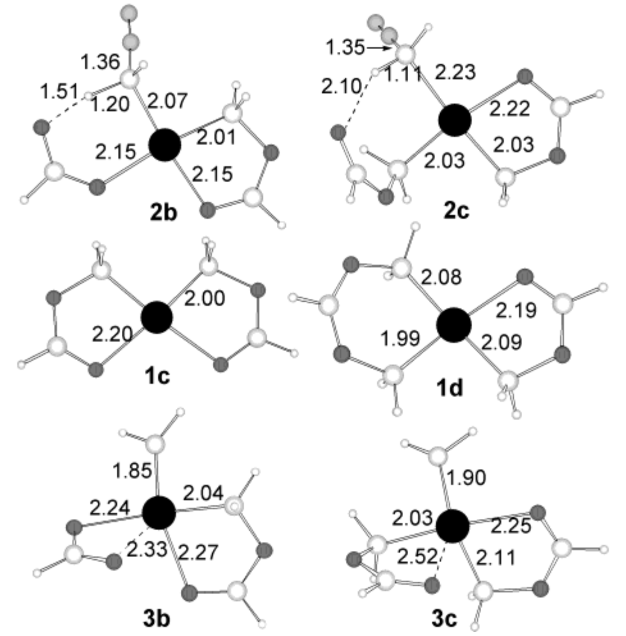


Figure 4. Geometries of the energy minima corresponding to the reactions shown in Scheme 4. Selected interatomic distances are given in Å.

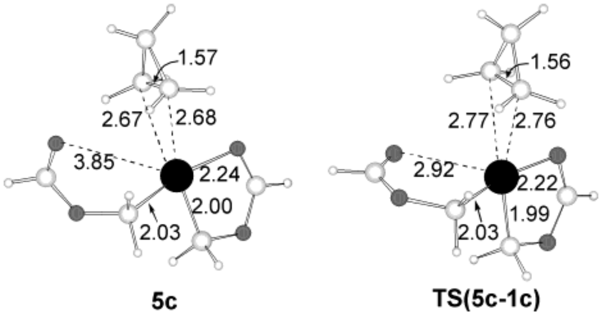


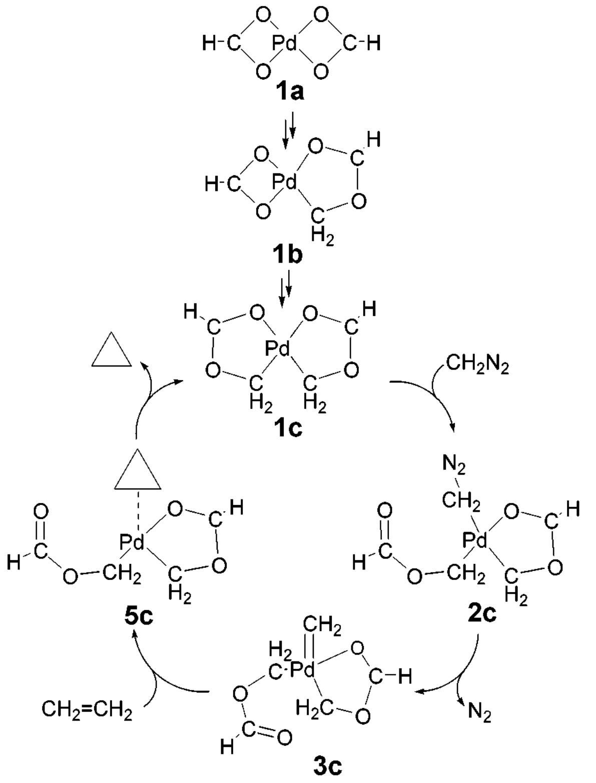
Figure 5. Geometries of the stationary points corresponding to the reaction between **3c** and ethylene. Selected interatomic distances are given in Å.

energy of 14.3 kcal mol^{-1}. The formation of the complex **1d**, with three inserted methylene groups, is less favorable, since the corresponding activation Gibbs energy is 17.3 kcal mol^{-1}. We have also located the transition state connecting **3c** and **1d**, which involves a Gibbs activation energy of 2.6 kcal mol^{-1}.

The attack of ethylene on **3c** leads to the formation of **5c** (see Figure 5) with no energy barrier. The corresponding reaction energy and Gibbs energy are −50.2 and −36.0 kcal mol^{-1}, respectively. This intermediate can evolve to palladacyclobutane **6c** or to **1c** and cyclopropane. The formation of **6c** is endothermic by 11.7 kcal mol^{-1}. On the other hand, the reaction energy for the direct formation of cyclopropane is −11.6 kcal mol^{-1}, so that the latter process is much more favorable. Moreover, entropy favors the formation of cyclopropane leading to a reaction Gibbs energy of −21.0 kcal mol^{-1}. The computed Gibbs activation energy for this process is 5.8 kcal mol^{-1}.

Scheme 6 summarizes the complete reaction mechanism. In this mechanism the bismethylene-inserted complex **1c** is the catalytic species. The formation of this complex requires the reaction of palladium diformate with two diazomethane molecules. In the presence of excess diazomethane, methylene insertion reactions could lead to the deactivation of the catalyst. This fact would be in accordance with the dependence of the reaction rate on the catalyst concentration observed at constant diazomethane concentration.[9]

Scheme 6



The Gibbs energy profile corresponding to the formation of **1c** is presented in Figure 6a. Reaction of **1c** with diazomethane

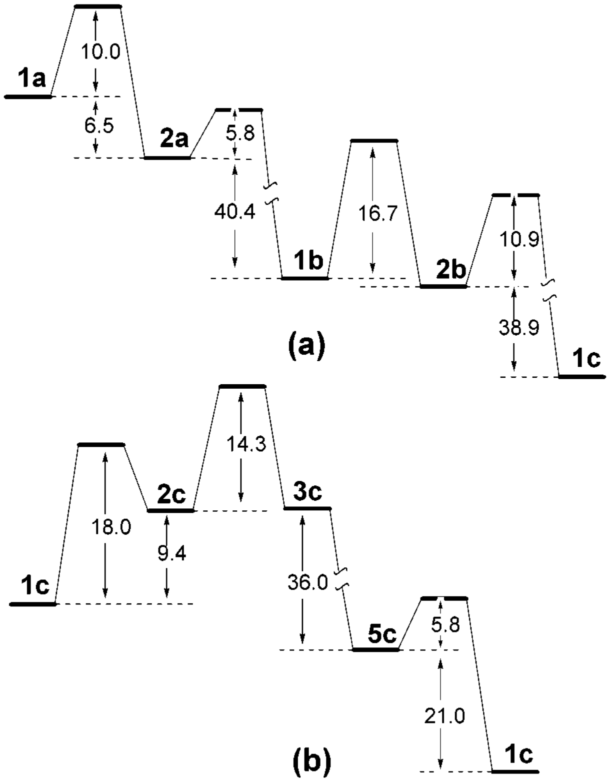


Figure 6. Gibbs energy profiles at 1 atm and 298.15 K corresponding to (a) the formation of the bismethylene-inserted complex **1c** and (b) to the catalytic cycle shown in Scheme 6. All values are given in kcal mol^{-1}.

leads to the formation of the Pd−methylene complex **3c** in two steps. Once this species is formed, reaction with the olefin to form cyclopropane should be very fast, restoring the catalytic complex **1c**. The Gibbs energy profile corresponding to the catalytic cycle is shown in Figure 6b.

Concluding Remarks

We have studied the cyclopropanation of ethylene by diazomethane in the presence of palladium diformate. We have shown that the first step of the process corresponds to the reaction between palladium diformate and diazomethane to form a methylene-inserted complex in two steps. The formation of the isomeric palladium−carbene complex is less favorable. The attack of ethylene on the methylene-inserted complex can lead to the formation of cyclopropane, but this process involves large Gibbs energy barriers. Reaction with additional diazomethane molecules can lead to the formation of complexes with more than one inserted methylene group. For the second diazomethane molecule, methylene insertion is more favorable than the formation of the isomeric palladium−carbene complex. On the other hand, the reaction with the third diazomethane molecule leads to the formation of the palladium−carbene complex as the most favorable product. Attack of ethylene on this palladium−carbene complex leads to the formation of cyclopropane in two steps. In the first one, an edge-coordinated cyclopropane is formed with no energy barrier. This complex evolves to cyclopropane and the bismethylene inserted complex, which would be the catalytic species in the catalytic cycle.

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Supporting Information Available: Total energies and geometries of energy minima and transition states. This material is available free of charge via the Internet at http://pubs.acs.org. See any current masthead page for ordering information and Web access instructions.

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