

Theoretical Study of the Mechanisms of Palladation of Methylene-cyclopropane and [3 + 2] Cycloadditions

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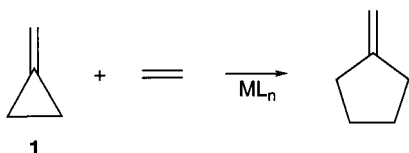
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Palladation of methylenecyclopropane and [3 + 2] cycloaddition with alkenes have been studied theoretically. In palladium complexes of methylenecyclopropane or trimethylenemethane, the η^2 forms have been shown to be more stable than the palladacyclobutane forms. However, the barrier heights to yield palladacyclobutanes are not very high and the methylene-bridged carbon can be converted to the metal-attached carbon on palladium via a ring-opened transition state, allowing the scrambling of hydrogens in methylenecyclopropane. With respect to the palladium-catalyzed [3 + 2] cycloaddition reaction of methylenecyclopropane with alkenes, the path via palladacyclobutanes has been demonstrated to be more favorable than the path via an η^2 complex. These results are discussed by using the paired interaction orbital scheme.

Introduction

Methylenecyclopropanes are known to undergo [3 + 2] cycloaddition with alkenes in the presence of some d^{10} metal catalysts.^{1–4} Azatrimethylenemethane (ATMM) and oxatrimethylenemethane (OTMM) also undergo the cycloadditions.⁵ Compounds having CO and CN groups add also to methylenecyclopropane **1** or trimethylenemethane (TMM) and to the hetero-substituted species.^{6,7}



It has been reported that **1** coordinates to the complexes of iron,⁸ molybdenum,⁹ nickel,^{10–12} and palladium.^{13–21} The

complexes of **1** have been characterized experimentally to have an η^2 and an η^4 form^{8,22} and the metallacyclic forms.¹⁸ Among those, the nickel and palladium complexes of **1** react with alkenes to yield five-membered-ring compounds. These coupling reactions have been investigated extensively by Noyori,¹⁰ Binger,^{11,13} and Trost.^{14,16,19} Some differences have been observed in the chemo- and stereoselectivity of those reactions.

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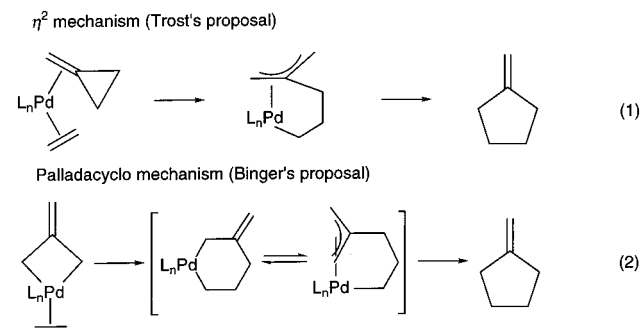
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Many questions still remain unanswered, but there seems to be no unifying mechanism to explain these experimental observations.

The initial complex has not yet been well clarified. In the [3 + 2] coupling reaction, a methylenecyclopropane-ML₂ (M = Ni or Pd) complex is suggested to be formed initially as a reaction intermediate, in which **1** coordinates to the metal center in an η^2 fashion or to form metallacyclic forms. There may be two metallacyclic forms, depending on whether the metal species attacks the distal bond or a proximal bond of **1**.

The mechanistic issues have recently been disclosed a great deal through the survey of the intramolecular cycloadditions.^{16–18} Theoretical works on d¹⁰ metal-TMM complexes have also revealed the possible mechanism of the reaction.²³ A stepwise mechanism has been suggested for the reaction of the TMM complexes with alkenes to explain the zwitterionic charge distribution. It consists of a nucleophilic attack of the electron-deficient double bond to the metal center and a ring closure between one of the metal-bound carbons of the TMM ligand and the β -carbon of the alkene molecule.^{19,21} On the other hand, complexes of **1** have been shown to react both with electron-rich alkenes and with electron-deficient alkenes.³ This difference might imply that another coupling mechanism is operating in the reaction of complexes of **1**.

For the [3 + 2] coupling reaction of **1**, there have been two proposals with respect to the initial reaction intermediates. Trost proposed the mechanism via an η^2 -methylenecyclopropane intermediate (eq 1), whereas Binger proposed the mechanism including a metallacyclobutane intermediate (eq 2).



In the mechanism proposed by Trost, the distal bond of **1** coordinated to the metal attacks the double bond of the acceptor ligand, and the complexation of the two partners follows to generate a π -allyl complex.²⁴ On the other hand, Noyori showed that the cycloaddition between 2,2,3,3-tetradeuteriomethylenecyclopropane and dimethyl fumarate in the presence of a catalytic amount of bis(acetonitrile)nickel yielded a mixture of cycloadducts derived both from the distal bond opening and from the proximal bond opening.^{10c} Upon the distal ring opening, complete scrambling of the carbons bearing deuterium occurs, whereas the scrambling will not be observed in the opening of a proximal bond. The recovered material also showed a partial scrambling.^{10c} Intervention of a σ -allyl complex in rapid equilibrium with the isomeric σ -allyl species or a π -allyl complex was suggested.

In this regard, it is important to investigate the mechanisms of the coupling between **1** and alkenes via an η^2 complex and via metallacyclic complexes, and to look for the reason for the deuterium scrambling. Theoretical calculations may be suitable

for searching the transition structures and short-lived species to get information on the plausible mechanism of the reactions. Orbital interaction analyses will allow us to draw a clear view of the interactions involved in the course of the reactions.

Method of Calculations

Theoretical calculations were carried out by applying the Gaussian 94 program.²⁴ All the geometrical parameters of the species appearing in this study were determined by the Møller–Plesset perturbation theory at the second-order (MP2) level,²⁵ and by the density functional method of Becke's three parameters with Lee, Yang, and Parr's correlations (B3LYP).²⁶ The Hay and Wadt ECP2 double- ζ basis with effective core potentials (ECPs) was employed for Pd,²⁷ and the 3-21G basis was used for the H, C, and P atoms in the organic ligands.²⁸ This set of basis functions is denoted by BS1. For the MP2 optimized structures, single-point calculations at the MP4(SDQ) level²⁹ were performed with another set of basis functions, BS2, in which one f -function was added to the Pd primitive functions³⁰ and all the other atoms were described by the 6-31G* basis functions.³¹ For the B3LYP/BS1 optimized structures, single-point calculations by B3LYP/BS2 were performed to include the effect of polarization functions for the atoms in the ligands. As for some important transition structures, we confirmed that UMP2(full)/BS1 calculations gave the same results as the MP2/BS1 calculations. The IRC analyses were carried out at the B3LYP level with the Dobbs–Hehre basis for Pd³² and the 3-21G basis for other atoms.³³

Results and Discussion

Palladation of Methylenecyclopropane. The palladation of cyclopropane was studied extensively by Siegbahn.³⁴ The first problem in this study is to see the structures and relative stabilities of the intermediates of the palladium-catalyzed [3 + 2] coupling reaction of **1**. There are two types of complexations in this case, an η^2 form and the metallacyclic forms. It is also of significance to clarify whether the distal bond or a proximal bond is broken, to form the palladacyclobutane intermediate. By simplifying the metal complex by Pd(PH₃)₂, **2**, we have obtained the geometries of three possible isomers for TMM–Pd(PH₃)₂ complexes, **4**, **7**, and **8** illustrated in Figure 1. The relative energies are given by taking the sum of the energies of **1** and **2** in an isolated state as the reference. η^2 complex **8** is

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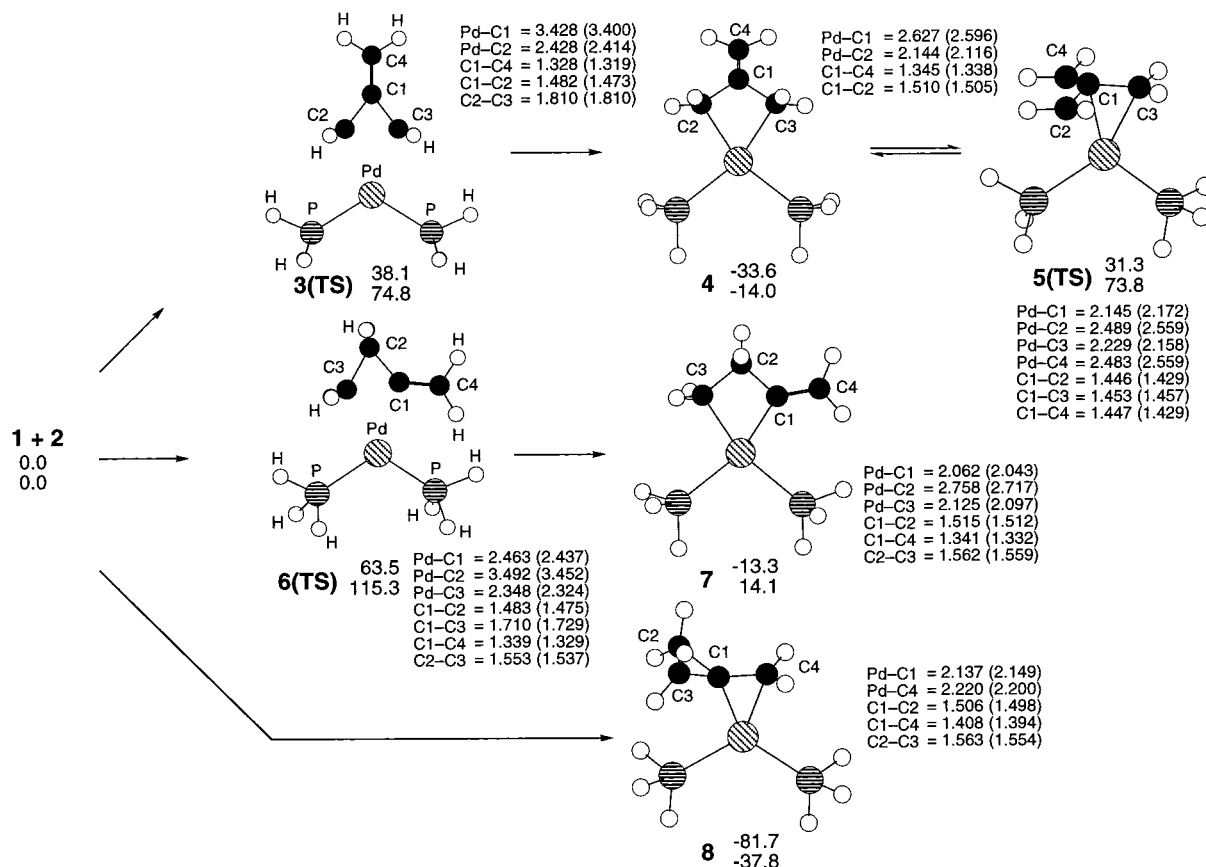
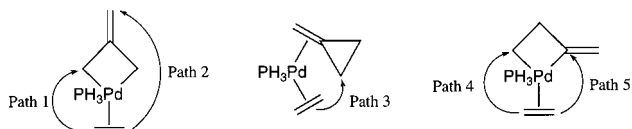


Figure 1. Structures of the ground and transition states of the species appearing on the paths of the palladation of methylenecyclopropane, calculated at the MP2 level of theory. Bond lengths are given in Å. Relative energies (kJ/mol) are given for the MP4/BS2//MP2/BS1 (above) and B3LYP/BS2//B3LYP/BS1 (below) calculations, by taking the starting materials as the reference. Bond lengths in parentheses are the B3LYP/BS1 optimized values.

shown to be stabilized by 82 kJ/mol at the MP4(SDQ)/BS2//MP2/BS1 level (38 kJ/mol at the B3LYP/BS2//B3LYP/BS1 level). Transition state **3(TS)** represents the path in which the distal C–C σ bond is broken to form **4**, whereas transition state **6(TS)** represents the path in which a proximal C–C bond is cleaved to form **7**. The activation energy of the path going through **3(TS)** has been calculated to be 38 kJ/mol at the MP4(SDQ)/BS2//MP2/BS2 level (75 kJ/mol at the B3LYP/BS2//B3LYP/BS1 level), which is lower than that for the path going through **6(TS)** by 25 kJ/mol (41 kJ/mol at the B3LYP/BS2//B3LYP/BS1 level). Palladacyclobutane **4** is shown to lie above η^2 complex **8**, but lower than the other palladacyclobutane form **7**.

In the palladacyclobutane structure **4**, the C⁴ atom and the C² or C³ atom may be exchanged via the transition state, **5(TS)**. The barrier height is slightly lower than that for **3(TS)**, and accordingly, **4** will lead to a scrambling of the hydrogens in **1** upon the elimination from **4**, as has been observed experimentally.^{10c} Transition structure **5(TS)** looks like an η^4 form.^{23a,b,35}

The [3 + 2] Addition via an η^2 Complex and via a Metallacyclobutane. Let us look at the process of palladium-catalyzed coupling of **1** with an alkene molecule, by taking a model complex, Pd(methylenecyclopropane)(ethylene)(PH₃).



Five paths are available for the alkene to attack **1** (or TMM) coordinated to the metal. In path 1, the ethylene molecule attacks

one of the carbon atoms of the TMM which is bound to the palladium center, while the ethylene molecule attacks the external methylenic carbon of the TMM in path 2. These paths involve the breaking of the distal bond of **1**. Path 3 starts from an η^2 -form intermediate. The ethylene molecule makes a bond with a carbon in the cyclopropane ring, accompanied by the opening of the ring. Paths 4 and 5 involve the breaking of one of the proximal bonds in **1**. In path 5, the ethylene molecule attacks a carbon atom of TMM which is bound to the external methylene group.

The calculated structures of the intermediates, the transition states, and the products in paths 1, 2, and 3 are illustrated in Figure 2. The relative energies are given by taking **9** as the reference. Species **9** and **10** show metallacyclic structures which differ from each other in the orientation of the coordinated ethylene. They are very close in energy to each other. Structures **12** and **13** differ in the orientation of **1** in the coordination to the metal. These η^2 complexes lie 64–67 kJ/mol below **9** or **10**. This is very similar to the trend observed in Figure 1 for the Pd(methylenecyclopropane)(PH₃)₂ system. Transition state **11(TS)** is located 68 kJ/mol above the palladacyclobutane **10**, through which C² and C³ can be exchanged by the methylenic carbon C⁴. The barrier height is considerably lower than that for transition state **14(TS)** or **15(TS)** to give **17** and **18**. The scrambling of hydrogens in the part of **1** observed in the product may be understood in this context.^{10c}

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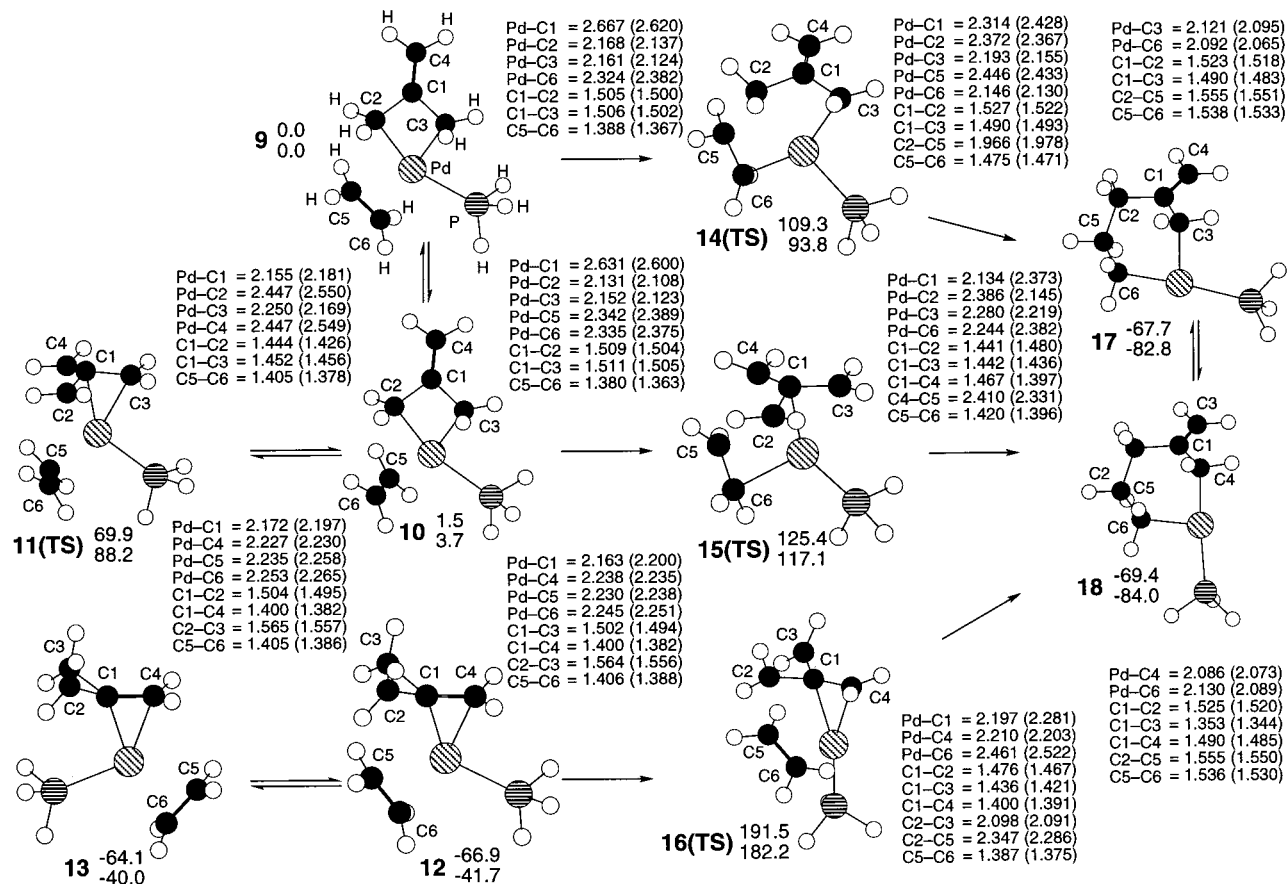


Figure 2. Structures of the ground and transition states of the species on the paths for the [3 + 2] cycloaddition reaction between methylenecyclopropane and ethylene, involving the cleavage of the distal bond of the cyclopropane ring or an η^2 complex. Bond lengths (in Å) have been calculated at the MP2 level of theory. Relative energies (kJ/mol) are given for the MP4/BS2//MP2/BS1 (above) and B3LYP/BS2//B3LYP/BS1 (below) calculations, by taking **9** as the reference. Bond lengths in parentheses are the B3LYP/BS1 optimized values.

In path 1, the coordinated ethylene attacks the Pd-attached carbon of **1** via transition state **14(TS)** with an activation energy of 109 kJ/mol at the MP4(SDQ)/BS2//MP2/BS1 level and 94 kJ/mol at the B3LYP/BS2//B3LYP/BS1 level. An IRC analysis has demonstrated that the formation of the new bond between C² and C⁵ takes place smoothly to give the product **17**. In path 2, the reaction goes through transition state **15(TS)** with an activation energy of 124 kJ/mol. The barrier height is slightly higher than that of **14(TS)**. The final stage of the reaction is reductive elimination of methylenecyclopentane from **17** and **18**, which has been investigated extensively.³⁶

We next examine path 3, which takes place via an η^2 complex of **1**. The ring opening has been shown to take place in a *disrotatory-out* mode. Transition state **16(TS)** is located above **12** by 258 kJ/mol at the MP4(SDQ)/BS2//MP2/BS1 level and 224 kJ/mol at the B3LYP/BS2//B3LYP/BS1 level. It should be noted here that this barrier is higher than those of paths 1 and 2 by ~130 kJ/mol. The path via an η^2 complex is suggested here to be not facile for the [3 + 2] cycloaddition of nonpolar alkenes. It is interesting to note that the ethylene molecule is forced to be more separated from the palladium atom, compared with its location in **12**, to bring the C⁵ atom in front of C² of the TMM part at the transition state.

In paths 4 and 5, illustrated in Figure 3, the reaction occurs via a metallacyclobutane in which a proximal bond of **1** is broken. The complexes **19**, **20**, and **21** are located ~19–22 kJ/mol above **9** at the MP4(SDQ)/BS2//MP2/BS1 level and ~26–28 kJ/mol above **9** at the B3LYP/BS2//B3LYP/BS1 level. In

path 4, the coordinated ethylene attacks the carbon atom of TMM via transition state **22(TS)** with an activation energy of 129 kJ/mol, while the coordinated ethylene attacks the methylene-attached carbon atom of TMM via transition state **23(TS)** in path 5, with an activation energy of 116 kJ/mol. It is seen that **22(TS)** and **23(TS)** lie above **14(TS)** by 30–40 kJ/mol. Now, we conclude that the [3 + 2] cycloaddition of **1** should take place most readily along path 1 via a palladacyclic intermediate which is produced by the breaking of the distal C–C bond of the cyclopropane ring in **1**. Incidentally, addition of the ethylene to the external methylene will lead also to [2 + 2] cycloaddition products.^{23a}

Orbital Interactions. Let us look at orbital interactions to see why path 1 via a palladacyclobutane intermediate has a lower activation energy than path 3 via an η^2 -coordinated intermediate. We divide here palladium complexes, **9**, **12**, **14(TS)**, and **16(TS)**, into two fragments, the TMM part and the Pd(C₂H₄)(PH₃) part. Now, we should populate electrons into the two fragments. The net electronic charge transferred from the metal reagent to the TMM fragment has been calculated to be ~0.2*e* by the Mulliken population analysis and ~0.6*e* by the natural bond orbital analysis in **9** and in **14(TS)**.^{37,38} The two species are less polarized in **12** and **16(TS)**. In all cases, the net charge on the TMM part has been found to be smaller than 1.0*e*. Therefore, we start our orbital interaction analysis from the two fragments having no net electronic charge in an isolated state, a Pd(0) complex and a methylenecyclopropane

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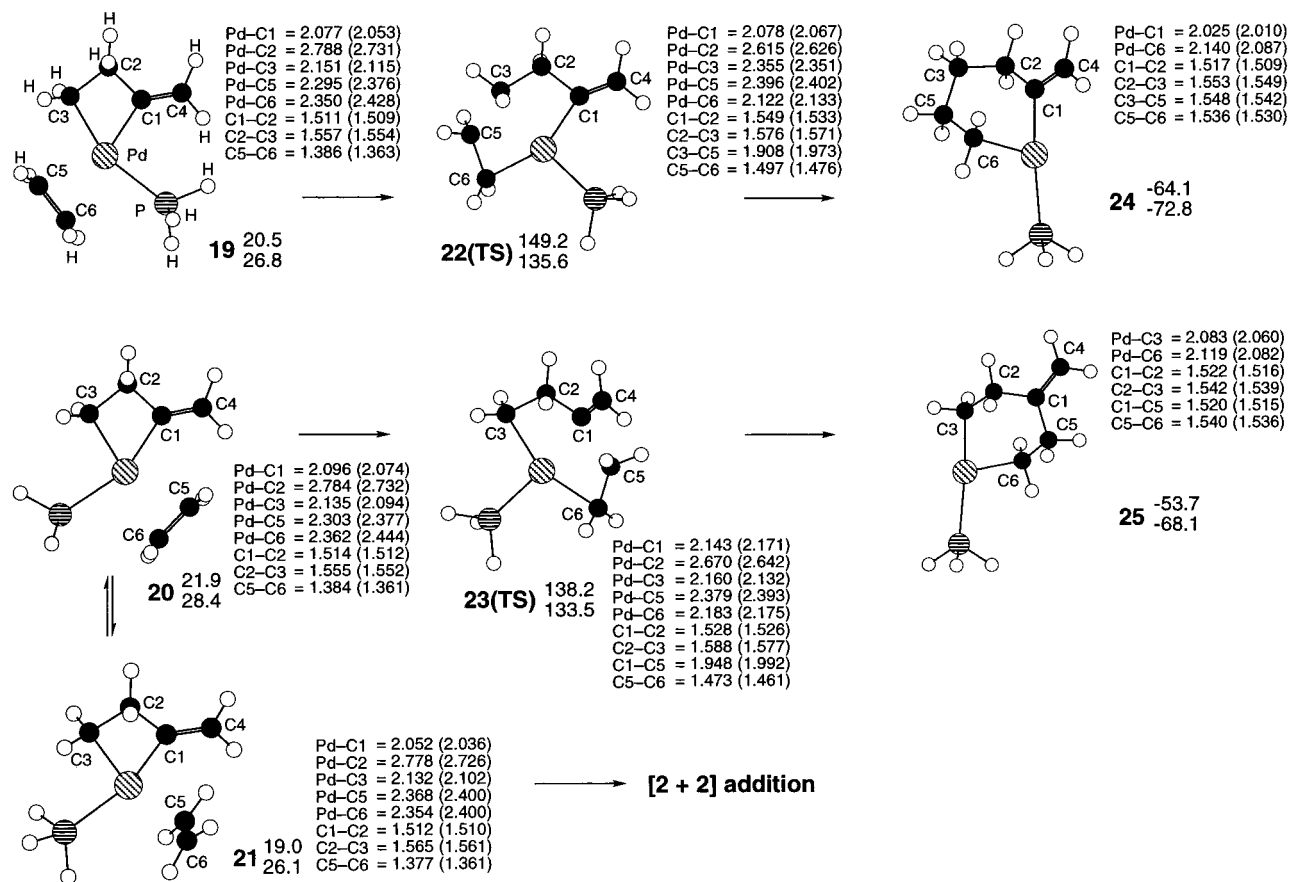


Figure 3. Calculated structures of the ground and transition states of the species on the paths for the [3 + 2] cycloaddition reaction between methylenecyclopropane and ethylene, involving the cleavage of a proximal bond of the cyclopropane ring.

or a TMM. The TMM fragment has been shown above to be distorted considerably from the D_{3h} symmetry structure in these species, and therefore, we have made RHF calculations on the TMM fragment to obtain its MOs.

In the frontier orbital scheme, one assumes a priori that the interaction is governed only by the highest occupied and lowest unoccupied MOs. To draw a more realistic view of interactions from the calculated wave function of the reacting system, we take here the contributions of all the occupied and unoccupied MOs of the two fragments into account. For this purpose, we have expanded first the wave function of the reacting system in a linear combination of various electron configurations of the two fragment species.³⁹ We have carried out next the unitary transformations of the fragment orbitals simultaneously within the occupied MO space of one fragment, A, and within the unoccupied MO space of the other fragment, B, referring to the coefficients of electron-transferred configurations in the wave function.⁴⁰ By this treatment, electron delocalization from A to B is represented compactly by a few pairs of fragment interaction orbitals (ϕ'_f, ψ'_f), by including properly not only the highest occupied and lowest unoccupied MOs but also all the occupied and unoccupied MOs of the fragments relevant for the interaction. The new orbital ϕ'_f is given by a linear combination of the occupied canonical MOs of A, and the orbital ψ'_f is given by a linear combination of the unoccupied canonical MOs of B.⁴¹ Electron delocalization from B to A can be represented similarly by another set of paired interaction orbitals.

Let us examine first the change in orbital interactions along with the progress of the [3 + 2] cycloaddition reaction via a metallacyclic intermediate. In palladacyclobutane **9** and transition structure **14(TS)** appearing on path 1, two pairs of interaction orbitals illustrated in Figure 4 play the dominant roles. The antisymmetric orbital pair (pair 1) of **9** participates strongly in electron delocalization from the Pd(C₂H₄)(PH₃) part to the TMM part. The interaction orbitals are seen to overlap efficiently in phase. The unoccupied orbital of the TMM fragment ϕ'_1 shows orbital lobes only on the two terminal carbons, having the extension toward the Pd center. The occupied orbital ψ'_1 of the Pd(C₂H₄)(PH₃) part consists primarily of a d AO of palladium, but a p AO mixes into the d AO to strengthen the bonding interaction with the TMM moiety. Pair 2 stands for electron delocalization from the TMM part to the Pd(C₂H₄)(PH₃) part. The interaction orbital of the TMM part ϕ'_2 is delocalized over all four carbons, though it has the largest amplitude on the two carbons bound to the palladium center. The paired counterpart of Pd(C₂H₄)(PH₃) ψ'_2 looks like an spd hybrid of the metal. These orbitals overlap also in phase.

At transition state **14(TS)**, the first pair of interaction orbitals ($\phi'_1; \psi'_1$) is distorted significantly. The unoccupied orbital ϕ'_1 of the TMM part looks more like the π_2 MO of an allyl, compared with that of **9**. The occupied partner ψ'_1 of the Pd(C₂H₄)(PH₃) fragment shows that the C² atom of the TMM fragment is bound both to the Pd center and to the C⁵ atom of

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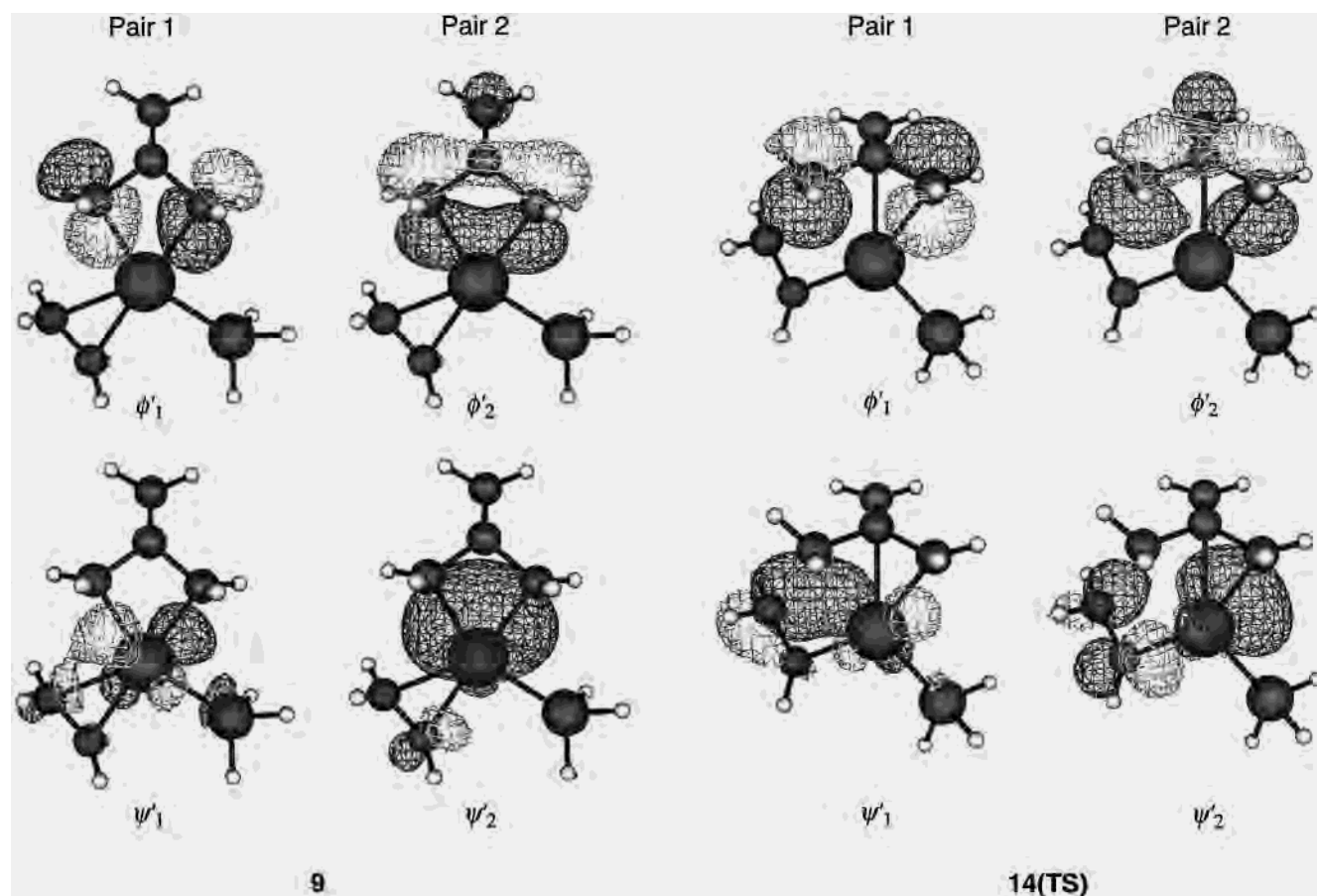


Figure 4. Two pairs of interaction orbitals representing electron delocalization from the Pd(C₂H₄)(PH₃) fragment to the methylenecyclopropane fragment (pair 1) and from the latter to the former (pair 2) in the Pd(methylenecyclopropane)(C₂H₄)(PH₃) complex, **9**, and in the transition-state structure, **14(TS)**. The orbitals ϕ' belong to the methylenecyclopropane fragment and the orbitals ψ' to the Pd(C₂H₄)(PH₃) part.

the coordinated ethylene at the transition state. In the second pair that represents electron delocalization from the TMM part to the Pd(C₂H₄)(PH₃) part, the C² atom of the TMM fragment is bound both to the Pd center and to the C⁵ atom of the ethylene unit. That is, in the [3 + 2] cycloaddition proceeding along path 1, a new C–C bond grows while a bonding interaction between the C² of TMM and the Pd center is partially retained. This reduces the destabilization of the reacting system and makes the cycloaddition facile to take place.

In η^2 complex **12** and transition structure **16(TS)** along path 3, two pairs of interaction orbitals illustrated in Figure 5 have been shown to play the principal roles. Orbital interactions in **12** are seen to bear a close resemblance to those proposed by Dewar, Chatt, and Duncanson.⁴² A p AO is seen to mix into the d AO on the metal in the occupied interaction orbital of ψ'_1 to strengthen back-donation of electrons from the Pd(C₂H₄)(PH₃) part to **1**. The occupied interaction orbital ϕ'_2 of **1** in pair 2 is shown to be localized almost completely on the C¹–C⁴ bond, having a large amplitude on the middle of the bond. Thus, orbital ϕ'_2 overlaps with paired orbital ψ'_2 of the Pd(C₂H₄)(PH₃) part efficiently and, accordingly, electron donation from **1** to the Pd(C₂H₄)(PH₃) part is stronger in **12**, compared with electron donation from the TMM part to the Pd(C₂H₄)(PH₃) part in **9**.

The present analysis of the wave function indicates clearly that the orbital interactions have been distorted significantly at the transition state, **16(TS)**, but the system still retains the η^2 -

type coordination. Then, localization of the interaction orbitals on C² of TMM is very poor, and therefore, the bonding interaction between C² and the ethylene C⁵ should be very weak in this case. When the reaction takes place via a palladacyclobutane intermediate, a Pd–C bond is converted smoothly to a C–C bond, being stabilized by the Pd–C bonding interaction which is kept partially at the transition state, as mentioned above. In contrast, in the path via an η^2 complex, the new C–C bond should be formed between an ethylene carbon C⁵ and the C² or C³ atom of **1** (or TMM) which has not been involved directly in the interaction with the metal center in the intermediate **12**. Thus, the reacting system tends to maintain a strong η^2 coordination between the C¹–C⁴ bond and Pd even at the transition state. The destabilization arising from the distortion of the η^2 coordination is not recovered sufficiently by stabilization which should be brought about by the formation of the new C–C bond. This must be the reason why the activation barrier is very high in path 3. The path going through an η^2 complex does not seem to be suited for [3 + 2] cycloaddition in the present system.

Conclusion

Palladation of **1** and the mechanisms of palladium-catalyzed [3 + 2] cycloaddition of **1** to alkenes have been studied theoretically, by adopting simple model palladium complexes, Pd(methylenecyclopropane)(PH₃)₂ and Pd(methylenecyclopropane)(ethylene)(PH₃). In the palladium complexes of **1**, the η^2 -coordinated form has been shown to be more stable than the palladacyclobutane forms. However, the barrier heights to form palladacyclobutanes are not so high and the [3 + 2] cyclo-

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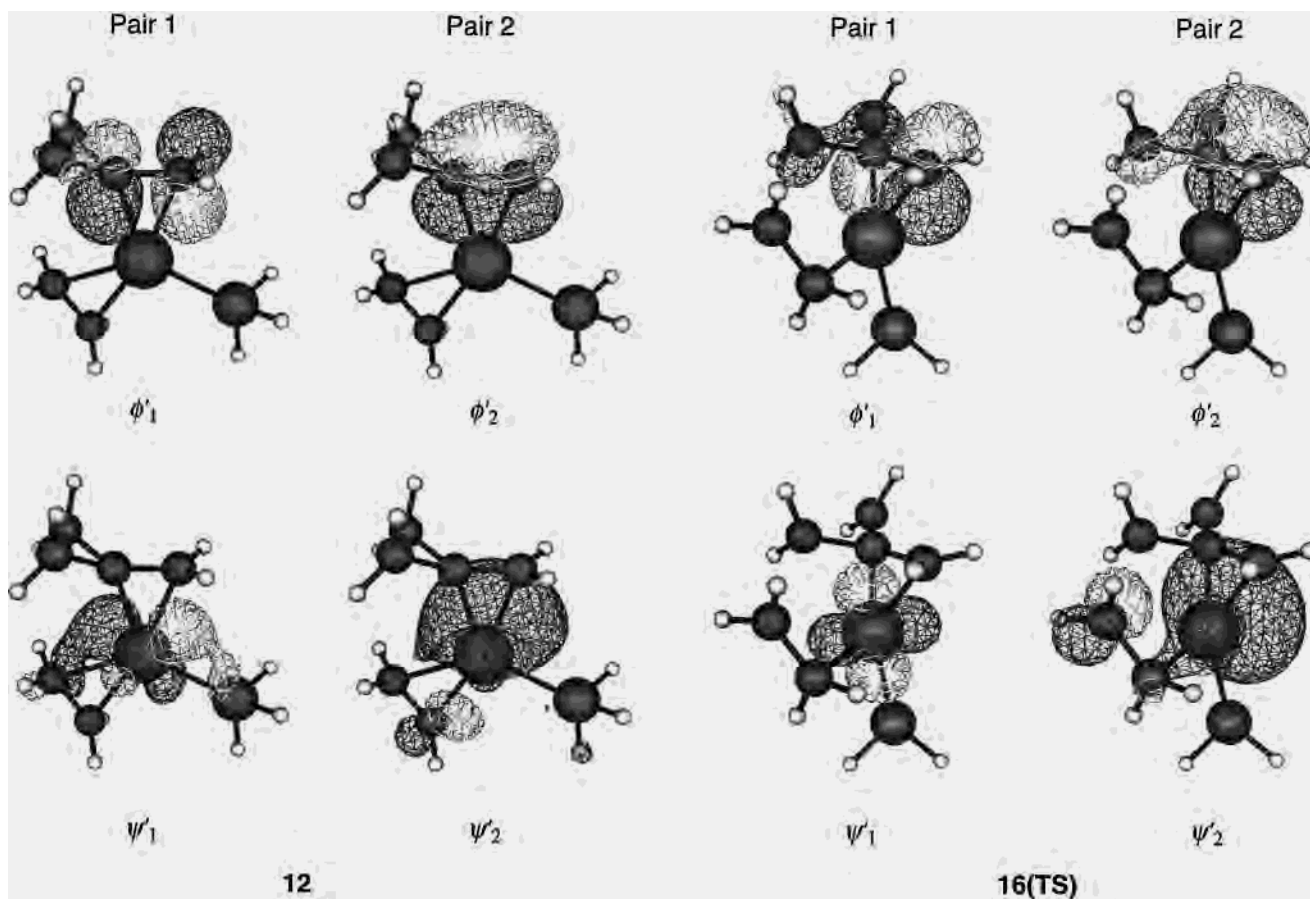


Figure 5. Two pairs of interaction orbitals representing electron delocalization from the Pd(C₂H₄)(PH₃) fragment to the methylenecyclopropane fragment (pair 1) and from the latter to the former (pair 2) in the Pd(methylenecyclopropane)(C₂H₄)(PH₃) complex, **12**, and in the transition-state structure, **16(TS)**.

addition with alkenes has been suggested to take place more readily via palladacyclobutane intermediates. The cleavage of the distal bond of the cyclopropane ring has been shown to be more favorable than that of a proximal bond. The calculations have revealed that the barrier height for the [3 + 2] cycloaddition via an η^2 complex is very high, compared with those for the reaction paths going through palladacyclobutane intermediates. Isomerization between palladacyclobutanes is probable on palladium, in which the methylene-bridged carbon is converted to a metal-attached carbon. Scrambling of the hydrogens in the reaction of 2,2,3,3-tetradeuteriomethylenecyclopropane with alkenes observed experimentally can be understood in this context.

The paired interaction orbital analyses have clarified the reason why the palladium-catalyzed [3 + 2] cycloaddition should take place more favorably via a metallacyclobutane

intermediate. The C(TMM)–Pd bond is switched smoothly to the C(TMM)–C(ethylene) bond in the path via a palladacyclobutane intermediate, by keeping the bonding interaction also between the C(TMM) atom and the Pd center. On the contrary, in the path via an η^2 -coordinated intermediate, the η^2 coordination is still retained strongly at the transition state, and therefore, the interaction orbitals do not provide significant amplitudes on the sites where the new C–C bond should appear.

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Supporting Information Available: Tables listing atomic positional parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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