Mechanisms of the Nucleophilic Substitution of the Allyl Carbons of (π-Allyl)platinum and (π-Allyl)palladium Complexes

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Mechanisms of platinum- and palladium-catalyzed nucleophilic substitutions of the allyl carbons of 2-chloro-2-propenyl ethyl carbonate have been studied by applying the *ab initio* molecular orbital method. By taking some model complexes, the nucleophilic substitution of the allyl carbon of (π-allyl)platinum complex has been demonstrated to consist of three steps, the formation of a π-allyl complex, conversion of the complex into a metallacyclic form, and the formation of an η^3-allyl product. The platinacyclo adduct and the η^2-complex are almost the same in stability. Replacement of the coordinated ligand in the η^2-product has been shown to be unfavorable from an energetic point of view. On the other hand, the palladium-catalyzed nucleophilic attack takes place at the terminal carbon of an allyl moiety to give an allylated product. It has been shown that the palladacyclobutane is less stable by ~15 kcal/mol than the η^2-complex. Thus, the formation of an η^3-allyl product *via* a metallacyclic adduct is unlikely in the palladium-catalyzed nucleophilic substitution. The replacement of the coordinated alkene ligand with the starting material will take place in this case to promote the catalytic process. The relative stabilities of the η^2- and the metallacyclic forms in platinum and palladium complexes have been discussed in terms of orbital interactions.

Introduction

The synthetic utility of transition-metal catalyzed allylic alkylation has been demonstrated since its introduction nearly three decades ago. Efficient and reliable amplification of chirality has been achieved by using enantioselective transition-metal catalyzed reactions.[1−6] In contrast to the processes where the allyl moiety acts as the nucleophilic partner, nucleophilic displacement processes on allylic substrates have also been investigated by Trost,[3] Tsuji,[4] and by others.[6] Soft nucleophiles attack the allyl carbons from the face opposite to the coordinated metal, whereas hard nucleophiles bind first to the metal and then attack the allyl moiety from the same face as the coordinated metal. Stereoselective syntheses by using chiral ligands have also been reported.[3c,5] The products of allylic alkylation, such as η^2-complexes,[7] η^3-complexes,[8] and metallacyclobutanes,[9,10] have been investigated.

In the allylic alkylation reactions, a nucleophile attacks the allyl moiety, either at the terminal carbon or at the central carbon. The nucleophilic attack at the central carbon of a π-allyl ligand attached to transition metals has attracted much attention.[11−15] For instance, the nucleophilic attack to the central carbon of an allyl moiety in (π-allyl)platinum complexes has been reported for the reactions of oxatrimethylenemethane,

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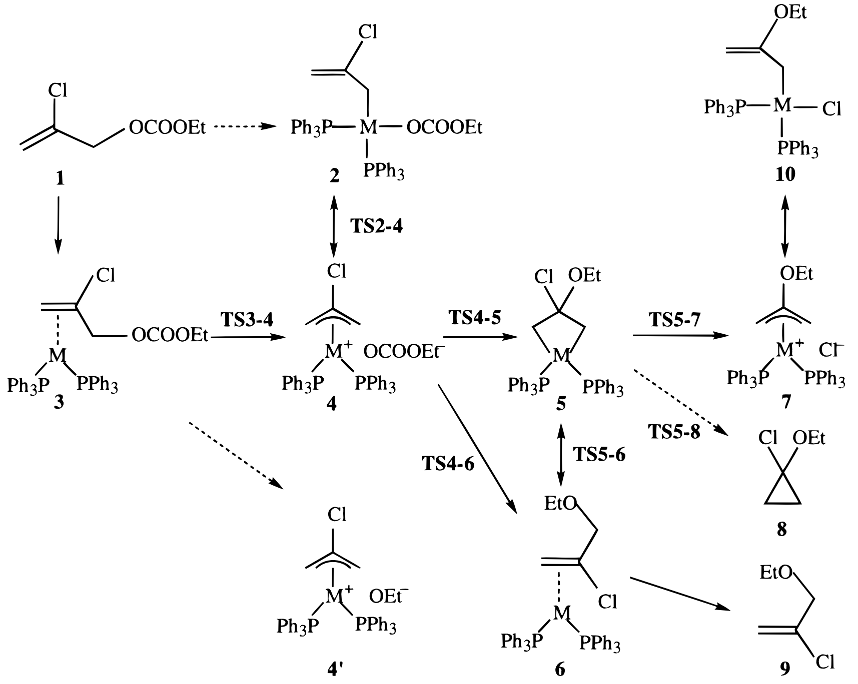
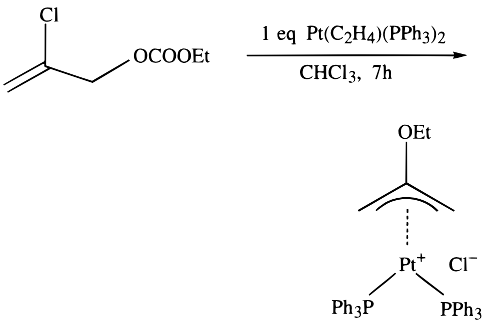
Scheme 1



azatrimethylenemethane, 2-chloro-2-propenyl ethyl carbonate, 2-chloro-2-propenyl-*N*,*N*-diethylcarbamate, and 2-chloro-2-propenyl acetate with platinum complexes.[15−17] Unlike the usual cases in which a nucleophile attacks a terminal carbon of an allyl moiety to give alkene complexes, this process converts (π-allyl)metal complexes into various metallacyclobutanes.[11−14] In some cases, it leads to the formation of cyclopropane derivatives through reductive elimination from metallacyclobutanes.[11−13] On the other hand, nucleophilic attacks at the terminal carbon have been reported for (π-allyl)palladium complexes. These reactions afford the allylated products,[16] except for the cases that have been carried out by using complexes with some amine ligands[11,13,14] (eq 1).



(1)

It has been revealed that 2-chloro-2-propenylethyl carbonate undergoes a reaction with a stoichiometric amount of $Pt(C_2H_4)(PPh_3)_2$ in $CHCl_3$ at 20 °C to afford (η^3-2-ethoxyallyl)bis(triphenylphosphine)platinum chloride in 48% yield.[15a]

The reaction has been suggested to take place *via* (η^3-2-chloroallyl)bis(triphenylphosphine)platinum ethoxide, followed by the formation of a platinacyclobutane. On the other hand, in the presence of a catalytic amount of zerovalent palladium complex, 2-chloro-2-propenyl ethyl carbonate yields 2-chloro-3-ethoxypropene as the major product *via* (η^2-2-chloro-3-ethoxypropene)bis(triphenylphosphine)palladium, as illustrated in Scheme 1.

Here the reaction is divided into three steps. In the first step, an η^3-complex **4** or **4′** is produced from 2-chloro-2-propenyl ethyl carbonate **1** and a zerovalent metal complex *via* an η^2-complex **3** or an η^1-complex **2**.[18] In the second step, the migration of an ethyl carbonate ion to the central carbon of the

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allyl unit gives rise to the metallacyclobutane **5**, while the addition of an ethoxide ion to the terminal carbon accompanied by liberation of carbon dioxide yields an η^2-complex **6**. In each case, the nucleophilic attack of an ethoxide ion may occur either from the same face as the metal or from the face opposite to the metal. In the last step, the metallacyclobutane **5** is converted to an η^3-complex **7**, or to a cyclopropane product through reductive elimination. The η^2-complex **6** may replace its ligand with the starting material, 2-chloro-2-propenyl ethyl carbonate, yielding **9** to complete a catalytic reaction.

Theoretical calculations seem to be useful for an investigation of these issues. Some meaningful information will be provided on the short-lived reactive species and the transition states.[19] The mechanisms of η^2-coordination, η^3-coordination, and of the formation of the metallacyclic adducts have been investigated by other groups.[20−22] Sakaki and co-workers have reported the results of MO calculations on interconversion between an η^1-complex and an η^3-complex and that between an η^2-complex and an η^3-complex.[23] Nucleophilic attacks to π-allyl ligands have been discussed theoretically by Sakaki[21a] and by Blöchl.[24] The oxidative addition to or reductive elimination from platinum and palladium have been investigated theoretically by Goddard[25] and by Sakaki.[26] Siegbahn and co-workers carried out elaborate MO analyses of oxidative additions to naked second transition metals.[22,27]

Our intention in this work is to determine the reaction paths for nucleophilic substitution in π-allylmetal complexes and to make a comparison of the reactivities between the platinum and palladium complexes, by using the *ab initio* MO method. We assume here that the solvent effects are similar in the platinum and palladium cases and that the reactivities of allyl carbons are not affected seriously by the presence of solvent molecules with little polarity such as $CHCl_3$.

Calculation Methods

Ab initio MO calculations have been carried out by the use of the Gaussian 92 and 94 programs.[28] As for the key intermediates, all the geometrical parameters have been optimized with the Møller−Plesset perturbation theory at the second order (MP2)[29] with the Hay and Wadt's ECP2 double-ζ basis with effective core potentials (ECP's) for the Pt and Pd atoms[30] and the 3-21G basis[31] for the C, H, O, P, and Cl atoms (denoted here by BS-I). All the species which appear in the reactions have been optimized at the restricted Hartree−Fock (RHF) level. Numerical vibration analyses have been carried out for the RHF-optimized structures to see whether a given structure is a transition state on the potential surface. For RHF optimized structures, two forms of single-point calculations have been performed at the MP2 level. One is the calculation with the same basis (MP2/BS-I//RHF/BS-I). The other is the calculation with the Stevens and Krauss's RCEP, triple-ζ basis quality *d* basis and double-ζ basis quality *sp* basis with relativistic compact effective potentials (RCEP's)[32] for Pt and Pd and the 6-31G* basis[33] for other atoms to include the effect of polarization in organic ligands (denoted here by BS-II). The PPh_3 ligands in the real species have been replaced by PH_3 groups for our computational feasibility. Unfortunately, MP4/BS-II calculations are beyond our computational feasibility, and hence, single point calculations have been carried out additionally at the MP4/BS-I//RHF/BS-I level to examine the relative stabilities of η^2-complexes and metallacyclobutanes in the platinum and palladium systems.

To begin with, we have compared the MP2/BS-I//RHF/BS-I energy of the η^2-, η^3-, and metallacyclic forms of the Pt and Pd complexes with the energy of the MP2 optimized structures, finding that the MP2/BS-I//RHF/BS-I calculations give the energy which lies 2.3−6.7 kcal/mol above those obtained at the MP2/BS-I level. The relative stabilities of the two most important species, metallacyclobutanes, **5**, and η^2-complexes, **6**, have been found to be very similar both at the MP2/BS-I//RHF/BS-I level and at the MP2/BS-I level. That is, **5** lies 0.0 kcal/mol below **6** at the MP2/BS-I//RHF/BS-I level and 0.5 kcal/mol

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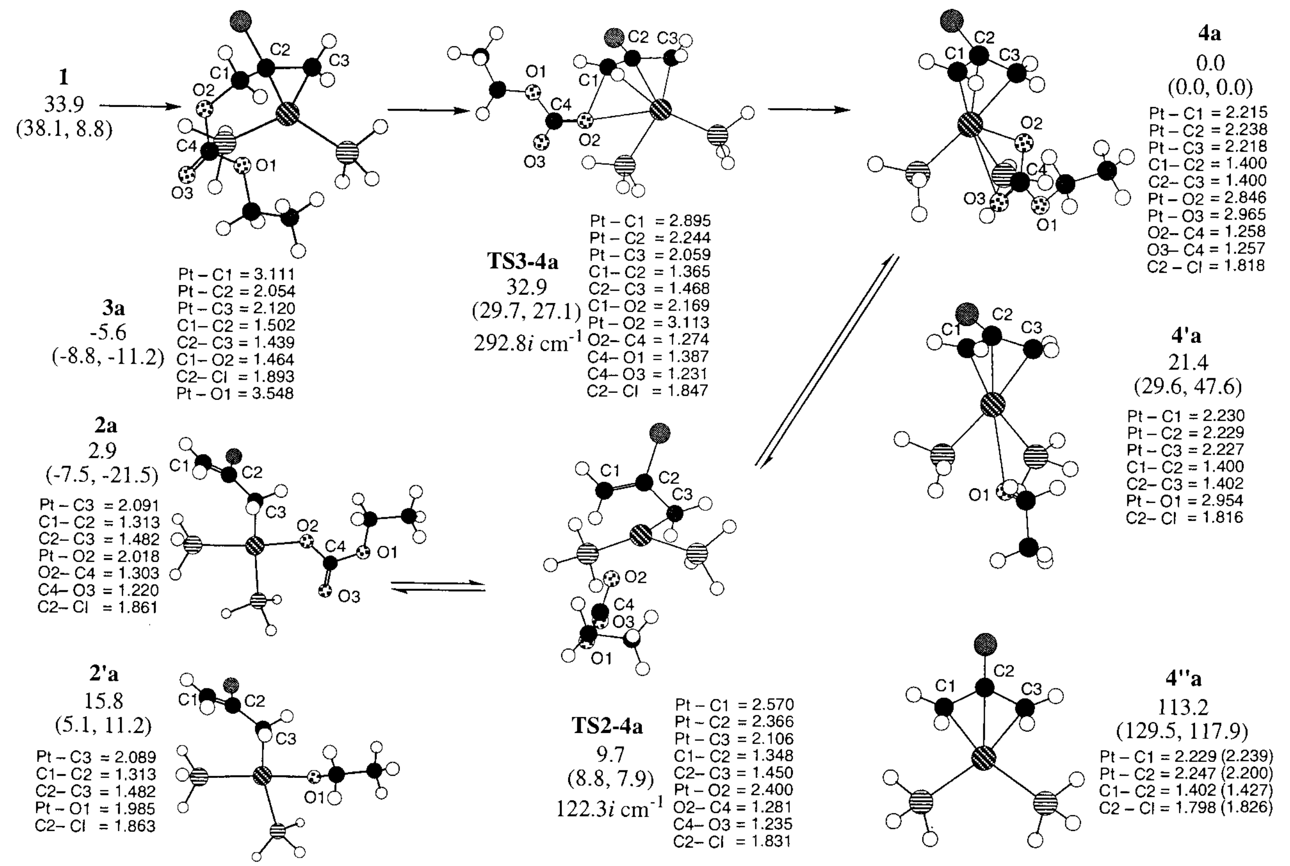

Figure 1. Calculated structures of the ground and transition states on the pathways generating the (η^3-allyl)platinum complexes. Relative energies (kcal/mol) are given for the MP2/BS-II//RHF/BS-I (above), MP2/BS-I//RHF/BS-I (below, left) and RHF/BS-I (below, right) calculations. Bond lengths in parentheses are the MP2/BS-I optimized values.

below **6** at the MP2/BS-I level in the platinum complex. In the palladium complex, **5** lies 11.3 kcal/mol above **6** at the MP2/BS-I//RHF/BS-I level and 12.0 kcal/mol above **6** at the MP2/BS-I level.

Results and Discussion

Formation of η^3-Complexes. We have compared next the calculated structures of $Pt(PH_3)_2$ with those given in the literature. Fantucci and co-workers have investigated the platinum(0) complex, $Pt(PH_3)_2$, by applying the Hartree–Fock, MP2, density functional and relativistic DF methods with large basis sets.[34] They have obtained the length ranging from 2.312 to 2.462 Å for the Pt–P bond. It has been shortened by ~0.07 Å when the polarization functions have been added to the atoms in the ligands. We have obtained 2.357 Å for the Pt–P bond by the calculation at the RHF/BS-I level. This is in good agreement with their results.

In the first step of the reaction between 2-chloro-2-propenyl ethyl carbonate **1** and a platinum–ethylene complex $Pt(C_2H_4)(PH_3)_2$, (η^2-2-chloro-2-propenyl ethyl carbonate)bis(phosphine)platinum, **3a**, is obtained. The coordination of **1** to the zerovalent platinum reagent $Pt(PH_3)_2$ stabilizes the complex by 39.5 kcal/mol at the MP2/BS-II//RHF/BS-I level. For the palladium complex, **3b**, the stabilization is 28.0 kcal/mol at the same level of theory. The structures of η^2-complexes, bis(phosphine)(alkene)metals, have been examined by X-ray analysis for platinum[7e,f] and by theoretical calculations for platinum and palladium.[20e–g] The structures of **3a** and **3b** are illustrated in Figures 1 and 2. The C^2–C^3 bond was lengthened upon complexation by 0.134 Å in **3a**, while the C^2–C^3 bond was lengthened by a smaller margin, only by 0.077 Å in **3b**. This implies that the platinum η^2-complex involves a stronger back-donation of electrons from the metal to the π^* MO of the C=C bond. The difference in the magnitude of stabilization is ascribed to the stronger back-donation in the platinum complex than that in the palladium complex, as will be discussed more in detail later.

The ethyl carbonate ion migrates from the η^2-2-chloroallyl moiety to the metal center to yield (η^3-2-chloroallyl)bis(phosphine)metal ethyl carbonate, **4**. A transition state, **TS3-4**, appears in the course of transformation of **3** to **4**. The activation energy for the migration is 38.5 kcal/mol in the platinum complex and 35.4 kcal/mol in the palladium complex at the MP2/BS-II//RHF/BS-I level of theory. Conversion between an η^2-complex and an η^3-complex induced by a hydride transfer was studied theoretically by Sakaki.[23] The activation energy was calculated to be 50.8 kcal/mol at the Hartree–Fock level and 35.6 kcal/mol at the SD-CI level in the platinum case and 43.2 and 32.9 kcal/mol in the palladium case. Sakaki found also that the platinum η^2-complex should be much more stable than the η^3-complex, the latter being located 40.5 kcal/mol at the Hartree–Fock level and 27.5 kcal/mol at the SD-CI level above the former. The energy difference was shown to be smaller in the palladium complexes, the η^3-complex being 17.4 and 9.6 kcal/mol higher than the η^2-complex at the Hartree–Fock level and the SD-CI level, respectively. In the present systems, the η^3-complex lies above the η^2-complex only by 5.6 kcal/mol in the platinum complex and by 6.7 kcal/mol in the palladium complex at the MP2/BS-II//RHF/BS-I level.

Now, the migration of an ethyl carbonate ion followed by liberation of a carbon dioxide molecule leads to (η^3-2-chloro-

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(34) Fantucci, P.; Polezzo, S.; Sironi, M.; Bencini, A. *J. Chem. Soc., Dalton Trans.* **1995**, 4121.

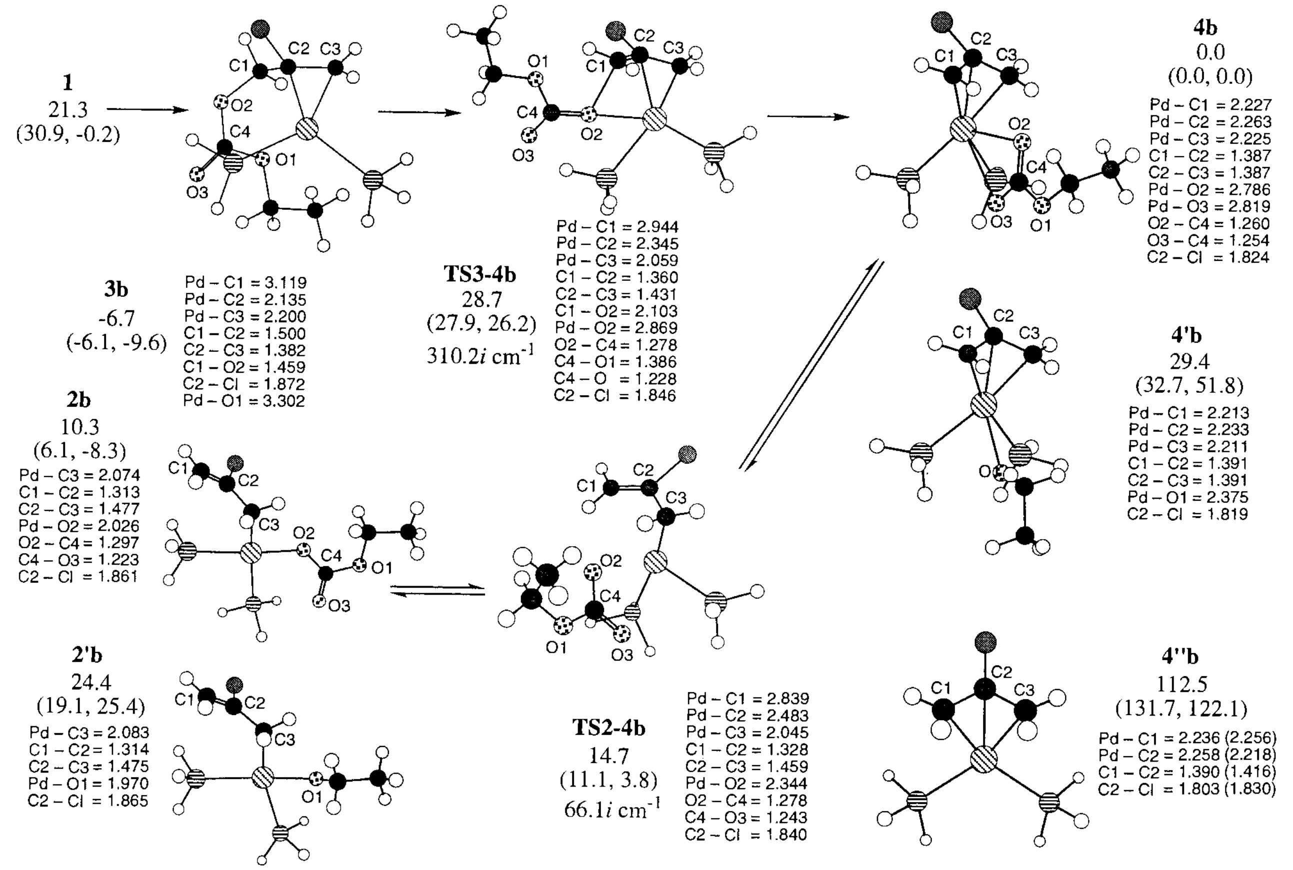

Figure 2. Calculated structures of the ground and transition states on the pathways generating (η^3-allyl)palladium complexes.

allyl)bis(phosphine)metal ethoxide, **4′**. This complex has been shown to be less stable than **4** by 21.4 kcal/mol in the platinum complex and by 29.4 kcal/mol in the palladium complex. We have also calculated the species **4″a** and **4″b** which show the structures of (η^3-2-chloroallyl)bis(phosphine)metal free from the coordination of an ethyl carbonate ion. The interaction between an ethyl carbonate ion and the metal has been calculated to be 113.2 kcal/mol in the platinum complex and 112.5 kcal/mol in the palladium complex. These values would be reduced significantly, if we consider the solvent effects. We may assume, however, that the complex **4** is an important intermediate both in the platinum-catalyzed and in the palladium-catalyzed reactions. Incidentally, it is interesting to see that the bond lengths are seen to remain almost unaffected in **4″** from those in **4** and in **4′**, the differences being in the range of ±0.03 Å. It is shown in Figures 1 and 2 that an ethyl carbonate ion coordinates to the metal center in a dihapto fashion in **4a** and in **4b**.[35]

Cleavage of the σ-bond between an ethyl carbonate ion and the π-allyl carbon in 2-chloro-2-propenyl ethyl carbonate yields an η^1-complex **2**. Siegbahn and co-workers suggested that π-coordination to form **2** is more favorable than the σ-bond cleavage.[27c] The platinum complex **2a** has been shown to lie above **4a** by 2.5 kcal/mol at the MP2/BS-II//RHF/BS-I level. In contrast, the palladium complex **2b** has been shown to lie above **4b** by 10.3 kcal/mol. The η^1-complexes of platinum and palladium have been investigated extensively.[25−27] Sakaki and co-workers have shown that the η^1-form of an allyl is 7.8−8.6 kcal/mol more stable in the platinum complex, whereas the η^3-form is more stable by 1.2−6.2 kcal/mol in the palladium complex, with two phosphine ligands.[23] The η^1-complexes are suggested to be produced through an allyl rotation from the η^3-complexes.[3a,18]

Conversion between the η^1-complexes and the η^3-complexes have not been clarified well, though some experimental observations have been reported.[3a,18] The barrier height found in the present study is not high, being 9.7 kcal/mol in the platinum case measured from **4a** and 14.7 kcal/mol in the palladium case measured from **4b**. In each case, this barrier is lower, compared with that for the conversion from an η^3-form to an η^2-form, and that from an η^3-form to a metallacyclic form. It is also lower compared with the activation energy for reductive elimination from the metal complex. It is suggested therefore that the η^1-complex **2a** and **2b** are produced through a rotation of the allyl group, starting from the η^3-complex, **4a** and **4b**.

Nucleophilic Attack to η^3-Complexes. An ethyl carbonate ion attacks the η^3-2-chloroallyl moiety in the second step of the reaction. The O^1 atom of **4** binds to one of the allyl carbons to yield the ethoxy compounds. Two paths are assumed here. First, the O^1 atom of the ethyl carbonate ion attacks the central carbon of the allyl moiety to yield metallacyclobutanes, **5** or **5′**, as illustrated in Figures 3 and 4. Alternatively, the anion attacks the terminal carbon of the allyl moiety to give (η^2-2-chloro-3-ethoxypropene)bis(phosphine)metal, **6**. The nucleophilic attack may occur either from the same face as the metal or from the opposite face to the metal.

Let us look at the paths in which the ethyl carbonate ion attacks the central carbon of an allyl unit accompanied by the desorption of carbon dioxide. The adduct **5** is produced by the attack of the anion from the face opposite to the metal, while the adduct **5′** is generated by the attack of the anion from the

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(35) Single crystal obtained by slow cooling of acetone solution showed that two ethyl carbonate ions were associated together by hydrogen bonds. The palladium atom was separated from the nearest oxygen atom by 3.63 Å. See ref 6d.

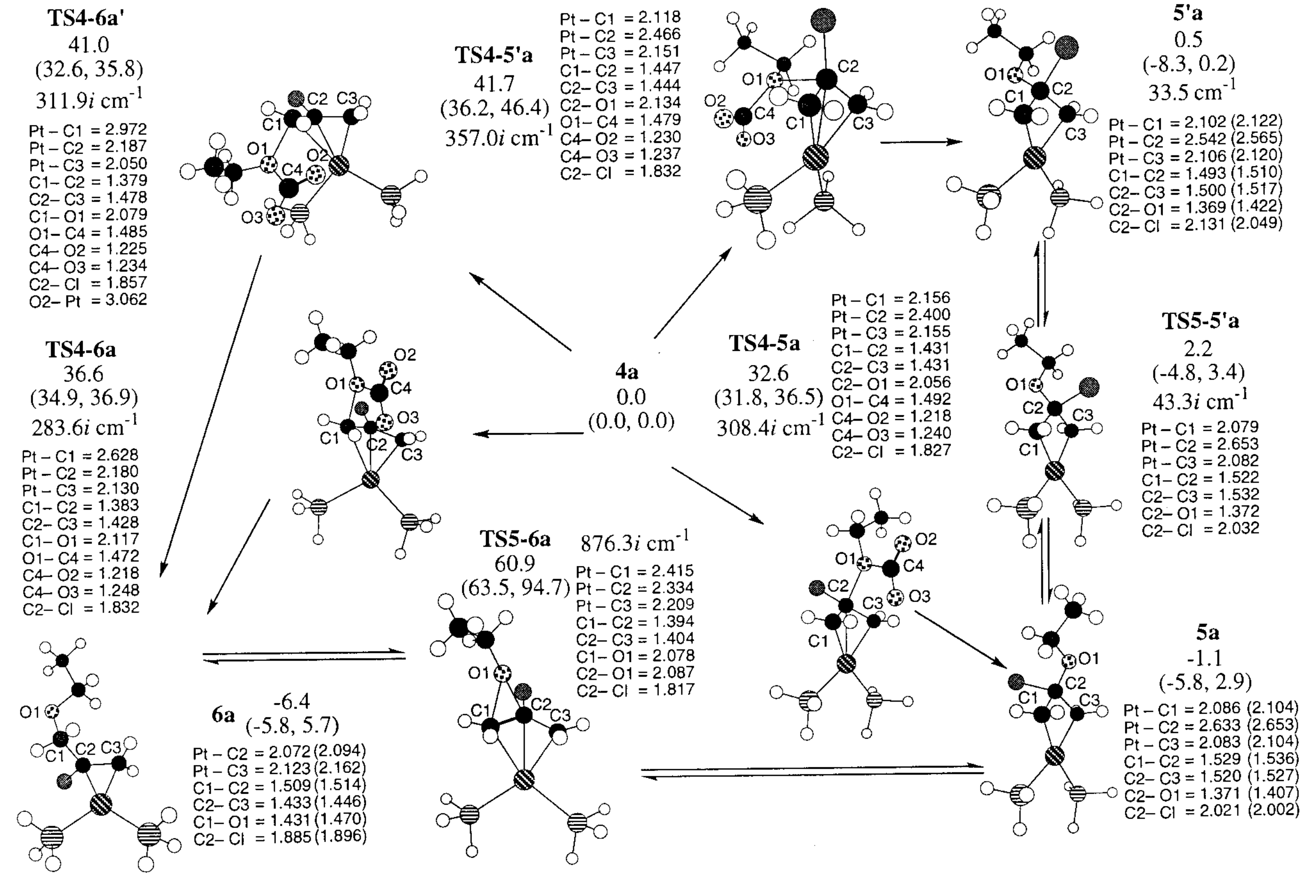
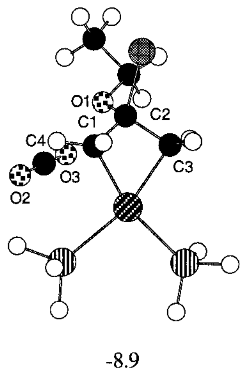


Figure 3. Calculated structures of the ground and transition states on the pathways for the nucleophilic attack to (η^3-allyl)platinum complexes and interconversions between the adducts.

same face. Platinacyclo complexes have been detected by an NMR spectroscopy in solution and by X-ray analysis in solid by Ibers and co-workers.[10d,f] The calculated value of the $C_1C_2C_3$ and C_1PtC_3 dihedral angle in platinacyclobutane is 37.5° in **5a** and 22.1° in **5′a**, in agreement with the observed values in solution. The platinum complex **5a** lies below **4a** by 1.1 kcal/mol at the MP2/BS-II//RHF/BS-I level. The activation energy to reach **5a** from **4a** is 32.6 kcal/mol (33.3 kcal/mol at the MP4/BS-I//RHF/BS-I level) and that to reach **5′a** from **4a** is 41.7 kcal/mol. This result implies that the ethyl carbonate ion attacks the allyl carbon preferably from the face opposite to the metal. However, it has been demonstrated in Figure 3 that the platinacyclobutane **5a** is converted very easily to its conformational isomer **5′a**. The energy barrier for the ring puckering is 1.7 kcal/mol starting from **5′a** and 3.3 kcal/mol starting from **5a**.[36]

The platinacyclobutane having a carbonate group has been calculated to be 3.9 kcal/mol less stable than **5′a** having an ethoxy group at the MP2/BS-II//RHF/BS-I level of theory. The platinacyclobutane **5′a** is stabilized further by 2.1 kcal/mol upon a loose coordination of a carbon dioxide molecule to the platinum metal in an side-on fashion, as illustrated below, after the correction of basis-set superposition error of 7.3 kcal/mol. The distance between the carbon and the platinum center is 3.590 Å, being very long compared with the Ni−C distance, 1.84 Å, in a nickel−carbon dioxide species.[37] On the other hand, it has been shown in Figure 1 that **4a** is located much lower in energy relative to the species **4′a** in which a carbon dioxide molecule has been eliminated. It is concluded therefore that it is the **4a** → **5a** (or **5′a**) stage that the ethyl carbonate group is converted to an ethoxy group. As has been shown above, the platinacyclobutane framework is not affected significantly by the coordination of a carbon dioxide molecule. Thus, we may eliminate the carbon dioxide ligand from our calculation model at this stage.



-8.9
(-21.0, -8.9)

Palladacyclobutane has been detected by X-ray analysis by Hoffmann and co-workers.[13d] In the present study, the palladium complex **5b** lies 8.0 kcal/mol above **4b** at the MP2/BS-II//RHF/BS-I level. The activation energy to reach **5b** from **4b** has been calculated to be high, being 34.8 kcal/mol (38.1 kcal/mol at the MP4/BS-I//RHF/BS-I level). The palladacyclobutane **5b** should be transformed very easily into an η^3-complex **7b** upon ring puckering *via* **TS5-7b**, as illustrated in Figure 4. The barrier

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(36) The wavenumber obtained by a numerical frequency analysis showed that **5′a** was located on a shallow potential minimum.

(37) (a) Aresta, M.; Nobile, F.; Albano, V. G.; Forni, E.; Manassero, M. *J. Chem. Soc., Chem. Commun.* **1975**, 636. (b) Aresta, M.; Nobile, F. *J. Chem. Soc., Dalton Trans.* **1977**, 708 (c) Sakaki, S.; Kitaura, K.; Morokuma, K. *Inorg. Chem.* **1982**, *21*, 760.

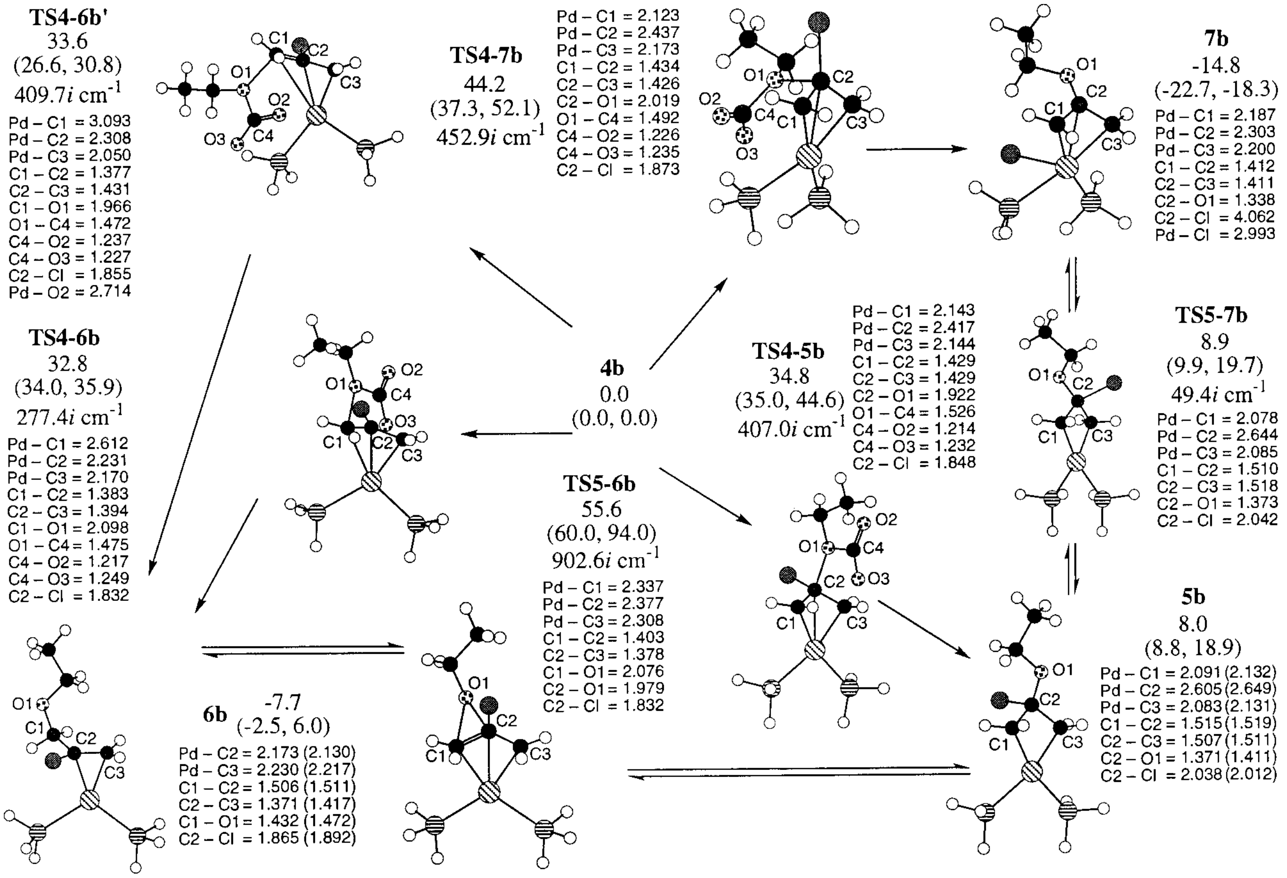

Figure 4. Calculated structures of the ground and transition states on the pathways for the nucleophilic attack to (η^3-allyl)palladium complexes and interconversions between the adducts.

height for the ring puckering is seen to be very small. The η^3-complex **7b** is produced also from **4b** by the attack of the O^1 atom of the ethyl carbonate group to the central carbon of the allyl moiety from the same face as the metal coordination.

The palladacyclobutane having an ethyl carbonate group has been calculated to be less stable than **5b** having an ethoxy group by 4.5 kcal/mol at the MP2/BS-II//RHF/BS-I level of theory. The palladacyclobutane **5b** is destabilized upon a loose coordination of a carbon dioxide molecule to the metal center in an side-on fashion by 1.8 kcal/mol, after the correction of the basis-set superposition error. The distance between the metal and the oxygen is very long, 3.247 Å, and therefore, the bonds in the palladacyclobutane framework have not been changed seriously (<0.01 Å) by removing the carbon dioxide from our model species. These results indicate that the ethyl carbonate group should be converted to an ethoxy substituent during the process in which **4b** is transformed into **5b**.

We discuss next the attack of an ethyl carbonate ion to the terminal carbon of the allyl moiety. The η^3-complex **4** is converted to an η^2-complex **6**. If carbon dioxide is not released in this stage, the reaction returns to the initial complex **3**. Liberation of carbon dioxide directly from **3** may not have to be considered in the experiments carried out under mild conditions. Now, two paths are suggested here. An ethyl carbonate ion may attack the allyl carbon from the same face or from the opposite face to the metal, yielding the same product, **6**. Transition states for these processes are **TS4-6** and **TS4-6′** illustrated in Figures 3 and 4. In the platinum complex, **TS4-6a′** lies above **TS4-6a** by 4.4 kcal/mol at the MP2/BS-II//RHF/BS-I level. The separation becomes smaller in the palladium complex, **TS4-6b′** being located 0.8 kcal/mol above **TS4-6b**. The activation energy for the path to give an η^2-complex **6a** starting from **4a** is higher than that to give the platinacyclobutane **5a** by 4.0 kcal/mol (2.0 kcal/mol at the MP4/BS-I//RHF/BS-I level). Interestingly, the path to give an η^2-complex **6b** has a lower activation energy in the palladium case by 2.0 kcal/mol (4.7 kcal/mol at the MP4/BS-I//RHF/BS-I level).

The η^2-complex **6a** lies below **5a** by 5.3 kcal/mol at the MP2/BS-II//RHF/BS-I level, but is almost the same in energy as **5a** at the MP2/BS-I level (0.6 kcal/mol above **5a** at the MP4/BS-I//RHF/BS-I level). The palladium complex **6b** lies below **5b** by 15.7 kcal/mol at the MP2/BS-II//RHF/BS-I level and 12.0 kcal/mol at the MP2/BS-I level (13.4 kcal/mol at the MP4/BS-I//RHF/BS-I level). That is, the palladium complex prefers the η^2-structure to the metallacyclobutane structure by ~15 kcal/mol, whereas the platinum complex may take either structure. This makes a big difference between the platinum and palladium catalyzed nucleophilic substitutions at the allyl carbons of 2-chloro-2-propenyl ethyl carbonate.

The interconversion between the η^2-complex **6** and the metallacyclobutane **5** is shown in Figures 3 and 4. The activation energy is very high, being 62.0 kcal/mol in the platinum complex starting from **6a**, and 63.3 kcal/mol in the palladium complex starting from **6b**. The interconversion between **5** and **6** is unlikely.

Reductive Elimination and *β*-Chloro Migrations. Now, we discuss the final step of the reactions. The metallacyclobutane **5** or **5′** may be converted to a cyclopropane **8** through reductive elimination. It may also afford (η^3-2-ethoxyallyl)bis(phosphine)-metal chloride **7** as a product, accompanied by a migration of the chloride ion from the allylic carbon to the metal center. The adduct **6** may generate **3** by replacing its ligand with the starting material **1** to liberate a product **9**.

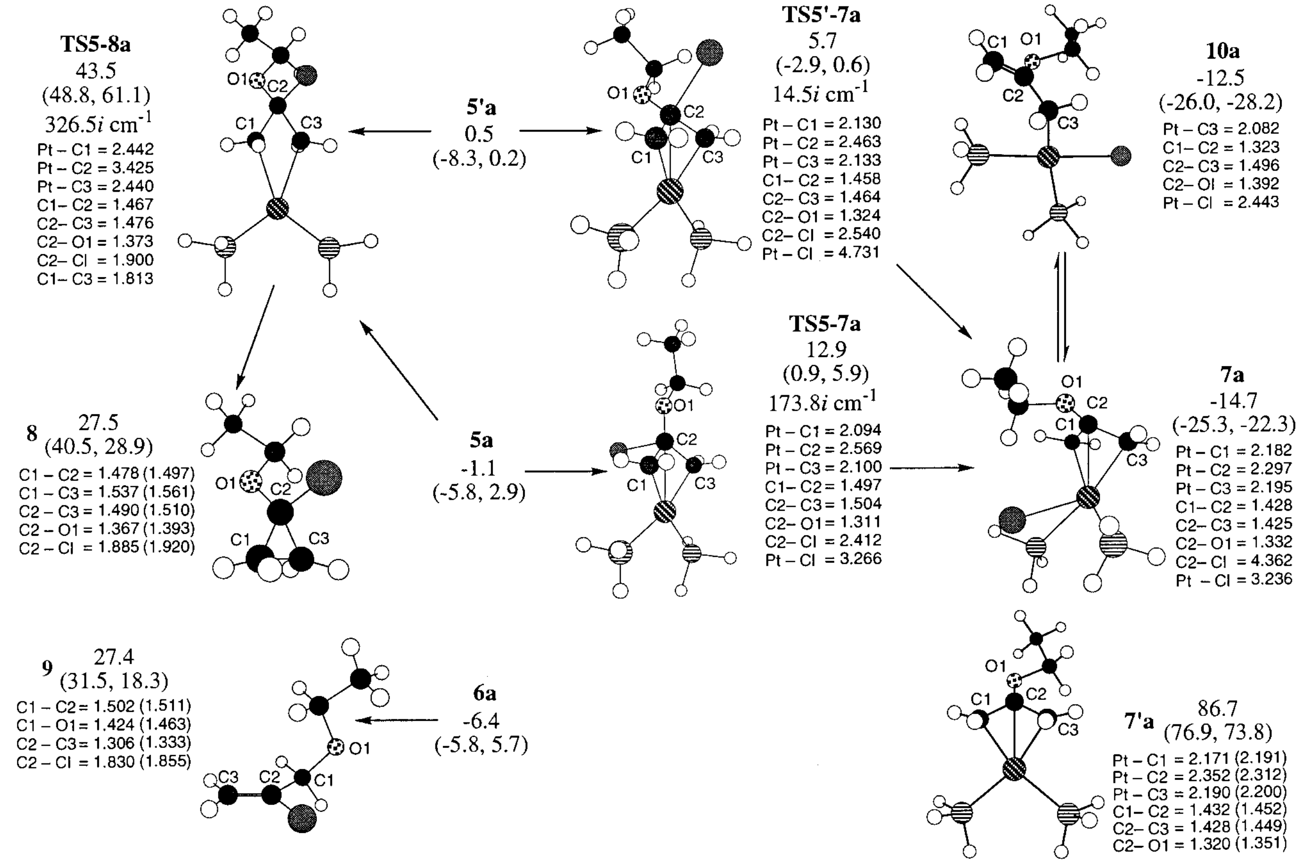

Figure 5. Calculated structures of the ground and transition states on the pathways of reductive elimination and *β*-chloro migration in platinacyclobutane. The product **9** *via* an η^2-complex **6a** is also indicated.

The path for the migration of the chloride ion to afford **7** is shown in Figures 5 and 6. Since the ring puckering between **5a** and **5′a** is very facile in the platinacyclobutane, two reaction paths are suggested. First, the metallacyclobutane may be converted to an η^3-complex *via* a transition state, **TS5-7a**. The activation energy for this path has been calculated to be 14.0 kcal/mol. The activation energy for the path passing through the transition state **TS5′-7a** is shown to be lower. However, the small vibrational frequency indicates that this corresponds to the path for the departure of a chloride ion from the system. In the product **7a**, the migrating chloride ion coordinates nearly perpendicular to the platinum square plane. The palladacyclobutane **5b** is also transformed to **7b** involving a migration of a chloride ion. The η^1-complex **10** is produced *via* **7** by rotating the allyl moiety. In the platinum case, the η^1-complex **10a** lies 2.2 kcal/mol above the η^3-complex **7a**, whereas the η^1-complex **10b** lies 6.6 kcal/mol above **7b**. Incidentally, in the pentacoordinated nickel complex, it has been suggested that an η^3-structure is more stabilized relative to an η^1-structure.[8b] The distance between a halogen atom and the metal has been demonstrated to be longer in a pentacoordinated structure relative to the usual metal−halogen bonds. In line with the observation in the nickel complex, the Pt−Cl bond in **7a** is seen to be considerably longer than that in **10a** and the Pd−Cl bond in **7b** is considerably longer than that in **10b**.

The metallacyclobutane **5** or **5′** may be converted to a cyclopropane derivative **8** by reductive elimination. The activation energy is 44.6 kcal/mol in the platinum complex measured from **5a** and 22.0 kcal/mol in the palladium complex measured from **5b**. The activation energy is higher in the platinum complex by ~23 kcal/mol. These values parallel those calculated for reductive elimination of ethane from metal complexes.[25,27] The cyclopropane **8** with a free Pt(PH$_3$)$_2$ molecule lies 28.6 kcal/mol above the platinacyclobutane **5a**, and **8** with a Pd(PH$_3$)$_2$ molecule lies 6.9 kcal/mol above **5b**. The activation energy to give the cyclopropane product is very high relative to the path that gives the η^3-complex **7**.

If the η^2-allyl ligand **9** is replaced by the starting carbonate, a catalytic cycle is realized.[6d] The stabilization energy due to the η^2-coordination is large in the platinum complex, being 33.8 kcal/mol in **6a** and 39.5 kcal/mol in **3a**. It is 22.4 kcal/mol in **6b** and 28.0 kcal/mol in **3b**. Both of the platinum and palladium complexes prefer **3** to **6**.

Figure 7 illustrates an energy profile of the reaction of the platinum complex. The η^2-complex **6a** is seen to be slightly more stable than the platinacyclobutane **5a**. The migration of the chloride ion *via* the transition state **TS5-7a** should occur easily. Thus, the reaction of 2-chloro-2-propenyl ethyl carbonate takes place *via* **3a**, **4a**, **5a**, and **7a**, consisting of the coordination of the starting carbonate ion to the platinum reagent, the migration of an ethyl carbonate ion from the allylic moiety to the platinum center, the nucleophilic attack of the ethyl carbonate ion (or an ethoxide ion) to the central carbon of the allylic moiety, and of the migration of a chloride ion from the allyl moiety to the platinum center. A stoichiometric amount of the platinum reagent is consumed.

In the palladium complex, the η^2-complex is more stable than the palladacyclobutane by ~15 kcal/mol, as illustrated in Figure 8. The η^2-coordination is weaker relative to that in the platinum complex by ~11 kcal/mol. These make the reaction of 2-chloro-2-propenyl ethyl carbonate proceed *via* **3b**, **4b**, and **6b**, involving the coordination of the carbonate to the palladium reagent, the migration of an ethyl carbonate ion from the allyl moiety to the palladium center, and the nucleophilic attack of the ethyl

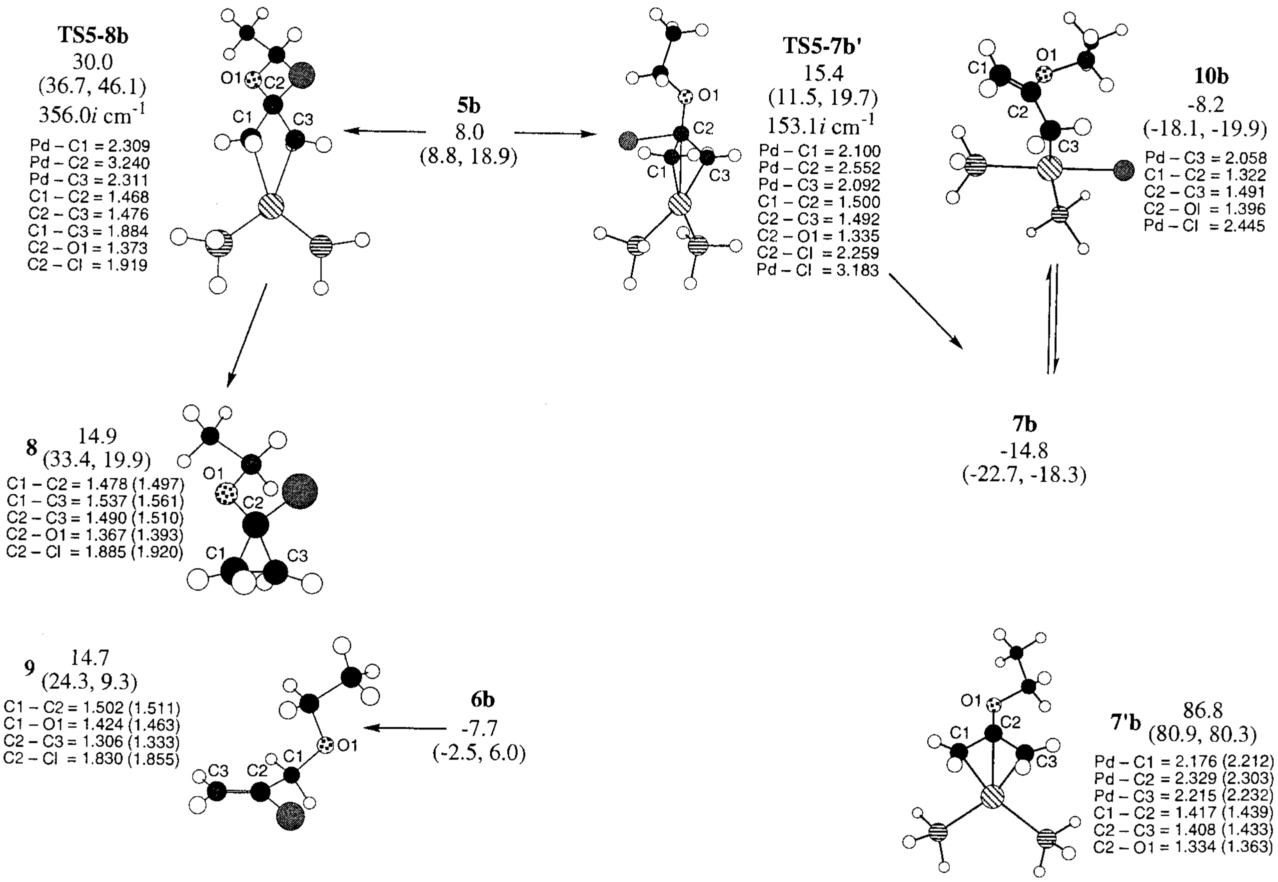

Figure 6. Calculated structures of the ground and transition states on the pathways of reductive elimination and β-chloro migration in palladacyclobutane. The product **9** *via* an η^2-complex **6b** is also indicated.

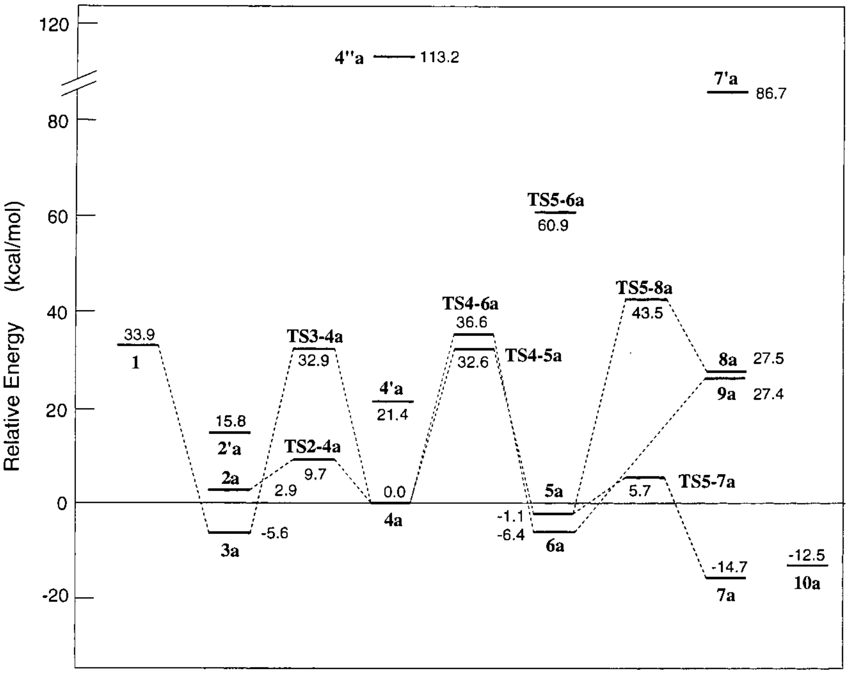

Figure 7. Energy profile of the reaction of Pt(PH$_3$)$_2$ with 2-chloro-2-propenyl ethyl carbonate. Relative energies (kcal/mol) have been measured from **4a**.

carbonate ion to the terminal carbon of the allyl moiety. Then, **6b** will liberate 2-chloro-3-ethoxypropene ligand **9** and makes again the complex **3b** with the starting carbonate. Then, the reaction should take place by a catalytic amount of the palladium complex. The η^3-complex **7** is also stable. This suggests that the palladium complex is consumed in part to form **7**. The experimental observation that the turnover of the catalyst is not high is understood in this context. If the energy difference between **5b** and **6b** is smaller or reversed compared with the present system, the nucleophilic attack at the central carbon will be more favorable in the palladium case. In fact, the nucleophilic attack on the central carbon of (π-allyl)palladium complexes

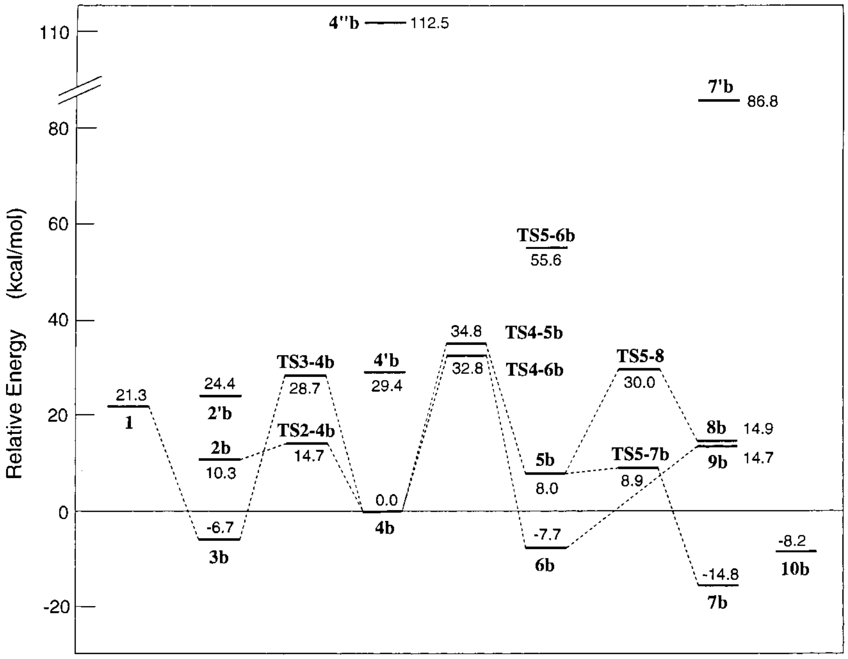

Figure 8. Energy profile of the reaction of Pd(PH_3)$_2$ with 2-chloro-2-propenyl ethyl carbonate. Relative energies (kcal/mol) have been measured from **4b**.

has been studied by Hoffmann and co-workers for several types of ligands.[13]

We have also carried out calculations on **5a**, **5′a**, **6a**, **7a**, **10a**, **TS5-5′a**, **TS5-6a**, **TS5-7a**, **TS5′-7a**, and **TS5-8a** with a carbon dioxide molecule coordinated to the platinum center, finding that they differ in energy by −2.1 to 1.7 kcal/mol from the species without a carbon dioxide ligand, the basis-set superposition errors being corrected. Calculations on **5b**, **6b**, **7b**, **10b**, **TS5-6b**, **TS5-7b**, **TS5-7′b** and **TS5-8b**, involving a carbon dioxide molecule have shown that they are destabilized by 0.8−2.5 kcal/mol relative to the species without a carbon dioxide. The metal−carbon (or oxygen) bond has been shown to be very long, ranging from 3.341 to 4.024 Å in the platinum complexes and from 3.105 to 3.916 Å in the palladium complexes. Coordination of a carbon dioxide molecule does not bring about significant changes in the relative stabilities and structures of the species examined in this study. Accordingly, the discussions made so far are unaffected by the presence or absence of a carbon dioxide molecule in our reaction models.

Orbital Interactions. To see the origin of the differences between the platinum-catalyzed reaction and the palladium-catalyzed reaction, we have studied orbital interactions. It has been suggested by Dewar and by Chatt and Duncanson that the bonds in metal-alkene complexes are represented by σ-donation from the occupied π MO of the olefin to the unoccupied *spd* hybrid orbital of the metal and by the π-back-donation from the occupied metal *d* orbital to the unoccupied π^* MO of the alkene.[38] Here, we compare the strength of bonds in the platinum η^2-complex and platinacyclobutane with those in the palladium species by examining orbital interactions between a metal reagent and the attached organic ligand. First, we divide a complex into two fragment species, M(PH_3)$_2$ and the remaining part. Both fragments are assumed to be neutral in η^2-complexes, but metallacyclobutanes are partitioned into charged fragments, M(PH_3)$_2^{2+}$ and a 2-chloro-2-ethoxytrimethylene dianion. Then, we have performed simultaneous transformations of the MOs within each of the two fragment species to represent the interaction by means of a few pairs of interaction orbitals.[39,40] To take not only the frontier MOs, but also all the occupied and unoccupied MOs properly into account, we used the components of the bond-order matrix ***P*** between the two fragment species as the scale of orbital interactions. They have been calculated from the MOs of the composite system of two fragments, and therefore, interaction orbitals are independent of the way of dividing the complex into fragments. It is natural, however, that the interpretation of interactions, e.g., donation and back-donation, depends on the way of populating electrons in the fragments. Figures 9 and 10 present two pairs of interaction orbitals which play dominant roles in the η^2 (**6a**) and metallacyclic (**5a**) forms of the platinum complexes, respectively.

It is seen that the orbitals of the metal fragment look very similar to each other in the η^2-coordinated and metallacyclic structures. The characteristics of interactions are demonstrated in the paired orbitals of the organic part. The interaction orbitals of the 2-chloro-3-ethoxypropene ligand in **6a** are seen to be localized well on the C=C bond, bearing close resemblance to the π^* and π MOs of ethylene. This indicates that 2-chloro-3-ethoxypropene combines its unoccupied MOs and its occupied MOs to give the unoccupied and occupied interaction orbitals which are most suitable for electron delocalization in this complex. It is very interesting to see that orbital interactions derived in this manner from the *ab initio* MO calculations are essentially the ones that have been suggested by Dewar and by Chatt and Duncanson more than forty years ago.[38] In the metallacyclic structure, **5a**, 2-chloro-2-ethoxytrimethylene ligand generates the occupied and unoccupied interaction orbitals that are suited to bring more oriented and tighter σ bonds.

Two pairs of interaction orbitals which play dominant roles in the palladium complex are presented in Figure 11 for the

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(38) (a) Dewar, M. J. S. *Bull. Chim. Soc. Fr.* **1951**, C71. (b) Chatt, J.; Duncanson, L, A. *J. Chem. Soc.* **1953**, 2939.

(39) Fukui, K.; Koga, N.; Fujimoto, H. *J. Am. Chem. Soc.* **1981**, *103*, 196.

(40) (a) Fujimoto, H.; Yamazaki, T.; Mizutani, H.; Koga, N. *J. Am. Chem. Soc.* **1985**, *107*, 6157. (b) Fujimoto, H.; Yamasaki, T. *J. Am. Chem. Soc.* **1986**, *108*, 578. (c) Fujimoto, H.; Koga, N.; Hataue, I. *J. Phys. Chem.* **1984**, *88*, 3539.

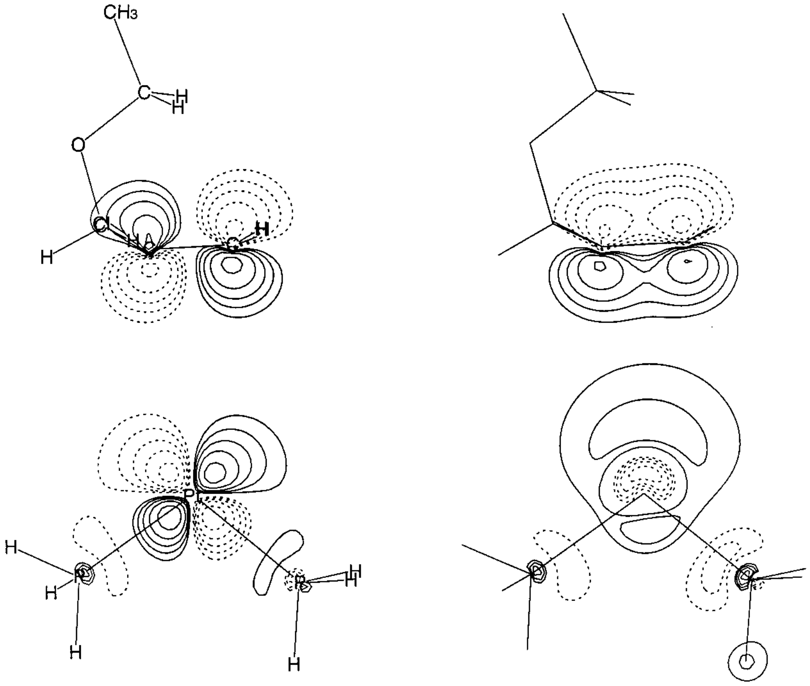

Figure 9. Orbital interactions in the η^2-complex, **6a** (pair 1 on the left-hand side, and pair 2 on the right-hand side).

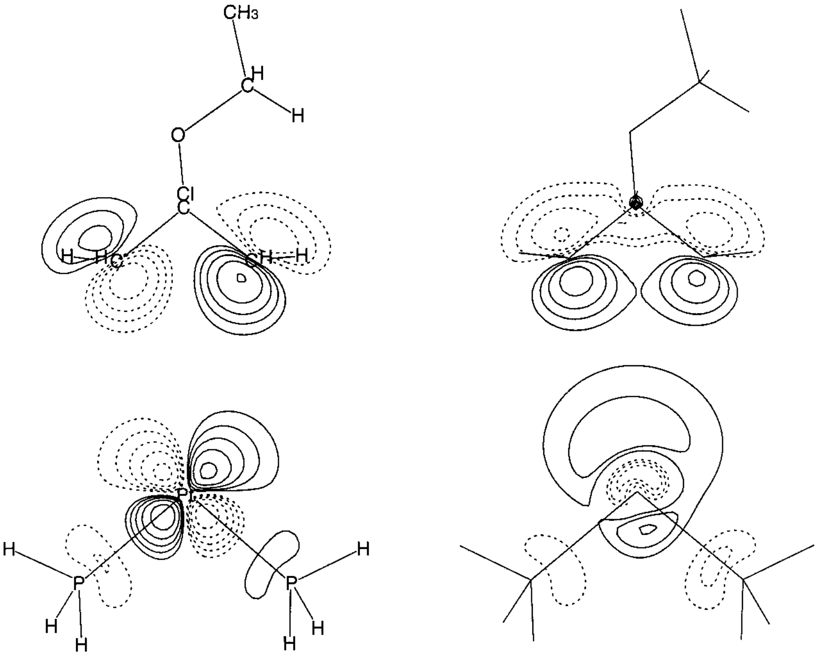

Figure 10. Orbital interactions in the platinacyclobutane, **5a** (pair 1 on the left-hand side, and pair 2 on the right-hand side).

η^2-coordinated form (**6b**) and in Figure 12 for the metallacyclobutane form (**5b**).

Table 1 summarizes the electron populations of the fragment interaction orbitals and the overlap population of the orbital pairs. In the η^2-coordinated form, **6a** and **6b**, the overlap population is larger in the orbital pair representing back-donation of electrons from the $M(PH_3)_2$ part (pair 1) than in the orbital pair representing donation of electrons from the organic ligand (pair 2). The net charge on the $Pt(PH_3)_2$ fragment has been calculated to be $+0.550e$ by the Mulliken population analysis and $+0.478e$ by the natural bond orbital analysis.[41,42] It is $+0.361e$ by the Mulliken population analysis and $+0.345e$ by the natural bond orbital analysis in the $Pd(PH_3)_2$ fragment. The calculated charges are in line with the results that back-donation of electrons from the metal fragment plays a more important role in the η^2-coordinated form of these complexes.

In **5a**, the net charge on the $Pt(PH_3)_2$ fragment has been calculated to be $+0.700e$ by the Mulliken population analysis and $+0.724e$ by the natural bond orbital analysis. It is $+0.539e$ and $+0.688e$ on the $Pd(PH_3)_2$ fragment of **5b**. The electronic charges are more separated in metallacyclobutanes than in the η^2-coordinated forms, but the formal charges assumed in partitioning the metallacyclobutane into fragments have been neutralized by strong electron shift from the trimethylene fragment to the metal fragment.[43-45] Here, the orbital pairs involve not only electron delocalization, but also the overlap

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(41) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841, 2338, 2343.
(42) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066.

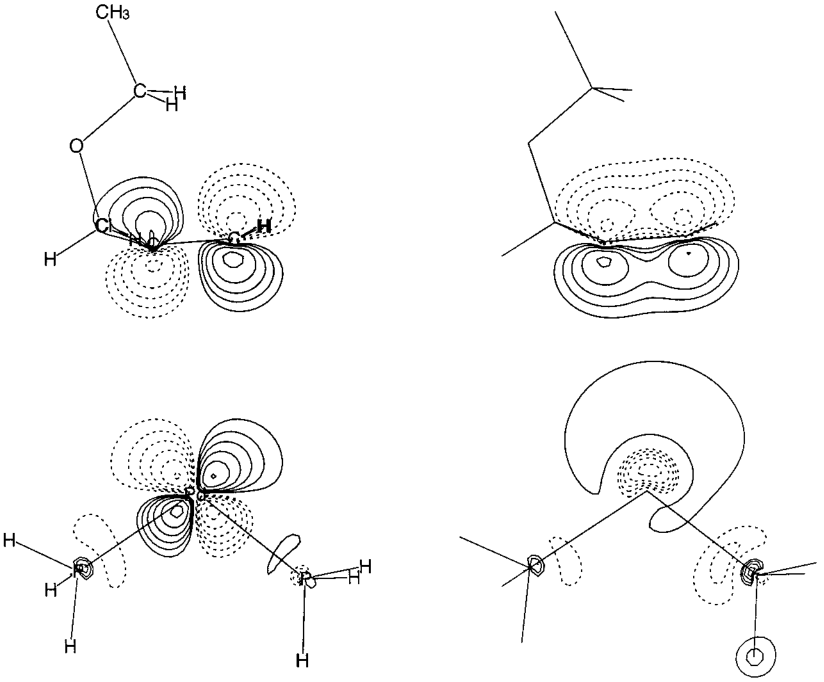

Figure 11. Orbital interactions in the η^2-complex, **6b** (pair 1 on the left-hand side, and pair 2 on the right-hand side).

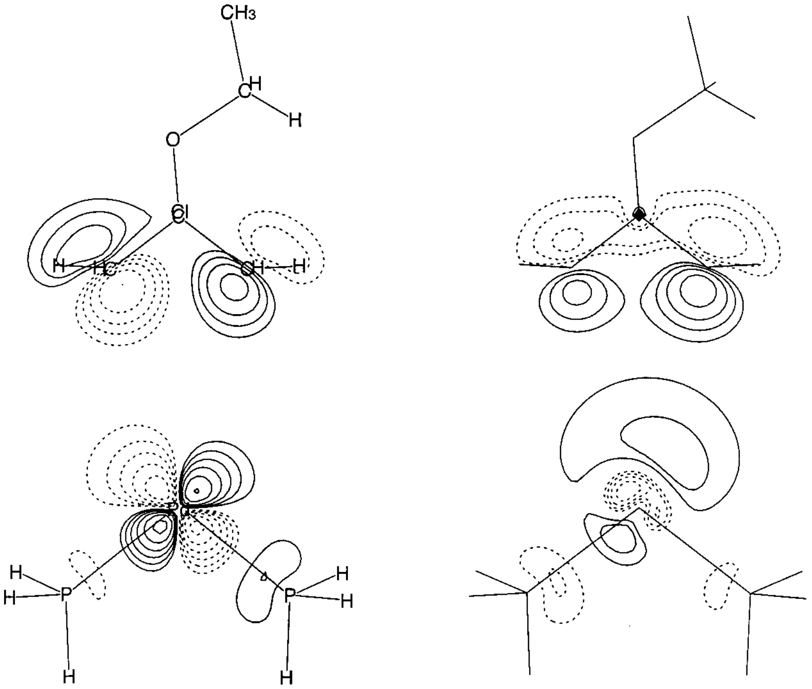

Figure 12. Orbital interactions in the palladacyclobutane, **5b** (pair 1 on the left-hand side, and pair 2 on the right-hand side).

repulsion arising between the reaction sites. Thus, the sum of the electron populations of each orbital pair is larger than 2, and therefore, it is rather difficult to find a direct correlation between the electron population of the interaction orbitals and the net charge on the metal fragment. One sees, however, that the ratio of electrons housed in the orbitals of the metal fragments to the total number of electrons housed in the two pairs of interaction orbitals is considerably smaller in **5a** and **5b** than in **6a** and **6b**, in line with the magnitude of the positive net charge on the metal fragment. The orbital of 2-chloro-2-ethoxytrimethylene ligand in the pair having a larger overlap

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(43) (a) Pauling, L. *J. Chem. Soc.* **1948**, 1461. (b) Connor, J. A.; Hillier, I. H.; Saunders, V. B.; Wood, M. H.; Barber, M. *Mol. Phys.* **1972**, *24*, 497.

(44) We divide a molecule into fragments to study the origin of bonds. The fragments are artificial and may not correspond to any realistic species. In the present case, the occupied orbital of the trimethylene dianion fragment is higher in energy than the unoccupied orbital of the metal fragment. In a simple perturbation scheme, a pair of electrons are shifted first from the occupied orbital of the anionic fragment to the unoccupied orbital of the cationic fragment, and then the electrons are brought into delocalization. The energy for dividing the complex into the ion pair is thus compensated.

(45) An alternative interpretation is that electronic charge is shifted from the anionic part to the cationic part until the local electron-donating and electron-accepting abilities of the two fragments (or chemical potentials of the two parts) are balanced. See: (a) Parr, R. G.; Zhou, Z. *Acc. Chem. Res.* **1993**, *26*, 256. (b) Fujimoto, H.; Satoh, S. *J. Phys. Chem.* **1994**, *98*, 1436.

Table 1. Overlap Populations and Electron Populations of the Interaction Orbitals

species	orbitals	fragment	electron population	overlap population
5a	pair 1	Pt(PH)$_3$	1.052	0.190
		ligand[a]	1.130	
	pair 2	Pt(PH)$_3$	0.672	0.057
		ligand[a]	1.672	
5b	pair 1	Pd(PH)$_3$	1.139	0.160
		ligand[a]	1.021	
	pair 2	Pd(PH)$_3$	0.583	0.026
		ligand[a]	1.731	
6a	pair 1	Pt(PH)$_3$	1.423	0.118
		ligand[b]	0.900	
	pair 2	Pt(PH)$_3$	0.580	0.087
		ligand[b]	1.732	
6b	pair 1	Pd(PH)$_3$	1.583	0.090
		ligand[b]	0.752	
	pair 2	Pd(PH)$_3$	0.535	0.055
		ligand[b]	1.822	

[a] 2-Chloro-2-ethoxytrimethylene. [b] 2-Chloro-3-ethoxypropene.

population in **5a** or in **5b** (pair 1) possesses a node between two terminal carbons. Two distinct σ bonds should be generated in metallacyclobutanes.[46]

The overlap populations are smaller in the palladacyclobutane compared with those in the platinacyclobutane, mainly due to smaller overlaps between the paired interaction orbitals in the former. This makes the formation of a metallacyclobutane less likely in the palladium-catalyzed reaction. The orbital interactions in platinacyclobutane are almost equivalent in strength in the two C−M bond regions. That is, the orbital of the trimethylene fragment shows approximately the same amplitude on both of the two terminal carbons. In contrast, there is some difference in the strength of orbital interactions between the two C−M bonds in palladacyclobutane. This may be another indication that the metallacyclobutane structure is not favored in the palladium case. It seems reasonable therefore that the palladacyclobutane lies above the η^2-complex in energy, but that the platinacyclobutane lies close in energy to the η^2-complex. The overlap populations are also smaller in the η^2-palladium complex relative to those in the η^2-platinum complex. This agrees with the result of calculations that the stabilization arising from the η^2-coordination of 2-chloro-3-ethoxypropene is smaller in the palladium complex. The weaker coordination in the palladium η^2-complex appears to be suitable for the replacement of the 2-chloro-3-ethoxypropene ligand with the starting compound.

Conclusion

It has been shown that 2-chloro-2-propenyl ethyl carbonate is liable to transform in the presence of a stoichiometric amount of Pt(C_2H_4)(PH_3)$_2$ to (η^3-2-chloroallyl)bis(phosphine)platinum ethyl carbonate **4a**, and then, affords (η^3-2-ethoxyallyl)bis(phosphine)platinum chloride **7a** *via* a metallacyclobutane, **5a** or **5′a**. In contrast, 2-chloro-2-propenyl ethyl carbonate is shown to be converted with a catalytic amount of a Pd(0) complex to (η^3-2-chloroallyl)bis(phosphine)palladium ethyl carbonate **4b**, which affords (η^2-2-chloro-3-ethoxypropene)bis(phosphine)palladium, **6b**. Then, an alkene **9** is produced. It is likely that the η^3-complexes, **4a** and **4b**, are yielded not from η^1-complexes, but from η^2-complexes. The stability of the η^3-complexes may depend on the counterion.

The nucleophilic attack takes place both at the central carbon and at the terminal carbon. In the platinum case, the activation energy to give the adduct at the central carbon has been calculated to be slightly smaller than that to give the adduct at the terminal carbon. In contrast, the nucleophilic attack to the central carbon costs a slightly higher activation energy than the attack to the terminal carbon in the palladium case. The ring puckering should be facile in metallacyclobutanes **5**, but the interconversion between **5** and the η^2-complex **6** has been shown to be difficult. Our calculations have demonstrated that the platinacyclobutane **5a** is converted to the η^3-complex **7a** and that this step governs the major product of the platinum-catalyzed reaction. In the palladium complex, the η^2-complex **6b** is more stable than the palladacyclobutane **5b** by ∼15 kcal/mol. The generation of **6b** *via* an η^3-complex **4b**, followed by the replacement of the 2-chloro-3-ethoxypropene ligand in **6b** with the starting carbonate, **1**, should determine the major product of the reaction. Orbital interactions favor the metallacyclic form, as well as the η^2-complex, in the platinum complex. In contrast, palladacyclobutane has an weaker orbital interaction relative to the platinum complex, making the η^2-complex more favorable than the metallacyclobutane.

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Supporting Information Available: Tables S1−S86 listing the calculated total energies and coordinates of the atoms in the optimized structures of the species examined in the present study (63 pages). Ordering information is given on any current masthead page.

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(46) The σ bonds in cyclobutane may be interpreted simply by partitioning the molecule into a trimethylene biradical fragment and a methylene biradical fragment (for a cycloporpane case, see: Fujimoto, H.; Ohwaki, S.; Endo. J.; Fukui, K. *Gazz. Chim. Ital.* **1990**, *120*, 229). Such a division may not be suitable for metallacyclobutane, since a considerable amount of charge is shifted from one to the other.