

A Theoretical Study of the Cyclopropane Ring Opening by Palladium

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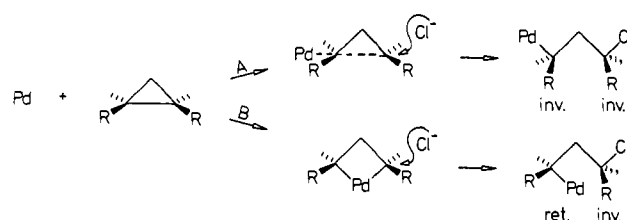
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Abstract: Quantum chemical methods including the effect of electron correlation have been used to study the reaction between palladium and cyclopropane. Geometries of the minima and saddle points have been determined by using the Complete Active Space SCF (CASSCF) method. For the optimized geometries contracted CI (CCI) calculations were performed. Two reaction pathways for the ring opening of cyclopropane were studied, edge and corner palladation. The edge palladation is clearly favored in these calculations with a barrier of 17 kcal/mol. The barrier for corner palladation is estimated to be 30–35 kcal/mol. The calculated energy for metallacyclobutane is slightly higher (6 kcal/mol) than the energy for palladium and cyclopropane. The radical intermediate formed after the corner attack is 18 kcal/mol less stable than metallacyclobutane.

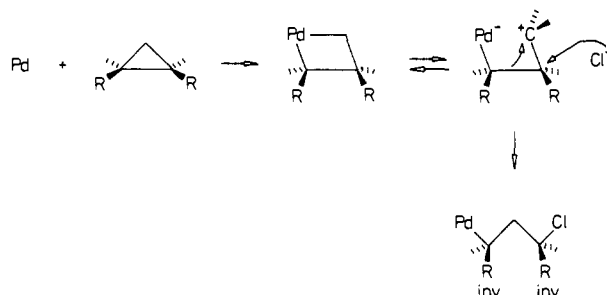
Reactions between transition metals and small strained ring hydrocarbons often result in a C–C bond cleavage.² In particular cyclopropanes readily react with transition metals, a reaction that has attracted considerable interest.^{3–7} In some cases the latter reaction leads to the formation of a metallacyclobutane, which can undergo further reactions.^{7,8}

We have recently studied the mechanism for palladium-induced ring opening of cyclopropanes experimentally.⁵ In these reactions a palladium(II) species activates the ring, followed by an addition of a nucleophile, e.g., chloride. We⁵ and others⁶ have found that the cyclopropane ring may be opened by the metal with either retention or inversion depending on the reaction conditions and the substrate. To account for these results, two types of ring activations were inferred (Scheme I). The reaction may occur either via a corner palladation (A) or an edge palladation (B). However, we also considered that the inversion may be a result of an initially formed metallacyclobutane followed by a rearrangement (Scheme II).^{5b,6} A similar rearrangement was suggested for the rearrangement of an iridacyclobutane.⁹ The rearrangement in Scheme II would lead to an apparent inversion at the carbon bound to palladium, but the mechanism involves an edge palladation. From the experimental results it cannot be established whether a corner activation or an edge activation according to Scheme II is operating in the cases where an inversion at the carbon bound to the metal is observed. The question arises

Scheme I. Ring Opening of Cyclopropane by Palladium



Scheme II. Ring Opening of Cyclopropane by Palladium



whether a corner activation (cf. Scheme I) exists at all, since an edge activation is more attractive from a chemical point of view.¹⁰

In a first attempt to elucidate the mechanism of transition metal promoted activation of cyclopropanes, we decided to study the problem theoretically by calculating important parts of the potential energy surface of the ring-opening process of cyclopropane by palladium for the edge and corner approaches, respectively. The model was chosen as simple as possible with use of a palladium atom without any ligands for two reasons. The first reason is obviously that the calculation becomes smaller which makes it possible to use refined theoretical methods and solve the model problem without any remaining question marks. The second reason is that it has been our experience that the same electronic structure mechanisms are operating with and without ligands.²³ It should in this context be mentioned that although most experimental studies of the cyclopropane ring opening by platinum metals have been done with palladium(II) and platinum(II) complexes, nickel(0),¹¹ palladium(0),¹² and platinum(0)^{4b} are also

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known to open cyclopropanes. We will attempt to add ligands in a forthcoming study, which will be much simplified by the present initial study. It is, for example, very likely that the geometries for the transition states and for the stable minima will only be moderately affected by the addition of ligands, thus simplifying the normally time-consuming search for the transition-state region. The model for the reaction including ligands is still much less straightforward to set up, however.

For chemical reactions where bonds are broken and formed, methods going beyond the Hartree-Fock approximation are generally required. It may be argued that for the present case with a reaction between a palladium atom, which has a closed-shell ground state, and cyclopropane, leading to a metallacycle with presumably rather strong bonds, the Hartree-Fock approximation may be sufficient. However, it is a characteristic feature for transition-metal complexes that even in molecules with strong bonds there will be large CI coefficients for excitations from bonding to antibonding orbitals. For the metallacycle there is indeed an antibonding orbital with occupation as high as 0.15, which would make the use of the Hartree-Fock approximation rather doubtful. For the radical-type structure formed after a corner attack the situation is even more complex with two orbitals having occupations of 1.36 and 0.66. In the present study we have used the CASSCF method¹³ to account for the near degeneracy effects and the contracted CI method¹⁴ for the changes of the dynamical correlation energy accompanying the rearrangements of the palladium d shell.

Details of the Calculations

Complete active space SCF¹³ (CASSCF) and contracted CI¹⁴ (CCI) calculations were performed for different regions of the potential surface of PdC₃H₆. The basis sets were of double- ζ quality in the valence space and for palladium an effective core potential (ECP) was used to replace the core orbitals.

For carbon the MIDI-4 basis of Tatewaki et al.¹⁵ was used. This is a 7s,3p set which is minimal basis contracted for the 1s orbital and double- ζ contracted for the valence orbitals. The 1s orbital was frozen in its atomic shape in all the calculations to avoid superposition errors.¹⁶ For hydrogen the 4s basis of Huzinaga¹⁷ was double- ζ contracted. The use of an ECP for metals like palladium is not without complications. In order to account for the fact that the 4d orbitals are not well separated from the 4s,4p core orbitals, the frozen core orbital ECP method¹⁸ was used. In this ECP method only the innermost core orbitals (1s-3p) are parametrized while the outer core orbitals (3d-4p) are expanded in the valence basis and frozen as atomic orbitals. The ECP for palladium was recently used in another study of palladium complexes¹⁹ and further details can be found in this article. In short, the general experience is that the loss of accuracy from using this ECP is negligible in comparison with other approximations and that about half the integral time is saved.

The geometries for the minima and saddle points of the PdC₃H₆ potential surface were optimized at the CASSCF level. The proper choice of active space in the CASSCF method is crucial for the accuracy of the calculations and some experimentation was done in the different regions of the potential surface before the choice was made. To fully specify each CASSCF calculation the symbol (*i,j,k,l/p,q,r,s*) will be used, where *i, j, k, l* are the number of inactive orbitals (doubly occupied in all configurations) in the A₁, B₂, B₁, and A₂ representations of C_{2v}, and *p, q, r, s* are the corresponding number of active orbitals. The inner core orbitals (contained in the ECP) and frozen core orbitals are not included in the inactive orbital space. The actual orbital choice for the different CASSCF calculations is described below in the subsections where the results are discussed.

CCI calculations were performed for these geometries on the potential energy surface which had been optimized at the CASSCF level. Not all

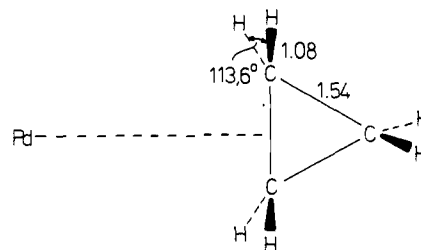


Figure 1. Optimized geometry for cyclopropane at long distance from palladium. Local D_{3h} symmetry assumed for cyclopropane.

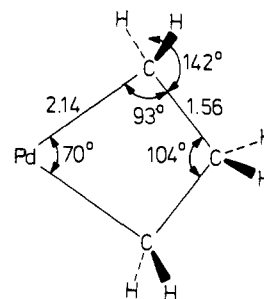


Figure 2. Optimized geometry for palladacyclobutane.

valence electrons were correlated in these CCI calculations since this would have been more expensive and also would have led to increased size consistency errors. It was decided that 12 electrons was the minimal number of electrons, which must be correlated, with 10 electrons on palladium and 2 electrons in the C-C bond cleaved by the palladium attack. The C-C bonding orbital is well defined in all points of interest on the potential surface. The inactive palladium d orbitals which came out of the CASSCF calculation were, however, somewhat mixed with C-H bonding orbitals. These d orbitals therefore had to be rotated with the other inactive orbitals to maximize the d contribution in the orbitals before the CCI calculation was performed. This procedure does not change the CASSCF wave function since only doubly occupied orbitals are involved in the rotations and has to be performed whenever a limited number of valence electrons are to be correlated. In the present case the rotations lead to perfectly clean palladium d orbitals. In the CCI calculations the configurations with coefficients larger than 0.05 were selected as reference states. This selection threshold for the reference states led to a rather small number of configurations, $3-7 \times 10^4$, and the CCI calculation required 5-15 s of CPU time on CRAY-1 after the integrals had been transformed and sorted. For all CCI calculations Davidson's correction²⁰ was finally added to account for unlinked cluster effects.

The Palladium Cyclopropane Potential Surface

As discussed in the introduction there are two different approaches of a palladium atom toward a cyclopropane molecule which are of special interest. The palladium atom will attack either the edge or the corner of the cyclopropane triangle. The first region of the potential surface of palladium cyclopropane which was studied was naturally where cyclopropane is still unperturbed with the palladium atom at long distance. This region is described briefly in the first part of this section, subsection a. After the edge attack a four-membered metallacycle, palladacyclobutane, is formed. This molecule is described in subsection b. The transition state for the edge attack was located and is described in subsection c. Finally, the radical-type structure formed after the corner attack is described in subsection d. The relative energies at the CASSCF and CCI levels are given in Table 1 and the CASSCF optimized geometries in Figures 1, 2, 3, and 5. The potential surface for the edge attack is shown in Figure 4.

a. Palladium at Long Distance from Cyclopropane. The geometry of cyclopropane was optimized in CASSCF calculations assuming D_{3h} symmetry. This means only three geometrical parameters—the C-C bond, the C-H bond, and the H-C-H angle. The orbital choice was (2,1,1,1/4,2,2,0) with 8 active electrons, which includes the C-C bonds. The resulting geometry and charge distribution are given in Figure 1. The bond distances

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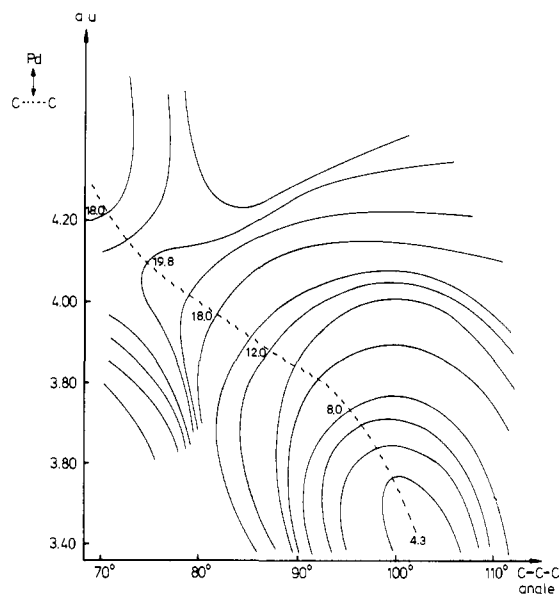


Figure 3. Potential energy surface in two dimensions for the edge attack of palladium on cyclopropane. The energy values are in kcal/mol. The dashed line is an approximate minimal energy path.

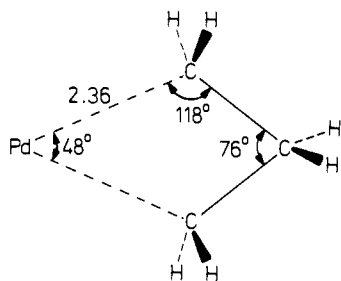


Figure 4. Optimized geometry for the transition state of the edge attack.

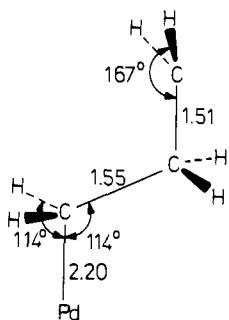


Figure 5. Optimized geometry for the radical formed after the corner attack.

are obtained slightly too long compared to experiments,²¹ 0.02 au for the C-C bond and 0.01 au for the C-H bond, which is expected with such a limited basis set and an MCSCF treatment. The most important configuration besides the Hartree-Fock determinant is a double excitation from the pure C-C p-bonding orbital in the in-plane second symmetry (B_2) of C_{2v} , with a coefficient of 0.08. The orbitals in the first symmetry will be mixed C-C and C-H bonding and lead to smaller CI coefficients.

At the optimized geometry of cyclopropane a CCI calculation was performed with palladium a distance of 20 au away. This calculation was designed to be as balanced as possible with the corresponding calculations on the metallacycle. A CASSCF calculation was therefore performed with the same active space as in the metallacycle calculation, (4,2,2,2/4,2,2,0) with 8 active electrons of which only 2 electrons are on cyclopropane. These 2 electrons, which are in the C-C bond closest to palladium, and

Table I. Relative Energies (kcal/mol) between Four Different Points on the PdC_3H_6 Potential Energy Surface

structure	CASSCF	CCI + Dav.
long distance	0.0 ^a	0.0 ^b
metallacycle	4.3	6.0
edge transition state	19.8	16.8
corner radical	24.6	24.4

^aTotal energy -642.74644 au. ^bTotal energy -642.82418 au.

the 10 4d electrons on palladium were correlated in the CCI calculation. Two reference states were selected of which the second state is the C-C bond correlating configuration, which had a coefficient of 0.11 in the CASSCF calculation. The resulting energy is given in Table I.

b. Palladacyclobutane. Optimizations of five geometrical parameters were performed at the CASSCF level for the four-membered metallacycle in Figure 2. These parameters were the C-Pd-C angle, the Pd-C bond distance, the C-C bond distance, the H-C₁-H angle, and the tilt angle of the C₁H₂ groups. The H-C₂-H angle and the C-H distances were taken from a measurement by Gillard et al.²² on the corresponding platinum metallacycle and set to 104° and 1.09 Å, respectively. The CASSCF orbital choice was (4,2,2,2/4,2,2,0) with 8 active electrons. This active space was reached after some experimentation with larger active spaces. The final optimized geometry given in Figure 1 is remarkably close to the geometry of the platinum metallacycle studied in ref 22; both the metal-carbon and carbon-carbon bond distances came out identical, 2.14 and 1.56 Å, respectively. The optimized C-Pd-C angle was slightly smaller, 70°, compared to 74° for C-Pt-C. This nearly perfect agreement between the structures of the two molecules must of course partly be a coincidence. It is, however, also a reflection of the fact that the same electronic state of palladium and platinum is involved in the bonding, namely the d^9 state. In earlier studies of nickel-containing molecules like NiCO, NiO₂, and NiC₂H₄²⁴⁻²⁶ it has been shown that it is always the d^9 (¹D) state of nickel which is the active state. The 3d occupation stays close to nine for all of these molecules. The dominance of this state of nickel may not be so surprising since d^9 is also the occupation of the ground state of the nickel atom. The situation is slightly different for palladium which has a d^{10} atomic ground state. If the perturbation on the palladium atom in a molecule is small, as, for example, in PdH₂, palladium will stay in the d^{10} state and have very weak bonds. With a larger perturbation as in Pd(H₂O)₂H₂ the d^9 state is more activated and dominates the binding with stronger bonds to the hydrogen atoms.²³ Characteristic of the d^9 state is the ability to form two covalent bonds. In chemical language this is expressed as a tendency for nickel and palladium to become Pd(II) and Ni(II) valence states, respectively. It is further our experience that nickel and palladium will seldom be significantly charged in these states contrary to what is normally assumed. A pure sd hybridization will optimally lead to bonds with a bond angle of 90°. Quite often, however, the bond angle will be smaller, because the s and d orbitals, coming from different shells, will not hybridize in an optimal way. There will often also be a small contribution from p orbitals in the bonding, which can also decrease the bond angle.

The CASSCF calculations on palladacyclobutane were performed with the orbital choice (4,2,2,2/4,2,2,0) with 8 active electrons. The bonds between palladium and carbon in the metallacycle are, as mentioned above, formed from sd hybrids on palladium. There are as usual for metal ligand bonds large oc-

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cupations of the antibonding orbitals. The most important configuration, besides the leading configuration, is a double excitation with coefficient 0.18 in the second symmetry from the d_{xz} -C bond to its antibonding orbital. The large occupation of the antibonding orbital of 0.15 is not necessarily a sign of a very weak bond but is merely a consequence of a nonoptimal overlap between the two atomic orbitals. A similar large occupation of the antibonding orbital is found also, for example, in NiH_2 between the d_{xz} orbital and the hydrogen s orbitals. This interaction is nevertheless responsible for breaking the fairly strong bond in H_2 . The reason for the nonoptimal overlap is that the d electrons are partly inside the s shell which will repel the ligand. The bond in the first symmetry of the metallacycle is formed with the 5s orbital of palladium and will lead to a much smaller occupation (0.04) of the antibonding orbital.

There are in total five configurations with coefficients larger than 0.05 in the CASSCF calculation, all of them of type bonding to antibonding excitations. These five configurations were selected as reference states for the CCI calculation which correlated 12 electrons. The energy difference compared to cyclopropane and a palladium atom at long distance is at the CCI (+Dav.), level 6.0 kcal/mol with the long distance lower in energy. This negative binding energy is actually somewhat smaller, 4.3 kcal/mol, at the CASSCF level, which is a rather unusual result. Judging from the experience from calculations on other molecules with similar basis sets, which have always led to too small binding energies, a positive binding energy of between 5 and 10 kcal/mol is predicted for palladacyclobutane. The population analysis leads to a positive palladium with charge +0.21 and an occupation of $4d^{9.29}5s^{0.42}5p^{0.08}$. The charge distribution on carbon and hydrogen will be exaggerated due to the small basis sets. The carbon nearest palladium is charged by -0.46 with its hydrogens +0.16 and the central carbon -0.21 with its hydrogens +0.13. In cyclopropane carbon has a charge of -0.30 and hydrogen +0.15. The charges on carbon and hydrogen would become smaller with polarization functions in the basis set.

c. The Transition State for Edge Attack. The transition state for formation of palladacyclobutane from palladium and cyclopropane was located in a two-dimensional optimization procedure keeping C_{2v} symmetry. The two geometrical parameters which were varied were the C-C-C angle and the distance between Pd and the midpoint between the two equivalent carbon atoms. All other degrees of freedom were retained from the metallacycle. The resulting two-dimensional potential surface is shown in Figure 3. The region around the saddle point is rather flat and easy to locate. The optimized geometry for the transition-state structure is shown in Figure 4. The CASSCF barrier is 19.8 kcal/mol compared to long distance between palladium and cyclopropane. At the CCI (+Dav.) level this energy drops to 16.8 kcal/mol. The barrier for dissociation of palladacyclobutane is 15.5 kcal/mol at the CASSCF level and 10.8 at the CCI level. Both a better basis set and a more complete geometry optimization will lower the barrier for formation of the metallacycle. A barrier of around 10 kcal/mol can be predicted on the basis of general experience from these types of calculations.

The edge attack of palladium on cyclopropane is a symmetry-allowed reaction and there are therefore no real problems in designing a CASSCF calculation which will describe a smooth passage from reactants to products. The active orbital choice was simply taken to be the same as that for the metallacycle and the 12-electron CCI calculations used two reference states. Even though the reaction is symmetry allowed in the sense that the total electron occupation per symmetry is not changed, there are some notable orbital occupation changes between the long distance and the saddle point region and further changes between the saddle point and the metallacycle region. The most important orbital changes are given in Table II. At long distance the C-C bonding orbital in the first symmetry has an occupation of 1.97. This orbital is transformed to a Pd(sp)-C bonding orbital with occupation 1.93 at the saddle point and with occupation 1.92 for the metallacycle. The antibonding orbital in the first symmetry has an occupation of 0.02 at the saddle point and reaches its maximum

Table II. Orbital Occupation Changes during the Edge Attack

orbital	long distance	saddle point	metallacycle
12a ₁ character	1.97 C-C	1.93 Pd-C	1.92 Pd-C
13a ₁ character	0.01 Pd(d*)	0.02 Pd-C*	0.04 Pd-C*
6b ₂ character	1.99 Pd(d)	1.98 Pd-C	1.90 Pd-C
7b ₂ character	0.02 C-C*	0.08 Pd-C*	0.15 Pd-C*

of 0.04 for the metallacycle. In the second symmetry the Pd-C bonding orbital is entirely a d-bonding orbital, which as expected will have a shorter range than the bonding orbital in the first symmetry. At the saddle point this weakly bonding orbital has an occupation of 1.97 which decreases markedly to 1.90 for the metallacycle. The corresponding antibonding orbital occupation increases from 0.08 at the saddle point to 0.14 for the metallacycle.

It is notable, and at first somewhat surprising, that the occupations of the antibonding orbitals increase as the bond gets stronger. This tendency must clearly change for shorter bond distances, which are then inside the equilibrium geometry, however. The reason for this unusual behavior of transition metals is that bonds are formed from two different shells with rather large differences in spatial extent. The equilibrium geometry will generally be inside the region of optimum overlap for the bonds formed from the ns and np orbitals but outside the optimum overlap region for the bonds formed from the (n-1)d orbitals. The occupation on palladium for the radical is $4d^{9.69}5s^{0.23}5p^{0.08}$. The CCI calculation used only two reference states.

d. Corner Palladation of Cyclopropane. The last region of the potential energy surface discussed in this section is the region of the radical-type structure formed after a corner attack of palladium on cyclopropane. The geometry of the radical structure was optimized with some parameters fixed. The H-C-H angles for the α and β carbons were set to 110° and for the γ carbon to 115°. The C-H distances were all fixed to 1.09 Å, and the C-C-C angle was set to 109°. The angle Pd-C-C was finally set equal to the Pd-C-H₂ angle. The remaining three distances and two angles were optimized and the resulting geometry is shown in Figure 5. The bond distances are around the expected values, with the C _{α} -C _{β} distance of 1.55 Å corresponding to a single bond and a shorter C _{β} -C _{γ} bond of 1.51 Å showing some slight double-bond character. The C _{β} -C _{γ} -H₂ angle 167° is closer to the angle for an sp² hybridized than an sp³ hybridized carbon. The CASSCF energy for the radical is 24.6 kcal/mol higher than the energy at long distance, and this energy difference is hardly modified at all at the CCI(+Dav.) level (24.4 kcal/mol). This means that the energy at the equilibrium for the radical is about 8 kcal/mol higher than the saddle point energy for the edge attack. With an additional estimated 10-kcal/mol barrier for the formation of the radical it is clear that the corner attack is a less favorable pathway for opening the cyclopropane ring than the edge attack.

The CASSCF calculations for the radical, which were done in C_s symmetry, were designed to be as similar as possible to the CASSCF calculations for the other regions of the potential energy surface. The orbital choice was therefore (6,4/6,2) with 8 electrons in the active space. The orbitals with open-shell character have occupations 1.36 and 0.66, and these orbitals are linear combinations (+ and -) of a Pd-C orbital and an orbital located at the γ carbon. The Pd-C orbital is bonding between Pd(s) and C and antibonding between Pd(d) and C. There is another Pd-C orbital with occupation 1.93 which has the opposite character, bonding between Pd(d) and C and antibonding between Pd(s) and C. This is one example of the complicated bonding patterns which can exist for transition-metal complexes. This wave function would clearly not be well approximated at the Hartree-Fock level. The occupation on palladium is $4d^{9.51}5s^{0.35}5p^{0.05}$, showing the typical mixture of the rather inert d¹⁰ ground state of palladium and the more chemically active d⁹s state. There were three reference states

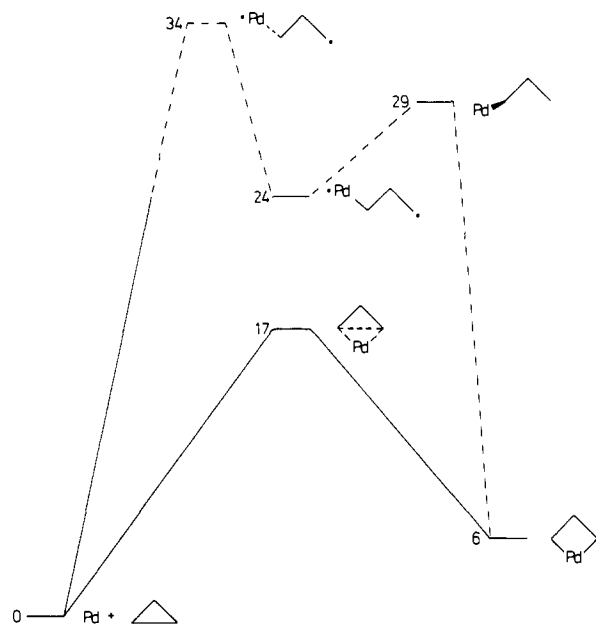


Figure 6. Schematic energy diagram for the different reaction paths followed after a palladium attack on cyclopropane. The energy values are in kcal/mol. The transition states for the corner palladation and for the formation of the metallacycle from the open radical structure are only estimated. The other energies are from the CCI(+Dav.) calculations.

in the CCI calculation leaving out a few reference configurations with coefficients slightly larger than 0.05.

Discussion

The calculated barrier for formation of a metallacyclobutane from palladium and cyclopropane is 17 kcal/mol. Considering

the approximations involved in the basis set and the geometry optimization a more realistic barrier is probably around 10 kcal/mol, which according to chemical experience is a reasonable value for this type of reaction. The calculations further show that the edge palladation is a lower energy pathway than the corresponding corner palladation. Thus, the energy minimum of the radical structure formed after a corner attack is 8 kcal/mol higher than the saddle point energy for the edge attack. The saddle point for the corner palladation should be an additional 10 kcal/mol higher in energy. It is thus clear that the effect of ligands on palladium, which will be investigated in a forthcoming study, has to be rather large in order to change the preference for the edge attack compared to the corner attack. The energies for the different structures on the potential energy surface of PdC_3H_6 are shown schematically in Figure 6.

It is clear that in principle a metallacyclobutane could also be formed from the open high energy radical structure by rotation around the $\text{C}_1\text{-C}_2$ bond and formation of a bond between palladium and C_3 . This would require another energy barrier of 4-5 kcal/mol on going from the radical to the metallacyclobutane, and the barrier for metalocyclobutane formation via a corner attack would then be around 30 kcal/mol. Formation of metallacyclobutane is therefore much favored via an edge activation. This is in agreement with experimental results, which have shown that the formation of a platinacyclobutane occurs with retention of configuration at both carbon atoms attacked by the metal.^{3f}

Acknowledgment. One of us (A.S) is grateful to the Swedish Natural Science Council (NFR) and the Swedish institute for financial support during his stay in Stockholm. A computer grant from NFR to use the CRAY-1 in Linköping is also gratefully acknowledged.

Registry No. Palladium, 7440-05-3; cyclopropane, 75-19-4; palladacyclobutane, 98875-35-5.

Temperature and Electrolyte Effects on the Electron-Transfer Reactions of Cytochrome *c*

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Abstract: The electron-transfer reaction partners of cytochrome *c* are both membrane-bound, imparting heterogeneous character to their reactions. The heterogeneous electron-transfer kinetics of cytochrome *c* reacting at indium oxide electrodes have been evaluated by cyclic voltammetry as a function of temperature in binding (phosphate) and nonbinding (Tris/cacodylic acid) neutral buffer media. The formal heterogeneous electron-transfer rate constant, k° , exhibited a biphasic dependence on temperature with a maximum value obtained at 41 °C in phosphate buffer and at 55 °C in Tris/cacodylic acid buffer at pH 7.0. The temperature dependence of the formal potential of cytochrome *c* was also determined under the same experimental conditions from reversible cyclic voltammograms acquired at a potential scan rate of 20 mV/s. The change in reaction center entropy, ΔS_{rc}° , and the formal potential, E° (at 25 °C), for cytochrome *c* were determined to be -13.4 eu and 0.264 V vs. NHE, respectively, in Tris/cacodylic acid buffer and -12.7 eu and 0.256 V vs. NHE in phosphate buffer. While the maximum k° occurred at different temperatures in the two buffer systems, it occurred at the same formal potential, ca. 0.247 V vs. NHE. These results suggest that there is an optimum conformation of ferricytochrome *c* for facile heterogeneous electron transfer that occurs at different temperatures in binding and nonbinding buffer media.

Mammalian cytochrome *c* is a water-soluble heme protein that functions as an electron carrier between cytochrome *c* reductase and cytochrome *c* oxidase, components of oxidative phosphorylation. The physiological redox partners of cytochrome *c* are membrane-bound (inner membrane of mitochondria), whereas

cytochrome *c* resides in the cytosol between the inner and outer membranes and is believed to be associated with the outer surface of the inner membrane.¹ Cytochrome *c* electron transfer is believed to occur at the solvent-exposed edge of the heme group by an outer-sphere mechanism.² The dipole moment of cyto-

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