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Mechanisms of the Cycloaddition Reaction of Methylenecyclopropane−Palladium and Oxa- and Azatrimethylenemethane−Palladium Complexes with Olefins

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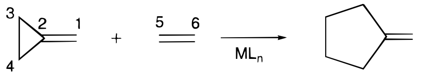
Mechanisms of palladium-catalyzed cycloaddition reactions of methylenecyclopropane with olefins and those of oxatrimethylenemethane (OTMM) and azatrimethylenemethane (ATMM) complexes with olefins have been studied by applying the *ab initio* molecular orbital method. Assuming an intramolecular coupling mechanism, we have examined some model complexes, Pd(η^2-methylenecyclopropane)(ethylene)(PH_3) and Pd(η^3-OTMM or η^3-ATMM)-(ethylene)(PH_3), to determine the transition state structures. The coupling of methylenecyclopropane, OTMM, and ATMM with ethylene on the metal center takes place in two steps. In the reaction of methylenecyclopropane, the first step involves an opening of the cyclopropane ring promoted by an attack of ethylene. The methylenecyclopropane moiety has a π-allylic form at the first transition state which leads to a metallacyclic intermediate. The first transition state of the reactions of OTMM and ATMM complexes looks very similar to that of the methylenecyclopropane complex, having π-allylic coordinations. The two paths are separated in the second step. A [3 + 2] addition product is obtained by a reductive elimination from the intermediate metallacycle, whereas a prototropic shift followed by a reductive elimination affords a [2 + 1] addition product. It is the energetics of the second stage starting from the metallacycles that differentiates the reactions of the OTMM and ATMM complexes from the reaction of the methylenecyclopropane complex. The relative stabilities of various isomeric forms of these complexes have also been studied.

Introduction

Methylenecyclopropanes are known to undergo [3 + 2] cycloaddition reactions with olefins in the presence of some d^{10} metal catalysts.[1,2]



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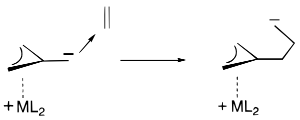
In this reaction a methylenecyclopropane−ML_2 complex should be formed initially as a reaction intermediate, in which at least two attachment modes of the methylenecyclopropane unit to the metal center have been suggested, i.e., an η^2-olefin form and a metallacyclic form or an η^3-trimethylenemethane (TMM) form as an equivalent. The structures of a variety of d^{10} and d^8 metal η^2-methylenecyclopropane complexes have been determined experimentally.[3] It has been shown that ring-opening reactions of d^8 metal−methylenecyclopropane complexes afford stable η^4-TMM complexes that have been characterized experimentally.[4] Palladium complexes of TMM have also been generated by another route and used for the [3 + 2] cycloaddition reactions.[5−7] Theoretical calculations of TMM−PdL_2 have been performed by Albright and by Trost.[8,9] They have shown that the complex adopts an unsymmetrical η^3 form.

Theoretical works on d^{10} metal−TMM complexes have revealed that they have a zwitterionic charge distribution.[9] Then, a stepwise mechanism has been suggested for the reaction of the TMM complexes with olefins. It consists of a nucleophilic attack of the uncomplexed carbon atom of the TMM ligand to the electron-deficient double bond and of a ring closure between one of the metal bound carbon atoms of the TMM ligand and the β-carbon atom of the olefin, as depicted in eq 2.[9] Experimental results support this mechanism: TMM−ML_2 complexes demand that the olefin has electron-deficient groups.[5] On the other hand, it has been shown that methylenecyclopro-



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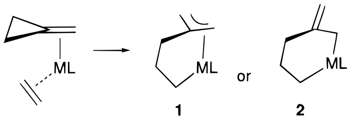
pane complexes react both with electron-rich olefins and with electron-poor olefins.[5] This difference seems to imply that there exists another route wherein a TMM species does not intervene as the reaction intermediate. A direct coupling mechanism has been suggested for the reaction of methylenecyclopropane complexes in which both methylenecyclopropane and olefin molecules are bound to the metal and the coupling takes place simultaneously with an opening of the three-membered ring.[5] In such a mechanism, the π-allyl complex **1** or the σ-complex **2** should be formed in the course of the reaction.



1 **2**

(3)

Heteroatom analogues of d^{10} metal−TMM complexes have also been explored. Recently, oxygen or nitrogen monosubstituted TMM (oxatrimethylenemethane (OTMM) and azatrimethylenemethane (ATMM), respectively) complexes of d^{10} metals have been isolated,[10,11c] and their structures have been determined by X-ray spectroscopy.[12] The observed geometries of those OTMM and ATMM complexes have a π-allylic form, in which the heteroatoms are placed at the uncomplexed position. A theoretical study of the OTMM complex also supports the π-allylic ground state.[8] In contrast to d^{10} metal−TMM complexes, heteroatom substituted species undergo [2 + 1] cycloadditions with norbornene rather than [3 + 2] cycloadditions. Although the OTMM or ATMM complexes are isoelectronic with the TMM complex and they seem to be more polarized than the TMM complex, they do not react with electron-deficient olefins but react only with strained electron-rich olefins. The coupling reaction of norbornene with the oxygen or nitrogen substituted analogue of d^{10} metal−TMM complexes[10−12] differs in this respect from the coupling reaction of d^{10} metal−TMM or d^{10} metal−methylenecyclopropane complex with olefins.

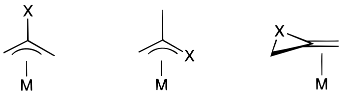
In this regard, it is interesting to compare the coupling of methylenecyclopropane complexes and olefins with the reactions of the OTMM or ATMM complexes with olefins. With a view to elucidating the mechanisms of these cycloaddition reactions, we have performed *ab initio* molecular orbital calculations on some model systems, including the geometry optimization of the transition states and the reaction intermediates.

Method of Calculations

Ab initio molecular orbital calculations were carried out by the use of the Gaussian 92 program.[13] In order to calculate a number of structures appearing in the overall processes of [3 + 2] and [2 + 1] coupling reactions, the M−P−H angle and the P−H bonds in a PH_3 ligand were fixed at 125.26° and 1.42 Å, respectively, and all the other geometrical parameters were optimized at the restricted Hartree−Fock (RHF) level. Hay and Wadt's ECP2 double-ζ basis with effective core potentials (ECP's) was employed for Pd,[14] the minimal basis with ECP's,[15] the STO-3G bases[16] were employed for the P and H atoms in a PH_3 ligand, respectively, and the 3−21G basis was used for the C, H, O, and N atoms in the organic ligands.[17] Single-point calculations using the Møller−Plesset perturbation theory at the second order (MP2) level were carried out to include the electron-correlation effect.

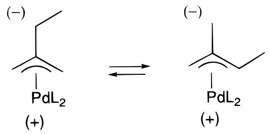
Results and Discussion

Structures of TMM−, MeTMM−, OTMM− and ATMM−PdL$_2$. To begin with, we want to know the difference in stabilities of three possible isomers **3**, **4**, and **5** of the TMM−PdL$_2$ complex and its heteroatom analogues. If the OTMM or ATMM complexes were fluxional, and if the isomers **4** and/or **5** were present, the [3 + 2] coupling would be possible: the isomer **4** would undergo nucleophilic addition similar to the TMM complex and the isomer **5** would also undergo the [3 + 2] coupling similar to the palladium-catalyzed coupling of methylenecyclopropane and olefins. In the [2 + 1] coupling reactions, these isomers still remain as potential candidates for the active intermediates and, therefore, must be taken into account. In this regard, a theoretical scrutiny is necessary for understanding the reactivity trends of the TMM complex and its analogues. So far, structure **5** is known to be stable and has been characterized experimentally in methylenecyclopropane (or TMM)−PdL$_2$ complexes.[1−3] Structure **3** is not stable in TMM complexes but is preferred in OTMM and ATMM complexes.[5−7,10−12]



3 **4** **5**

We have obtained the geometries of three possible isomers for TMM−Pd(PH$_3$)$_2$. For comparison, the geometries of the isomers of methyltrimethylenemethane (MeTMM)−Pd(PH$_3$)$_2$ have also been determined, wherein two forms **6** and **7** are possible for the η^3-coordination. Starting from different precursors, either **6** or **7** may be generated. Experiments have shown, however, that the rearrangement between these two isomeric structures takes place in the course of the cycloaddition reactions.[7]



6 **7**

The calculated geometries of the TMM− and MeTMM− complexes are illustrated in Figure 1. The relative energies calculated at the Hartree−Fock level and at the MP2 level are presented in parentheses by taking the structures **8** and **11** as the reference. In the ground-state structure of complex **8**, the TMM ligand is bound to the Pd center mainly by two carbons, having an η^3-coordination. The metal−bridging C distance and the metal−central C distance are 2.097 and 2.570 Å, respectively. The overlap population between Pd and the central C

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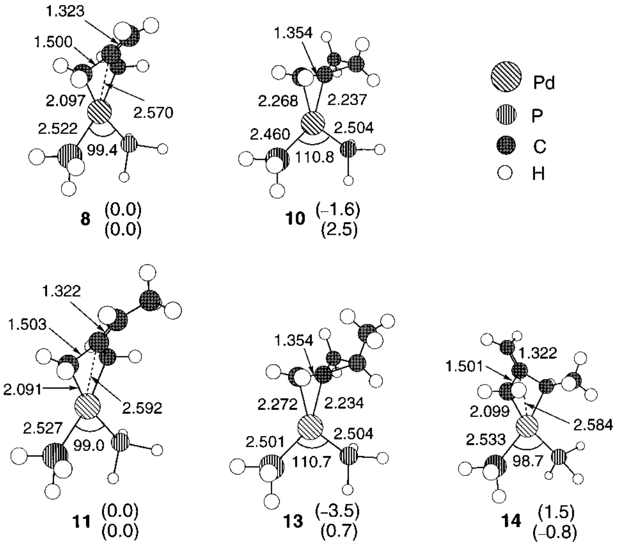


Figure 1. Calculated structures of Pd(TMM)$(PH_3)_2$, **8** and **10**, and of Pd(MeTMM)$(PH_3)_2$, **11**, **13**, and **14**. Relative energies (kcal/mol) are given in parentheses for HF (above) and MP2 (below) calculations.

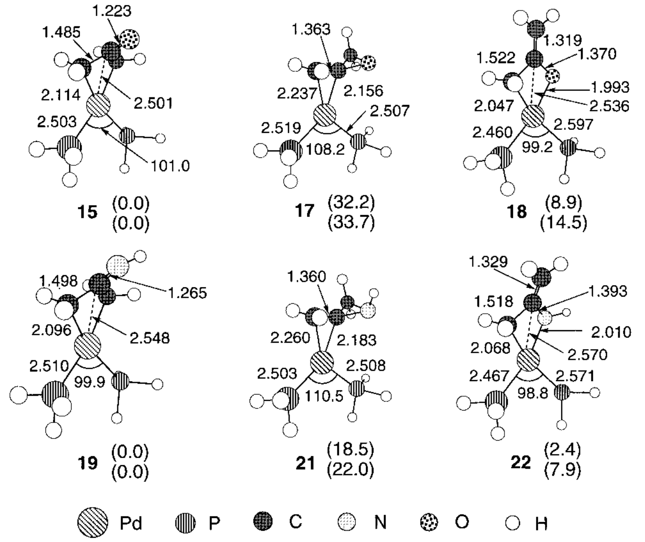
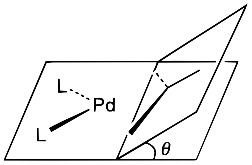


Figure 2. Calculated structures of Pd(OTMM)$(PH_3)_2$, **15**, **17**, and **18**, and of Pd(ATMM)$(PH_3)_2$, **19**, **21**, and **22**. Relative energies (kcal/mol) are given in parentheses for HF (above) and MP2 (below) calculations.

was calculated to be −0.168 in **8**,[18] implying that there is an overlap repulsion between the two atoms. The angle of ring puckering *θ*, defined in the following manner, has been calculated to be 37.4°.



We have found also a planar coordination mode of the TMM ligand ($\theta = 0°$), **9**. It has been located at a shallow energy minimum that is higher than **8** by 2.6 kcal/mol at the Hartree−Fock level and by 2.4 kcal/mol at the MP2 level. Structure **10** represents an η^2-methylenecyclopropane complex that has been shown to lie 1.6 kcal/mol below **8** at the Hartree−Fock level but 2.5 kcal/mol above **8** at the MP2 level. Introduction of a methyl substituent into TMM produces only a subtle change. Two coordination modes **11** and **13**, corresponding respectively to **3** and **5** mentioned above, do not differ much in stability from each other. The two isomeric structures **11** and **14** are shown to be approximately the same in energy.

In the OTMM and ATMM complexes, there are four possible coordination modes, three of which are very similar to those found in the TMM or methylenecyclopropane complex. The optimized geometries and the calculated energies are shown in Figure 2.

In the OTMM complex, the most stable is **15**, as has been reported by Fawcett et al.[8c] The Pd−bridging C, C−C, and C−O distances, 2.114, 1.485, and 1.223 Å at the current level of theory, are in good agreement with the experimental ones, 2.09−2.17, 1.47−1.49, and 1.22−1.24 Å.[12] The Pd−central C distance, 2.501 Å, was calculated to be about 0.1 Å longer than the experimental one, 2.37−2.38 Å. The angle *θ* defined above is 46.6° in the present calculation and is 51.3−53.3° in experiments. Structure **19** is the lowest in energy in the ATMM complex. The angle *θ* was calculated to be 40.2° in this structure. The order of value of *θ* places TMM < ATMM < OTMM in our calculations, which is inconsistent with the experimental results observed for OTMM−Pt and ATMM−Pt complexes, 51.0° and 53.9°, respectively.[12] This is probably due to the replacement of the electron-withdrawing tosilate group on the nitrogen atom in the real system by a hydrogen atom in our calculation model of the ATMM complex. The overlap populations between Pd and the central C atom have been calculated to be negative, −0.162 and −0.165 in **15** and **19**, respectively.[18]

In addition to the structures presented in Figure 2, we have obtained planar geometries for the OTMM and ATMM complexes, **16** and **20**, in which the OTMM or ATMM ligand coordinates to the metal at the two terminal carbons of the allylic unit. A fluxionality due to the flipping motion of the ATMM portion *via* a planar form has been observed in the NMR spectra.[11c] The activation energy going from **15** to the planar metallacyclic form **16** has been calculated to be 6.8 kcal/mol at the Hartree−Fock level and 7.8 kcal/mol at the MP2 level, respectively. The barrier height for flipping in **19** has been calculated to be smaller, being 3.3 kcal/mol at the Hartree−Fock level and 3.7 kcal/mol at the MP2 level.

Corresponding to the η^2-methylenecyclopropane form **10**, there are two isomeric forms to be considered, *i.e.*, one with the heteroatom at the complexed position (an oxocyclopropane or azocyclopropane form) and the other with the heteroatom at the uncomplexed position. The former structure has been shown to be unstable, and only the latter structure, **17** or **21**, has been obtained. However, as shown in Figure 2, **17** and **21** are considerably higher in energy than the other isomers. The η^2-coordination seems to be unfavorable in the present OTMM and ATMM systems. The heteroatom is bound to the metal center in **18** and in **22**. The former is planar, whereas the latter is slightly bent. The nitrogen atom tends to have a pyramidal arrangement in **22**. The energy difference between **22** and **19** is not so large, being 2.4 kcal/mol at the Hartree−Fock level and 7.9 kcal/mol at the MP2 level, but the energy difference between the corresponding structures in the OTMM complex, **18** and **15**, is seen to be significantly large.

In summary at this moment, the methylenecyclopropane complex **5** (≡**10** with X = CH_2) is suggested to be similar in energy to its isomeric TMM complex form, **3** (**8**). In contrast, the η^2-coordination mode **5** is unfavorable both in the OTMM complex (**17**) and in the ATMM complex (**21**). They prefer an η^3-coordination at the carbon centers, **3** (**15** in the OTMM complex and **19** in the ATMM complex). Another η^3-coordination mode **4** (**18** and **22**) is lower in energy than **5** but is considerably higher in energy than **3** in these species.

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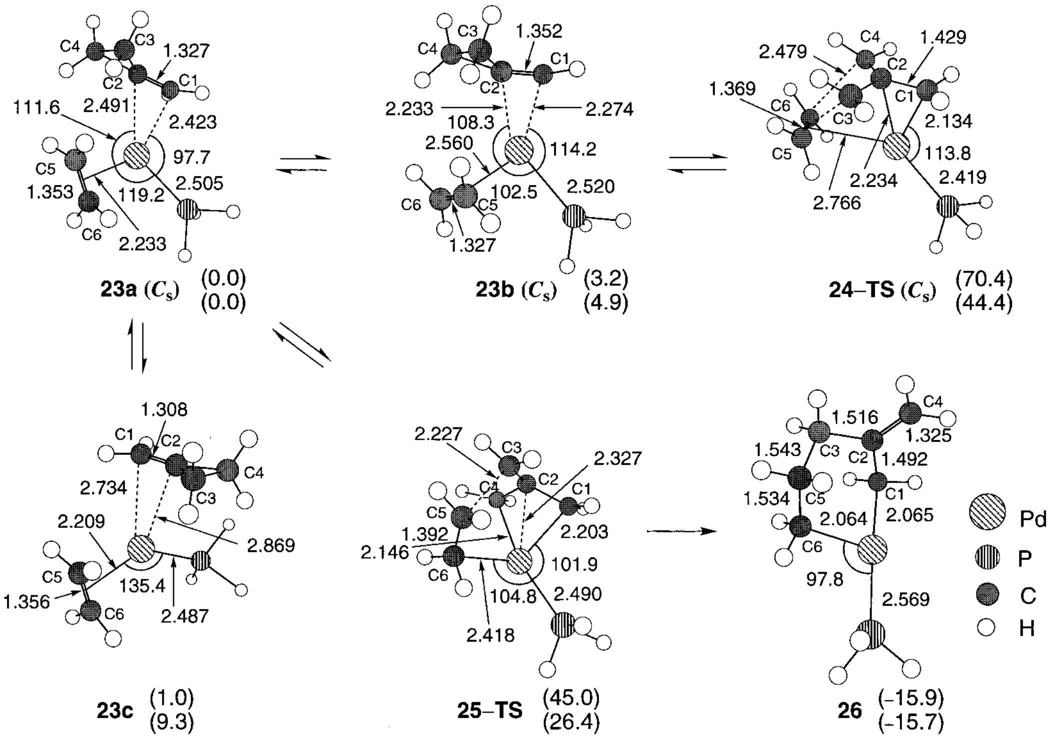
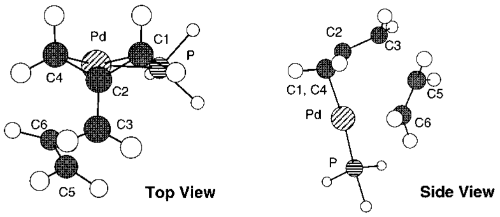


Figure 3. Calculated structures of the ground and transition states of Pd(methylenecyclopropane)(ethylene)(PH_3). Relative energies (kcal/mol) are given in parentheses for HF (above) and MP2 (below) calculations.

Coupling of Palladium–η^2-Methylenecyclopropane Complex with Olefins. We assume here that the [3 + 2] coupling of methylenecyclopropane with olefins takes place by forming initially a Pd(η^2-methylenecyclopropane)(olefin)L complex as a reaction intermediate. Then, we study the process of ring-opening and coupling with the coordinated olefin molecule on the metal, with respect to a model complex Pd(η^2-methylenecyclopropane)(ethylene)(PH_3). The structures of the intermediates, the transition states, and the product are illustrated in Figure 3. Their relative energies are given in parentheses by taking **23a** as a standard.

Here, **23a** and **23b**, which differ from each other in the orientation of the coordinated ethylene molecule, represent the initial intermediates. Conformation **23a**, in which the carbon atoms of the ethylene ligand, the Pd atom, the C1 and C2 atoms of the methylenecyclopropane unit, and the P atom of the phosphine ligand sit in a plane, is lower in energy, being stabilized by a bonding overlap between the occupied d orbital of the metal center and the π^* orbital of the ethylene, as in ethylene–ML_2 complexes. The bonding interaction is not so strong; the energy difference between **23a** and the out-of-plane geometry **23b** is 3.2 kcal/mol at the Hartree–Fock level and 4.9 kcal/mol at the MP2 level of theory. In both of these two conformations, the methylenecyclopropane ligand adopts a simple η^2-coordinated structure. Another stable intermediate **23c** has an in-plane orientation of the ethylene ligand, as in **23b**, and an out-of-plane orientation of the unsaturated bond of the methylenecyclopropane ligand.

The cyclopropane ring is seen to be opened at the transition state **25**, having a π-allylic structure to interact with the ethylene ligand. The mode of ring-opening has been shown to be *disrotatory out*. Another transition state is **24** which has been found under the constraint of a C_s symmetry. When the symmetry constraint is lifted, **24** collapses spontaneously to give **25**. The activation energy to reach **24** has been calculated to be 70.4 kcal/mol at the Hartree–Fock level and 44.4 kcal/mol at the MP2 level relative to **23a**, which is considerably higher than that of the path to go through **25**. Two representations of **25** are given as follows to characterize the transition state of the reaction.



In the transition state **25**, Pd, P, C1, and C4 sit approximately in the same plane, as illustrated above. The C1–C2–C4 moiety has an ideal π-allylic form, and the calculated Pd–C2 distance, 2.327 Å, has been shortened significantly relative to that bond in the η^3-TMM–Pd(PH_3)$_2$ complex, **8**, 2.570 Å. The C1 and C4 atoms are seen to be nearly equivalent in the transition state, **25**, the Pd–C1 and Pd–C4 bond distances being 2.203 and 2.146 Å, respectively. This indicates that the ring-opening and a rotation of the methylenecyclopropane ligand around the Pd–C2 bond take place prior to the bond formation between C3 of the methylenecyclopropane ligand and the ethylene ligand, and the former is brought into the position suitable for an η^3-coordination. Going through the transition state **25**, a metallacyclic product **26** is formed. The ethylene molecule can add to either of the C3–C1 and C3–C4 allylic units, because the C1–C2–C4 unit in **26** may rearrange to break the Pd–C1 bond and to form the Pd–C4 bond. This is in line with the experimental observation that 1-substituted and 3-substituted methylenecyclopropanes result in the same product mixture.[5]

The result presented above makes a clear contrast to the reaction of methylenecyclopropane–nickel complexes. It is known that the nickel-catalyzed coupling of methylenecyclopropane and olefin occurs at the C3–C4 bond of methylenecyclopropane,[5] whereas olefin adds both at C1 and C3 and at C3 and C4 in the palladium-catalyzed reactions. Our calculations at the MP2 level of theory could locate only the transition state

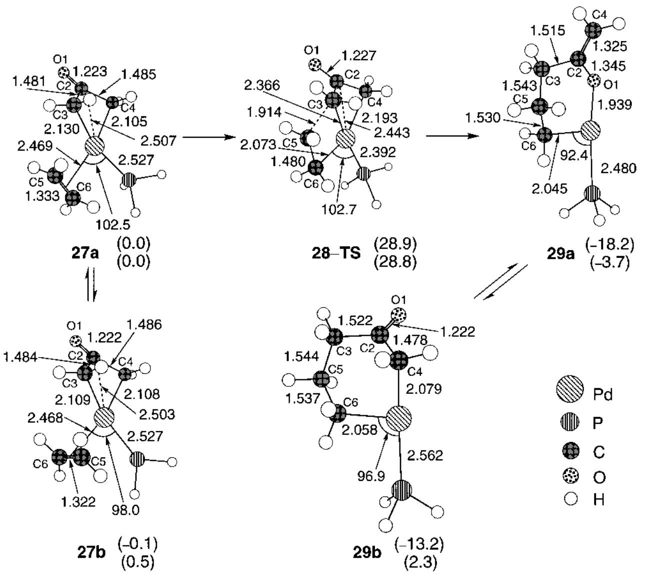
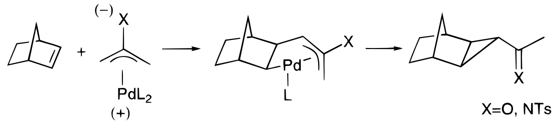


Figure 4. Calculated structures of the ground and transition states of Pd(OTMM)(ethylene)(PH$_3$). Relative energies (kcal/mol) are given in parentheses for HF (above) and MP2 (below) calculations.

having a C_s symmetry for the Ni(η^2-methylenecyclopropane)(ethylene)(PH$_3$) model system. The activation energy has been found to be 56 kcal/mol. This indicates that the transition state **25** plays a crucial role in giving the [3 + 2] addition product in the present system. Details of the difference between the palladium-catalyzed and nickel-catalyzed couplings of methylenecyclopropane and olefins will be discussed elsewhere.

Coupling of Pd−OTMM and Pd−ATMM Complexes with Olefins. The [3 + 2] coupling between TMM−Pd complexes and electron-deficient olefins has been suggested to be initiated by the nucleophilic attack of the uncomplexed carbon atom to a C−C double bond.[6,9] In contrast, the first step of the coupling of the OTMM− or ATMM−Pd complex with norbornene seems to be the insertion of olefin into the metal−carbon bond to generate a metallacyclic intermediate. The mechanism suggested so far is depicted in eq 4.[10]



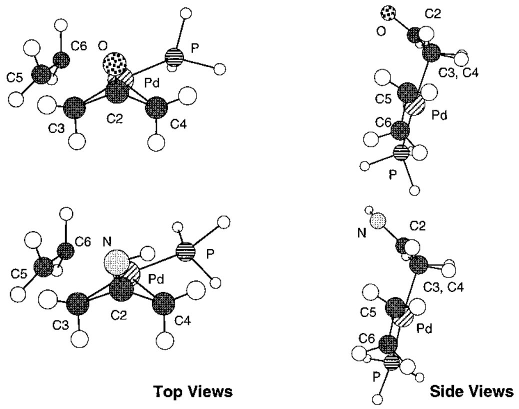
(4)

To look into the course of this reaction, we have carried out calculations on the model compounds, Pd(OTMM)(ethylene)(PH$_3$) and Pd(ATMM)(ethylene)(PH$_3$). The tosilate group on the nitrogen center of ATMM in an experimental system[11a] has been replaced by a hydrogen atom for a computational feasibility. The structures of the complex, the transition state, and the product are illustrated in Figure 4 with respect to the OTMM complex.

The two structures, **27a** and **27b**, represent the intermediates of the reaction for our model OTMM complex. The former has an in-plane orientation of the ethylene ligand around the Pd center, and the latter has an out-of-plane orientation. The OTMM ligand has a π-allylic or a metallacyclic form in these conformations. The Pd−C3 bond has been calculated to be a little longer than the Pd−C4 bond in **27a**, whereas the two bonds are almost the same in length in **27b**. Other structural parameters are approximately the same in these two conformations, and the energy change associated with the rotation of the ethylene ligand is negligibly small. Starting from **27a** or **27b**, we obtain the transition state **28**. In this transition state, a carbon atom of the ethylene ligand is attacking the coordinated C3 atom of the OTMM ligand, and the bond between the metal and the ethylene part is shifted from a π type to a σ type. The Pd−C6 distance in **28**, 2.073 Å, is much shorter than that found in **27a** or **27b**. The coordination mode of the OTMM unit remains π-allylic in **28**, the oxygen atom being located away from the palladium center. This makes a contrast to the transition state for the coupling of methylenecyclopropane and ethylene, in which the uncomplexed carbon of the former interacts with the latter. The calculated activation energy in going from **27a** to **28** is 28.9 kcal/mol at the Hartree−Fock level and 28.8 kcal/mol at the MP2 level. The product is **29a**, in which the Pd−O bond has been formed by rotating the OTMM moiety to break the Pd−C3 and Pd−C4 bonds. The total energy of **29a** has been calculated to be lower than **27a** by 18.2 kcal/mol at the Hartree−Fock level and 3.7 kcal/mol at the MP2 level. An alternative metallacyclic form is **29b**, in which the Pd−C4 bond is formed instead of the Pd−O bond. This structure is 5−6 kcal/mol less stable than **29a**.

The result obtained for the ATMM complex is similar to that obtained for the OTMM complex, as illustrated in Figure 5. The replacement of the electronegative oxygen atom with an imino group affects to some extent the transition-state structure. The C3−C5 distance has been calculated to be 1.975 Å in **31**, which is about 0.06 Å longer than that found for **28**. The activation energy has been calculated to be 2.2−2.8 kcal/mol lower than the reaction of the OTMM complex.

In the OTMM and ATMM complexes, the transition states are shown to have π-allylic structures and the calculated activation energies are comparable to that found for the [3 + 2] coupling of methylenecyclopropane with ethylene. Top and side views of the transition states **28** and **31** are shown as follows.



One sees that not only the Pd, P, C3, and C4 atoms but also the C5 and C6 atoms of the attacking ethylene ligand are located approximately in the same plane in the transition state.

In the reaction of methylenecyclopropane complex, the transition state is relatively late, the cyclopropane ring being almost opened. The C−C bond in methylenecyclopropane is loosened easily, and the resulting TMM complex is fluxional.[7] The transition state should be stabilized by orbital interaction between the HOMO of the metal part and the *out-of-phase* combination of p type atomic orbitals of the two terminal carbons in the TMM part. The ring-opening is accompanied by a decrease in the C3−C5 distance to facilitate the cycloaddition reaction (see **25** in Figure 3 for the numbering scheme). In contrast, in the reaction of the OTMM or ATMM complex, the TMM moiety is not distorted much in the transition state. It has been shown above that **18** is less stable than **15** in the OTMM complex and **22** is less stable than **19** in the ATMM

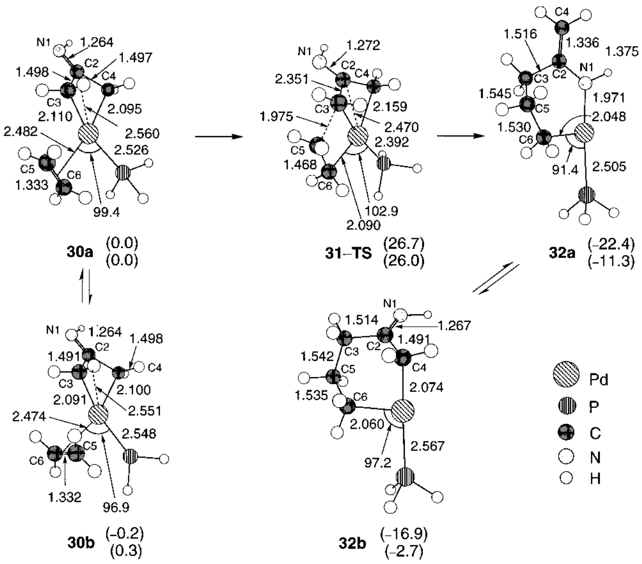
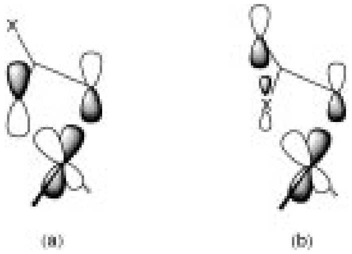


Figure 5. Calculated structures of the ground and transition states of Pd(ATMM)(ethylene)(PH_3). Relative energies (kcal/mol) are given in parentheses for HF (above) and MP2 (below) calculations.

complex. The p orbitals of the oxygen or nitrogen atom in the OTMM or ATMM ligand are more contracted than the pπ orbital of C3 in the metylenecyclopropane unit. The OTMM or ATMM fragment may interact with the metal at the C−C−X (X = O or NH) site by mixing its low-lying unoccupied MO's (**b**),[19] but orbital interaction involving the oxygen or nitrogen atom would not be effective relative to interaction at the allylic unit (**a**). If the OTMM or ATMM ligand is coordinated to the metal by the C−C−X unit, the complex will collapse immediately to give the metallacycle **29** or **32**, upon the coordination of an ethylene ligand.



The bonding interaction between the oxygen or the nitrogen with C5 of the coordinated ethylene molecule would also be weaker than that between C5 and the external methylene carbon in the methylenecyclopropane complex. Therefore, the C5 atom tends to be bound to one of the terminal carbons in the allylic unit in the OTMM and ATMM complexes. It is interesting to see here that the resulting metallacycles **29** and **32** are very similar to that found in the reaction of methylenecyclopropane, **26**.

Ring-Closing Step. We have seen above that there are sizable differences in configurational stabilities between the methylenecyclopropane−Pd(PH_3)$_2$ complex and the OTMM−Pd(PH_3)$_2$ or ATMM−Pd(PH_3)$_2$ complex. In spite of such differences, we have also seen that they follow the routes similar to each other to produce metallacyclic intermediates at the first stage of the reaction with olefins. Then, it is asked why methylenecyclopropane prefers the [3 + 2] cycloaddition, while the OTMM and ATMM species follow the [2 + 1] cycloaddition mode. A clue is found in the second stage of the reactions.

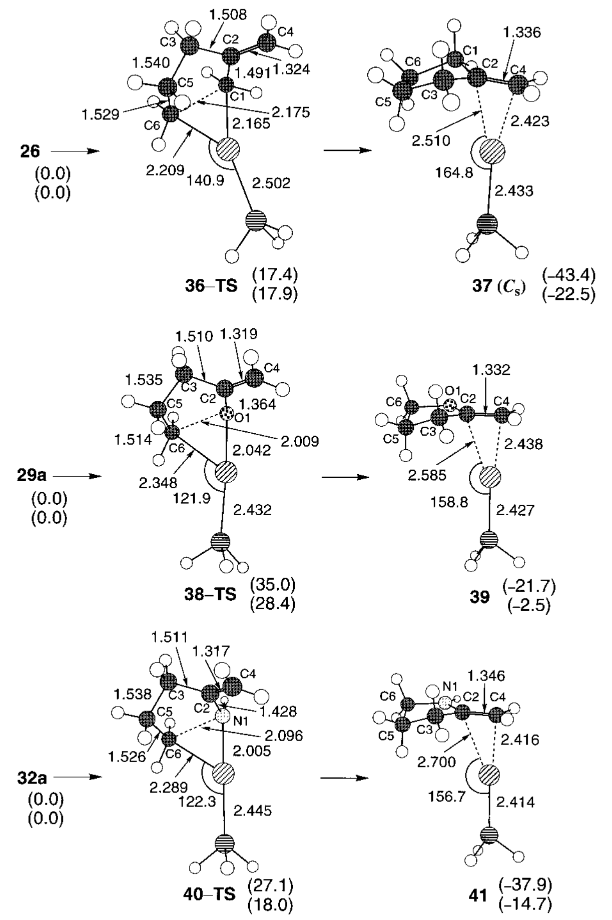
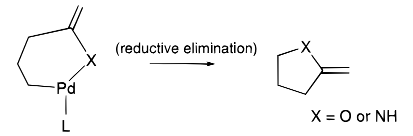
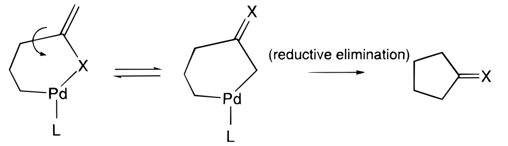


Figure 6. Calculated structures of the transition states and products on the pathways starting from the metallacyclic intermediates **26**, **29a**, and **32a** to give the [3 + 2] adducts. Relative energies (kcal/mol) are given in parentheses for HF (above) and MP2 (below) calculations.

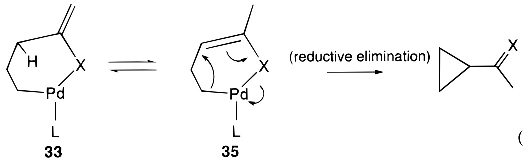


33 (5)



33 **34** (6)

As illustrated in eqs 5 and 6, the [3 + 2] cycloaddition occurs by a reductive elimination of metallacyclic isomers, **33** and **34**. On the other hand, to give the [2 + 1] cycloaddition product, a prototropic shift from **33** to **35** must be followed by a reductive elimination.



33 **35** (7)

Then, we have calculated the reaction pathways for the ring-closing process starting from the metallacyclic structures. The optimized geometries are illustrated in Figure 6.

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[19] (a) Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370. (b) Imamura, A.; Hirano, T. *J. Am. Chem. Soc.* **1975**, *97*, 4192. (c) Inagaki, S.; Fukui, K. *J. Am. Chem. Soc.* **1975**, *97*, 4445. (d) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4693.

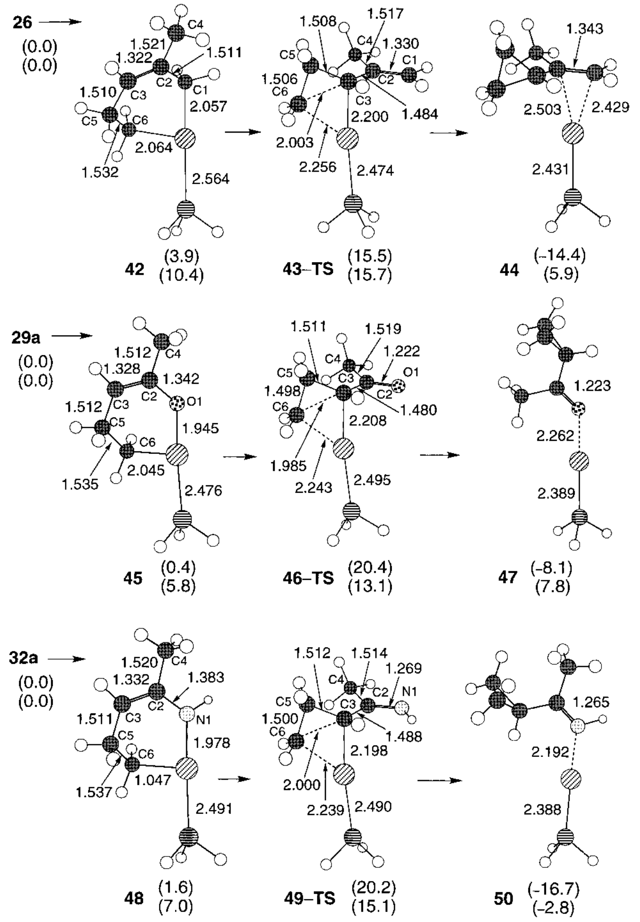


Figure 7. Calculated structures of the transition states and products on the pathways starting from the metallacyclic intermediates **26**, **29a**, and **32a** to give the [2 + 1] adducts. Relative energies (kcal/mol) are given in parentheses for HF (above) and MP2 (below) calculations.

In the [3 + 2] cycloaddition, the C6 atom of **26** interacts with the C1 atom to produce a C−C σ bond, and the C2−C4 double bond comes in the position to fill the vacant site of the palladium center in the transition state **36**. Then, **36** leads to a methylenecyclopentane complex **37**. Although the [3 + 2] cycloaddition mode has not been observed for the heteroatom substituted species, we obtained similar transition states and products starting from **29a** and from **32a**.

For the [2 + 1] cycloaddition, we have obtained the reaction intermediates **42**, **45** and **48** and the transition states **43**, **46**, and **49** shown in Figure 7. Product **44** is shown to have a coordination mode that is different from that in **47** and in **50**. The relative energies of these structures are given in parentheses by taking **26**, **29a**, and **32a** as the references.

Figure 8 shows an energy profile of the cycloaddition reactions. The first transition state is **TS1** that leads to the metallacyclic intermediates **26**, **29**, and **32**. The [3 + 2] cycloaddition products, **37**, **39**, and **41**, are generated by going through the second transition state, **TS2**. The energy diagram for the [2 + 1] cycloaddition is illustrated on the right-hand side. In this process, the reaction intermediates **42**, **45**, and **48** are formed from **26**, **29**, and **32**, respectively, followed by the transition state **TS2′** for cyclopropanation or ring-closure. The results are very instructive. The activation energy for **TS2** becomes larger on going from the methylenecyclopropane complex to the ATMM complex and to the OTMM complex. In the case of methylenecyclopropane, reaction intermediate **26** is transformed immediately into the methylenecyclopentane complex **37**, because the activation energy for **TS2** is 8.5 kcal/mol lower than that for **TS1**. On the other hand, the barrier for **TS2** is approximately the same as that for **TS1** in the reaction of the OTMM complex. If the reacting system is relaxed at the intermediate stage **29**, the [3 + 2] coupling would not be favorable. In the [2 + 1] cycloadditions, the barrier heights for **TS2′** are similar in magnitude among the methylenecyclopropane, OTMM, and ATMM species, showing a good contrast to the [3 + 2] reaction. Since **TS2′** is much lower in energy than **TS2** for the OTMM complex, the [2 + 1] mode must be followed preferentially in this case. In the case of methylenecyclopropane, **TS2′** is located a little lower in energy than **TS2**. Therefore, the [2 + 1] reaction should compete with the [3 + 2] reaction. Then, the predominance of the [3 + 2] mode over the [2 + 1] mode in the methylenecyclopropane complex would depend on the rate of prototropic shift from **33** to **35**.

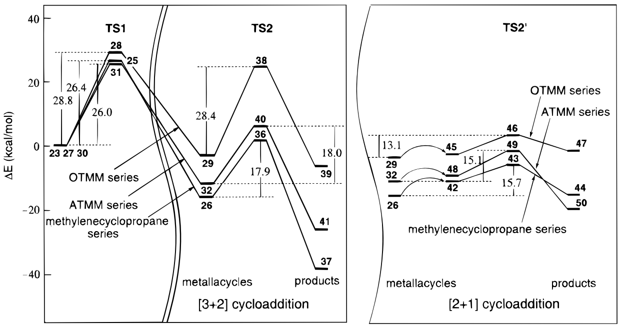
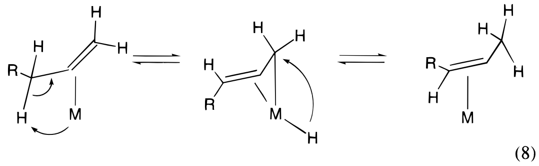


Figure 8. Sketch of energetics of the reactions of Pd(methylenecyclopropane)(ethylene)(PH$_3$), Pd(OTMM)(ethylene)(PH$_3$), and Pd(ATMM)(ethylene)(PH$_3$) complexes. The [3 + 2] addition is shown on the left-hand side and the [2 + 1] addition on the right-hand side.

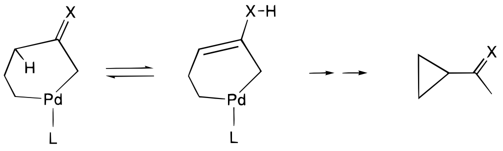
In an analogous isomerization reaction of olefins involving 1,3 hydride shifts, a mechanism presented in eq 8 has often been suggested.[20] Thus, we have investigated whether or not



(8)

hydride complexes intervene in the process connecting **33** and **35**. The ground-state structures of the hydride complexes obtained are illustrated in Figure 9. By abstracting an allylic proton from C3 and attaching it onto the metal center in **26** and **29**, we obtained some unusual structures **51** and **53** and methylenecyclopropane complexes **52** and **54**. In contrast, we found only a methylenecyclopropane complex **55** from **32**. These complexes are shown to be higher in energy than **TS2′** in each system. The formation of hydride complexes is unlikely.

An alternative may be the mechanism which involves deprotonation and protonation by a base added. In such a process, a tautomeric shift from **34** to **56** may intercept the reductive elimination (eq 9). For this process, we have



34 **56** (9)

calculated the geometry of intermediates **56** in the OTMM and ATMM cases. The optimized structures are illustrated in Figure 10. Both in the OTMM complex and in the ATMM complex, **57** and **58** (of the type **56**) are shown to be higher in energy

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(20) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 179.

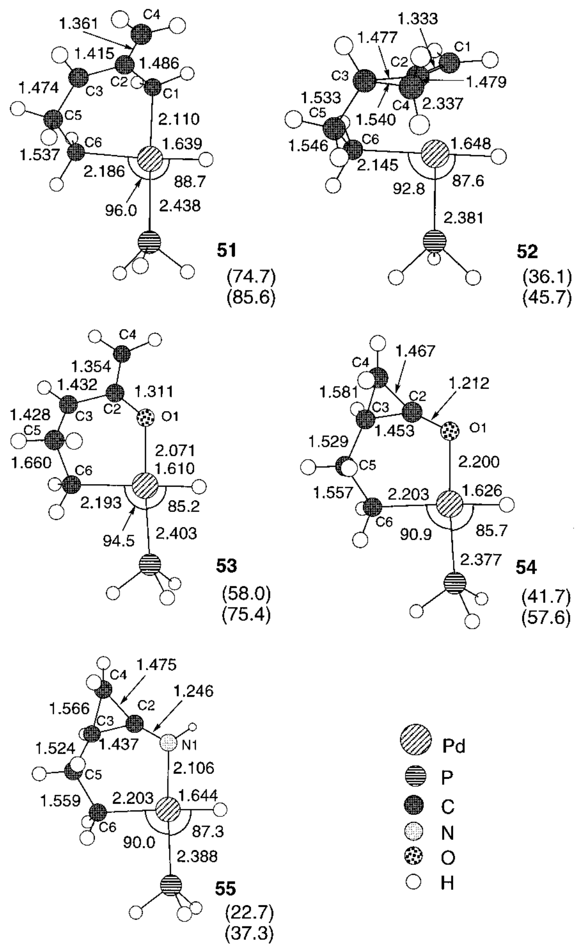

Figure 9. Calculated structures of intermediates **51**−**55**. Energies (kcal/mol) of **51** and **52** relative to **43**, of **53** and **54** relative to **46**, and of **55** relative to **49** are given in parentheses for HF (above) and MP2 (below) calculations.

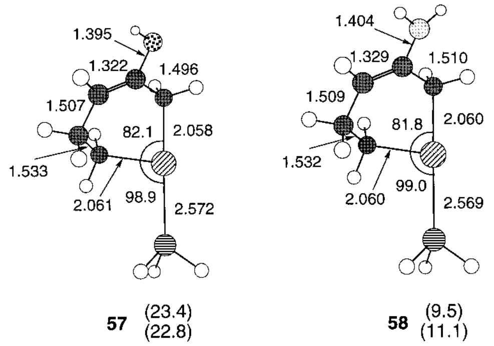

Figure 10. Calculated structures of intermediates **57** and **58**. Energies (kcal/mol) of **57** relative to **45** and of **58** relative to **48** are given in parentheses for HF (above) and MP2 (below) calculations.

than **45** and **48** (of the type **35**) by 22.8 and 11.1 kcal/mol, respectively, at the MP2 level. Therefore, the direct **33** → **35** → re (reductive elimination) route must be preferred to the **33** → **34** → **56** → re route or the **33** → **34** → **56** → **35** → re route. In any case, the rate of prototropic shift must depend heavily on the solvent used.

Conclusion

It has been demonstrated that the η^2-methylenecyclopropane Pd complex, **5**, and an isomeric TMM Pd complex, **3**, are roughly the same in stability. Introduction of a heteroatom favors an η^3-coordination, **3**, at the carbon sites, and neither the isomer **4** nor the isomer **5** seems to exist as a stable intermediate for the OTMM and ATMM complexes.

The d^{10} metal induced [3 + 2] coupling between methylenecyclopropane and olefin takes place in two steps, **23a** → **25 (TS1)** → **26** and **26** → **36 (TS2)** → **37**. The first step possesses a higher activation barrier, 26.4 kcal/mol, than the second one, 17.9 kcal/mol. The transition state, **TS1**, is of an ideal π-allylic structure, in which the external methylene carbon C1, the adjacent carbon C2, and one of the carbons in the methylenecyclopropane ring, C4, are bound to the metal center upon ring-opening. The concerted one-step mechanism, **23b** → **24**, is shown to be unfavorable, having a much higher activation energy, 44.4 kcal/mol.

In the [2 + 1] coupling reactions of the OTMM and ATMM complexes with olefins, the first step of the reaction is **27a** → **28 (TS1)** → **29a** and **30a** → **31 (TS1)** → **32a**, respectively. The transition states and the metallacyclic intermediates bear close resemblance to those found in the reaction of the methylenecyclopropane complex. From those metallacyclic intermediates, a mechanism, **29a** →→ **45** → **46 (TS2′)** → **47** or **32a** →→ **48** → **49 (TS2′)** → **50**, that involves a prototropic shift in the presence of solvent molecules would operate to give the [2 + 1] products. The [3 + 2] mode has been clarified to be unfavorable in the case of the OTMM complex, giving a higher activation energy. The ATMM complex has been located between the OTMM complex and the methylenecyclopropane complex in its reactivity trend for the coupling reactions. In experiments, both the OTMM and ATMM complexes are known to react only with strained electron-rich olefins.[10−12] In this study, we have used an ethylene molecule instead of larger olefins like norbornene because of computational limitation. The possible effects of substituent groups on olefins will be a topic of our future study.

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Supporting Information Available: Tables S1−S52 listing calculated total energies and the coordinates of atoms in the optimized structures of **8**−**32**, **36**−**55**, and **57**−**58** (35 pages). Ordering information is given on any current masthead page.

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