Computational Study of C–C Coupling on Diruthenium Bis(µ-vinyl) Ethylene π-Complex

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We have performed a computational study of the C–C coupling reaction between coordinated ethylene and two vinyl ligands in the binuclear bis(vinyl)-ethylene complex CpRu(η^2-C_2H_4)(µ-H)(CHMe-CMe)RuCp (1) to yield the ruthenacyclopentadiene complex CpRu(η^2-C_2H_4)(CHMe-CH=CHMe)RuCp (28), described by Suzuki et al. This reaction is a sophisticated multistep process with a large number of possible pathways. Agostic interactions and the cooperativity of both Ru centers play a crucial role in the mechanism of the reaction. Our calculations provide support for Suzuki et al.’s proposal that the conversion of the reactant 1 to the final product 28 proceeds through the intermediate Cp(H)(µ-H)(CMe-CH=CH=CMe)RuCp (20). However, the pathway originally proposed by Suzuki et al. leading to the intermediate 20 is unfavorable (ΔG^298 = 33 kcal mol^{-1}). We found a new, more favorable pathway with a ΔG^298 of 20 kcal mol^{-1}. The rate-determining step of the mechanism is ethylene coordination to the intermediate CpRu(µ-H)(CHMe-CH=CH=CMe)RuCp (22). The free energy barrier is about 29 and 24 kcal mol^{-1} at the BP86 and MPWLYP1M level, correspondingly.

Introduction

Bi- and polynuclear transition metal complexes are of great interest for organometallic chemists; due to the cooperativity of multiple metal centers, they exhibit unusual reactivity not found with mononuclear complexes. An illustrative example is the versatile chemistry of multinuclear transition metal polyhydride complexes with pentamethylcyclopentadienyl (Cp*) as auxiliary ligand. In particular, complexes Cp^*Ru(µ-H)_2RuCp^* and (Cp^*Ru)_2(µ-H)_2, synthesized and studied by H. Suzuki and co-workers, are capable of activating a variety of substrates. These complexes have been found to be efficient in bond activation reactions, such as H–H, C=C, H–C=C, Si–H, Si–C=C, P=C, C=S, C=N, and N=N.2–20

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bond cleavages. Also, these complexes have been shown to favor reactions affording new C–H, C–Si, C–C, C–O bonds.26

The mechanisms of these processes are generally rather complicated and involve a large number of steps. The course of reaction is largely governed by cooperativity of metal centers and by flexibility of hydride ligands. Interconversion between bridging and terminal hydrides can occur frequently in the course of the reaction. There were few examples of earlier computational studies of the mechanism of such reactions.27–29 More recently, on the basis of the experimental work,30 we have studied the hydride exchange process in the binuclear complex CpRu(µ-H)_2RuCp according to the equation CpRu(µ-H)_2RuCp + 2D_2 ⇄ CpRu(µ-D)_2RuCp + 2H_2.30 Both dissociative and associative mechanisms for the hydrogen exchange were considered. The associative pathway was shown to be more favorable. However, we found that the reaction does not necessarily occur through simple addition–elimination steps. In fact, there are several possible pathways and a large number of hexahydride intermediates with either bridging or terminal hydrides. This illustrates...
that even in such a seemingly simple reaction very versatile processes can occur.

Subsequently, we have performed a computational study\(^{31}\) of the C–H bond activation in ethylene on CpRu(µ-H)\(_2\)RuCp to form bis(vinyl)-ethylene complex CpRu(η\(^2\)-C\(_2\)H\(_4\))(η\(^2\)-CMe)\(_2\)RuCp, which corresponds to Cp\(^*\)Ru(η\(^2\)-C\(_2\)H\(_4\))(η\(^2\)-CMe)\(_2\)RuCp\(^*\) (A) obtained in the experimental work.\(^{3}\) We found that this is a sophisticated multistep reaction with a large number of possible pathways. The rate-determining step of the C–H bond activation reaction is the initial coordination of ethylene to the reactant with a \(\Delta^rG^{298}\) barrier of 27 kcal \(\cdot\) mol\(^{-1}\). Metadynamics calculations yielded a somewhat lower barrier of 20 kcal \(\cdot\) mol\(^{-1}\).

Cooperative involvement of the two Ru centers plays an important role in the C–H bond activation. Bridging hydrides play a role of an electron-mediating “buffer”, facilitating the coordination of the incoming ethylene on the metal center and its further transformations. The bridging Ru–H–Ru bonds compete with C–H···Ru agostic interactions. As a result, a very large number of intermediates and possible pathways emerge, contributing to the complexity of the mechanism.

The C–C coupling reactions are of enormous importance in synthetic organic chemistry, with thousands of papers published on this subject every year. In this connection, the C–C coupling reaction between coordinated ethylene and two vinyl ligands in complex A to yield the ruthenacyclopentadiene complex Cp\(^*\)Ru(η\(^2\)-C\(_2\)H\(_4\))(CMe=CH-CH=CMe)RuCp\(^*\) (C), also discovered by Suzuki and co-workers,\(^{3}\) is quite intriguing. It is a rare example of the functionalization of alkynyl groups formed as a result of C–H bond activation in alkenes by a transition metal complex. However, it should be noted that formation of a ruthenacyclopentene\(^2\) or ruthenacyclopentadiene\(^2\) intermediate can play a key role in mononuclear ruthenium-mediated alkynyl C–C coupling reactions.

The reaction of A with ethylene affords C and ethane (Scheme 1). A small amount of 1-butene is also formed. Heating of A in benzene in the absence of ethylene yields the ruthenacycle Cp\(^*\)Ru(CMe=CH-CH=CMe)RuCp\(^*\) (B). Exposed to light, B reacts with ethylene at atmospheric pressure to produce C and ethane. From these results it was concluded that the conversion of A to C occurs through the intermediate B in the first reaction. Therefore, the cyclopentadienyl framework of the metallacycle C should be formed from the two vinyl groups and the ethylene ligand coordinated in A. Thus, an incoming ethylene molecule A converts to ethane, while the coordinated ethylene is incorporated in the metallacycle C.

Scheme 1. Coupling Reaction among Coordinated Ethylene and Two Vinyl Ligands on the Ruthenium Complex (after ref \(^{3}\))

Scheme 2. Mechanism of the C–C Coupling Reaction Based on Suzuki et al.’s Proposal\(^{3}\)

The mechanism of the C–C coupling reaction shown in Scheme 2 was proposed mostly on the basis of the related reactions, since \(^{1}\)H NMR studies did not indicate the existence of any stable intermediate.\(^{3}\) Initially the activation of a C(sp\(^3\))-H bond at the α-carbon of the vinyl group in A yields the µ-vinylidene species II. The insertion of the remaining vinyl group into a Ru–H bond produces the µ-ethyldiene-µ-vinylidene intermediate I2. The oxidative addition of a C–H bond of the coordinated ethylene followed by the reductive coupling of the resulting vinyl ligand with the vinylidene ligand yields an intermediate I4 by way of I3. The insertion of a vinylc C≡C bond into a Ru–H bond gives the µ-ethyldiene intermediate I5. Reductive C–C coupling at the Ru center yields the ruthenacyclopentene I6. Activation of an allylic C–H bond followed by hydrogen abstraction at C(α′) affords the ruthenacyclopentadiene B. Finally, in the presence of ethylene B converts to C to give ethane.

In the present work we report a computational study of the mechanism of the coupling reaction in the bis(vinyl) complex CpRu(C\(_2\)H\(_4\))(µ-η\(^2\)-CH\(_2\)=CH\(_2\))RuCp between coordinated ethylene and two vinyl ligands to yield ruthenacyclopentadiene complex CpRu(η\(^2\)-C\(_2\)H\(_4\))(CMe=CH-CH=CMe)RuCp. The main goal is to establish a detailed mechanism of this unprecedented reaction, taking into account Suzuki’s suggestion (Scheme 2). We have located possible intermediates and the transition states and evaluated standard enthalpies \(\Delta H^{298}\), standard Gibbs free energies \(\Delta G^{298}\), and standard free energy barriers \(\Delta^rG^{298}\) for the corresponding reaction steps. Throughout the paper, we mostly operate with and discuss the Gibbs free energy rather than enthalpy changes. We focus on the formation of the ruthenacyclopentadiene complex C and have not studied the formation of the coproduct, 1-butene.

A significant number of computational mechanistic studies of various C–C coupling reactions catalyzed by mononuclear complexes have been done.\(^{35–48}\) However, their conclusions are hardly transferable to binuclear complexes, since the reactivity


\(^{(34)}\) Kirchner, K. Monatsh. Chem. 2008, 139, 337–348.
of the latter is dominated by cooperativity between the metal centers. Computational studies of C–C coupling reactions on bi- and trinuclear complexes are still scarce.49

**Computational Details**

The computational study was performed with the complex CpRu(η5-C5H5)(μ-η5,η5′-C5H5-CH2)2RuCp (1). The replacement of Cp by the cyclopentadienyl ligand (Cp) should not critically affect the chemistry, but allows for large savings of computer time. We adopted the same practice in our previous studies.30,31

The quantum-chemical calculations were carried out using the density functional theory (DFT)50,51 with the Gaussian 03 program package.52 The gradient-corrected BP86 functional was employed, which combines Becke’s nonlocal exchange53 and Perdew’s correlation64 functionals. We used the quasi-relativistic effective core relation54 functionals. We used the quasi-relativistic effective core potential of LaJohn et al. with the associated double-ζ valence basis set55 for ruthenium, 6-311G(dp)56 for C and H, and 6-31G(dp)57 for the spectator Cp ligands. For transition metal compounds, the chosen DFT approach normally provides realistic geometries, relative energies, and vibrational frequencies.50,58–61 Metal hydride complexes are no exception.62 In selected cases, we performed additional calculations using MPWLYP1M, a hybrid functional developed by Zhao et al.63 It is considered to be especially suitable for transition metal complexes.64 It combines modified

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<th>Scheme 3. Part 1 of the Mechanism of the C–C Coupling Reaction</th>
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| Relative Gibbs free energies are in kcal mol⁻¹. The numbers above arrows are ΔG°C values in kcal mol⁻¹. |

Perdew–Wang65 exchange with Hartree–Fock exchange (5%) along with the Lee–Yang–Parr66,67 correlation functional. The reactant, transition state, and product geometries were fully optimized without any constraints. The nature of optimized stationary points was confirmed by analytic computation of harmonic force constants. The transition states were connected to the related minima by means of an energy minimization following a small geometry displacement along the reaction coordinate obtained from the vibrational frequency calculation.

**Results and Discussion**

Initially, we decided to follow the mechanism proposed by Suzuki and co-workers. The mechanism is divided into three parts. Part 1 (Scheme 3) describes the reactant and its isomer, as well as subsequent steps leading to the intermediate 3 (corresponds to 13 in Scheme 2). Part 2A and Part 2B (Schemes 4 and 5) represent possible pathways of the formation of rhenacycle 20 (B). The final conversion of the latter to the product 28 (C) is described in Part 3 (Scheme 6).

**Part 1.** In our previous work,31 the two isomeric structures 1 and 1' have been found that correspond to the bis(vinyl) ethylene complex A observed experimentally. Their optimized geometries are depicted in Figure 1. The two μ-vinyl ligands in 1 are bonded in σ-mode to one Ru, with ethylene coordinated

(44) Matsubara, T. Organometallics 2003, 22, 4286.
(52) Frisch, M. J.; et al. Gaussian 03, Revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
(61) See special issue on computational transition metal chemistry: Chem. Rev. 2000, 100, 351.
(64) Zhao, Y.; Truhlar, D. G. J. Chem. Phys. 2006, 124, 224105.
to the same center, and π-bonded to the other. However, in 1′ both μ-vinyl ligands are bonded to Ru in σ,π-mode. Thus, the coordination numbers of the metal centers are different in 1′ due to the coordinated ethylene; Ru₁ is more electron-rich than Ru₂, which remains partly unsaturated. It is probably for this reason that 1′ is 6.6 kcal·mol⁻¹ less stable than 1 on the ΔG°₂⁹₈ scale (Table S1). In this work we have examined the C–C coupling reaction on complex 1.

According to the Suzuki mechanism, the first step is the activation of a C(sp²)–H bond of the vinyl group in 1 to form the μ-vinylidene species 2 (Scheme 3, Figure 1). The C–H bond activation proceeds through transition state TS(1–2) with a moderate ΔG°₂⁹₈ barrier of 14.9 kcal·mol⁻¹. The resulting complex 2 is 3.9 kcal·mol⁻¹ more stable than 1 on the ΔG°₂⁹₈ scale. The following insertion of the remaining vinyl group into a newly formed Ru–H bond produces the μ-ethylidene–μ-
Computational Study of C–C Coupling

Figure 2. Optimized structures of intermediates 4, 4', and 4'' as well as C=C coupling transition states TS(4–5), TS(4–7), and TS(4–8). Selected bond lengths are in angstroms. “Cp” denotes the center of mass of a Cp ring, which is omitted for clarity.

vinylidene intermediate 3 (Figure 1). This transformation is slightly endergonic (ΔG°298 = 2.4 kcal·mol⁻¹) with a Δ¹G°298 barrier of 7.0 kcal·mol⁻¹. The vacant space generated on Ru is suggested as a binding site for ethylene coordination.

Part 2A. Beginning from complex 3, several pathways are possible (see Schemes 4 and 5). In this part, we discuss the routes proposed by Suzuki and co-workers, starting with the C–H bond activation in ethylene ligand in 3 (Scheme 4). Depending on which of the carbon atoms is involved in the C–H bond cleavage, two vinyl hydride intermediates, 4 and 4’, are possible. In 4, the C° atom of the vinyl ligand is oriented toward the μ-vinylidene ligand, while the hydride ligand is positioned next to the ethylene group; in 4’ the ligand orientation is opposite (Figure 2). The C–H bond activation step to produce 4 or 4’ is substantially endergonic (ΔG°298 = +18.1 and +16.8 kcal·mol⁻¹, correspondingly).

In the original Suzuki mechanism, the two pathways split because the coupling in the vinyl hydride complex 13 can occur in two ways: between vinyl and μ-vinylidene ligands or between vinyl and μ-ethyldiene ligands. Here we show that the branching can also take place due to the existence of two vinyl hydride intermediates, 4 and 4’.

Route 2A.1. The transition state TS(3–4) is only 0.6 kcal·mol⁻¹ higher in energy than 4 on the ΔG°298 scale. Moreover, the difference in their zero-temperature enthalpy H°0 = E° + v298 is less than 0.1 kcal·mol⁻¹. Thus, 4 is a very shallow minimum and the reverse step (4–3) proceeds virtually without a barrier. According to the proposed mechanism, the subsequent step is the C–C coupling between the C° atoms of the vinyl and vinylidene group in 4 to yield 5 (Scheme 2). The coupling 4–5 proceeds with a moderate energy barrier of 14.5 kcal·mol⁻¹. Taking into account the fact that the energy barrier of the conversion 4–3 is very low, we conclude that the effective rate of formation of 5 is determined by the free energy difference between TS(4–5) and 3. This corresponds to an effective Δ¹G°298 barrier of 32.6 kcal·mol⁻¹ for the reaction from 3 to 5. This reasoning could be destroyed if 4 were a deeper minimum, in which case the 3–4 and 4–5 barriers need to be considered separately. Thus, it is important to make sure that the minimum 4 is indeed a shallow one.

For this purpose, we performed test calculations for the chain of conversions 3–4–5 using the MPWLYP1M functional. At this level, the 3–4 barrier (Δ¹G°298 = 23.8 kcal·mol⁻¹) is found to be 5 kcal·mol⁻¹ higher than at BP86. For the reverse step, the MPWLYP1M functional gives an energy barrier very close to the BP86 value (Δ¹G°298 = 0.7 kcal·mol⁻¹). This result supports the conclusion that 4 is a short-lived intermediate. The free energy barrier of the following C–C coupling step (4–5) is only 1.2 kcal·mol⁻¹ higher than the BP86 value (Δ¹G°298 = 15.7 kcal·mol⁻¹ at MPWLYP1M). Thus, the overall energy barrier of the formation of 5 is 39.5 kcal·mol⁻¹ at the MPWLYP1M level, which is even higher than the BP86 value. At both the BP86 and MPWLYP1M levels, this barrier is prohibitively high. Therefore, this pathway must be rejected.

We have examined the possibility of ethane formation in 4 through the hydrogenation of μ-ethyldiene. The hydride reductive coupling to the C° atom of the ethyldiene group in 4 yields the ethyl complex 6. The insertion of the μ-ethyldiene into the Ru–H bond is facile (Δ¹G°298 = 4.3 kcal·mol⁻¹). Further C–H bond activation at the C° atom of the vinyl ligand in 6 can yield a hydride ligand that is needed for further hydrogenation of ethyl. However, extensive potential energy scans indicate that the neighboring Cp ring in 6 sterically hinders the cleavage of the C–H bond, which is therefore inactive.

Route 2A.2. The vinyl hydride species 4’ is 0.2 kcal·mol⁻¹ higher in ΔG°298 than the corresponding transition state TS(3–4’) (Table S1, Supporting Information). Via a hydride rotation, 4’ can easily (Δ¹G°298 of 1.2 kcal·mol⁻¹) convert to 4”, which is 3.0 kcal·mol⁻¹ more stable. In the course of the rearrangement the hydride migrates through the C° atom of the μ-vinylidene ligand to the position between the μ-vinylidene and μ-ethyldiene ligands (Figure 2).

The subsequent C–C coupling in 4” can proceed in two ways (Scheme 4). The first possibility is the coupling between the C° atoms of μ-vinyl and μ-ethyldiene ligands to yield 7. The coupling occurs through the transition state TS(4”–7), the optimized geometry of which is shown in Figure 2. The length of the newly forming C–C bond in TS(4”–7) of 1.751 Å indicates that the bond formation has partially occurred. The conversion is thermodynamically favorable (ΔG°298 = −11.5 kcal·mol⁻¹), but the free energy barrier of 36.7 kcal·mol⁻¹ is very high.

On the other hand, the coupling can take place between the C° atom of μ-vinyl and C° atom of μ-vinylidene to produce 8. The optimized geometry of the corresponding transition state TS(4”–8) is shown in Figure 2. The newly forming C–C bond in TS(4”–8) is 0.086 Å longer than in TS(4”–7). This step is endergonic (ΔG°298 = 8.4 kcal·mol⁻¹) and has a very high free energy barrier of 32.6 kcal·mol⁻¹.
It follows that the coupling pathways proposed by Suzuki et al. are very unfavorable energetically. Therefore, we have to elaborate alternative pathways. The new pathways found in this work are described in the next part.

**Part 2B.** In principle, the direct C–C coupling can occur in complex 3. Considering the equilibrium structure of 3 (Figure 1), one can envision two alternative C–C coupling channels.

**Route 2B.1.** The coupling between \( \mu \)-vinylidene and the coordinated ethylene in 3 occurs via transition state TS\((3-9)\) to give the methyleneruthenacyclobutane complex 9 (Scheme 5), with the methylenic double bond bound in a \( \eta^2 \)-manner to the other ruthenium. The coupling proceeds with a \( \Delta^G_{298} \) barrier of 24.2 kcal \( \cdot \) mol\(^{-1}\). The product 9 lies 4.6 kcal \( \cdot \) mol\(^{-1}\) above the reactant 3. The optimized geometries of TS\((3-9)\) and 9 are shown in Figure 3. The length of the newly forming C–C bond is 1.794 \( \text{Å} \) in the transition state TS\((3-9)\) and 1.506 \( \text{Å} \) in the minimum 9.

The following step is the C–H bond cleavage at C\(^\alpha\) of the \( \mu \)-ethylidene ligand in 9 to yield intermediate 10. The C\(^\alpha\)–H bond cleavage proceeds through transition state TS\((9-10)\) with a \( \Delta^G_{298} \) barrier of 7.6 kcal \( \cdot \) mol\(^{-1}\). The hydride ligand formed in this step can further migrate to the methylene group to form complex 11. This step is exergonic (\( \Delta^G_{298} = -10 \) kcal \( \cdot \) mol\(^{-1}\)), but the calculated free energy barrier is too high (\( \Delta^G_{298} = 32.3 \) kcal \( \cdot \) mol\(^{-1}\)). Therefore, this route has been rejected.

**Route 2B.2.** Alternatively, the coupling between the coordinated ethylene and \( \mu \)-ethylidene can occur in 3 to yield the methylruthenacyclobutane complex 12. This step proceeds through the transition state TS\((3-12)\) with a large \( \Delta^G_{298} \) barrier of 28.5 kcal \( \cdot \) mol\(^{-1}\). Thus, the C–C coupling with a more saturated \( \mu \)-ethylidene ligand is less favorable compared to a less saturated \( \mu \)-vinylidyne ligand. This step is endergonic (\( \Delta^G_{298} = +13.9 \) kcal \( \cdot \) mol\(^{-1}\)). The optimized geometries of TS\((3-12)\) and 12 are presented in Figure 3. As can be seen from Figure 3, the C\(^3\)–H bond in 12 is strongly elongated (1.17 Å) due to agostic interaction with the Ru\(^2\) atom. This facilitates the C–H bond activation to produce 13 (\( \Delta^G_{298} = 10.0 \) kcal \( \cdot \) mol\(^{-1}\)).

More routes arise if one considers the possibility of the C–H bond activation in the \( \mu \)-ethylidene ligand in 3 taking place before the corresponding C–C coupling step (Scheme 5). The cleavage of the C\(^\alpha\)–H bond of the \( \mu \)-ethylidene ligand in 3 produces the vinyl hydride complex 14. The activation takes place through the transition state TS\((3-14)\) with a \( \Delta^G_{298} \) barrier of 7.5 kcal \( \cdot \) mol\(^{-1}\), which is very close to the value for the C–H bond cleavage in 9 (7.6 kcal \( \cdot \) mol\(^{-1}\)). The subsequent C–C coupling can again occur in two ways in 14.

**Route 2B.3.** The C–C coupling between the coordinated ethylene and \( \mu \)-vinylidene in 14 yields the \( \mu \)-butenediy1 complex 15, instead of the expected ruthenacyclobutane 10. Thus, the change in the order of the C–C coupling and C–H bond activation steps results in the formation of a different product (Scheme 4). The structural isomers 10 and 15 differ by the manner of coordination of the C\(_4\) moiety. The methylene group is, in particular, \( \eta^2 \)-coordinated to Ru\(^1\) in 15, while it is \( \eta^3 \)-coordinated to Ru\(^2\) in 10 (Figures 3 and 4). The formation of two different structures can be understood from the consideration of the optimized geometries of the transition states TS\((3-9)\) and TS\((14-15)\). As seen in Figure 4, the following \( \eta^3 \)-coordinated of the methylene group to Ru\(^2\) is more favorable since the metal center Ru\(^2\) is occupied by the terminal hydride in the transition state TS\((14-15)\), while Ru\(^2\) is vacant in TS\((3-9)\) (Figure 3). As a consequence, the \( \Delta^G_{298} \) barrier of the C–C coupling in 14 is 4.6 kcal \( \cdot \) mol\(^{-1}\) lower than the barrier of the corresponding step 3–9.

The subsequent C–C coupling between the \( \mu \)-butenediy1 and \( \mu \)-CCH\(_3\) ligand takes place through the transition state TS\((15-16)\) to produce 16 with a moderate free energy barrier of 14.0 kcal \( \cdot \) mol\(^{-1}\). The optimized geometries of TS\((15-16)\) and 16 are depicted in Figure 4. The newly forming C–C bond

**Figure 3.** Optimized structures of the transition states TS\((3-9)\) and TS\((3-12)\), corresponding to the process of the direct C–C coupling in 3, as well as of the products 9 and 12. Selected bond lengths are in angstroms. “Cp” denotes the center of mass of a Cp ring, which is omitted for clarity.
is still rather long in the transition state $\text{TS}(17-18)$ (1.961 Å) and shortened to 1.495 Å in minimum 16. The latter lies between typical lengths of a single and double C–C bond. The latter has a partly double-bond character since one of the adjacent C–H bonds is weakened due to an agostic interaction. As can be seen from Figure 4, the C–H bond is strongly elongated (1.282 Å), indicating a strong agostic interaction. This bond is cleaved to give ruthenacyclopentene 17 without barrier (Scheme 5, Figure 5).

The next step is the insertion of the methylene group into the Ru–H bond to give the agostic ethyl complex 18. The hydrogenation of the methylene group occurs via the transition state $\text{TS}(17-18)$ with a $\Delta^qG^o_{298}$ barrier of 14.7 kcal · mol$^{-1}$. The resulting agostic ethyl complex 18 is a shallow minimum, lying only 0.3 kcal · mol$^{-1}$ below the transition state $\text{TS}(17-18)$ in terms of $\Delta^qG^o_{298}$. Therefore it converts to a much more stable nonagostic ethyl complex 19 in a nearly barrier-free step ($\Delta^qG^o_{298} = 0.1$ kcal · mol$^{-1}$). The total 17–19 conversion is substantially exergonic ($\Delta^qG^o_{298} = -13.1$ kcal · mol$^{-1}$).

The rotation of the hydride in 19 in the direction coplanar to the ruthenacycle yields 20 (Figure 5), which corresponds to the experimentally isolated complex B (Scheme 1). The rearrangement occurs through the transition state $\text{TS}(19-20)$ with a very low $\Delta^qG^o_{298}$ barrier of 2.7 kcal · mol$^{-1}$.

Another possibility was a coupling between the coordinated ethylene and $\mu$-CCH$_3$ in 14 to give 13. However, extensive PES scans indicated that there is no minimum energy path for this transformation. Therefore, the coupling product 13 can be formed only indirectly on the route 2B.2 described above.

Part 3. The conversion of the ruthenacycle 20 (B) to the product complex 28 (C) is described in this part. It involves two ethylene coordination steps and elimination of ethane (Scheme 6).

**Route 3.1.** This pathway consists of only one step of ethylene coordination to the ruthenacycle 20 to yield ethylene $\pi$-complex 21. The coordination takes place through the transition state $\text{TS}(20-21)$ with a prohibitively high energy barrier ($\Delta^qH^o_{298} = +52.7$ kcal · mol$^{-1}$, $\Delta^qG^o_{298} = +63.1$ kcal · mol$^{-1}$). Moreover, this step is very endothermic ($\Delta^qH^o_{298} = +28.3$ kcal · mol$^{-1}$, $\Delta^qG^o_{298} = +43.1$ kcal · mol$^{-1}$). The high energy barrier is due to the fact that the coordination of the upcoming ethylene is hindered by the terminal hydride in $\text{TS}(20-21)$ (Figure 5). The latter is approximately perpendicular to the plane of ruthenacycle (the C–C–Ru–H dihedral angle of 82°) in 20, while in the transition state $\text{TS}(20-21)$ and the minimum 21 it is bent by about 40–50° toward the ruthenacycle plane.

**Route 3.2.** In the alternative pathway, the terminal hydride migration to the C$^a$ atom of the ruthenacycle in 20 to produce 22 takes place before the ethylene coordination step (Scheme 6). The hydride transfer occurs through transition state $\text{TS}(20-22)$ with a very low $\Delta^qG^o_{298}$ barrier of 2.9 kcal · mol$^{-1}$. The resulting structure 22 is only 1.6 kcal · mol$^{-1}$ less stable than 20. The optimized geometries of the transition state $\text{TS}(20-22)$ and the corresponding minimum 22 are shown in Figure 6. The bonds Ru–C$^a$ (2.300 Å) and C$^a$–H (1.202 Å) are elongated in 22, indicating a quite strong $\alpha$-agostic interaction. The Ru–C$^a$ bond is broken as a result of the ethylene coordination to 22. As can be seen from Figure 6, the bond Ru–C$^a$ (3.129 Å) is already broken in
the transition state \( TS(22-23) \). The coordination of ethylene proceeds with a free energy barrier of 28.6 kcal \( \cdot \) mol\(^{-1} \), which is more than 2 times less than the \( \Delta^i G^o_{298} \) barrier of the direct coordination step \( 20 \rightarrow 21 \).

For the sake of comparison, we performed calculations using the MPWLYP1M functional. The resulting free energy barrier of 23.8 kcal \( \cdot \) mol\(^{-1} \) is 4.8 kcal \( \cdot \) mol\(^{-1} \) lower than at the BP86 level. As MPWLYP1M is generally considered to be a more reliable functional, the barrier in reality is expected to be somewhat lower than the BP86 values. Moreover, for a reaction in a solvent, where entropy effects are less pronounced than in the gas phase, the actual \( \Delta^i G^o_{298} \) barrier will be even lower by some 5 kcal \( \cdot \) mol\(^{-1} \). Therefore, ethylene coordination to \( 22 \) is certainly a kinetically affordable step.

In the following steps, the coordinated ethylene is hydroge-

nated and eliminated as free ethane (Scheme 6). The insertion of the coordinated ethylene into the Ru\( ^{\text{H}} \) bond yields agostic ethyl complex \( 24 \). The insertion proceeds through the transition state \( TS(23-24) \) with a \( \Delta^i G^o_{298} \) barrier of 12.0 kcal \( \cdot \) mol\(^{-1} \). The agostic ethyl complex \( 24 \) is a shallow minimum, lying only 0.3 kcal \( \cdot \) mol\(^{-1} \) below the transition state \( TS(23-24) \) on the \( \Delta H^o_{298} \) scale, but 0.2 kcal \( \cdot \) mol\(^{-1} \) above it in terms of \( \Delta G^o_{298} \). Therefore, it readily converts to the nonagostic ethyl complex \( 25 \), which is by far more stable (\( \Delta G^o_{298} = -19.6 \) kcal \( \cdot \) mol\(^{-1} \)).

The subsequent migration of hydrogen to the ethyl ligand in \( 25 \) produces the ethane \( \sigma \)-complex \( 26 \) (Scheme 6). Hydrogena-
tion of the ethyl moiety proceeds through transition state \( TS(25-26) \) with a low free energy barrier of 3.7 kcal \( \cdot \) mol\(^{-1} \). The C\( ^{\text{H}} \) bond in the ethane ligand is significantly elongated (1.15 Å), indicating a rather strong C\( ^{\text{H}} \)\( \cdots \)Ru interaction. This transformation is accompanied by ruthenacycle closure (Figure 7).

Elimination of ethane from \( 26 \) yields the ruthenacycle \( 27 \). It is a favorable step mostly due to the entropy effects (\( \Delta H^o_{298} \) = \( -2.4 \) kcal \( \cdot \) mol\(^{-1} \), \( \Delta G^o_{298} \) = \( -13.1 \) kcal \( \cdot \) mol\(^{-1} \)). The negative \( \Delta H^o \) of dissociation of ethane can be explained by an additional stabilizing C\( ^{\text{C}} \)\( \text{ring} \) \( \rightarrow \) Ru donation in \( 27 \). No transition state for this process has been located, but a low dissociation barrier (within several kcal \( \cdot \) mol\(^{-1} \)) is expected for dissociation of a weakly bound ligand such as ethane.

It is evident from Scheme 6 that complex \( 27 \) can be formed directly from \( 20 \) (which corresponds to intermediate B) as a result of \( \text{H}_2 \) dissociation. This is an endothermic reaction with a \( \Delta H^o_{298} \) of about \( +19 \) kcal \( \cdot \) mol\(^{-1} \) and a \( \Delta G^o_{298} \) of about \( +10 \) kcal \( \cdot \) mol\(^{-1} \). The reaction barrier can be even higher. We propose that the dissociation can occur as a result of a photochemical reaction. As will be shown below, the coordination of an ethylene molecule to \( 27 \) to yield \( 28 \) has a much lower energy barrier than the ethylene coordination to \( 20 \). Thus, a

**Figure 5.** Optimized structures of the minima \( 17-21 \), as well as of the transition state \( TS(20-21) \), corresponding to the direct ethylene coordination to \( 20 \). Selected bond lengths are in angstroms.
photochemical dissociation of H₂ can facilitate the formation of the final product 28.

The final step of the mechanism is the coordination of the second ethylene molecule to the complex 27 (Scheme 6). The incoming ethylene can attack either in cis or trans position with respect to the ruthenacycle to yield 28 or 28', respectively. The formation of ethylene π-complex 28, which corresponds to the final product C in Scheme 1, occurs via transition state TS(27–28) with a moderate barrier (Δ¹H°298 = 2.7 kcal·mol⁻¹, Δ¹G°298 = 12.6 kcal·mol⁻¹). In contrast, the formation of complex 28' through the transition state TS(27–28') is considerably less favorable (Δ¹H°298 = 12.2 kcal·mol⁻¹, Δ¹G°298 = 22.5 kcal·mol⁻¹). In transition state TS(27–28) the incoming ethylene is coordinated in a symmetrical manner, with both Ru–C distances of about 3.66 Å.

Relative Gibbs free energies are in kcal·mol⁻¹. The numbers above arrows are Δ¹G°298 values in kcal·mol⁻¹.

Figure 6. Optimized structures of the transition state of the C–H bond activation step TS(20–22) leading to 22, and the transition state of the subsequent ethylene coordination step to produce ethylene π-complex 23. Selected bond lengths are in angstroms. “Me” denotes the carbon atom of a methyl group.
Å (Figure 7). On the contrary, in TS(27−28′) ethylene attacks asymmetrically, with one shorter Ru–C distance and the other much longer (3.29 and 4.08 Å, respectively).

Thus, our calculations demonstrate that the ruthenacycle 20 (B) plays a role of the intermediate in the transformation 1 (A) → 28 (C) (Scheme 1).

Figure 7. Optimized structures of the agostic and nonagostic ethyl complexes 24 and 25, the ethane σ-complex 26, and the product of ethane elimination, 27. Selected bond lengths are in angstroms. “Me” denotes the carbon atom of a methyl group.

Figure 8. Optimized structures of the transition states of the ethylene coordination step TS(27−28) and TS(27−28′) to produce the final product 28 and its isomer 28′. Selected bond lengths are in angstroms.
Conclusions

We present the computational study of the C–C coupling reaction between coordinated ethylene and two vinyl ligands on the binuclear bis(vinyl)-ethylene complex 1 to yield a ruthenacyclopentadiene complex 28.

The rate-determining step of the mechanism is the coordination of the first ethylene molecule to the intermediate 22 to give the ethylene π-complex 23. The enthalpy barrier $\Delta H^\circ_{298}$ is 18 kcal·mol$^{-1}$, and $\Delta G^\circ_{298}$ barrier is about 29 kcal·mol$^{-1}$ at the BP86 level. On the other hand, the barrier calculated at the MPWLYP1M level is about 5 kcal·mol$^{-1}$ lower than the BP86 value. Thus, the actual barrier for the rate-determining step is expected to be below 24 kcal·mol$^{-1}$. It should be also borne in mind that the actual $\Delta S^\circ$ of a coordination reaction in solution is much less negative than in the gas phase. Thus, the actual ethylene coordination barrier in solution is expected to be about 20 kcal·mol$^{-1}$. Another high-barrier step is the C–C coupling between the coordinated ethylene and $\mu$-vinylidene in 14 to yield 15. The corresponding free energy barrier is 20 kcal·mol$^{-1}$.

The calculations show that, in general, the C–C coupling occurs more readily between less saturated carbon atoms, as a higher π-electron population facilitates the formation of a new C–C bond. For instance, the C–C coupling between $\mu$-vinyl and $\mu$-vinylidene ligands in 4 has a much lower energy barrier ($\Delta G^\circ_{298} = 14$ kcal·mol$^{-1}$) than the C–C coupling between $\mu$-vinyl and $\mu$-ethylidene in 14 to yield 15 ($\Delta G^\circ_{298} = 37$ kcal·mol$^{-1}$). The coordination environment of both ruthenium atoms also strongly influences the coupling barrier. For example, the C–C coupling between the coordinated ethylene and $\mu$-vinylidene in 3 proceeds with a higher energy barrier ($\Delta G^\circ_{298} = 24$ kcal·mol$^{-1}$) than in 14 ($\Delta G^\circ_{298} = 20$ kcal·mol$^{-1}$).

Our computational study shows that the mechanism originally proposed by Suzuki et al. needs some modifications, since the subsequent C–C coupling steps 3–4–5 turn out to proceed with a very high barrier.

A new, more favorable pathway has been found. The actual C–C coupling occurs in the vinyl hydride complex 14, which results from the C–H bond activation in $\mu$-ethylidene in 3. The ruthenacyclopentyl complex 16 is then formed as a result of two consecutive C–C coupling steps in this pathway. The following hydrogenation and rearrangement steps yield the ruthenacyclopentadiene complex 20, which corresponds to the experimentally isolated intermediate B in Scheme 1.

We have demonstrated that the intermediate 20 can be transformed to the final product 28 with an affordable free energy barrier (below 24 kcal·mol$^{-1}$). Thus, the presented computational results provide evidence for Suzuki et al.’s conclusion that conversion of the reactant 1 to the final product 28 occurs through the ruthenacyclopentadiene complex 20.

In summary, the title reaction is a sophisticated multistep reaction with a large number of possible pathways.

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Supporting Information Available: Calculated relative equilibrium energies, standard Gibbs free energies, and standard enthalpies of the reactant, intermediates, and products. Absolute energies, Gibbs free energies, and Cartesian coordinates of all the structures under study. Complete ref 52. This material is available free of charge via the Internet at http://pubs.acs.org.