

Unusual Intramolecular [2 + 2] Cycloaddition of Allyl and Vinylidene C=C Bonds under Mild Conditions: A Theoretical Analysis

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A theoretical analysis allows for the rationalization of the recently reported unusual formation under mild conditions of a cyclobutylidene ring from a diastereoselective [2 + 2] intramolecular cycloaddition of two C=C systems. The reaction takes place by heating in dichloromethane the vinylidene complexes $[\text{Ru}(\eta^5, \eta^3\text{-C}_9\text{H}_7)\{\text{C}=\text{C}(\text{R})\text{H}\}\{\kappa^1\text{-}(P)\text{-PPh}_2(\text{C}_3\text{H}_5)\}(\text{PPh}_3)][\text{BF}_4]$ ($\text{R} = \text{Ph}$, $p\text{-Me-C}_6\text{H}_4$) (**1**) yielding the bicyclic alkylidene complexes $[\text{Ru}(\eta^5, \eta^3\text{-C}_9\text{H}_7)\{\kappa^2\text{-}(P, C)\text{-}(=\overline{\text{C}}\text{C}(\text{R})\text{HCH}_2\text{CHCH}_2\text{-PPh}_2)\}(\text{PPh}_3)][\text{BF}_4]$ (**2**). The proposed mechanism represents an alternative to the classical Woodward–Hoffmann's supra-antara approach.

Introduction

The [2 + 2] cycloadditions are very important processes from both the synthetic and mechanistic viewpoints.¹ According to the Woodward–Hoffmann rules,² the [2 + 2] cycloaddition reactions are forbidden when proceeding through a supra-supra reaction path. Seminal experimental work by Huisgen³ and Bartlett⁴ on the stereoselectivity of these processes accumulated evidence to elucidate their mechanism.

Theoretical investigations^{5–7} and experimental work⁸ concluded that no true transition structure exists on the

potential energy surface for such reactions. A concerted supra-antara process is allowed according to the above-mentioned symmetry rules,² but in general it is expected to have high activation energy because of large steric effects and will be favored only in very special cases.⁹

Following Epiotis et al.'s suggestions,¹⁰ Bernardi et al.¹¹ reported that for polarized π -systems they were able to locate a true supra-supra transition structure, although as a result of its high energy, it will eventually become important only when solvent effects are considered. In this context, it has been reported that sometimes the high polarization of one reactant makes the [2 + 2] concerted cycloaddition reaction symmetry allowed.¹²

After extensive theoretical and experimental investigations on simple thermal [2 + 2] cycloaddition reactions, a stepwise process through either zwitterionic¹³ or bi-radical¹⁴ intermediates is the commonly accepted mechanism for these reactions.

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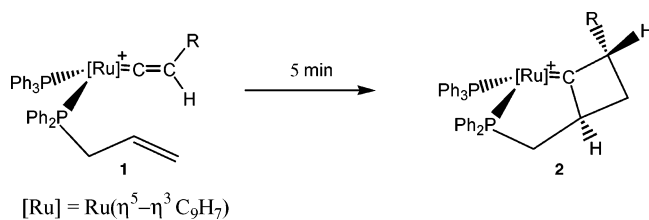
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SCHEME 1. Reaction Scheme



In a very recent work,¹⁵ an unusual diastereoselective [2 + 2] cycloaddition of two C=C bonds under mild thermal conditions was reported. The process takes place by heating the vinylidene complexes [Ru(η^5 , η^3 -C₉H₇){=C=C(R)H}{ κ^1 -(P)-PPh₂(C₃H₅)}(PPh₃)] [BF₄] (R = Ph, *p*-Me-C₆H₄) (**1**) yielding the bicyclic alkylidene complexes [Ru(η^5 , η^3 -C₉H₇){ κ^2 -(P,C)-(=CC(R)HCH₂CHCH₂PPh₂)-(PPh₃)] [BF₄] (**2**) (see Scheme 1).

In this work, we report the results of a theoretical analysis of the above reaction. We will show that (a) the reaction proceeds through a concerted although asynchronous mechanism; such a mechanism is fully consistent with the experimentally observed diastereoselectivity of the process as well as with the kinetic measurements; (b) the barrier of the transition structure is unexpectedly low as a consequence of the formation of a temporary stabilizing bonding Ru–C interaction. This theoretical observation justifies the experimental fact that the reaction proceeds under mild conditions, and (c) the theoretically estimated activation Gibbs free energy agrees rather well with the corresponding experimental value.

A biradical mechanism was not considered in the present work as we focused on the possibility of rationalizing the experimental facts in terms of a concerted mechanism under thermal conditions. According to the previous paragraphs, this perspective represents a novel contribution to the field of the [2 + 2] cycloaddition reactions. Although our experimental work has shown that the use of radical inhibitors (BHT, i.e., 2,6-di-*tert*-butyl-4-methylphenol) did not alter the experimental observations at all, the feasibility of a stepwise mechanism cannot be fully discarded.

Computational Methods

Density functional theory (DFT) calculations at the B3LYP level¹⁶ were carried out in order to explore the corresponding potential energy surface (PES). The LANL2DZ effective core potential¹⁷ was chosen for Ru and P, while the standard 6-31G-(d,p) basis sets¹⁸ were employed for the rest of the atoms. Experience has shown that this level of theory provides reasonable predictions for transition-metal-containing compounds.¹⁹ Graphical analysis of the imaginary frequencies of the transition structures as well as intrinsic reaction coordinate (IRC)²⁰ calculations allowed us to interconnect the dif-

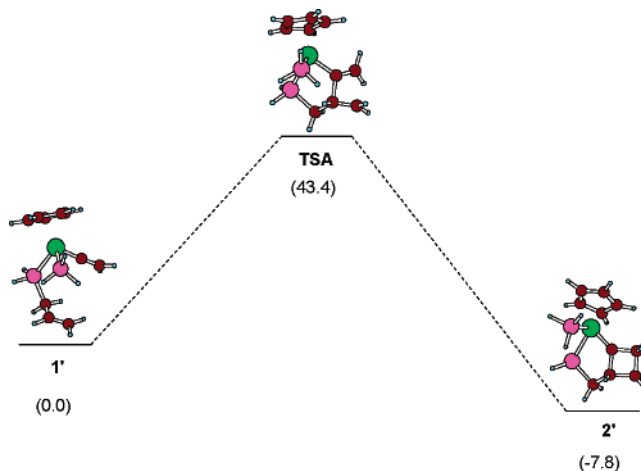
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SCHEME 2. Energy Profile, As Computed at the B3LYP/6-31G(d,p) + LANL2DZ Level, for the Single-Step [2 + 2] Intramolecular Cycloaddition Reaction in [Ru(η^5 -C₅H₅)(=C=CH₂){ κ^1 -(P)-PPh₂(C₃H₅)}(PPh₃)]⁺ (**1'**)

ferent structures located on the PES and then construct the energy profiles.

Two different tools were employed in order to characterize the bonding interactions: (a) natural bond orbital (NBO) analysis²¹ in which a given wave function is optimally transformed into localized form according to a Lewis structure picture (lone pairs and two-center bonds), and (b) Bader's atoms in molecules theory,²² which is based on the topological analysis of the electron densities.

Solvation effects were estimated by performing single-point calculations with the self-consistent reaction field (SCRFF) Onsager model.²³ In this model, the solute is placed in a spherical cavity immersed in a continuous medium with a dielectric constant ϵ . The solute radius is computed by a gas-phase molecular volume calculation. The thermodynamic functions were estimated within the ideal gas, rigid rotor, and harmonic oscillator approximations.²⁴ The Gaussian 98 package of programs²⁵ were used to carry out the calculations. A temperature of 298.15 K and a pressure of 1 atm were assumed.

Because energies are much more sensitive than geometries to the choice of methodology, we explored, through single-point calculations, the basis set effects [considering various basis from different laboratories: Pople's 6-31+G(2d,2p),¹⁸ Dunning–Huzinaga's D95, D95+(2d,2p),²⁶ and Dunning's cc-pVDZ,

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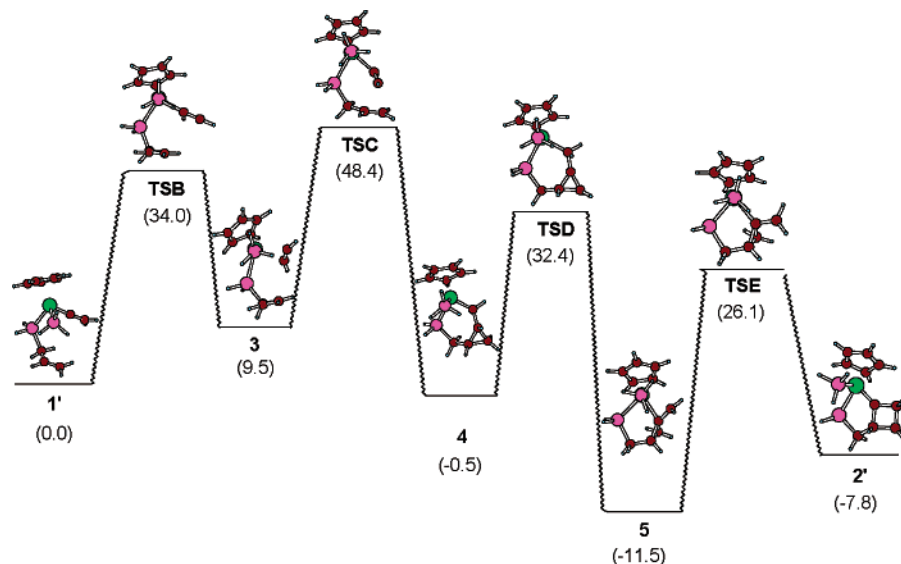
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SCHEME 3. Energy Profile, As Computed at the B3LYP/6-31G(d,p) + LANL2DZ Level, for the Multistep [2 + 2] Intramolecular Cycloaddition Reaction in $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(=\text{C}=\text{CH}_2)\{\kappa^1\text{-}(\text{P})\text{-PH}_2(\text{C}_3\text{H}_5)\}(\text{PH}_3)]^+$ (**1'**)**TABLE 1.** B3LYP/6-31G(d,p)+LANL2DZ Relative (to 1') Electronic Energies (ΔE^\ddagger), Enthalpies (ΔH^\ddagger), Entropies (ΔS^\ddagger), and Gibbs Free Energies (ΔG^\ddagger) for All Structures Located on the PES for Pathways I and II^a

system	ΔE^\ddagger	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger
		pathway I		
TSA	39.9	39.8	-12.017	43.4
		pathway II		
TSB	37.3	34.5	1.499	34.0
3	10.0	9.9	1.322	9.5
TSC	47.1	46.0	-8.094	48.4
4	-6.2	-4.5	-13.324	-0.5
TSD	30.3	28.8	-11.850	32.4
5	-17.5	-15.6	-14.046	-11.5
TSE	23.4	23.4	-9.204	26.1
2'	-12.8	-10.9	-10.436	-7.8

^a All values in kcal/mol except ΔS^\ddagger (cal/mol·K). A temperature of 298 K and a pressure of 1 atm were assumed.

aug-cc-pVDZ]²⁷ and the performance of other methods, including different DFT functionals (BPW91)¹⁶ and MP2 theory.¹⁸

Results and Discussion

A preliminary exploration of the PES corresponding to the [2 + 2] intramolecular cycloaddition reaction in $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(=\text{C}=\text{CH}_2)\{\kappa^1\text{-}(\text{P})\text{-PH}_2(\text{C}_3\text{H}_5)\}(\text{PH}_3)]^+$ (**1'**), resulting from the substitution of $\eta^5, \eta^3\text{-C}_9\text{H}_7$ and the Ph groups in **1** by the computationally more tractable species $\eta^5\text{-C}_5\text{H}_5$ and H, respectively, suggested the existence of two different pathways. Schemes 2 and 3 show the two energy profiles. The minima and transition structures located on the PES are summarized in Figures 1 and 2 where the most representative geometrical parameters are also given (two additional views for each structure are provided as Supporting Information to facilitate spatial visualization). Table 1 collects the energetic data for all of the structures.

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TABLE 2. ΔG and ΔG^\ddagger ^a Values (in kcal/mol and relative to 1') for the Transition Structure (TS) and Product (2'') of the Intramolecular [2 + 2] Cycloaddition Reaction between Allyl and Vinylidene C=C Bonds in $[\text{Ru}(\eta^5, \eta^3\text{-C}_9\text{H}_7)(=\text{C}=\text{CH}_2)\{\kappa^1\text{-}(\text{P})\text{-PH}_2(\text{C}_3\text{H}_5)\}(\text{PH}_3)]^+$ ^b

method	system	basis sets		
		6-31+G(2d,2p)	D95+(2d,2p)	aug-cc-pVDZ
B3LYP ^c	TS	31.5 (29.7)	31.0 (31.5)	31.4 (29.9)
	2''	-40.3 (-39.2)	-42.6 (-39.4)	-41.2 (-39.3)
BPW91 ^c	TS	26.3 (26.4)	25.9 (24.9)	26.2 (25.1)
	2''	-45.5 (-43.0)	-47.9 (-46.2)	-46.3 (-44.7)
MP2	TS	22.1	21.1	19.6
	2''	-57.9	-60.1	-62.2

^a Frequency calculations were carried out at the B3LYP/6-31G(d,p) + LANL2DZ level of theory (see text for more details).

^b A temperature of 298 K and a pressure of 1 atm were assumed.

^c Solvation effects (see text) in parentheses. As these effects are rather small they were not estimated at the very expensive MP2 level.

The first pathway (I) consists of a single-step mechanism through a concerted although asynchronous transition structure (**TSA**). The second via (II) represents a multistep mechanism starting from the formation of a π -alkyne species (**3**) in equilibrium with the corresponding vinylidene complex (**1'**). The interaction between a terminal carbon in the alkyne with the terminal double bond forming a three-member ring gives rise to a slightly stable complex (**4**). Further 1,2-hydrogen migration leads to a rather stable complex (**5**) exhibiting a terminal olefin π -coordination. A rearrangement from the three-membered carbon ring in **5** gives the four-membered cyclobutylidene final product (**2'**).

In a global sense, whereas the multistep mechanism represents the coupling of the allylic double bond with the π -alkyne complex, the single-step process proceeds through the coupling of the allylic double bond with the vinylidene C=C. The analysis of these two energy profiles indicates that the concerted mechanism involves a lower energy barrier and consequently is the favored pathway. It should be stressed, however, that the energy difference (about 5 kcal/mol), although important, suggests that the two mechanisms might become competitive under ap-

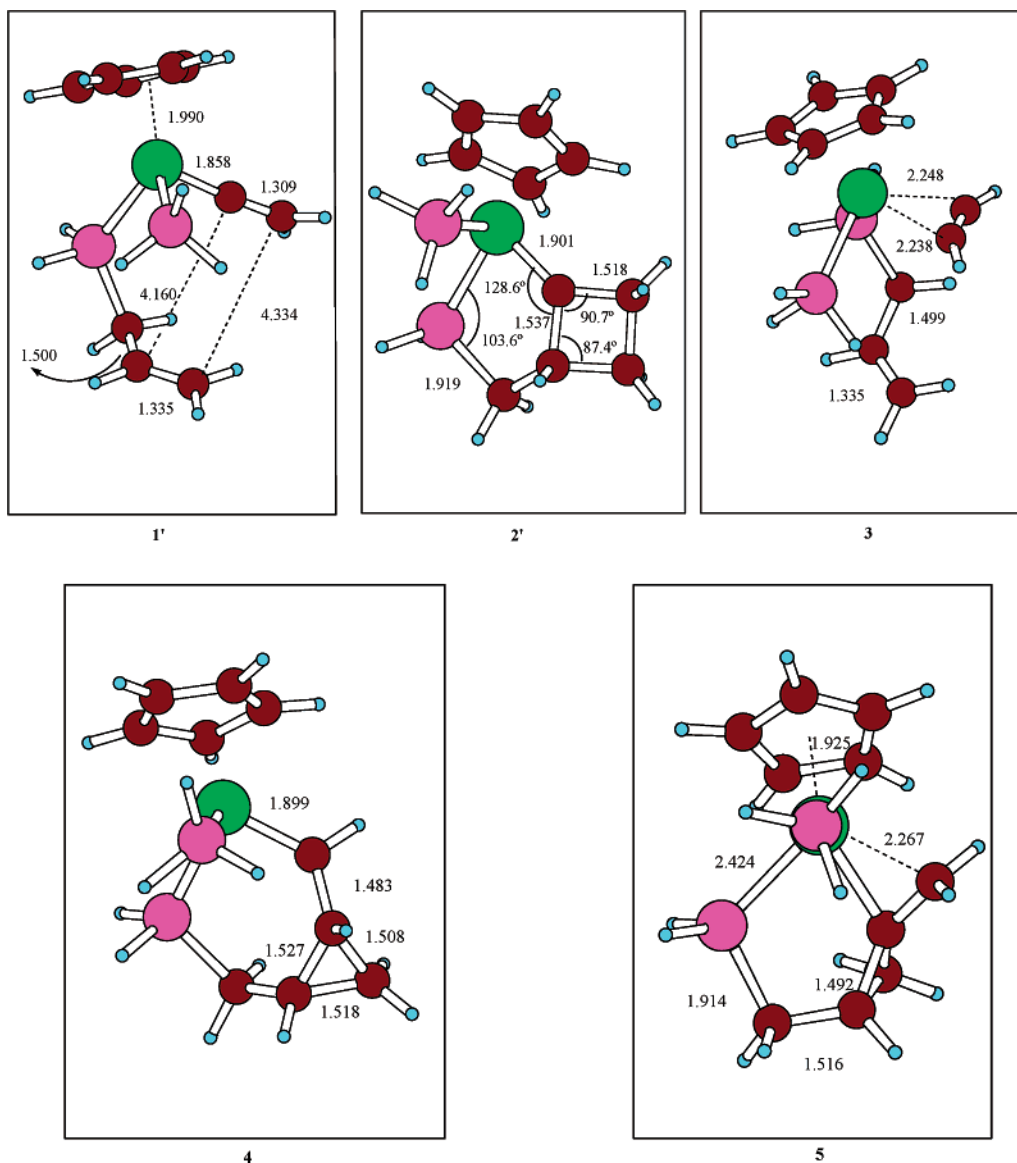


FIGURE 1. Minima structures located on the potential energy surface, as computed at the B3LYP/6-31G(d,p) + LANL2DZ level, of the intramolecular cycloaddition reaction in $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(=\text{C}=\text{CH}_2)\{\kappa^1\text{-}(P)\text{-PH}_2(\text{C}_6\text{H}_5)\}(\text{PH}_3)]^+$ (**1'**).

appropriate circumstances. However, the kinetics experimental measurements,¹⁵ which are consistent with a single-step process, show that this is not the case for the reaction in Scheme 1.

Examination of the energy profiles in Schemes 2 and 3 shows that, in sharp contrast with the experimental observation, the theoretically predicted final product for the studied reaction should be **5** instead of **2'**. Indeed, the reaction would proceed through the kinetically favored mechanism (single-step pathway in Scheme 2) giving **2'** as the product. However, according to Scheme 3, **2'** will transform into the more exothermic product **5** through the transition structure **TSE** with an energy barrier (33.9 kcal/mol) lower than that corresponding to the single-step **TSA** transition structure.

A close inspection of the geometry of the structures collected in Schemes 2 and 3 (see Figures 1 and 2) suggests that the steric effects, minimized in our theoretical modeling to make the calculations affordable,

should affect in some extent the stabilizations and barrier heights of such structures. To analyze the influence of the steric effects we carried out calculations on a model compound, closer to the experimental system, where we included the PPh_3 and $=\text{C}=\text{CHPh}$ substituents instead of the PH_3 and $=\text{C}=\text{CH}_2$ groups employed in the simpler model. To keep the computational cost within practical limits (70 atoms and 679 basis functions are involved) we focused on the B3LYP/6-31G(d,p) + LANL2DZ geometry optimizations of structures **II** (**2'**) and **V** (**5**). The final geometries are shown in Figure 3.

As a consequence of the influence of steric effects, the structure **II** becomes lower in energy than the structure **V** by 1 kcal/mol. Furthermore, as **TSA** and **TSE** closely resemble **2'** and **5** structures, respectively (see Figures 1 and 2), a similar steric effect should be expected for the barrier heights associated with the transition structures including the phenyl groups. Therefore, from a kinetic viewpoint, the conversion **II** \rightarrow **V** should also involve a

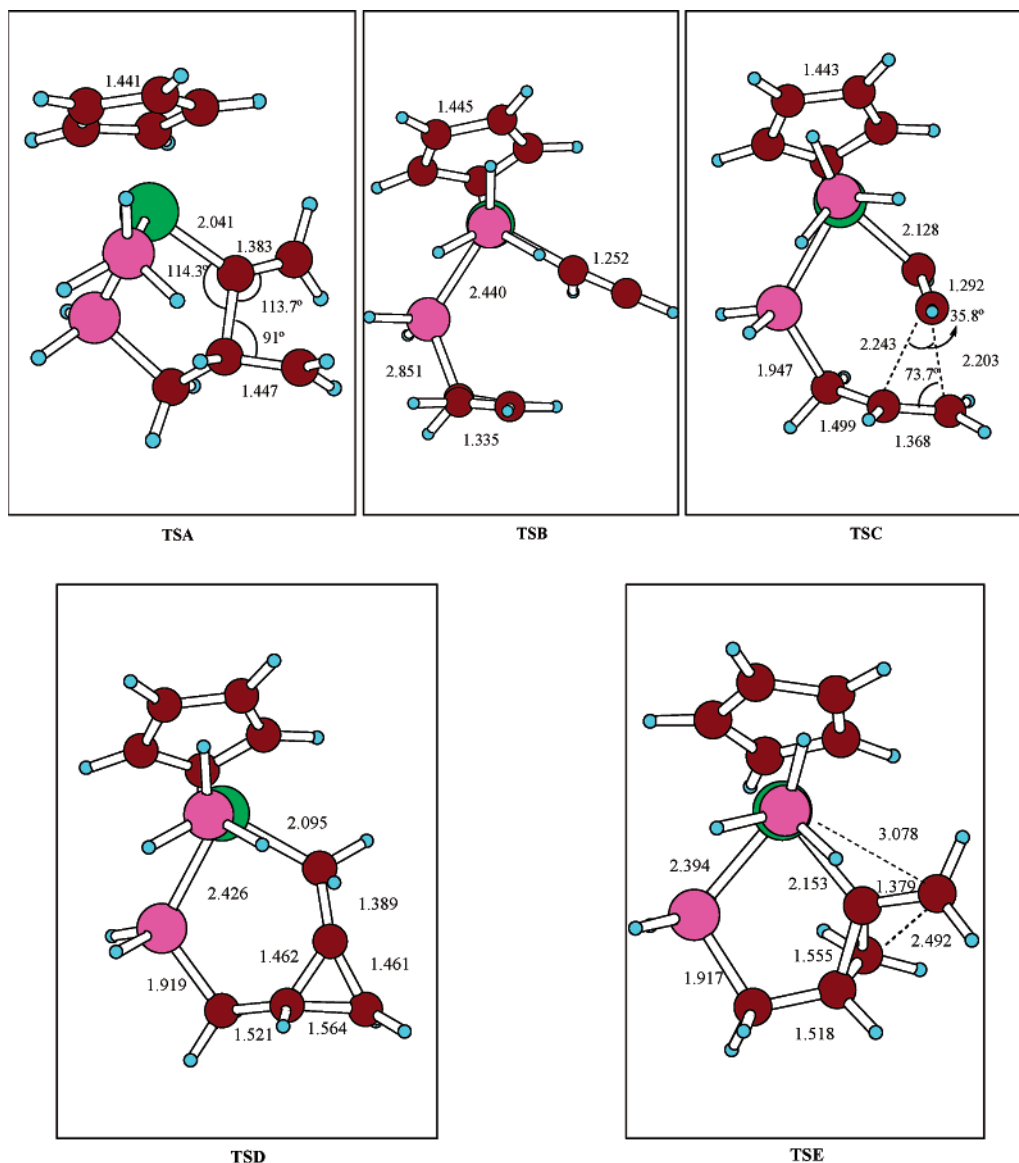


FIGURE 2. Transition structures located on the potential energy surface, as computed at the B3LYP/6-31G(d,p) + LANL2DZ level, of the intramolecular cycloaddition reaction in $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(=\text{C}=\text{CH}_2)\{\kappa^1\text{-}(P)\text{-PH}_2(\text{C}_3\text{H}_5)\}(\text{PH}_3)]^+$ (**1**).

barrier higher than that for the $2' \rightarrow 5$ conversion (see Scheme 3). As a conclusion, from both the thermodynamic and kinetic viewpoints, the steric effects will lead to favor the formation of **2** (i.e., model compounds **2'**, **II**, and **2''**, see below) as the final product of the reaction, in agreement with the experimental observation.

Bearing in mind the above results, we focused on the single-step mechanism using $\eta^5, \eta^3\text{-C}_9\text{H}_7$ instead of $\eta^5\text{-C}_5\text{H}_5$ to mimic in a more realistic way the experimental vinylidene complex (**1**). Scheme 4 shows the energy profile, and Figure 4 contains the two minima (**1''**, **2''**) and the transition structure (**TS**) located on the PES (see Supporting Information for two additional views of each structure). Table 2 collects the corresponding energies as estimated by the larger size basis set, including diffuse functions, employed in this work (results from the rest of the theoretical levels employed are available as Supporting Information). The BPW91//B3LYP and MP2//B3LYP activation Gibbs free energies (19.6–26.2 kcal/

mol) are good estimates of the corresponding experimental value (23.8 ± 3.2 at 298.15 K).¹⁵

The fully optimized geometries obtained for models **1''** and **2''** preserve a three-legged piano stool geometry as determined by the spectroscopic characterization of **1** and **2** and the X-ray structural determination of complex **2**.¹⁵ The models show a relatively high indenyl distortion ($\eta^5 \rightarrow \eta^3$ slippage). This structural feature correlates well with the observed indenyl distortion of complexes **1** and **2** in solution as determined by the value of the slip-fold parameter $\Delta\delta$. This parameter has been widely used for the evaluation of the indenyl hapticity and can be calculated spectroscopically by comparing the ¹³C NMR chemical shifts of the ring-junction carbon atoms of the indenyl ring in the metal complex with those of the sodium indenyl.^{28a} $\Delta\delta$ having values in the range -10 to -20 ppm have been proposed as an indication of a partially slipped η^5, η^3 indenyl ligand.^{28b} The $\Delta\delta$ values for complexes **1** and **2** are -15.85 and -17.1 ppm,

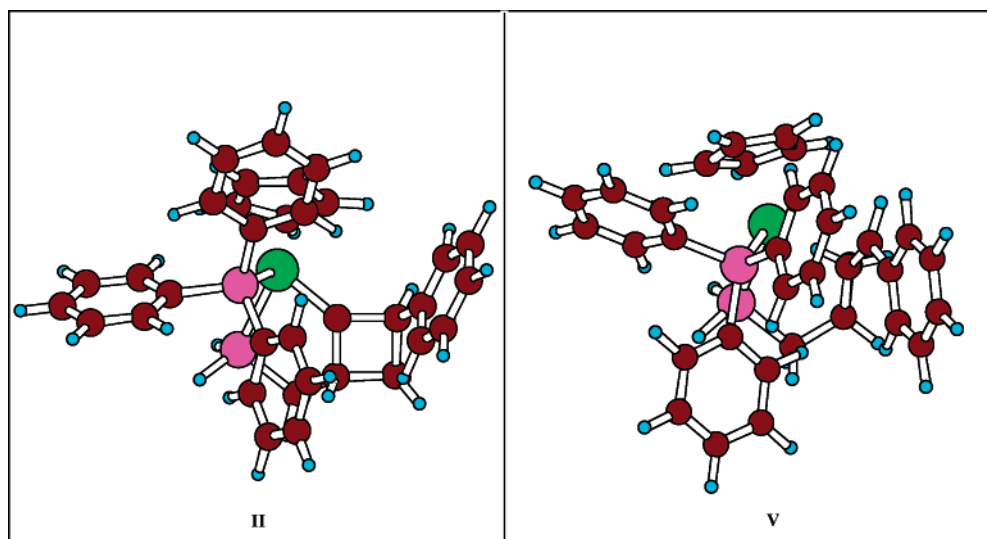


FIGURE 3. Minima structures located on the potential energy surface, as computed at the B3LYP/6-31G(d,p) + LANL2DZ level, of the intramolecular cycloaddition reaction in the model $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(=\text{C}=\text{CHPh})\{\kappa^1\text{-}(P)\text{-PH}_2(\text{C}_3\text{H}_5)\}(\text{PPh}_3)]^+$. Structures II and V correspond to the structures 2' and 5 for the intramolecular cycloaddition reaction in $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(=\text{C}=\text{CH}_2)\{\kappa^1\text{-}(P)\text{-PH}_2(\text{C}_3\text{H}_5)\}(\text{PH}_3)]^+$ (see Figure 1).

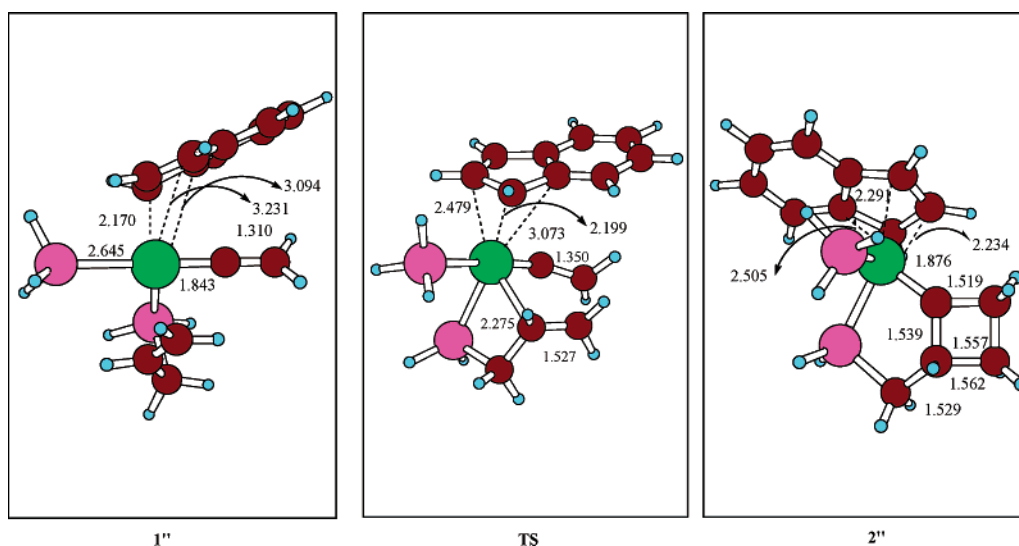


FIGURE 4. Stationary points located on the potential energy surface, as computed at the B3LYP/6-31G(d,p) + LANL2DZ level, of the intramolecular cycloaddition reaction in $[\text{Ru}(\eta^5, \eta^3\text{-C}_9\text{H}_7)(=\text{C}=\text{CH}_2)\{\kappa^1\text{-}(P)\text{-PH}_2(\text{C}_3\text{H}_5)\}(\text{PH}_3)]^+$ (1'').

respectively. These values are similar to those found in representative ruthenium(II) complexes (ranging from -16.3 to -22.3 ppm)^{28c-e} for which the X-ray structures show a slip-fold distortion in the solid state

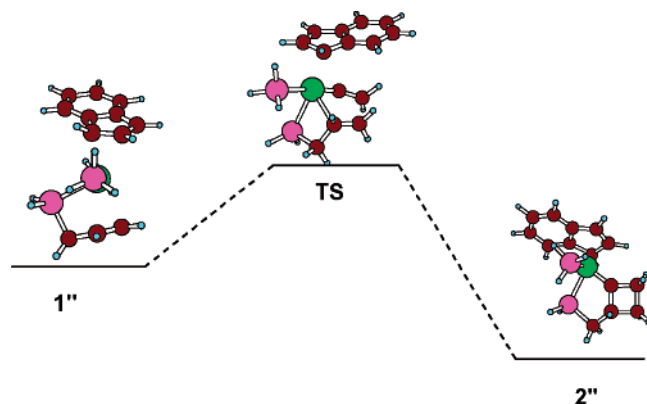
The geometry of the transition structure for the concerted mechanism (TS) is presented in Scheme 5. A careful analysis of the interactions helps us to rationalize the experimental result that the reaction proceeds under

mild conditions, contrary to expectations for a [2 + 2] cycloaddition between two C=C bonds.

Indeed, the most striking outcome of our studies is the observation that both NBO²⁴ and Bader's²⁵ topological analyses detected the presence of a bonding interaction Ru-C4 ($\text{Ru}-\text{C4} = 2.275 \text{ \AA}$) in TS. According to NBO, the corresponding bonding orbital is described as a roughly half and half mixture of a Ruthenium sd^3 hybrid with a carbon p orbital. Bader's analysis locates bond critical points between Ru and C4 [$\rho(r_c) = 0.0796 \text{ au}$, $\nabla^2\rho(r_c) = 0.0995 \text{ au}$, $H(r_c) = -0.0269 \text{ au}$] and between C2 and C3 [$\rho(r_c) = 0.0463 \text{ au}$, $\nabla^2\rho(r_c) = 0.0619 \text{ au}$, $H(r_c) = -0.0048 \text{ au}$]. Therefore, the expected high barrier associated with the [2 + 2] transition structure TS is partly mitigated by the stabilization involved in the

(28) (a) Baker, R. T.; Tulip, T. H. *Organometallics* **1986**, *5*, 839. (b) Cadierno, V.; Diez, J.; Gamasa, M. P.; Gimeno, J.; Lastra, E. *Coord. Chem. Rev.* **1999**, *193-195*, 147. (c) Alvarez, P.; Gimeno, J.; Lastra, E.; Garcia-Granda, S.; Van der Maelen, J. F.; Bassetti, M. *Organometallics* **2001**, *20*, 3762. (d) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J.; Garcia-Granda, S.; Pérez-Carreño, E. *Organometallics* **1996**, *15*, 2137. (e) Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Borge, J.; Garcia-Granda, S. *Organometallics* **1997**, *16*, 3178.

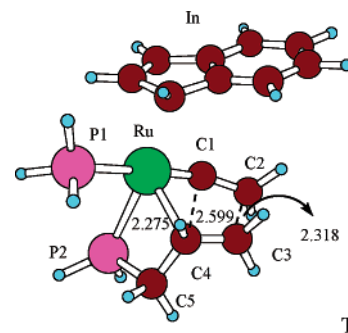
SCHEME 4. Energy Profile for the Single-Step [2 + 2] Intramolecular Cycloaddition Reaction in $[\text{Ru}(\eta^5, \eta^3\text{-C}_9\text{H}_7)(=\text{C}=\text{CH}_2)\{\kappa^1\text{-}(\text{P})\text{-PH}_2(\text{C}_3\text{H}_5)\}(\text{PH}_3)]^+$ ($1''$)



formation of the Ru–C4 bond. It is interesting to mention at this point that the presence of bonding interactions has been shown to play a relevant role in the stabilization of transition structures in the case of [4 + 2] cycloadditions.²⁹ The C2–C3 bond is partly formed at this stage (C2–C3 = 2.318 Å), while the formation of the C1–C4 bond is still incipient (C1–C4 = 2.599 Å). **TS** evolves toward the four-membered cyclobutylidene final product **2''** via an energetically favorable asynchronous process involving the simultaneous rupture of the Ru–C4 bond

(29) (a) Suárez, D.; Sordo, T. L.; Sordo, J. A. *J. Am. Chem. Soc.* **1994**, *116*, 763. (b) Suárez, D.; González, J.; Sordo, T. L.; Sordo, J. A. *J. Org. Chem.* **1994**, *59*, 8059.

SCHEME 5. Transition Structure (TS) for the Single-step [2 + 2] Intramolecular Cycloaddition Reaction in $[\text{Ru}(\eta^5, \eta^3\text{-C}_9\text{H}_7)(=\text{C}=\text{CH}_2)\{\kappa^1\text{-}(\text{P})\text{-PH}_2(\text{C}_3\text{H}_5)\}(\text{PH}_3)]^+$ ($1''$)



and the complete formation of the C2–C3 and C1–C4 bonds.

Conclusion

The theoretical analysis presented above allows for the rationalization of the recently reported unusual formation under mild conditions of a cyclobutylidene ring from a diastereoselective [2 + 2] intramolecular cycloaddition of two C=C systems. The proposed mechanism represents an alternative to the classical Woodward–Hoffmann's supra-antara approach.

Supporting Information Available: Absolute electronic energies, enthalpies, entropies, and Gibbs free energies as computed with different methods and basis sets, geometrical parameters, and Cartesian coordinates for the different structures located on the PES. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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