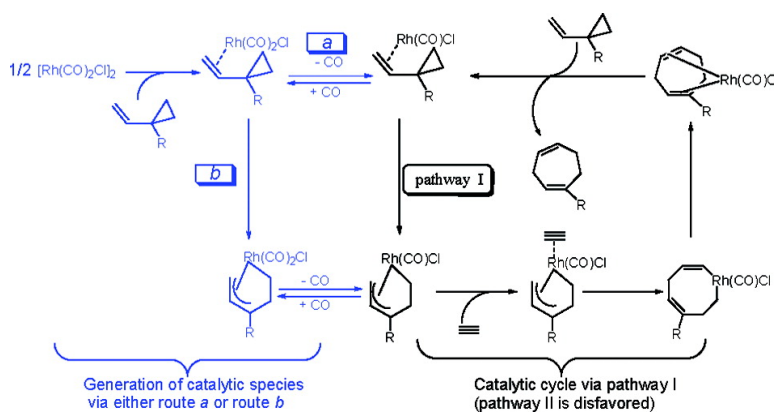


On the Mechanism of $[\text{Rh}(\text{CO})\text{Cl}]$ -Catalyzed Intermolecular (5 + 2) Reactions between Vinylcyclopropanes and Alkynes

Zhi-Xiang Yu, Paul A. Wender, and K. N. Houk

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On the Mechanism of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ -Catalyzed Intermolecular (5 + 2) Reactions between Vinylcyclopropanes and Alkynes

Zhi-Xiang Yu,[†] Paul A. Wender,^{*,‡} and K. N. Houk^{*,†}

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569, and
Department of Chemistry, Stanford University, Stanford, California 94305

Received March 4, 2004; E-mail: houk@chem.ucla.edu; wenderp@stanford.edu

Rh(I)-catalyzed (5 + 2) reactions between vinylcyclopropanes (VCPs) and 2- π components such as alkynes, alkenes, and allenes provide a very efficient and straightforward method to construct seven-membered rings.^{1,2} Three Rh(I) complexes, the Wilkinson catalyst $\text{RhCl}(\text{PPh}_3)_3$, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, and $[(\text{arene})\text{Rh}(\text{COD})]\text{SbF}_6$ complexes, have been shown to catalyze these transformations.¹ The dimeric rhodium complex catalyzes not only the intramolecular, but also the intermolecular (5 + 2) reactions between VCPs and alkynes. This dimer has also been used to catalyze (6 + 2), (5 + 2 + 1), and hetero-(5 + 2) reactions.³ Mechanisms for these reactions have been proposed but not investigated theoretically or experimentally. We have applied density functional theory (DFT)⁴ to explore the potential energy surfaces for these catalyzed cycloadditions, and report here the energy surface for the intermolecular (5+2) reactions between VCPs and alkynes.

Two mechanisms (see Figures 1 and 4) have been considered in previous publications.¹ Pathway I is found to be favored by DFT calculations for the intermolecular (5+2) reactions, and this mechanism is summarized in Figure 1. Initially, the rhodium dimer dissociates⁵ and coordinates to the VCP, leading to the formation of a VCP– $\text{Rh}(\text{CO})_2\text{Cl}$ complex. This complex can enter the catalytic cycle via either route *a* or *b* (the blue part of Figure 1). This communication describes the catalytic cycle (represented in black in Figure 1). Figure 2 shows the computed energies for the catalytic cycle via pathway I, and the corresponding structures of the stationary points involved are given in Figure 3.

Complex **1** formed by VCP and $\text{Rh}(\text{CO})\text{Cl}$ is a 16-electron (16e) complex and adopts a square-planar geometry, where the cyclopropyl group acts as the fourth ligand binding to the Rh center. The computed bond distance and bond order of the C₅–Rh bond in **1** are 2.68 Å and 0.07, respectively.⁶ Cleavage of the cyclopropyl bond in **1** via **TS2** results in the formation of an η^3 -complex **3d** which adopts a trigonal bipyramidal conformation with a CO ligand at the axial position; **3d** can then relax to the more stable square-pyramidal conformers of **3a** and **3b**, where CO and Cl are in the equatorial plane. **3a** and **3b** are expected to be in equilibrium in the reaction system since **3a** and **3b** can convert back to **3d**. Transforming **1** to **3a–b** requires activation free energies of 13.6 and 15.2 kcal/mol, respectively. Coordinating solvents stabilize **1** and other intermediates but not the transition states (see Figure S4 of the Supporting Information).

An alkyne and **3a–d** can form several 18e complexes.⁶ The most efficient route for alkyne insertion to generate 16e **6** starts from complex **4c**, which is generated through coordination of the alkyne to **3b** when the Cl ligand in **3b** moves to its axial position. An intrinsic reaction coordinate (IRC) calculation shows that the most energetically favored alkyne insertion transition structure **TS5** is connected to **4c** and **6**. The alkyne insertion, transforming **3a** and

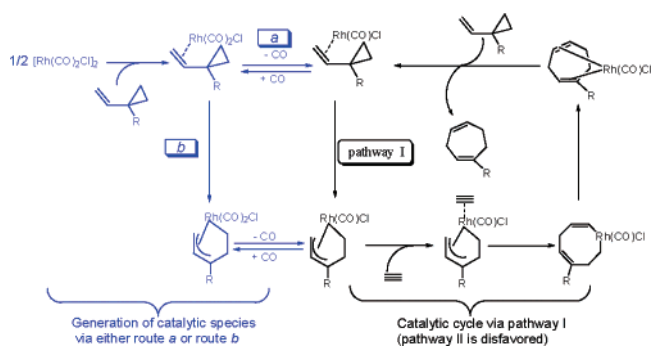


Figure 1. The mechanism of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ catalyzed intermolecular (5 + 2) reactions between VCPs and alkynes.

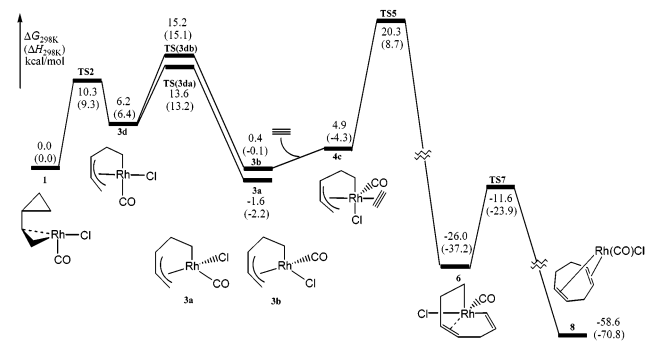


Figure 2. The energy surface of the catalytic cycle of (5 + 2) reaction.⁴

alkyne to **6**, is the most difficult step of the catalytic cycle and requires an activation free energy of 21.9 kcal/mol ($\Delta\Delta H_{298\text{K}}^\ddagger = 10.9$ kcal/mol). The alkyne insertion step is very exothermic.

The final step of the catalytic cycle is a reductive elimination process, where Rh(III) in **6** is reduced to Rh(I) in **8** via the transition structure **TS7**. Comparison of the bond distances of Rh–C₅ and Rh–C₆ in **6** and **TS7** shows that, in the transition structure, the former bond is partially broken and is elongated (2.09 vs 2.26 Å), whereas the latter bond is almost intact (2.02 vs 2.08 Å). This phenomenon suggests that **TS7** resembles a carbon-migration transition structure; therefore this step is better described as a migratory reductive elimination (MRE) step. Similar MRE processes have been observed in other $\text{C}(\text{sp}^3)$ –metal– $\text{C}(\text{sp}^2$ or $\text{sp})$ complexes.⁷ If the sp^2 hybridized C₆ in **6** is replaced by an sp^3 hybridized C, the reductive elimination process becomes more difficult. The rhodium dimer has not been shown to catalyze the (5 + 2) reactions between VCPs and alkenes.^{1d} The present MRE step is very facile with an activation free energy of only 14.4 kcal/mol.

Overall, the catalytic cycle via pathway I (Figure 2) has a reasonable activation free energy and is highly exergonic (58.6 kcal/mol).⁸

[†] University of California.
[‡] Stanford University.

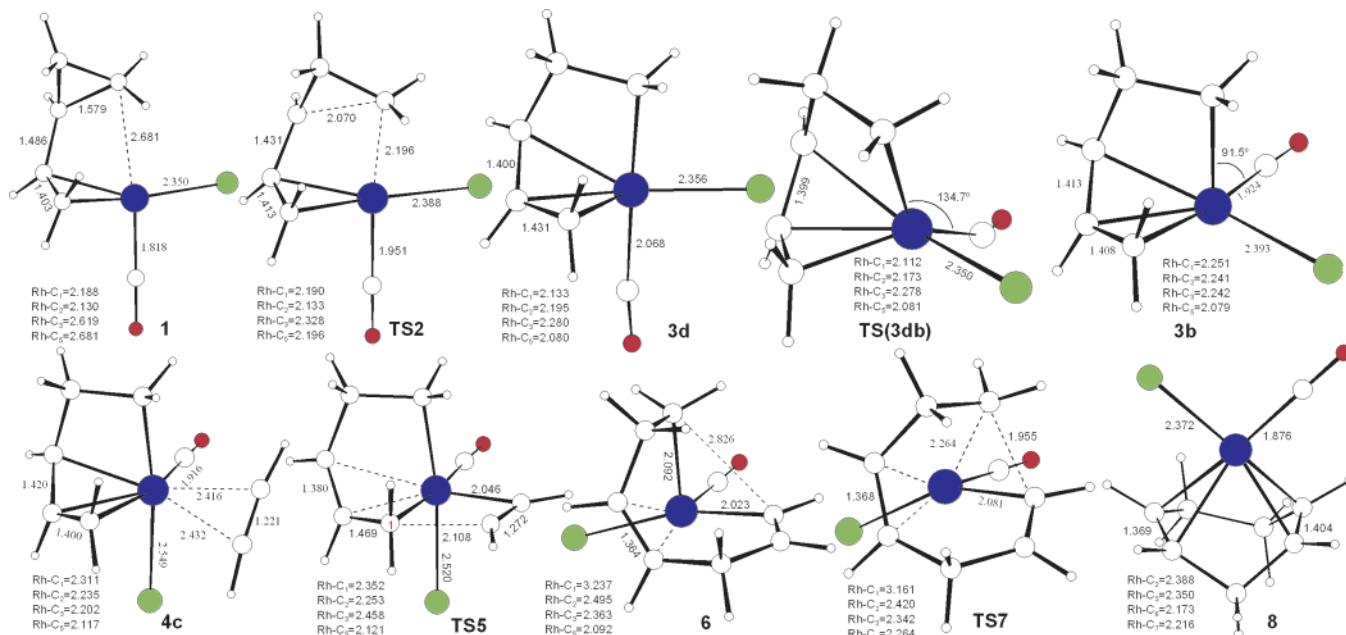


Figure 3. DFT computed structures of the stationary points in Figure 2 (Distances in Å).

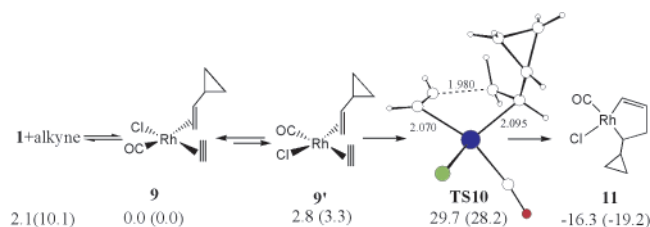


Figure 4. Alternative mechanism (relative energies in kcal/mol and distances in Å).⁴

Figure 4 shows an alternative pathway (pathway II) which has been postulated for the catalytic cycle of the (5 + 2) processes. This pathway starts with oxidative coupling converting **9** to **11**, which can then be transformed to **8** via cyclopropyl cleavage and MRE steps. The oxidative coupling step of this pathway requires an activation free energy that is 7.8 kcal/mol higher than that in pathway I. The higher activation barrier for the oxidative coupling is attributed to the square-planar conformation of **9**, which has the alkyne and alkene fragments perpendicular to the square plane to maximize the back-donation interactions from d orbitals of the d⁸ Rh(I) to π* orbitals of the alkene and alkyne moieties. However, to form **11**, the alkyne and alkene fragments must twist from the parallel conformation to a planar conformation, and this geometrical requirement costs additional energy for the present case compared to the facile oxidative coupling processes of Ti, Zr, and Ta systems, where the metals and the coordinating alkenes are in the same plane.⁹

While Rh(CO)₂⁺ is predicted to be an excellent catalyst, the energy of heterolysis of Rh(CO)₂Cl prevents its formation from the neutral Rh dimer. Instead, dissociation of CO gives an active catalyst, Rh(CO)Cl. The active catalyst Rh(CO)Cl catalyzes the intermolecular (5 + 2) reactions between VCPs and alkynes through catalytic cycle I, involving the sequential reactions of cyclopropyl cleavage of vinylcyclopropane, alkyne insertion (rate-determining step), and a migratory reductive elimination.

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Supporting Information Available: Computational details and references, including structures and energies of all stationary points. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (5) See, for example: Wilson, M. R.; Prock, A.; Giering, W. P. *Organometallics* **2002**, *21*, 2758.
- (6) For the relative energies of other conformers of the stationary points shown in Figure 2, see Figure S1 of the Supporting Information.
- (7) See: Ozawa, F.; Mori, T. *Organometallics* **2003**, *22*, 3593 and references therein.
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