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# Full Quantum Mechanical Investigation of the Unimolecular versus Bimolecular Acetylene to Vinylidene Rearrangement in the Prototype *trans*-Cl-Rh(P*i*-Pr$_3$)$_2$ Complex

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We report a full quantum mechanical investigation, based on DFT calculations, on the unimolecular and bimolecular alkyne−vinylidene rearrangements in the prototype [Cl-Rh(P*i*-Pr$_3$)$_2$(HC≡CH)] complex, to solve the discrepancy between theory and recent experimental data and to provide a definitive answer concerning the largely debated molecularity issue of the 1,3-shift in d$^8$ metal complexes. We calculate the intramolecular pathway to be kinetically favored over the intermolecular one by 15.0 kcal/mol, in agreement with recent crossover experiments. Comparison of our DFT calculations performed on the real systems with reduced models shows that a full quantum mechanical description of the investigated systems is mandatory for a correct description of their reactivity, owing to the relevant role played by the electron-donating phosphine ligands.

## Introduction

The acetylene−vinylidene rearrangement in the coordination sphere of a transition metal has attracted much interest both from experimental and theoretical points of view,[1−12] owing to the importance of this class of reactions in homogeneous catalysis.[1b] Two different mechanisms have been proposed for the metal-assisted isomerization of 1-alkynes to vinylidenes,[1] whose fundamental steps involve either a 1,2- or a 1,3-hydrogen shift (paths I and II in Scheme 1, respectively). Path I takes place from the alkyne complex **1** via a mechanism analogous to that occurring in the free acetylene−vinylidene tautomerization or occurs through the intermediacy of an $\eta^2$-CH-bound alkyne intermediate.[5,6] Antonova et al.[2] proposed an alternative mechanism in which an oxidative addition of the 1-alkyne to the metal center gives a hydrido-alkynyl complex, **2**, which then isomerizes to the vinylidene product **3** by a 1,3 hydrogen shift from the metal to C$_\beta$ (path II). Either unimolecular (IIA) or bimolecular (IIB) 1,3-shifts can take place in principle, the latter possibly involving the coupling of two hydrido-alkynyl moieties.[1,3,10] Discrimination between pathways I and II is strictly related to the stability of the hydrido-alkynyl intermediate, which in turn depends on the electron count or electron richness of the metal center.[4] Indeed, while for the alkyne−vinylidene isomerizations on d$^6$ metal fragments a straightforward 1,2-shift pathway has been experimentally and theoretically proved,[5,6] for d$^8$ and highly electron-rich d$^6$ systems the same process occurs via hydrido-alkynyl intermediates, which have also been intercepted and in some cases structurally characterized.[7−10]

The 1,3-shift step from the hydrido-alkynyl is more elusive and is still a matter of debate.[1a,7−11] Bianchini et al. have shown that the isomerization of 1-alkynes on [P(CH$_2$CH$_2$PPh$_2$)$_3$Co]$^+$ complexes occurs through the intermediacy of a hydrido-alkynyl species, the subsequent isomerization to the vinylidene product being a unimolecular process, as supported by its occurrence even in the solid state.[8] Werner and co-workers showed that the rearrangement of RhCl(P*i*-Pr$_3$)$_2$(HC≡CR) alkyne complexes to the vinylidene proceeds via the intermediacy of a hydrido-alkynyl complex.[7] Although a unimolecular mechanism has been initially proposed on the basis of kinetic data, including the evidence that the reaction occurs is some cases in the solid state,[7b] an unusual bimolecular mechanism (IIB) has been

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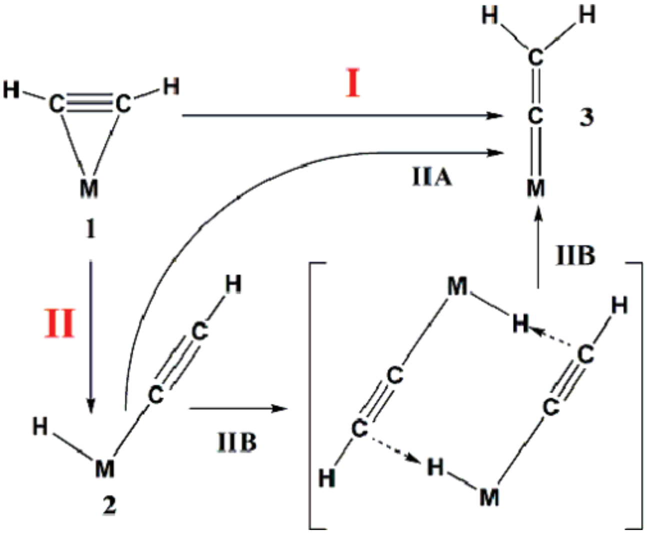
**Scheme 1. Reactivity of Acetylene−Vinylidene Isomerizations**



suggested for the alkyne−vinylidene isomerization on this RhCl(P*i*-Pr$_3$)$_2$ fragment and supported by a theoretical study[10] and some circumstatial evidence.[3] In particular a pioneering computational study by Wakatsuki et al.,[10] based on integrated quantum mechanics/molecular mechanics (QM/MM) calculations on the [Cl-Rh(P*i*-Pr$_3$)$_2$(HC≡CH)] complex, revealed an energetically accessible bimolecular pathway, involving coupling of two hydrido-alkynyl complexes, which was found to be favored over the unimolecular 1,3-shift. Recent double-crossover experiments performed on the same complex, however, have been reported that are inconsistent with a bimolecular pathway.[11]

To solve the discrepancy between theory and experiment and to provide a definitive answer concerning the largely debated molecularity issue of the 1,3-shift in d$^8$ metal complexes, in this article we report a full quantum mechanical DFT investigation on both the unimolecular (IIA) and bimolecular (IIB) alkyne−vinylidene rearrangements in the [Cl-Rh(P*i*-Pr$_3$)$_2$(HC≡CH)] complex.

## Computational Details

The DFT calculations reported in this paper have been performed using the Gaussian 98 program package.[13] To check the effect of the exchange−correlation functional, we employed both the B3LYP[14] and B97-1[15] functionals. The LANL2DZ basis set along with the corresponding pseudopotential[16] was used for the Rh atom, while a 6-31G* basis set was employed for the remaining atoms;[17] we will hereafter label this basis set as BS1. Geometry optimizations followed by frequency calculations have been performed using BS1. Single-point calculations with the larger LANL2DZ/6-31+G** basis set (BS2) have then been carried out, adding BS1 thermal corrections to obtain the free energy data labeled Δ*G*(BS2), which we discuss here. In all cases small differences, within ca. 3 kcal/mol, were found between BS1 and BS2 energies; see Table 1. No simplification in the molecular structures or symmetry constraints have been employed.

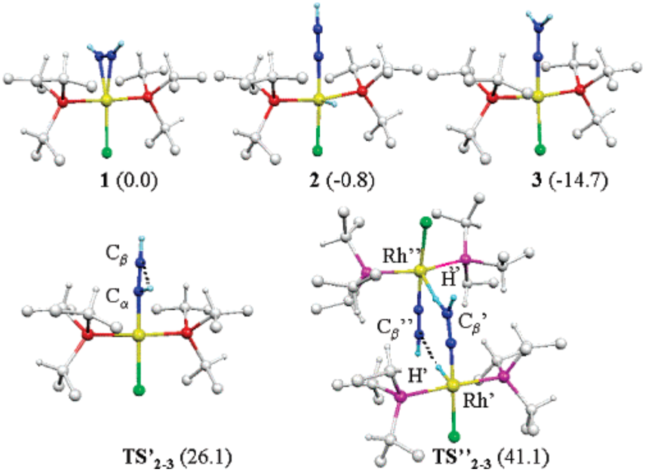


**Figure 1.** Optimized geometrical structures and relative energies of species **1**−**3** and of the transitions states **TS′$_{2-3}$** and **TS″$_{2-3}$**. The H atoms of the Me groups of the *i*-Pr ligands are omitted for clarity.

**Table 1. Calculated Energetics Using Different Basis Sets and Functionals**

| | **1** | **TS$_1$−2** | **2** | **TS′$_2$−3** | **TS″$_2$−3** | **3** |
|---|---|---|---|---|---|---|
| | | | B3LYP | | | |
| Δ*E* (BS1) | 0.0 | 12.6 | 1.5 | 32.4 | 29.6 | −12.8 |
| Δ*G* (BS1) | 0.0 | 10.1 | 1.4 | 28.7 | 42.7 | −14.2 |
| Δ*E* (BS2) | 0.0 | 9.3 | −0.7 | 29.8 | 28.0 | −13.3 |
| Δ*G* (BS2) | 0.0 | 6.8 | −0.8 | 26.1 | 41.1 | −14.7 |
| | | | B97-1 | | | |
| Δ*E* (BS1) | 0.0 | | 1.7 | 33.3 | 24.1 | |
| Δ*G* (BS1) | 0.0 | | 2.6 | 30.0 | 40.6 | |
| Δ*E* (BS2) | 0.0 | | −0.6 | 30.8 | 24.3 | |
| Δ*G* (BS2) | 0.0 | | −0.7 | 27.4 | 40.9 | |

## Results and Discussion

We calculate the reaction free energies of both pathways IIA and IIB considering the experimentally characterized systems, which for path IIB amounts to taking into account 136 atoms. In agreement with previous studies on the acetylene−vinylidene isomerization on d$^8$ metal fragments,[10] we found only three minima on the reaction potential energy surface, i.e., the acetylene, **1**, the hydrido-alkynyl, **2**, and the vinylidene, **3**, complexes, their optimized structures being reported in Figure 1. The $\eta^2$-C−H-coordinated acetylene, which was found as a minimum in previous studies performed on d$^6$ metal complexes,[4,6] turned out to be a transition state in the present d$^8$ case.[10]

Considering Δ*G*(BS2) data, the vinylidene product **3** is calculated to be 14.7 kcal/mol below the starting acetylene species **1**, thus representing the reaction global energy minimum, with the hydrido-alkynyl intermediate **2** almost isoenergetic with

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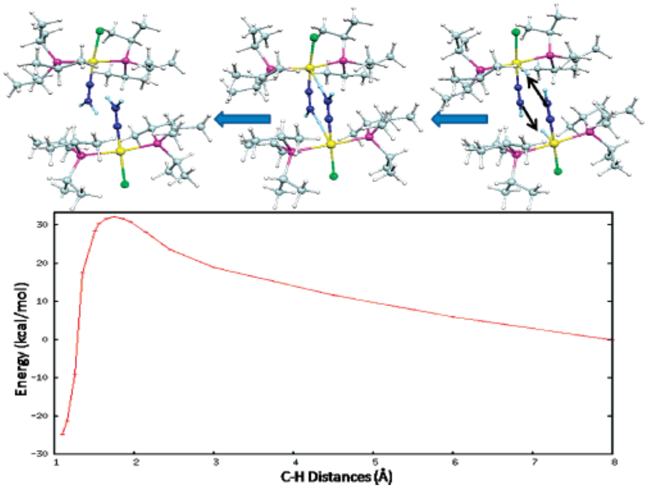

**Figure 2.** Potential energy surface (kcal/mol) along the linear transit scan connecting two isolated hydrido-alkynyl units to the vinylidene product, performed at the B3LYP/BS1 level. The *x*-axis corresponds to a concerted shortening of the two intermolecular C–H distances (Å). The zero of the energy has been set to the sum of the energies of two noninteracting hydrido-alkynyl species, set arbitrarily at a C–H distance of 8 Å. The calculated points have been interpolated by a cubic spline.

**1**, lying only 0.8 kcal/mol below **1**; see Figure 1. The relative stability of the three minima is drastically different from that found in ref 10, where the vinylidene and hydrido-alkynyl species were reported to lie, respectively, 7.8 below and 9.4 kcal/mol above the alkyne for the [Cl-Rh(PH$_3$)$_2$] model by means of MP2 calculations. This discrepancy is not related to the different level of theory used in this work and in ref 10, as confirmed by B3LYP/BS1 and MP2/BS1 calculations performed on the same [Cl-Rh(PH$_3$)$_2$] fragment, which consistently indicated the vinylidene and hydrido-alkynyl, respectively, 6.6–5.3 and 15.1–15.7 kcal/mol (DFT-MP2, respectively) below and above the alkyne species. Our results point, on the other hand, to a remarkable stabilizing effect of the electron-donating P*i*-Pr$_3$ phosphine ligands on both the vinylidene and hydrido-alkynyl species, which cannot be captured by use of simplified PH$_3$ ligands or by QM/MM calculations including the PH$_3$ ligands in the QM subsystem. This stabilizing effect of electron-donating ligands on the energy of the hydrido-alkynyl species in d$^6$ metal fragments was identified by us in a previous study.[4] We notice that destabilization of the alkyne relative to the hydrido-alkynyl by the steric hindrance exerted by the bulky P*i*-Pr$_3$ ligands might also contribute to a lesser extent to reduce the energy gap between **1** and **2**.[9b]

We then searched for the transition states connecting **1** to **2** ($\mathbf{TS_{1-2}}$) and **2** to **3** ($\mathbf{TS'_{2-3}}$) along the unimolecular pathway IIA, finding the two TS structures to lie 6.8 and 26.1 kcal/mol above **1**, respectively. The geometries of $\mathbf{TS_{1-2}}$ and $\mathbf{TS'_{2-3}}$ are similar to those found in ref 10, with $\mathbf{TS_{1-2}}$ showing an $\eta^2$-CH interaction with the metal and $\mathbf{TS'_{2-3}}$ showing the migrating hydrogen exploiting the bonding interaction to $C_\alpha$; see Figure 1.

The bimolecular pathway IIB was investigated by performing a linear transit scan of the potential energy surface for the system constituted by two interacting hydrido-alkynyl moieties, constraining the two intermolecular $C_\beta$–H distances to vary in a concerted fashion in the range 4.5–1.1 Å, the latter value corresponding to the C–H distance in the vinylidene product **3**. The resulting potential energy curve, reported in Figure 2 along with selected optimized geometrical structures, shows a repulsive interaction at short range and no evidence of formation of an adduct between the two interacting moieties. The maximum energy structure encountered along the linear transit scan, corresponding to the approximate transition state for a synchronous reaction pathway, is found for C–H values of 1.75 Å and calculated 31.6 kcal/mol higher than twice the energy of the hydrido-alkynyl **2**, i.e., 34.7 kcal/mol above twice the energy of the starting alkyne complex **1** at the B3LYP/BS1 level.

Starting from the linear transit maximum energy structure, we have been able to optimize the transition state for the bimolecular coupling of the two hydrido-alkynyl moieties, leading to two uncoupled vinylidene products, $\mathbf{TS''_{2-3}}$ in Figure 1. Surprisingly, $\mathbf{TS''_{2-3}}$ corresponds to an asynchronous reaction mode, with an almost formed vinylidene $C'_\beta$–H′ bond (1.22 Å), an elongated Rh′–H′ bond (1.90 Å), a noninteracting $C'_\beta$–H″ distance (2.36 Å), and a Rh″–H″ distance of 1.56 Å, close to its value in the equilibrium structure of **2** (1.51 Å). Frequency eigenvector analysis performed on $\mathbf{TS''_{2-3}}$ confirmed the asynchronous reaction mode of the unique negative frequency; see Supporting Information. $\mathbf{TS''_{2-3}}$ is calculated 2.3 kcal/mol below the energy of the approximate synchronous transition state, considering B3LYP/BS1 data. Despite several attempts, no real transition state corresponding to a synchronous reaction pathway could be located. Considering $\Delta G$(BS2) data, $\mathbf{TS''_{2-3}}$ is calculated 41.1 kcal/mol above twice the energy of **1**, therefore 15.0 kcal/mol higher than the transition state for the unimolecular pathway IIA, $\mathbf{TS'_{2-3}}$, in agreement with recent experimental evidence.[11] It is interesting to note that, without inclusion of thermal corrections, $\mathbf{TS'_{2-3}}$ and $\mathbf{TS''_{2-3}}$ are almost isoenergetic, 29.8 versus 28.0 kcal/mol at the B3LYP/BS2 level, the discrimination between unimolecular and bimolecular pathways being essentially determined by the unfavorable entropy loss associated with the bimolecular pathway. We notice that our calculated (free) energy barrier for the bimolecular pathway IIB might be slightly affected by basis set superposition error, which should lead, however, to an underestimation of the energy barrier. Finally, to check that our results are independent of the employed exchange–correlation functional, we performed additional calculations using the B97-1 functional,[16] which was shown by Zhao and Truhlar to provide energetics of comparable quality to MP2 results for weakly interacting systems.[18] The activation free energies for pathways IIA and IIB calculated with B97-1 are 27.4 and 40.9 kcal/mol, respectively (see Table 1), only marginally different from B3LYP results, thus confirming the unimolecular pathway.

## Conclusions

To solve the discrepancy between theory and experiment and to provide a definitive answer concerning the largely debated molecularity issue of the 1,3-shift in d$^8$ metal complexes, we have performed a full quantum mechanical DFT investigation on both the unimolecular (IIA) and bimolecular (IIB) alkyne–vinylidene rearrangements in the [Cl-Rh(P*i*-Pr$_3$)$_2$(HC≡CH)] complex. Reaction free energies of both pathways IIA and IIB have been calculated considering the experimentally characterized systems without any symmetry constraints, which for path IIB amounts to taking into account 136 atoms.

In agreement with previous studies on the acetylene–vinylidene isomerization on d$^8$ metal fragments, we found only three minima on the reaction potential energy surface, corresponding to the acetylene, the hydrido-alkynyl, and the vinylidene complexes. Conversely to what was previously found for the simplified [Cl-Rh(PH$_3$)$_2$] model complex, for which the

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hydrido-alkynyl was found to lie 9.4 kcal/mol above the alkyne complex, we find the hydrido-alkynyl and the alkyne to be almost isoenergetic. This discrepancy is not related to the different level of theory used (DFT or MP2), as confirmed by additional MP2 calculations. Our results point, on the other hand, to a remarkable stabilizing effect of the electron-donating P*i*-Pr$_3$ phosphine ligands on both the vinylidene and hydrido-alkynyl species, which we identified also in d$^6$ metal fragments and appears therefore to be of general significance.

Considering our calculated free energy data, the transition state for the bimolecular pathway IIB is calculated to be 41.1 kcal/mol above twice the energy of the alkyne complex, therefore, 15.0 kcal/mol higher than the transition state for the unimolecular pathway IIA. It is interesting to note that, without inclusion of thermal corrections, the two transition states are almost isoenergetic, the discrimination between unimolecular and bimolecular pathways being essentially determined by the unfavorable entropy loss associated with the bimolecular pathway.

In conclusion we have demonstrated that a full quantum mechanical description of the investigated systems is mandatory for a correct description of their reactivity, owing to the relevant role played by the phosphine ligand substituents. Our results are fully in agreement with recent crossover experiments and strongly indicate that a unimolecular pathway is favored for the alkyne−vinylidene isomerization in this prototype rhodium d$^8$ system, thus solving the long-standing issue of the molecularity of the 1,3-shift in this important class of organometallic reactions.

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**Supporting Information Available:** Optimized molecular structures and a movie showing the reaction mode in $\mathbf{TS''_{2-3}}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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