An ab Initio MO Study on the Transformation of Acetylene to Vinylidene in the Coordination Sphere of Rhodium(I). The Intra- and Intermolecular Proton Transfer Mechanism

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Abstract: The transformation of a rhodium(I) η^2-alkyne model complex $RhCl(PH_3)_2(HC\equiv CH)$ (**A**) into the vinylidene form $RhCl(PH_3)_2(C=CH_2)$ (**E**) has been examined by ab initio theoretical calculations using MP2 level geometry optimizations and localized molecular orbital (LMO) analysis. The vinylidene form **E** has been found to be 7.8 kcal/mol more stable than **A**. The previously found intraligand 1,2-hydrogen shift mechanism in the Ru(II)-coordinated alkyne−vinylidene isomerization is not relevant for the present Rh system. The reaction proceeds via the oxidative addition product $RhCl(PH_3)_2(H)(C\equiv CH)$ (**C**), followed by a bimolecular hydrogen shift from the metal to the terminal carbon of a second molecule rather than by intramolecular 1,3-hydrogen transfer. The LMO analysis of the transition state of the unimolecular 1,3-hydrogen shift indicates that the hydrogen moves as a proton while it interacts with the three centers simultaneously, i.e., Rh, Cα, and Cβ in the transition state. The hydrogen was analyzed to migrate also as a proton in the bimolecular mechanism. The barrier of the bimolecular pathway has been further calculated for a more realistic system with substituted phosphines, $RhCl(P^iPr_3)_2(H)(C\equiv CH)$, using the integrated MO + MM (MP2:MM3) method. It was concluded that in the real system with substituents on both the phosphines and the alkyne, $RhCl(P^iPr_3)_2(HC\equiv CR)$, the bimolecular hydrogen shift is still favored by ca. 15 kcal/mol in free energy of activation; unimolecular 1,3-H migration should become important in special cases like solid state isomerizations.

Introduction

The tautomerization between free acetylene ($HC\equiv CH$) and vinylidene ($:C=CH_2$) has been the subject of a number of theoretical[1] and physicochemical studies.[2,3] While formation of vinylidene from free acetylene is strongly endothermic, by 44−47 kcal/mol, and is observed only under special conditions,[2,3] the same isomerization occurring in the coordination sphere of transition metals has numerous examples, apparently vinylidene being stabilized in many transition-metal complexes.[4] This phenomenon may be relevant to a number of transition metal catalyzed reactions of alkynes, and indeed some of them have been established to involve alkyne and vinylidene isomerization in their catalytic cycles.[5,6] There are, however, surpris-

ingly few reports on the theoretical analysis of how and why an η^2-coordinated acetylene undergoes isomerization for the vinylidene very easily in transition metal complexes.

Ten years ago, the extended Hückel calculations by Silvestre and Hoffmann on $Mn(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_2)$ suggested that a direct 1,2-hydrogen shift from the α- to β-carbon, a route similar to that calculated for the tautomerization of free acetylene, might be plausible also in the complex.[7] In relevance to the intermediate in a unique catalytic dimerization of 1-alkyne to 1,4-disubstituted butatriene,[6] we have recently carried out detailed analysis by ab initio molecular orbital calculations on the $RuCl_2(PH_3)_2(C_2H_2)$ system.[8] It also supported the intraligand 1,2-hydrogen shift mechanism, a route similar to (i) indicated in Scheme 1. The major role of the metal in this isomerization is to stabilize the lone pair electrons at the α-carbon which develop already in the transition state.

A different mechanism, where the role of a transition metal is more pronounced, was proposed by Antonova and co-workers already 20 years ago; i.e., the tautomerization takes place via an alkynyl(hydrido)metal intermediate formed by oxidative addition of a coordinated terminal alkyne. Subsequent 1,3-shift of the hydride from the metal to β-carbon of the alkynyl might then give the vinylidene complex.[9] However, the extended

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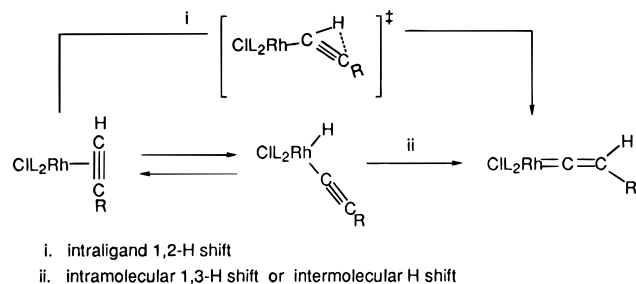
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Scheme 1

i. intraligand 1,2-H shift
ii. intramolecular 1,3-H shift or intermolecular H shift

Hückel calculations showed the 1,3-H shift was unlikely in the $Mn(\eta^5\text{-}C_5H_5)(CO)_2(C_2H_2)$ system, the barrier for this step being too high.[7]

Although the two foregoing theoretical simulations on d^6-metal complexes support the intraligand 1,2-hydrogen transfer mechanicam, enough experimental evidence has been accumulated for the intermediacy of alkynyl(hydrido) complexes in the case of the Co, Rh, and Ir family.[10−12] Werner and co-workers have demonstrated that the five-coordinated rhodium complexes of the type $RhCl(P^iPr_3)_2(H)(C\equiv CR)$ where R = ^{t}-Bu, $SiMe_3$, and $CH=CH(OMe)$,[10c−e] rearrange smoothly to the vinylidene form. In analogous iridium complexes and for R = Me, Ph, CO_2Me, and $SiMe_3$, all three isomers $IrCl(P^i\text{-}Pr_3)_2(HC\equiv CR)$, $IrCl(P^iPr_3)_2(H)(C\equiv CR)$, and $IrCl(P^iPr_3)_2(C=CHR)$ have been isolated, and the conversion of the η^2-alkyne complexes to alkynyl(hydrido) and of the alkynyl(hydrido) to vinylidene complexes has been achieved.[12] Bianchini's cationic cobalt system $[P(CH_2CH_2PPh_2)_3CoL]^+$ also illustrates a stepwise rearrangement of L, $\eta^2\text{-}CH\equiv CR \rightarrow (H)(C\equiv CR) \rightarrow C=C(H)R$, where the alkyne complexes were characterized spectroscopically while the solid state structures of alkynyl(hydrido) and vinylidene complexes have been determined.[11] On the basis of kinetic data, the isomerization of the alkynyl(hydrido)cobalt-(+) complex to the vinylidene form in solutions has been concluded to be a unimolecular process. The positive entropy of activation was consistent with a "dissociative" mechanism. In some cases, the isomerizations have been observed in the solid state, both in Biachini's Co^+ system[11] and in Werner's Rh complexes,[10f] also suggesting that the change can take place via a unimolecular pathway. Despite this evidence, there still remains a little uncertainty if the alkynyl(hydrido) complex is a true intermediate since its equilibrium with the η^2-alkyne complex has been observed in the case of Werner's Rh system;[13] i.e., the alkynyl(hydrido) complex might go back to the η^2-alkyne complex before it isomerizes via intraligand 1,2-hydrogen shift as path (i) in Scheme 1.

It seemed, therefore, interesting to carry out theoretical simulations on the isomerization reaction of one of these alkynyl(hydrido)metal complexes to examine if it was a true intermediate followed by the 1,3-H shifts as Antonova had proposed, or a side product equilibrating with the η^2-alkyne complex which slowly undergoes 1,2-H shift. In other words, it is of critical importance to check if path (ii) in Scheme 1 is a reasonable process. Given that the alkynyl(hydrido)metal species is a true intermediate, it was also of our interest to compare the unimolecular and bimolecular hydrogen shift mechanisms; aside from experimental observations to support unimolecular reactions, the possibility of harmonized mutual hydrogen exchange between the two alkynyl(hydrido)metal molecules, from the metal of one molecular to $C\beta$ of the other molecule, has been first pointed out by Werner for an Ir system.[12c]

In this paper we describe the ab initio molecular orbital analysis on a model system of Werner's reaction, rearrangement in a square planar rhodium d^8 system. This model system replaces the P^iPr_3 ligand and monosubstituted acetylene used in the real reactions by PH_3 and $HC\equiv CH$, respectively. For the simulation of the bimolecular process where steric interactions could be critical, we further performed calculations on the "real" P^iPr_3 ligand system using the integrated molecular orbital + molecular mechanics (IMOMM) method recently developed by Maseras and Morokuma[14a] and applied successfully to oxidative addition of H_2 to $Pt(PR_3)_2$ (R = H, Me, ^tBu, Ph) by Matsubara et al.[14b] The isomerization route and the transition state structures we obtained for the present Rh complex are much different from those of our previous conclusions on the Ru(II) system[8] and demonstrate the importance of the electronic configuration of the metal center.

Methods of Calculation

Simulations were performed by means of ab initio molecular orbital calculations (GAUSSIAN 92 program[15]). Throughout the calculations, geometries of the stationary points were optimized at the MP2 level (electron correlation by second-order Møller−Plesset perturbation). All the unimolecular complexes were assumed to have C_s symmetry and calculated using the 17 valence electron effective core potential of Hay and Wadt[16a] with the [3s3p2d]/[5s5p4d] basis functions for Rh, 4-31G basis set[17] for P, 3-21G set[18] for H of PH_3, 4-31G* basis set[19] for C and Cl, and TZP set[20] for H of the C_2H_2 moiety or Rh−H. Interactive states of the two Rh complex units were optimized at the MP2 levels with [2s2p2d]/[3s3p4d] basis functions and the 9-valence-electron effective core potential[16b] for the metal, and STO-3G basis sets[21] for all other atoms. The MP2 energies of thus optimized bimolecular structures were recalculated using the same effective core potential and basis sets as for the unimolecular complexes.

Transition state structures for the unimolecular and bimolecular reactions were relaxed after giving small perturbation to ensure that they are connected to corresponding reactants and products. A vibrational analysis was performed for the two important transition

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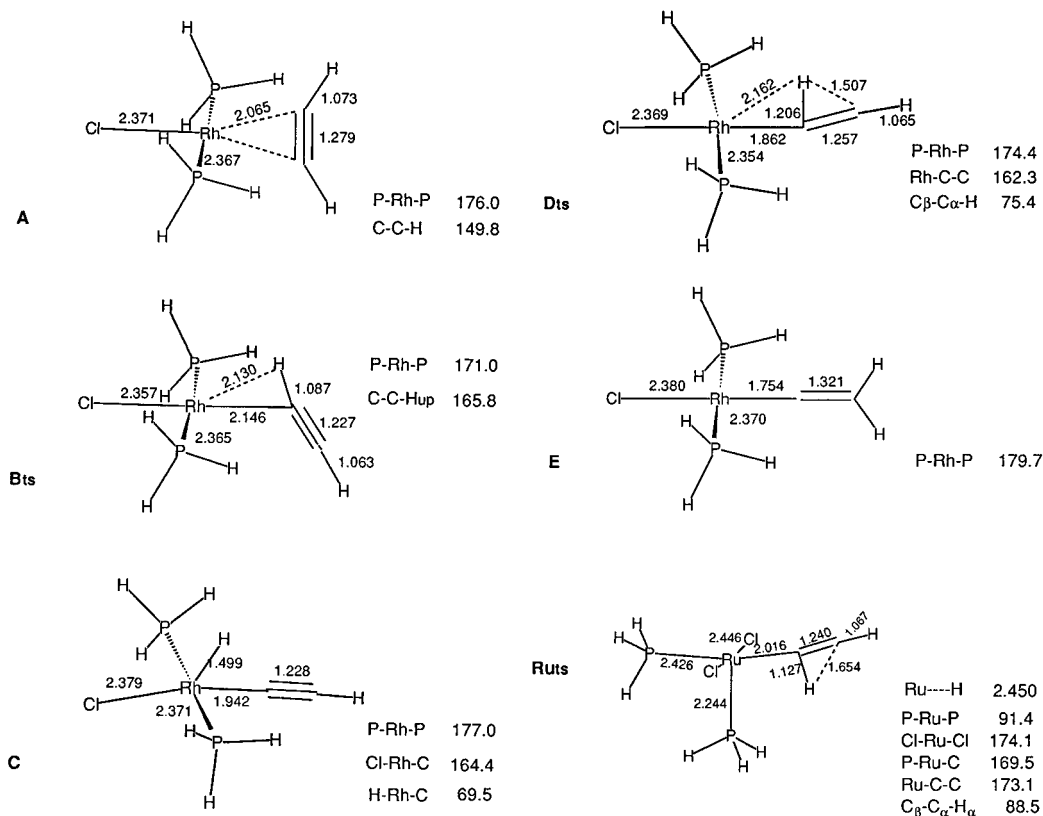
Figure 1. Optimized structures (Å and deg) for η^2-alkyne complex **A**, alkynyl(hydrido) complex **C**, vinylidene complex **E**, and transition states **B$_{ts}$** and **D$_{ts}$**. **Ru$_{ts}$** is the previously calculated transition state for the 1,2-H shift in RuCl$_2$(PH$_3$)$_2$(C$_2$H$_2$).

states, **D$_{ts}$** and **G$_{ts}$** (vide infra), to confirm that they have only one imaginary frequency.

The IMOMM[14] calculations were carried out for a pair of interacting RhCl(P^{i}Pr$_3$)$_2$(H)(CCH) complexes as well as for isolated Rh-ClP^{i}Pr$_3$)$_2$(H)(CCH) and RhCl(P^{i}Pr$_3$)$_2$(CCH$_2$) molecules. In the simulations of [RhCl(PR$_3$)$_2$(H)(CCH)]$_2$ for example, the "model system", [RhCl(P)$_2$(H)(CCH)]$_2$, was treated by the MP2 method and the ^{i}Pr groups were treated by the MM3[22] method. As shown in the following equation, the total energy of the ^{i}Pr-substituted complex is expressed as the sum of the MP2 energy for the unsubstituted complex (E_{MP2}(R=H)) and the MM3 energy for the ^{i}Pr-substituted complex, which was modified so that any MM contribution already included in the MP2 calculation has to be zeroed out to avoid double counting (E_{mMM3}(R=^{i}Pr)):[14]

$$E_{tot} = E_{MP2}(R{=}H) + E_{mMM3}(R{=}^iPr)$$

In the IMOMM method, the structures of the P^{i}Pr$_3$ complexes were optimized using the gradient of E_{tot} without symmetry restrictions, under the prescribed geometry constraint that the P−C bonds in the R = ^{i}Pr system lie on top of the corresponding P−H bonds in the R = H system with the P−C bond lengths frozen to a value of 1.843 Å. Consequently, the MP2 geometry of the model system, [RhCl(P)$_2$(H)(CCH)]$_2$, is perturbed by the steric effect due to the ^{i}Pr substituents evaluated by the MM3 method. In the IMOMM calculations, the 9-valence-electron core potential with the better basis functions shown above was used for the MP2 part and standard parameters and the van der Waals parameters for Rh by Rappé et al.[23] were used for the MM3 part. Finally, E_{MP2}(R=H) was refined using the same effective core potential and basis sets as for the unimolecular complexes.

Results and Discussion

(1) Optimized Structures of RhCl(PH$_3$)$_2$(HC≡CH) (A), RhCl(PH$_3$)$_2$(H)(C≡CH) (C), and RhCl(PH$_3$)$_2$(C=CH$_2$) (E).

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We first optimized the structures of the three stable complexes involved in the present reaction, RhCl(PH$_3$)$_2$(HC≡CH) (**A**), RhCl(PH$_3$)$_2$(H)(C≡CH) (**C**), and RhCl(PH$_3$)$_2$(C=CH$_2$) (**E**), which are shown in Figure 1. To our knowledge the only known X-ray structure of a monomeric Rh(I) η^2-alkyne complex is that of a 1,4-bis(trimethylsilyl) diyne complex RhCl(P^{i}Pr$_3$)$_2$(Me$_3$-SiC$_4$SiMe$_3$) (**a**).[24a] The calculated Rh−C (2.065 Å) and the C≡C (1.279 Å) distances in **A** are very close to those found in complex **a**, 2.03(1) and 2.16(1) Å for the Rh−C and 1.26(2) Å for the coordinating C≡C bond. The Rh−P (2.367 Å) and Rh−Cl (2.317 Å) bond lengths in **A** are also in agreement with the observed values, Rh−P (2.376(5) and 2.353(5) Å) and Rh−Cl (2.353(4) Å) in the crystal of **a**. For comparison, the Rh−P and Rh−Cl bond lengths observed experimentally in the ethylene analog RhCl(P^{i}Pr$_3$)$_2$(H$_2$C=CH$_2$) are 2.362(1) and 2.365(1) Å, respectively.[24b]

A five-coordinated (alkynyl)(hydrido)rhodium(III) compound corresponding to **C** has not been structurally characterized, but the structures of the six-coordinated complexes Rh(PMe$_3$)$_3$-(H)(C≡CPh)$_2$ (**c**) and RhCl(P^{i}Pr$_3$)$_2$(Py)(C≡CCMe=CH$_2$)$_2$ (**d**) have been determined.[25,10e] The Rh^{III}−H distances found in a dinuclear complex, Rh$_2$H$_2$(O$_2$CO)(PhC≡CPh)(P^{i}Pr$_3$)$_3$,[26] are 1.48(3) and 1.42(3) Å and thus in good agreement with the calculated value of **C** (1.499 Å). While the Rh^{III}−H bond length in **d** is only slightly longer, 1.56(4) Å, the bond length of 1.90 Å in **c** is unusually long which is probably due to the strongly electron donating PMe$_3$ group present in the trans position. The Rh−C (1.958(4) Å) and C≡C (1.206 Å) distances in complex **d** agree with those in **C**, Rh−C (1.942 Å) and C≡C (1.228 Å).

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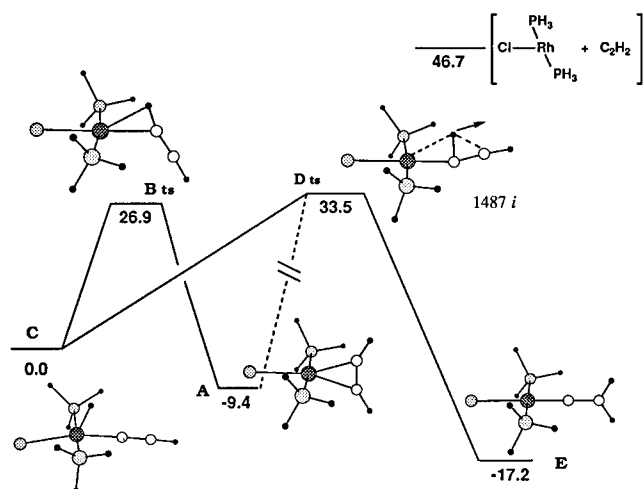
Figure 2. Energy diagram (kcal/mol) of unimolecular rearrangement: RhCl(PH$_3$)$_2$(HC≡CH) (**A**), RhCl(PH$_3$)$_2$(H)(C≡CH) (**C**), RhCl(PH$_3$)$_2$-(C=CH$_2$) (**E**), and transition states. For **D$_{ts}$**, the reaction coordinate vector is shown with the associating imaginary frequency (cm^{-1}).

The geometry around the Rh center in **C** is distorted square pyramidal: the Cl–Rh–C(alkynyl) angle is 164.4°, and the H–Rh–C(alkynyl) angle is only 69.5°. Though five-coordinate d^6 metal complexes have been calculated to adopt a square-pyramidal structure rather than a trigonal-bipyramidal one, the energy surface is knownto be flat and various intermediate forms are possible.[27]

The vinylidene complex RhCl(P^{i}Pr$_3$)$_2$(C=C(H)Me) (**e**) has also been structurally characterized.[10b] The Rh–C (1.775(6) Å), C=C (1.32(1) Å), Rh–P (2.343(2) Å), and Rh–Cl (2.366(2) Å) distances are all close to the values calculated for **E**, Rh–C (1.754 Å), C=C (1.321 Å), Rh–P (2.370 Å), and Rh–Cl (2.380 Å).

(2) Path from RhCl(PH$_3$)$_2$(HC≡CH) (A) to RhCl(PH$_3$)$_2$-(H)(C≡CH) (C), the Oxidative Addition of the Acetylenic CH unit. It is generally accepted that the initial interaction between a metal center and a terminal alkyne molecule is of the η^2-CC coordination mode. The most reasonable reaction which follows is the oxidative addition of the C–H bond to form an alkynyl(hydrido)metal species; isolation of an η^2-alkyne complex and its transformation into an alkynyl(hydrido) complex have been observed in many instances. The calculated energy difference between **A** and **C** is 9.4 kcal/mol, as shown in Figure 2, in favor of the alkyne complex. In the actual reaction, where a bulky phosphine like P^{i}Pr$_3$ and a bulky substitutent on the alkyne are employed, the η^2-alkyne complex should be less stable than the present model system because the substituent on the alkyne has obviously much more steric interaction with the phosphine in **A** than in the alkynyl complex **C**. Furthermore, the more basic nature of the central metal with P^{i}Pr$_3$ ligands, as compared with PH$_3$, should favor the alkynyl(hydrido) complex.

The transition state structure (**B$_{ts}$**) between **A** and **C** was calculated to have an η^2 type interaction of the C–H σ-bond with the metal as shown in Figure 1, with an energy of +26.9 kcal/mol relative to that of **C** (Figure 2). A similar interaction of the HC≡CH unit with a metal through its C–H σ-bond has been found in our previous calculation for RuCl$_2$(PH$_3$)$_2$(C$_2$H$_2$), as an unstable η^2-C–H intermediate.[8] The calculated geometry of **B$_{ts}$** in Figure 1, C–C 1.227 Å and C–H 1.087 Å, indicates that the alkyne unit distorts only slightly from its calculated

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free state, C–C 1.215 Å and C–H 1.061 Å, and that the bending of the C–C– H angle is also small (165.8°).

In the Ru case, the route to an alkynyl(hydrido)ruthenium complex from the η^2-C–H complex does not exist due to thermodynamic instability of the oxidative addition product which must have an octahedral Ru(IV) center.[8] This is a reason why one finds the η^2-C–H intermediate state in the Ru system albeit its shallow minimum; in marked contrast, the present η^2-C–H species (**B$_{ts}$**) is a transition state which has a steep slope down to the alkynyl(hydrido)metal complex **C**, reflecting the ease of oxidative addition reaction in d^8 metal complexes to form d^6 products.

(3) Path from RhCl(PH$_3$)$_2$(H)(C≡CH) (C) to RhCl(PH$_3$)$_2$-(C=CH$_2$) (E), the 1,3-Hydrogen Shift from the Metal to Cβ. As expected, the vinylidene complex (**E**) has been calculated to be the most stable species with its energy 17.2 kcal/mol lower than that of **C** (Figure 2).

The transition state (**D$_{ts}$**) for the transformation of **C** to **E** has been determined, the energy of which is 33.5 kcal/mol higher than that of **C**. The transition structure for the 1,3-hydrogen shift process calculated here (Figure 1) differs from the transition state for the intraligand 1,2-hydrogen shift calculated previously for RuCl$_2$(PH$_3$)$_2$(C$_2$H$_2$)[8] (**Ru$_{ts}$** in Figure 1); in **D$_{ts}$** the interaction between the metal and the C$_2$H$_2$ unit is much stronger than in **Ru$_{ts}$**. The Rh–Cα (1.862 Å) and Rh–H$_{migrating}$ (2.162 Å) distances are shorter than Ru–Cα (2.016 Å) and Ru–H$_{migrating}$ (2.450 Å) while the Cα–H$_{migrating}$ distance is longer in the 1,3-migration (1.206 Å) than in 1,2-migration (1.127 Å). Owing to the bending of the Rh–Cα–Cβ angle toward the migrating hydrogen (angle 162°), the Cβ–H$_{migrating}$ distance in the present 1,3-shift (1.507 Å) is distinctively shorter than in the 1,2-migration process (1.654 Å).

Figure 3 illustrates contour diagrams of four important occupied localized molecular orbitals (LMOs), (a)–(d), of **D$_{ts}$** in its C$_s$ plane. The metal component and the :C$_2$H$_2$ component of each LMO are shown schematically on the left and right sides, respectively, of Figure 3. The behavior of LMOs in this reaction process can be best understood if the migrating hydrogen is viewed as a proton rather than a hydride; i.e., the migrating hydrogen leaves behind two electrons used for the Rh–H bond. During the reaction, the Rh–C σ-bond turns into the lone pair on carbon, which is represented by LMO (a) at the transition state **D$_{ts}$**. In LMO (b) the migrating proton is accepting two electrons from the in-plane C=C π-bonding orbital, and these electrons are used to form the new Cβ–H σ-bond in the final vinylidene complex **E**. LMO (c) represents back-donation from the occupied d$_{z^2}$ oribtal to an empty C$_2$H$_2$ fragment orbital which is antibonding between H and Cα. On the path from the reactant complex **C** to **D$_{ts}$**, the vacant d$_{z^2}$ MO of the five-coordinate d^6 species **C** accepts the two electrons of the M–H bond to accomplish the reductive elimination process and to convert the Rh to d^8. In LMO (d) another back-donation can be seen from the metal d$_{xz}$ to the "empty pπ" of Cα in the final vinylidene complex product **E**.

The LMO analysis above clearly indicates that **D$_{ts}$** is not correlated to the η^2-alkyne complex **A**. This is confirmed by following the energy gradient from the vicinity of **D$_{ts}$**, which actually leads to the alkynyl(hydrido)metal complex **C**. Despite all our efforts, we could not find a transition state for the 1,2-hydrogen shift within the alkyne ligand, and we have to conclude that such a transition state does not exist.

(4) Bimolecular Rearrangement of [RhCl(PH$_3$)$_2$(H)-(C≡CH)]$_2$ (F) to [RhCl(PH$_3$)$_2$(C=CH$_2$)]$_2$ (H). Besides the intramolecular 1,3-hydrogen shift mechanism discussed above,
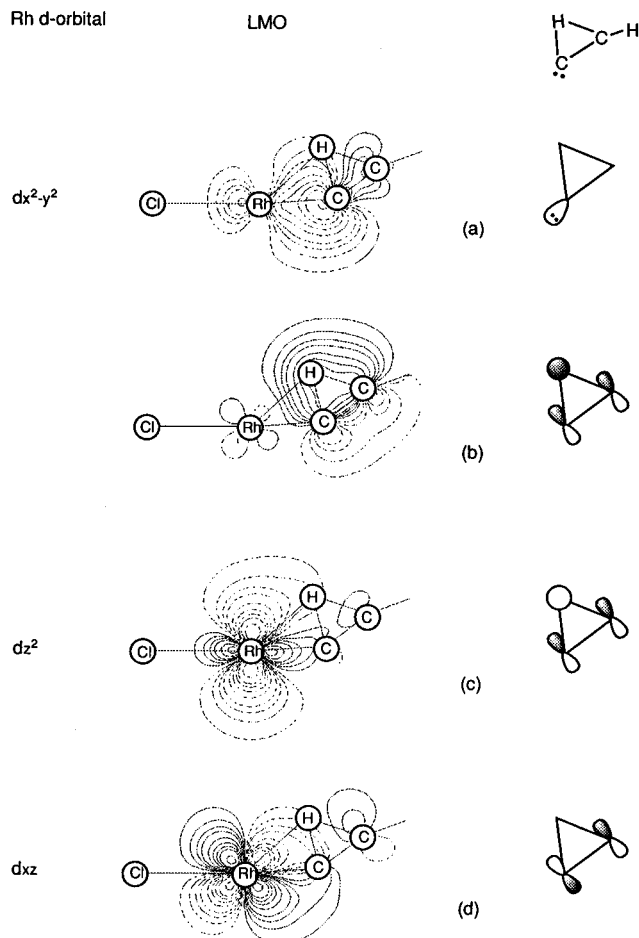
Figure 3. Important localized molecular orbitals in the plane of Cl−Rh−CH−CH (xz plane) for transition state $\mathbf{D_{ts}}$.

Figure 4. Optimized structures (Å and deg) for bimolecular units of alkynyl(hydrido) complex **F**, vinylidene complex **H**, and the transition state $\mathbf{G_{ts}}$, under the C_{2h} constraint.

we have studied the possibility for a concerted bimolecular hydrogen transfer process taking place between two alkynyl-(hydrido)rhodium units. Throughout the calculations of the present bimolecular reactions, C_{2h} symmetry was assumed for the spatial arrangement of the two metal complex units. Since we obtained C_{2h}-like structures in the IMOMM calculations without symmetry restriction, as will be shown later, this assumption is reasonable. We found the equilibrium structures for the interaction of two alkynyl(hydrido)rhodium molecules (**F**), two vinylidene complex units (**H**), and the transition state between them ($\mathbf{G_{ts}}$). Their calculated structures and the energy profile are shown in Figures 4 and 5, respectively.

Since these dimeric structures have been calculated with minimal basis sets for all non-metal atoms and, therefore, cannot be compared directly with the monomer structures, the alkynyl-(hydrido)rhodium complex **C** was recalculated using the minimal basis sets. The alkynyl(hydrido)metal moiety in **F** is virtually the same in geometry as the recalculated **C** except that the C≡C bond is slightly longer. The intermolecular distance between the hydride and alkynyl carbons of the other unit are 2.80 Å to Cα and 2.85 Å to Cβ, distances too large to expect direct orbital interactions but well within the sum of van der Waals radii. The interaction is thus expected to be of a weak electrostatic type between the hydride and the alkynyl group.

In the transition state $\mathbf{G_{ts}}$, the intermolecular distance between the hydride of one molecule and Cβ of the other is shortened to 1.384 Å while the metal−hydride bond is elongated to 1.660 Å. The angle Cα−Cβ−Hβ is bent from linearity to 148.9° so that Cβ can form the new C−H bond. The Rh−Cα−Cβ angle is also bent by 165.3° toward the incoming H. In the final product **H** the hydrogen that has migrated now interacts very
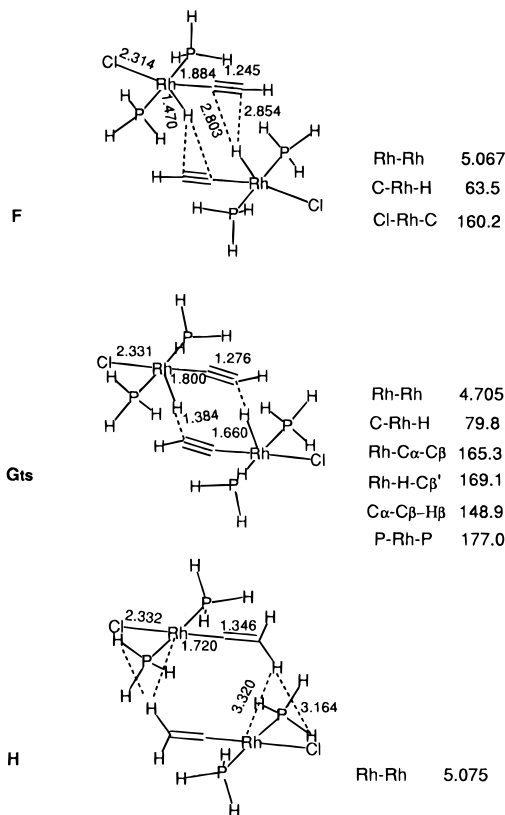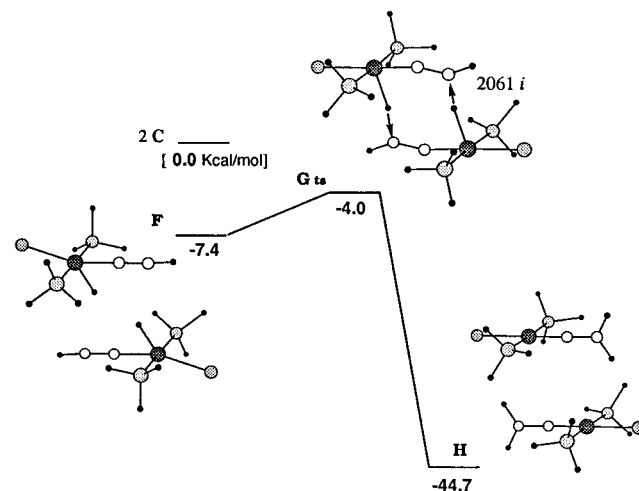
Figure 5. Energy diagram (kcal/mol) for bimolecular rearrangement: [RhCl(PH$_3$)$_2$(H)(C≡CH)]$_2$ (**F**), [RhCl(PH$_3$)$_2$(C=CH$_2$)]$_2$ (**H**), and transition state $\mathbf{G_{ts}}$. For $\mathbf{G_{ts}}$, the reaction coordinate vector is shown with the associating imaginary frequency (cm^{-1}).

weakly with the Rh−Cl bond of the other molecule, the H···Cl distance being 3.164 Å vs van der Waals radii of 1.2 Å for H and 1.8 Å for Cl.

Finally, the energies of these optimized structures were refined employing the same basis sets as used for the calculations of the unimolecular process, and the energy profile thus calculated is illustrated in Figure 5. The association energy to form **F** from two units of **C** has been calculated to be 7.4 kcal/mol. The most important finding is that the bimolecular rearrangement from [RhCl(PH$_3$)$_2$(H)(C≡CH)]$_2$ (**F**) to [RhCl(PH$_3$)$_2$-(C=CH$_2$)]$_2$ (**H**) takes place with a very low activation energy of 3.4 kcal/mol. The unimolecular rearrangement requires more than 33 kcal/mol of the activation energy, and the bimolecular
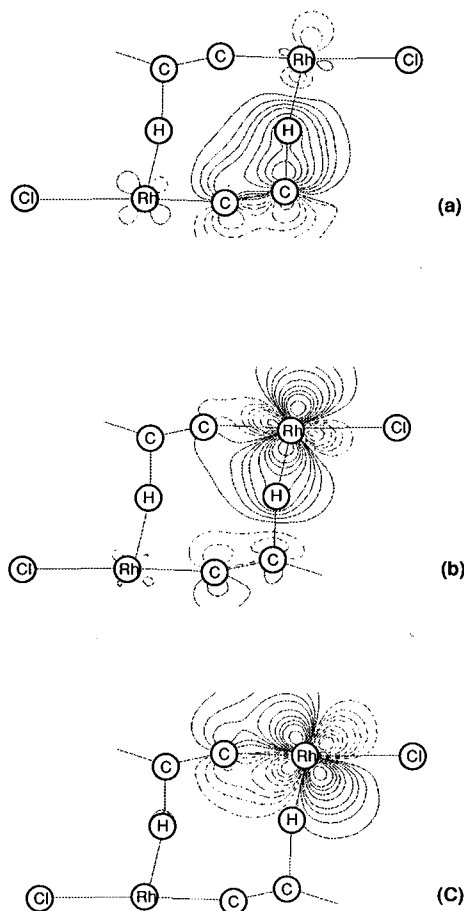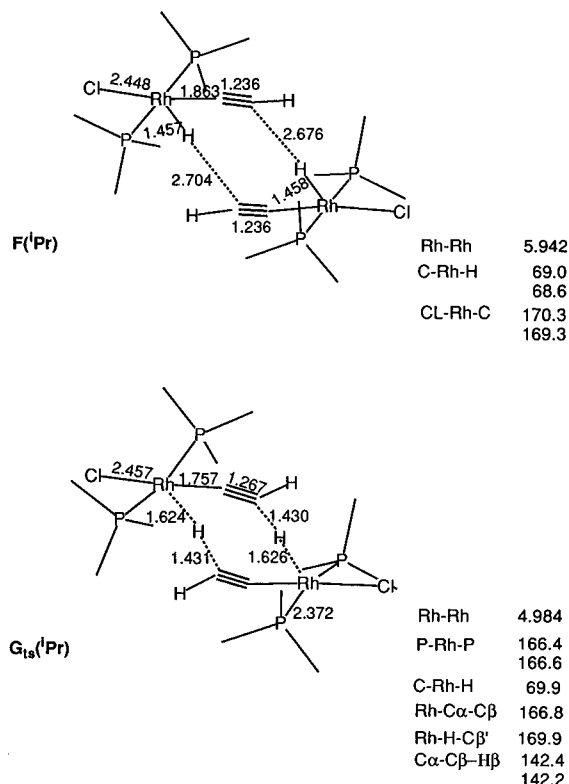
Figure 6. Important localized molecular orbitals in the plane of 2(Cl−Rh−CH−CH) for the bimolecular transition state $\mathbf{G_{ts}}$.

pathway is much preferred over the unimolecular pathway for the rearrangement from the alkynyl(hydrido) complex to the vinlidene complex.

Three important LMOs of transition state $\mathbf{G_{ts}}$ shown in Figure 6 strongly suggest again that the migrating hydrogen should be regarded as a proton rather than a hydride. In LMO (a), the migrating proton is interacting with the in-plane CC π-orbital which turns to the new $C\beta$−H bond on going to the product. This leaves the in-plane p-orbital at $C\alpha$ empty and, as seen in LMO (c), back-donation from the Rh d_π is already becoming effective at the transition state $\mathbf{G_{ts}}$. In LMO (b), the Rh−H bond is turning into the d_{z^2} orbital localized on Rh. The linear combination of (a) and (b) gives three-centered (Rh$\cdots$H$\cdots$Cβ) 4-electron interaction which explains why this proton-bridged species forms a low-energy transition state.

(5) Integrated MO + MM (IMOMM) Calculations on the Bimolecular Hydrogen Migration of RhCl(P^{i}Pr$_3$)$_2$(H)-(C≡CH). In a series of Rh−vinylidene-forming reactions from terminal alkynes, the ancillary phosphine ligand employed by Werner and co-workers has been P^{i}Pr$_3$.[10] Since the bimolecular pathway was found to be an energetically preferred route in the case of the model complex with the PH$_3$ ligand as discussed in the preceding section, we need to examine if two alkynyl-(hydrido) molecules with bulky P^{i}Pr$_3$ ligands RhCl(P^{i}Pr$_3$)$_2$-(H)(C≡CH) (C(^{i}Pr)) can likewise interact with each other and rearrange easily. As shown in Figure 7, the IMOMM calculations have shown that such interaction indeed takes place (F(^{i}Pr)) and the transition state for the intermolecular hydrogen shift (G$_{ts}$(^{i}Pr)) exists at more or less expected geometries. We did not perform an IMOMM calculation for the corresponding pairing of the final vinylidene complex because of the cpu time limitation, but such an intermediate, "H(^{i}Pr)", must be more


Rh-Rh	5.942	
C-Rh-H	69.0	
	68.6	
CL-Rh-C	170.3	
	169.3	

Rh-Rh	4.984	
P-Rh-P	166.4	
	166.6	
C-Rh-H	69.9	
Rh-Cα-Cβ	166.8	
Rh-H-Cβ'	169.9	
Cα-Cβ-Hβ	142.4	
	142.2	

Figure 7. Structures (Å and deg) of [RhCl(P^{i}Pr$_3$)$_2$(H)(C≡CH)]$_2$ (**F(iPr)**) and transition state **G$_{ts}$(iPr)** optimized with the IMOMM method. The ^{i}Pr groups of phosphines are not shown for clarity.

stable than a pair of **E(^{i}Pr)**, for which we performed IMOMM calculations.

Comparing the structure of **F(^{i}Pr)** with that of **F** in Figure 4, one notices that the Rh−Rh distance is longer in **F(^{i}Pr)** by 0.88 Å, as expected by a much larger steric repulsion between the isopropyl groups on phosphines. However, in **G$_{ts}$(^{i}Pr)** the Rh−Rh distance is longer than in **G$_{ts}$** only by 0.28 Å. The interaction between Rh−CCH of one molecule and Rh−H of the other is similar in **G$_{ts}$(iPr)** and **G$_{ts}$**, the same bond exchange taking place. Bending of the P−Rh−P bond angle (from 180° in **F-(^{i}Pr)** to 166° in **G$_{ts}$(^{i}Pr)**) away from the reaction center in the transition state, combined with the flexible nature of isopropyl groups on P, must have relieved the steric repulsion. Though the Rh−Rh distance in **G$_{ts}$(^{i}Pr)** is 0.96 Å shorter than in **F(iPr)**, its MM3 energy (E_{mMM3}) is only 6.5 kcal/mol larger than that for **F(iPr)**, and this reduced steric repulsion in the transition state **G$_{ts}$(^{i}Pr)** has contributed to lowering of the activation barrier for the bimolecular rearrangement, as will be discussed later.

Some preliminary study on the steric effect brought about by a bulky substituent on acetylene has been carried out. The hydrogens on the two terminal alkynyl carbons in **G$_{ts}$(^{i}Pr)** were replaced with ^{t}Bu groups, and their conformations as well as those of ^{i}Pr groups on the phosphine ligands were optimized with MM2 calculations, while the geometry of the central part, (P−Rh−P)−CC−H$_{migrating}$ was kept frozen to that of **G$_{ts}$(^{i}Pr)**. The ^{t}Bu hydrogens have some steric interaction with the ^{i}Pr hydrogens on phosphines of the partner molecule, the shortest contact being 2.126 Å, but it is not very severe. This is mainly due to the large bend angle of C≡C−Hβ or C≡C−^{t}Bu (in the MM2 calculation frozen at 142° which is taken from **G$_{ts}$(^{i}Pr)** in Figure 7) which directs the substituent (^{t}Bu group) toward open space.

The association of two **C(^{i}Pr)** to form **F(^{i}Pr)** has been calculated to be 4.2 kcal/mol exothermic, and the barrier from this level to transition state **G$_{ts}$(^{i}Pr)** is 10.3 kcal/mol, as shown
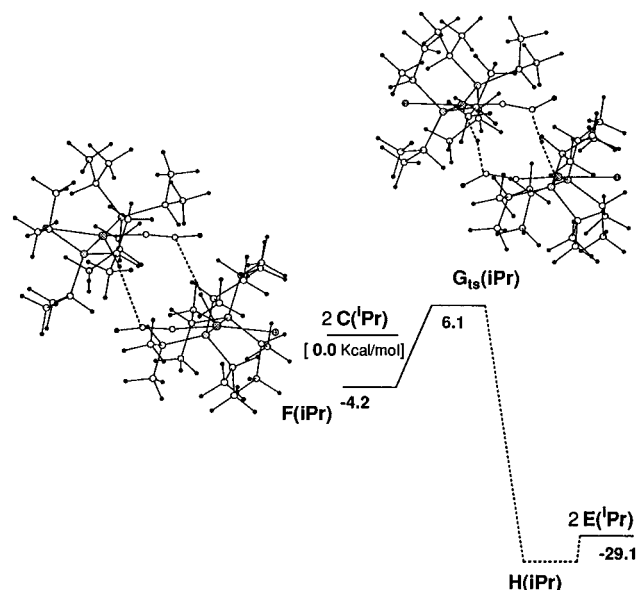
Figure 8. Energy diagram (kcal/mol) for bimolecular rearrangement: $[RhCl(P^iPr_3)_2(H)(C\equiv CH)]_2$ (**F(iPr)**) and the transition state $\mathbf{G_{ts}(iPr)}$.

in Figure 8. The energy level of $\mathbf{G_{ts}(^iPr)}$ is then endothermic from $\mathbf{C(^iPr)}$ by 6.1 kcal/mol, a reasonable change from the exothermic formation of $\mathbf{G_{ts}}$ for $\mathbf{C}$ in the model complex with less bulky PH_3 ligands (Figure 5). The entropy change for forming a "tight" transition state in bimolecular reactions has been described to be approximately -150 J K^{-1} mol^{-1} which is equal to free energy of 10.6 kcal/mol at 298 K.[28] If we assume the entropy change of -150 J K^{-1} mol^{-} on going from two $\mathbf{C(^iPr)}$ to $\mathbf{G_{ts}(^iPr)}$, the free energy of activation in the present bimolecular process should then be approximately 17 kcal/mol at 298 K.

Concluding Remarks

While our previous MO calculations have indicated tht the transformation of an η^2-coordinated alkyne to a vinylidene ligand on Ru(II) proceeds via an intraligand 1,2-hydrogen shift mechanism,[8] a similar rearrangement in the present Rh(I) complex has been found to take place via the oxidative addition product, alkynyl(hydrido)rhodium. Starting from an η^2-$C\equiv C$ complex, both systems give a [metal-η^2-CH] species in a subsequent step. In the case of the d^6-Ru(II) system, this η^2-CH complex is an intermediate which then climbs up the hill to the 1,2-hydrogen shift transition state. In contrast, the η^2-CH coordinated state is a transition state in the d^8-Rh(I) system, the oxidative addition being a very facile process. The alkynyl-(hydrido)rhodium complex thus formed can then rearrange to the vinylidene form by transferring the metal-bound hydrogen to the β-carbon of the alkynyl group via either unimolecular 1,3-H shift or bimolecular hydrogen exchange between the two alkynyl(hydrido)rhodium units. The unimolecular hydrogen migration was calculated to have an activation enthalpy of 33.5 kcal/mol, meaning that the free energy of activation is larger than this value, the entropy certainly having a negative value. In contrast, the free energy of activation for the bimolecular hydrogen exchange was estimated to be ca. 17 kcal/mol even for the "real" complex with bulky P^iPr_3 ligands.

The pathways for the isomerization reactions of d^6- and d^8-

(28) Page, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 449.
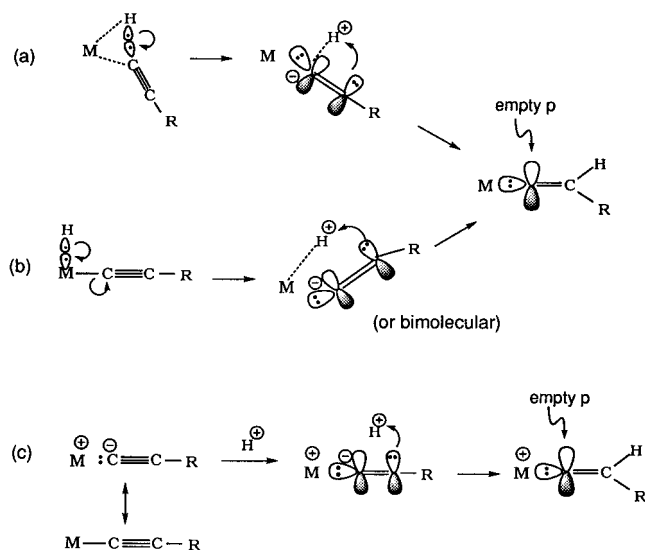
Scheme 2

metal complexes are thus very different, but they have similarities in that the hydrogen moves as a proton, regardless if it is bound to $C\alpha$ or to the central metal before the shift starts (Scheme 2a,b), so that a lone pair orbital is generated at $C\alpha$. The two electrons necessary to form the new $C\beta-H$ bond are supplied by the in-plane $C-C$ π-orbital, and this process leaves the in-plane p-orbital at $C\alpha$ empty, which thus ends up as an accepting orbital for the back-donation from the metal. In this respect, the resemblance to the mechanism in well-known protonation reactions[4] of metal–alkynyl complexes may be pointed out (Scheme 2c) where the proton is added externally to form cationic vinylidene complexes.

Bianchini's vinylidene-forming reaction[11] from the cationic alkynyl(hydrido)cobalt complex, $[P(CH_2CH_2PPh_2)_3Co(H)-(C\equiv CR)]^+ \rightarrow [P(CH_2CH_2PPh_2)_3Co(C=CHR)]^+$, may be viewed as situated between (b) and (c) in Scheme 2. The proton is originally bonded to Co, but after dissociation from the metal, the reaction should follow Scheme 2c. Their kinetic data suggests that the proton dissociation is the rate-determining step (first-order kinetics and positive $\Delta S^\ddagger$), and the observed enthalpy of activation, $\Delta H^\ddagger = 31 \pm 1$ kcal/mol for R = Ph, happens to be in the same range as the calculated here for the Rh complex in its unimolecular process. It is worth noting that the cobalt center is guarded by six phenyl groups of the conformationally rigid tetrapod phosphine ligand and a bimolecular pathway is apparently not possible here.

Finally, the solid state transformation of alkynyl(hydrido) complexes to the vinylidene isomer observed in $RhCl(P^iPr_3)_2-(H)(C\equiv CSiR_3)^{10f}$ most likely proceeds via the unimolecular 1,3-H shift transition state outlined in Figure 2.