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Two possible reaction pathways for the formation of a ruthenium carbene complex by addition of acetylene to $[\mathrm{RuH_2Cl_2(PH_3)_2}]$: a quantum chemical study[☆]

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Abstract

$[\mathrm{RuH_2Cl_2(P^iPr_3)_2}]$ reacts with terminal alkynes to give the vinylidene complex $[\mathrm{RuCl_2({=}C{=}CHR)(P^iPr_3)_2}]$. As a side product the carbene complex $[\mathrm{RuCl_2({=}CHR)(P^iPr_3)_2}]$ is formed. The formation of the vinylidene compound has been studied widely and is well understood whereas the reaction mechanism that leads to the carbene complex is still unclear. We have studied two possible reaction paths at the B3LYP level of theory: on the one hand the addition of acetylene and two subsequent 1,3-H shifts from the metal center to the C2 carbon of the acetylene ligand; on the other hand the dissociation of HCl from the starting compound, rearrangement of acetylene to vinyl and the formation of the carbene by addition of HCl. Both reaction paths have been found to be possible. The former can be understood as a 1,3-H shift followed by a 1,2-H shift due to the unusual η^2 coordination mode of the vinyl intermediate. The latter proceeds via protonation of the vinyl ligand and addition of $\mathrm{Cl^-}$ to the metal center. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ruthenium complexes; Carbene complexes; Reaction pathways; Quantum chemical study

1. Introduction

Homogeneous catalysts based on the late transition metals ruthenium and osmium have gained great importance in olefin metathesis due to their high stability toward oxygen and protic solvents and their wide functional group tolerance. Ruthenium carbene complexes such as $[\mathrm{RuCl_2({=}CHR)(PR_3)_2}]$ have proved to be especially efficient [1]. These compounds can be prepared in good yields and are easy to handle. However, the classic syntheses require carbene precursors such as 3,3-diphenyl cyclopropene or phenyl diazomethane, which are reactive compounds that are difficult to obtain. The growing demand for these catalysts has led to the search for new methods of synthesis that do not need any carbene precursors [2–6].

Recently Werner and coworkers developed a new synthesis that proceeds from ruthenium hydride complexes and terminal alkynes [7–9] (Fig. 1): $[\mathrm{RuCl_2(C_8H_{12})_n}]$ (**A**) reacts in 2-butanol at 80°C with $\mathrm{H_2}$ and diisopropyl phosphane forming a red solution. If consecutively terminal alkynes are added to the solution at 25°C, the carbene complex $[\mathrm{RuCl_2({=}CHR)(P^iPr_3)_2}]$ (**C**) is obtained with good yields. If the red solution is worked up with ether, one can isolate the ruthenium dihydride complex $[\mathrm{RuH_2Cl_2(PH_3)_2}]$ (**D**) with nearly 100% yield. Surprisingly it was found that **D** reacts with alkynes to give mainly the vinylidene complex $[\mathrm{RuCl_2({=}C{=}CHR)(P^iPr_3)_2}]$ (**E**). In this case the carbene complex is only formed as a side product. It could be shown that the red solution contains the monohydride(dihydrogen) complex $[\mathrm{RuClH(H_2)(P^iPr_3)_2}]$ (**B**) as well as $[\mathrm{HP^iPr_3}]\mathrm{Cl}$ [10].

For the formation of the carbene complex Werner has proposed the following mechanism [8] (Fig. 2): **B** first reacts with the alkyne to give a vinylidene complex (**F**). Addition of HCl to the C=C double bond then

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leads to the formation of the chlorocarbene intermediate **G**. The 14 VE α-chloroalkyl species **H** is formed by insertion of the carbene into the Ru–H bond. **H** finally rearranges to give the carbene complex **C**. Grubbs and coworkers have described similar α-chloroalkyl compounds as intermediates for the formation of ruthenium carbenes from ruthenium hydrides and vinyl chloride [11]. The proposed mechanism is also in agreement with ^{2}H-NMR studies of the reaction of **F** with DCl.

The formation of the vinylidene complex **E** by addition of a terminal alkyne to the ruthenium dihydride **D** is also quite well understood. The acetylene–vinylidene rearrangement in the coordination sphere of transition metals constitutes an important step in the catalytic cycle of the polymerization of alkynes and has been studied experimentally and theoretically [12–17]. Recently Caulton and Eisenstein have studied the influence of hydride ligands at the metal center on the mechanism of the acetylene–vinylidene rearrangement [18]. DFT calculations as well as deuteration experiments indicate that the first step of the reaction consists of an insertion of acetylene into the metal–H bond through which a 14 VE vinyl intermediate is formed. The reaction then proceeds via an α-H shift to the metal (Fig. 3).

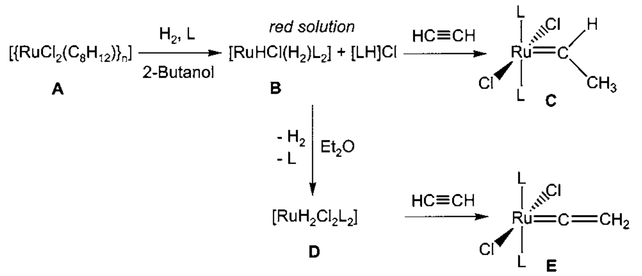

Fig. 1. Synthesis of ruthenium carbene and vinylidene complexes (L = $\mathrm{P}^i\mathrm{Pr}_3$).

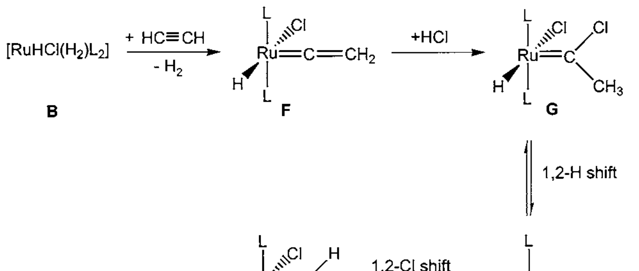

Fig. 2. Possible mechanism for the formation of the carbene from the vinylidene complex (L = $\mathrm{P}^i\mathrm{Pr}_3$).

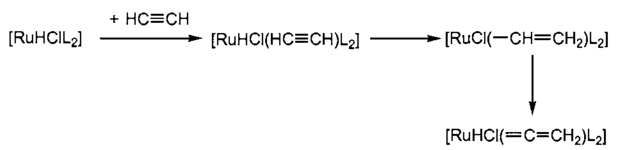

Fig. 3. Mechanism of the acetylene–vinylidene rearrangement (L = PH$_3$).

In this work we have studied the formation of the carbene complex **C** as a side product of the addition of acetylene to [RuH$_2$Cl$_2$($\mathrm{P}^i\mathrm{Pr}_3$)$_2$], i.e. the reaction step **D**→**C** in Fig. 1. On the one hand it is conceivable that the reaction might take place via formation of a hydride vinyl complex and a subsequent 1,3-H shift from the metal center to the C2 carbon of the vinyl ligand. However, it has been shown that such 1,3-H shift reactions of transition metal compounds usually have a very high activation barrier [14,16]. On the other hand it is well known that hydride vinylidene complexes react in the presence of HCl and other acids to give the corresponding carbene complexes [8]. When Werner and coworkers carried out the reaction in the absence of acids they still observed the formation of a certain amount of carbene side product. Therefore we have also examined the possibility that HCl might dissociate from the starting compound.

2. Computational details

In all calculations PH$_3$ has been used as a model ligand for the $\mathrm{P}^i\mathrm{Pr}_3$-groups present in the experiment.

The geometry optimizations have been carried out at the DFT level of theory using the B3LYP hybrid functional [19] with the program packages Gaussian 94 [20] and Gaussian 98 [21]. The 28 innermost electrons of Ru have been replaced by a relativistic core potential (ECP) of Hay and Wadt [22]. The valence electrons have been described by a (441/2111/21) basis set. An ECP by Stoll and Preuβ [23] with a (31/31) valence basis and an additional polarization function by Huzinaga [24] has been used for Cl, while 6-31G(d,p) all electron basis sets [25] were used for the other atoms. The H-atoms of the PH$_3$-groups have been described without polarization functions, however. This basis set corresponds to our standard basis set II [26]. The nature of the equilibrium structures has been determined by calculation of the vibrational frequencies. Energy minimum structures have only positive eigenvalues of the Hessian matrix while transition states have one negative eigenvalue. For most transition state structures it was obvious how to specify the corresponding reaction path. In one case we carried out a calculation of the intrinsic reaction coordinate [27,28].

3. Results and discussion

3.1. Reaction path 1: addition of acetylene to $[RuH_2Cl_2(PH_3)_2]$ and intramolecular rearrangement

Fig. 4 shows the equilibrium structures and transition states which are predicted at the B3LYP level of theory. Only the most important isomers are sketched here. The energy scheme for the reaction path is shown in Fig. 5.

The energetically lowest isomer of the six-coordinate model complex $[RuH_2Cl_2(PH_3)_2]$ (**1a**) has an octahedral geometry with the phosphine ligand in a *trans* position. Isomer **1b**, which is 3.89 kcal mol^{-1} less stable than **1a**, is a bicapped tetrahedron. The Ru–H bond lengths are 1.562 and 1.569 Å respectively. Both isomers can be considered as dihydrides rather than dihydrogen complexes. The H–H distance in **1a** is 1.450 Å, which indicates negligible hydrogen–hydrogen interactions. The H–H distance in **1b** is even longer (2.674 Å). In a recent work by Chaudret and coworkers [29] the geometry of $[RuH_2Cl_2(PH_3)_2]$ was calculated at the B3LYP level with a double-ζ basis with polarization functions. The two most stable isomers correspond to **1a** and **1b**. The bond lengths and angles are very similar to our values. The crystal structure of $[RuH_2Cl_2(P^iPr_3)_2]$ has been solved by X-ray analysis by Werner and coworkers [7]. It can be described as a trigonal prism, with the two triangular faces each defined by the atoms P–Cl–H. This structure can be deduced from **1b** if the

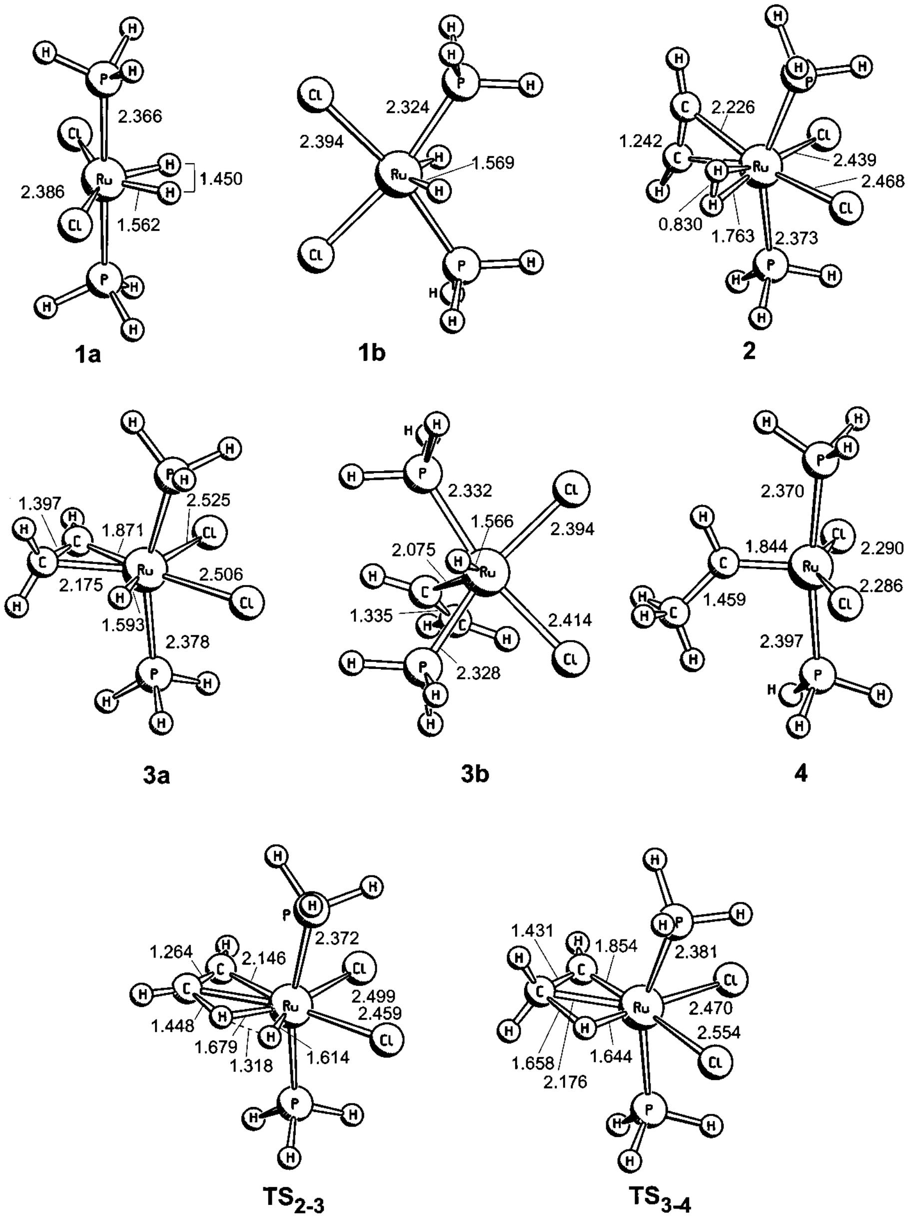

Fig. 4. Optimized structures (Å) of reactants, intermediates, products and transition states for the reaction path 1.

Cl-atoms move away from the P–Ru–P plane. The distortion is due to steric repulsion of the large P^iPr_3 ligands. This effect cannot be reproduced by the small model ligands, as shown by Eisenstein and Maseras for the corresponding osmium compound $[OsH_2Cl_2(P^iPr_3)_2]$ [30].

The formation of the acetylene π-complex **2** is exothermic by 14.4 kcal mol^{-1} although the 16 VE starting compound has already the coordination number eight. The reductive elimination of the two hydrides and the formation of one dihydride ligand facilitate the coordination of an additional ligand leading to the formation of an 18 VE complex with a slightly distorted octahedral geometry. Due to the higher coordination number all metal–ligand bonds in **2** are slightly longer compared to **1**. The Ru–H bonds are lengthened by 0.2 Å and the H–H distance is shortened by 0.6 Å. The H–H bond length of 0.830 Å lies within the range of transition metal dihydrogen complexes that has been found by X-ray analysis and molecular orbital calculations [29,31,32]. The calculated barrier for the rotation of the H_2-ligand in **2** is very low (1.4 kcal mol^{-1}). We also located four energy minima of $[RuH_2Cl_2(PH_3)_2]$ which have a dihydride structure, i.e. the ruthenium atom is seven coordinated in these complexes. The two Ru–H bonds are always separated by another Ru–L bond and thus can not be considered as η^2-bonded dihydrogen complex with a stretched H–H bond. The energetically lowest-lying dihydride form of $[RuH_2Cl_2(PH_3)_2]$ lies 19.3 kcal mol^{-1} above **2**.

The 1,2-H shift that leads to the formation of the vinyl complex **3** is slightly exothermic (3.5 kcal mol^{-1}). The corresponding activation barrier is 14.4 kcal mol^{-1}. During the reaction the acetylene as well as the dihydride ligand move into the Cl–Ru–Cl plane. In the transition state $\mathbf{TS_{2-3}}$ the Ru–C bond lengths are al-

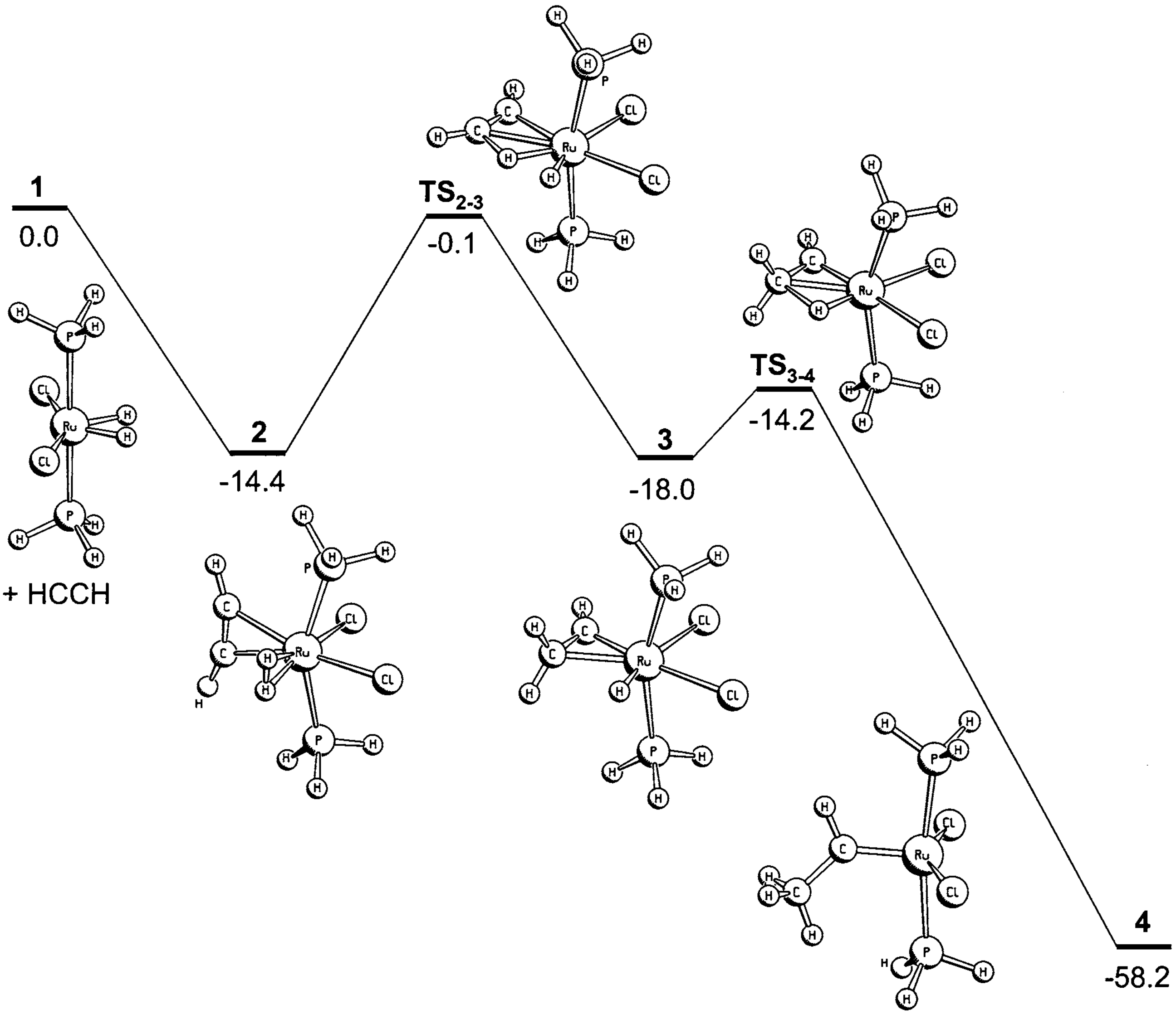

Fig. 5. Energy diagram (kcal mol^{-1}) for the reaction path 1.

ready significantly different (2.146 and 2.292 Å) and the C–C bond is lengthened. Both Ru–H bonds are shortened and the H–H bond is essentially broken (1.318 Å) while the nascending C–H bond has started to form (1.448 Å). This step results in the formation of an η^2-vinyl complex. A similar η^2-vinyl complex has been described by Caulton and Eisenstein as an intermediate for the addition of acetylene to [OsHCl(PH$_3$)$_2$] [33]. For the corresponding Ru(II) compound they could only locate the σ-bonded η^1-vinyl isomer. Due to the stronger Lewis acidity of Ru(IV) compared to Ru(II), the formation of the η^2-vinyl complex is facilitated in the present case although it leads to a higher coordination number on the metal. The η^2-vinyl complex has a long C–C bond (1.397 Å). The Ru–(CH) bond is very short (1.871 Å) while the Ru–(CH$_2$) bond is rather long (2.173 Å). We have also localized various η^1-vinyl isomers, the most stable of which lies 12.1 kcal mol^{-1} below **3**. However a calculation of the intrinsic reaction coordinate (IRC) [27,28] starting from the transition structure **TS$_{2-3}$** indicates that **3** is actually the product of the 1,2-H shift.

Because the vinyl ligand in **3** is η^2-coordinate, the carbene complex is not formed via a 1,3-H shift, as had been assumed before, but via a second 1,2-H shift. The latter hydrogen transfer has a very low activation barrier of only 3.8 kcal mol^{-1}. The structure of the corresponding transition state **TS$_{3-4}$** resembles **3** with a Ru–(CH$_2$) bond that is hardly changed. The Ru–(CH) bond is slightly shortened and the C–C bond slightly elongated. The hydride has moved significantly towards the vinyl ligand and the Ru–H bond is stretched. The formation of the carbene is highly exothermic with a reaction energy of -40.3 kcal mol^{-1}. The coordination of the metal in the carbene complex resembles a distorted trigonal bipyramid with the carbene ligand lying in the Cl–Ru–Cl plane. This geometry has been observed before and has been widely discussed [18,34]. It is favored by the presence of the π-donor ligands Cl and by Ru → C back-donation.

3.2. Reaction path 2: addition of HCl to the 14 VE vinyl complex [RuHCl(–CH=CH$_2$)(PH$_3$)$_2$]

Fig. 6 shows the most important isomers of the energy minima which are predicted at the B3LYP level of theory. The energy scheme for this reaction path is shown in Fig. 7.

Elimination of HCl from the starting compound **1** leads to the 14 VE monohydride [RuHCl(PH$_3$)$_2$]. The monohydride has a sawhorse geometry, which resembles an octahedron with two empty *cis*-oriented coordination sites. This coordination geometry has also been found by Eisenstein and coworkers. It makes it possible to keep the six metal electrons in non-bonding t$_{2g}$-like d orbitals [33]. Surprisingly the isomer with *trans* phosphines (**5b**) is 11.6 kcal mol^{-1} less stable than the one with *cis* PH$_3$-groups (**5a**). This order may change when the steric effects of the large phosphines in the real system are included in the calculation. The elimination is endothermic (18.0 kcal mol^{-1} with respect to **5a** and 29.6 kcal mol^{-1} with respect to **5b**), but under experimental conditions the coordination of solvent molecules and solvatation of HCl might favor this step.

Elimination of HCl might also occur from the acetylene complex **2**. In this case the reaction is less endothermic (11.0 kcal mol^{-1}) and the energy of the resulting 16 VE acetylene complex **6** lies slightly below the energy of the reactants. Elimination of HCl during the addition of acetylene to the starting compound therefore seems to be a possible reaction step. In the acetylene complex **6** the coordination geometry is that of a square pyramid, where the hydride as the strongest σ-donor occupies the apical position. The C–C bond is moderately elongated (1.252 compared to 1.205 Å in free acetylene). Due to the electron deficiency and the lower coordination number the acetylene ligand in **6** is more strongly coordinated than in the corresponding Ru(IV) compound **2**. This can be seen from the longer C–C bond (1.252 instead of 1.230 Å) and the shorter Ru–C bonds (2.263 and 2.206 instead of 2.305 Å).

The formation of the 14 VE vinyl complex **7b** from **6** has been studied by Eisenstein and coworkers as part of the acetylene–vinylidene rearrangement [33] at the B3LYP level of theory with a basis set slightly different from ours. Reaction energies as well as bond lengths and angles which are presented here are in very good agreement with their work. Eisenstein and coworkers found an activation barrier of 6.6 kcal mol^{-1} for the 1,2-H shift. In agreement with our results for the four-coordinate hydride complex **5**, we found that the most stable isomer of the vinyl complex has the phosphine ligands in *cis* position (**7a**). The isomer where the PH$_3$-groups are in *trans* position (**7b**) is 8.9 kcal mol^{-1} less stable. The geometry reported by Eisenstein and coworkers corresponds to **7b**. In contrast to the corresponding Ru(IV) complex **3**, species **7** is an η^1-vinyl complex. Compared to **3** the Ru–C bond in **7** is clearly longer (1.974 Å in **7b** compared to 1.871 Å in **3**) and the C–C bond is shorter (1.337 compared to 1.397 Å).

For the transformation of the vinyl complex **7** into a carbene complex a mechanism had been proposed that proceeds via the formation of a vinylidene and subsequent rearrangement to the carbene (see Fig. 2). Eisenstein and coworkers have shown that the vinylidene complex is easily accessible [33]. One can however imagine a more direct reaction path to the carbene: Protonation of the C(2)-carbon of the vinyl ligand and addition of chlorine to the metal center would also result in the formation of **4**. The formation of a cationic carbene complex [RuCl(=CH–CH$_3$)(PH$_3$)$_2$]$^+$ (**8b**) is highly endothermic (104.0 kcal mol^{-1}). This extremely

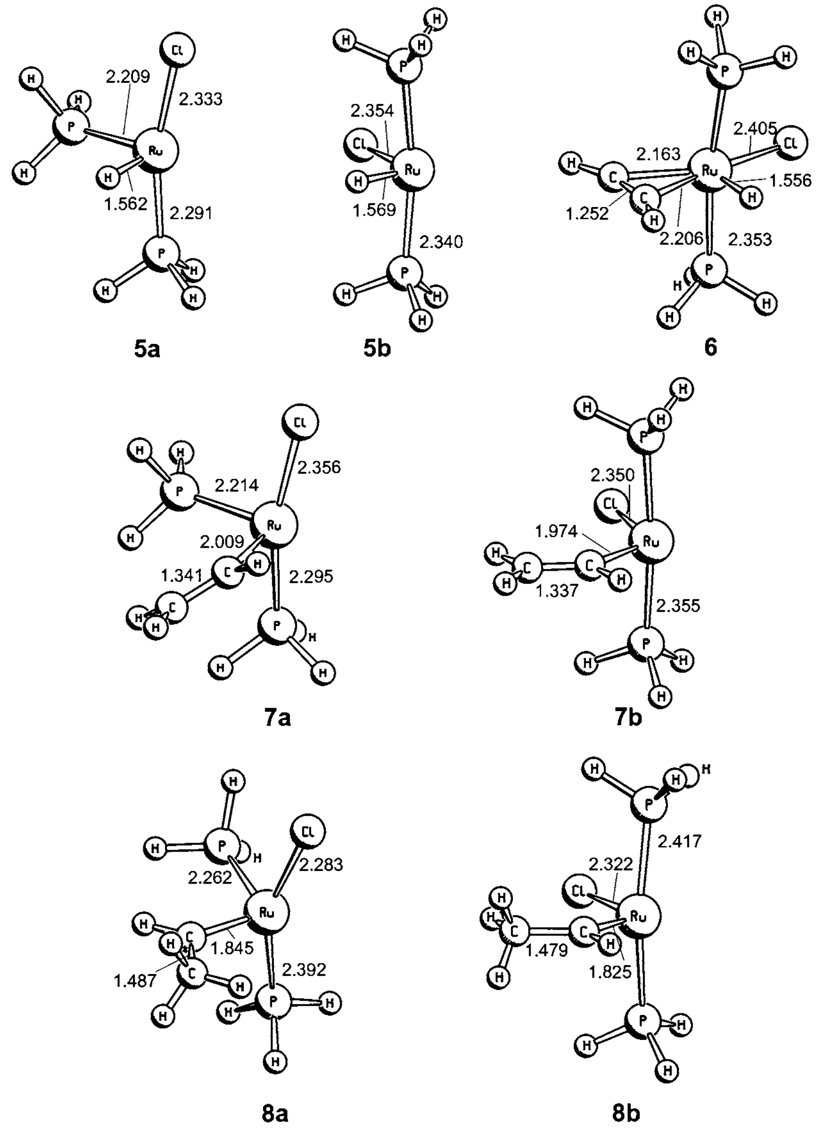

Fig. 6. Optimized structures (Å) of the intermediates for the reaction path 2.

high expenditure of energy however does not correspond to the actual situation in solution but is due to the fact that in the present work the system has been limited to $[RuCl(-CH{=}CH_2)(PH_3)_2]$ (**7b**) and HCl and that no solvent effects have been taken into account. This results in an unfavorable charge separation during the formation of **8** from **7** and HCl. The energy of the latter reaction will be strongly affected by the coordination of the ions which are formed in the reaction. We want to point out that this reaction is not the rate determining step in the overall reaction. In order to estimate the probability of a protonation of the vinyl ligand, the proton affinity of **7** has been calculated. The calculated values are 240.4 kcal mol^{-1} for **7a** and 240.8 kcal mol^{-1} for **7b**. These are very high values. The calculated proton affinity of NH_3 at the same level of theory is 218.4 kcal mol^{-1}. The high proton affinity of **7**, which lies within the range of the experimental values for strong bases [35], indicates that the carbene complex **4** should be accessible through protonation of the vinyl complex. In the cationic carbene complex **8** the Ru–P bonds are slightly lengthened compared to the vinyl compound (~ 0.1 Å) whereas the Ru–Cl bond is shortened (~ 0.07 Å). The electron deficiency at the metal center favors the binding of the electron-donating chloro ligand, whereas the bonds to the electron-deficient phosphine ligands are weakened. The overall addition of HCl to the vinyl complex is exothermic by 39.4 kcal mol^{-1} with respect to **7a** and 46.4 kcal mol^{-1} with respect to **7b**.

3.3. Comparison of the reaction pathways

Two possible reaction paths for the formation of a ruthenium carbene complex by addition of acetylene to the ruthenium dihydride complex $[RuH_2Cl_2(PH_3)_2]$ have been found, both of which show several interesting features. Reaction path 1 starts with the addition of acetylene to the Ru(IV) starting compound. Coordination of an additional ligand to the six-coordinate ruthenium dihydride is facilitated by reductive elimination of the two hydride ligands. Thereby a Ru(II) complex with an undissociated dihydrogen ligand is formed.

The formation of the carbene then proceeds via two subsequent 1,2-H shifts instead of one 1,2- and one 1,3-H-shift. This is due to the fact that the Ru(IV) vinyl intermediate shows an unusual η^2-coordination as it had only been described for Os(II) complexes before [33]. The first hydrogen migration is the rate-determining step with an activation barrier of 14.4 kcal mol^{-1}. The η^1-coordinate isomer of the vinyl complex is noticeably more stable than the η^2-coordinate one. Nevertheless the very low activation barrier of the 1,2-H shift suggests that the η^1-vinyl compound is not relevant for the reaction, as the reaction to the carbene should occur immediately, once the η^2-vinyl complex is formed.

The reaction path 2 starts with elimination of HCl during the addition of the acetylene. The reaction is slightly exothermic. It can be expected that consideration of solvent effects in the calculation should further facilitate the dissociation. In analogy to reaction path 1, a 1,2-H shift then leads to the formation of a vinyl complex. Due to the lower Lewis acidity of Ru(II) compared to Ru(IV), the vinyl ligand in the Ru(II) complex is η^1-coordinated. Eisenstein and coworkers have calculated an activation barrier of 6.6 kcal mol^{-1} for this reaction step [33]. The carbene complex is finally formed by protonation of the vinyl ligand and addition of an additional chloro ligand to the metal center. In the present work no solvent effects were taken into account, so no realistic reaction energy for the formation of the cationic carbene complex could be calculated. The high proton affinity however suggests

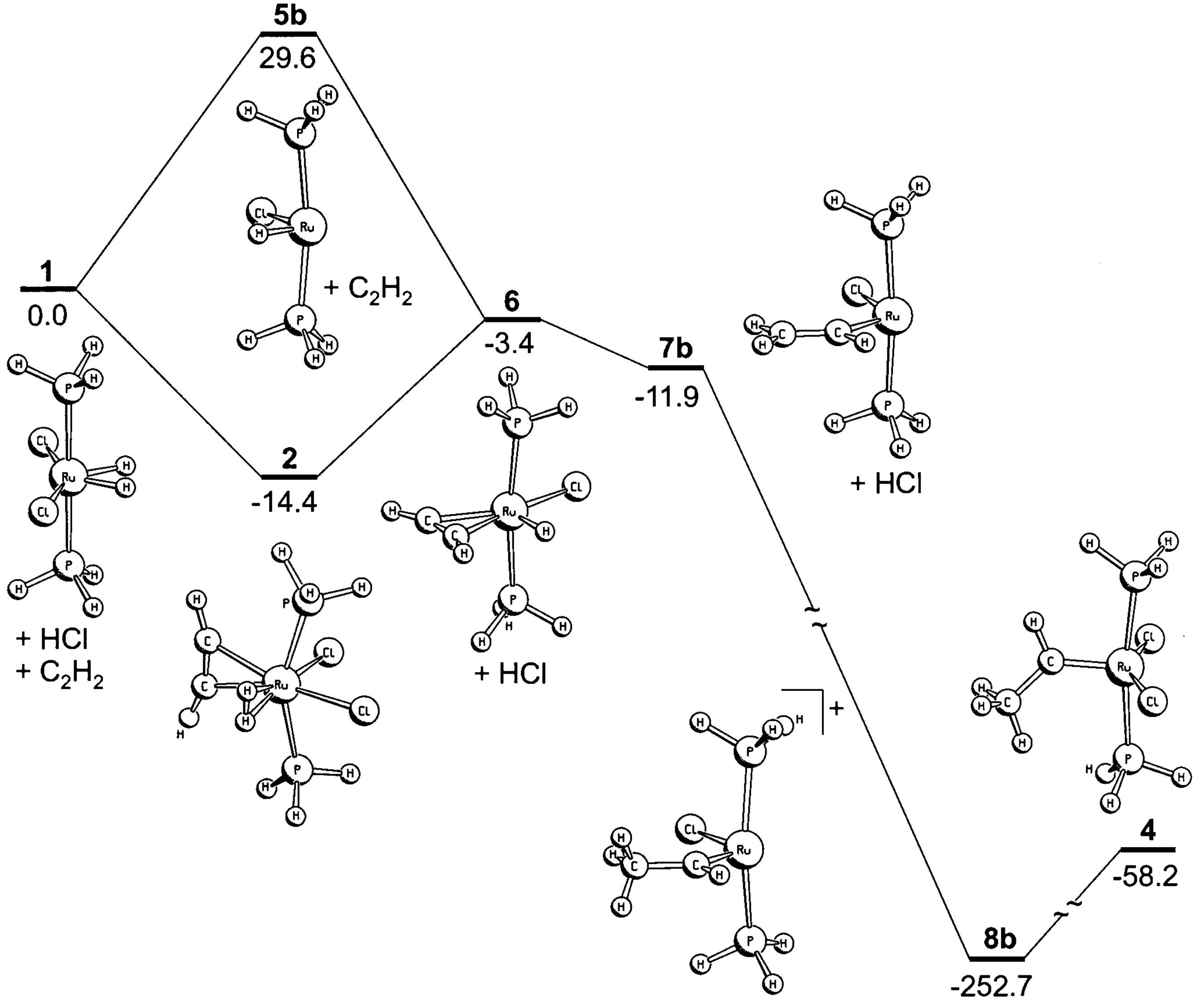

Fig. 7. Energy diagram (kcal mol^{-1}) for the reaction path 2.

that protonation of the vinyl complex should be favorable. Addition of HCl to the vinyl complex represents a more simple and direct way to the carbene than the formation of a vinylidene and a subsequent rearrangement to the carbene, as had been suggested initially.

Surprisingly we have found that for the 14 VE intermediates the isomers with *trans* phosphines are noticeably less stable than the ones with *cis* phosphines. This might be due to the fact that steric effects of the large phosphines used in the experiment have not been taken into account.

The calculated energies of the two reaction pathways are not very different. Thus, it is not possible to predict which of the two reaction channels is operative. The actual reaction pathway may be dictated by the reaction conditions, particularly by the solvent, and by the substituents. The main conclusion of this work is that two reaction pathways are possible for the formation of the carbene complex **C** from **D** and acetylene.

Acknowledgements

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