Mechanism of the Acetylene−Vinylidene Rearrangement in the Coordination Sphere of a Transition Metal[1]

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Quantum mechanical calculations at the CCSD(T) level of theory using BP86-optimized geometries indicate that the high-valent d^0 tungsten acetylene complex $[F_2W(HCCH)]$ (**1**) is 10.4 kcal/mol lower in energy than the isomeric vinylidene complex $[F_4W(CCH_2)]$ (**2**). Two energetically high-lying reaction pathways are calculated for the tautomerization reaction **1 → 2**. The direct 1,2-hydrogen migration has a barrier of 84.8 kcal/mol and proceeds via the transition state **TS1**, which has a nonplanar C_2H_2 moiety. **TS1** resembles the transition states for the rearrangement of the free C_2H_2 species in the triplet state and as an anion. The alternative rearrangement involves the alkynyl(hydrido) complex **3** as an intermediate, which is 50.5 kcal/mol higher in energy than **1**. The rate-determining step of the two-step process **1 → 3 → 2** is the 1,3-hydrogen migration **3 → 2**, which has an energy barrier of 85.5 kcal/mol with respect to **1**. The high barriers for the two alternative pathways of the tautomerization reaction **1 → 2** make it unlikely that they play a role in the acetylene polymerization reaction, which is catalyzed by high-valent transition-metal compounds. The analysis of the bonding situation using the NBO and CDA methods show that **1** and **2** should not be considered as acetylene and vinylidene complexes but rather as metallacyclopropene and metallaallene, respectively.

Introduction

There are two energy minima on the C_2H_2 singlet ground-state potential-energy surface, acetylene (HCCH) and vinylidene (CCH_2). Theoretical[2] and experimental[3] work have established that vinylidene is 44−47 kcal/mol higher in energy than acetylene and that there is only a small barrier (<1 kcal/mol) for the vinylidene → acetylene rearrangement. It follows that free vinylidene has the character of a transient species, which is difficult to observe experimentally.[3] The relative energies of the two isomers change drastically when they are coordinated to a transition metal. Vinylidene complexes are stable compounds which may even be lower in energy than the isomeric alkyne complexes.[4] An important question concerns the tautomerization of the alkyne complex to the vinylidene complex, because the latter is frequently formed via rearrangement of the alkyne complex. The isomerization of the complexes is also an important process which occurs during the reaction course of transition-metal-catalyzed processes

of alkynes.[5] However, the mechanism of the reaction is still not completely understood. Recent experimental[6,7] and theoretical[8,9] studies suggest that the rearrangement may take place via different pathways, depending on the oxidation state of the metal and the type of ligands.

Two reaction mechanisms have been suggested earlier, which are schematically shown in Scheme 1. The results of photochemical studies performed 20 years ago of vinylidene complexes of manganese and rhenium led Antonova and co-workers[10] to conclude that the rearrangement of the alkyne complex **A** to the vinylidene complex **B** takes places via an alkynyl(hydrido)metal intermediate **C** (path 1, Scheme 1). However, theoreti-

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Scheme 1. Previously Suggested Mechanisms for the Intramolecular Tautomerization between Alkyne and Vinylidene Complexes
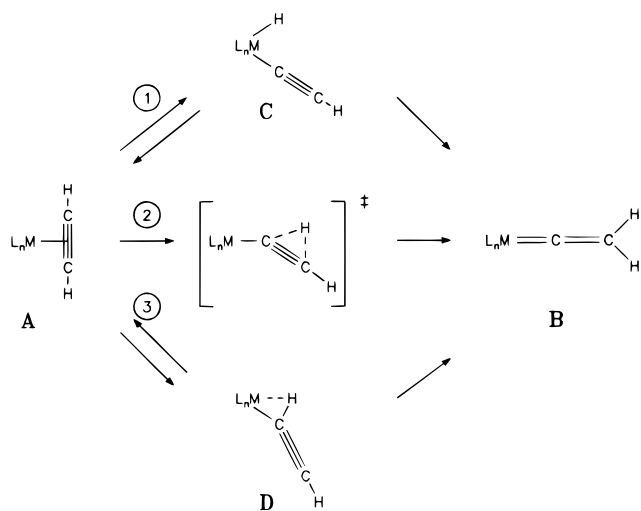
cal studies at the EHT level of theory of Silvestre and Hoffmann[11] indicated that the 1,3-rearrangement **C → B** has a high activation barrier, which is much higher than for the direct 1,2-rearrangement **A → B**, for which a transition state with a "slipping" alkyne ligand was proposed (path 2, Scheme 1). For a long time, experimental studies did not give evidence that **C** plays a role in the **A → B** tautomerization until Werner and co-workers[7] showed unequivocally that the alkyne complex [Cl(P*i*Pr₃)₂Ir(HCCMe)] rearranges to the corresponding vinylidene complex via the intermediate [Cl(P*i*Pr₃)₂IrH-(CCMe)]. The same stepwise pathway was found by Bianchini and co-workers[12a] for the cationic system [P(CH₂CH₂PPh₂)₃Co(HCCR)]⁺. From kinetic studies in solution, it was concluded that the isomerization process occurs unimolecularly.[12a] However, the reaction of the related [Rh(PPh₃)]⁺ cation with alkynes yields only the alkynyl(hydrido) complexes, which do not rearrange further to the corresponding vinylidenes.[12b]

Important information about the mechanism of the rearrangement came from combined experimental and theoretical work of Wakatsuki, Morokuma, and co-workers[8] who studied the reaction of [X₂Ru(PPh₃)₃] (X = Cl, Br) with HCC*t*Bu which yields [X₂(PPh₃)₂Ru-(CCH*t*Bu)]. The calculations indicated that the initially formed alkyne complex rearranges in a slippage process to the vinylidene product via an intermediate **D**, which has an agostic interaction of the CH bond with the metal center (path 3, Scheme 1). However, the same authors recently published together with Koga and Werner theoretical work which showed that the acetylene → vinylidene rearrangement in the coordination sphere of a Rh(I) complex, i.e., [Cl(PH₃)₂Rh(HCCH)], takes place via the hydrido intermediate [Cl(PH₃)₂RhH(CCH)][9] The existence of a alkynyl(hydrido)metal isomer as a mini-

mum on the potential energy surface seems to depend on the electronic configuration of the metal. A further interesting result of this study was the finding that formation of the vinylidene complex from the hydrido intermediate should occur via an intermolecular process rather than an intramolecular 1,3-rearrangement, which is much higher in energy.[9] Finally, an important experimental study of the formation of cationic [Cp*-(dippe)Ru(CCHR)]⁺ (R = CO₂Me, Ph, SiMe₃) has recently been published by Puerta and co-workers, who proposed an alternative mechanism of the alkyne to vinylidene isomerization.[13] It was suggested that the initially formed hydrido intermediate [Cp*(dippe)RuH-(CCR)]⁺ yields the vinylidene complex via a deprotonation/reprotonation route. It seems that the 1,3 rearrangement step **C → B** (path 1, Scheme 1) takes place only under special conditions, and kinetic studies are essential to firmly establish that the reaction is indeed an intramolecular process.

Two reasons prompted us to theoretically investigate the acetylene−vinylidene rearrangement in the coordination sphere of a transition metal. One reason is that one of the present authors previously studied the 1,2-rearrangement of the free C₂H₂ species.[14] It was found that neutral and cationic vinylidene are both shallow minima on the potential-energy surface and that there is only a small barrier for the tautomerization to the acetylene form. However, the vinylidene radical anion CCH₂⁻ is only slightly higher in energy than HCCH⁻ (3.8 kcal/mol at MP2/6-31+G*//HF/4-31G). Even more important is that the calculated barrier for the isomerization process of the C₂H₂ anions is very high and that the transition state has a nonplanar geometry (Scheme 2). The large activation barrier is in agreement with the experimental observation that the long-lived C₂H₂⁻ species is probably the vinylidene anion and not the acetylene anion, which has a negative electron affinity.[15] The large activation barrier and the nonplanar transition state for the 1,2-rearrangement of the anions was explained with the electronic structure of the vinylidene form (Scheme 2). Neutral and cationic CCH₂ have an empty in-plane p(π) AO at the carbenic center, which facilitates the hydrogen migration, leading to an energetically low-lying in-plane transition state. This orbital is singly occupied in the anion and in the triplet state of neutral CCH₂ (Scheme 2). This explains why the triplet state of neutral vinylidene is also separated from the acetylene form by a substantial barrier, which is associated with a nonplanar transition state.[16] It is reasonable to assume that the in-plane p(π) AO of the C$_\alpha$ atom of the vinylidene ligand in transition-metal complexes L$_n$MCCR₂ is partly occupied by L$_n$M→CCR₂ back-donation, which could lead to a nonplanar structure for the transition state of the 1,2-rearrangement of the ligand (path 2, Scheme 1). Previous theoretical studies did not consider this transition structure. Because the calculations of Wakatsuki, Morokuma, et al.[8,9] were carried out with the restriction of C_s symmetry for

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Scheme 2. Transition States for the Tautomerization between Free Acetylene and Vinylidene (Top). Schematic Representation of the Orbital Occupancies in CCH₂ Species (Bottom)
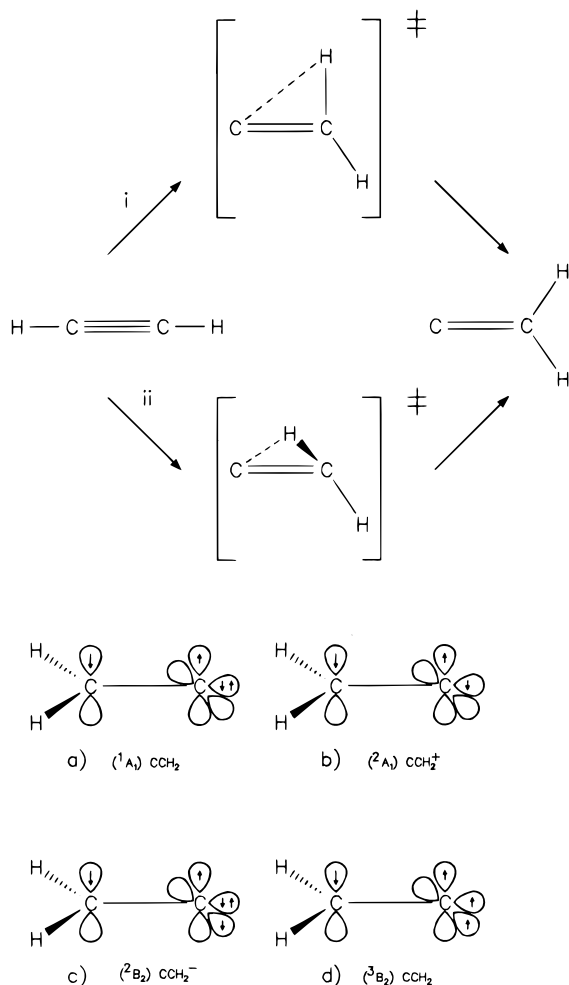
the optimized geometries, nonplanar transition states could not be found.

A second reason for this work is our ongoing interest in the structure and reactivity of high-valent transition-metal complexes with π-bonded ligands,[17] which may be important intermediates in catalytic processes. For example, WCl_6 is a very efficient catalyst for acetylene polymerization.[18] The initial step of the catalytic process is probably the formation of $[Cl_4W(HCCH)]$. Several substituted alkyne complexes $[Cl_4W(RCCR)]$ could be isolated and have been characterized as chlorine-bridged dimers by X-ray structure analysis.[19] The nature of the initial chain formation step of the acetylene polymerization is not clear, however, and it has been suggested that $[Cl_4W(HCCH)]$ may first rearrange to the vinylidene complex $[Cl_4W(CCH_2)]$ which then

adds another acetylene.[20] We previously studied the structures and energies of the acetylene and difluoroacetylene complexes of W(VI) and Mo(VI) and the corresponding vinylidene isomers, but the reaction path of the tautomerization was not investigated.[17d] It is important to find out if the intramolecular rearrangement of the two forms is energetically possible. Previous theoretical work focused on metals in low oxidation states having a formal d^6 or d^8 configuration (Rh(I) or Ru(II))[8,9] It is interesting to compare those results with the theoretical predictions for W(VI) compounds, which have a formal d^0 configuration at the metal. In this work, we report the quantum chemical calculations at the DFT level of theory using the BP86 functional forms[21,22] in conjunction with relativistic effective core potentials for tungsten for the rearrangement of the acetylene complex $[F_4W(HCCH)]$ (**1**) to the vinylidene isomer $[F_4W(CCH_2)]$ (**2**). We have chosen fluorine rather than chlorine in order to save computer time. Particularly, the calculations of the reaction coordinate were very expensive, and it would not have been possible for us to carry them out for the chlorine system. However, we believe that the results of the fluorine system are very similar to the chlorine compounds.

Theoretical Details

The geometry optimizations have been carried out at the gradient-corrected DFT level using the exchange and correlation functionals of Becke[21] and Perdew,[22] respectively (BP86). Our standard basis set II,[23] which has relativistic effective core potentials (ECP)[24] with a (441/2111/21) valence basis set for W and 6-31G(d,p) all-electron basis sets for the other atoms,[25] was employed for calculating geometries and vibrational frequencies. Single-point energy calculations of BP86/II-optimized structures have been performed using coupled-cluster theory[26] with singles and doubles and noniterative estimation of triple excitations CCSD(T)[27] The valence basis set at tungsten was augmented with an additional set of f-type polarization functions (exponent 0.823)[28] for the CCSD(T) energy calculations. This is denoted as basis set III.[23] We also report energy values at the HF and MP2 levels[29] with basis set III (HF/III and MP2/III) using the BP86/II-optimized geometries. Unless otherwise specified, we discuss energies at the highest level of theory employed in this study, i.e., CCSD(T)/III//BP86/II.

The geometry optimizations and frequency calculations were carried out with program package Gaussian 94.[30] For the CCSD(T) calculations, the program Molpro was employed.[31]

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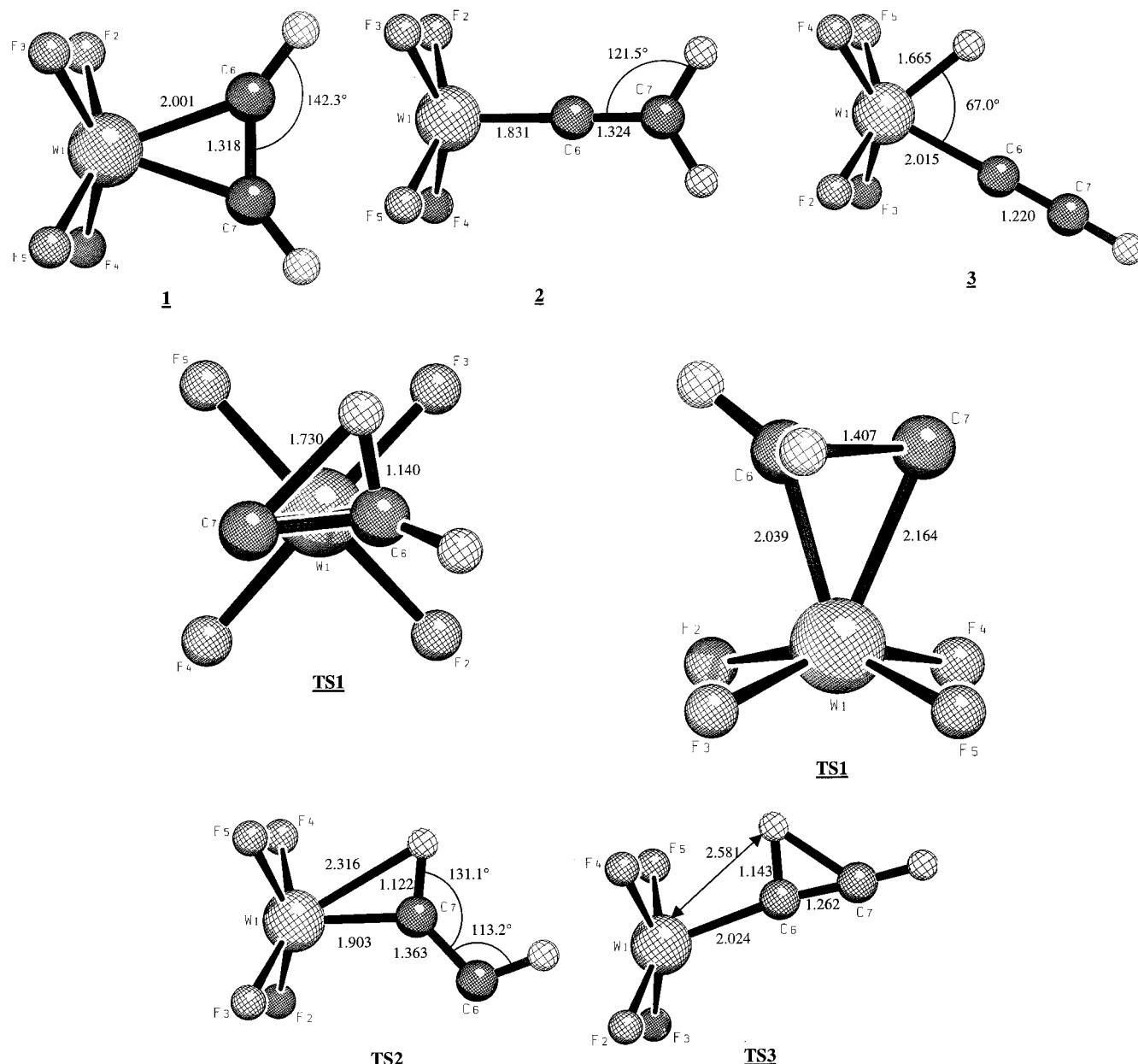
Figure 1. Optimized geometries (BP86/II) of the equilibrium structures **1**−**3** and the transition states **TS1**−**TS3**. Distances are given in angstroms and angles in degrees.

The nature of the stationary points was investigated by calculating the Hessian matrixes at the BP86/II level. All structures reported here are either minima (number of imaginary frequencies $i = 0$) or transition states ($i = 1$) on the potential-energy surface. To receive a more detailed picture of the reaction pathway, we calculated the intrinsic reaction coordinate (IRC)[32] starting from the optimized transition states. The bonding situation of the molecules has been analyzed with the help of the NBO partitioning scheme.[33]

Reaction Paths

Figure 1 shows the calculated equilibrium structures and transition states which are predicted at the BP86/II level of theory. The energies are listed in Table 1.

There are three energy minima at BP86/II on the $WF_4C_2H_2$ singlet potential-energy surface, i.e., the acetylene complex [$F_4W(HCCH)$] (**1**), the vinylidene complex [$F_4W(CCH_2)$] (**2**), and the alkynylhydrido complex [$F_4WH(CCH)$] (**3**). The acetylene complex **1** is predicted as the global energy minimum structure. The vinylidene complex **2** is 10.4 kcal/mol higher in energy than **1**, and the alkynylhydrido complex **3** is 50.5 kcal/mol less stable than **1**. We want to point out that the relative energies of the isomeric forms **1**−**3** at BP86, HF, MP2, and CCSD(T) are very similar (Table 1).[34] The calculations indicate that the rearrangement **1** → **2** is

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Table 1. Calculated Total Energies E_{tot}, (au), Zero-Point Energies, ZPE (kcal/mol), Relative Energies, E_{rel} (kcal/mol), and Number of Imaginary Frequencies, i

	BP86/II				RHF/III//BP86/II		MP2/III//BP86/II		CCSD(T)/III//BP86/II	
	E_{tot}	i	ZPE	E_{rel}[a]	E_{tot}	E_{rel}	E_{tot}	E_{rel}	E_{tot}	E_{rel}
1 (C_{2v})	−545.93428	0	25.17	0.0 (0.0)	−541.91862	0.0	−543.25222	0.0	−543.28227	0.0
2 (C_{2v})	−545.91635	0	24.50	11.3 (10.6)	−541.89374	15.6	−543.22749	15.5	−543.26573	10.4
3 (C_s)	−545.85315	0	23.25	50.9 (49.1)	−541.82800	56.9	−543.16605	54.1	−543.20185	50.5
TS1 (C_1)	−545.80249	1	22.18	82.7 (79.7)	−541.78670	82.8	−543.10230	94.1	−543.14721	84.8
TS2 (C_s)	−545.81917	1	21.65	72.2 (68.7)	−541.79295	78.9	−543.12319	81.0	−543.16136	75.9
TS3 (C_s)	−545.79982	1	20.68	84.4 (79.9)	−541.78433	84.3	−543.08134	107.2	−543.14608	85.5

[a] Values in parentheses include zero-point corrections at BP86/II.
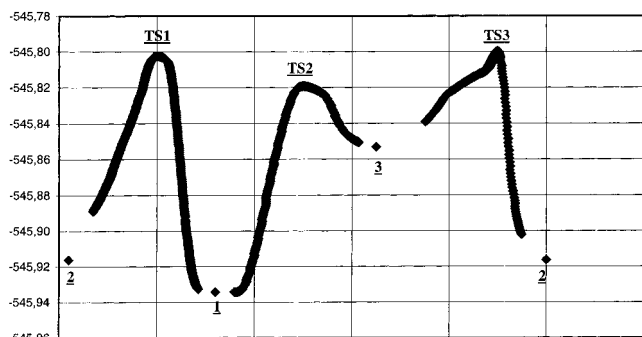
Figure 2. Calculated intrinsic reaction coordinate (BP86/II) using the transition states **TS1**, **TS2**, and **TS3** as starting points.

an endothermic process, which should also be kinetically unfavorable if intermediate **3** is involved in the reaction path.

Three transition-state structures **TS1−TS3** have been located on the potential energy surface, which connect the equilibrium structures **1−3**. When the transition-state search calculations were constrained to structures with C_s symmetry, only **TS2** and **TS3** could be found as transition states. Calculations of the intrinsic reaction coordinate (IRC)[32] starting from **TS2** and **TS3** show (Figure 2) that the transition structures belong to the reaction steps **1** → **3** (**TS2**) and **3** → **2** (**TS3**). A transition state for the direct tautomerization **1** → **2** with a planar arrangement of the C_2H_2 moiety could not be found. A transition state for the direct isomerization could only be located when the search was carried out without symmetry constraint. Using a nonplanar starting geometry for the C_2H_2 moiety, which was similar to the transition state for the rearrangement of the free anions,[14] and the triplet state of the neutral C_2H_2 species[16] lead to the transition state **TS1**. An IRC calculation showed that **TS1** is the transition state for the direct rearrangement **1** → **2** (Figure 2).

Table 1 and Figure 1 show that both reaction channels which connect the acetylene complex **1** and the vinylidene complex **2** have very high barriers. The rate-determining step of the two-step mechanism via intermediate **3** is the 1,3-hydrogen migration **3** → **2**, which has an activation barrier of 85.5 kcal/mol with respect to **1** (Table 1). However, the direct 1,2-hydrogen migration **1** → **2** is only marginally favored over the two-step process, because **TS1** is 84.8 kcal/mol higher in energy than **1**. It follows that the intramolecular formation of

the vinylidene complex should not play a role in the acetylene polymerization reaction.

It is instructive to compare the two-step process **1** → **3** → **2** with the recently published results of Wakatsuki, Morokuma, et al.[9] for the same reaction sequence of the system [Cl(PH$_3$)$_2$Rh(HCCH)] → [Cl(PH$_3$)$_2$RhH(CCH)] → [Cl(PH$_3$)$_2$Rh(CCH$_2$)]. The main difference is that the hydridoacetylide intermediate [Cl(PH$_3$)$_2$RhH(CCH)] is only 9.4 kcal/mol higher in energy than the acetylene complex [Cl(PH$_3$)$_2$Rh(HCCH)] while in our system **3**, is 50.5 kcal/mol less stable than **1**. The energy differences can be traced back to the different M−CCH interactions in [Cl(PH$_3$)$_2$RhH(CCH)] and **3**. The calculated Rh−C distance in [Cl(PH$_3$)$_2$RhH(CCH)] is 0.123 Å shorter than that in [Cl(PH$_3$)$_2$Rh(HCCH)], while the W−C bond length in 3 is 0.014 Å longer than that in **1**. The more electron-rich d^8 metal Rh(I) can interact better with the CCH ligand than the d^0 metal W(VI). The activation barriers of the two-step mechanism become very similar for the two systems studied by Wakatsuki, Morokuma, et al.[9] and by us when the energies of the hydridoacetylide intermediates are used as reference values.

Structures and Bonding

The acetylene complex **1** and the vinylidene complex **2** have been previously calculated at the HF/II level of theory.[17d] The BP86/II-optimized geometries are very similar to the HF/II-derived structures. This is not surprising because systematic studies have shown that the geometries of transition-metal compounds in high oxidation states which are calculated at the HF level are in good agreement with experiment and correlation effects are not very important.[23] The theoretically predicted W−C and C−C bond lengths of **1** at BP86/II (2.001 and 1.318 Å) conform with the experimental values for the related complex [Cl$_4$W(PhCCPh)] (1.990 and 1.330 Å).[19c] We think that the geometries shown in Figure 1 are quite accurate.

The calculated bond lengths of the hydridoacetylide compound **3** indicate a W−C single bond and a C=C triple bond. The NBO analysis discussed below supports the interpretation. The W−C distances and particularly the C−C bond length of **TS1** are clearly longer than in **1**. The migrating hydrogen atom H* is much closer to C6 than to C7 (Figure 1). The long W−H* distance of 2.422 Å shows that there is only a negligible interaction between tungsten and H*. Transition-state **TS1** resembles a complex with a π-bonded vinylidene ligand, which is not a minimum on the WF$_4$C$_2$H$_2$ potential-energy surface. The strong deformation of the C$_2$H$_2$ ligand and the rather long distances between the WF$_4$ moiety and the C$_2$H$_2$ fragment com-

(34) To investigate the influence of the different basis sets II and III on the relative energies calculated at BP86, we carried out energy calculations at BP86III using BP86/II-optimized geometries. The relative energies ΔE are **2**, 12.6 kcal/mol; **3**, 51.2 kcal/mol; **TS1**, 83.6 kcal/mol; **TS2**, 72.8 kcal/mol; **TS3**, 87.2 kcal/mol.

pared to **1** and **2** explain why **TS1** is energetically so unfavorable. Acetylene and vinylidene are much more stabilized than the nonplanar transition state by bonding interactions with WF_4.

The transition-state structure **TS2** which connects the acetylene complex **1** and the hydridoacetylide compound **3** is quite interesting because the C–C distance is longer (1.363 Å) than in **1** (1.318 Å) and **3** (1.220 Å). Also, the terminal CCH moiety has a rather acute bonding angle of 113.2°. This is very different than the reported transition state for the corresponding rearrangement in the system $[Cl(PH_3)_2Rh(HCCH)] \rightarrow [Cl(PH_3)_2RhH-(CCH)]$.[9] Here, the transition state has a nearly linear CCH geometry and a rather short C–C distance (1.227 Å). The W–C interaction in **TS2** is very strong, as indicated by the rather short distance of 1.903 Å, which is only slightly longer than the W=C double bond length in **2** (1.831 Å, Figure 1). The Rh–C distance in the transition state for the reaction $[Cl(PH_3)_2Rh(HCCH)] \rightarrow [Cl(PH_3)_2RhH(CCH)]$ becomes even longer than in the acetylene complex.[9] The difference emphasizes the importance of the electron configuration of the transition metal. The transition state for the 1,3-hydrogen migration **TS3** also shows clear differences from the transition state for the process $[Cl(PH_3)_2RhH(CCH)] \rightarrow [Cl(PH_3)_2-Rh(CCH_2)]$. **TS3** has a W–C distance which is even longer, 0.023 Å, than the W–C single bond in **1**, while the corresponding transition state in the Rh(I) system has a Rh–C bond length which is 0.203 Å shorter than in the acetylene complex.[9] The rather short W–C bond lengths of **1** and **2** indicate that the acetylene complex **1** should be considered as a metallacyclopropene and that **2** is a metallaallene rather than a vinylidene complex. We recently presented an analysis of the bonding situation in transition-metal complexes in high and low oxidation states with π-bonded ligands.[17a–c] By employing the charge decomposition analysis (CDA)[35] to the wave function of $[Cl_4W(HCCH)]$ and $[(CO)_5W(HCCH)]$, it could be shown that the former compound is a metallacyclopropene while the latter is a true donor–acceptor complex where the W–(HCCH) interactions can be interpreted in terms of the Dewar–Chatt–Duncanson model.[36] In the CDA method, the wave function of the complex is formed by a linear combination of the molecular orbitals of the chosen fragments. Analysis of the mixing of the occupied and unoccupied orbitals of the fragments reveals quantitative information about the extent of donation, back-donation, and repulsive polarization between the fragments. The crucial difference between the metallacycle and the π-complex was that the former compound had a significant contribution of the mixing of the unoccupied orbitals of both fragments to the electron density of the complex, which is not a physical result. The conclusion is that the electronic structure of the metallylcyclic compound cannot be discussed in terms of orbital mixing between the electronic ground state of the closed-shell fragments.[17a–c] Application of the CDA method to **1** and **2** using WF_4 and C_2H_2 as fragments gave the same

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(36) (a) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C79. (b) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2929.

Table 2.   NBO Analysis of the Bond Orbitals at BP86/II

bond orbital		1	2	3	TS1	TS2	TS3
W–C6 (σ)	occ.	1.93	2.00	1.92	1.92	1.78	1.86
	%W	37.71	32.74	29.38	36.34	12.80	32.62
	%s	11.98	16.91	25.87	13.87	0.04	21.31
	%p	0.15	0.03	1.21	0.17	3.14	0.07
	%d	87.87	83.06	72.92	85.96	96.82	78.62
	%C	62.29	67.26	70.62	63.66	87.20	67.38
	%s	25.19	48.81	46.92	20.78	9.98	21.69
	%p	74.74	51.16	53.06	79.15	89.90	78.28
W–C6 (π)	occ.		1.96				
	%W		52.85				
	%s		0.00				
	%p		0.63				
	%d		99.37				
	%C		47.15				
	%s		0.00				
	%p		99.95				
W–C7 (σ)	occ.	1.93			1.89	1.87	1.77
	%W	37.71			49.55	37.29	65.53
	%s	11.98			9.54	23.63	0.49
	%p	0.15			0.37	0.63	0.88
	%d	87.87			90.09	75.74	98.62
	%C	62.29			50.45	62.71	34.47
	%s	25.19			5.20	17.82	0.45
	%p	74.74			94.52	82.08	99.52
C6–C7 (σ)	occ.	1.98	2.00	1.99	1.96	1.98	1.99
	%C6	50.00	49.22	49.12	56.84	46.24	50.77
	%s	34.77	51.02	52.41	27.43	50.63	43.21
	%p	65.13	48.91	47.52	72.43	49.23	56.67
	%C7	50.00	50.78	50.88	43.16	53.76	50.23
	%s	34.77	38.05	51.62	25.27	42.84	50.60
	%p	65.13	61.85	48.30	74.43	57.08	49.33
C6–C7 (π)	occ.	1.66	1.78	1.94			1.93
	%C6	50.00	54.99	49.29			53.28
	%s	0.22	0.00	0.31			0.00
	%p	99.78	99.99	99.61			99.87
	%C7	50.00	45.01	50.71			46.72
	%s	0.22	0.00	0.15			0.00
	%p	99.78	99.92	99.77			99.90
C6–C7 (π)	occ.		1.84				
	%C6		55.54				
	%s		0.00				
	%p		99.96				
	%C7		44.46				
	%s		0.00				
	%p		99.91				
W1–H7 (σ)	occ.		1.82				
	%W		47.92				
	%s		17.38				
	%p		2.66				
	%d		79.96				
	%H		52.08				
	%s		99.84				

results, i.e., mixing of the unoccupied orbitals of the fragments contributes significantly to the charge distribution of the compounds. It follows that **1** and **2** are not really complexes but metallacyclopropene (**1**) and metallaallene (**2**). Since the electronic state of the CCH_2 moiety of an allene corresponds to triplet ($^3B_2$) vinylidene, it is not surprising that the rearrangement **1** $\rightarrow$ **2** proceeds via transition state **TS1**, which has a nonplanar C_2H_2 moiety.

The NBO analysis of **1** and **2** is in agreement with the conclusions from the CDA results. Table 2 shows the occupied natural bond orbitals of the calculated structures. Compound **1** has two W–C σ-bonds and a C=C double bond. The W–C bonds of **1** are clearly polarized toward the carbon end (62.3% at C). The hybridization at C is sp^3, while the bonding at tungsten has mainly d character (88% d).[37] Compound **2** has W=C and C=C double bonds. The W–C ρ-bond in **2** is even

Table 3. NBO Partial Atomic Charges q and Atom Electronic Configuration at BP86/II

	q						W				C$_6$		C$_7$	
	W	C$_6$	C$_7$	H$_8$	H$_9$	F	6s	5d	6p	6d	2s	2p	2s	2p
1	2.25	−0.40	−0.40	0.26	0.26	−0.49	0.29	3.38	0.02	0.01	1.11	3.26	1.11	3.26
2	2.19	−0.41	−0.33	0.26	0.26	−0.49	0.31	3.44	0.03	0.05	1.15	3.23	1.10	3.21
3	2.18	−0.42	−0.12	−0.04	0.26	−0.46/−0.47	0.36	3.40	0.02	0.05	1.12	3.27	1.04	3.07
TS1	2.23	−0.88	−0.07	0.30	0.37	−0.47/−0.50	0.30	3.37	0.01	0.07	1.18	3.67	1.63	2.42
TS2	2.36	−0.19	−0.77	0.19	0.29	−0.46/−0.48	0.31	3.27	0.02	0.05	1.37	2.80	1.14	3.61
TS3	2.06	−0.65	−0.11	0.28	0.43	−0.49/−0.51	0.38	3.48	0.03	0.05	1.17	3.44	1.05	3.05

more polarized toward the carbon atom which is sp-hybridized (67.3% at C) than in **1**, while the W–C π-bond is slightly polarized toward tungsten (52.9% at W). The hydridoacetylene compound **3** has a W–C single bond which is strongly polarized toward the carbon end (70.6% at C) and has a C≡C triple bond (Table 2). The W–H bond is slightly polarized toward hydrogen (52.1% at H).

Table 3 shows the calculated charge distribution and the atomic electron configurations of the calculated structures. The C$_2$H$_2$ ligand always carries a small negative partial charge. The C$_\alpha$ atom of the vinylidene ligand in **2** has nearly the same electron configuration as C$_\beta$(H$_2$). Thus, the in-plane p(π) orbital of C$_\alpha$, which is formally empty in free vinylidene, is occupied in **2**. This explains why the direct tautomerization **1** → **2** proceeds via a nonplanar transition state as calculated for the negatively charged free species[14] and neutral triplet states.[16]

Summary and Conclusion

Two energetically nearly degenerate pathways have been found for the rearrangement of the tungsten acetylene complex **1** to the energetically higher lying vinylidene complex **2**, which is 10.4 kcal/mol less stable than **1**. The direct 1,2-hydrogen migration proceeds via transition-state **TS1**, which has a nonplanar C$_2$H$_2$ moiety. The activation barrier for this process is 84.8 kcal/mol. The alternative pathway involves the alkynyl-(hydrido)metal complex **3**, which is 50.5 kcal/mol higher in energy than **1**. The rate-determining step of the two-step process is the 1,3-hydrogen migration **3** → **2**, which has a barrier of 85.5 kcal/mol. Because both reaction pathways have very large activation barriers, it seems unlikely that the intramolecular rearrangement between the acetylene and vinylidene complex plays a role in the transition-metal-catalyzed acetylene polymerization reaction using high-valent transition-metal compounds as the catalyst. The NBO bonding analysis and the results of the CDA partitioning scheme show that **1** and **2** should be considered as metallacyclopropene and metallaallene, respectively. The C$_2$H$_2$ ligand always carries a small negative partial charge. The C$_\alpha$ atom of the CCH$_2$ ligand in **2** has an occupied in-plane p(π) orbital. This explains why the transition state **TS1** has a nonplanar C$_2$H$_2$ ligand, which is similar to the transition state for the rearrangement of the free C$_2$H$_2$ ligand in the triplet state or as an anion.

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(37) One referee pointed out that the sp³ hybridization at the carbon atoms does not agree with the description of **1** as metallacyclopropene, which should have sp²-hybridized carbon atoms. Table 2 shows that the C–C σ-bonds of **1** are indeed sp² hybridized. The W–C bonds are bent bonds, which have higher p character at the carbon end than a normal bond with a 120° bond angle at C. There would be a deviation from sp² even with a 120° bond angle, because of the different electronegativities of the atoms.[38] While the W–C bonds have a higher %p character at carbon than sp², the C–H bonds have a higher %s character (40%, not shown in Table 2).

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