

Insertion and σ -bond metathesis reactions of acetylene with $(C_5H_5)_2ZrCH_3^+$. All-electron density functional (B3LYP) study

Isabella Hyla-Kryspin*, Rolf Gleiter

Organisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

Dedicated to Professor Günter Helmchen on the occasion of his 60th birthday

Abstract

All-electron DFT (B3LYP) calculations with a split-valence basis set of double- and triple- ξ quality have been used to study the reaction paths of the first and second step insertion as well as of the σ -bond metathesis for the reaction of acetylene with $(C_5H_5)_2ZrCH_3^+$. Geometry optimizations of the reactants, intermediates, transition states and products were carried out without symmetry constraints. The nature of the particular points on the potential energy surfaces was verified by the analytical calculation of the Hessian matrices. The relative electronic energies are corrected for ZPVE, entropic and thermal contributions, and correspond to the Gibbs free energies ($\Delta\Delta G^{298}$). It is shown that the propagation step of acetylene polymerization is a facile process from kinetic and thermodynamic point of view, and that the investigated insertion reactions are kinetically and thermodynamically favoured over the σ -bond metathesis reaction. The calculated energetics and structures of either reaction are compared with available theoretical and experimental data of relevant complexes of group III and IV transition metals. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Theoretical study; DFT (B3LYP); Acetylene polymerization; Cationic zirconocene; Insertion reaction; σ -Bond metathesis reaction

1. Introduction

The reactions of hydrocarbons with electron-deficient d^0 transition metal complexes and d^0f^n lanthanide complexes are of considerable practical importance [1]. The usefulness of these reac-

tions comes from the ability of the d^0 and d^0f^n metals to mediate the breaking and formation of H–H and C–H bonds. To the wide range of these reactivities belong the industrially important Ziegler–Natta catalysis of olefin polymerization [2–5] as well as σ -bond metathesis with both, saturated and unsaturated, hydrocarbons [6,7]. The reaction of unsaturated hydrocarbons are of special interest, because alternative pathways were observed. Thus, alkenes and alkynes can react either by insertion into metal–R (R = H, alkyl, alkynyl) [8–13] bonds, or by an activation of the C–H bonds in a σ -bond

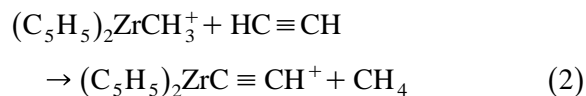
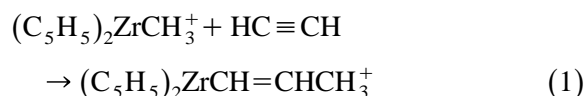
* Corresponding author. Tel.: +49-6221-544367; fax: +49-6221-544205.

E-mail address: ihk@oskar.oci.uni-heidelberg.de (I. Hyla-Kryspin).

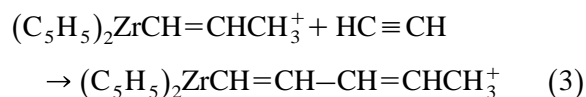
metathesis reaction [6,14–21]. Several experimental [8–25] and theoretical [26–33] studies have been undertaken in order to understand the mechanism of these reactions. However, there is no experimental information about what happens on the molecular level when unsaturated hydrocarbons approach the active catalyst. It has been postulated that both reactions begin with the precoordination of the hydrocarbon to the vacant coordination site of the metal and proceed via a four-membered transition state. In the case of the insertion reactions, π -complexes (**A**) (Scheme 1) are commonly accepted as intermediates in the beginning of the reaction [33]. There is no agreement about the intermediates of the early stage of the σ -bond metathesis reaction.

On the basis of DFT calculations on the activation of the alkenylic and alkynylic C–H bonds by $(C_5H_5)_2Sc-R$ ($R = H, CH_3$), Ziegler et al. [28] postulated that σ -bond metathesis begins with the formation of the tight adducts (**B**) (Scheme 1) in which the C–H bond undergoes an agostic interaction with scandium. However, our previous MP2//HF (single-point Møller–Plesset perturbation calculations for structures optimized at the Hartree–Fock level) on the reaction of acetylene with the model compounds Cl_2Zr-R^+ ($R = H, CH_3$) pointed out, that σ -bond metathesis begins with the same intermediate as the insertion reaction, i.e. with the π -complex (**A**) [29]. Our results demonstrated, that C–H adducts, such as structures (**B**) do not correspond to local minima on the potential energy surface. Since in our previous study [29,32,34] correlation effects were not

taken into account for geometry optimizations as well as due to the simplified nature of the model catalyst Cl_2Zr-R^+ , in the present paper we will report the results of DFT investigations with the B3LYP method on the reaction of acetylene with $(C_5H_5)_2ZrCH_3^+$ (Eqs. (1) and (2)).

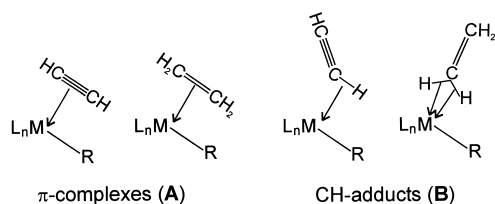


It has been repeatedly shown that the B3LYP approach is the most reliable one in modern DFT, especially for the investigations of transition metal compounds [35,36]. Furthermore, we will also discuss the calculated energetics and structures of the second step of acetylene insertion (Eq. (3)), which should give some insight on the propagation step of Ziegler–Natta acetylene polymerization.



2. Calculation details

All calculations were carried out with the hybrid Hartree–Fock/density functional theory method, known in the literature by its acronym B3LYP [37–39]. We have chosen this method since, in addition to some benchmark jobs, a number of recent studies have convincingly demonstrated that the B3LYP functional is quite reliable in both geometry and energy, and in the case of transition metal compounds, affords correct results at moderate computational costs [35,36,40–43]. A single all-electron basis set was used throughout the present studies. The Zr atom was described by a (14s,9p,7d) basis set obtained by adding a p-type exponent (0.12) to the optimized (14s,8p,7d) set by Hyla–Kryspin



Scheme 1.

et al. [44]. The choice of the additional p-exponent guarantees a comparable distribution of the radial density functions of 5p and 5s orbitals. The contraction is [6s,4p,4d] and corresponds to a single- ξ description for the inner and the 5p shell, double- ξ for 5s and triple- ξ for 4d. Carbon and hydrogen were described by Dunning's standard split-valence D95 basis set [45]. All geometries were optimized using analytical gradient procedures. The presented structures correspond to fully converged geometries with gradients and displacements below the standard thresholds implemented in Gaussian 98. The analytically calculated force constant matrices were used for characterization of the stationary points (minima or transition states) and for determination of zero point vibrational energy (ZPVE) and thermal corrections. For the location of the transition states we have used the QST3 transition state searcher procedure. All geometry optimizations were carried out without symmetry constraints, since unexpected negative eigenvalues appeared for minima in the case of symmetric structures. The relative energies are corrected for ZPVE, entropic and thermal contributions and correspond to Gibbs free energies at 298 K, ($\Delta\Delta G^{298}$). Thus, the calculated results provide informations directly comparable to the experimental observations. The calculations were carried out with the Gaussian 98 program [46] installed on the IBM RS/6000 workstations of our laboratory and of the Universitätsrechenzentrum Heidelberg.

3. Results and discussion

The optimized stationary structures of the investigated reaction paths are shown in (Figs. 1, 3 and 4) and the most important bond distances are collected in Tables 1 and 3. The calculated electronic and thermochemical data are presented in Tables 2 and 4. The theoretical $\Delta\Delta G^{298}$ values for the reaction paths from Eqs. (1) and (2) are compared in Fig. 2.

3.1. Early stage of the insertion and σ -bond metathesis reactions of acetylene-2 with $(C_5H_5)_2ZrCH_3^+-1$

In reactant **1** the optimized Zr–C2–H3 bond angle of 93.3° deviates from the normal sp^3 value and the C2–H3 bond distance is elongated to 1.123 Å. Both features are indicative for an α -agostic interaction between the C2–H3 σ -bond of the methyl group and the zirconium center [47]. The agostic C2–H3 bond lies in the plane of Zr($d\sigma$)–LUMO [32,48], as required for a three-center two-electron (3c-2e) interaction. To our knowledge cationic complex **1** has never been directly observed in experimental investigations, but its THF analogue $(C_5H_5)_2Zr-(CH_3)(THF)^+-1a$ has been isolated and studied by Jordan et al. [25]. Thus, we can compare the optimized structure of **1** with the X-ray data measured for **1a** [25]. The average Zr–C(Cp) (Cp = C_5H_5) distance of **1a** (2.487 Å) is in excellent agreement with our finding (2.491 Å), but the Zr–C2 distance of **1** is by 0.043 Å shorter. This small discrepancy we ascribe to the THF ligand which, though labile, influences the coordination of the methyl group in **1a**. The methyl hydrogen atoms were not located in **1a** [25]. If we approach acetylene to complex **1**, the resulting structure converges to the π -complex **3**. During acetylene coordination, the methyl group rotates around the Zr–C2 bond and the “in-plane” α -agostic interaction $\sigma(C2-H3) \rightarrow Zr$ vanishes. The rotation of the methyl group allows an electron density transfer from acetylene π -orbital to the low lying Zr($d\sigma$)–LUMO [32,48], which in complex **1** was involved in the interaction with the C3–H3 σ -bond. Nevertheless, the C2–H3 bond of **3** receives a weak interaction with the empty high lying “out-of-plane” Zr($d\pi$)-orbital, as it can be seen from the slightly elongated C2–H3 distance (1.101 Å) with respect to the “out-of-plane” C2–H4/H5 bonds of complex **1**. For complex **3** we observe an elongation of the Zr–C2 distance from 2.213 Å in **1** to 2.243 Å in **3** and a small elongation of acetylene C6≡C7 triple

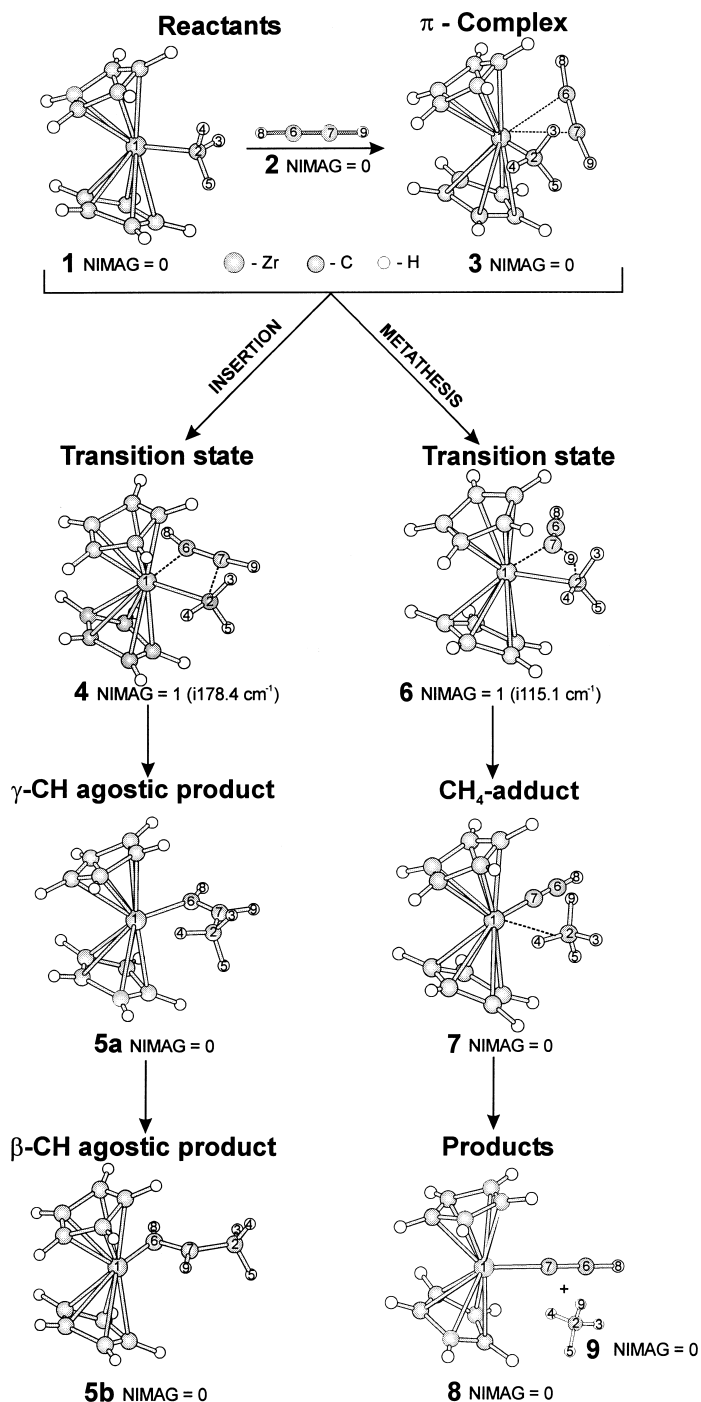


Fig. 1. Optimized stationary structures and number of imaginary frequencies (NIMAG) for the first step insertion and σ -bond metathesis reactions.

bond, from 1.222 Å in **2** to 1.230 Å in **3**. The coordination of acetylene in complex **3** is not

symmetric. The distance Zr–C7 is by 0.147 Å shorter than Zr–C6. The Zr, C2, C6, and C7

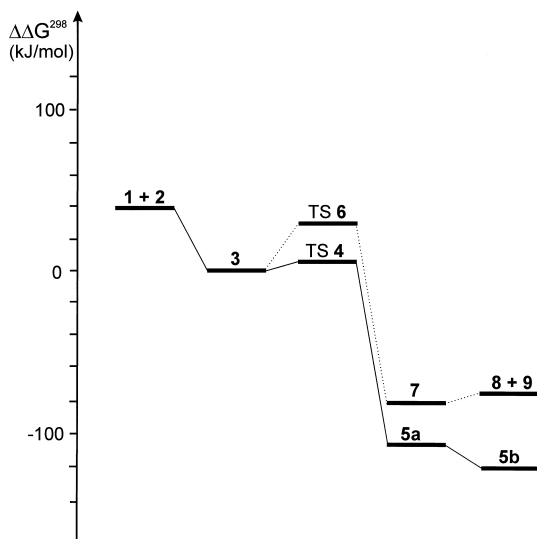


Fig. 2. Theoretical thermochemical data for the first step insertion and σ -bond metathesis reactions.

atoms of **3** do not lie in the same plane, as it is normally the case when π -complexes **A** are

optimized under the C_s -symmetry constraints [26–33]. The optimized dihedral angle C7–C6–Zr–C2 is 64.3° . The “out-of-plane” geometry of the acetylene ligand in complex **3** leads to a greater bending of the Zr(C₅H₅)₂-unit, which in turn lowers the energy of the Zr(d π) orbitals [48] and allows the zirconium center to utilize more efficiently all its empty d-orbitals for bonding interactions in a non-planar conformation. The computed Gibbs free energy ($\Delta\Delta G^{298}$) for the bonding of acetylene in complex **3** amounts to -39.1 kJ/mol, and the calculated ΔE_{elec} , ΔE_0 , and $\Delta\Delta H$ range from -88.7 to -82.3 kJ/mol (Table 2). These values as well as those presented later clearly demonstrate that accounting for theoretical entropy differences is important for a reliable discussion of the calculated data. Similar as in the case of the model catalysts Cl₂ZrR⁺ (R = H, CH₃) [29] we were not able to locate the CH-adduct, such as **B** from Scheme 1, as a local minimum on the

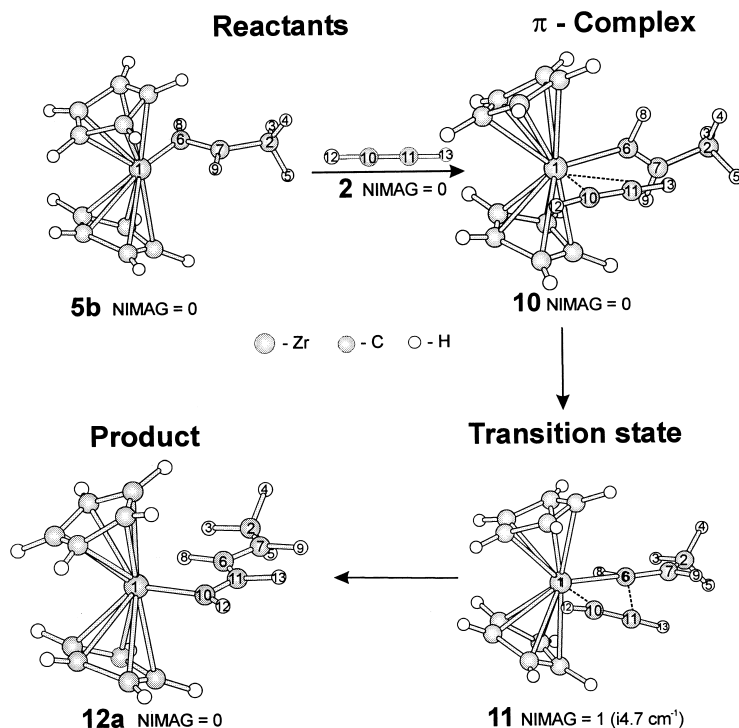
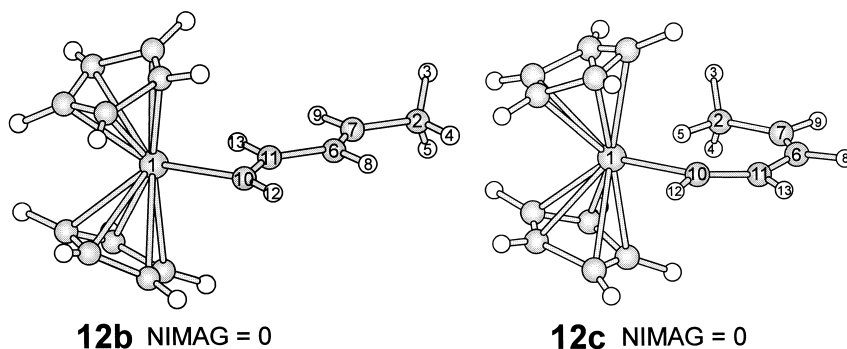


Fig. 3. Optimized stationary structures and number of imaginary frequencies (NIMAG) for the propagation step of Ziegler–Natta acetylene polymerization.

Fig. 4. Optimized structure of the isomers **12b** and **12c**.

potential energy surface. Thus, we assume that both insertion and σ -bond metathesis reactions continue from the π -complex **3**.

3.2. Transition states, intermediates and products of the first step insertion and σ -bond metathesis reactions

The transition states (TS) **4** and **6** for the processes from Eqs. (1) and (2) are planar, four-membered cycles (Fig. 1). It is seen that different distortions in acetylene coordination are necessary to bring the reaction from the π -complex **3** in the two competitive reaction channels. The insertion reaction proceeds via TS **4** to the γ -CH product **5a**, which corresponds to a local minimum on the potential energy surface. Complex **5a** rearranges to the β -CH struc-

ture **5b**, which represents the global minimum for the product from Eq. (1). With respect to **5a**, the β -CH agostic structure **5b** is by 12 kJ/mol more stable. The σ -bond metathesis proceeds via TS **6** to the local minimum of the CH_4 -adduct **7**, which in the late stage of the reaction rearranges to the acetylide product **8** and methane **9** (Fig. 1). The TS **4** and **6** are stabilized by an α -agostic interaction, as suggested by the Zr–C2–H4 bond angles of 85.1° (TS **4**) and 95.6° (TS **6**) and the elongated C2–H4 bond distance of 1.124 Å (TS **4**) and 1.107 Å (TS **6**) (Table 1). It is interesting to note, that α -CH agostic interactions have been proposed to assist the mechanism of olefin insertion reaction on the basis of either experimental [49–51] or theoretical [29–33,52] studies. To our knowledge α -CH agostic interactions were so far not discussed to be operative in the transition states

Table 1

Optimized bond distances (Å) of complexes **1–9**. Bold numbers refer to “agostic bonds”

	1	2	3	TS 4	5a	5b	TS 6	7	8	9
Zr1–C(Cp) _{avr}	2.491		2.518	2.517	2.505	2.505	2.508	2.509	2.489	
Zr1–C2	2.213		2.243	2.242	2.734		2.293	2.692		
C2–H3	1.123		1.101	1.093	1.096	1.095	1.097	1.096		1.095
C2–H4	1.092		1.098	1.124	1.118	1.098	1.107	1.110		1.095
C2–H5	1.092		1.099	1.093	1.096	1.098	1.097	1.095		1.095
Zr1–C6			2.787	2.475	2.157	2.171				
Zr1–C7			2.640	2.798	2.662	2.566	2.384	2.171	2.163	
C6–C7		1.222	1.230	1.240	1.361	1.345	1.233	1.242	1.244	
C6–H8		1.068	1.070	1.075	1.089	1.088	1.072	1.070	1.070	
C7–H9		1.068	1.071	1.072	1.092	1.136	1.147	3.068		
C2–C7			3.413	2.665	1.548	1.511		3.476		
C2–H9			3.486	2.626	2.181	2.180	1.800	1.096		1.095

Table 2

Calculated electronic and thermodynamical data (kJ/mol) for the first step insertion and σ -bond metathesis reactions ($T = 298.15$ K, pressure = 1 atm)

	Compounds	ΔE_{elec} MP2//HF ^a	ΔE_{elec}	ΔE_0^b	$\Delta\Delta H$	$\Delta\Delta G$
Insertion	1 + 2	+124.6	+88.7	+82.3	+83.6	+39.1
	3	0.0	0.0	0.0	0.0	0.0
	TS 4	+15.5	+10.2	+6.2	+4.4	+5.7
	5a	-67.3	-121.2	-108.6	-119.9	-108.6
	5b		-130.5	-119.0	-121.9	-120.7
Metathesis	1 + 2	+124.6	+88.7	+82.3	+83.6	+39.1
	3	0.0	0.0	0.0	0.0	0.0
	TS 6	+75.6	+33.7	+29.3	+27.1	+28.6
	7	-54.8	-84.1	-78.4	-77.7	-81.0
	8 + 9	+13.2	-33.8	-34.5	-32.7	-75.7

^aModel catalyst $\text{Cl}_2\text{ZrCH}_3^+$; Ref. [29].

^b $E_0 = E_{\text{elec}} + \text{ZPVE}$.

of the σ -bond metathesis reactions. It should be mentioned, however, that the α -CH agostic interaction of the TS **6** is weaker than of the TS **4**. Both TS are asynchronous with regard on the formation of the new bonds. The formation of the Zr–C6 (2.475 Å: TS **4**) and Zr–C7 (2.384 Å: TS **6**) is more advanced than for the C2–C7 (2.665 Å: TS **4**) and C2–H9 (1.800 Å: TS **6**) bonds. The alkylylic CH activation in the TS **6** is more advanced than the transformation of the acetylic triple bond to the vinylic double bond in the TS **4** (Table 1). Cationic 14 valence electrons (VE) Zr–acetylide complexes are un-

known. Nevertheless, the optimized Zr–C7 and C7–C6 bond lengths as well as the average Zr–C(Cp) distance in complex **8** reproduce almost exactly the X-ray data reported for 16 VE $\text{Cp}_2\text{Zr}(-\text{C}\equiv\text{CR})_2$ species [53–55]. Cationic 14VE Zr–vinyl complexes are known, and the optimized bond distances of the insertion product **5b**, Zr–C6 (2.171 Å), C6–C7 (1.345 Å) and $\text{Zr}-\text{C}(\text{Cp})_{\text{avr}}$ (2.505 Å) agree very well with the respective values of 2.180, 1.334 and 2.513 Å, from the X-ray data of $\text{rac-C}_2\text{H}_4(\text{indenyl})_2\text{ZrC}(\text{SiMe}_3)=\text{CMe}_2^+$ [10]. The computed $\Delta\Delta G^{298}$ values of both reactions are displayed in Fig. 2. The calculated energy barrier of the σ -bond metathesis (28.6 kJ/mol) is about five times greater than in the case of the insertion reaction (5.7 kJ/mol). In the TS **6**, the loss of energy from CH activation is not recompensated for by the energy of new bond formations.

Table 3

Optimized bond distances (Å) of the stationary structures for the propagation step of acetylene polymerization. Bold numbers refer to “agostic bonds”

	10	TS 11	12a	12b	12c
Zr1–C(Cp) _{avr}	2.516	2.522	2.509	2.507	2.508
Zr1–C6	2.197	2.173			
C6–C7	1.372	1.345	1.357	1.359	1.360
C7–C2	1.508	1.514	1.503	1.504	1.507
C6–H8	1.105	1.159	1.116	1.088	1.090
C7–H9	1.093	1.096	1.092	1.095	1.091
C2–H3	1.100	1.096	1.097	1.099	1.098
C2–H4	1.095	1.099	1.099	1.095	1.098
C2–H5	1.100	1.098	1.099	1.099	1.108
Zr1–C10	2.650	2.479	2.150	2.155	2.135
Zr1–C11	2.884	2.791			
C10–C11	1.229	1.241	1.371	1.356	1.355
C6–C11	3.088	2.719	1.495	1.461	1.478
C10–H12	1.073	1.074	1.090	1.089	1.130
C11–H13	1.071	1.069	1.091	1.133	1.093

Table 4

Theoretical thermochemical data (kJ/mol) for the propagation step of acetylene polymerization ($T = 298.15$ K, pressure = 1 atm)

Compounds	ΔE_{elec}	ΔE_0^a	$\Delta\Delta H$	$\Delta\Delta G$
5b + 2	+72.1	+65.8	+66.0	+32.8
10	0.0	0.0	0.0	0.0
TS 11	+15.4	+10.9	+7.8	+16.5
12a	-132.5	-121.4	-125.7	-118.9
12b	-133.5	-122.9	-126.7	-122.3
12c	-119.4	-107.7	-112.5	-105.9

^a $E_0 = E_{\text{elec}} + \text{ZPVE}$.

Furthermore, with respect to TS **4**, the TS **6** loses π -complexation energy, which in addition to the strong agostic interaction keeps the energy barrier of the insertion reaction at a small value. The calculated overall exothermicity of the insertion reaction (-159.8 kJ/mol) is greater than in the case of σ -bond metathesis reaction (-114.8 kJ/mol). From our estimates it follows that insertion reaction from Eq. (1) should be kinetically and thermodynamically favoured over the σ -bond metathesis reaction from Eq. (2). Note that zirconium does, in fact, favour insertion [56]; both reactions are feasible with lutetium [57], while for scandium only CH-activation was observed [16]. The reaction of acetylene with $(C_5H_5)_2ScCH_3$ was theoretically investigated by Ziegler et al. [28]. In contrast to the experimental observations [16], the authors found that insertion should be favoured over the σ -bond metathesis. Similar conclusions were presented by Rappe [27] for the model complex Cl_2ScH . Note, however, that experiments for scandium were carried out with methylated derivatives of the pentadienyl ligands and theoretical investigations with C_5H_5 or Cl should be only viewed as a model picture for the really existing systems. The calculated by Ziegler et al. [28] alkylic CH-activation at Sc proceeds with low energy barrier of 14 kJ/mol and is by -128 kJ/mol exothermic, while the exothermicity of the insertion reaction is greater (-193 kJ/mol). These values can only be compared with our ΔE_{elec} , since ZPVE, thermal corrections and entropy differences were not considered for the $(C_5H_5)_2ScCH_3-C_2H_2$ system [28]. From the comparison, it follows that CH-activation at Sc has a lower energy barrier and greater exothermicity than at Zr, which approximatively agrees with the experimentally observed trends [16,56,57].

3.3. Propagation step of Ziegler–Natta acetylene polymerization

We proceed with the second step of acetylene insertion from the global minimum of the first

step insertion, i.e. from the β -CH agostic product **5b**. The corresponding stationary structures are shown in Fig. 3 and the calculated energetics are presented in Table 4. At the start of propagation, we encounter again the π -complex, structure **10**, whose geometry differs slightly from those of complex **3** (Figs. 1 and 3). In complex **10** the incoming acetylene adopts an “in-plane” conformation and it is seen that the vinyl ligand is rotated around the Zr–C6 bond. As in the case of **3**, complex **10** is stabilized by an “out-of-plane” $\sigma(C6-H8) \rightarrow Zr$ agostic interaction (Table 3). The Zr–C10 distance in complex **10** (2.650 Å) is virtually the same as the Zr–C7 distance (2.640 Å) in the precursor **3**, but the Zr–C11 distance is by 0.097 Å longer. The bonding energy of acetylene in **10** (-32.8 kJ/mol) is slightly lower than in **3** (-39.1 kJ/mol) (Tables 2 and 4). TS **11** is stabilized by a strong α -CH agostic interaction, as manifested by the acute Zr–C6–H8 bond angle of 73.7° and a short Zr–H8 distance of 2.158 Å. We notice that “agostic hydrogens” in cationic zirconocene complexes have been located experimentally at Zr–H_a distance of 2.160 Å [12]. In spite of the strong agostic interaction in TS **11**, the activation barrier is higher ($+16.5$ kJ/mol) than in the case of the first step insertion ($+5.7$ kJ/mol). This is due to the distortion of the vinyl ligand, which is necessary for the development of the C6–C11 bond (Fig. 3, Table 3). However, in TS **11**, the C6–C11 distance is still long (2.719 Å) and the distortion energy of the vinyl ligand cannot be recompensated for by the energy from C–C coupling. The direct insertion product, **12a**, is stabilized by a γ -CH agostic interaction. The overall exothermicity of the second step insertion (-151.7 kJ/mol) does not differ much from the first step insertion (-147.7 kJ/mol). The 1,3-dienyl ligand of **12a** may be regarded as a building block for polyacetylene with predominantly *cis* conformation. In Fig. 4, we present the optimized structures of two isomers **12b** and **12c**, which may be regarded as starting materials for polyacetylene in *trans* (**12b**) and

cis (**12c**) conformations. Both structures are stabilized by an agostic interaction (β -CH (**12b**), α -CH (**12c**)) (Table 3). The most stable structure corresponds to *trans*-**12b**, which is lower in energy than the *cis* conformers **12a** (+3.4 kJ/mol) and **12c** (+16.4 kJ/mol) (Table 4). It is interesting to note, that acetylene polymerization in the presence of $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4/\text{Al}(\text{C}_2\text{H}_5)_3$ as catalyst system, known as the Shirikawa route for polyacetylene [58–64], leads at lower temperature to a material containing a high percentage of *cis* double bonds, which upon heating isomerizes to the predominantly *trans* isomer [61,62]. Furthermore, it has been found experimentally that the *cis/trans* polyacetylene isomerization is an exothermic reaction [61,62]. Our results concerning the mechanism of the propagation step in Ziegler–Natta (C_5H_5)₂ZrCH₃⁺ acetylene polymerization as well as the relative stability of *trans* **12b** over *cis* **12a/12c** agree well with the experimental findings.

4. Conclusions

In the present paper we investigated the competing reactions of $(\text{C}_5\text{H}_5)_2\text{ZrCH}_3^+$, **1**, with acetylene, **2**, concerning the insertion of **2** into Zr–C bond of **1** and the activation of alkynyl C–H bond in a σ -bond metathesis reaction. Both reactions start with the formation of the π -complex, **3**, and proceed through a four-membered transition state (TS **4** (Eq. (1)) or TS **6** (Eq. (2))) to the vinyl product, **5a**, (Eq. (1)) or acetylide complex, **8**, and methane, **9** (Eq. (2)). Characteristic for both transition states are α -CH agostic interactions. The direct insertion product, **5a**, is stabilized by γ -CH agostic interaction and rearranges to the more stable β -CH agostic isomer, **5b**. Our calculations indicate that insertion of acetylene into the Zr–C bond (Eq. (1)) is preferred kinetically ($\Delta\Delta G^\ddagger(\text{TS } \mathbf{4}) = +5.7$ kJ/mol, $\Delta\Delta G^\ddagger(\text{TS } \mathbf{6}) = +28.6$ kJ/mol) and thermodynamically ($\Delta\Delta G(\mathbf{5b}) = -159.8$ kJ/mol, $\Delta\Delta G(\mathbf{8} + \mathbf{9}) = -114.8$

kJ/mol) over the alkynyl CH activation (Eq. (2)). Although the investigations with a model catalyst $\text{Cl}_2\text{ZrCH}_3^+$ led to similar conclusions, the calculated energetics differ significantly from those of the more realistic systems (Table 2). The second part of our studies was concerned with the propagation step in Ziegler–Natta acetylene polymerization (Eq. (3)). The mechanism of the second step of acetylene insertion does not differ much from those of the first step insertion. The reaction proceeds from **5b** to the π -complex **10** ($\Delta\Delta G(\mathbf{10}) = -32.8$ kJ/mol) and continues through TS **11** ($\Delta\Delta G^\ddagger(\text{TS } \mathbf{11}) = +16.5$ kJ/mol) to the γ -CH agostic product **12a** ($\Delta\Delta G(\mathbf{12a}) = -151.7$ kJ/mol). The activation barrier of the second step insertion reaction is higher and the overall exothermicity slightly lower than in the case of the first step insertion. The 1,3-dienyl ligand of **12a** and **12c** may be regarded as a building unit for polyacetylene in predominantly *cis*-conformation. The *trans* isomer **12b** is lower in energy and should be regarded as the thermodynamically favoured product in the propagation step of Ziegler–Natta acetylene polymerization. Our computed data are in all aspects in agreement with the available experimental observations concerning the investigated reaction mechanisms.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft (SFB 247), the state Baden-Württemberg (Landesforschungsschwerpunkt “Katalyse”) and the Fonds der Chemischen Industrie is gratefully acknowledged.

References

- [1] G.W. Parshal, Homogenous Catalysis, Wiley, NY, 1980.
- [2] G. Natta, P. Pino, G. Mazzanti, U. Giannini, J. Inorg. Nucl. Chem. 8 (1958) 612.
- [3] K. Ziegler, H.G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Söll, W.R. Kroll, Justus Liebigs Ann. Chem. 629 (1960) 121.

- [4] J. Boor Jr., Ziegler–Natta Catalysts and Polymerization, Academic Press, NY, 1979.
- [5] G. Fink, R. Mühlaupt, H.H. Brintzinger (Eds.), Ziegler Catalysts, Springer, Heidelberg, 1995.
- [6] J.A. Davis, P.L. Watson, J.F. Liebmann, A. Greenberg (Eds.), Selective Hydrocarbon Activation, VCH, NY, 1990.
- [7] F. Quignard, C. Lecuyer, A. Choplin, D. Olivier, J.M. Basset, *J. Mol. Catal.* 74 (1992) 353.
- [8] R.F. Jordan, R.E. La Point, N.C. Baenziger, G.D. Hinch, *Organometallics* 9 (1990) 1539.
- [9] W. Kaminsky, K. Kulper, H.H. Brintzinger, F.R.W.P. Wild, *Angew. Chem. Int. Ed. Engl.* 31 (1992) 1347.
- [10] A.D. Horton, A.G. Orpen, *Organometallics* 10 (1991) 3910.
- [11] A.D. Horton, A.G. Orpen, *Organometallics* 11 (1992) 8.
- [12] A.S. Guram, R.F. Jordan, 2nd edn., in: M.F. Lappert (Ed.), *Comprehensive Organometallic Chemistry* 4 (1995) p. 589, and references cited.
- [13] A. Haskel, T. Straub, A.K. Dash, M.S. Eisen, *J. Am. Chem. Soc.* 121 (1999) 3014.
- [14] G. Jeske, H. Lauke, H. Mauermann, H. Schumann, T.J. Marks, *J. Am. Chem. Soc.* 107 (1985) 8111.
- [15] J.W. Bruno, G.M. Smith, T.J. Marks, C.K. Fair, A.T. Shulz, J.M. Williams, *J. Am. Chem. Soc.* 108 (1986) 40.
- [16] M.E. Thompson, S.M. Buxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, *J. Am. Chem. Soc.* 109 (1987) 203.
- [17] B.J. Burger, M.E. Thompson, W.D. Cotter, J.E. Bercaw, *J. Am. Chem. Soc.* 112 (1990) 1566.
- [18] M. St. Clair, W.P. Schaefer, J.E. Bercaw, *Organometallics* 10 (1991) 525.
- [19] T. Straub, A. Haskel, M.S. Eisen, *J. Am. Chem. Soc.* 117 (1995) 6364.
- [20] J.L. Polse, R.A. Andersen, R.G. Bergman, *J. Am. Chem. Soc.* 117 (1995) 5393.
- [21] T. Straub, W. Frank, G.J. Reiss, M.S. Eisen, *J. Chem. Soc. Dalton Trans.* (1996) 2341.
- [22] P. Cossee, *J. Catal.* 3 (1964) 80.
- [23] E.J. Arlman, P. Cossee, *J. Catal.* 3 (1964) 99.
- [24] F.S. Dyachkovskii, A.K. Shilova, A.E. Shilov, *J. Polym. Sci.* 16 (1967) 2333, Part C.
- [25] R.F. Jordan, C.S. Bajgur, R. Willet, B. Scott, *J. Am. Chem. Soc.* 108 (1986) 7410.
- [26] M.L. Steigerwald, W.A. Goddard, *J. Am. Chem. Soc.* 106 (1984) 308.
- [27] A.K. Rappe, *Organometallics* 9 (1990) 466.
- [28] T. Ziegler, R. Folga, A. Berces, *J. Am. Chem. Soc.* 115 (1993) 636.
- [29] I. Hyla-Kryspin, S.J. Silverio, S.-Q. Niu, R. Gleiter, *J. Mol. Catal.* 115 (1997) 183.
- [30] H. Weiss, C. Ehrig, R. Ahlrichs, *J. Am. Chem. Soc.* 116 (1994) 4919.
- [31] T. Yoshida, N. Koga, K. Morokuma, *Organometallics* 14 (1995) 746.
- [32] I. Hyla-Kryspin, S.-Q. Niu, R. Gleiter, *Organometallics* 14 (1995) 964.
- [33] P. Margl, L. Deng, T. Ziegler, *J. Am. Chem. Soc.* 120 (1998) 5517.
- [34] R. Gleiter, I. Hyla-Kryspin, S.-Q. Niu, G. Erker, *Organometallics* 12 (1993) 3828.
- [35] C.W. Bauschlicher Jr., A. Ricca, H. Patridge, S.R. Langhoff, in: D.P. Chang (Ed.), *Recent Advances in Density Functional Methods*, World Scientific, Singapore, 1997, Part II.
- [36] B.B. Laird, R.B. Ross, T. Ziegler (Eds.), *Chemical Application of Density Functional Theory*, ACS Symposium Series 629, WA, DC, 1996.
- [37] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [38] C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [39] S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [40] M.R.A. Blomberg, P.E.M. Siegbahn, M. Svensson, *J. Chem. Phys.* 104 (1966) 9546.
- [41] L.A. Curtiss, K. Ragavachari, P.C. Redfern, J.A. Pople, *J. Chem. Phys.* 106 (1997) 1063.
- [42] R.D.J. Froese, D.G. Musaev, T. Matsubara, K. Morokuma, *J. Am. Chem. Soc.* 119 (1997) 7190.
- [43] I. Hyla-Kryspin, J. Koch, R. Gleiter, T. Klettke, D. Walther, *Organometallics* 17 (1998) 4724.
- [44] I. Hyla-Kryspin, J. Demuynck, A. Strich, M. Benard, *J. Chem. Phys.* 75 (1981) 3954.
- [45] T.H. Dunning Jr., *J. Chem. Phys.* 53 (1970) 2823.
- [46] Gaussian 98 (revision A. 5), M.J. Frisch et al., Gaussian Inc., Pittsborough, USA, 1998.
- [47] M. Brookhart, M.L.H. Green, L.-L. Wong, *Prog. Inorg. Chem.* 36 (1988) 1.
- [48] J.W. Lauher, R. Hoffmann, *J. Am. Chem. Soc.* 98 (1976) 1729.
- [49] W.E. Piers, J.E. Bercaw, *J. Am. Chem. Soc.* 112 (1990) 9406.
- [50] W. Roell, H.-H. Brintzinger, R. Rieger, R. Zolk, *Angew. Chem. Int. Ed. Engl.* 29 (1990) 279.
- [51] G.F. Schmidt, M. Brookhart, *J. Am. Chem. Soc.* 107 (1985) 1443.
- [52] M.-H. Prosenc, C. Janiak, H.H. Brintzinger, *Organometallics* 11 (1992) 4036.
- [53] G. Erker, W. Frömberg, R. Benn, R. Mynott, K. Angermund, C. Krüger, *Organometallics* 8 (1989) 911.
- [54] J.L. Atwood, R.D. Rogers, W.E. Hunter, C. Floriani, G. Fachinetti, A. Chiesi-Villa, *Inorg. Chem.* 19 (1980) 3812.
- [55] H. Lang, S. Blau, B. Nuber, L. Zsolnai, *Organometallics* 14 (1995) 3216.
- [56] C. McDade, J.E. Bercaw, *J. Organomet. Chem.* 279 (1985) 281.
- [57] P.L. Watson, G.W. Parshall, *Acc. Chem. Res.* 18 (1985) 51.
- [58] T. Itoh, H. Shirikawa, S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.* 12 (1974) 11.
- [59] H. Shirikawa, E.J. Louis, A.G. McDiarmid, C.K. Chiang, A.J. Heeger, *J. Chem. Soc., Chem. Commun.* (1977) 578.
- [60] C.K. Chiang, C.R. Fincher Jr., Y.W. Park, A.J. Heeger, H. Shirikawa, E.J. Louis, S.C. Gau, A.G. MacDiarmid, *Phys. Rev. Lett.* 39 (1977) 1098.
- [61] B.E. Kohler, *J. Chem. Phys.* 88 (1988) 2788.
- [62] P. Robin, J.P. Pouget, R. Comes, H.W. Gibbsin, A.J. Epstein, *J. Phys.* 44 (1983) 77.
- [63] T. Itoh, H. Shirikawa, S. Ikeda, *J. Polym. Sci., Polym. Chem. Ed.* 13 (1975) 1943.
- [64] M. Tanaka, H. Yasuda, J. Tanaka, *Bull. Chem. Soc. Jpn.* 55 (1982) 3639.