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An ab initio investigation of σ -bond metathesis and insertion reactions of acetylene with Cl_2ZrH^+ and $\text{Cl}_2\text{ZrCH}_3^+$

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Abstract

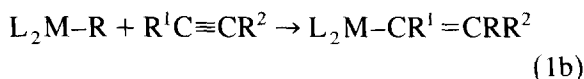
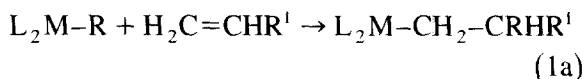
All-electron RHF and RMP2 ab initio calculations with split-valence basis sets of double- and triple- ξ quality have been used to study reaction paths for the reaction of acetylene (1) with the model compounds Cl_2ZrH^+ (2) and $\text{Cl}_2\text{ZrCH}_3^+$ (3). At the RMP2//RHF level the acetylide-complex formation reaction is calculated to have a barrier of 15.8 (2), 20.8 (3) kcal/mol with respect to complexed acetylene and to be 44.4 (2), 18.9 (3) kcal/mol exothermic with respect to free acetylene. The transition states are four-membered cycles. The calculated energy barriers are greater than the theoretical values obtained for σ -bond metathesis of acetylene with Cl_2ScR and Cp_2ScR ($\text{R} = \text{H}, \text{CH}_3$). The calculated energetics of the metathesis reaction path are compared with the theoretical values determined for the alternative insertion reaction of acetylene into Zr–H and Zr–C σ bonds. The insertion reactions are kinetically and thermodynamically favoured over the corresponding metathesis reactions.

Keywords: Ab initio; Acetylene; Cationic zirconocene; Insertion reactions; σ -bond metathesis reaction; Molecular orbital investigations

1. Introduction

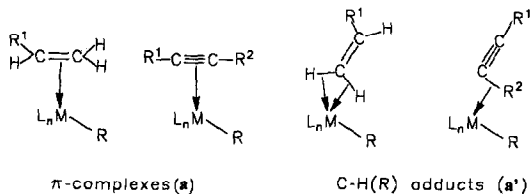
Electron deficient d^0 transition-metal complexes and d^0f^n lanthanide complexes are very active at both stoichiometric and catalytic transformation of organic substrates [1–3]. To the wide range of their reactivities belong the industrially important Ziegler–Natta catalysis of olefin polymerization [4–9] as well as metathesis reactions with both saturated and unsaturated hydrocarbons [10]. It is commonly accepted that the high reactivity of these species comes from the ability of metal centers to mediate the breaking and formation of carbon–carbon and car-

bon–hydrogen bonds. Several experimental [11–34] and theoretical [32–66] studies have been undertaken in order to understand the mechanism of these particular reactions as well as the role of the metal center for the activation of C–C and C–H bonds. The reactions of alkenes and alkynes with $\text{L}_2\text{M–R}$ ($\text{L} = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$; $\text{M} = d^0, d^0f^n$ metals, $\text{R} = \text{H}, \text{CH}_3$) species are of special interest because alternate pathways were observed [8–31]. Alkenes and alkynes can react either by classical β -insertion into the M–R bond (Eqs. (1a) and (1b)).



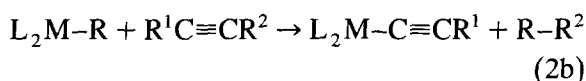
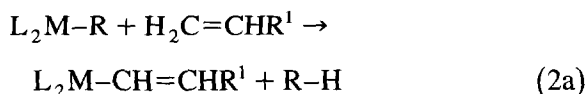
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Scheme 1.

or by an activation of the alkenylic and alkynylic C–H bonds in a σ -bond metathesis reaction (Eqs. (2a) and (2b)).



There is no experimental information about what happens on the molecular level when unsaturated hydrocarbons enter the sphere of the L_nM-R species. In the case of the insertion reactions the commonly accepted mechanism was proposed by Cossee and Arlman [68,69].

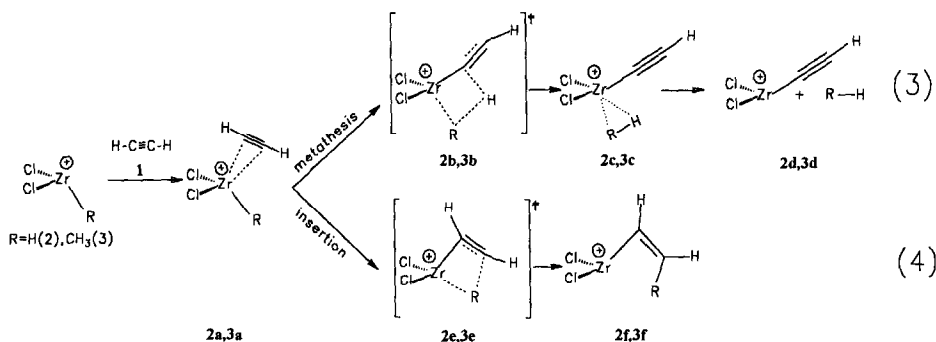
According to this mechanism, the insertion reaction begins with the precoordination of the hydrocarbon to the vacant coordination site on the metal center, leading to the formation of the π -complexes (a). In the case of the σ -bond metathesis reactions the hydrocarbon adducts (a') in which the metal center receives some bonding interaction from C–H/R bond (s) were

proposed for the primary step of the reaction, see Scheme 1 [63,66].

Thus, the answer to the question, if either of these structures represents a local minimum on the potential energy surface can be crucial for the prediction and understanding of the preferred reaction path. The β -insertion reactions of Eqs. (1a) and (1b) are far more common than the σ -bond metathesis of Eqs. (2a) and (2b). For lutetium, ethylene and propene react by insertion whereas more bulky olefins give rise to C–H activation [10].

Electron-poor complexes of early f-block elements are also known to activate C–H bonds according to reactions of Eqs. (2a) and (2b) [24,27]. For scandium, ethylene and internal acetylenes ($R^1, R^2 = \text{alkyl}$) insert into Sc–R bond whereas σ -bond metathesis product acetylide is exclusively observed in the reaction of terminal acetylenes ($R^1 = \text{alkyl}, R^2 = H$) with Cp_2^*ScR ($Cp^* = C_5Me_5; R = H, CH_3$) [10,28,31].

The reaction of alkenes and alkynes with cationic titanocenes and zirconocenes give the insertion products according to reactions of Eqs. (1a) and (1b) [4–9,11–21]. The recent experimental [11–21] and theoretical [44–46,48–50,52,54–60] work of many groups provides compelling support that the insertion reactions of Eq. (1) play the key role in the propagation step of Ziegler–Natta olefin polymerization. For the reactions of Eqs. (1) and (2) it has been postulated, that they proceed via a four-mem-

Scheme 2. Postulated reaction paths for the σ -bond metathesis and the insertion reactions.

bered transition state [63,66,68,69]. In our previous studies we have investigated the insertion reactions of acetylene with the model compounds Cl_2ZrR^+ according to path (4) displayed in Scheme 2 [51,56].

In order to examine the factors that favor one pathway over another, for the present study we have chosen the σ -bond metathesis reactions displayed in path (3).

Although one can suppose that the results obtained for the model systems may deviate from experimental observations, it has been shown in previous studies that Cl_2M moieties not only provide a good theoretical substitute for the actual bent metallocene system but also an appropriate conceptual basis for an understanding of experimental results [55,63,66,67].

2. Computational details

All-electron *ab initio* calculations were carried out with a single basis set using the Gaussian 94 system of programs [70]. For Zr we

selected a (14, 9, 7) basis set obtained by adding a p-type orbital exponent (0.12) to the optimized (14, 8, 7) set from Ref. [71]. The choice of the additional p-exponent guarantees a comparable distribution of the radial density function of the 5p and 5s orbitals. The most diffuse exponent for the valence d shell is 0.134708, and the maximum of the associated density distribution is located 1.76 Å from the nucleus. The contraction is [6,4,4] corresponding to a single- ξ description for the inner and the 5p shell, double- ξ for 5s and triple- ξ for 4d. Basis sets of respective size (10, 6), (9, 5) and (4) were used for chlorine, carbon and hydrogen and contracted to split-valence [72–74]. The geometry optimizations of the reactants, intermediates, transition states and products were carried out using the energy gradient technique at the restricted Hartree–Fock (RHF) level. In order to check the stationary nature of the particular points on the potential energy surface, the optimized equilibrium structures were used for analytical calculations of the Hessian matrices. For an estimation of correlation effects and

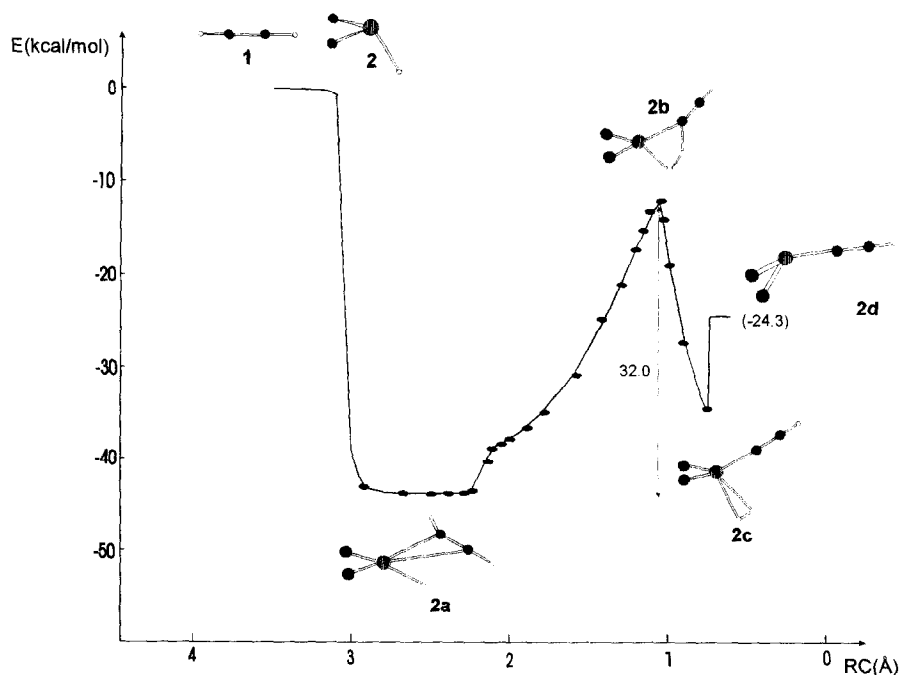


Fig. 1. RHF energy profile for the σ -bond metathesis reaction of C_2H_2 with Cl_2ZrH^+ .

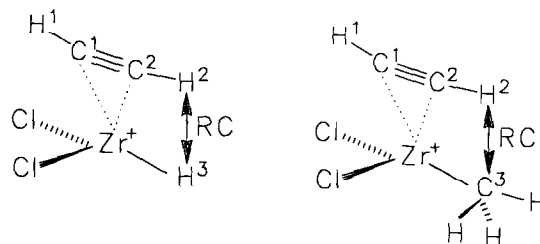
better energetics, restricted second-order Møller–Plesset perturbation (RMP2) calculations [75] were carried out with geometries optimized at the RHF level (RMP2//RHF). In the case of second-row early transition metal compounds it is known from previous studies that the energetics determined with SCF-optimized geometries are very similar to those obtained for geometries optimized on correlated levels [76].

3. Results and discussion

For the investigation of the energy profiles of the σ -bond metathesis reactions we have begun with a reaction coordinate (RC) approach [77]. As an RC we have chosen the distance between the two atoms that form the new bond.

Please refer to Scheme 3.

For the alternative insertion reactions the natural choice of RC should be the distance between C(2)–H(3) and C(2)–C(3) atoms [54]. To simplify the analysis the optimizations were carried out under C_s symmetry constraint, at fixed distances of the RC. Theoretical investiga-

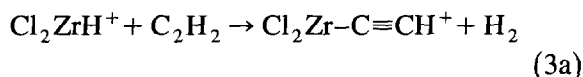


Scheme 3. Please provide text if so required.

tions on similar systems showed that sometimes more stable equilibrium structures can be found with C_1 symmetry whose energy, however, is only 0.5–1.0 kcal/mol lower than those of the corresponding C_s structures [48,49,78].

3.1. RHF structures and energy profiles of the σ -bond metathesis reactions

The calculated energy profile for the σ -bond metathesis reaction from Eq. (3a) is shown in Fig. 1.



At the beginning of the reaction (RC = 2.9–

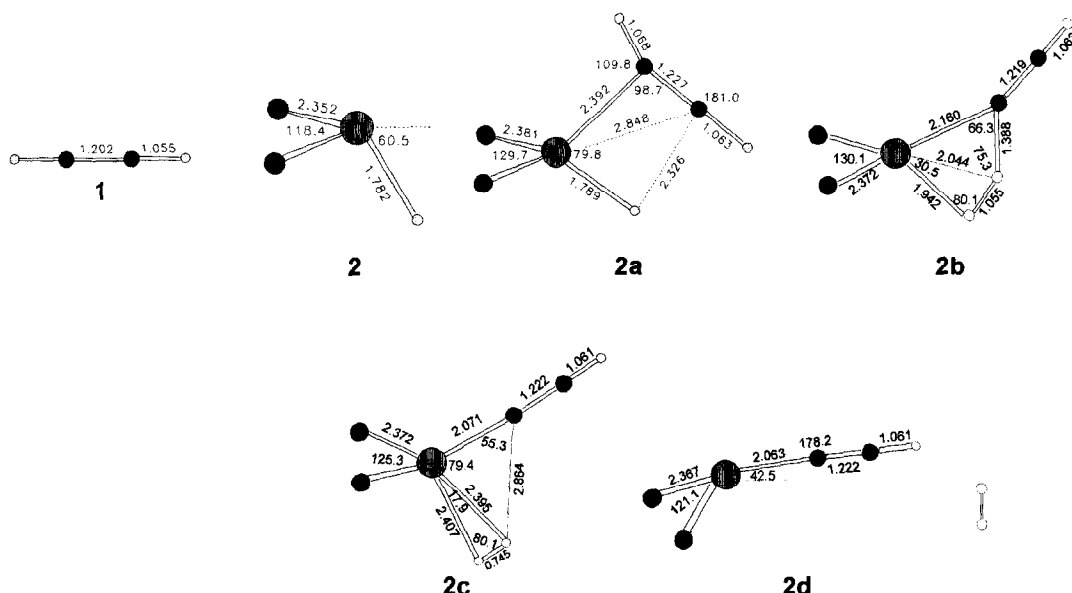


Fig. 2. Fully optimized structures corresponding to the stationary points in the potential energy surface of the σ -bond metathesis reaction between C_2H_2 and Cl_2ZrH^+ .

2.2 Å) the potential energy surface is extremely flat and corresponds to the structures that are about 43 kcal/mol more stable than the reactants. If in this region we also relax the RC the resulting structure converges to the π -complex **2a** whose energy is 43.9 kcal/mol below the reactants (Table 1). The fully optimized structure **2a** is shown in Fig. 2. The subsequent frequency analysis confirmed that **2a** represents a local minimum on the potential energy surface (no imaginary frequencies were detected; $i = 0$). For **2a** the optimized H(2)–H(3) bond distance is 2.454 Å. This value is about 1 Å longer than in the case of the C–H adduct, like **a'**, proposed for the primary step of the σ -bond metathesis of acetylene with Cp_2ScH [66].

Our results predict that for the region with

RC between 2.0 Å and 1.1 Å there is no structure that corresponds to a local minimum as is demonstrated by the energy profile plotted in Fig. 1. Thus, the σ -bond metathesis (Eq. (3a)) can not begin with the formation of the C–H adduct like **a'** but it should begin with the formation of the π -complex **2a**. We note that the structure of the acetylene C–H adduct to the Cp_2ScH complex was not verified to be a local minimum on the potential energy surface [66]. By relaxing the RC = 1.1 Å and applying the saddle point searcher algorithm we were able to locate a four-membered transition state (TS) **2b** with one and only one imaginary frequency at $1720i \text{ cm}^{-1}$. The TS **2b** is by 32.0 kcal/mol less stable than the π -complex **2a**.

For the TS **2b** we find the saddle point to be

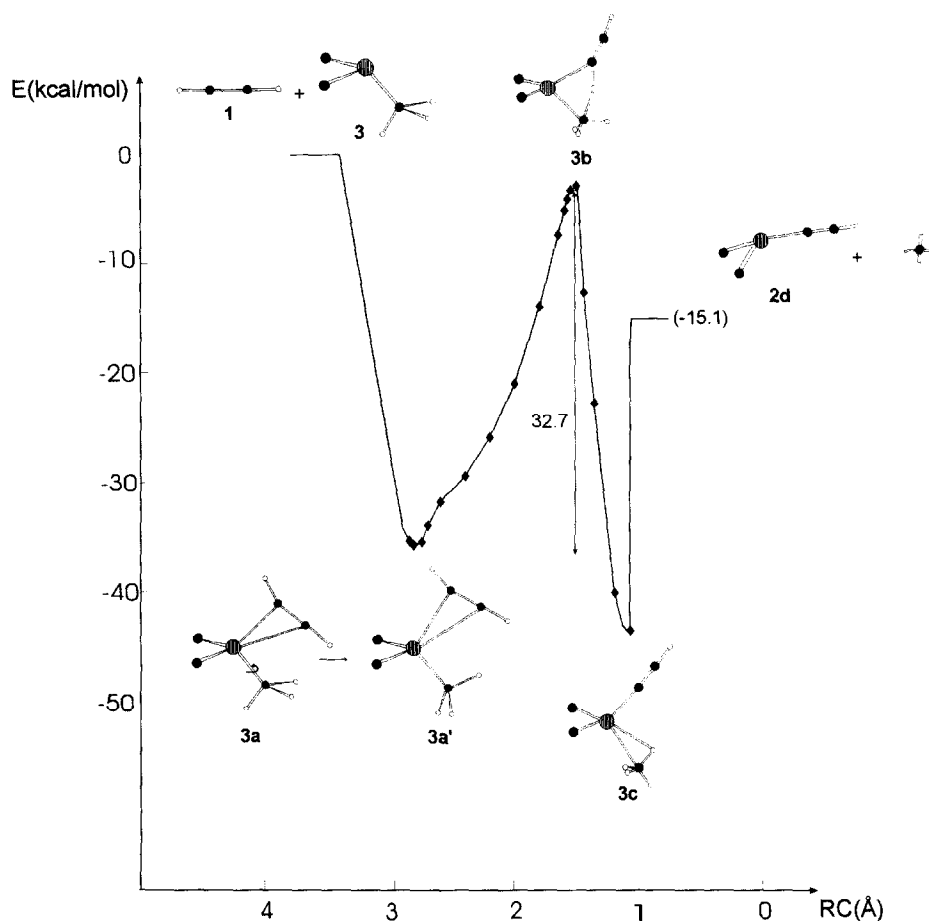


Fig. 3. RHF energy profile for the σ -bond metathesis reaction of C_2H_2 with $\text{Cl}_2\text{ZrCH}_3^+$.

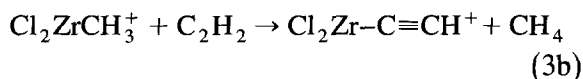
Table 1
Total energies of the investigated structures for the reactions of C_2H_2 (**1**) with Cl_2ZrR^+ ($R = H(2), CH_3(3)$)

Structure	RHF (a.u.)	<i>i</i>	RMP2//RHF (a.u.)
1	-76.79666	0	-76.96855
2	-4448.57791	0	-4448.92525
3	-4487.65160	0	-4488.09797
3'	-4487.64958	1	-4488.09468
2a	-4525.44446	0	-4525.97605
3a	-4564.50911	0	-4565.13267
3a'	-4564.50493	2	-4565.12808
2b	-4525.39358	1	-4525.95087
3b	-4564.45283	1	-4565.09955
2c	-4525.42963	0	-4525.98359
3c	-4564.51776	0	-4565.15198
2d	-4524.28667	0	-4524.82064
H2	-1.126658	0	-1.143867
CH4	-40.185602	0	-40.276001
2e	-4525.44417	1	-4525.97578
3e	-4564.49298	1	-4565.12445
2f	-4525.50092	0	-4526.03231
3f	-4564.53637	0	-4565.15138

rather 'late'. The Zr–C(2) distance has shortened by 0.69 Å and is only 0.097 Å longer than in the acetylide product **2d**. The Zr–H(3) distance has stretched by 0.153 Å and the newly

formed H(2)–H(3) bond has a distance of 1.055 Å (Fig. 2). In the late stage of the reaction the TS **2b** transforms through a local minimum of the H₂-adduct **2c** to the acetylide product **2d** and H₂ (Figs. 1 and 2). The frequency analyses confirmed that **2c** and **2d** represent local minima on the potential energy surface.

The energy profile for the activation of the acetylic C–H bond by $Cl_2ZrCH_3^+$ (Eq. (3b)) is displayed in Fig. 3.



In the early stage of the reaction we encounter again a deep local minimum ($i = 0$) of the π -complex **3a** (Fig. 4). The π -complex **3a'** differs from **3a** by rotating the CH₃ group around the Zr–C bond. For **3a** two CH σ -bonds are staggered with respect to the Zr–Cl bonds; in **3a'** they are eclipsed. **3a'** is by 2.6 kcal/mol less stable than **3a** and does not correspond to a local minimum ($i = 2$). However, **3a'** provides an appropriate structure for the σ -bond metathe-

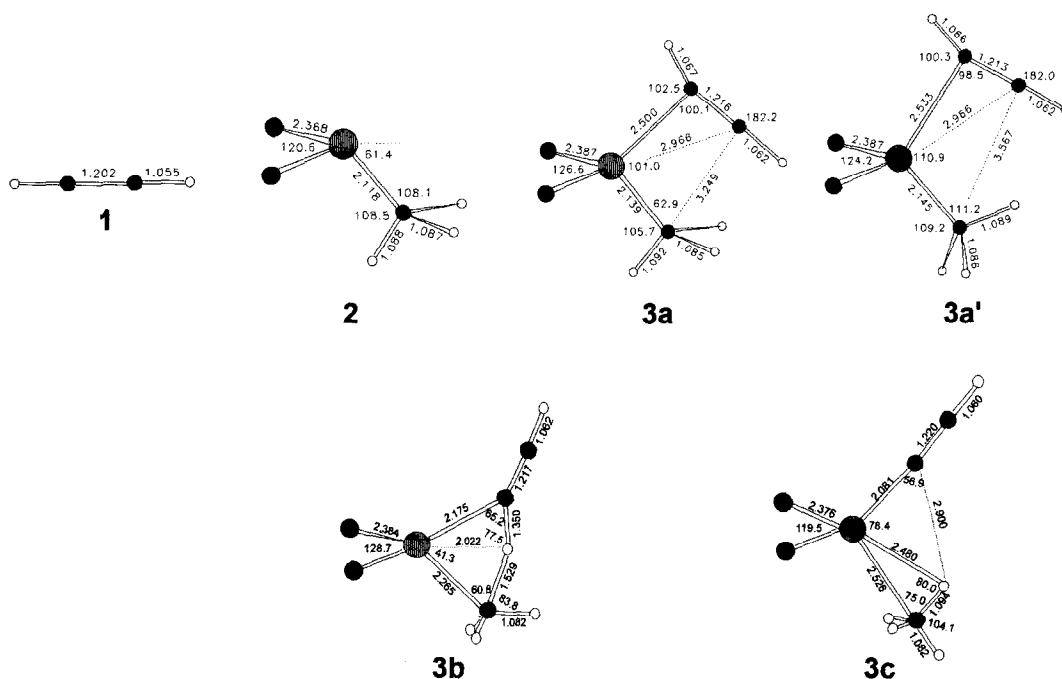
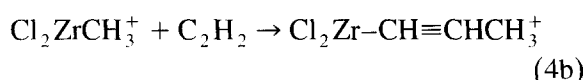
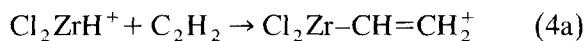


Fig. 4. Fully optimized structures for the σ -bond metathesis reaction of C_2H_2 with $Cl_2ZrCH_3^+$.

sis reaction. Thus, in the early stage of the reaction the formation of the π -complex **3a** is followed by an energetically less demanding rotation of the CH_3 group around the $\text{Zr}-\text{C}(3)$ axis, leading to the π -complex **3a'**. Due to strong donor–acceptor interactions between the electrophilic zirconium center and the acetylene π -system, **3a'** is by 35.6 kcal/mol more stable than the reactants (Fig. 3, Table 1). For **3a'** the optimized $\text{H}(2)-\text{C}(3)$ bond distance is 2.818 Å. By relaxing the RC to around 1.5 Å we have located the four-membered TS **3b** (Fig. 4) having one imaginary frequency at 1679i cm^{-1} . The TS **3b** lies 2.9 kcal/mol below the reactants but is by 32.7 kcal/mol less stable than the π -complex **3a'**. With respect to **3a'** the activated $\text{C}(2)-\text{H}(2)$ bond as well as the $\text{Zr}-\text{C}(3)$ bond of **3b** are considerably weakened and stretched to 1.35 Å and 2.265 Å, respectively. The destabilization connected with this process is to some extent recompensated for by the formation of the $\text{Zr}-\text{C}(2)$ and $\text{C}(3)-\text{H}(2)$ σ -bonds at 2.175 Å and 1.529 Å, respectively. The new bond formation at the TS is asynchronous in the sense that the $\text{Zr}-\text{C}(2)$ bond formation is more advanced than that for the $\text{C}(3)-\text{H}(2)$ bond which is still very long. In the late stage of the reaction we encounter the deep local minimum ($i = 0$) corresponding to the CH_4 -adduct **3c** (Figs. 3 and 4) which transforms to the acetylide product and methane.

3.2. Comparison of σ -bond metathesis reactions with the alternative insertion reactions

The insertion reactions displayed in Eqs. (4a) and (4b) were discussed in detail in Ref. [56].



For the sake of clarity we present in Fig. 5 the optimized structures of the insertion TS **2e**, **3e** and of the products **2f**, **3f**. The TS are four-membered cycles and have one imaginary fre-

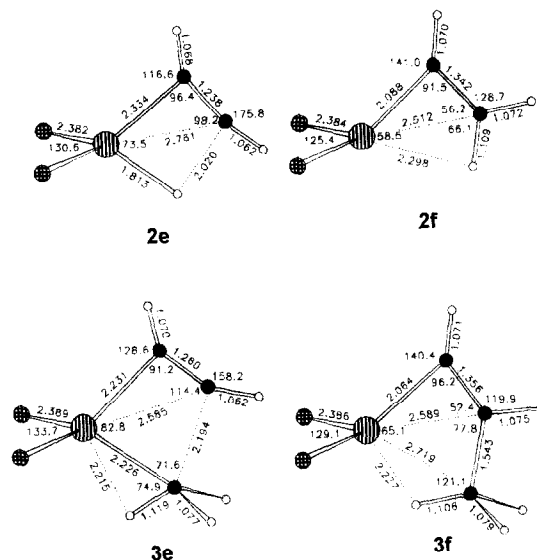


Fig. 5. Fully optimized structures of the TS (**2e**, **3e**) and products (**2f**, **3f**) for the insertion reactions displayed in Eqs. (4a) and (4b).

quency at 319i cm^{-1} (**2e**) and 426i cm^{-1} (**3e**). Both TS are early. With respect to π -complexes **2a** and **3a** the $\text{Zr}-\text{H}(3)$ and $\text{Zr}-\text{C}(3)$ bonds have only stretched by 0.024 Å and 0.087 Å; the newly formed $\text{C}(2)-\text{H}(3)$ and $\text{C}(2)-\text{C}(3)$ bonds have a distance of 2.020 Å and 2.194 Å, respectively. In the TS **3e** the geometry of the CH_3 group deviates from the normal sp^3 structure. The CH bond directed towards the Zr -atom is elongated to 1.119 Å, the corresponding ZrCH angle is lower than the sp^3 value (Fig. 5). Such structural deformation suggest, that **3e** is stabilized through an α -agostic interaction. The α - CH agostic interaction has been proposed to assist the mechanism of olefin insertion reactions on the basis of both, experimental [79–84] and theoretical [42,48–56] investigations. The products **2f** and **3f** are stabilized through β - CH and γ - CH agostic interactions, respectively [56].

The RMP2//RHF energetics of the insertion reactions (Eqs. (4a) and (4b)) and of the corresponding σ -bond metathesis reactions (Eqs. (3a) and (3b)) are compared in Figs. 6 and 7. The total energies of the particular structures are collected in Table 1. Both, insertion and σ -bond metathesis reactions begin with the formation of

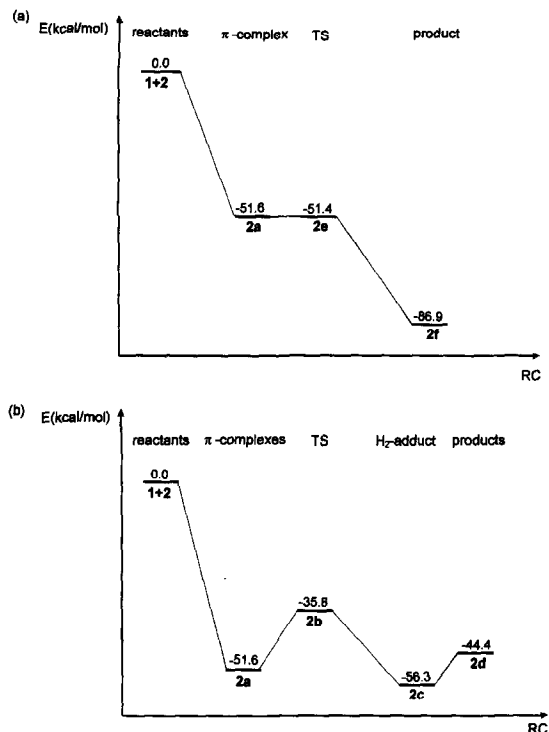


Fig. 6. RMP2//RHF energy profiles for the insertion (a) and σ -bond metathesis reaction (b) of C_2H_2 with Cl_2ZrH^+ .

the π -complexes which are by 51.6 kcal/mol (**2a**) and 41.5 kcal/mol (**3a**) more stable than the reactants. The calculated energy barriers of 0.2 kcal/mol (**2e**), 5.1 kcal/mol (**3e**) and overall exothermicity of -86.9 kcal/mol (**2f**), -53.3 kcal/mol (**3f**) suggest that the insertion

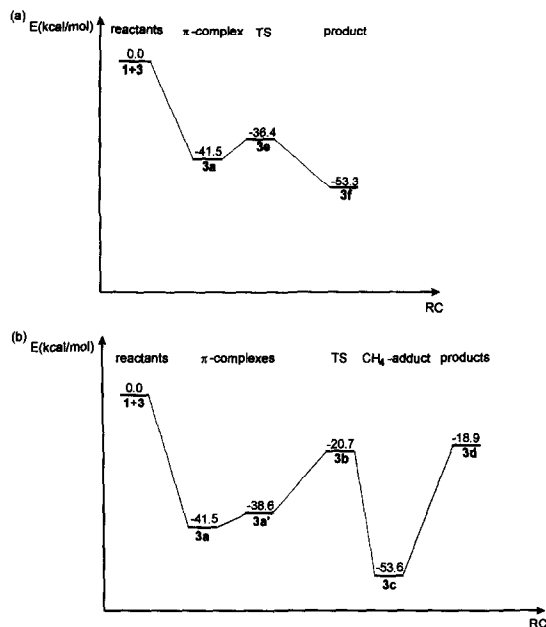


Fig. 7. RMP2//RHF energy profile for the insertion (a) and σ -bond metathesis reaction (b) of C_2H_2 with $Cl_2ZrCH_3^+$.

processes (Eqs. (4a) and (4b)) are facile reactions from a kinetic as well as a thermodynamic point of view. The insertion reaction of acetylene into Zr–H bond has lower energy barrier and greater exothermicity than into Sc–H bond (Table 2). Due to high energy barriers of 15.8 kcal/mol (**2b**), 20.8 kcal/mol (**3b**) and lower exothermicity (-44.4 kcal/mol (**2d**), -18.9 kcal/mol (**3d**)) with respect to the correspond-

Table 2

Calculated with respect to the reactants relative energies of the investigated structures for the reaction of acetylene with Sc and Zr complexes. All values are given in kcal/mol

Metathesis reaction	Calculation method	π -complex	TS	H ₂ /CH ₄ adducts	Products	Ref.
$Cp_2ScH + C_2H_2$	DFT	-8.8^a	-6.9	-25.8	-20.5	[66]
$Cl_2ScH + C_2H_2$	GVB-CI//RHF		$+9.1$		-15.2	[63]
$Cl_2ZrH + C_2H_2$	RMP2//RHF	-51.6	-35.8	-56.3	-44.4	this work
$Cp_2ScCH_3 + C_2H_2$	DFT	-4.3^a	-1.0	-37.5	-30.6	[66]
$Cl_2ScCH_3 + C_2H_2$	GVB-CI//RHF				-40.9	[63]
$Cl_2ZrCH_3 + C_2H_2$	RMP2//RHF	-41.5	-20.7	-53.6	-18.9	this work
Insertion reaction						
$Cp_2ScH + C_2H_2$	DFT				-45.6	[66]
$Cl_2ScH + C_2H_2$	GVB-CI//RHF	-15.4	-9.1		-36.9	[63]
$Cl_2ZrH + C_2H_2$	RMP2//RHF	-51.6	-51.4		-86.9	[56]
$Cl_2ZrCH_3 + C_2H_2$	RMP2//RHF	-41.5	-36.4		-53.3	[56]

^a Acetylene C–H adduct.

ing insertion reactions, it is clear, that both σ -bond metathesis reactions (Eqs. (3a) and (3b)) can not be preferred reactions. The calculated energy barriers of the metathesis reactions of acetylene with Cl_2ZrH^+ and $\text{Cl}_2\text{ZrCH}_3^+$ are greater than those determined for the L_2ScR ($\text{L} = \text{Cl}, \text{C}_5\text{H}_5$; $\text{R} = \text{H}, \text{CH}_3$) species [63,66] (Table 2). To our knowledge, cationic 14 valence electron (VE) Zr-acetylide complexes are unknown. However, the optimized Zr–C and C–C triple bond lengths of **2d** do not deviate much from the X-ray data reported for 16 VE Zr-acetylide $\text{Cp}_2\text{Zr}(-\text{C}\equiv\text{CR})_2$ [85–88]. The optimized C–C bond distance of **2d** (1.222 Å) agree very well with the reported X-ray data, but the Zr–C bond length is about 0.1 Å shorter [85–88]. This discrepancy is traced back to the introduced structural approximation for our model compound (Cl^- instead C_5H_5^- or C_5Me_5^-) We note, that for $(\text{C}_5\text{H}_5)_2\text{Zr}-\text{C}\equiv\text{CH}^+$ the optimized Zr–C bond distance of 2.189 Å agree well with those of neutral Zr-acetylide compounds [89].

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