Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 671 (2003) 75–90

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Mechanism of metal-catalyzed CC-coupling reactions with titanocene vinylidene. A theoretical study

Uwe Böhme *

Technische Universität Bergakademie Freiberg, Institut für Anorganische Chemie, Leipziger Straße 29, D-09596 Freiberg, Germany

Received 13 November 2002; received in revised form 8 January 2003; accepted 8 January 2003

Abstract

The activation barriers and reaction energies for the [2+2]-cycloaddition of titanocene vinylidene with different reagents with double and triple bonds have been investigated at the B3LYP level of theory, using an effective core potential for Ti with a large valence basis set. For nonpolar reagents like ethylene or acetylene the reaction proceeds via a facile [2+2]-cycloaddition. In contrast to that polar reagents like formaldehyde or HCN react via primary formation of a donor–acceptor complex with the electrophilic titanium atom. This adduct rearranges to the transition state of the [2+2]-cycloaddition yielding the four membered titanacyclus. The analysis of the molecular orbitals of the 2-methylenetitanacyclobutene $Cp_2\overline{TiC(=CH_2)CH=C}H$, the 2-methyleneazatitanacyclobutene $Cp_2\overline{TiC(=CH_2)CH=N}$ and the 2-methyleneoxatitanacyclobutane $Cp_2\overline{TiC(=CH_2)CH_2-O}$ with the extended Hückel method makes the different reactivity of these compounds understandable. Subsequent reactions of the titanacyclobutanes and -butenes have been investigated as well: Cycloreversion occurs for titanacyclobutane, and with a substantial higher activation barrier for titanacyclobutene. Electrocyclic ring opening is proposed for azatitanacyclobutene. Metathesis reactions are possible for titanaoxetanes. A mechanism for the rearrangement of titanaoxetanes with the exocyclic methylene group in α-position to Ti into titanaoxetanes with the exocyclic methylene group in β-position has been proposed.

Keywords: Density functional calculations; Cycloaddition; Titanocene vinylidene; Titanacyclobutanes; Titanacyclobutenes

1. Introduction

Titanacyclobutanes and -butenes are encountered throughout the literature [1–9]. For instance the conversion of organic carbonyl compounds to alkenes via methylenation reactions has been facilitated by the 'Grubbs reagent' [3,4]. Titanacyclobutanes have been used as polymerization catalysts for syndiotactic polymerization of styrol [6].

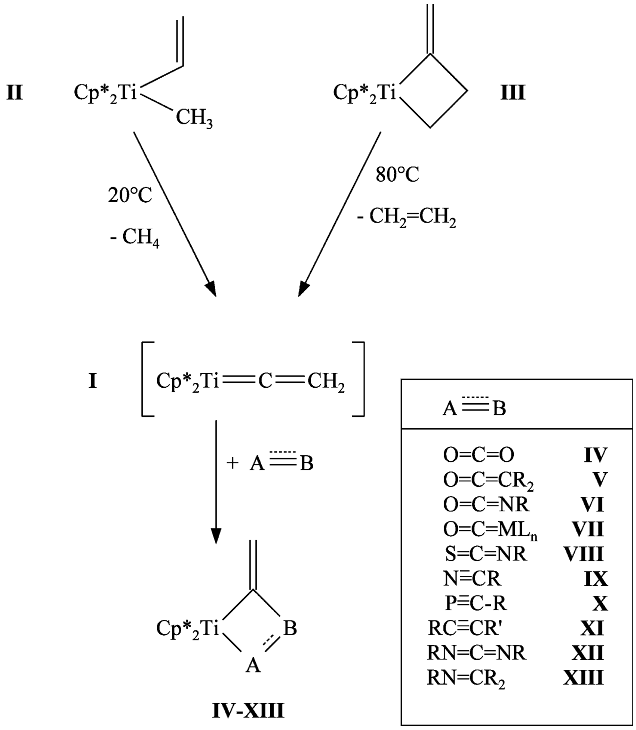
The titanium vinylidene species ($Cp^*_2Ti{=}C{=}CH_2$) (**I**) can easily be generated from 2-methylenetitanacyclobutane $Cp^*_2TiC(=CH_2)CH_2CH_2$ (**III**) or by α-H-elimination of methane from the methylvinyltitanocene $Cp^*_2Ti(CH{=}CH_2)CH_3$ (**II**). The titanium vinylidene intermediate can be used in a great number of [2+2]-cycloadditions to prepare titanacyclobutanes and -butenes (**IV**–**XIII**) (see Scheme 1) [1,2].

Oxatitanacyclobutanes and azatitanacyclobutenes are discussed as intermediates in reactions of carbenoid titanium compounds with carbonyl compounds or nitriles [10,11]. The high electrophilicity of the metal centre has prohibited the isolation and characterization of oxa- and azatitanacyclobutanes. Spontaneous ring opening reactions afford carbonyl olefination [4], or products of vinylimido intermediates [12,13]. The titanacyclobutanes and titanacyclobutenes **IV**–**XIII** are isolable products which have been characterized by X-ray structure analyses [14]. These compounds are more stable than corresponding derivatives without the exocyclic methylene group, which undergo spontaneous cycloreversion or electrocyclic ring opening reactions [3,4]. The thermal stability of the metallacycles **IV**–**XIII** is the major advantage of using **I** instead of the titanium methylene intermediate. Compound **I** acts as a highly nucleophilic titanium carbene.

---

* Tel.: +49-3731-392-050; fax: +49-3731-394-058.
E-mail address: uwe.boehme@chemie.tu-freiberg.de (U. Böhme).

0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00046-9



Scheme 1.

The titanacycles **III**–**XIII** can serve as substrates to investigate several subsequent reactions (Scheme 2). Metathesis products (reaction a) are found for the oxetanes **IV**–**VI** [8], whereas electrocyclic ring opening reactions (b) are proposed for **IX** [15] and in part for **XI** [16]. Cycloreversions (e) dominate for the titanacyclobutane **III** and the nonclassical oxetanes **VII**. The cycloreversion of the latter one leads to five membered rings via an acetylene vinylidene rearrangement (c) [17,18]. Regioisomerization (d) was found to occur by thermal treatment of titanathietanes **VIII** [19].

Quantum chemical calculations on titanacyclobutanes and -butenes have been done before, the reactivity of the compounds was only estimated from thermodynamic data [9]. We wanted to gain a more detailed knowledge of the electronic properties of **III**–**XIII** in order to explain structure–reactivity relations by using DFT calculations. In our calculations the Cp* groups of the experimentally investigated molecules **III**–**XIII** were replaced by Cp ligands.

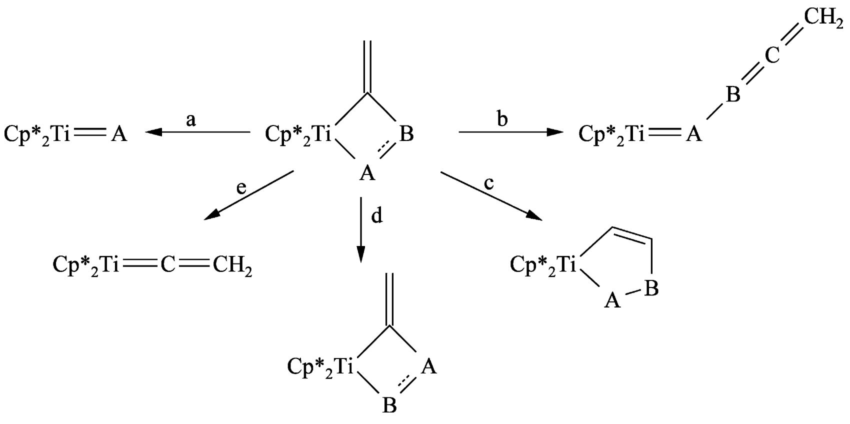
2. Results and discussion

2.1. Structures of reactants and titanacycles

The structure of the titanocene vinylidene intermediate (**1**) was fully optimized and has nearly perfect C_{2v} geometry. There was not found any evidence for a lateral distortion of the vinylidene group as it was proposed some years before on the basis of extended Hückel calculations [20]. The torsion angle (center Cp1)–Ti-(center Cp2)–C1 was found to be 0° in **1**. Nevertheless the lateral distortion of the vinylidene group should proceed easy since there were found only small activation barriers for the cyclodaddition reactions. There are only very few structurally characterized carbene complexes of titanium. For a compilation of these data see Ref. [14]. The calculated titanium–carbon bond length in **1** is rather short with 1.909 Å. The X-ray structures shows values from 1.911 to 1.979 Å. For a dititanacumulene with a linear Ti=C=C=Ti fragment were found bond lengths of 1.809 and 1.757 Å [21].

Two rotamers of the methylvinyltitanocene **2** have been optimized. They differ in the orientation of the vinyl C–H group. The C–H outside rotamer is 0.2 kJ mol^{-1} lower in energy than the C–H inside rotamer. Only the structure of the C–H inside rotamer **2** is shown in Fig. 1, since only this rotamer is relevant for a methane elimination reaction leading to **1**. The torsion angle C3–Ti–C1–C2 is 133.8°.

The conformations of four-membered rings in carbon chemistry have been studied extensively [22]. Cyclobutane is puckered with a dihedral angle of 34°, while oxetane is planar. Mostly the metallacycles **III**–**XIII** are



Scheme 2.

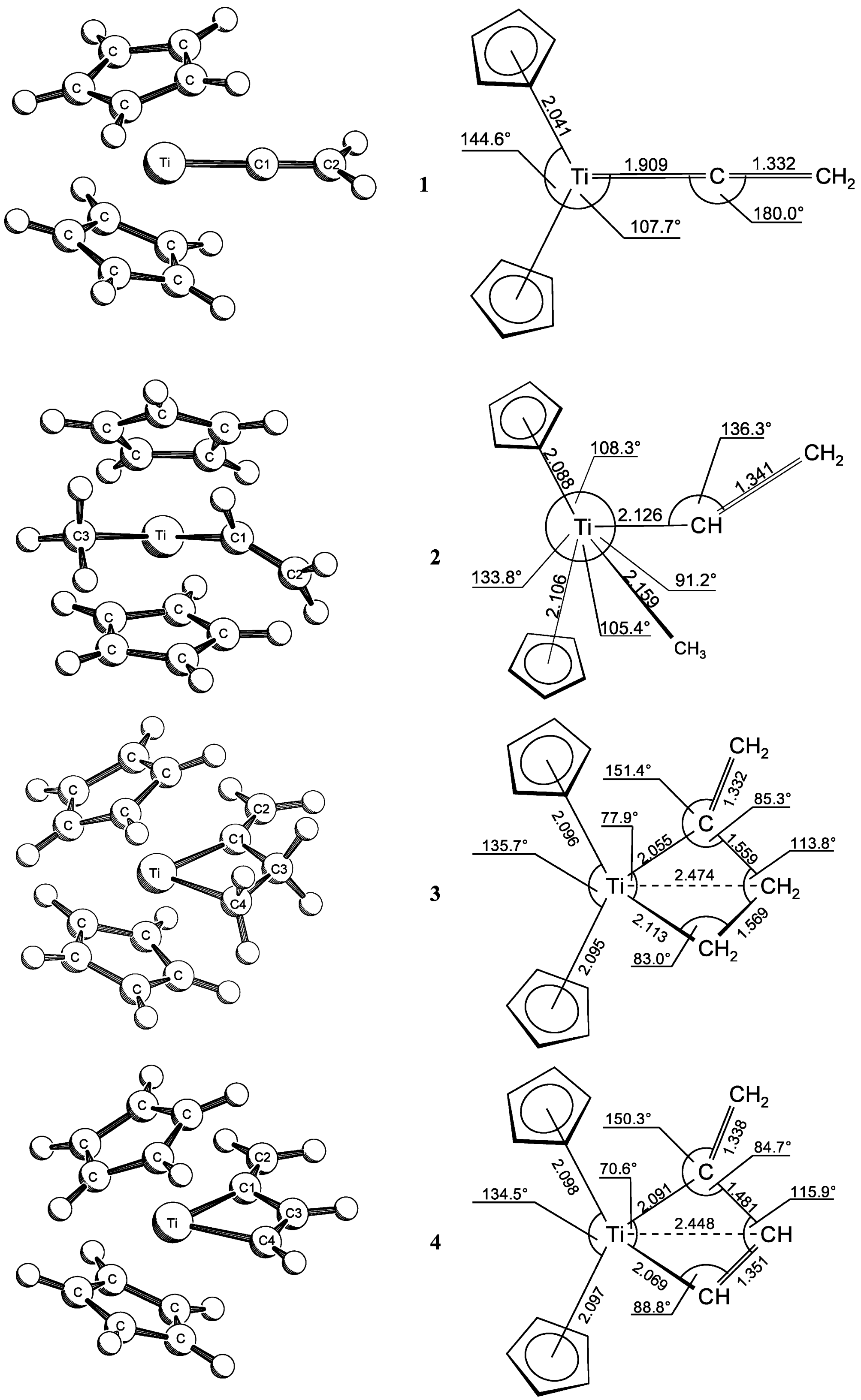


Fig. 1. Calculated structures of **1**–**7**.

found to be planar. Sometimes also puckering effects are discussed, particularly in the case of four-membered metallacycles with exocyclic double bonds in β-position, like **XIV** [23]. 'Square' molecules such as cyclobutane

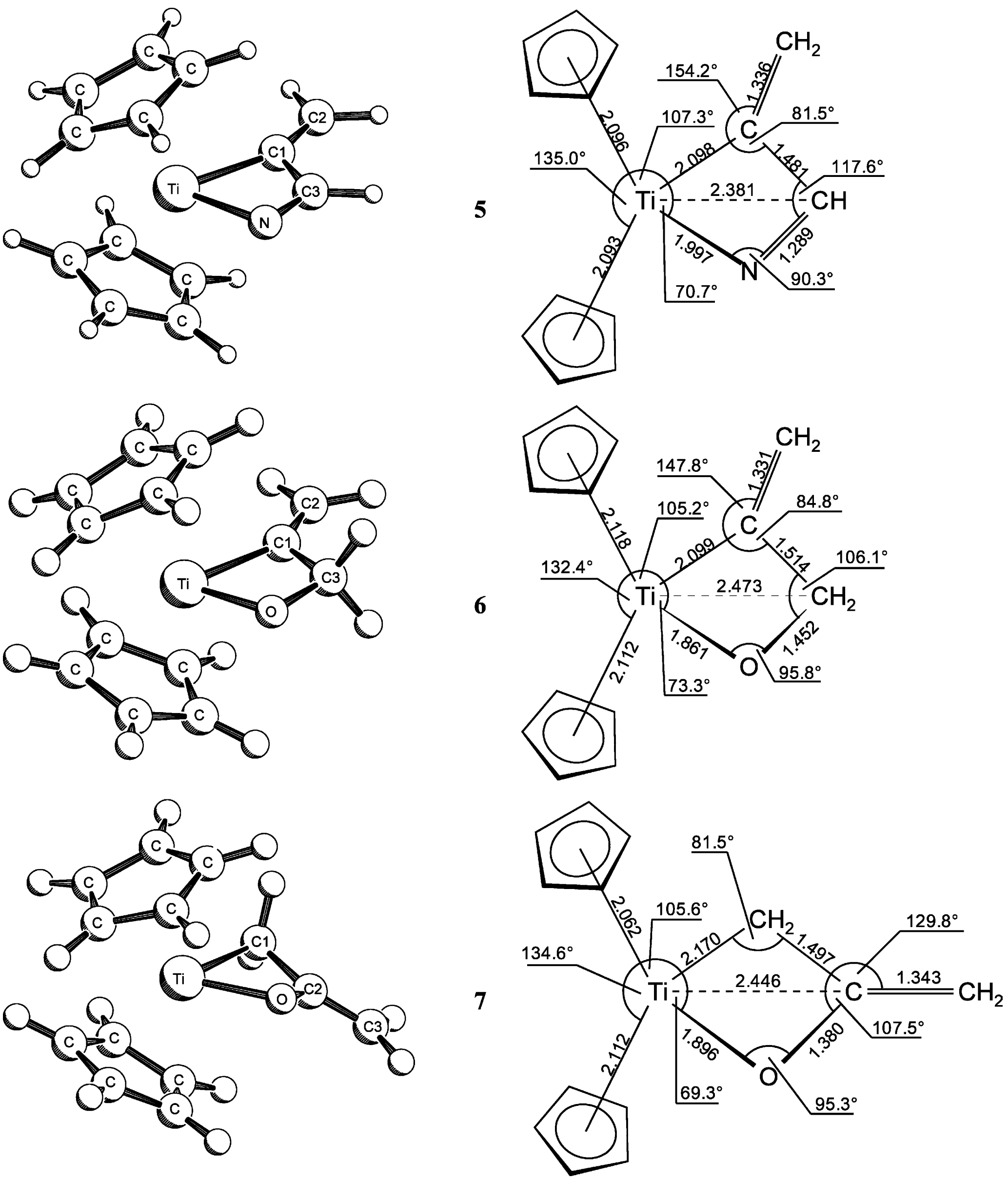
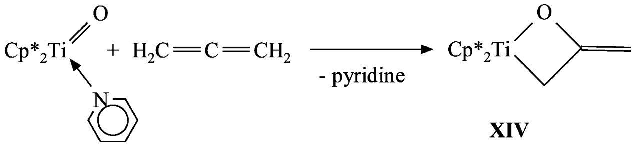


Fig. 1 (*Continued*)

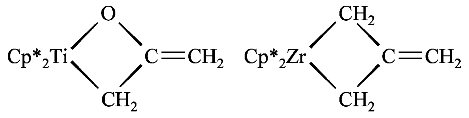
are nonplanar. This fact might be explained with a gain in energy by the partial staggered conformation of the hydrogen atoms. The 1,3-interaction between the carbon atoms is relieved by a lengthening of the C–C bonds (1.568 Å) [24]. When one of the methylene groups is replaced by a more electronegative atom or group, the molecule will adapt a planar geometry and the 1,3-nonbonded distance is shortened. σ-bridged π-bonds have been discussed as a way of stabilizing such square-planar heterocycles [25].



XIV

In order to rationalize the structure and reactivity behaviour of the titanium containing metallacycles, we have carried out DFT calculations on the Cp_2Ti-model complexes. The bond angles in the titanacyclic rings are reproduced with some errors, there are maximal deviations up to 8.8°, the average error is ±1.7°. It is well understandable that the angle Cp–Ti–Cp is smaller for the model complexes than the Cp*–Ti–Cp* angle in the real molecules due to the different spatial requirements of a pentamethylcyclopentadienyl- (Cp*) and a cyclopentadienyl-ligand (Cp). For the same reasons the angle between the substituents at the titanium atom (R–Ti–R) becomes smaller for the real molecules and larger for the calculated derivatives. Similar effects are observed for the bond lengths, which are reproduced with maximal deviations of 0.1 Å, the average error is ± 0.023 Å.[1]

The four-membered titanacycles in the model complexes **4** and **5** were found to be planar. Molecules **3** and **6** are nearly planar with torsion angles in the ring of 1.0 and 0.6°, respectively. Due to a molecular orbital analysis which has been done previously on titanaoxetanes there is no gain in energy by puckering of the ring [26]. Planar-four membered rings have also been found in the X-ray structures of **III**, **VIII**, **IX**, **X**, **XI** Puckered four-membered metallacycles have been found in **XIV** and **XV**, with 22.5 and 33.0°, respectively [27,28]. In these compounds the *exo*-methylene group is situated in β-position to the metal atom. The calculated molecule **7** has a puckered ring with an angle of 21.0°. This is in excellent agreement with the X-ray structure data of **XIV**.



XIV **XV**

The geometry of the organic reactants and side products ethylene, acetylene, formaldehyde, allene, HCN and methane have been optimized with the same method and basis set as the titanocene derivatives. Total energies and zero-point energies of all calculated molecules are listed in Table 1.

2.2. *Mechanism of [2+2]-cycloadditions*

The [2+2]-cycloaddition with the transition metal carbene or vinylidene as reaction partner is symmetry allowed in contrast to the [2+2]-cycloaddition of two alkenes. Previous work on the cycloaddition of $Cp_2Ti{=}CH_2$ with $O{=}CH_2$ has shown that a formally 2π+2π reaction path is made allowed due to the existence of a very polarized titanium–carbon π-type orbital providing two electrons more for the cycloaddition, that means this reaction was considered as a six-electron reaction. The second argument was that the two new bonds result from different orbital interactions, which was interpreted as a'non-symmetric' concerted cycloaddition [26].

Scheme 3 shows three potential energy surfaces which include the titanocene vinylidene intermediate. Methylvinyltitanocene (**2**) and the titanacyclobutane **3** need similar activation energies to reach the transition states $\mathbf{TS_{1-2}}$ and $\mathbf{TS_{1-3}}$, respectively (Scheme 3). It was found that $Cp^*_2Ti{=}C{=}CH_2$ is formed in solution already at 20 °C starting from bis(η-pentamethylcyclopentadienyl)methylvinyltitanium (**II**) and at about 80 °C starting from $Cp^*_2\overline{Ti(C{=}CH_2)CH_2CH_2}$ (**III**) [29,30].

The transition state $\mathbf{TS_{1-2}}$ shows the preformed titanocene vinylidene unit with an angle Ti–C1–C2 of 176.7° and a Ti–C1 bond which is 0.018 Å longer than in titanocene vinylidene (**1**). The bond from titanium to the carbon atom of the methyl group is 0.272 Å longer than in the reactant **2**. The hydrogen atom H1 which is eliminated from the vinyl goup in **2** is nearly midway between the carbon atoms C1 and C3. An interaction between this hydrogen atom and the titanium atom should be discussed, since the distance between both atoms is only 1.761 Å. The whole unit Ti, C1, C2, H1, C3 is planar (Fig. 2). The Hessian matrix for $\mathbf{TS_{1-2}}$ has one imaginary frequency. The normal mode of this frequency shows the displacement of H1 between C1 and C3.

The transition states $\mathbf{TS_{1-3}}$ and $\mathbf{TS_{1-4}}$ have planar units Ti–C1–C3–C4. The imaginary frequencies of both transition states correspond to the movement of the ethylene or acetylene towards the titanocene vinylidene unit. Both reagents react via a cyclic transition state to form the product of the [2+2]-cycloaddition. This is in contrast to polar reagents like carbonyl compounds or nitrils which react via a primary coordination of the negatively charged heteroelement to the electrophilic titanium atom (see Schemes 4 and 5). This process is accompanied by a lowering of the total energy of the system which was calculated to be 32.1 kJ mol^{-1} for $Cp_2Ti{=}C{=}CH_2+O{=}CH_2$ and 36.8 kJ mol^{-1} for $Cp_2Ti{=}C{=}CH_2+NCH$. This primary adduct rearranges to a transition state with an already preformed four membered titanacycle. The gain in energy from the titanocene vinylidene to the adducts $\mathbf{AD_{1-5}}$ and $\mathbf{AD_{1-6}}$ can be explained with the high energy of the titanocene vinylidene, which is a reactive intermediate.

HCN coordinates at titanocene vinylidene in the plane between the cyclopentadienyl ligands in $\mathbf{AD_{1-5}}$ with a torsion angle C1–Ti–N–C3 of 0.2°. This is in contrast to the torsion angle C1–Ti–O–C3 in $\mathbf{AD_{1-6}}$ which is 91.3°. This gives one electron pair of the oxygen atom the opportunity to overlap with the acceptor orbital of $Cp_2Ti{=}C{=}CH_2$. The formaldehyde unit tries to find the best orientation to minimize the steric repulsion from the cyclopentadienyl ligand and the hydrogen atoms at the vinylidene group. The transition state $\mathbf{TS_{1-5}}$ has a planar arrangement of the unit C3–N–Ti–C1. It is remarkable, that the distance Ti–N is substantially shorter (2.675 Å) than the distance C1–C3 (3.385 Å). This is very similar to the geometry $\mathbf{TS_{1-6}}$ where the distance Ti–O is 0.748 Å shorter than C1–C3. This hints to a concerted nonsynchronous process as it was outlined for the cycloaddition of ketenes [31].

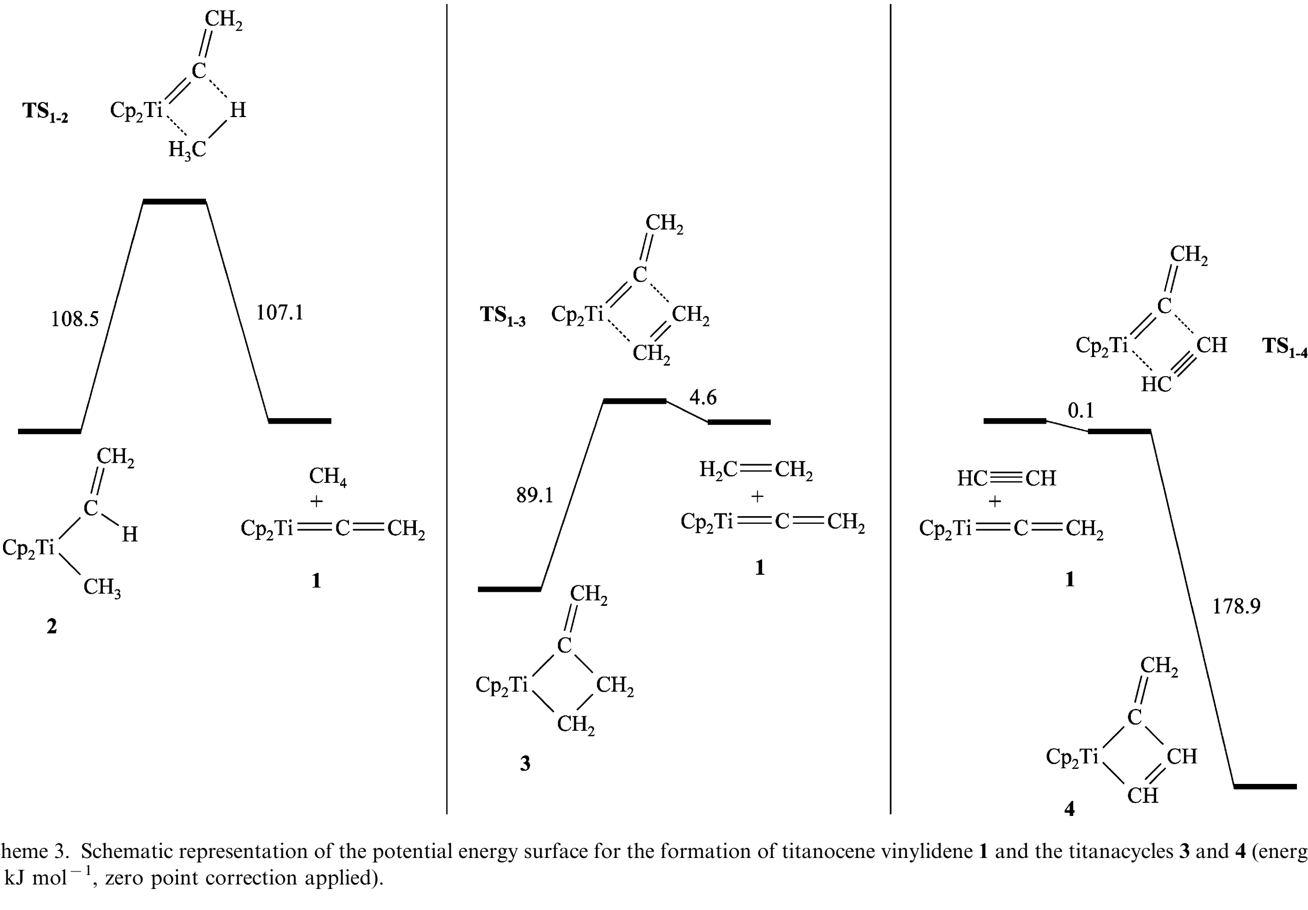
The donor–acceptor interaction in the transition states of the [2+2]-cycloadditions and the adducts

---

[1] A comparison of structural parameters of the calculated molecules with data from X-ray structure analyses is available as supplementary material.

Table 1
Calculated total energies E, zero-point energies ZPE, number of imaginary frequencies n(imag) and frequencies

Molecule	E (au)	ZPE (au)	E+ZPE (au)	n(imag)	Frequency (cm^{-1})
1	−522.54234	0.19838	−522.34396	0	–
2	−563.06538	0.24771	−562.81767	0	–
3	−601.16856	0.25612	−600.91243	0	–
4	−599.94296	0.23174	−599.71122	0	–
5	−616.01258	0.22062	−615.79196	0	–
6	−637.11662	0.23202	−636.88461	0	–
7	−637.13066	0.23241	−636.89824	0	–
8	−520.44243	0.17104	−520.27139	0	–
9	−615.99558	0.21920	−615.77637	0	–
AD(1–5)	−615.98115	0.21700	−615.76416	0	–
AD(1–6)	−637.05880	0.22812	−636.83068	0	–
TS(1–2)	−563.02002	0.24367	−562.77635	1	−1403.27
TS(1–3)	−601.12913	0.25062	−600.87851	1	−42.52
TS(1–4)	−599.86894	0.22588	−599.64306	1	−58.76
TS(1–5)	−615.96581	0.21600	−615.74981	1	−197.02
TS(1–6)	−637.05285	0.22785	−636.82501	1	−313.09
TS(5–9)	−615.97648	0.21869	−615.75779	1	−148.14
TS(6–8)	−637.08544	0.23011	−636.85533	1	−334.50
TS(7–8)	−637.08976	0.22946	−636.86030	1	−382.90
Ethen	−78.58751	0.05123	−78.53628	0	–
Ethin	−77.32570	0.02663	−77.29906	0	–
Formaldehyde	−114.50134	0.02683	−114.47450	0	–
Allene	−116.65771	0.05550	−116.60221	0	–
HCN	−93.42262	0.01646	−93.40616	0	–
Methane	−40.51841	0.04521	−40.47320	0	–



Scheme 3. Schematic representation of the potential energy surface for the formation of titanocene vinylidene **1** and the titanacycles **3** and **4** (energy in kJ mol^{-1}, zero point correction applied).

$\mathbf{AD_{1-5}}$ and $\mathbf{AD_{1-6}}$ have been examined using the charge-decomposition analysis (CDA) [32]. In the CDA method, the Kohn–Sham molecular orbitals of a complex are expressed in terms of the MOs of appropriately chosen fragments. In the present case, the Kohn–Sham orbitals of the transition states ($\mathbf{TS_{1-5}}$, $\mathbf{TS_{1-6}}$, $\mathbf{TS_{1-3}}$, $\mathbf{TS_{1-4}}$) and the adducts ($\mathbf{AD_{1-5}}$, $\mathbf{AD_{1-6}}$) are expressed by a linear combination of the orbitals of $Cp_2Ti{=}C{=}CH_2$ and the reagent in the calculated geometry. The orbital contributions are divided into the mixing of the occupied MOs of the reagent and the unoccupied MOs of $Cp_2Ti{=}C{=}CH_2$ (donation — *d*), mixing of the unoccupied MOs of the reagent and the occupied MOs of $Cp_2Ti{=}C{=}CH_2$ (backdonation — *b*), and mixing of the occupied MOs of the reagent and the occupied MOs of $Cp_2Ti{=}C{=}CH_2$ (repulsive polarization — *r*). The transition states $\mathbf{TS_{1\text{-}3}}$ and $\mathbf{TS_{1-4}}$ can be considered as weak donor acceptor complexes, since there is a small electron donation from the ligand to the titanocene vinylidene in both cases. The donation is stronger in the adducts $\mathbf{AD_{1-5}}$ and $\mathbf{AD_{1-6}}$ and in the transition state $\mathbf{TS_{1-6}}$. All three structures have also some backdonation from the titanocene vinylidene to the reagent. The donation term of $\mathbf{TS_{1-5}}$ is negative, which is a physically unreasonable result. Therefore, $\mathbf{TS_{1-5}}$ should be discussed as transition state without donor–acceptor interaction. More striking are the results of the residue term Δ, which gives the contribu-

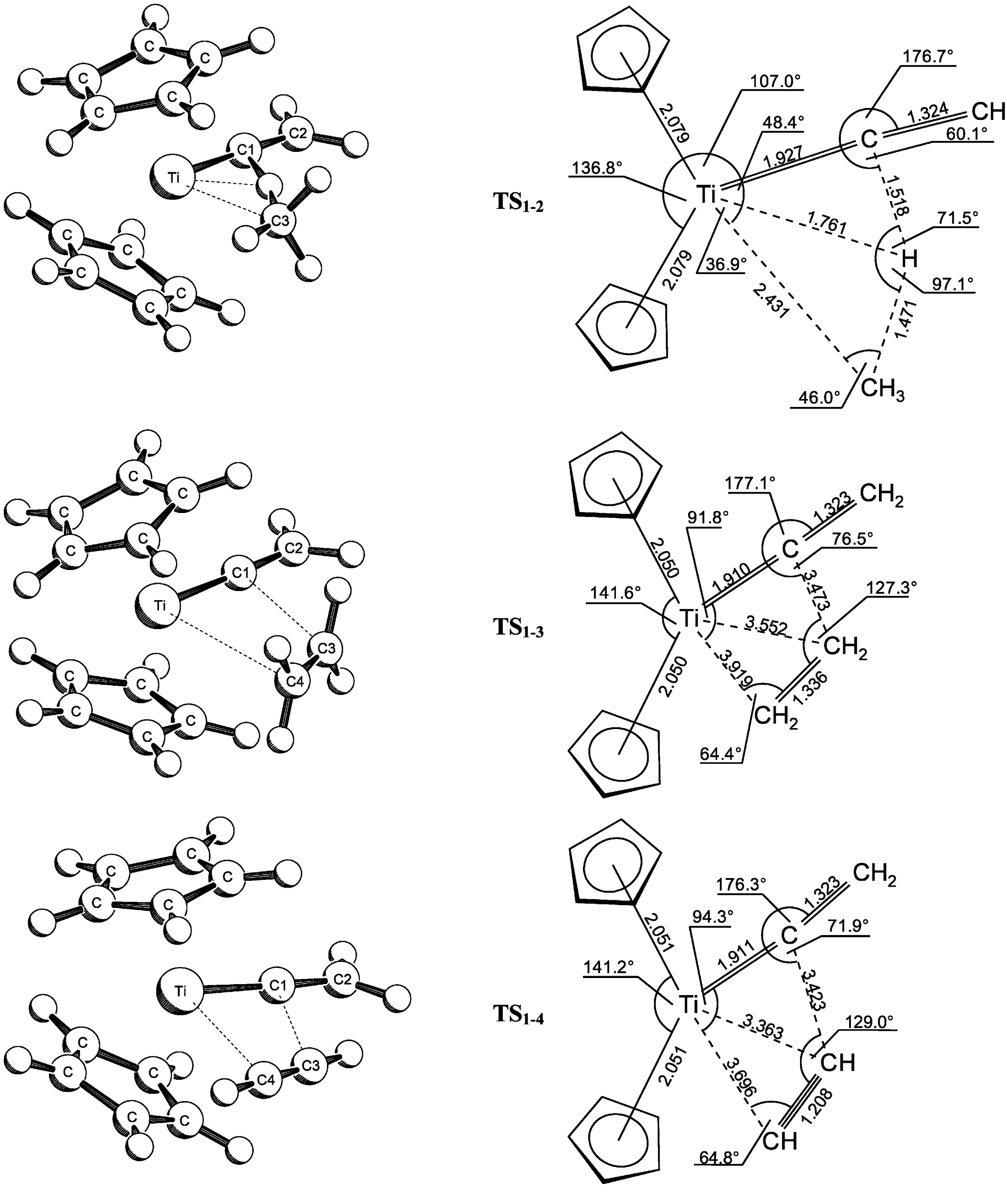
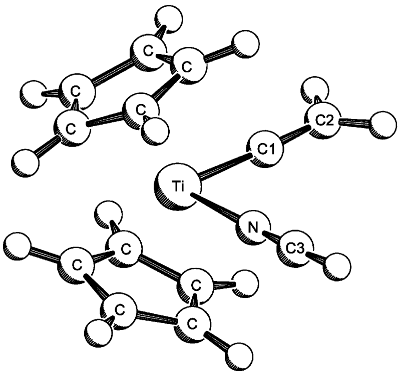
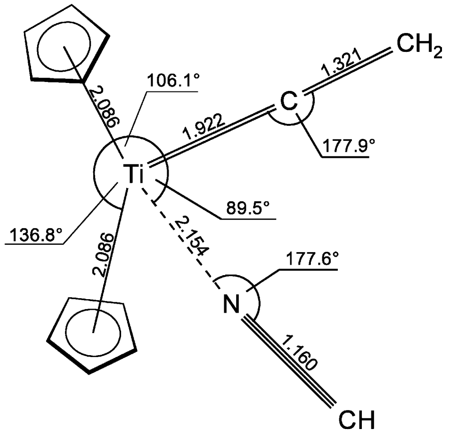
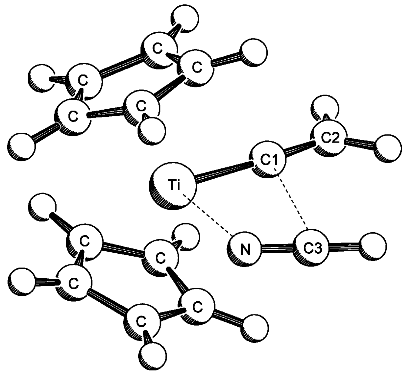


Fig. 2. Transition states of formation of $Cp_2Ti{=}C{=}CH_2$ and [2+2]-cycloaddition reactions.

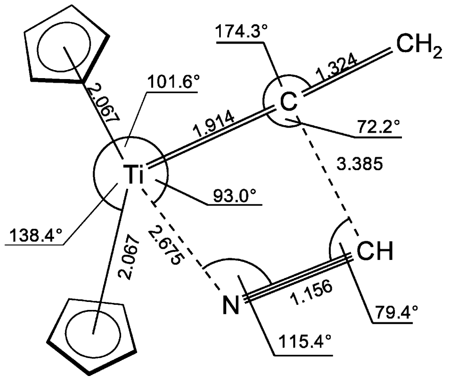


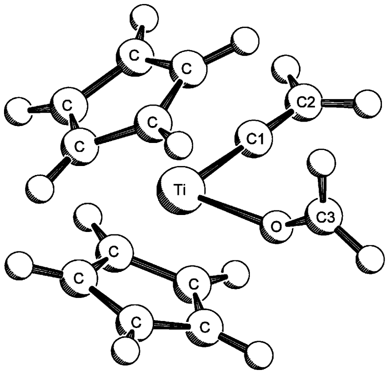
AD_{1-5}



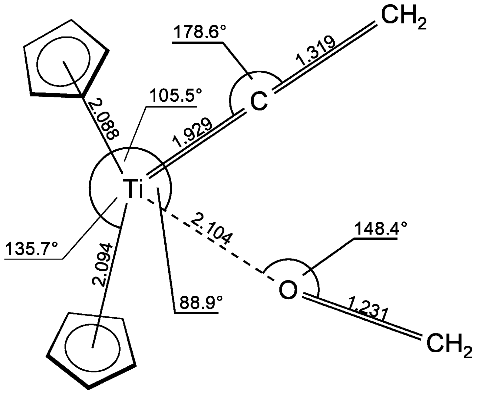


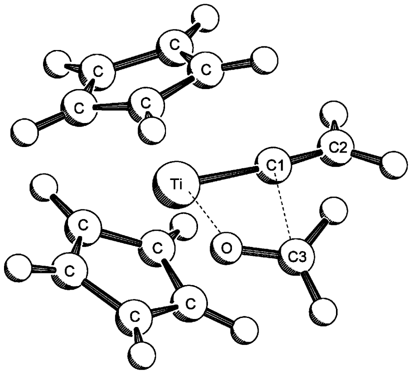
TS_{1-5}





AD_{1-6}





TS_{1-6}

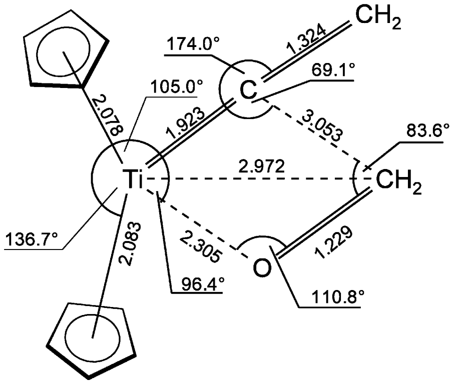
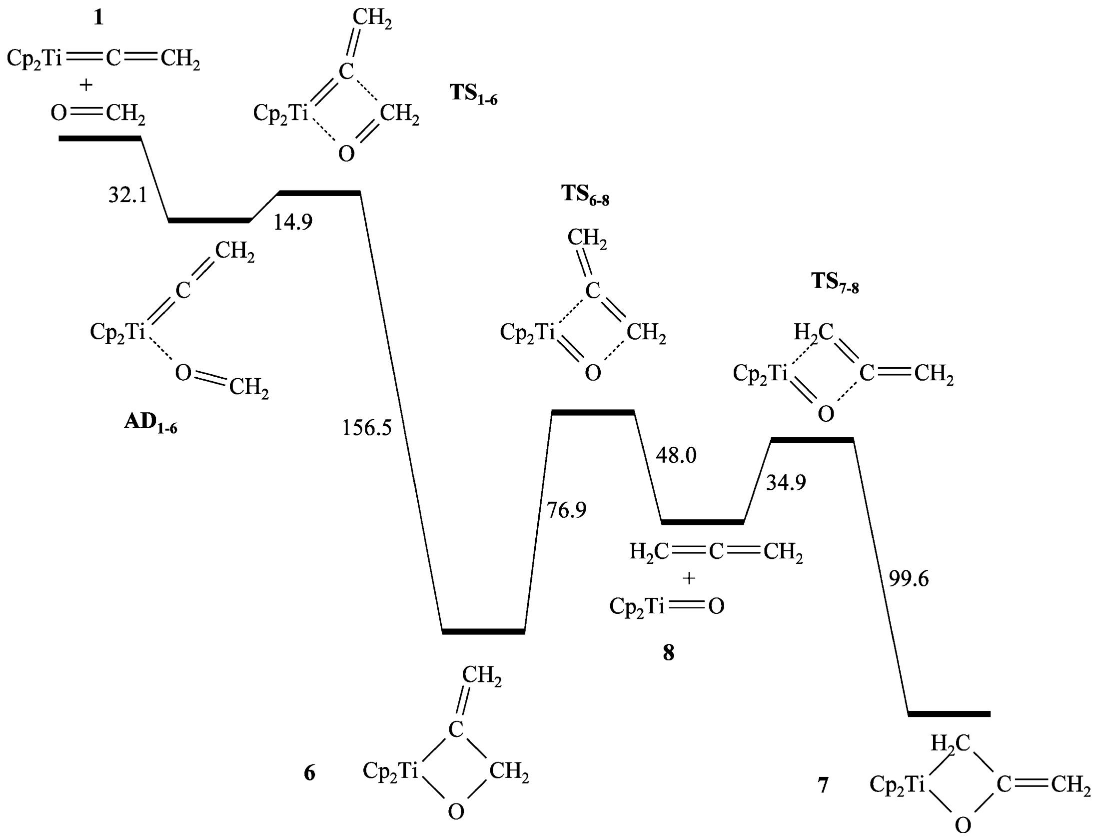
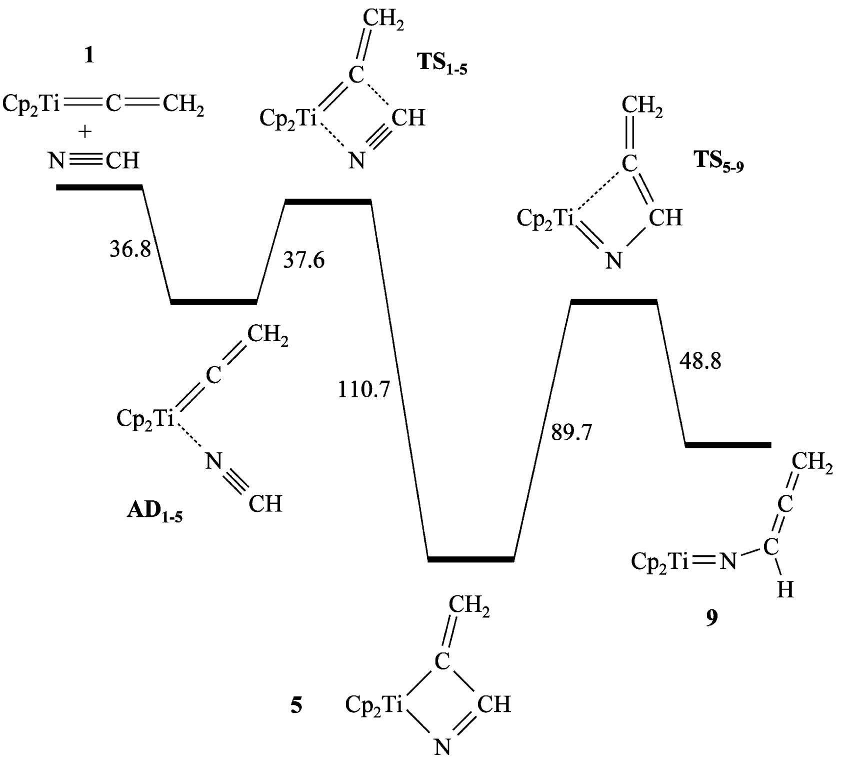


Fig. 2 (*Continued*)



Scheme 4. Schematic representation of the potential energy surface for the formation of the titanaoxetanes **6** and **7** (energy in kJ mol^{-1}, zero point correction applied).



Scheme 5. Schematic representation of the potential energy surface for the formation of the azatitanacyclobutene **5** and the titanocene imide **9** (energy in kJ mol^{-1}, zero point correction applied).

tions of the unoccupied MOs of the reagents and the unoccupied MOs of $Cp_2Ti{=}C{=}CH_2$ to the electronic structure of the complexes. The term Δ should be about zero if the transition states of the [2+2]-cycloaddition can be discussed in terms of donor–acceptor interactions between the fragments and the reactions are thermally symmetry-allowed [33,34]. The values of this term are indeed in all cases about zero as shown in Table 2. The CDA results of transition states for [2+2]−2 cycloadditions involving M=O groups in $CpReO_3$ were shown to provide limited insight and electrostatic interactions are potentially important in addition to orbital interactions [35].

2.3. *Reactivity of titanacycles*

It is possible to draw conclusions about the reactivity of the compounds under investigation if one compares the energy differences between reactants, transition states and reaction products. Therefore, transition states for different reaction pathways as outlined in Scheme 2 have been calculated. The reaction pathways have been examined by following the intrinsic reaction coordinate starting from the transition states.

2.3.1. *Titanacyclobutane and titanacyclobutene*

The formation of the titanacyclobutene **4** is more exothermic than that of the titanacyclobutane **3** by 94.5 kJmol^{-1} (Scheme 3). Indeed by reacting **III** with acetylenes the formation of **XI** occurs straight away [16,36], indicating the higher stability of titanacyclobutenes.

2.3.2. *Oxatitanacyclobutane*

Metallaoxetanes such as $Cp_2\overline{TiCH_2CR_2O}$ (R = Organyl) have been proposed as intermediates in various transition-metal catalyzed oxygen-transfer reactions [10,37,38]. Oxatitanacyclobutanes of this type have not yet been isolated. They undergo spontaneous ring opening under formation of $Cp_2'Ti{=}O$ and alkene, a reaction which is widely applied in the methylenation of carbonyl compounds [1,3]. [2+2]-Cycloadditions of group 6 metallocene oxo complexes with ethylene have been studied computationally and it was concluded that the oxo chemistry of the compounds $Cp_2M{=}O$ with M = Mo, W is dominated by addition processes which preserve M–O bonding. Complete M–O bond scission is driven only by processes which form very strong product bonds to oxygen, e.g. Si–O or H–O [39].

The titanaoxetane **6** is protected against metathesis reaction by an energy barrier of 76.9 kJ mol^{-1} (Scheme 4). Titanaoxetanes $Cp^*_2\overline{Ti(C{=}CH_2)CR_2O}$ with $R_2 = O$ (**IV**), CPh_2 (**V**), NC_6H_{11} (**VI**) have been isolated and **V** and **VI** have been characterized structurally [2,40]. All three compounds are thermally stabile up to nearly 150 °C. The fragmentation of these compounds in the mass spectrometer indicates the formation of $Cp^*_2Ti{=}O$. On the other hand, compounds of type **7** with the *exo*-methylene group in the β-position have been isolated as well, for instance **XIV** [23]. A rearrangement of **6** to **7** or vice versa should be possible due to the calculated energy barriers of 76.9 kJ mol^{-1} starting from **6** to $\mathbf{TS_{6-8}}$ or 99.6 kJ mol^{-1} from **7** to $\mathbf{TS_{7-8}}$. However this type of rearrangement was not yet experimentally detected.

The addition of formaldehyde to the titanocene vinylidene (**1**) proceeds via the primary formation of an adduct $\mathbf{AD_{1-6}}$, as mentioned above. There is a very low activation barrier of 14.9 kJ mol^{-1} from this adduct to the transition state $\mathbf{TS_{1-6}}$, which is an early transition state if we compare the geometries of $\mathbf{AD_{1-6}}$, $\mathbf{TS_{1-6}}$ and **6**. This is in accordance with the Hammond postulate, which says that more exothermic reactions usually have earlier transition states [41,42]. It is remarkable that the TiO distance in $\mathbf{TS_{1-6}}$ is longer than in the adduct $\mathbf{AD_{1-6}}$ (2.305 vs. 2.104 Å, respectively). The metathetic ring opening reaction from the titanaoxetanes **6** and **7** proceeds via the cyclic transition states $\mathbf{TS_{6-8}}$ and $\mathbf{TS_{7-8}}$ to the products $Cp_2Ti{=}O$ (**8**) and allene. The distances O–C3 ($\mathbf{TS_{6-8}}$) and O–C2 ($\mathbf{TS_{7-8}}$) are about 2.0 Å in both transition states. The bond length Ti–C1 is at 2.284 Å in $\mathbf{TS_{6-8}}$ and at 2.324 Å in $\mathbf{TS_{7-8}}$. There is not such a big difference between the distances of the reacting atoms like in $\mathbf{TS_{1-6}}$. This hints to a concerted synchronous [2+2]-cycloreversion. No further adduct complexes were found in these reactions, which meets our expectations since allene is a nonpolar reagent (Fig. 3).

Table 2
Results of the charge decomposition analysis of transition states and adducts

Molecule	*d* (donation) $L \rightarrow Cp_2Ti{=}C{=}CH_2$	*b* (backdonation) $L \leftarrow Cp_2Ti{=}C{=}CH_2$	*r* (repulsive polarization) $L \leftrightarrow Cp_2Ti{=}C{=}CH_2$	Δ (residue term)
$\mathbf{TS_{1-3}}$	0.128	0.020	−0.055	−0.003
$\mathbf{TS_{1-4}}$	0.166	0.006	−0.049	0.001
$\mathbf{AD_{1-5}}$	0.193	0.086	−0.258	−0.002
$\mathbf{TS_{1-5}}$	−0.028	0.002	−0.116	−0.009
$\mathbf{AD_{1-6}}$	0.225	0.059	−0.205	−0.002
$\mathbf{TS_{1-6}}$	0.241	0.062	−0.198	−0.011

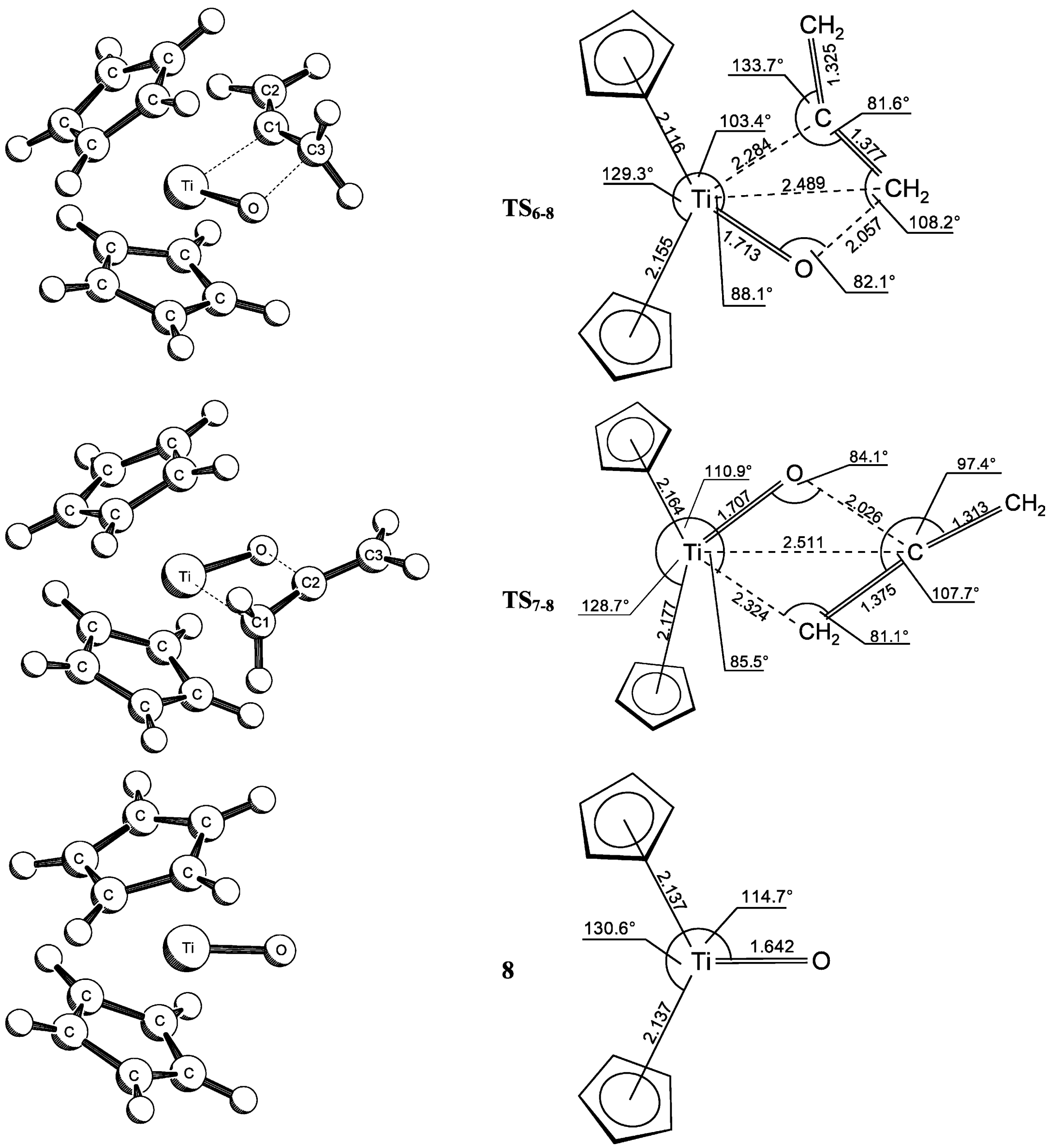


Fig. 3. Transition states $\mathbf{TS_{6-8}}$ and $\mathbf{TS_{7-8}}$ and product **8** of metathesis of titanaoxetanes.

2.3.3. Azatitanacyclobutene

Azametallacyclobutenes are subject to facile ring opening reactions [15]. In contrast azametallacyclobutanes with an exocyclic methylene group like **IX** are isolable products which were characterized by X-ray structure analysis [43]. The calculated energy profile confirms that the azatitanacyclobutene with exocyclic methylene group (**5**) is the thermodynamic stable product (Scheme 5). The reaction of **1** with HCN proceeds via the formation of the adduct $\mathbf{AD_{1-5}}$ where the free electron pair of the nitrogen atom coordinates at the electrophilic titanium atom. This adduct rearranges to the transition state $\mathbf{TS_{1-5}}$ with a planar [2+2]-arrangement of the atoms to form the azatitanacyclobutene ring. The azatitanacyclobutene **5** is protected against ring opening reactions by a considerable energy barrier of 89.7 kJ mol^{-1}. This is in accordance with experimental findings, since compound **IX** (R = *t*-Bu) reacts at higher temperature with an excess of nitrile to give a diazatitanacyclohexadiene derivative [43]. Primary step of this reaction should be the opening of the azatitanacyclobutene ring between titanium and C1. The transition state $\mathbf{TS_{5-9}}$ of this reaction is shown in Fig. 4. The unit Ti–N–C3–C1 in $\mathbf{TS_{5-9}}$ is not planar as in **5** with a torsion angle of −57.2°. The bond lengths Ti–N and C1–C3 are shortened to 1.771 and 1.344 Å, respectively. The allene unit C3–C1–C2 gets linearized with an angle of 169.6°. This trend is continued in the imidotitanocene **9**, which has an angle C3–C1–C2 of 177.4°. Striking difference between $\mathbf{TS_{5-9}}$ and **9** is the conformation of the substituent C3–C1–C2 at the imido nitrogen atom. This group has a lateral orienta-

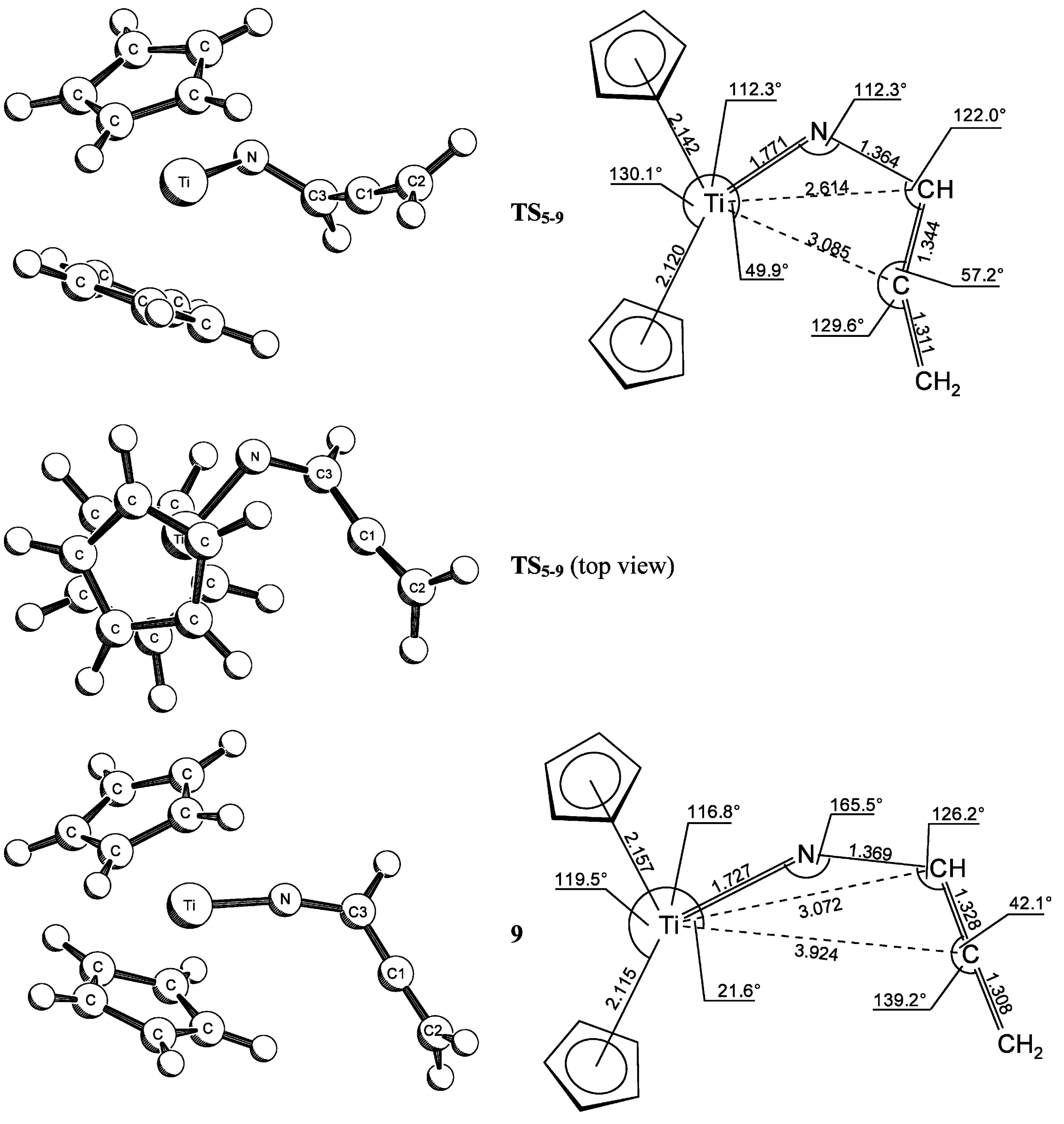


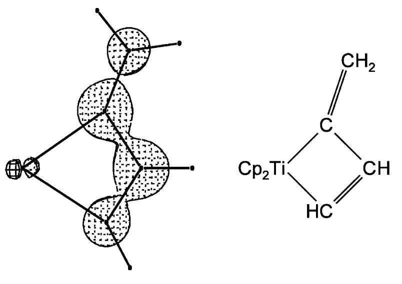
Fig. 4. Transition state $\mathbf{TS_{5-9}}$ and product **9** of ring opening reaction of azatitanacyclobutene.

tion in $\mathbf{TS_{5-9}}$, whereas it is oriented ‘down’ in **9**. This reorientation is accompanied by a widening of the angle Ti–N–C3 to 165.5° and a further shortening of the Ti–N bond by 0.044 Å

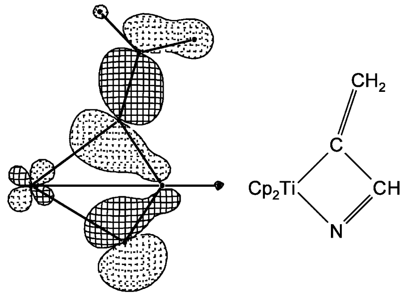
2.3.4. Molecular orbital analysis of four-membered titanacycles

In order to understand the electronic structure of four membered titanacycles a MO analysis with the extended Hückel method was performed with some derivatives [44–48]. Selected molecular orbitals of **4**, **5** and **6** are shown in Fig. 5. All three compounds have very similar sigma-type orbital interactions between the titanocene fragment and the organic substituents in the bisecting plane of the metallocene and will be not further discussed. Striking differences are only found for the orbital interactions between the atom **A** and the titanocene unit.

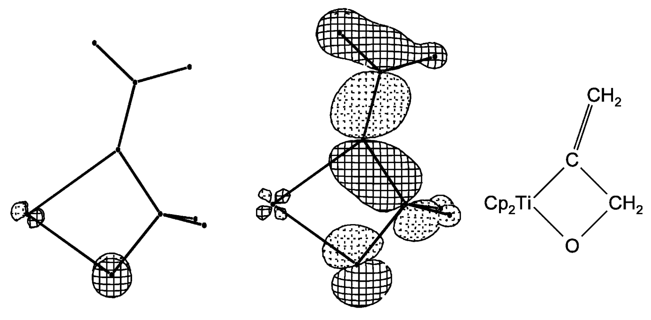
The carbon atoms bound to the titanocene fragment in **4** are all sp^2-hybridized. The π-orbitals of the substituents have only weak interactions with d-orbitals at the titanium atom as it is shown in Fig. 5 (top). The most favorable orbital interaction between the titanium atom and the atom **A** in α-postion can be expected for atoms **A** which have suitable occupied orbitals in the bisecting plane of the titanocene unit. These orbitals may attain overlap with the empty b_2 orbital of the titanocene moiety. In fact this type of interaction is found in the azatitanacyclobutenes **5** and the titanaoxetanes **6** (Fig. 5, middle and bottom). The lone pair at the nitrogen atom in **5** is situated in the bisecting plane of the metallocene and overlaps with the b_2 acceptor orbital at the titanium atom. A similar situation is found in **6**: one electron pair of the oxygen atom is situated in the bisecting plane of the metallocene unit, the other one is orientated perpendicular. The influence of these



MO 55 E = -14.09 eV **4**



MO 47 E = -13.02 eV **5**



MO 58 E = -14.52 eV MO 52 E = -14.02 eV **6**

Fig. 5. Molecular orbitals of **4**, **5** and **6** from EHT-analysis.

different orbital interactions on the reactivity of titanacyclobutane and titanacyclobutene derivatives will be discussed in the next section.

The orbital interactions described above were also found in the Kohn–Sham MO's from the DFT-calculations. Since the Kohn–Sham MO's do not carry quite the same significance as MO's in Hartree–Fock or extended Hückel theory we relied on the orbital interactions from extended Hückel calculations [49,50].

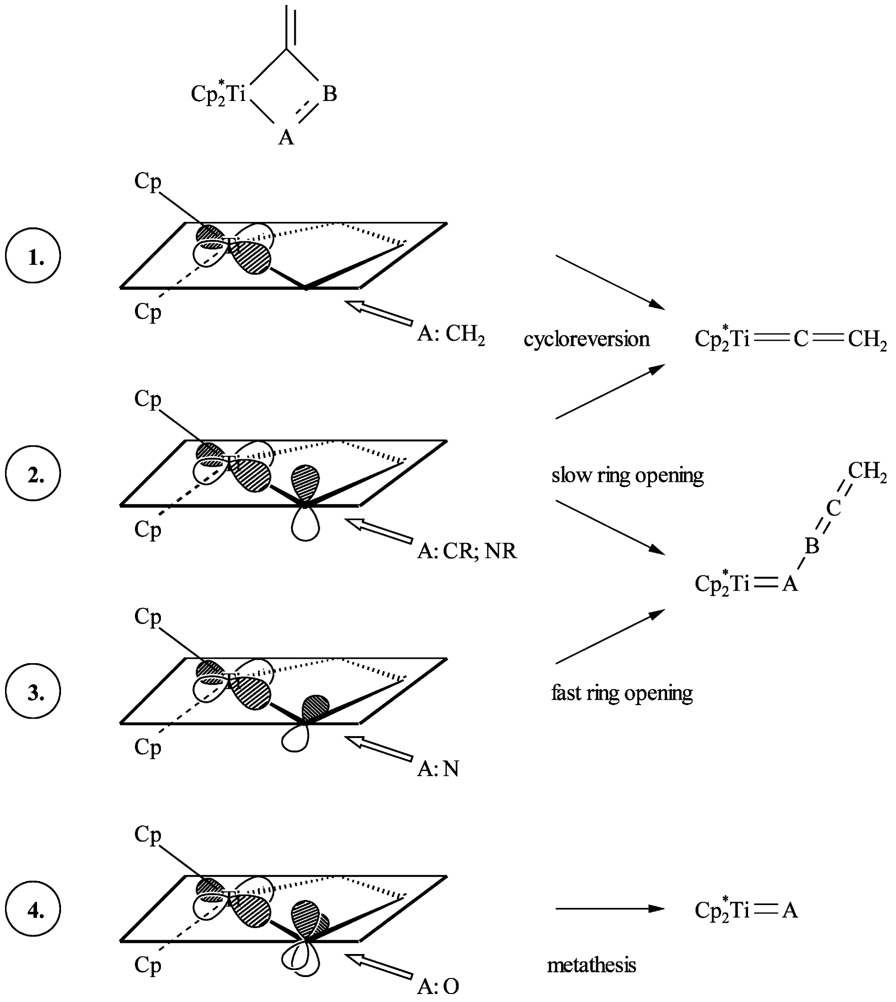
2.3.5. Comparative discussion of reactivity

Depending on the nature of hetero atom **A** and the orbital situation at this atom, different types of subsequent reactions of the titanacycles **III**–**XIII** are observed (Scheme 6).

1) Compounds without donor orbitals at **A**: In the case of the titanacyclobutane **III**, cycloreversion reactions dominate, leading to the vinylidene intermediate **I**.
2) Compounds with a donor orbital at **A** perpendicular to the bisecting plane of the metallocene: For the titanacyclobutenes **XI** and azatitanacyclobutanes **XII** and **XIII** the p_z-orbital of the double bond (**XI**) respectively the lone pair at the nitrogen atom (**XII** and **XIII**) is orientated perpendicular to the bisecting plane of the titanocene unit. This causes only weak π-interactions between the titanocene unit and the atom **A**. Cycloreversion or slow electrocyclic ring opening reactions are observed. Electrocyclic ring opening reactions leading to the formation of polyacetylene are found in case of unsubstituted titanacyclobutenes **XI** [16]. The reactivity of the titanacyclobutenes **XI** with substituents at **A** and **B** is mainly controlled by the steric and electronic properties of these substitutents [36]. The azatitanacyclobutanes **XII** and **XIII** are thermally stable up to 150 °C. Above this temperature the azatitanacyclobutane **XII** with $R = C_6H_{11}$ undergoes a cycloreversion under liberation of the carbodiimide [8].
3) Compounds with a donor orbital at **A** in the bisecting plane of the metallocene: Fast ring opening reactions leading to formally insertion products of nitrils in the Ti–C bond occur in the case of the azatitanacyclobutenes **IX** [43]. The lone pair at the nitrogen atom (**A**) is located in the same plane as the acceptor orbital at the titanium atom (see Scheme 6). This orbital interaction represents de facto a 'preformed' double bond and allows a fast ring opening to form intermediate titanaimides and derivatives thereof.
4) Compounds with one donor orbital in the bisecting plane of the metallocene and one perpendicular orientated occupied orbital at **A**: Two lone pairs are present in the titanaoxetanes **IV**–**VI**. They do not cause any electrocyclic ring opening because of their low energy. Strong interactions between the oxygen atom **A** and the metallocene unit are already present in the titanaoxetane. Therefore metathesis reactions are mainly observed which retain the Ti–O bond. The metathesis reaction forming [$Cp_2Ti{=}O$] is allowed by symmetry and has an accessible energy barrier, as shown above. In case of the oxetanes **IV**–**VI** metathesis reactions are observed by mass spectroscopy, whereas from the nonclassical oxetanes **VII** the reactants are formed [1,18].

3. Conclusions

The results of quantum mechanical calculations at the DFT level of theory on a number of titanium complexes have been discussed. [2+2]-cycloadditions of the titanocene–vinylidene [$Cp_2Ti{=}C{=}CH_2$] intermediate with organic π-systems yields four-membered titana-



Scheme 6.

cycles. The transition states and reaction pathways for these cycloadditions have been investigated. Nonpolar reagents like alkenes or alkynes react via a [2+2]-cycloaddition to give titancyclobutanes and -butenes. In contrast to that the polar reagents containing CO or CN groups react via a titanium donor ligand complex followed by rearrangement to the titanacycles. A mechanism for the rearrangement of titanaoxetanes with the exocyclic methylene group in α-position to Ti into titanaoxetanes with the exocyclic methylene group in β-position has been proposed.

The influence of the group **A** (CH$_2$, CR, NR, O, N) in titanacyclobutanes and -butenes $Cp_2\overline{TiC(=CH_2)BA}$ becomes understandable from the electronic ground state structure of these complexes. Compounds without lone pairs at **A** in the bisecting plane of the metallocene unit undergo cycloreversion or slow electrocyclic ring opening reaction. Compounds with a lone pair at **A** in the bisecting plane of the metallocene unit undergo metathesis or fast electrocyclic ring opening.

4. Computational details

4.1. DFT calculations

Calculations have been performed with Gaussian 98 [51]. All geometries have been fully optimized with density functional methods. Beckes three-parameter hybrid-exchange functional and the correlation functionals from Lee, Yang and Parr were used (B3LYP) [52,53]. Geometry optimization and frequency calculations have been performed with an effective core potential and valence double zeta basis set for titanium [54] and 6-31G* basis set for all main group elements [55,56]. The structures of all molecules have been identified as minima with 0 imaginary frequencies or as transition states with one imaginary frequency by calculating the Hessian–Matrices. To receive a more detailed picture of the reaction pathways the intrinsic reaction coordinates (IRC) have been calculated starting from the transition states [57,58]. The energies in

Schemes 3–6 are in kJ mol^{-1} and have been calculated from the total energies of the optimized molecules including zero point corrections. The CDA calculations have been performed using the program CDA 2.1 [59]. A detailed presentation of the method and the interpretation of the results is given in Ref. [32].

4.2. Extended Hückel calculations

Molecular orbital calculations were performed with CACAO [48]. The molecules were constructed for this purpose according to the data of X-ray structure analyses.

Acknowledgements

I wish to express my thanks to Rüdiger Beckhaus for helpful discussions. Special thanks are given to the Computing Center of the TU Bergakademie Freiberg for supplying disk space and computing time.

References

[1] R. Beckhaus, Angew. Chem. 109 (1997) 694; Angew. Chem. Int. Ed. Engl. 36 (1997) 686.

[2] R. Beckhaus, in: D. Enders, H.-J. Gais, W. Keim (Eds.), Organic Synthesis via Organometallics (OSM 4) Methylidentitanacyclobutane vs. Titanocene–Vinylidene — Versatile Building Blocks in Organic Synthesis via Organometallics (OSM 4), Proceedings of the Fourth Symposium in Aachen, 15–18 July, 1992, Vieweg Verlag Braunschweig, 1993, p. 131.

[3] S.H. Pine, in: L.A. Paquette (Ed.), Carbonyl Methylenation and Alkylidation using Titanium-Based Reagents in Organic Reactions, vol. 43, Wiley, New York, 1993, p. 1.

[4] R.H. Grubbs, R.H. Pine, in: B.M. Trost (Ed.), Comprehensive Organic Synthesis; Alkene Metathesis and Related Reactions in Comprehensive Organic Synthesis, vol. 5, Pergamon, New York, 1991, p. 1115.

[5] K.M. Doxsee, J.B. Farahi, J. Am. Chem. Soc. 110 (1988) 7239.

[6] S. Yamada, Y. Akihiro, Tosoh Corporation, EP0587141 and EP 0587143.

[7] R. Beckhaus, J. Chem. Soc. Dalton Trans. (1997) 1991.

[8] R. Beckhaus, J. Oster, J. Sang, I. Strauß, M. Wagner, Synlett (1997) 241.

[9] U. Böhme, R. Beckhaus, J. Organomet. Chem. 585 (1999) 179.

[10] B. Schiøtt, K.A. Jørgensen, J. Chem. Soc. Dalton Trans. (1993) 337.

[11] K.M. Doxsee, J.K.M. Mouser, J.B. Farahi, Synlett (1992) 13.

[12] K.M. Doxsee, J.B. Farahi, H. Hope, J. Am. Chem. Soc. 113 (1991) 8889.

[13] K.M. Doxsee, J.B. Farahi, J. Chem. Soc. Chem. Commun. (1990) 1452.

[14] R. Beckhaus, C. Santamaría, J. Organomet. Chem. 617-618 (2001) 81.

[15] R. Beckhaus, C. Zimmermann, T. Wagner, E. Herdtweck, J. Organomet. Chem. 460 (1993) 181.

[16] R. Beckhaus, J. Sang, T. Wagner, B. Ganter, Organometallics 15 (1996) 1176.

[17] R. Beckhaus, J. Oster, T. Wagner, Chem. Ber. 127 (1994) 1003.

[18] R. Beckhaus, J. Oster, Z. Anorg. Allg. Chem. 621 (1995) 359.

[19] R. Beckhaus, J. Sang, T. Wagner, U. Böhme, J. Chem. Soc. Dalton Trans. (1997) 2249.

[20] R. Beckhaus, S. Flatau, S. Trojanov, P. Hofmann, Chem. Ber. 125 (1992) 291.

[21] S. De Angelis, E. Solari, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Angew. Chem. 107 (1995) 1200; Angew. Chem. Int. Ed. Engl. 34 (1995) 1092.

[22] A.C. Legon, Chem. Rev. 80 (1980) 231.

[23] D.J. Schwartz, M.R. Smith, III, R.A. Andersen, Organometallics 15 (1996) 1446.

[24] G. Hauptmann, Organische Chemie, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1985, p. 216.

[25] C. Liang, L.C. Allen, J. Am. Chem. Soc. 113 (1991) 1878.

[26] B. Schiøtt, K.A. Jørgensen, J. Chem. Soc. Dalton Trans. (1993) 337.

[27] D.J. Schwartz, M.R. Smith, III, R.A. Andersen, Organometallics 15 (1996) 1446.

[28] G.E. Herberich, C. Kreuder, U. Englert, Angew. Chem. 106 (1994) 2589; Angew. Chem. Int. Ed. Engl. 33 (1994) 2465.

[29] R. Beckhaus, J. Sang, J. Oster, T. Wagner, J. Organomet. Chem. 484 (1994) 179.

[30] R. Beckhaus, M. Wagner, R. Wang, Eur. J. Inorg. Chem. (1998) 253.

[31] F.A. Carey, R.J. Sundberg, Advanced Organic Chemistry, 3rd ed., Plenum Press, New York, 1993, p. 638.

[32] S. Dapprich, G. Frenking, J. Phys. Chem. 99 (1995) 9352.

[33] D.V. Deubel, G. Frenking, J. Am. Chem. Soc. 121 (1999) 2021.

[34] D.V. Deubel, S. Schlecht, G. Frenking, J. Am. Chem. Soc. 123 (2001) 10085.

[35] D.V. Deubel, J. Phys. Chem. A 106 (2002) 431.

[36] R. Beckhaus, J. Sang, U. Englert, U. Böhme, Organometallics 15 (1996) 4731.

[37] K.A. Jørgensen, B. Schiøtt, Chem. Rev. 90 (1990) 1483.

[38] K.A. Jørgensen, Chem. Rev. 89 (1989) 431.

[39] L. Luo, G. Lanza, I.L. Fragalà, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 3111.

[40] R. Beckhaus, I. Strauß, T. Wagner, P. Kiprof, Angew. Chem. 105 (1993) 281; Angew. Chem. Int. Ed. Engl. 32 (1993) 264.

[41] G.S. Hammond, J. Am. Chem. Soc. 77 (1955) 334.

[42] D.V. Deubel, T. Ziegler, Organometallics 21 (2002) 4432.

[43] R. Beckhaus, I. Strauß, T. Wagner, Angew. Chem. 107 (1995) 738; Angew. Chem. Int. Ed. Engl. 34 (1995) 688.

[44] R. Hoffmann, J. Chem. Phys. 39 (1963) 1397.

[45] R. Hoffmann, W.N. Lipscomb, J. Chem. Phys. 36 (1962) 2179.

[46] R. Hoffmann, W.N. Lipscomb, J. Chem. Phys. 37 (1962) 2872.

[47] J.W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.

[48] C. Mealli, D.M. Proserpio, J. Chem. Educ. 67 (1990) 399.

[49] P. Politzer, F. Abu-Awwad, Theor. Chem. Acta 99 (1998) 83.

[50] For a comparative discussion of molecular orbitals from EHT, HF and DFT-methods see: R. Stowasser, R. Hoffmann, J. Am. Chem. Soc. 121 (1999) 3414.

[51] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.6, Gaussian Inc., Pittsburgh, PA, 1998.

[52] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[53] C. Lee, W. Yang, R.G. Parr, J. Phys. Chem. B37 (1988) 785.
[54] (a) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270;
(b) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 284;
(c) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299.
[55] P.C. Hariharan, J.A. Pople, Theoret. Chim. Acta 28 (1973) 213.
[56] M.M. Francl, W.J. Pietro, W.J. Hehre, J.S. Binkley, M.S. Gordon, D.J. DeFrees, J.A. Pople, J. Chem. Phys. 77 (1982) 3654.
[57] K. Fukui, Acc. Chem. Res. 14 (1981) 363.
[58] C. Gonzalez, H.B. Schlegel, J. Chem. Phys. 95 (1991) 5853.
[59] S. Dapprich, G. Frenking, Marburg, CDA 2.1, 1994. The program is available via: ftp.chemic.uni-marburg.de/pub/cda.