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Structure and reactivity of four-membered titanacycles—theoretical studies

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Abstract

The equilibrium geometries of a series of four-membered titanacycles with exocyclic methylene group $\mathrm{Cl_2\overline{Ti-X-Y-C}{=}CH_2}$ (X: CH_2, CH, O, S, N, P; Y: CH_2, CH, C=O, $C{=}CH_2$, $N-CH_3$) and two derivatives without exocyclic methylene group $\mathrm{Cl_2\overline{Ti-X-CH_2-C}H_2}$ (X: CH_2, O) have been calculated at the HF level of theory by using an effective core potential basis set. The geometries were compared with data from X-ray structures for the corresponding compound $\mathrm{Cp^*_2\overline{Ti-X-Y-C}{=}CH_2}$. The structures of the planar four-membered titanacycles are well represented by the model complexes. The chloride ligands are good theoretical substitutes for the bent metallocene system with cyclic ligand systems in the intersecting plane between the Cp* ligands. The calculated metal–carbon bond distances are found to be shorter than in the X-ray structures of the real molecules. Total energies are calculated at the MP2 level and are used to predict the reactivity of the compounds. Titanacyclobutanes with an exocyclic methylene group are more stable than titanacyclobutanes without this group. Oxatitanacyclobutanes are subject to cycloreversion under formation of $Cl_2Ti{=}O$ and allene. Azatitanacyclobutenes undergo spontaneous ring opening reactions. These statements are further supported by the analysis of the molecular orbitals of some selected derivatives. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ab initio calculations; Titanium; Metallacycles; Titanacyclobutanes

1. Introduction

Titanacyclobutanes and -butenes are encountered throughout the literature [1–21]. For instance, the conversion of organic carbonyl compounds to alkenes via methylenation reactions has been facilitated by 'Grubbs reagent' [2]. Titanacyclobutanes have been used as polymerization catalysts for syndiotactic polymerization of styrol [3]. During our investigations, which concerned the chemistry of vinyl complexes of electron poor transition metals, we were able to find a low temperature route to the versatile titana-allene building block $[Cp^*_2Ti{=}C{=}CH_2]$ (Cp*: C_5Me_5) (**1**) [4–6]. Reactions between the intermediate **1** and unsaturated substrates lead to the four-membered titanacycles **3**–**12** [7–15]. Generally, oxatitanacyclobutanes [16] and azatitanacyclobutenes [17] are discussed as intermediates in reactions of carbenoid titanium compounds with carbonyl compounds or nitriles. The high electrophilicity of the metal centre has generally prohibited the isolation and characterization of oxa- and azatitanacyclobutanes; spontaneous ring opening reactions afford carbonyl olefination [2b], or products of vinylimido intermediates [18,19]. The high thermal stability of the metallacycles **3**–**12** is the major advantage of using **1** instead of titanium methylene intermediates. Therefore, **1** acts as an excellent highly nucleophilic titanium carbene, but it also shows the characteristic properties of a metalla-allene.

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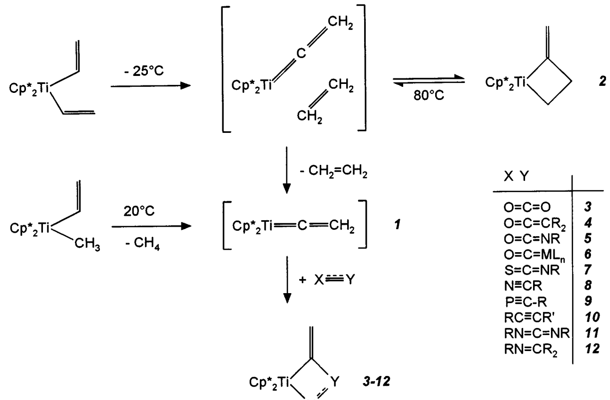


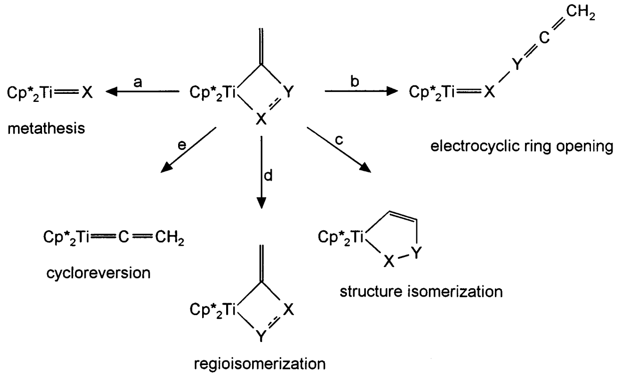
The titanacycles **3**–**12** are isolable products and can therefore serve as substrates to investigate several subsequent reactions (Scheme 1). Metathesis products (reaction **a**) are found for the oxetanes **3**–**5** [4], whereas electrocyclic ring opening reactions (**b**) are proposed for **8** [20] and in part for **10** [13]. Cycloreversions (**e**) dominate for the nonclassical oxetanes **6**, leading via a acetylene vinylidene rearrangement to five-membered rings (**c**) [10,21]. Regioisomerization (**d**) was found to occur by heating titanathietanes **7** [11].

In a series of such studies we wanted to gain a more detailed knowledge of the electronic properties of **2**–**12** in order to explain structure–reactivity relations by using ab initio calculations at the restricted Hartree–Fock level of theory. In our ab initio calculations the Cp* groups of the real molecules **2**–**12** were replaced by chloride ligands, which provides a good theoretical substitute for the actual bent metallocene system, as has been shown in other studies [11,22].

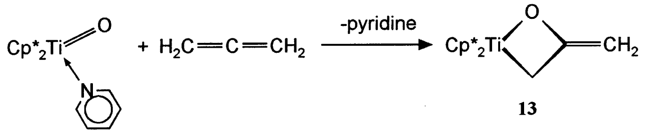
2. Results and discussion

2.1. Structures of titanacycles

The conformations of four-membered rings in carbon chemistry have been extensively studied [23]. Cyclobutane is puckered with a dihedral angle of 34°, while oxetane is planar. Mostly the metallacycles **2**–**12** are found to be planar. Occasionally puckering effects also are discussed, particularly in the case of four-membered metallacycles with exocyclic double bonds in the β-position, like **13** [24].



Scheme 1.



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The structures of the model complexes will be discussed in the following part. The geometries of various titanaoxetanes have been optimized some years before, using the STO-3G* basis set and a general basis set (GBS) [16].

It is well known that 'square' molecules such as cyclobutane are nonplanar because of the repulsion among the eclipsing hydrogens and angle strain. When one of the methylene groups is replaced by a more electronegative atom or group, the molecule will assume 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]. In order to rationalize the structure and reactivity behaviour of the titanium containing metallacycles **3**–**12**, we have carried out ab initio calculations on the Cl_2Ti-model complexes **I**–**XV**. The results are shown in Figs. 1 and 2.

The comparison of structure relations in the real complexes **2**, **4**, **5**, **7**–**10** and **13** with those in the model complexes **I**–**IX** is shown in Fig. 2. It is well understandable that the angle α is smaller for the model complexes than the Cp*–Ti–Cp* angle in the real molecules due to the different spatial requirements of a Cp* and a Cl-ligand. For the same reasons the β angle becomes smaller for the real molecules and larger for the calculated derivatives by about 5°.

The titanium–carbon bond distances **a**, **b** and **c** are found to be shorter in the calculated molecules by 0.1 Å (Fig. 2). Good agreement of the bond lengths are found for the distances **d**, **e** and **f**. From the structural data of **10a**–**c** it is obvious that the substituents at the titanacyclobutene ring considerably influence the geometry [13,14]. (For **10a**–**10c** X–Y is RC≡CR′ with R, R′ = Me for **10a**; R = $SiMe_3$, R′ = Ph for **10b**; R = $CCSiMe_3$, R′ = $SiMe_3$ for **10c**.) Therefore, the geometry of a simple model compound like **II** has to suffice to obtain basic information about energetics and composition of molecular orbitals. The ring diagonal distance **c** is identical for the titanacyclobutane **I**/**2**, the oxetanes **IV**/**4**–**5**, and **V**/**13**, but shorter for the titanacyclobutenes **II** and the S, N and P substituted derivatives.

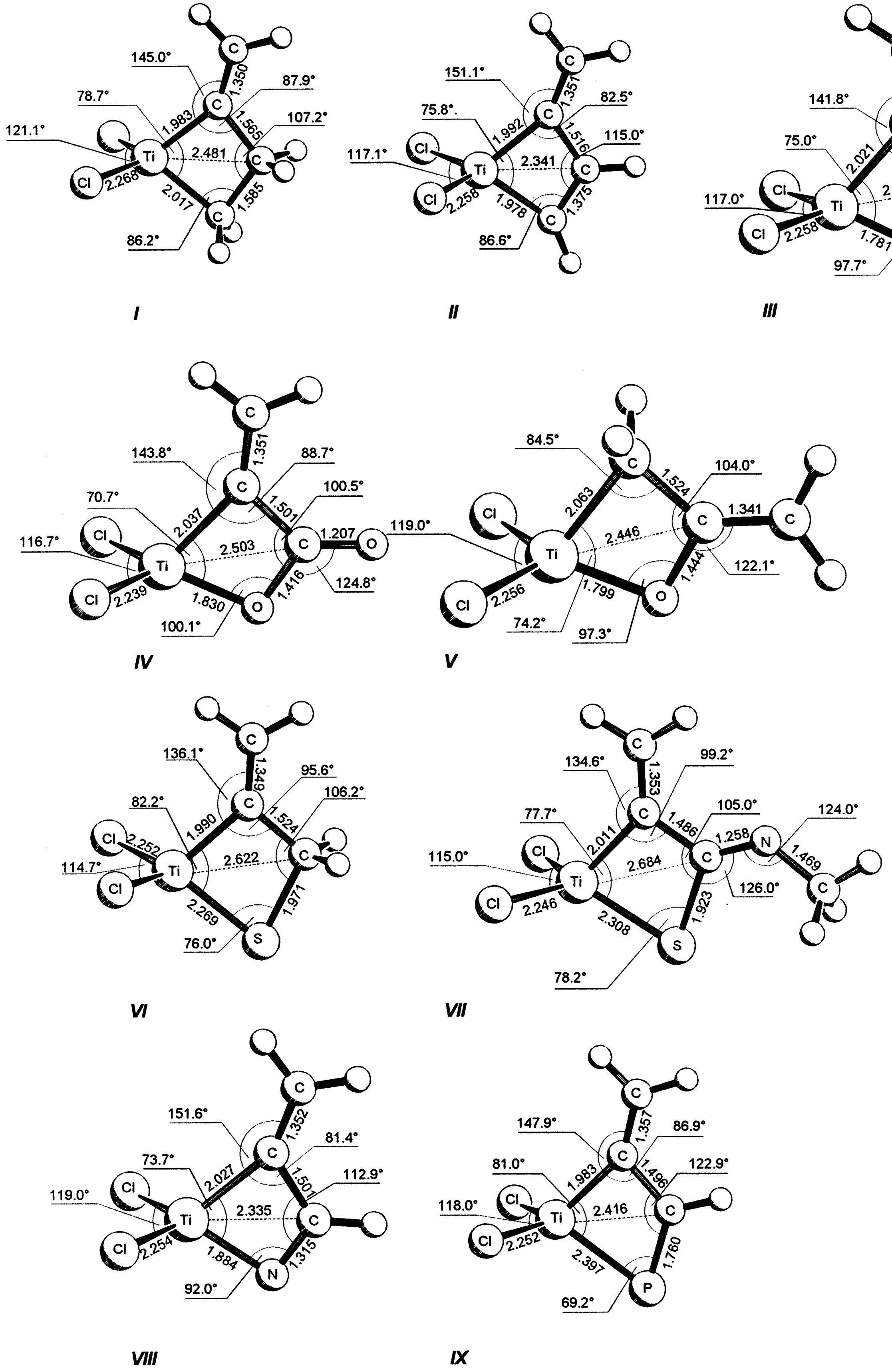


Fig. 1. Optimized geometries of **I**–**XV** at the RHF level.

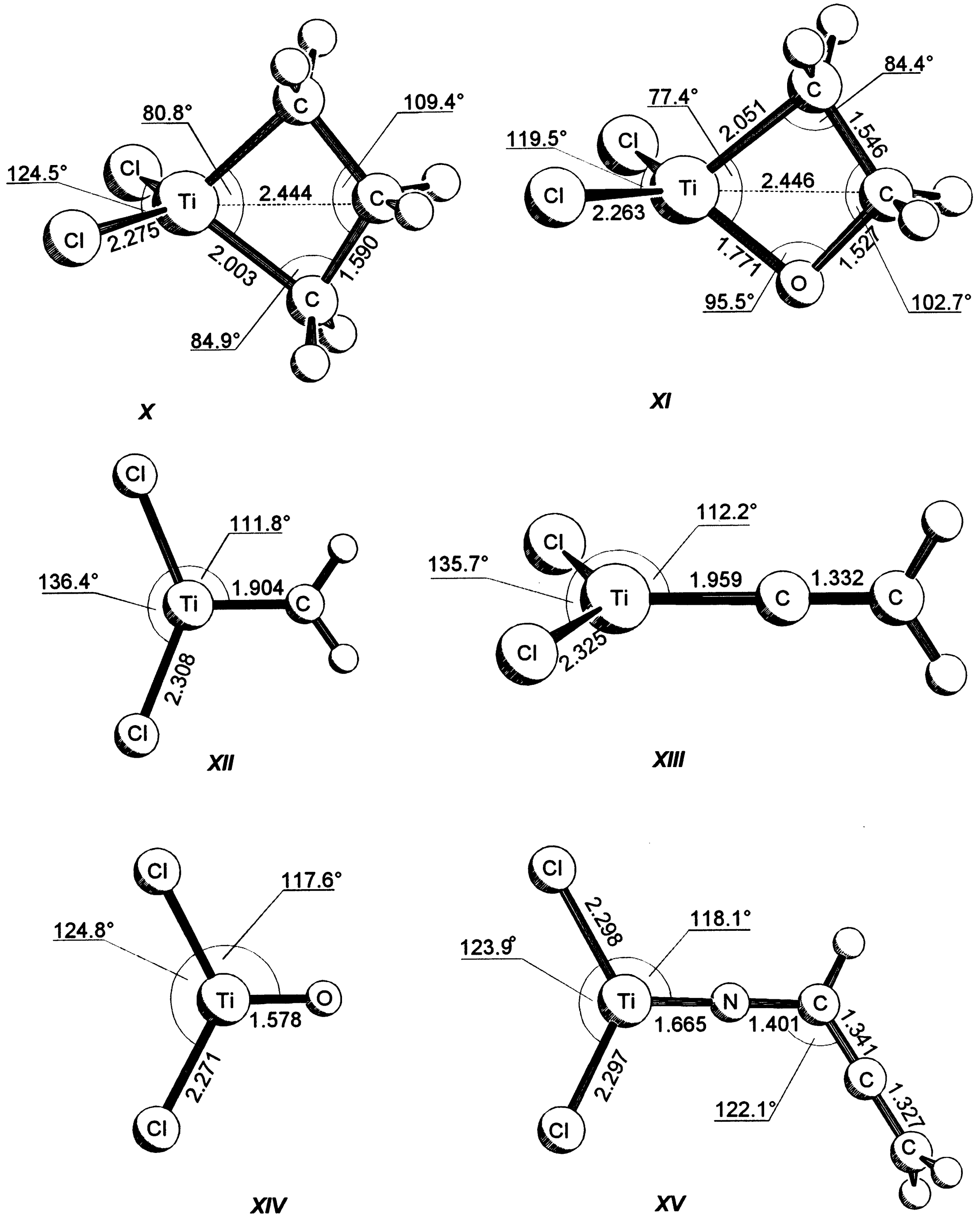


Fig. 1. (*Continued*)

The four-membered titanacycles in the model complexes **I**–**XI** were found to be planar in all cases. Due to a molecular orbital analysis which has been done previously on titanaoxetanes, there is no gain in energy by puckering of the ring [16]. Planar four-membered rings have also been found in the X-ray structures of **2**, **7**, **8**, **9**, **10**. For these types of complexes the simple Cl_2Ti model should meet the requirements for reproducing the geometries from X-ray structures. Puckered four-membered metallacycles have been found in **13** and **14**, with 22.5 and 33.0°, respectively [24,26]. In these compounds

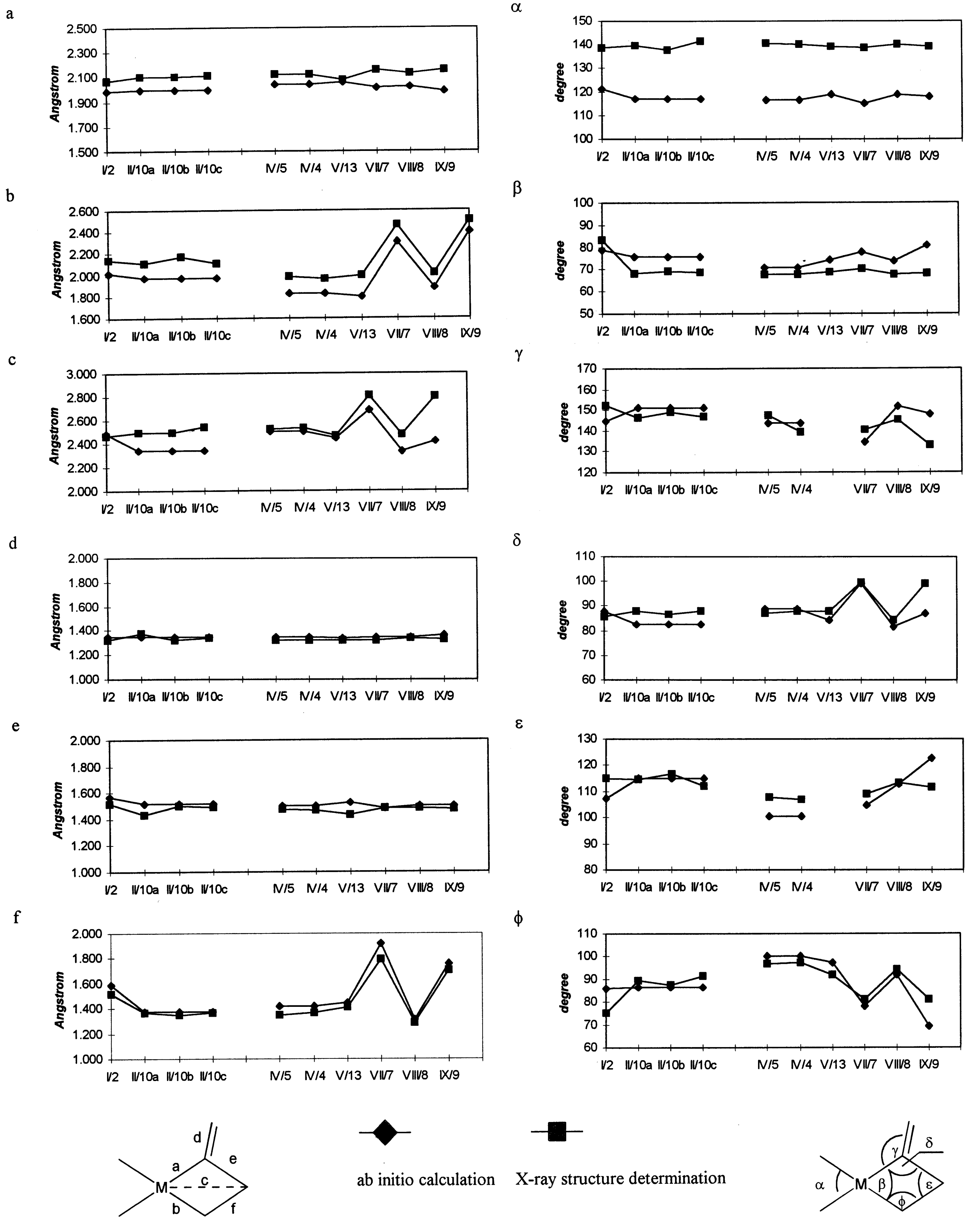
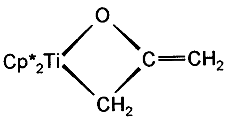


Fig. 2. Distances and angles in **2**, **4**, **5**, **7**–**10**, **13** compared to the model complexes **I**–**IX** (beginning left: **I**/**2**; **II**/**10a**–**10c**; **IV**/**5**,**4**; **V**/**13**; **VII**/**7**; **VIII**/**8**; **IX**/**9**).

the *exo*-methylene group is situated in β-position to the metal.



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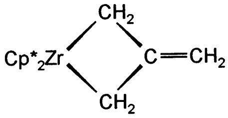

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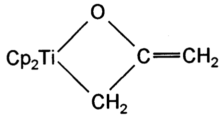
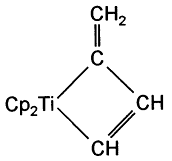
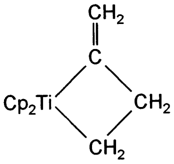


Va



IIa



Ia

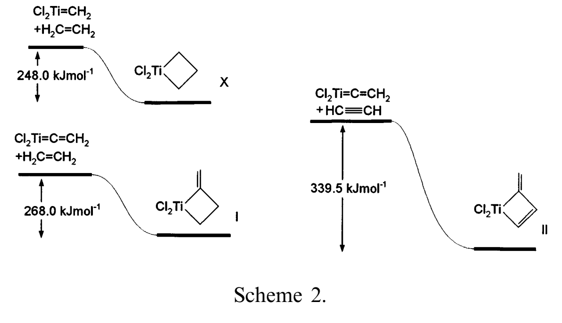
The geometry optimization was repeated with the Cp_2Ti framework for the model complexes **Ia**, **IIa**, **Va** in order to demonstrate the effect of ring puckering. **IIa** was found to be completely planar. For **Ia** and **Va**, small ring torsion angles of 6.8 and 3.9° were found. Both **Ia** and **Va** have CH_2 ring groups in α-position to the metal atom. These hydrogen atoms are directed away from the metallacycles. It was concluded by Anderson [24] that this puckering effect arises from repulsive interactions between the cyclopentadienyl groups (Cp* in the real molecules) and the α-hydrogen atoms. Naturally, this effect would be larger if the sterically demanding Cp* ligands were taken into account in the calculations.

2.2. Reactivity of titanacycles

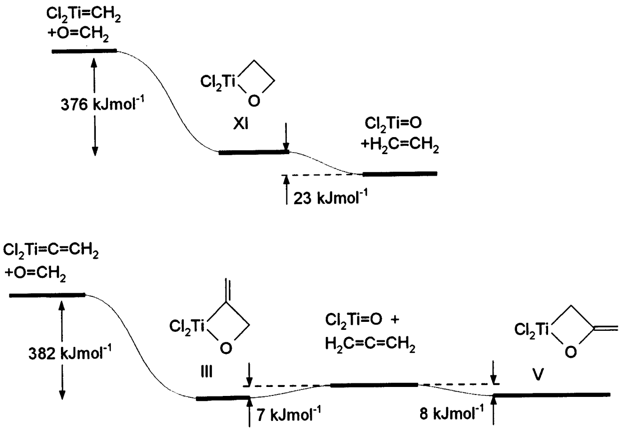
The titanacycles **X** and **XI** without an exocyclic methylene group and the titana-ethylene **XII**, titana-allene **XIII**, titanoxide **XIV** and the titanimine derivative **XV** were also optimized (Fig. 1) in order to compare reaction enthalpies.

2.2.1. Titanacyclobutanes and titanacyclobutene

As shown in Scheme 1, different reaction types are observed for the metallacycles **2**–**12**. The greatest advantage of the metallacycles derived from the titana-allene **1** compared with methylene building blocks of the $[Cp_2Ti{=}CH_2]$ type lies in the high thermal stability of the metallacycles **2**–**12**. In this regard, it can be deduced from the results of our calculations that the formation of the titanacyclobutane **I** is more exothermic than the formation of the titanacycle $Cl_2\overline{TiCH_2CH_2CH_2}$ (**X**) by 20.0 kJ mol^{-1} (Scheme 2).



Scheme 2.



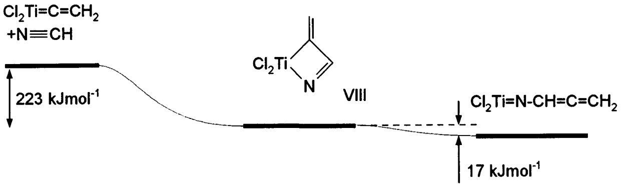
Scheme 3.

The formation of the titanacyclobutene **II** is more exothermic than that of the titanacyclobutane **I** by 71.5 kJ mol^{-1} (Scheme 2). Indeed by reacting **2** with acetylenes the formation of **10** occurs in a few minutes [13,14], indicating the higher stability of titanacyclobutenes.

2.2.2. Oxatitanacyclobutanes

Metallaoxetanes such as $Cp_2\overline{TiCH_2CR_2O}$ (R = H, Me, Ph) have been proposed as intermediates in various transition-metal-catalyzed oxygen-transfer reactions [16,27,28]. Generally, metallaoxetanes have been prepared by two principal synthetic routes: reaction of a metal carbene with a carbonyl functional group [8,9,29–31], or via oxygen atom insertion into a coordinated olefin [32]. Other examples of metallaoxetanes characterized by X-ray diffraction methods are also known (Ta [30], Mo [29], Ti [8,9] Cr [33]). Additionally, the reverse reaction of a terminal metal oxide fragment $(Cp_2^*Ti{=}O)$ and allene also leads to the formation of metallaoxetanes [24]. Using the acetone dianions $[CH_2C(O)CR_2]^{2-}$ (R = Ph, H), monomeric metalloxetanes are formed in solution by reaction with Group 4 metallocene dihalides (M = Zr, Hf) [34]. These compounds are 'dimers' in the solid state exhibiting a 1,5-dimetalla-2,6-dioxacyclooctane structure. The formation of titanaoxetanes is also possible by the addition of a methylene fragment to a titanium ketene complex, in the case of the addition of two equivalents of dimethylsulfoxonium methylide to titanaocene chloro-acyl complexes [35].

Oxatitanacyclobutanes of the type **XI** have not yet been isolated. They undergo spontaneous ring opening under formation of $X_2Ti{=}O$ and alkene, a reaction which is widely applied in the methylenation of car-



Scheme 4.

bonyl compounds [1,2]. The course of this reaction is reproduced by the energy profile in Scheme 3. The coupling of [$Cl_2Ti{=}CH_2$] with the carbonyl compound is exothermic and leads, via the oxatitanacyclobutane **XI**, to the product of carbonyl olefination. Contrary to the intermediate character of **XI**, the metallacycle **III** is protected against ring opening by a small energy difference (7 kJ mol^{-1}). On the other hand, the compound with the *exo*-methylene group in the β-position (**V**) is also stable (Scheme 3). A rearrangement of **III** to **V** or vice versa has not yet been experimentally detected, but should be possible due to the low energy difference.

2.2.3. Azatitanacyclobutene

Azametallacyclobutenes are subject to facile ring-opening reactions [20]. This experimental fact could indeed be reproduced by comparing the energetics of the reactants and products (Scheme 4). For further discussion see the next section.

2.2.4. Subsequent reactions of four-membered titanacycles

The analysis of the molecular orbitals of **II**, **III** and

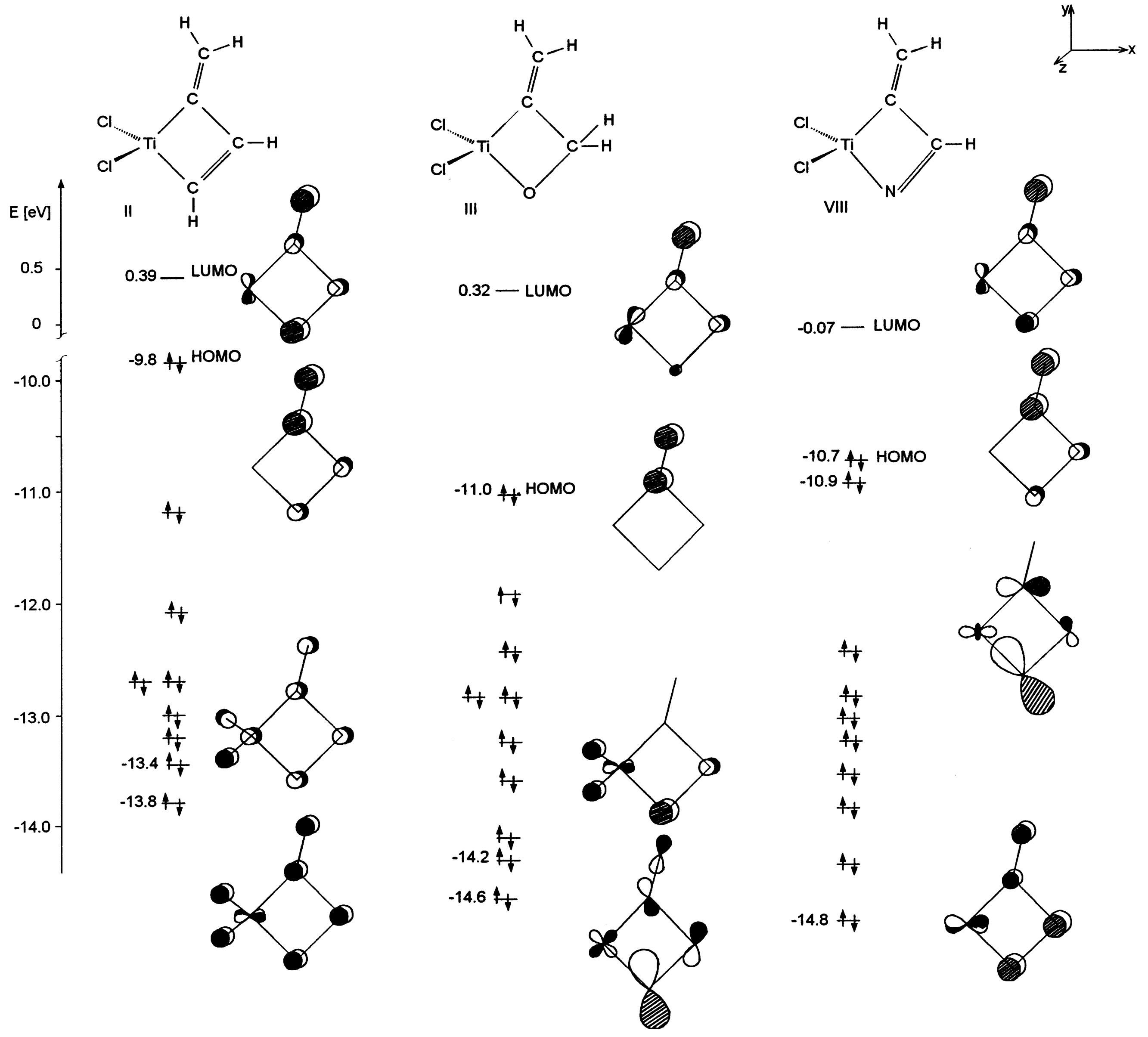


Fig. 3. Molecular orbitals of **II**, **III** and **VIII**. Orbitals of the σ-bond framework and electron pairs at the chlorine atoms are omitted for clarity.

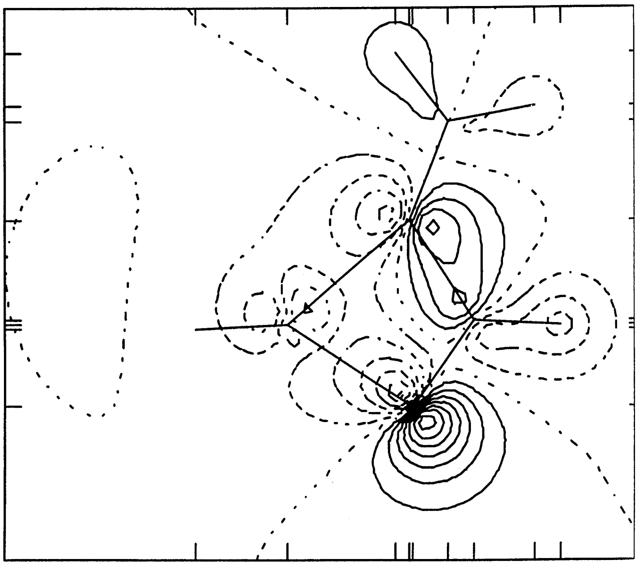


Fig. 4. Molecular orbital plot of HOMO-1 at − 10.9 eV in **VIII**. The relative position of the molecule and the viewing direction are the same as in Fig. 3. The lowest magnitude contour shown is − 0.3 Bohr − 3/2, the highest magnitude contour is 0.35 Bohr − 3/2. The increment between successive lines is 0.05 Bohr-3/2.

VIII shows some interesting features (Fig. 3). The combination of the butadiene system with the Cl_2Ti fragment is depicted in the molecular orbital scheme of **II**. The π-orbitals interact with suitable d- and p-orbitals of the titanium atom, forming a stable metallacyclic ring system. Similar stabilising effects are known in the titanaoxetanes **3**–**5**, which are formal derivatives of **III**. The molecular orbital scheme confirms this stability. One of the lone pairs of oxygen, which has an energy of − 14.2 eV, is orientated perpendicular to the titanaoxetane ring and thus attains overlap with the titanium orbitals. The other lone-pair is situated in the plane at − 14.6 eV. Neither of these are valence orbitals and they should not promote ring-opening reactions.

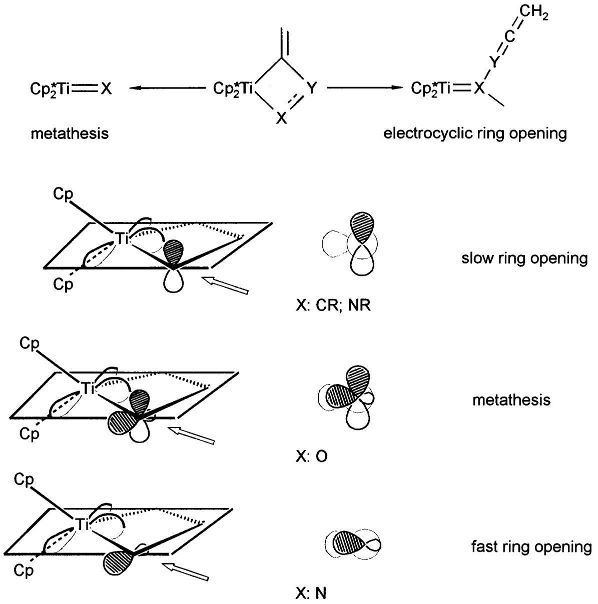
The molecular orbital scheme of **VIII** shows interesting differences in **II** and **III**. The LUMO has remarkably low energy, which should enable the system to react with nucleophiles or even to add further ligands if steric requirements of the Cp* ligands in the real molecules do not prevent it. Furthermore, the lone-pair at nitrogen is the second highest occupied orbital (HOMO-1) at − 10.9 eV. Small portions of the $d_{z^2-x^2}$ orbitals at titanium and p_x and p_y orbitals at the carbon atoms are mixed to the lone pair (see also Fig. 4). This orbital with dominating lone-pair character has high energy compared with the inner lone pairs in **III**. This high-energy orbital is probably the main reason for the fast ring-opening reactions that occur in azatitanacyclobutenes.

Depending on the nature of heteroatoms **X**, **Y**, different types of subsequent reactions of the titanacycles **2**–**12** are observed. In the case of the titanacyclobutane **2**, cycloreversion reactions dominate, leading to the vinylidene intermediate **1**. In the case of the oxetanes **3**–**5** metathesis reactions are observed in the mass spectrometer, whereas from the non-classical oxetanes **6** the educts are formed. Electrocyclic ring-opening reactions are observed in the case of unsubstituted titanacyclobutenes [13]. Fast ring-opening reactions occur in the case of the azatitanacyclobutenes leading to formal insertion products in the Ti–C bond [12]. This behaviour is explained by the orientation of the lone pair in the heteroatom **X** to the acceptor orbitals in the equatorial plane of the metallocene Cp^*_2Ti-fragment. Two lone pairs are present in the titanaoxetane **III**, which do not cause electrocyclic ring-opening because of their low energy. The metathesis reaction forming [$Cl_2Ti{=}O$] is allowed by symmetry and has a small energy barrier, as shown above (Scheme 5).

The best orbital interaction between the titanium atom and the atom **X** in the α-position can be expected in the case of the azatitanacyclobutenes **8**, because the lone pair at the nitrogen atom and the lateral acceptor orbital of the titanium centre are orientated in the same mirror plane, leading to a fast ring opening to form imido-intermediates and derivatives thereof. On the other hand, in the azatitanacyclobutanes **11**, where the hybridization of the nitrogen atoms is different, no electrocyclic ring-opening reactions are observed. In the molecule **11** the lone pair at the sp^2-hybridized nitrogen is orientated perpendicular to the acceptor orbital on titanium [15]. A similar orientation of donor and acceptor orbitals is also present in the case of titanacyclobutenes, leading to substituent controlled reactions. Electrocyclic ring-opening reactions are only observed for the non-substituted titanacyclobutene leading to the formation of polyacetylene [13].

3. Conclusions

The results of ab initio calculations on a number of titanium complexes have been discussed. The calculated energy differences between the different four-membered titanacycles, derived by formal [2 + 2]-cycloadditions from the titana-ethylene [$Cl_2Ti{=}CH_2$] and the titana-allene [$Cl_2Ti{=}C{=}CH_2$] intermediate, allow conclusions on the reactivity and stability of the titanacycles derived thereof. The exocyclic methylene group in the α-position of the titanacycles formed from [$L_2Ti{=}C{=}CH_2$] leads to products of higher stability compared with those from [$L_2Ti{=}CH_2$]. The four-membered titanacycles in the model complexes were found to be planar in all cases. Planar four-membered rings have also been found in a number of X-ray structure analyses of titanacycles.



Scheme 5.

The influence of the heteroatom X in heterotitanacyclobutanes and -butenes (X: CH_2, CH, O, N) becomes understandable from the electronic ground-state structure of these complexes. The regiochemistry of the addition of allene to $[L_2Ti{=}O]$ fragments compared to the inverse orientation of $[L_2Ti{=}C{=}CH_2] + R_2C{=}O$ is in good agreement with experimental results. Azatitanacyclobutenes undergo a spontaneous ring opening reaction due to the LUMO orbital which is located at remarkable low energy and the lone pair character of the HOMO-1. This reactivity is quite different from the reactivity of titanaoxetanes and titanacyclobutenes. In summary, the results obtained with calculations on $[Cl_2Ti{=}C{=}CH_2]$ subsequent products is in good agreement with the reactivity of the titanacycles derived from the $[Cp_2^*Ti{=}C{=}CH_2]$ intermediate. Simplifications in the theoretical model have been applied to obtain the results of the ab initio calculations in a reasonable time scale. Additional calculations with DFT methods would certainly help to provide more accurate information.

4. Experimental

4.1. Ab initio calculations

The model complexes **I**–**XV** and some organic derivatives have been optimized at the restricted Hartree–Fock (RHF) level of theory with an effective core potential basis set (ECP) [36,37]. The ECP replaces the innermost core orbitals for titanium and all core orbitals for the main group elements (C, N, S, Cl). For titanium and zirconium ns, np, nd, $(n+1)$s and $(n+1)$p are treated explicitly by a quadruple-zeta quality sp and a triple-zeta quality d basis set. For the main group elements ns and np are treated explicitly by a double-zeta basis set. It has been shown that this ECP basis set is suitable for transition metal compounds [39]. The geometries of the bis(cyclopentadienyl)metallocene complexes (**Ia**, **IIa**, **Va**) have been optimized at the restricted Hartree–Fock (RHF) level of theory with the STO-3G basis set [38]. The presence of stationary points has been proved for all geometry optimizations by evaluating the second energy derivative matrix at the Hartree–Fock level of theory. The correlation contribution for complexes **I**–**XV** was taken into consideration with single-point energy calculations (at the geometries obtained at the RHF level) according to Møller–Plesset second-order pertubation theory (MP2/RHF) [40]. The combination of RHF geometry optimization and MP2 energy scheme is a computationally effective choice and has been used with success in probing the structure and energetics of transition metal compounds [41]. The calculations have been carried out using the program packages SPARTAN 3.1 [42] on IBM RS6000-355 and GAMESS [43] on CONVEX-C3420. Tables with bond lengths, angles and total energies of the optimized molecules are available on request from the corresponding author.

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