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Bis(η^5-cyclopentadienyl)titanium(II) in the gas phase: Mass spectrometric and computational study of the structure and reactivity

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Abstract

Bis(η^5-cyclopentadienyl)titanium(II), titanocene, was generated in the gas phase by a thermolysis of the titanocene complex with bis(trimethylsilyl)acetylene. This elusive compound was characterized by means of mass spectrometric methods. Density functional theory (DFT) calculations indicated that the triplet ground state titanocene is kinetically stable towards the unimolecular isomerizations. Based on a DFT calculated energetics, a mechanism of the formation of a titanocene dimer, was proposed, which was based on a formation of bis(η^5-cyclopentadienyl)titanium hydride as a key intermediate.

Keywords: Titanocene; Titanocene hydride; Titanocene dimer; Mass spectrometry; DFT calculation

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1. Introduction

The story of the bis(η^5-cyclopentadienyl)titanium(II), so called titanocene (**1**), begun in the early 1950s, when motivated by the recent discovery of ferrocene [1], the electronic structure of all bis(η^5-cyclopentadienyl) compounds have been considered from the molecular orbital theory point of view [2–4]. In 1956 Fischer and Wilkinson reported the first synthesis of what they called di(π-cyclopentadienyl)titanium(II) [5]. However, their bright green "titanocene" appeared to be a dimer with the fulvalene ligand and two (μ-hydrido) bridges connecting titanium atoms. Strong evidence for dimeric structure was given by Brintzinger and Bercaw [6], the presence of fulvalene moiety was established by the ^{13}C NMR [7] and by the X-ray crystallographic studies of various derivatives of the titanocene dimer [8,9], and finally, a direct proof provided the X-ray structure solved by Mach et al. [10]. A clear conclusion has been drawn from numerous experimental studies, that in spite of extensive effort devoted to its preparation and characterization, the free titanocene is obviously not isolable [11], and as such it remained the last experimentally unknown metallocene in the 3d series transition metals.

Zagorevskii and Holmes [12] utilized neutralization-reionization mass spectrometry (NRMS) [13] in an attempt to prepare and characterize monomeric titanocene in the gas phase. The NRMS represents a "non-chemical" way of generating neutral species by the femtosecond electron transfer to or from precursor gas phase ions during the high-energy collision with suitable atom or molecule and has already proved to be a powerful tool for studies of elusive organometallic compounds [14,15]. For the NRMS experiment they used "titanocenium" $C_{10}H_{10}Ti^+$ ion precursors prepared by the dissociative electron ionization of bis(η^5-cyclopentadienyl)titanium dichloride and diiodide. They concluded that the $C_{10}H_{10}Ti^+$ ions in the gas phase might be envisaged as a dynamic system, which exists in several isomeric forms. Therefore, owing to a vertical nature of electron transfer in NRMS, the structure assignment of the apparently stable neutral $C_{10}H_{10}Ti$ species was rather ambiguous.

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More then a half century long history of theoretical studies of titanocene was thoroughly reviewed by Freitag and Gordon [16]. They also performed high-level ab initio and density functional theory (DFT) calculations on titanocene with C_s, C_{2v}, D_{5h} and D_{5d} symmetries [16]. In their quantum chemical survey of the electronic structure of these titanocenes they found that at all levels of theory they used, the triplet geometries were all lower then the lowest energy singlet and that the $^3B_1$ (C_{2v}) state was a ground state at MP2, B3LYP and CCSD(T) levels of theory. Based on results of their MCSCF calculation, Freitag and Gordon also concluded that a single-reference wave function is appropriate for theoretical treatment of titanocene [16]. Some DFT calculation results concerning titanocene can also be found in papers by Harrod et al. [17] and Lee et al. [18].

In the present paper, we report on a generation of titanocene from its complex of bis(trimethylsilyl)acetylene (BTMSA) [19] by thermolysis in the ion source of the mass spectrometer. Neutral gas phase monomeric titanocene was characterized by mass spectrometry and its unimolecular chemistry was studied using DFT calculations. Several aspects of possible mechanism of formation of the titanocene dimer are also addressed in this paper.

2. Experimental

The titanocene complex with BTMSA, $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ ($Cp_2 = \eta^5\text{-}C_5H_5$), was prepared according to a procedure described previously [20]. Mass spectrometric measurements were performed on ZAB2-SEQ hybrid tandem mass spectrometer of BEqQ geometry. Namely the magnetic (*B*) and electrostatic (*E*) sectors were used in the experiments presented in this study. The mass spectrometer was equipped with the electron ionization (EI) ion source, which was operated at the typical EI conditions, i.e. electron energy of 70 eV and 50 μA of ionizing electron current. Samples for mass spectrometric measurements were prepared under vacuum using all-sealed glass device equipped with breakable seals. Capillaries with samples were opened and inserted into the direct inlet under argon in order to totally avoid sample exposure to the air. The ion source temperature was varied from 100 °C to 250 °C. High-resolution mass spectrometry (HRMS) measurements were performed at the resolution of 10000 (10% valley definition) with perfluorkerosene as internal standard. Accuracy of the HRMS measurements was 3 ppm. Collisionally activated dissociation (CAD) mass spectra were measured in a collision cell located in the first field-free region (FFR1) between the ion source and the magnetic sector. Helium gas was admitted into the collision cell at pressure necessary to achieve 50% transmittance of the precursor ion beam. The spectra from the FFR1 were obtained by simultaneously scanning *B* and *E* while maintaining a constant B/E ratio (B/E linked scan).

The quantum chemistry calculations were performed using the GAUSSIAN03 suite of programs [21]. Hybrid DFT method was used employing the Becke's three-parameter hybrid functional B3LYP [22,23] that uses correlation functional of Lee et al. [24]. Geometries were optimized using 6-31G(d,p) polarized basis set applied to all atoms using the Gaussian 03 default grid size. Stationary points were characterized by harmonic frequency calculations as local minima (all frequencies real) or first-order saddle points (one imaginary frequency). Harmonic frequencies were used to obtain zero-point vibration energy (ZPVE) corrections, enthalpies and Gibbs free energies. No scaling factor was applied to the B3LYP/6-31G(d,p) frequencies. An improved set of energies was obtained using B3LYP/6-311+G(2d,p) single point calculations on B3LYP/6-31G(d,p) optimized geometries and B3LYP/6-31G(d,p) ZPVE corrections.

3. Results and discussion

3.1. Mass spectrometry

Mass spectra of BTMSA complexes with various titanocenes are characterized by a weak or even absent signal due to a molecular ion and by abundant peaks corresponding to BTMSA and a respective titanocene [19,20,25–31]. With all samples of $'Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$, ($'Cp_2 = \eta^5\text{-}C_5H_5$ or substituted $\eta^5\text{-}C_5H_5$) complexes measured in our laboratory, the abundance of $BTMSA^{+\cdot}$ ion (*m*/*z* 170) relative to $'Cp_2Ti^{+\cdot}$ and $'Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)^{+\cdot}$ ions fluctuated in the course of measurement depending on the direct inlet probe (DIP) as well as on the ion source temperatures. On the contrary, the abundances of BTMSA fragment ions relative to $BTMSA^{+\cdot}$ molecular ion remained practically constant and independent to the DIP and ion source temperature changes, and the same applied to $'Cp_2Ti^{+\cdot}$ and its fragment ions. Such a behavior of pure chemical compound under the conventional EI conditions in the mass spectrometer is usually explained in terms of thermal instability of the compound, which decomposes in the sample inlet system or directly in the ion source. In such a case, the resulting mass spectra correspond rather to a mixture of decomposition products. Thus, there was a chance in this particular case that beside free BTMSA, a respective free neutral titanocene was generated during the mass spectrometry measurements.

To examine for such a possibility, several different experiments were run with the simplest titanocene–BTMSA complex, $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$, which was chosen as a model system as it exhibited the most abundant molecular ion $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)^{+\cdot}$ of all $'Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ complexes. The EI mass spectrum of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ is shown in Fig. 1 together with EI mass spectrum of pure BTMSA measured at the same experimental conditions.

The former spectrum is characterized by the signal at *m*/*z* 348 (^{48}Ti, ^{28}Si) that corresponds to the molecular radical-cation of the parent complex and by the base peak at *m*/*z* 178, which was found to have an elemental composition

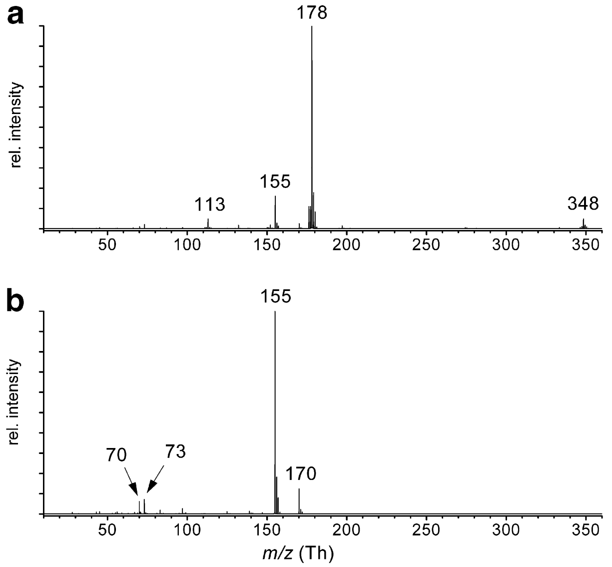


Fig. 1. EI mass spectra of (a) titanocene–BTMSA complex and (b) BTMSA at ion source temperature of 100 °C.

of $C_{10}H_{10}{}^{48}Ti$ as revealed by the accurate mass measurement at HRMS conditions. The peaks due to the presence of BTMSA are also seen in this spectrum. The mass spectrum of pure BTMSA shows major peaks at *m*/*z* 170 ($M^{+\cdot}$), *m*/*z* 155 ($M^{+\cdot} - {}^{\cdot}CH_3$), *m*/*z* 73 ($(CH_3)_3Si^+$) and *m*/*z* 70. The latter ion is accompanied by isotopic satellites at *m*/*z* 70.5 and 71 indicating that it is a stable dication, which most probably corresponds to the loss of methyl radical from both of the trimethylsilyl groups in unstable or metastable BTMSA molecular dication, formed by electron ionization. The accurate mass measurement of this characteristic ion is indeed consistent with elemental formula $C_6H_{12}Si_2{}^{2+}$.

Typically, only one of 10^4–10^6 molecules is ionized under the standard EI conditions. The probability of subsequent ionization of singly charged ion in the interaction with second electron is even much lower due to smaller ionization cross-section and much shorter residence time of the ion in the EI ion source (typically 10^{-6} s whereas the neutral molecule residence time is $\sim 10^{-3}$ s). Hence, the BTMSA dications can only be formed by the ionization of free BTMSA in a single electron–molecule collision, or by the elimination of the neutral titanocene from the EI-formed dication of the titanocene–BTMSA complex. However, the latter possibility seems very unlikely considering that the second ionization energy of BTMSA is expected to be higher then that of titanocene (in analogy to the first ionization energies, vide infra), and therefore, Cp_2Ti^{2+} and neutral BTMSA, or $Cp_2Ti^{+\cdot}$ and $BTMSA^{+\cdot}$ corresponding to the charge separation reaction are supposed to be formed preferentially from $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)^{2+}$.

Interestingly, the relative ion abundances of all major BTMSA ions normalized to *m*/*z* 155 are virtually the same in both of the mass spectra in Fig. 1. The same extent of fragmentation indicates that the internal energy deposited in $BTMSA^{+\cdot}$ was the same in both cases, which further supports the concept that the free BTMSA molecules were already present in the ion source before the ionization event takes place. It should be mentioned at this point, that the presence of substantial amount of free BTMSA as an impurity in the samples of titanocene–BTMSA complex used in the experiments is excluded by the fact, that at the constant experimental conditions (ionization energy, source and DIP temperatures, etc.), the abundance of BTMSA ions relative to total ion current became constant after a few "warming-up" minutes from the beginning of the experiment, and such a steady state lasted for a long period of time of sample evaporation (i.e. several hours, depending on the total amount of complex dosed in the experiment). Owing to the sizeable difference in volatilities of BTMSA and $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$, such behavior would be impossible, if sample was contaminated with large amount of more volatile free BTMSA.

Can singly charged BTMSA ions be the products of unimolecular fragmentation of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)^{+\cdot}$? The ions at *m*/*z* 178 and 170 are complementary species, abundances of which are controlled by their ionization energies according to the Stevenson's rule [32–34] saying that the charge remains at the species with lower ionization energy. The ionization energy of BTMSA was measured by the photoelectron spectroscopy [35] and the adiabatic value was evaluated to be 9.2 eV [36]. To our best knowledge however, no value of ionization energy of titanocene was available in the literature. Therefore, the quantum chemistry calculations were used to estimate this quantity. Adiabatic ionization energy of titanocene, taken as the energy difference between the ${}^3B_1$ (C_{2v}) ground state of neutral titanocene and the lowest energy ${}^2A_1$ (C_{2v}) doublet titanocene cation, is 5.6 eV at the B3LYP/6-311+G(2d,p) level of theory. For completeness it should be mentioned that the adiabatic ionization energy of BTMSA is 8.8 eV at the same level of theory.

These ionization energies implicate that the $BTMSA^{+\cdot}$ (*m*/*z* 170) should not be formed by the unimolecular fragmentation of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)^{+\cdot}$, because the ionization energy difference of 3.6 eV strongly favors formation of complementary $Cp_2Ti^{+\cdot}$ cation-radical. In order to address this issue experimentally, the tandem mass spectrometry experiments were run, in which the mass-selected $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)^{+\cdot}$ was activated by the collisions with He or Ar atoms. During the collision, a portion of the ion kinetic energy is transformed into the internal energy of the ion. This results in a vibrational excitation, which promotes ion dissociations. Products of these unimolecular dissociations are analyzed by means of mass spectrometry. The CAD mass spectrum of mass-selected $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)^{+\cdot}$ ion (Fig. 2) shows only one major product ion at *m*/*z* 178 corresponding to $C_{10}H_{10}Ti^{+\cdot}$ whereas there is absolutely no signal at *m*/*z* 170 that would correspond to the $BTMSA^{+\cdot}$.

The above-mentioned facts support the assumption that the free BTMSA observed in the mass spectra of $Cp_2Ti(\eta^2$-

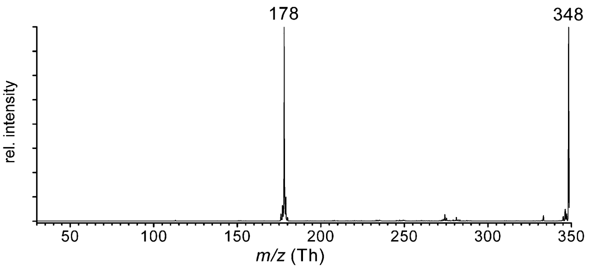


Fig. 2. CAD mass spectrum (He/50%T) of titanocene–BTMSA complex radical-cation at ion source temperature of 100 °C.

$Me_3SiC_2SiMe_3$) is formed by the thermal decomposition of this complex prior to ionization. Furthermore, the observed long-term stability of the partial vapor pressures is inconsistent with eventual decomposition of the solid $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ taking place in DIP. The constant vapor pressure in the ion source indicates that the complex is evaporated from the DIP practically without decomposition and that a partial decomposition takes place in the ionization chamber, which is usually held at the temperature that is higher then that of DIP.

To support this conclusion the EI mass spectra of the $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ were measured with the DIP temperature kept at constant value of approximately 50 °C and with the ion source temperature gradually increasing from 100 °C, which was the lowest temperature at least temporarily sustainable in the EI/CI ion source on the mass spectrometer used in this study, up to 250 °C at the rate of approximately 20 °C min^{-1} (Fig. 3).

It is clearly seen from the source temperature dependent mass spectra, that the abundances of all BTMSA ions nearly retained their mutual ratios while the contribution of the BTMSA ions to the total ion current increased dramatically with the source temperature, and at the same time, the abundance of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)^{+\cdot}$ at m/z 348 decreased. At the source temperature of 250 °C, only very weak signals due to the molecular ions of titanocene–BTMSA complex were present in the mass spectra indicating that a majority of the molecules of the complex decomposed and free titanocene and BTMSA molecules were present in the ion source. Therefore, this mass spectrum (Fig. 3d) represents a spectrum of 1:1 mixture of titanocene and BTMSA. After subtracting the mass spectrum of free BTMSA measured at the source temperature of 250 °C, the mass spectrum of titanocene was obtained, which represents direct experimental characterization of the elusive monomeric titanocene (Fig. 4a) provided the nascent titanocene is sufficiently stable to survive a time delay between its formation and subsequent ionization. CAD mass spectrum of the titanocene molecular ion is shown in Fig. 4b. The most abundant fragment ions in the mass spectra of titanocene, m/z 113 and 152, correspond to the elimination of cyclopentadienyl radical and a molecule of acetylene, respectively.

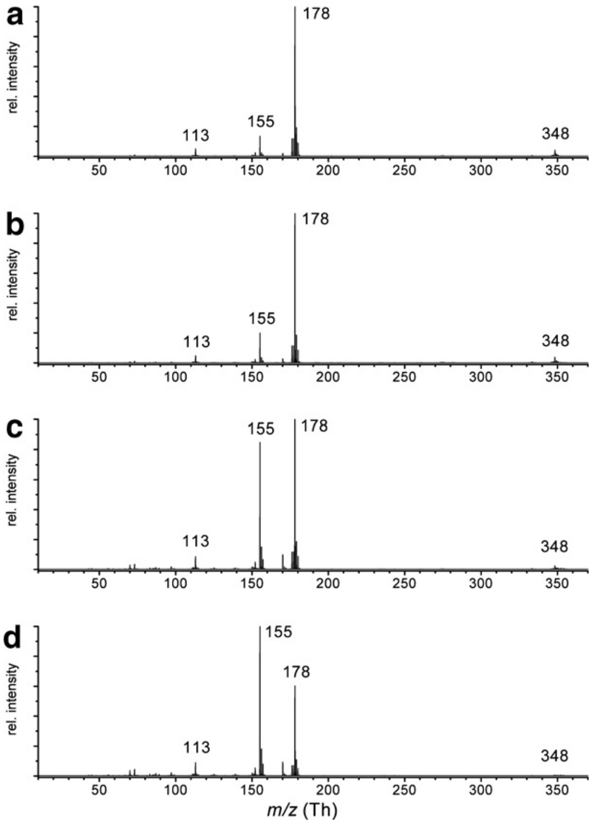


Fig. 3. EI mass spectra of titanocene–BTMSA complex at ion source temperatures of (a) 100 °C, (b) 150 °C, (c) 200 °C and (d) 250 °C.

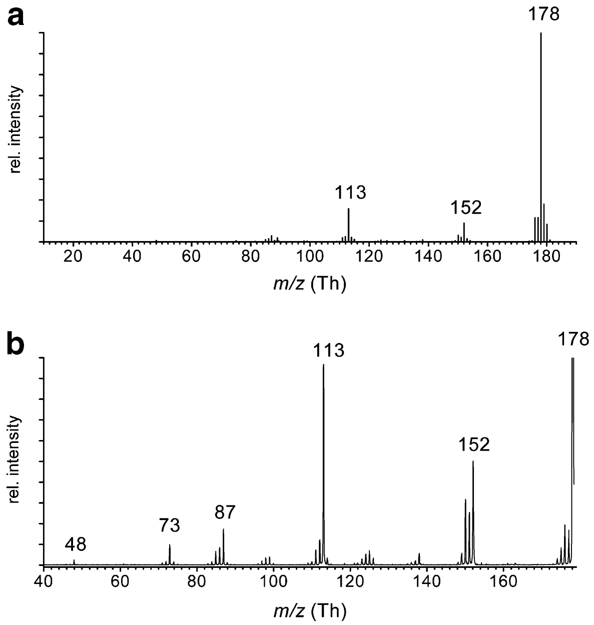


Fig. 4. (a) EI mass spectrum of Cp_2Ti generated by ion source thermolysis of titanocene–BTMSA complex at 250°C (see text for details), (b) CAD mass spectrum (He/50%T) of ions at m/z 178 from titanocene–BTMSA complex at ion source temperature of 250 °C.

At ion source temperatures above 200 °C, weakly abundant group of isotopomers of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)^{+\cdot}$ at m/z 346–350 were interfered with a similarly abundant group of ions at m/z 346–356 corresponding to the dimeric titanocene [6,20]. The presence of these ions in the mass spectra at higher source temperatures can be explained by the fact that decomposition of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ takes place at inner walls of the ion source. After decomposition, some of the titanocene molecules can remain adsorbed, undergo a dimer forming bimolecular reaction, which is improbable in the gas phase at the pressures of $\sim 10^{-3}$ Pa typical for EI conditions, and get released at higher temperatures necessary for evaporation of dimer. Traces of titanocene dimer as an impurity in the samples of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$, can not be excluded as well.

It should be mentioned that the reversed experiment with the ion source temperature gradually decreasing from 250 °C down to 100 °C was impossible because the standard EI ion source used in this study was not capable of efficient active cooling. However, after switching off the filament and waiting for approximately one hour, which was a time period necessary for the ion source to cool down, the entire experiment could be repeated provided that a sufficient amount of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ was dosed for the experiment.

3.2. Calculations

From the experiments described in the previous section, a chance arose that the elusive titanocene could be prepared and characterized by the mass spectrometry. However, a question could be asked about a kinetic stability of titanocene under the conditions used in our experiments. In other words, if the nascent titanocene is not sufficiently stable towards the unimolecular isomerization, the $C_{10}H_{10}Ti$ molecules, which are to be ionized within $\sim$1 ms time interval, will loose their original structure and the mass spectrum obtained from these molecules will not be a spectrum of titanocene. Therefore, the calculations were carried out in order to explore the energetics of the unimolecular isomerizations of the neutral $C_{10}H_{10}Ti$ system.

The quantum chemistry calculations of the titanocene and its various isomers were preformed employing B3LYP method at two levels of theory. The energy minima and transition states found on the singlet and triplet PES are shown in Fig. 5 and the corresponding total and relative energies are listed in Table 1.

Brintzinger and Bercaw postulated a rearrangement, in which the η^5-cyclopentadienyl-η^1-cyclopentadienylidenetitanium hydride is formed via the η^5-cyclopentadienyl-η^1-cyclopentadienyltitanium intermediate as shown in Scheme 1 [6].

These two species were considered as possible intermediates in a formation of dimeric titanocene. Therefore, we primarily focused on exploration of a reaction pathway leading from the triplet ground state titanocene **1t** to some kind of isomeric hydride species.

Freitag and Gordon [16] calculated using various correlated methods that the triplet ground state ($^3B_1$) C_{2v} titanocene is 21–88 kJ mol^{-1} (5.0–21.0 kcal mol^{-1}) below the lowest energy singlet (C_{2v} $^1A_1$). Our value of energy difference between ground state titanocene **1t** and lowest energy singlet titanocene **1s** obtained at B3LYP/6-311+G(2d,p) level of theory is 33 kJ mol^{-1}.

Two minima (structures **2t** and **3t**) exhibiting the Ti–H bond were found on the triplet PES. The η^5-cyclopentadienyl-η^5-cyclopentadienylidenetitanium hydride structure **2t** has C_s symmetry and is 218 kJ mol^{-1} less stable then **1t**. Structure **3t** is similar to **2t**, but exhibits distorted C_1 geometry. **2t** is formed through the C_s symmetrical transition

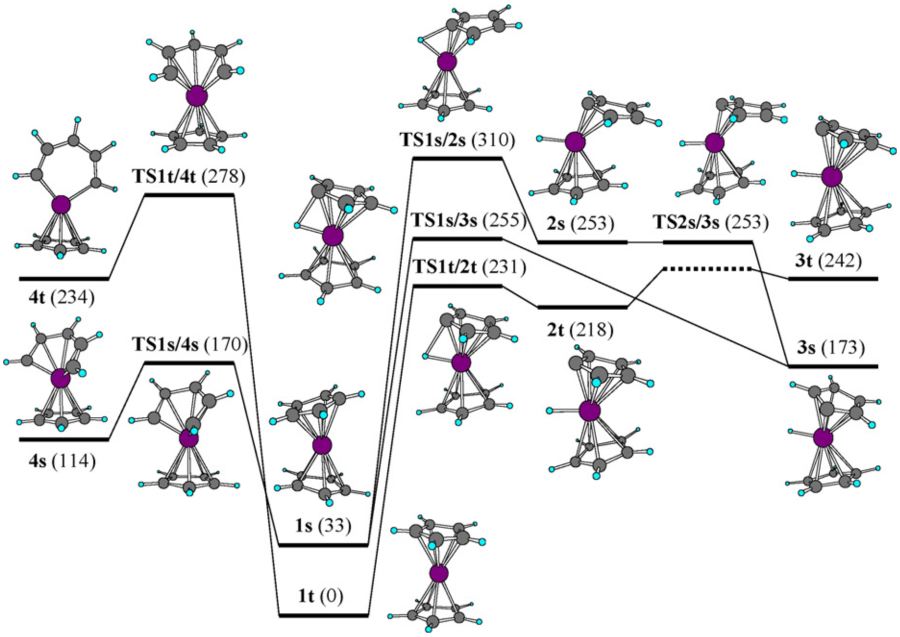
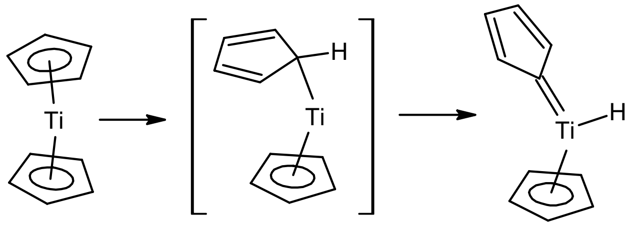


Fig. 5. Potential energy profile for isomerizations of Cp_2Ti in singlet and triplet state. B3LYP/6-311+G(2d,p) relative energies (in kJ mol^{-1}) shown in parentheses.

Table 1
B3LYP total energies, zero-point energy corrections and relative energies at 0 K of the titanocene isomers and transition states

Structure	B3LYP/6-31G(d,p)			B3LYP/6-311 + G(2d,p)	
	E (hartree)	ZPVE (hartree)	Relative energy (kJ mol^{-1})	*E* (hartree)	Relative energy (kJ mol^{-1})
1s	−1236.509345	0.165287	65	−1236.655097	33
1t	−1236.535651	0.166590	0	−1236.668863	0
2s	−1236.425615	0.160767	274	−1236.566822	253
2t	−1236.440513[a]	0.161131	236	−1236.580303	218
3s	−1236.460777	0.163071	187	−1236.599578	173
3t	−1236.440493	0.161069	235	−1236.571211	242
4s	−1236.481163	0.164312	137	−1236.623105	114
4t	−1236.437294	0.162296	247	−1236.575411	234
5s	−1236.457997	0.160259	187	−1236.597310	171
5t	−1236.444404	0.161959	227	−1236.588584	199
TS1s/2s	−1236.401556	0.158601	331	−1236.542782	310
TS1t/2t	−1236.432936	0.160703	254	−1236.575018	231
TS2s/3s	−1236.425525	0.160599	273	−1236.566542	253
TS1s/3s	−1236.423938	0.160338	277	−1236.565569	255
TS1s/4s	−1236.458975	0.163044	192	−1236.600526	170
TS1t/4t	−1236.414252	0.161069	304	−1236.557487	278

[a] Small imaginary frequency (−7 cm^{-1}) with zero intensity was obtained using default GAUSSIAN03 grid size.



Scheme 1.

state **TS1t/2t** with relative energy of 231 kJ mol^{-1} respective to **1t**. Similar situation was found on the singlet PES. Contrary to **2t**, its singlet C_s symmetrical analog **2s** has η^3-cyclopentadienylidene ligand with the shortest Ti–C bond being 1.93 Å. Distorted C_1 species **3s** has structure of η^5-cyclopentadienyl-η^5-cyclopentadienylidenetitanium hydride, and is 69 kJ mol^{-1} more stable then its triplet analog **3t**. The structure **3s** can be formed through transition states **TS1s/2s** and **TS2s/3s** having the relative energies 310 and 253 kJ mol^{-1}, respectively. However, a "shortcut" pathway was also found that leads from **1s** directly to **3s** through transition state **TS1s/3s** with relative energy 255 kJ mol^{-1}.

Two other types of titanocene isomers were found on both the singlet and triplet PES. Insertion of titanium atom in to the C–C bond in titanocenes **1s** and **1t** through transition states **TS1s/4s** and **TS1t/4t** leads to the structures **4s** and **4t**. These reactions are energetically more feasible than the above described hydrogen migration, as the relative energies of **TS1s/4s** and **TS1t/4t** are 170 and 278 kJ mol^{-1} above **1t**. The structures **4s** and **4t** are substantially different. The **4t** features a planar titanabenzene ring oriented almost perpendicularly with respect to the Cp ring, whereas the C_s symmetric **4s** exhibits a fan-shaped arrangement of the open-ring C_5H_5 ligand. Structures **5s** and **5t** (Fig. 6) have relative energies 171 and 199 kJ mol^{-1}, respectively.

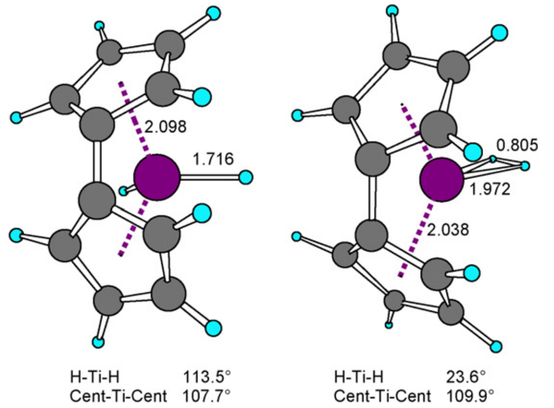


Fig. 6. B3LYP/6-31G(d,p) optimized geometries of C_{2v} symmetric **5s** and **5t**. Bond lengths in Å.

They contain a bent fulvalene ligand, in which the angles between the Cp ring planes are 99.8° (**5s**) and 95.3° (**5t**). Major difference in geometries of **5s** and **5t** is that **5s** is a dihydride structure with Ti–H bond length of 1.716 Å and H–Ti–H angle of 113.5° whereas in **5t** a molecule of dihydrogen act as a neutral two electron sigma donor. The back-donation of electrons from a filled titanium orbital to the σ^* orbital on the dihydrogen elongates the H–H bond to 0.805 Å and the Ti–H bond length is 1.972 Å. Formation of **5s** and **5t** requires a hydrogen atom migration from the η^5-cyclopentadienyl ligand to Ti center in **3s** and **3t**, respectively, however, the corresponding transition states were not found.

Since the triplet C–C insertion transition state energy of **TS1t/4t** is higher than that of **TS1s/4s**, a crossing occurs between the singlet and triplet surfaces in this region (Fig. 5). This implies that the triplet ground state titanocene can isomerize to singlet **4s**, if the intersurface coupling interactions are sufficiently large. During the eventual isomerization of **1t** to **4s** the system must reach a point where both spin states have the same energy and geometry. The line connecting **1t** and**4s** in Fig. 5 only represents an idealized pathway along one-parameter projection of the 3N-6 dimensional space and therefore it is not excluded that the crossing occurs in fact at energy that is even higher than that of **TS1s/4s** [37,38]. Therefore, the energy of **TS1s/4s** can be taken as lower limit of activation energy for the formation of **4s** from **1t**. Similarly also the hydride structures **3s** and **3t** exhibit a reversed order of stability than titanocenes **1s** and **1t**. Therefore, another crossing point between singlet and triplet PES must be present on the hydrogen migration pathways leading to **3s** and **3t**. Again, a more stable hydride **3s** can be formed from **1t**, provided the appropriate spin–orbit coupling constants are favorable.

A conclusion can be drawn from the above-discussed calculation results, that the unimolecular isomerization of the ground state titanocene in the gas phase is a demanding process. The lowest energy isomerization of **1t** to **4s** requires at least 170 kJ mol^{-1} of internal energy to be available in the molecule. In addition, favorable spin–orbit coupling constants are also required in order to alter the course of otherwise energetically prohibitive reaction (note that the energy of **TS1t/4t** is 278 kJ mol^{-1} above **1t**) to allow an isomerization of the triplet titanocene to proceed on the energetically more feasible singlet PES. Also the hydrogen migration from Cp ring to the titanium center in **1t**, a proposed key step in formation of titanocene dimer, requires 231 kJ mol^{-1} of activation energy. Moreover, the formation of the most stable singlet η^5-cyclopentadienyl-η^5-cyclopentadienylidenetitanium hydride **3s** requires the spin isomerization as well.

In the EI ion source of the mass spectrometer at typical working conditions, the gas phase molecules quickly reach a thermal equilibrium with the inner surfaces of the ionization chamber. In our experiments the ion source temperatures were kept in the range of 100–250°C. The thermal energy of ground state titanocene at the upper limit of this range (523 K) is 76 kJ mol^{-1}, and a probability of additional excitation by collisions with electrons prior to ionization is negligible. Therefore the $C_{10}H_{10}Ti$ species formed by the thermolysis of titanocene–BTMSA complex should retain their original ''sandwich'' structure and the EI mass spectrum obtained from these molecules can be taken as an experimental characteristic of the elusive titanocene.

3.3. Formation of titanocene dimer

It has been proposed that green titanocene dimer, μ-(η^5:η^5-fulvalene)-di-(μ-hydrido)-bis(η^5-cyclopentadienyltitanium), **6** is formed via the $Cp(C_5H_4)TiH$ intermediate (vide supra) [6]. It has been found in the previous section that the unimolecular gas phase isomerization of the ground state titanocene to such intermediate requires an activation energy of at least 231 kJ mol^{-1} and favorable spin–orbit coupling constants to allow for efficient PES crossing. However, the formation of **6** in solution is known to take place at mild conditions. For example, the reduction of the titanocene dichloride, Cp_2TiCl_2, with sodium naphthalene in tetrahydrofurane yields **6** at 25 °C [39]. Also the titanocene–BTMSA complex dissolved in xylene decomposes at 100 °C to give **6** in a high yield [20]. This compound is usually prepared in less- or non-polar aprotic solvents. These solvents are known to have only small effects on rates and activation energies of the gas phase reactions, particularly the unimolecular ones. Therefore, a formation of the proposed η^5-cyclopentadienyl-η^1-cyclopentadienylidenetitanium hydride intermediate by the unimolecular isomerization of titanocene in solution seems to be improbable. Instead, a different mechanism of the formation of **6** will be considered in the following section.

The bis(η^5-cyclopentadienyl)titanium hydride **7** was postulated to play a role in the formation of **6** from Cp_2TiCl_2 by the reduction with $LiAlH_4$ in aromatic [40] and olefinic [41] solvents. In the reaction systems without presence of $LiAlH_4$, e.g. during the thermolysis of titanocene–BTMSA complex [20], the titanocene hydride **7** can be formed by the reaction of two molecules of nascent titanocene

$$Cp_2Ti + Cp_2Ti \rightarrow Cp_2TiH + CpTiC_5H_4 \quad (1)$$

In this reaction, one molecule of titanocene abstracts hydrogen from the Cp ring of the second molecule producing hydride **7** and η^5-cyclopentadienyl-η^5-cyclopentadienylidenetitanium **8**. The enthalpy of this reaction was calculated at the B3LYP/6-311+G(2d,p) level of theory to be *only* 120 kJ mol^{-1}, which makes this reaction significantly less endothermic than all the relevant unimolecular reactions in **1t**.

The lowest energy $^2A_1$ state of **7** has C_{2v} symmetry and exhibits a conformation, in which the hydride hydrogen atom is eclipsed with one hydrogen atom on each Cp ring. Such an orientation of Cp rings is different from that in bis(η^5-cyclopentadienyl)titanium dihydride **9** [18] as shown in Fig. 7.

The B3LYP optimized C_s symmetric structure **8** has a η^5-coordinated cyclopentadienylidene ligand (Fig. 8). According to the total spin density calculation, the unpaired electron in **8** is localized entirely on the Ti atom.

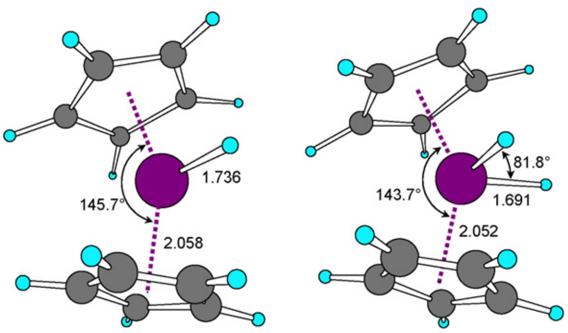


Fig. 7. B3LYP/6-31G(d,p) optimized geometries of C_{2v} symmetric **7** and **9**. Bond lengths in Å.

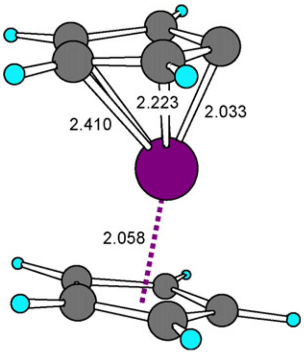


Fig. 8. B3LYP/6-31G(d,p) optimized geometry of C_s symmetric **8**. Bond lengths in Å.

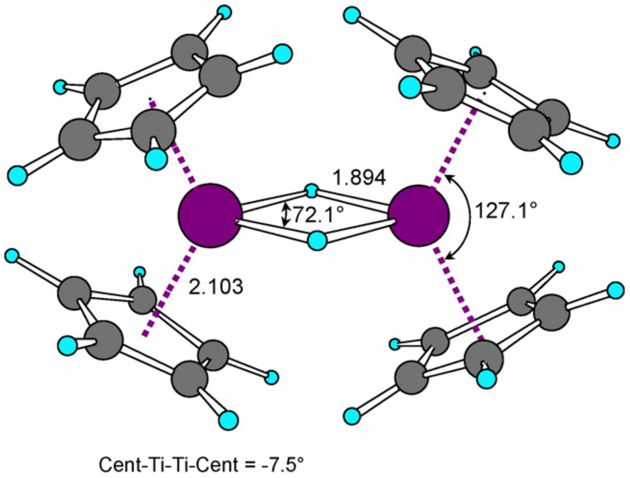


Fig. 9. B3LYP/6-31G(d,p) optimized geometry of D_2 symmetric **10**. Bond lengths in Å.

Alternatively, the titanocene hydride **7** can be formed directly in the reaction with solvent such as toluene:

$$Cp_2Ti + CH_3C_6H_5 \rightarrow Cp_2TiH + {}^{\bullet}CH_2C_6H_5$$

The reaction energies, enthalpies and Gibbs free energies of reactions of triplet ground state titanocene **1t** with several solvents routinely used in titanocene chemistry are listed in Table 2. It follows from the data in Table 2 that the abstraction of methyl hydrogen from toluene, *p*-xylene and mesitylene are the least energetically demanding reactions of **1t** examined in this study.

Titanocene dimer **6** can be formed from two molecules of **7** via formation of intermediate titanocene hydride dimer **10**.

$$Cp_2TiH + Cp_2TiH \rightarrow [Cp_2TiH]_2 \tag{2}$$

$$[Cp_2TiH]_2 \rightarrow \text{dimeric titanocene} + H_2 \tag{3}$$

Dimer **10** has D_2 symmetry with all Ti–H bonds being identical (Fig. 9). The structure is distorted around the Ti–Ti axis and the Cent(Cp)–Ti–Ti–Cent(Cp) dihedral angle is 7.5°. Our B3LYP/6-31G(d,p) optimized structure of **10** exhibit the geometrical parameters similar to those of Lee et al. [18]. Titanocene dimer **6** has C_2 symmetry (Fig. 10). The experimental geometrical parameters of **6** [10] are well reproduced by the calculation presented in this study. The only significant exception is the Ti–Ti distance, which was found shorter than the experimental value of 2.989 Å [10] by 0.112 Å. It should be noted that also the calculated Ti–H bond lengths and Ti–H–Ti and H–Ti–H angles were found notably different from the X-ray data. However, these differences can be attributed to the inaccuracy of the determination of hydrogen atom positions from X-ray data and to the fact that the experimental molecular structure of **6** was determined from the titanocene dimer cocrystallized with 1.5 equiv. of benzene [10], whereas the calculated structure corresponds to **6** in the gas phase.

The calculated energy of reaction (2) is 48 kJ mol^{-1} and the elimination of dihydrogen from **10** giving rise to **6** (reaction (3)) is 91 kJ mol^{-1} exothermic. Formation of a

Table 2
B3LYP/6-311 + G(2d,p) reaction energies (ZPVE corrected, at 0 K), enthalpies and Gibbs free energies (both at 298 K) in kJ mol^{-1}

Reaction	ΔE	ΔH	ΔG
1t + **1t** → **7** + **8**	122	120	128
1t + H_2 → **9**	−26	−34	9
8 + H_2 → **7**	−194	−200	−168
1t + toluene → **7** + benzyl	104	103	110
1t + toluene → **6** + *p*-tolyl	205	205	204
1t + *p*-xylene → **7** + *p*-$^{\bullet}CH_2C_6H_4CH_3$	103	102	106
1t + mesitylene → **7** + $^{\bullet}CH_2C_6H_3(CH_3)_2$	103	102	110
1t + THF → **7** + tetrahydrofuran-2-yl	119	118	119
1t + THF → **7** + tetrahydrofuran-3-yl	135	136	135
7 + **7** → **10**	48	46	126
1t + **9** → **10**	2	−1	76
10 → **6** + H_2	−91	−86	−116
1t + **1t** → **6**	−115	−121	−31
7 + **8** → **11**	−153	−155	−79
11 → **6**	−84	−86	−79
8 + **8** → **12**	−224	−227	−153
8 + **8** → **13**	−215	−215	−155
8 + **8** → **14**	−294	−296	−222

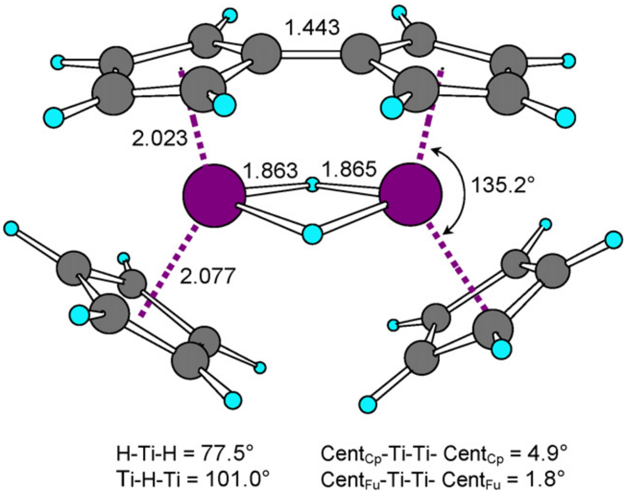


Fig. 10. B3LYP/6-31G(d,p) optimized geometry of C_2 symmetric **6**. Bond lengths in Å.

conjugated fulvalene ligand may represent a possible driving force for the formation of **6**.

The dihydrogen eliminated from this reaction can immediately react with either **8** or titanocene **1t**.

$$CpTi\,C_5H_4 + H_2 \rightarrow Cp_2TiH \tag{4}$$

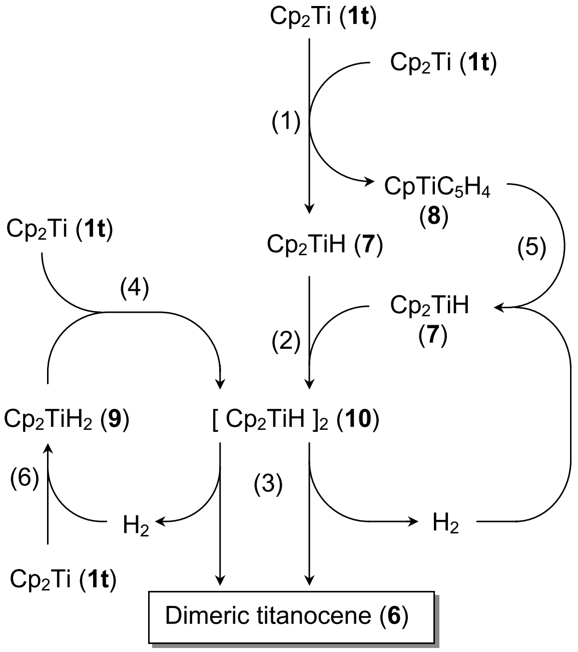
$$Cp_2Ti + H_2 \rightarrow Cp_2TiH_2 \tag{5}$$

The energies of reactions (4) and (5) are −194 and −26 kJ mol^{-1}, respectively. Lee et al. calculated the enthalpy of reaction (5) to be −17 kJ mol^{-1} [18], which is in reasonable agreement with the B3LYP/6-311+G(2d,p) value of −34 kJ mol^{-1} presented in this study. Titanocene dihydride **9** formed by the reaction (5) can be consumed by the reaction with another molecule of **1t** giving rise to intermediate titanocene hydride dimer **10**, which eliminates H_2 and forms **6**.

$$Cp_2TiH_2 + Cp_2Ti \rightarrow [Cp_2TiH]_2 \tag{6}$$

The energy of reaction (6) was calculated to be 2 kJ mol^{-1}. The enthalpy of this reaction was calculated to be −1 kJ mol^{-1}, not too far from the value of 19 kJ mol^{-1} (4.6 kcal mol^{-1}) published previously [18]. Thus, an overall reaction scheme can be proposed, in which a titanocene dimer **6** is formed from the externally generated **1t** (Scheme 2). The molecules of dihydrogen eliminated from **10** by the reaction (3) are used for the formation of the titanocene hydrides **7** and **9** in reactions (4) and (5).

Alternatively, the dimer **6** can be formed via simpler reaction pathway without participation of titanocene hydride dimer **10**. Once the intermediates **7** and **8** are formed by reaction (1), they can react together to form a dimer intermediate **11** featuring one μ-hydride bridge between Ti atoms and a covalent bond between Ti atom derived from **7** and carbene-like carbon atom from **8** (see Fig. 11).



Scheme 2.

The reaction $Cp_2TiH + CpTiC_5H_4 \rightarrow Cp_2Ti(H)C_5H_4\text{-}TiCp$ is 153 kJ mol^{-1} exothermic and subsequent rearrangement of **11** to **6** leads to additional gain of 84 kJ mol^{-1}.

In order to further complete a complex picture of the chemistry of titanocene derived species considered in this chapter, yet another possible dimeric species were studied, which can be formed by reaction of two molecules of **8**. Three different interesting structures exhibiting two intact $CpTiC_5H_4$ subunits were found on the $C_{20}H_{18}Ti_2$ singlet PES. Structures **12** and **13** have fulvalene ligand with Ti atoms coordinated to the same and opposite sides, respectively. The structure **12** has C_2 symmetry. The distance between Ti atoms in **12** is rather long (3.243 Å), however the fact that the fulvalene ligand is bent markedly towards the Ti atoms (angle between five-membered ring planes is 161.2°) indicates that there is a bonding interaction between Ti atoms. This interaction was confirmed by examination of the highest occupied molecular orbital (HOMO) from B3LYP/6-31G(d,p) calculation (see Fig. 12).

In C_{2h} symmetric structure **13**, which can be viewed as "*trans*-" isomer of **12**, the Ti atoms are apparently η^4-coordinated to fulvalene as seen in Fig. 13. Interestingly, the fulvalene C-1 and C-1′ atoms are involved in bonding interaction with both Ti atoms. The bond length between the fulvalene rings (1.555 Å) indicated a single bond.

In C_2 symmetric dimer **14**, the Ti atom from one molecule of **8** is bonded to carbene-like carbon atom from the second $CpTiC_5H_4$ unit. Analogous compounds, $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ and $[(C_5H_2Me_3)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5HMe_3)Ti]_2$ were synthesized and their X-ray structures were determined [42]. The calculated Ti–C σ bond length in **14** (2.183 Å) is slightly shorter than that in $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (2.284 Å) and the Cent(Cp)–Ti and Cent(C_5H_4)–Ti distances in **14** are very close to those reported for its tetramethylated analog [42]. Dramatic difference in Ti–Ti distances in **14** (2.873 Å) and $[(C_5HMe_4)(\mu\text{-}\eta^1{:}\eta^5\text{-}C_5Me_4)Ti]_2$ (3.543 Å) can be ascribed to a steric hindrance caused by massive methyl substitution in the latter compound.

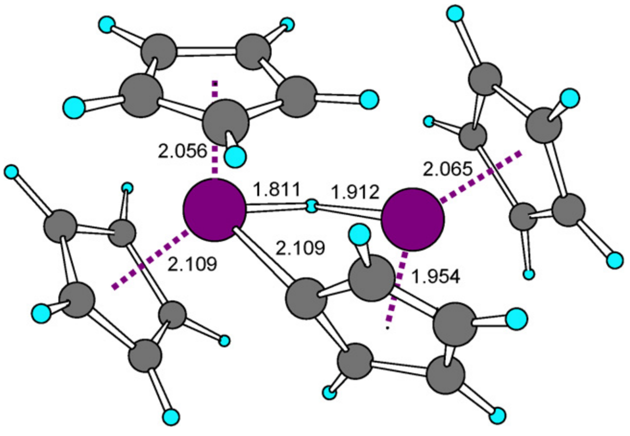


Fig. 11. B3LYP/6-31G(d,p) optimized geometry of C_1 symmetric **11**. Bond lengths in Å.

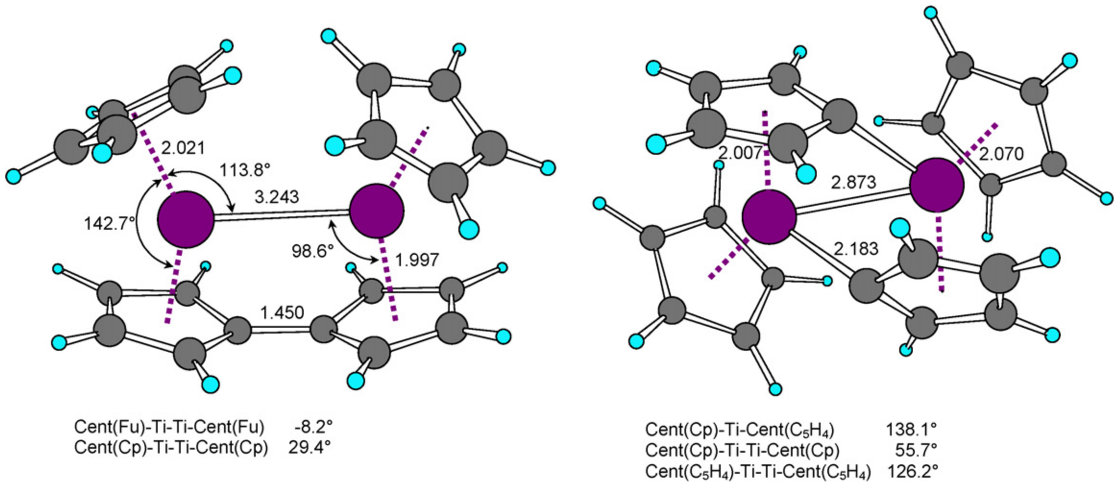


Fig. 12. B3LYP/6-31G(d,p) optimized geometries of C_2 symmetric **12** (on the left) and **14**. Bond lengths in Å.

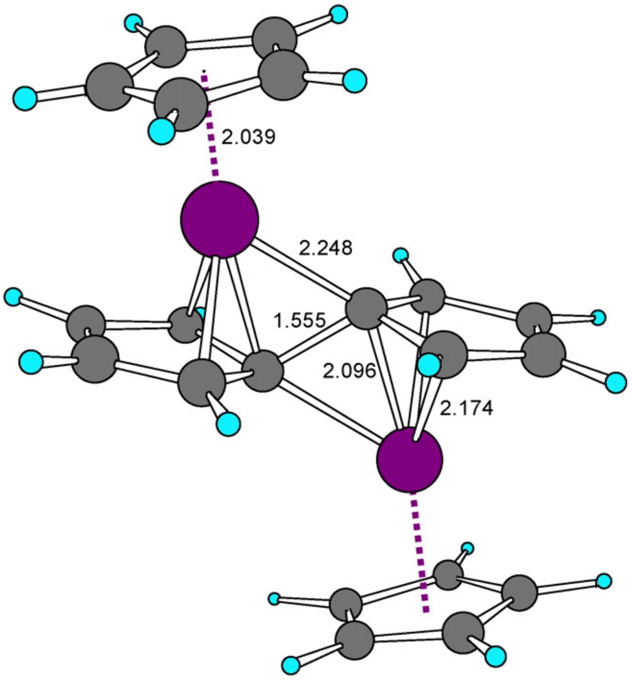


Fig. 13. B3LYP/6-31G(d,p) optimized geometry of C_{2h} symmetric **13**. Bond lengths in Å.

The overall exothermicity of the formation of **6** from two molecules of **1t** is 115 kJ mol^{-1}. Therefore one can imagine an even more straightforward way of formation of **6** in some kind of reaction complex formed from two molecules of **1t**. Due to the size and complexity of the system, however, a detailed description of the $C_{20}H_{20}Ti_2$ PES necessary to untangle the possible reaction mechanism still represents a challenging task.

4. Conclusions

The thermolysis of the complex of titanocene with BTMSA was used to generate titanocene molecules in the rarefied gas phase in the EI ion source of the mass spectrometer. Various mass spectrometric methods were used to characterize this elusive chemical species. B3LYP hybrid DFT method in connection with the 6-31G(d,p) and 6-311+G(2d,p) basis sets was used to explore parts of both the singlet and triplet PES that were relevant to unimolecular isomerizations of bis(η^5-cyclopentadienyl)titanium(II). It was found that the hydrogen migration from Cp ring to the Ti center and the insertion of Ti into the C–C bond in the triplet ground state titanocene **1t** that form isomers **2t** and **4t** require activation energies of 355 and 332 kJ mol^{-1}, respectively. The analogous isomerizations of **1t** to the thermodynamically more stable singlet species **2s** and **4s** require favorable spin–orbit coupling constants to allow for efficient PES crossing. A conclusion can be drawn from our calculations that the titanocene molecules formed by the thermolysis in the EI source of the mass spectrometer at 250 °C should retain their original sandwich structure, and therefore the mass spectra obtained from these molecules represent in fact the first experimental characteristics of bis(η^5-cyclopentadienyl)titanium(II) possessing no additional ligand. Based on the DFT calculated energetics, a mechanism of the formation of titanocene dimer **6** was proposed, in which the bis(η^5-cyclopentadienyl)titanium hydride **7** is formed by a hydrogen atom abstraction from a solvent or second Cp_2Ti molecule. Two molecules of **7** may form a titanocene hydride dimer $[Cp_2TiH]_2$, **10**. This intermediate is subsequently stabilized by elimination of dihydrogen, which is immediately recycled in the formation of titanocene dihydride **9** or another molecule of hydride **7**. Alternatively, the titanocene dimer can be formed directly by reaction of hydride **7** and η^5-cyclopentadienyl-η^5-cyclopentadienylidenetitanium **8**.

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