Activation of CH_4 and H_2 molecules by cationic zirconium(IV) complexes: a DFT study

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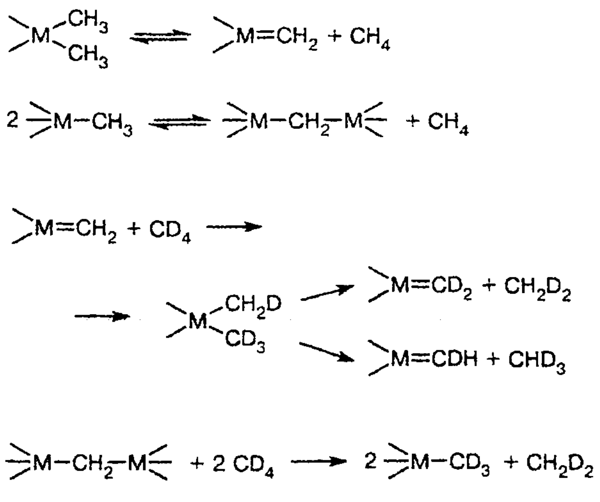
Reactions of methane and hydrogen molecules with $[(\eta^5\text{-}C_5H_5)_2ZrCH_3]^+$ (**1**) and $[(\eta^5\text{-}C_5H_5)_2ZrH]^+$ (**2**) cations were studied using nonempirical density functional theory (DFT). In all cases, the reactions begin with the formation of agostic complexes between the substrate molecules and **1** or **2**. Transformation of these intermediates into transition states when moving along the reaction coordinate requires only slight changes in the geometry. The dihydrogen molecule reacts with **1** exothermically (−8.8 kcal mol^{-1}) and barrierlessly to form **2** and CH_4. Exchange of σ-bonded ligands in the **1**—CH_4 system proceeds through a symmetric transition state with an activation energy of 15.0 kcal mol^{-1}. According to calculations, organometallic Zr^{IV} complexes are promising for activation of C—H and H—H bonds under mild conditions.

Key words: activation of C—H bonds in methane, bis(cyclopentadienyl)zirconium complexes, activation of H—H bond, nonempirical quantum-chemical calculations, density functional theory.

Activation of C—H-bonds in alkanes for their functionalization under mild conditions is an important and complex problem. Among processes in which such activation was observed,[1—3] of considerable interest is the H/D isotope exchange in CD_4 under the action of the Ziegler—Natta catalysts $TiCl_4+Et_2AlCl$, $(C_5H_5)_2TiCl_2+Et_2AlCl$, and $(acac)_2TiCl_2+Et_2AlCl$.[4] A hypothetical mechanism[4] of this process is shown in Scheme 1.

Scheme 1



$^{13}C/^{12}C$ isotope exchange was observed[5—7] in reactions of $^{13}CH_4$ with bis(cyclopentadienyl)lutetium, bis(cyclopentadienyl)yttrium, and bis(cyclopentadienyl)scandium complexes in cyclohexane at 70—80 °C:

$$Cp^*{}_2MCH_3 + {}^{13}CH_4 \rightleftharpoons Cp^*{}_2M^{13}CH_3 + CH_4,$$

where Cp* is a substituted cyclopentadienyl ligand. Reactions of benzene-d_6 with bis(cyclopentadienyl)zirconium complexes also result in H/D isotope exchange.[8]

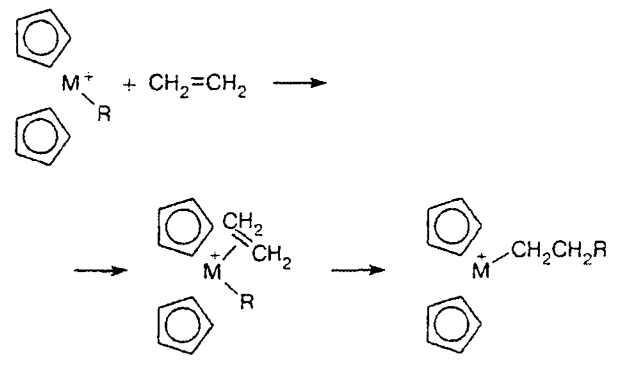
Catalytic polymerization of olefins in systems based on cyclopentadienyl complexes of titanium and zirconium has likely much in common with hydrogen exchange reactions of alkanes in the same systems. Polymerization has been extensively studied experimentally and theoretically. In particular, it was established with certainty that $[L_nMR]^+$ (M = Ti, Zr) cationic complexes are key intermediates in these processes. The complexes are formed due to elimination of one of the σ-bonded ligands from the metal atom by Lewis acids such as organoaluminum compounds (R_2AlCl, methylaluminoxane) or $(C_6F_5)_3B$. These cationic complexes are coordinatively unsaturated and readily bind an olefin molecule. Cleavage of the M—R bond and the formation of a C—R bond within the coordination sphere of the metal ion results in elongation of the hydrocarbon polymer chain. After addition of a new olefin molecule the cycle is repeated (Scheme 2).[9]

Detailed theoretical studies of ethylene polymerization by $[(\eta^5\text{-}C_5H_5)_2ZrR]^+$ cations (R = Me, Et),[9—12] carried out using the density functional theory (DFT) approach, showed an important role of agostic interactions in the mechanism and rate of the process. These

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2248—2254, December, 1999.

1066-5285/99/4812-2222 $22.00

Scheme 2



interactions favor partial donation of the electron pair of the C—H σ-bond to the transition-metal atom and partially saturate its coordination vacancy. Agostic interactions are observed by X-ray analysis and NMR spectroscopy in many 16- and 14-electron transition-metal complexes and their important role in stoichiometric and catalytic reactions has been studied in detail.[13] At the same time, no theoretical studies of alkane reactions with cationic titanium(IV) and zirconium(IV) complexes have been carried out as yet. The aim of this work is to perform a DFT study of σ-bonded ligand exchange reactions in the systems

$$Cp_2ZrCH_3^+ + CH_4 \rightleftharpoons Cp_2ZrCH_3^+ + CH_4$$

and

$$Cp_2ZrCH_3^+ + H_2 \rightleftharpoons Cp_2ZrH^+ + CH_4.$$

Calculation procedure

Calculations were carried out in the framework of an approach described earlier.[14] The approximate PBE density functional[15] belonging to the most appropriate approximations with inclusion of the electron density gradient was used. An original program written by one of the authors uses Gaussian basis sets for solving the Kohn—Sham equations and the electron density expansion in an auxiliary basis set for faster calculations of necessary integrals.[16] The orbital basis sets had the following contraction patterns: (5s1p)/[3s1p] for H, (11s6p2d)/[6s3p2d] for C, and (21s16p12d)/[15s12p7d] for Zr. The auxiliary basis sets were uncontracted sets of Gaussian functions of dimensions (5s1p) for H, (10s3p3d1f) for C, and (21s9p9d8f8g) for Zr. Molecular geometries were optimized without imposing symmetry restrictions. The types of stationary points found on the potential energy surface (PES) were determined from analytical calculations of the second energy derivatives.

Results and Discussion

Agreement between the calculated and experimental geometric parameters of bis(cyclopentadienyl)zirconium complexes can be shown taking $Cp_2Zr(CH_3)_2$ and $Cp_2ZrCH_3^+$ systems as examples (Table 1). The data listed in Table 1 indicate that the computational method employed in this work adequately reproduces the geometries of the systems under study. The geometric parameters of $Cp_2ZrCH_3^+$, obtained previously using the DFT method,[12] are also listed in Table 1. It is well known[20] that the DFT approach is highly efficient in calculations of the structures and energies of organometallic compounds and transition states of their reactions. Recently,[14] we successfully used the above-mentioned implementation of this method in studies of haptotropic rearrangements.

Structure of $Cp_2ZrCH_3^+$ and Cp_2ZrH^+ complexes

Stationary points corresponding to two isomeric forms of the $Cp_2ZrCH_3^+$ cation (**1a** and **1b**) were localized on the PES of this system. Each of the structures **1a** and **1b** shown in Fig. 1 has a symmetry plane passing through the Zr, C, and one of the H atoms of the Me group. These structures differ in orientation of the Me group with respect to the symmetry plane.

Table 1. Bond lengths (*d*) and bond angles (ω) in $Cp_2Zr(CH_3)_2$ and $Cp_2ZrCH_3^+$ complexes

Parameter	$Cp_2Zr(CH_3)_2$		$Cp_2ZrCH_3^+$		
	Experiment[17,18]	Calculation*	Experiment[12,19]	Calculation	
				I**	II*
Bond			*d*/Å		
$Zr—C_{Me}$	2.27	2.30	2.22—2.25	2.18	2.25
$Zr—C_{Cp}$ (average)	2.52	2.56	2.52	2.50	2.51
Zr—Cp (centr.)	2.23	2.25	2.21	2.19	2.20
Angle			ω/deg		
$C_{Me}—Zr—C_{Me}$	132.6	134.3	—	—	—
Cp_1 (centr.)—Zr—Cp_2 (centr.)	95.6	101.1	132.5	138.6	135.4

* This work.

** See Ref. 12.

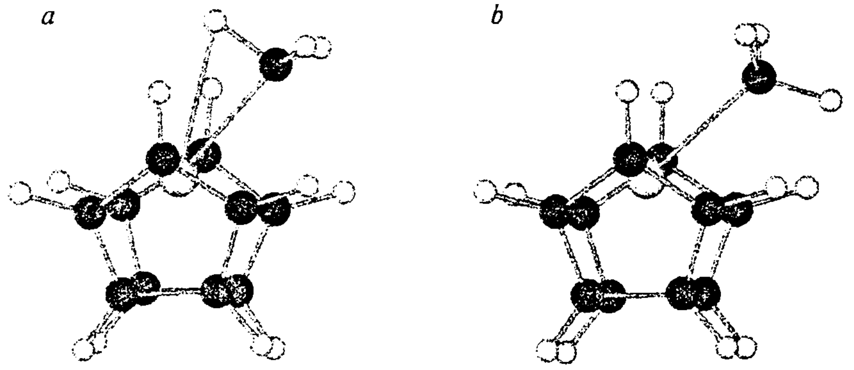


Fig. 1. Structure of the $Cp_2ZrCH_3^+$ cation: forms **1a** (*a*) and **1b** (*b*).

The agostic Zr—H bond in form **1a** (see Fig. 1) is a salient distinction between structures **1a** and **1b**. The presence of such a bond is indicated by the following peculiarities of the structure of complex **1a**. One of the Zr—H distances is 2.39 Å, which is less than the sum of the van der Waals radii (2.5 Å). In Fig. 1, the corresponding H atom of the Me group is denoted as H_a. The Zr—C—H_a bond angle is 84°. The C—H_a bond (1.14 Å) is somewhat lengthened as compared to the ordinary C—H bond in alkanes (1.10 Å).

No agostic bond is observed in form **1b** (see Fig. 1). All Zr—H distances lie in the range from 2.96 to 2.78 Å and the bond angles lie in the interval from 107 to 120°. All C—H bonds in the Me group have the same length of 1.10 Å.

The agostic Zr—H_a bond in form **1a** stabilizes this structure as compared to **1b**. The energies of the two isomeric forms differ by ~0.4 kcal mol^{-1}. Conversion of isomer **1a** into **1b** requires overcoming of an energy barrier of ~0.5 kcal mol^{-1} only and occurs by rotating the Me group about the Zr—C bond. This results in the cleavage of the agostic bond. The reverse process requires overcoming of an energy barrier of ~0.1 kcal mol^{-1}. Since these barriers do not exceed the thermal energy (RT) at room temperature (0.6 kcal mol^{-1}), free rotation of the Me group can be suggested. With inclusion of zero-point vibrational energy corrections obtained in the harmonic approximation, the relative energies (H_0) of isomer **1a**, the transition state of the isomerization reaction, and isomer **1b** are 0, ~0.3, and ~0.5 kcal mol^{-1}, respectively. This indicates the absence of an activation barrier, *i.e.*, free rotation of the Me group. It should be noted that, in this case, the use of an harmonic approximation for assessing the zero-point vibrational energy corrections can lead to large errors.

Since pathways of $Cp_2ZrCH_3^+$ reactions with methane and hydrogen molecules pass through form **1b**, hereafter it will be considered a reagent.

The structure of the Cp_2ZrH^+ cation (**2**) is shown in Fig. 2. As can be seen, the zirconium ion in **2** has considerably more opportunities for coordinating extra ligands than in derivative **1**. This is likely a reason for the higher reactivity of hydride zirconium complexes compared to alkyl complexes.[8]

Reaction of $Cp_2ZrCH_3^+$ with CH_4

The reaction of $Cp_2ZrCH_3^+$ with CH_4 was studied as a model for isotope exchange reaction. We investigated its mechanism and the energy profile. Stationary points corresponding to the intermediate complex $[Cp_2Zr(CH_3)CH_4]^+$ (**3**) and transition state (**TS-1**) were localized on the PES of the system under study. The structures of **3** and **TS-1** are shown in Figs. 3 and 4, respectively, and their geometric parameters are listed in Table 2.

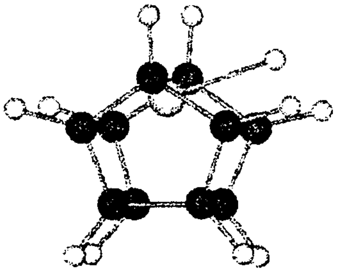


Fig. 2. Structure of the Cp_2ZrH^+ cation (**2**).

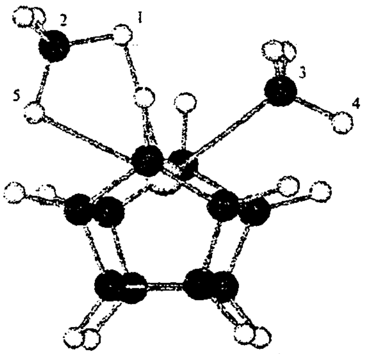


Fig. 3. Structure of the $[Cp_2Zr(CH_3)CH_4]^+$ complex (**3**).

Table 2. Bond lengths (*d*) and bond angles (ω) in the reagents ($Cp_2ZrCH_3^+$, CH_4), intermediate complex $[Cp_2Zr(CH_3)CH_4]^+$ (3), and **TS-1** of the $Cp_2ZrCH_3^+ + CH_4 \rightleftharpoons Cp_2ZrCH_3^+ + CH_4$ reaction*

Parameter	**1b** + CH_4	3	**TS-1**
Bond		*d*/Å	
Zr—H(1)	—	2.40	1.95
Zr—C(2)	—	2.77	2.40
Zr—C(3)	2.25	2.27	2.40
Zr—H(4)	2.96	2.92	2.52
Zr—H(5)	—	2.37	2.52
H(1)—C(2)	1.10	1.11	1.45
H(1)—C(3)	—	2.67	1.45
H(4)—C(3)	1.10	1.10	1.11
Angle		ω/deg	
C(2)—Zr—C(3)	—	93	74
C(2)—H(1)—C(3)	—	151	177
Zr —C(2)—H(1)	—	59	54
Zr —C(3)—H(1)	—	57	54
Zr —C(2)—H(5)	—	58	83
Zr —C(3)—H(4)	120	115	83

* The numbering of atoms is shown in Figs. 3 and 4.

Table 3. Energy and thermodynamic parameters of the reaction between $Cp_2ZrCH_3^+$ and CH_4

Parameter*	3	**TS-1**
ΔE/kcal mol^{-1}	−9.9	7.1
ΔH_0/kcal mol^{-1}	−8.4	6.6
ΔH_{298}/kcal mol^{-1}	−8.6	5.6
ΔS_{298}/cal mol^{-1} K^{-1}	−33.1	−38.3
ΔG_{298}/kcal mol^{-1}	1.2	14.5

* Listed are the energies calculated without (ΔE) and with (ΔH_0) inclusion of zero-point vibrational energy corrections, enthalpies (ΔH_{298}), entropies (ΔS_{298}), and the Gibbs free energies (ΔG_{298}); all values are given relative to corresponding values for noninteracting reagents (**1b** + CH_4), which were taken as zero.

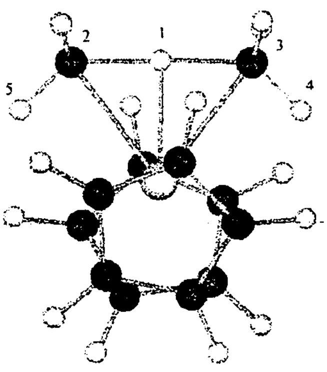


Fig. 4. Transition state of the reaction of inner-sphere migration of H atom in complex **3** (**TS-1**).

Bonding of the CH_4 molecule in the coordination sphere of the zirconium atom in intermediate complex **3** occurs with participation of electrons of two C—H bonds. The formation of 3 from **1b** and a CH_4 molecule decreases the energy of the system by 9.9 kcal mol^{-1}. The relative energies of complex **3** and **TS-1**, calculated without and with inclusion of zero-point vibrational energy corrections, as well as the standard enthalpies, entropies, and the Gibbs free energies are listed in Table 3.

The structure of the transition state **TS-1** of the $Cp_2ZrCH_3^+ + CH_4$ ligand exchange reaction is characterized by C_2 symmetry. The H(1) atom is equidistant from the C(2) and C(3) atoms of the Me groups. The interaction between the H(1) and Zr atoms stabilizes **TS-1**. The Zr—H(1) distance is 1.95 Å (*cf.* 2.40 Å in the intermediate complex **3**), which is less than the sum of the atomic radii of Zr and H (2.06 Å); thus, a Zr—H bond is formed in **TS-1**. For comparison, the Zr—H bond length in the Cp_2ZrH^+ cation is 1.82 Å.

The energy of **TS-1** is 17.0 kcal mol^{-1} higher than that of the intermediate complex **3**. We can assess the rate constant for inner-sphere migration of a H atom in complex **3** in the framework of the Eyring gas-phase model[21]:

$$
\begin{aligned}
k &= kT/h \cdot \exp[-\Delta G^{\neq}/(RT)] = \\
&= kT/h \cdot \exp(\Delta S^{\neq}/R) \cdot \exp[-\Delta H^{\neq}/(RT)] = \\
&= k_0 \cdot \exp[-\Delta H^{\neq}/(RT)].
\end{aligned}
$$

At $T = 298.15$ K, $k_0 = 4.4 \cdot 10^{11}$ s^{-1}, and $\Delta H^{\neq} = 14.2$ kcal mol^{-1}, the k value was estimated at 18.4 s^{-1}, which should be considered as the upper bound expected for the experimental rate constant.

Reactions of $Cp_2ZrCH_3^+$ with H_2 and of Cp_2ZrH^+ with CH_4

Formation and interconversion of $[Cp_2Zr(CH_3)H_2]^+$ complexes

Two stationary points corresponding to two complexes (**4a** and **4b**) formed as primary products in the reaction of $Cp_2ZrCH_3^+$ with dihydrogen were localized on the PES of the $Cp_2ZrCH_3^+ + H_2$ system. The structures of these complexes (Fig. 5) differ in orientation of the H_2 molecule in the coordination sphere of the zirconium ion with respect to Cp ligands. In form **4a**, the H_2 molecule is perpendicular to the symmetry plane passing through the Zr, C, and one of the H atoms of the Me group. In isomer **4b**, it lies in the symmetry plane and is coordinated to the Zr ion in the same way as the CH_4 molecule in complex **3**.

Apart from the coordination mode, there are also some other distinctions between the structures of the two isomers. First of all, it should be noted that the Zr—H(4) distance, Zr—C(3)—H(4) bond angle, and C(3)—H(4) bond length in complex **4a** are the same as those in the initial compound $Cp_2ZrCH_3^+$ (**1b**) (2.96 Å, 120°, and 1.10 Å, respectively, Table 4). All this makes it possible to argue that no agostic bond with participation of the H(4) atom of the Me group is formed in isomer **4a**. At the same time, the Zr—H(4) distance in

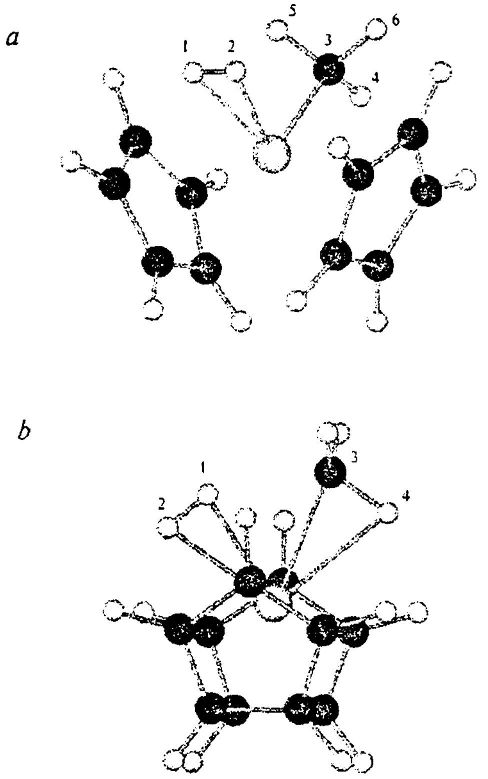


Fig. 5. Structure of the $[Cp_2Zr(CH_3)H_2]^+$ complex: isomers **4a** (*a*) and **4b** (*b*).

Table 4. Bond lengths (*d*) and bond angles (ω) in the reagents ($Cp_2ZrCH_3^+$, H_2), complex $[Cp_2Zr(CH_3)H_2]^+$ (**4b**), **TS-3**, complex $[Cp_2Zr(H)CH_4]^+$ (**5**), and products (Cp_2ZrH^+, CH_4) of the $Cp_2ZrCH_3^+ + H_2 \rightleftharpoons Cp_2ZrH^+ + CH_4$ reaction*

Parameter	**1b** + H_2	**4b**	**TS-3**	**5**	**2** + CH_4
Bond			*d*/Å		
Zr—H(1)	—	2.04	1.96	2.27	—
Zr—H(2)	—	2.08	1.98	1.83	1.82
Zr—C(3)	2.25	2.27	2.33	2.70	—
Zr—H(4)	2.96	2.32	2.36	2.39	—
H(1)—H(2)	0.75	0.82	0.91	2.11	—
H(1)—C(3)	—	1.99	1.66	1.12	1.10
H(4)—C(3)	1.10	1.13	1.13	1.11	1.10
Angle			ω/deg		
H(2)—Zr—C(3)	—	78	71	85	—
H(2)—H(1)—C(3)	—	150	157	150	—
Zr—H(2)—H(1)	—	75	75	70	—
Zr—C(3)—H(1)	—	57	56	56	—
Zr—C(3)—H(4)	120	78	78	62	—

* The numbering of atoms is shown in Figs. 5—7.

complex **4b** is 2.32 Å. Appreciable shortening of this distance, the lengthening of the C(3)—H(4) bond to 1.13 Å, and a decrease in the Zr—C(3)—H(4) angle to 78° indicate the formation of an agostic bond.

We failed to localize a minimum on the PES, corresponding to the $Cp_2ZrCH_3^+$ complex with an agostic bond. However, we calculated the energy of a $Cp_2ZrCH_3^+$ core (this species remains after elimination of an H_2 molecule from complex **4b**). According to calculations, such a hypothetical species would be 2.7 kcal mol^{-1} less stable than form **1b**.

Among other distinctions, it should also be noted that the distances between the Zr atom and H atoms of the H_2 molecule in complex **4a** (2.25 Å) are slightly lengthened as compared with those in complex **4b** (2.04 and 2.08 Å). Complex **4a** is 1.4 kcal mol^{-1} less stable than **4b**, which is first of all due to the formation of the Zr—H(4) agostic bond in **4b**.

Complex **4a** isomerizes into **4b** *via* rotation of the H_2 molecule by 90° and simultaneous displacement toward the Me group. These two motions proceed concertedly and are accompanied by the formation of a Zr—H(4) agostic bond. The energy of the transition state for such a transformation (**TS-2**) is 1.2 and 2.6 kcal mol^{-1} higher than those of complexes **4a** and **4b**, respectively. With inclusion of zero-point vibrational energy corrections calculated in the harmonic approximation, the relative energies H_0 of **4a**, **TS-2**, and **4b** are 0.6, 1.0, and 0 kcal mol^{-1}, respectively.

The $Cp_2ZrCH_3^+$ cation can form two adducts (**4a** and **4b**) with dihydrogen; however, the pathway of the ligand exchange reaction

$$Cp_2ZrCH_3^+ + H_2 \rightleftharpoons Cp_2ZrH^+ + CH_4$$

passes through complex **4b** only. For this reason, hereafter only this complex will be considered as the intermediate.

Transformation of $[Cp_2Zr(CH_3)H_2]^+$ into $[Cp_2Zr(H)CH_4]^+$

The structure of the transition state (**TS-3**) for inner-sphere migration of the H(1) atom in form **4b** is shown in Fig. 6. Complex **4b** is structurally close to **TS-3**. It is transformed into **TS-3** *via* slight displacements of the atoms of the Me ligand and the coordinated H_2 molecule. The reverse reaction ($Cp_2ZrH^+ + CH_4$) also involves a stage in which the $[Cp_2Zr(H)CH_4]^+$ intermediate complex (**5**) is formed (Fig. 7). In this complex, electrons of two C—H bonds participate in bonding the CH_4 molecule to the central ion. The geometric parameters of intermediates **4b**, **5**, and transition state **TS-3** are listed in Table 4.

The interaction between the H(1) atom and Zr ion stabilizes **TS-3**. The Zr—H(1) distance is 1.96 Å (*cf.* 2.04 Å in form **4b** and 2.27 Å in complex **5**), which, as in the case of **TS-1** of the $Cp_2ZrCH_3^+ + CH_4$ reaction, indicates the formation of a Zr—H bond. Stabilization is also achieved by retention of the Zr—H(4) agostic bond in **TS-3** (see Table 4).

The relative energies of complexes **4b**, **5**, and **TS-3**, calculated without and with inclusion of zero-point vibrational energy corrections, as well as the standard enthalpies, entropies, and the Gibbs free energies are listed in Table 5.

The energy of **TS-3** is 0.4 and 14.0 kcal mol^{-1} higher than those of complexes **4b** and **5**, respectively. The $\Delta H^{\neq}$ value of −0.34 kcal mol^{-1} ($\Delta H^{\neq} = H(\mathbf{TS\text{-}3}) - H(\mathbf{4b})$) indicates a barrierless ligand exchange at room temperature. Assuming that an equilibrium is established between intermediates **4b** and **5**, we can assess the equilibrium constant as

$$K = \exp\{-[G(\mathbf{5}) - G(\mathbf{4b})]/(RT)\} = 3 \cdot 10^4,$$

i.e., the equilibrium mixture contains mostly **5**.

Thus, we obtained detailed information on the mechanisms of ligand exchange reactions in the systems

$$Cp_2ZrCH_3^+ + CH_4 \rightleftharpoons Cp_2ZrCH_3^+ + CH_4$$

and

$$Cp_2ZrCH_3^+ + H_2 \rightleftharpoons Cp_2ZrH^+ + CH_4.$$

The results of our calculations are in good agreement with the known experimental data[4] on H/D isotope exchange in CH_4. At the same time, the mechanism of such an exchange with participation of bis(cyclopentadienyl)zirconium(IV) complexes differs from the known mechanism proposed[4] for analogous Ti^{IV} compounds.

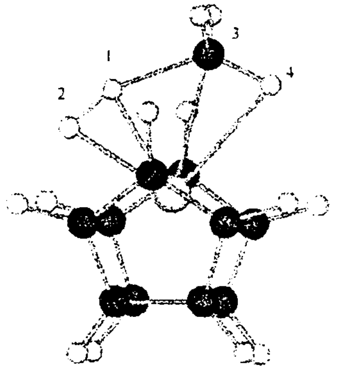


Fig. 6. Transition state of the reaction of inner-sphere migration of H atom in complex **4b** (**TS-3**).

Table 5. Energy and thermodynamic characteristics of the reaction between $Cp_2ZrCH_3^+$ and H_2

Parameter*	**4b**	**TS-3**	**5**	**2** + CH_4
ΔE/kcal mol^{-1}	−10.2	−9.8	−23.8	−11.8
ΔH_0/kcal mol^{-1}	−6.3	−6.3	−18.3	−7.6
ΔH_{298}/kcal mol^{-1}	−8.0	−8.3	−19.7	−8.8
ΔS_{298}/cal mol^{-1} K^{-1}	−30.9	−32.5	−27.5	4.8
ΔG_{298}/kcal mol^{-1}	1.2	1.3	−11.6	−10.3

* Listed are the energies calculated without (ΔE) and with (ΔH_0) inclusion of zero-point vibrational energy corrections, enthalpies (ΔH_{298}), entropies (ΔS_{298}), and the Gibbs free energies (ΔG_{298}); all values are given relative to corresponding values for noninteracting reagents (**1b** + CH_4), which were taken as zero.

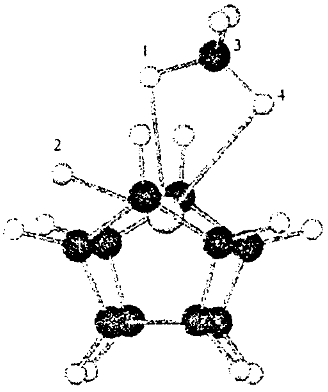


Fig. 7. Structure of the $[Cp_2Zr(H)CH_4]^+$ complex (**5**).

Investigations of the $Cp_2ZrCH_3^+$—CH_4/H_2 systems showed that the binding energy of CH_4 in the coordination sphere of the Zr atom in complex **3** is 9.9 kcal mol^{-1}, while the corresponding values for H_2 in complexes **4a** and **4b** are 8.7 and 10.2 kcal mol^{-1}, respectively. These values are comparable with the binding energy of ethylene (8.8 kcal mol^{-1} [11] and ~19 kcal mol^{-1} according to our results). Based on these results, it is believed that bis(cyclopentadienyl)zirconium complexes will also be rather efficient in binding of various donor molecules, as well as in the activation of C—H bonds in alkanes in other reactions. A theoretical investigation of this type of systems is currently in progress.

This work was financially supported by the "Russian Universities — Basic Research" Higher School Scientific Program (Project No. 5223), the Russian Foundation for Basic Research (Project No. 99-03-32792), the "Leading Scientific Schools of the Russian Federation" Program (Project No. 96-15-97469), and by the Russian State Scientific-Technical Program "Ecologically Safe Processes in Chemistry and Chemical Engineering".

The authors express their gratitude to B. M. Bulychev, V. I. Pupyshev, D. A. Tyurin, and V. L. Yarnykh for useful discussions and help in preparation of this work.

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Received May 19, 1999