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Activation of C—H bonds in C_1—C_3 alkanes by titanium(IV) and zirconium(IV) cationic complexes: a DFT study

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A DFT study of a model reaction $[(\eta^5\text{-}C_5H_5)_2MCH_3]^+ + RH \rightleftharpoons [(\eta^5\text{-}C_5H_5)_2MR]^+ + CH_4$ (M = Ti^{IV}, Zr^{IV}; R = Me, Et, Pr, Pr^i) was carried out with the PBE density functional. Exchange of σ-bonded ligand proceeds through the formation of agostic complexes $[Cp_2M(RH)CH_3]^+$ followed by their isomerization into complexes $[Cp_2M(CH_4)R]^+$ *via* an inner-sphere migration of a hydrogen atom. The calculated rate constants for such migrations involving the primary and secondary C—H bonds of propane molecule differ by 930 times for Ti^{IV} complexes and by 47 times for Zr^{IV} complexes, which is due to the effect of steric factors.

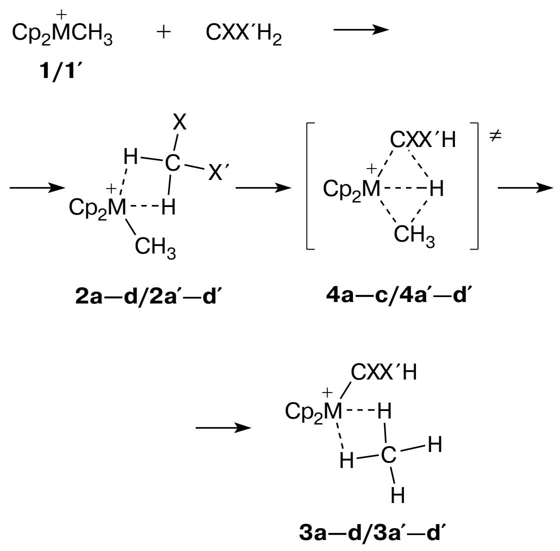
Key words: alkanes, activation of C—H bonds, bis(cyclopentadienyl) complexes of Zr and Ti, nonempirical quantum-chemical calculations, density functional approach.

Activation of C—H bonds in alkanes for their functionalization under mild conditions is an important and intricated problem.[1—3] Among processes in which such an activation was observed (reactions involving transition-metal complexes, lanthanides, and actinides[4—7]), of particular interest are the reactions of alkanes with electron-deficient complexes Cp^*_2M—L (Cp^* = η^5-C_5R_5, R = H, Me; M = Sc, Lu, Y). A characteristic feature of these reactions is their high selectivity. In particular, the C—H bonds at the secondary C atom of the alkane molecule are much less reactive than those at the primary C atom. This is inconsistent with the order in which the dissociation energies of these bonds and their reactivities in most of chemical reactions change. The selectivity of the above-mentioned reactions is known to be so high that cyclohexane or cyclohexane-d_{12} are often used as inert solvents in studies of the reactions of *n*-alkanes with Cp^*_2M—L complexes and in kinetic studies.[3]

Recently,[8,9] we studied the mechanism of the experimentally observed[4] H/D isotope exchange in methane in the reactions with cationic complexes of Zr^{IV} and Ti^{IV} using the density functional approach. We found that model reactions of complexes $[Cp_2MCH_3]^+$ (M = Zr (**1**), Ti (**1′**))[★] with CH_4 molecule (Scheme 1) involve the formation of agostic intermediate $[Cp_2M(CH_4)CH_3]^+$ (**2a**/**2a′**) in which hydrogen transfer occurs through an inner-sphere migration *via* a symmetric transition state (TS) (**4a**/**4a′**).

The calculated activation barriers are low, which is in excellent agreement with the experimental results. In this work, we investigated the reactions of the next two representatives of the alkane series (C_2—C_3) with the $[Cp_2MCH_3]^+$ (M = Ti, Zr) complexes. The results obtained were compared with those reported earlier for CH_4.[8,9]

Scheme 1



M = Zr (**1—4**), Ti (**1′—4′**)

2—4	**a**	**b**	**c**	**d**
X	H	Me	Et	Me
X′	H	H	H	Me

Calculation Procedure

All calculations were carried out in the framework of an approach used in our previous studies[8,9] with the gradient-corrected PBE density functional.[10] An original program[11] uses Gaussian basis sets for solving the Kohn—Sham equations and

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[★] Hereafter, the primed and unprimed notations refer to the compounds with M = Ti and M = Zr, respectively.

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the electron density expansion in an auxiliary basis set. 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 size (5s1p) for H, (10s3p3d1f) for C, and (21s9p9d8f8g) for Zr. Molecular geometries were optimized without imposing symmetry restrictions. The characters of stationary points located on the potential energy surfaces (PES) were determined from analytical calculations of the second energy derivatives.

Results and Discussion

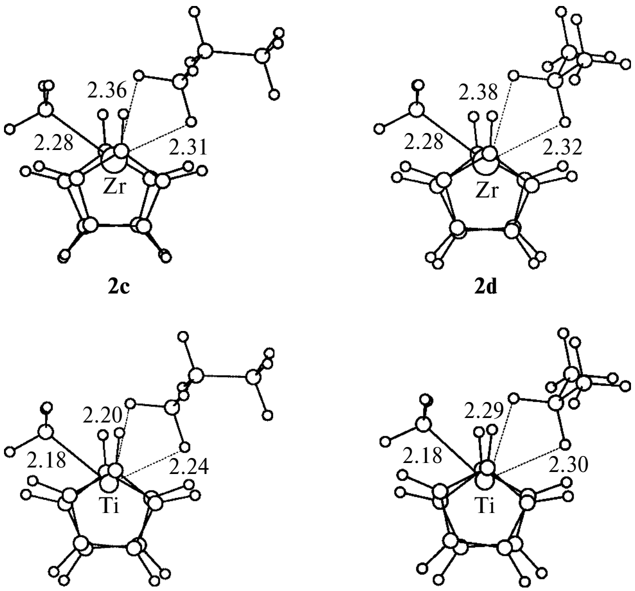
In this work, we optimized the geometries and calculated the thermodynamic characteristics of the complexes $[Cp_2M(RH)CH_3]^+$ (**2b—d/2b′—d′**) and $[Cp_2M(CH_4)R]^+$ (**3b—d/3b′—d′**); the same was also done for the TS **4b—d/4b′—d′** of the reactions of hydrocarbons RH, where R = Et (**b**), Pr^n (**c**), and Pr^i (**d**) (see Scheme 1). The corresponding structures for R = Me (**a**) were calculated earlier.[8,9] The total energies of the reagents **1/1′** and RH are listed in Table 1.

Agostic complexes 2b—d/2b′—d′ and 3b—d/3b′—d′. As for methane, gas-phase reactions of complexes **1/1′** with ethane and propane molecules begin with the barrierless formation of agostic complexes $[Cp_2M(RH)CH_3]^+$ (**2b—d/2b′—d′**) in which the alkane molecule is coordinated involving two C—H bonds. The structures and selected geometric parameters of the complexes **2c/2c′** and **2d/2d′** are shown in Fig. 1 and the thermodynamic characteristics of all the complexes of the types **2/2′** are listed in Table 2. The binding energies of ethane and propane in the intermediates **2b—d/2b′—d′** are higher than those of methane. For propane, the involvement of one out of two CH_3 groups in coordination leads to the strongest bonding. Coordination of the propane molecule involving secondary C—H bonds is much less energetically favorable. The decrease in the binding energy on going from R = Pr^n (**c**) to R = Pr^i (**d**) is most pronounced for the complexes with M = Ti. This indicates that intermediates **2d/2d′** are more sterically strained than **2c/2c′** and that the effect of steric hindrances manifests itself to the greatest extent in the Ti complex **2d′** (titanium has a smaller atomic radius compared to zirconium).

The addition of an alkane molecule is accompanied by a substantial loss of entropy, which increases on going from R = Me to R = Pr^i. In this connection, the ΔG_{298} values (see Table 2) are close to zero for the Zr complexes and positive for the Ti complexes.

Table 1. Total energies of reagents calculated without (E) and with inclusion (H_0) of zero-point vibrational energy correction

Reagent	$-E$	$-H_0$
	au	
$[Cp_2ZrCH_3]^+$ (**1**)	3967.07450	3966.87677
$[Cp_2TiCH_3]^+$ (**1′**)	1275.66246	1275.46350
CH_4	40.46518	40.42166
C_2H_6	79.73423	79.66170
C_3H_8	119.00567	118.90535



2c **2d**

2c′ **2d′**

Fig. 1. Structures of complexes **2c**, **2d**, **2c′**, and **2d′**; here and in Tables 2 and 3 the interatomic distances are given in Å.

The influence of steric factors on the reactions of alkanes with $[Cp_2MCH_3]^+$ complexes can be even more clearly followed by analyzing the structure (Fig. 2) and thermodynamic characteristics (Table 3) of complexes $[Cp_2M(CH_4)R]^+$ (**3a—d/3a′—d′**) which are products of the reactions under study. It is easily seen that the binding energies of methane in these complexes decrease on going from methyl to other alkyl radicals. This decrease is particularly large for the isopropyl complexes

Table 2. Thermodynamic characteristics of complexes $[Cp_2M(RH)CH_3]^+$ (**2a—d/2a′—d′**)*

Complex	R	$-\Delta E$	$-\Delta H_0$	$-\Delta H_{298}$	ΔG_{298}	$-\Delta S_{298}$ /cal mol^{-1} K^{-1}
		kcal mol^{-1}				
			M = Zr			
2a	Me	9.4	7.9	8.0	1.4	31.7
2b	Et	11.8	10.5	10.4	0.2	35.5
2c	Pr^n	12.5	11.3	11.1	−0.2	36.6
2d	Pr^i	12.4	11.2	11.0	0.5	38.6
			M = Ti			
2a′	Me	4.2	2.0	2.4	8.3	35.9
2b′	Et	6.1	4.3	4.4	7.6	40.2
2c′	Pr^n	6.8	5.1	5.1	6.8	39.9
2d′	Pr^i	5.8	4.3	4.2	8.2	41.4

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

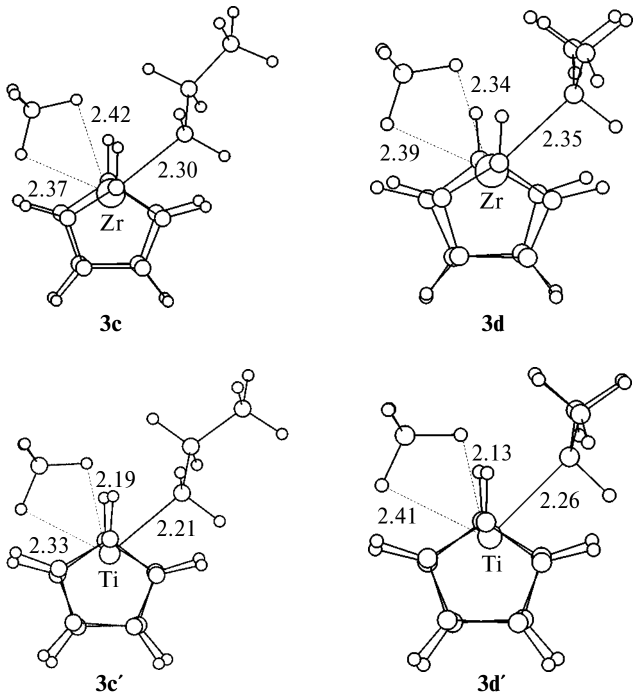


Fig. 2. Structures of complexes **3c**, **3d**, **3c′**, and **3d′**.

(**3d**/**3d′**). In this case, steric strain is so large that we failed to localize the minima corresponding to $[\mathrm{Cp_2M(CH_4)(Pr^i)}]^+$ (M = Ti, Zr) complexes on the PES of the systems under consideration, since these complexes barrierlessly decompose into methane molecule and β-agostic complexes $[\mathrm{Cp_2M(Pr^i)}]^+$ (Scheme 2).

By point-by-point scanning the PESs of these systems we found some points (they are not local minima) corresponding to the structures whose geometric parameters and energies can be considered as rough estimates of the parameters of complexes **3d**/**3d′**. In other words, these points on the PESs are characterized by the smallest energy gradient on the reaction pathway in the region of geometric parameters corresponding to the complexes $[\mathrm{Cp_2M(CH_4)(Pr^i)}]^+$.

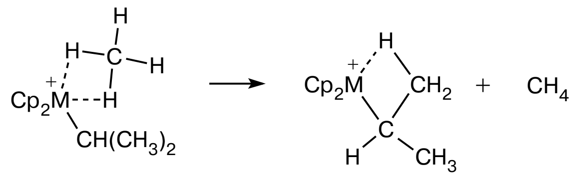
Table 3. Thermodynamic characteristics of complexes $[\mathrm{Cp_2M(CH_4)R}]^+$ (**3a**—**d**/**3a′**—**d′**)*

Complex	R	$-\Delta E$	$-\Delta H_0$	$-\Delta H_{298}$	ΔG_{298}	$-\Delta S_{298}$ /cal mol^{-1} K^{-1}
		kcal mol^{-1}				
			M = Zr			
3a	Me	9.4	7.9	8.0	1.4	31.7
3b	Et	7.3	6.6	6.0	3.1	30.7
3c	Pr^n	7.8	7.2	6.5	3.3	32.8
3d	Pr^i**	2	—	—	—	—
			M = Ti			
3a′	Me	4.2	2.0	2.4	8.3	35.9
3b′	Et	2.0	0.7	0.6	11.1	39.1
3c′	Pr^n	2.5	1.3	0.9	13.5	39.9
3d′	Pr^i**	−4	—	—	—	—

* See note to Table 2.

** As follows from the text, complexes **3d** and **3d′** do not correspond to local minima on the PES of the system under study; therefore, the ΔE values for **3d** and **3d′** listed in this Table can be considered only as rough estimates.

Scheme 2



Again, large negative entropy contributions increase in the following order of R: Me < Et < Pr. This leads to a considerable increase in the ΔG_{298} values, which is most pronounced for the Ti complexes.

Transition states 4a—d/4a′—d′. Previously,[8,9] in studies of the reactions of **1**/**1′** with methane we have shown that each reaction is characterized by one energy barrier corresponding to TS **4a**/**4a′** and that this barrier is overcome in the stage of inner-sphere migration of H atom. The geometries of the TS **4c**/**4c′** and **4d**/**4d′** of such a hydrogen migration for M = Ti, Zr and R = Pr^n, Pr^i are shown in Fig. 3. The activation parameters for this stage (figures in the columns labeled by I) were calculated as the differences between the corresponding values for the TS **4**/**4′** and intermediate complexes **2**/**2′**. They are listed in Table 4 together with the thermodynamic characteristics of TS **4**/**4′** calculated relative to

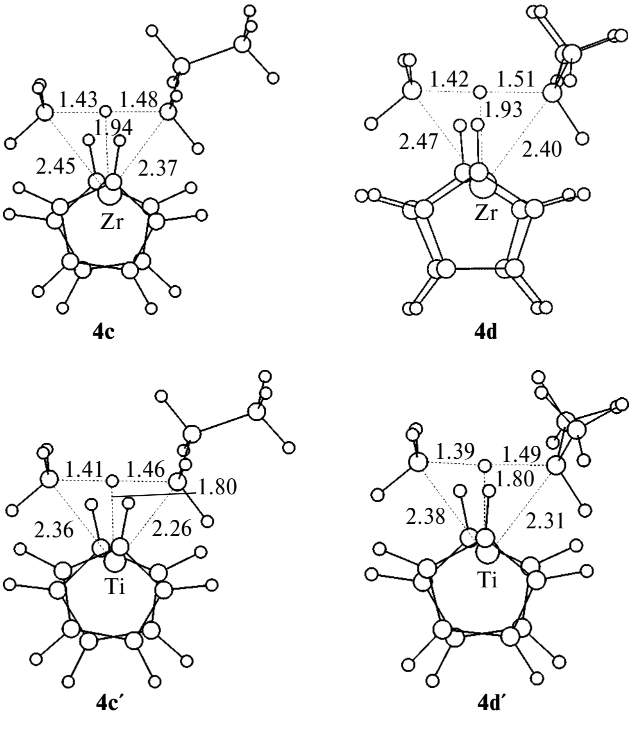


Fig. 3. Transition states **4c**, **4d**, **4c′**, and **4d′** of the inner-sphere proton migration.

Table 4. Thermodynamic characteristics of transition states of the inner-sphere hydrogen migration in complexes $[Cp_2M(RH)CH_3]^+$ (**4a—d/4a′—d′**)*

Complex	R	$\Delta E^{\neq}$		$\Delta H_0^{\neq}$		$\Delta H_{298}^{\neq}$		$\Delta G_{298}^{\neq}$		$-\Delta S_{298}^{\neq}$ /cal mol^{-1} K^{-1}	
		kcal mol^{-1}									
		I**	II*	I**	II*	I**	II*	I**	II*	I**	II*
						M = Zr					
4a	Me	17.0	7.6	15.0	7.1	14.2	6.2	15.7	17.1	5.2	36.0
4b	Et	18.4	6.6	16.0	5.5	15.4	5.0	17.0	17.2	5.3	40.8
4c	Pr^n	18.6	6.1	16.1	4.8	15.6	4.5	17.0	16.8	4.7	41.3
4d	Pr^i	20.5	8.1	17.9	6.7	17.5	6.5	18.6	19.1	3.4	42.0
						M = Ti					
4a′	Me	13.5	9.3	11.6	9.6	10.9	8.5	12.3	20.6	4.7	40.6
4b′	Et	14.8	8.7	12.4	8.1	11.9	7.5	13.2	20.8	4.4	44.6
4c′	Pr^n	14.9	8.1	12.5	7.4	12.0	6.9	13.4	20.2	4.6	44.5
4d′	Pr^i	17.5	11.7	15.6	11.3	14.5	10.3	16.1	24.3	5.2	46.6

* See note to Table 2.

** Relative to the corresponding values for complexes **2a—d/2a′—d′**.

the noninteracting reagents (figures in the columns labeled by II).

The activation energies $\Delta H_0^{\neq}$ (see Table 4) and Gibbs free activation energies $\Delta G_{298}^{\neq}$ (see Table 3) of the inner-sphere migration of H atom in the Ti complexes are lower than those calculated for the corresponding Zr complexes. This also holds for the overall energy barrier to the reaction which was calculated relative to the noninteracting reagents. These characteristics of the reactions do not correlate with changes in the strength of the R—H bonds for both the Ti and Zr complexes. According to calculations, the strengths of the C—H bonds in corresponding hydrocarbons decrease by ~5 kcal mol^{-1} on going from R = Me to R = Et and Pr^n and by ~9 kcal mol^{-1} on going to R = Pr^i. This is in agreement with the experimental results (103 to 107, 95 to 99, 98 to 99, and 94 to 95 kcal mol^{-1} for R = Me, Et, Pr^n, and Pr^i, respectively[12]). The $\Delta H_0^{\neq}$ values of TS **4/4′** calculated relative to those of noninteracting reagents (**1** + RH) insignificantly decrease on going from R = Me to R = Pr^n; however, they substantially increase for R = Pr^i (by 3.9 kcal mol^{-1} for M = Ti and by 1.9 kcal mol^{-1} for M = Zr) as compared to R = Pr^n (see Table 4). This indicates that the structures of transition states of inner-sphere migration of H atom are sterically strained.

Thus, the effect of steric factors manifests itself in all the systems studied and is most pronounced for R = Pr^i, especially in Ti complexes. The rate constant (k') for the inner-sphere hydrogen migration can be assessed from the data listed in Table 4 in the framework of Eyring's gas-phase model[13]:

$$k' = (kT/h)\exp(-\Delta G^{\#}/RT) =$$
$$= (kT/h)\exp(\Delta S^{\#}/R)\exp(-\Delta H^{\#}/RT) = k'_0\exp(-\Delta H^{\#}/RT).$$

The calculated rate constants of these gas-phase reactions (Table 5) should be considered as the upper bounds expected for the experimental rate constants. Assuming that the equilibrium between the reagents (**1/1′** + RH) and corresponding intermediate complex (**2/2′**) is established rapidly, the overall rate constant for the reaction of hydrogen exchange can be estimated using the formula

$$K_e k' = (kT/h)\exp(-\Delta G_e/RT)\exp(-\Delta G^{\#}/RT).$$

Here, $\Delta G_e = \Delta G_{298}$(**2a—d/2a′—d′**) − ΔG_{298}(**1/1′** + RH) is the difference between the Gibbs free energies of the intermediate **2a—d/2a′—d′** and reagents (**1/1′** + RH) (see Table 2), which characterizes the equilibrium in the system, and $K_e = \exp(-\Delta G_e/RT)$ is the constant of equilibrium between the noninteracting reagents (**1/1′** + RH) and corresponding complex **2a—d/2a′—d′**. This assumption can be considered justified since the addition of alkane to cation **1/1′** to give complex **2/2′** proceeds barrierlessly.

The data listed in Table 4 indicate that the conditions for inner-sphere migration of H atom in Ti complexes are much better than in Zr complexes. Nevertheless, the formation of intermediates $[Cp_2M(RH)CH_3]^+$ is more energetically favorable for M = Zr. This has a

Table 5. The calculated relative rate constants for the inner-sphere migration of H atom (k') and the rate constants for exchange of σ-bonded ligand $[\eta^5\text{-}C_5H_5)_2MR]^+$ ($K_e k'$)*

R	k'	$K_e k'$	R	k'	$K_e k'$
	M = Zr			M = Ti	
Me	2	160000	Me	620	480
Et	0.2	140000	Et	140	340
Pr^n	0.2	270000	Pr^n	90	930
Pr^i	0.01	5800	Pr^i	1	1

* The corresponding values for M = Ti, R = Pr^i were taken as unity.

pronounced effect on the rate constant for the exchange of σ-bonded ligand, $K_e k'$, so that these rate constants for M = Zr are much higher than those for M = Ti.

Thus, in this work we found that cationic complexes $[Cp_2MCH_3]^+$ (M = Zr, Ti) (**1/1′**) can form agostic intermediates with ethane and propane molecules and that they are more stable than analogous complexes with methane. The involvement of primary C—H bonds of the alkane molecule in coordination is more energetically favorable as compared to secondary C—H bonds due to an increase in steric strain in the latter case. The results of calculations suggest that the primary C—H bonds of propane molecule are most reactive in the exchange reaction of the σ-bonded ligand. The energy barrier to the reaction slightly decreases in the following order of R: Me > Et > Pr^n; however it substantially increases for R = Pr^i, which is particularly clearly seen for the Ti complexes (titanium has a smaller atomic radius compared to zirconium). Therefore, activation of C—H bonds in alkanes by bis(cyclopentadienyl) complexes of Zr and Ti is highly selective, that is, the calculated rate constants for the exchange of σ-bonded ligand involving the primary and secondary C—H bonds differ by ~930 times for Ti complexes and by 47 times for Zr complexes. This is due to the effect of steric hindrances on the energies of the TS and intermediates of this reaction.

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