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DFT study of new binuclear zirconium(IV) hydride complexes as prospective catalysts for alkane hydrogenolysis under mild conditions

Leila Yu. Ustynyuk,* Yuri A. Ustynyuk and Valery V. Lunin

Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation. Fax: +7 495 939 2677; e-mail: leila_ust@mail.ru

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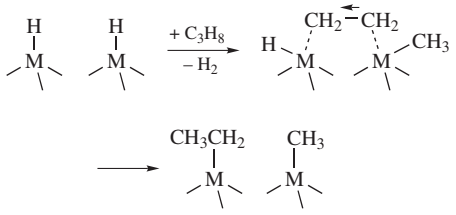
The results of DFT study of the reaction between binuclear Zr^{IV} hydride complex $(\equiv SiO)_2(H)Zr(H)_2Zr(H)(OSi\equiv)_2$ and propane show that centres of this type would be more prospective catalysts for alkane hydrogenolysis under mild conditions (T < 450 K, P ~ 1 atm) than previously studied mononuclear Zr^{IV} complexes.

The Ermakov–Basset catalytic system based on silica-supported zirconium and titanium hydrides has been extensively studied (refs. 1–5 and cited therein). This system catalyzes both olefin polymerization reactions and C–C and C–H bond hydrogenolysis in alkanes under mild conditions (T < 450 K, P ~ 1 atm). Three types of hydride centres are found in the Ermakov–Basset catalytic system: (i) monohydrides of tetravalent metals $(\equiv Si–O)_3MH$ (M = Zr, Ti), (ii) dihydrides of tetravalent metals $(\equiv Si–O)_2MH_2$, and (iii) hydrides of trivalent metals $(\equiv Si–O)_2MH$. Among them, centres (ii) (M = Zr) and (iii) (M = Ti) are the most efficient in C–C and C–H bond cleavage processes. Monohydrides (i), which are dominant in the Ermakov–Basset system, are much less reactive toward the C–C and C–H bonds of alkanes.[6–11] At the same time, the most reactive centres (ii) $(\equiv Si–O)_2ZrH_2$ reveal significantly lower oxidative and hydrolytic stabilities than (i) $(\equiv Si–O)_3ZrH$. This precludes their practical use.

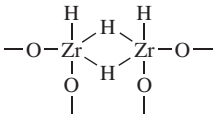
Earlier, we suggested[12] that the introduction of a bulky π-ligand (Cp) would lead to stabilization of centres (ii). Here we consider an alternative way of stabilization based on the synthesis of binuclear metal hydride complexes of zirconium.

DFT calculations were performed with the original program Priroda[13] using PBE functional,[14] TZ2p Gauss type basis sets and electron core potentials for the core electrons of C, O, F, Si and Zr.[15] Vibrational spectra and thermodynamic characteristics were calculated in the approximation of harmonic oscillator, rigid rotator and ideal gas.

The construction of binuclear catalytic centres containing two transition metal atoms could serve for two purposes. First, the olefin molecule formed in the course of the reaction could be hydrogenated on the neighbouring metal hydride site, thus avoiding energy expenses for its removal from one catalytic site and transfer to another distant centre for hydrogenation. For example, in the case of propane molecule:

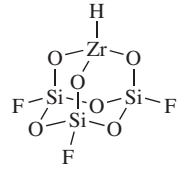


The second purpose is the stabilization of highly reactive centres (ii) due to the formation of bridging hydride or other bonds. We consider the following surface hydride centre and its interaction with propane:



We suppose that catalytic centres of this type could be formed by the reaction of the $R_3Zr–CH_2–ZrR_3$ compound with a partially dehydroxylated silica surface with subsequent heating in a hydrogen atmosphere.

In model compound **4** for binuclear catalytic centre cut of fragments (–O–Si≡) were replaced by F atoms by analogy with the models of the mononuclear Zr^{IV} centres of compounds **1–3** previously studied:[6–12]



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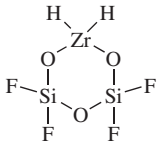

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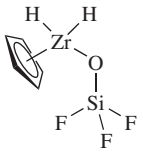

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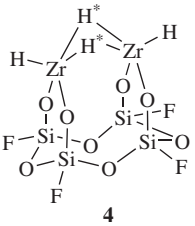
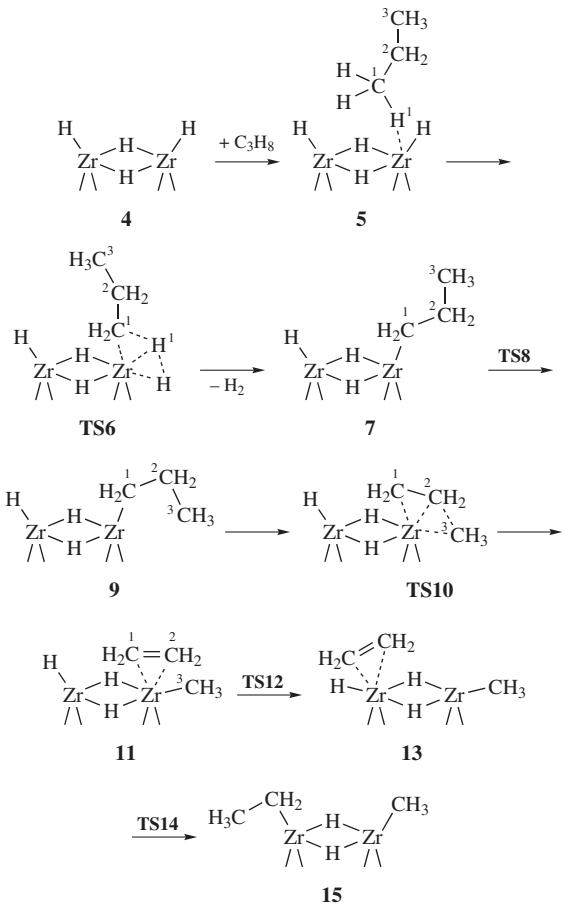


4

In compound **4** two of four hydride ligands are terminal, two other are bridges (marked with asterisks) forming the non-planar four-membered chelate cage. The geometry of model **4** was optimized. Two Zr atoms are positioned at the distance of 3.27 Å from each other. Bond angles Zr–H*–Zr are 107.6°, and the bond angles H*–Zr–H are 117.7°. All distances between Zr atoms and H* bridging atoms are 2.02 Å; those between Zr atoms and terminal H atoms are 1.87 Å.

The local minimum on the potential energy surface (PES) of the system corresponding to the structure without bridging hydrogen atoms was found, in which the Zr–Zr distance is 5.69 Å. We do not consider it since the energy of this structure is 21.1 kcal mol^{-1} higher than that of compound **4**. Due to a high strength of two Zr–H*–Zr bridge bonds, bridging H* ligands do not participate in the reaction with propane. Only the terminal hydrides H are involved. The mechanism of the inter-



Scheme 1

action is presented in Scheme 1. Energy characteristics of the intermediates and transition states are presented in Table 1.

Interaction starts with the formation of weak pre-reactional complex **5** in which one of C–H bonds of C^1 atom of propane interacts with one of two Zr atoms (ΔE = –3.0 kcal mol^{-1}). The distances Zr–H^1 and Zr–C^1 in **5** are 2.52 and 3.36 Å, respectively. Complex **5** should be unstable at room or higher temperatures (ΔG_{298} = 6.1 kcal mol^{-1}, see Table 1). The C^1–H^1 bond of propane is involved in the following exchange reaction with a hydride ligand *via* transition state **TS6**. As a result, *n*-propyl derivative **7** is formed, and the H_2 molecule is released. The energy of the system increases slightly. Energy effects ΔE of the formation of *n*-propyl compound **7** [reaction (1)] are 5.6, 2.1, 5.5, and 3.2 kcal mol^{-1} for **1**–**4**, respectively.

$$\equiv Zr–H + C_3H_8 \rightarrow \equiv Zr–C_3H_7 + H_2 \quad (1)$$

The C–H bonds at the C^2 atom of propane can also be involved in the interaction with ≡Zr–H resulting in the formation of an *iso*-propyl derivative.[10] Since this reaction channel does not lead to the cleavage of C–C bonds of propane, we do not consider it here.

Energy barriers $\Delta E^{\#}$ of stage (1) (**TS6** in the case of **4**, calculated relatively to non-interacting reagents) are 18.8, 12.8, 12.6, and 19.9 kcal mol^{-1} for **1**–**4**, respectively. **TS6** is a standard four-centred transition state for hydrogen atom migration with the key distances Zr–C^1–H^1–H–Zr of 2.43, 1.57, 0.95 and 2.04 Å, respectively.

Internal rotation around the C^1–C^2 bond of the propyl fragment leads to the formation of conformer **9**. The torsion angle Zr–C^1–C^2–C^3 changes by ~120° upon this rotation. The energy barrier **TS8** of the conformational change **7** → **9** is 2.4 kcal mol^{-1} with respect to **7**. In **9**, the C^2–C^3 bond can be cleaved by methyl group migration to the Zr atom *via* transitional state **TS10**. Key distances Zr–C^1–C^2–C^3–Zr in **TS10** are 2.39, 1.42, 2.05, and 2.34 Å, respectively. Breaking bond length of 2.05 Å is typical of a transitional state of this type. Moreover, two short contacts (α-agostic bonds) Zr–H (2.48 Å) between Zr and H atoms at C^3 are formed in **TS10**. As a result, complex **11** with coordinated olefin molecule appears.

$$\equiv Zr–C_3H_7 \rightarrow \equiv Zr(CH_2{=}CH_2)CH_3 \quad (2)$$

TS10 is a global energy maximum along the reaction path. Energy barriers $\Delta E^{\#}$ of stage (2) (**TS10** in the case of **4**, calculated relatively to non-interacting reagents) are 36.1, 35.0, 38.5 and 32.9 kcal mol^{-1} for **1**–**4**, respectively. Thus, in the line of metal hydrides considered here, binuclear centre **4** has the lowest global energy barrier.

Further transformations of the ethylene molecule formed as a result of the C–C bond cleavage depend on the ligand surrounding of the Zr atom, being different for centres of different types. In the case of monohydride centres **1**, the ethylene molecule has to be removed from the catalytic centre [reaction (3)] and transferred to another catalytic centre for hydrogenation [reaction (4)] and subsequent transformation into ethane.

$$\equiv Zr(CH_2{=}CH_2)CH_3 \rightarrow \equiv Zr–CH_3 + CH_2{=}CH_2 \quad (3)$$

$$\equiv Zr–H + CH_2{=}CH_2 \rightarrow \equiv Zr–CH_2CH_3 \quad (4)$$

The loss of binding with the catalytic centre, where the ethylene molecule is formed, increases the energy of the system. For instance, the removal of the ethylene molecule from complex **11** is characterized by the energy effect of 5.2 kcal mol^{-1} (with respect to **11**), and general energy effect for the reaction (1) + (2) + (3) is 27 kcal mol^{-1} with respect to non-interacting reagents (Table 1).

In the case of dihydride centres **2** and **3**, the neighbouring H ligand participates in hydrogenation of the ethylene molecule. The relaxation of the transitional state of the C–C bond cleavage leads directly to the dialkyl compound [reaction (5)].

$$=Zr(H)C_3H_7 \rightarrow =Zr(C_2H_5)CH_3 \quad (5)$$

Such hydration without the loss of binding with the Zr atom promotes the reaction and increases its efficiency.[6–12]

For system **4**, in complex **11** the ethylene molecule is still bound to a catalytic site where it was formed. This molecule migrates readily to the neighbouring Zr atom where the hydrogenation reaction takes place. Figure 1 shows the plot of the

Table 1 Energy characteristics of the reaction of model compound **4** with propane calculated with respect to the sum of energies of non-interaction reagents (**4** + C_3H_8).

Compound	ΔE/ kcal mol^{-1}	ν_i[a]/cm^{-1}	ΔE_0 (ZPVE)/ kcal mol^{-1}	ΔG_{298}[b]/ kcal mol^{-1}
5	–3.0	—	–2.4	6.1
TS6	19.9	796i	17.7	27.8
7	3.2	—	–1.6	1.7
TS8	5.6	105i	0.6	4.3
9	3.4	—	–1.5	1.0
TS10	32.9	349i	27.3	31.7
11	21.8	—	15.4	18.7
11-C_2H_4[c]	27.0	—	18.2	10.5
TS12[d]	22.8	25i	—	—
13	17.6	—	10.5	13.0
TS14[d]	17.8	56i	—	—
15	–10.3	—	–15.6	–14.0

[a]In the vibrational spectra of all the transition states (**TS**) only one imaginary frequency was obtained, and no imaginary frequencies were found for other structures. [b]T = 298.15 K. In the case of surface hydride centres (in contrast to free H_2, C_3H_6, C_2H_4 molecules), translational and rotational degrees of freedom were out of consideration. [c]Energies of formation of $(\equiv SiO)_2(H)$-$Zr(H)_2Zr(Me)(OSi\equiv)_2$ and free ethylene molecule. [d]Estimates obtained using the PES scanning procedure (Figure 1). In other cases, complete geometry optimization was performed.

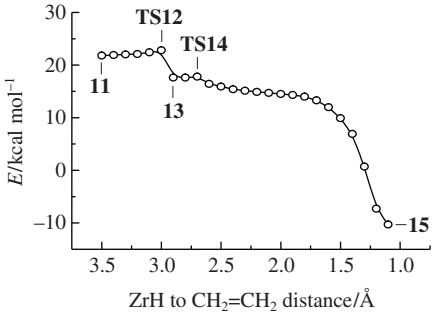


Figure 1 Energy profile of the transformation **11** → **15**.

system energy *versus* the distance $ZrH\cdots CH_2{=}CH_2$ between the C^1 atom of the ethylene molecule and the hydride ligand of the neighbouring Zr atom corresponding to the transformation of ethylene complex **11** to product **15**. The distance was varied from 3.60 Å in **11** to 1.10 Å in **15** by steps of 0.1 Å. The transformation **11** → **15** proceeds without noticeable energy barriers.

The local energy minimum on the PES of the system, corresponding to complex **13** in which the ethylene molecule coordinates to the neighbouring Zr atom in the immediate vicinity of the terminal hydride ligand, has been found. In complex **13**, the distance $ZrH\cdots CH_2{=}CH_2$ is 2.85 Å, the C^1–C^2 bond of the ethylene molecule is perpendicular to the Zr–Zr direction, and both $Zr–C(H)_2$ (Zr–C^1 and Zr–C^2) distances are 2.96 Å.

The rotation of an ethylene molecule in the coordination sphere of Zr in **13** results in its insertion into the Zr–H bond. Energy barrier of the insertion **TS14** with respect to **13** (Table 1) is negligible. The formation of dialkyl product **15** results in a decrease in both energy E and free energy G_{298} of the system. This means that the transformation $\mathbf{4} + C_3H_8 \rightarrow \mathbf{15} + H_2$ is favourable from the thermodynamic point of view. The subsequent exchange of two alkyl ligands (CH_3, C_2H_5) in **15** for hydrides as a result of the reaction with two hydrogen molecules from the gas phase leads to the regeneration of initial catalytic centre **4**. If ethyl fragment reacts first with H_2 molecule, the energy barriers of the first and the second alkyl–hydride exchange reactions are 7.7 and 4.2 kcal mol^{-1} with respect to $\mathbf{15} + m H_2$ and –2.6 and –6.1 kcal mol^{-1} with respect to $\mathbf{4} + C_3H_8 + (m-1)H_2 - lC_2H_6$ (m, l are 1, 0 for the first step and 2, 1 for the second step of the exchange). If the methyl ligand exchanges first, the corresponding values are 8.7 and 4.1 kcal mol^{-1} with respect to $\mathbf{15} + mH_2$ and –1.6 and –6.2 kcal mol^{-1} with respect to $\mathbf{4} + C_3H_8 + (m-1)H_2 - lCH_4$.

Thus, the rate-limiting stage of alkane hydrogenolysis reaction on metal hydride centres **1**–**4** is the C–C bond cleavage. Energy barriers of this process on mononuclear Zr^{IV} hydride complexes **1**–**3** (with respect to non-interacting reagents) usually fall in the range from 35 to 40 kcal mol^{-1}.[6–10] For the test system ($\mathbf{4} + C_3H_8$), we obtained a somewhat lower value of 32.9 kcal mol^{-1}. Thus, the formation of binuclear catalytic centres of type **4** can be promising for the modification of the Ermakov–Basset catalytic system.

The results of our calculations also suggest that binuclear hydride compounds with two bridges M–X–M (in particular, M = Zr) including both hydride- (X = H) and non-hydride-bridged (X = O, OR, NR_2, *etc.*) systems are very prospective for further development of catalysts for alkane hydrogenolysis under mild conditions ($T < 450$ K, $P \sim 1$ atm).

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