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Quantum chemical study of C—H bond activation in methane molecule by Au^{III} aqua chloride complexes

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The mechanism of the reactions of methane with the gold(III) complexes $[AuCl_x(H_2O)_{4-x}]^{3-x}$ (x = 2, 3, or 4) was studied by the DFT/PBE method with the SBK basis set. High activation barriers obtained for the reactions of $[AuCl_4]^-$ and $[Au(H_2O)Cl_3]$ with methane suggest these reactions cannot proceed under mild conditions. The reaction of the $[Au(H_2O)_2Cl_2]^+$ complex with methane has a rather low energy barrier and proceeds through the formation of an intermediate complex.

Key words: gold complexes, methane, methane activation, quantum chemical calculations.

Catalytic functionalization of methane and its homologs is one of the most important problems of modern chemistry.[1,2] It is known that saturated hydrocarbons are very inert under ambient conditions and react only with reactive radicals, but these processes are poorly selective and of little use for the effective practical use.[3] In this connection, catalytic transformations of alkanes in the presence of transition metal complexes under mild conditions are of considerable interest. The C—H bond activation in alkanes by Pt^{II} aqua chloride complexes (Shilov reaction)[4] has stimulated studies in this field of metal complex catalysis. Unlike radical and electrophilic processes, in which the reactions occur predominantly at the least stable tertiary bond, an opposite situation is observed for Pt^{II} complexes, in which the C—H primary bond is more reactive than the secondary and tertiary bonds.

Different explanations for the observed selectivity of the process were presented. At low temperature, the $[Pt(en)(CH_2Ph)Cl]$ complex can be involved in the addition reaction with HCl to form the $[HPt(en)(CH_2Ph)Cl_2]$ complex. Based on this fact, it was hypothesized[5] that the C—H bond activation in the Shilov reaction occurs as oxidative addition. This hypothesis was experimentally

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confirmed.[4] To clarify the situation, the reaction of methane with the platinum(II) aqua chloride complex *trans*-$[PtCl_2(H_2O)_2]$ was simulated[6] by the quantum chemical DFT/B3LYP method. This process can be divided into three steps: 1) H_2O—CH_4 ligand exchange, 2) C—H bond activation, and 3) formation of the product. In the Shilov reaction, methane can replace the aqua ligand in spite of the difference in the bond energy, and this occurs in the first step. The energy barrier estimated by the quantum chemical simulation of the reaction of the *trans*-$[PtCl_2(H_2O)_2]$ complex with methane is 24 kcal mol^{-1}. Based on a comparison of these data with the energy barriers for the mechanism of electrophilic substitution, the conclusion about the predominant direction of electrophilic substitution was drawn,[6] although two processes have similar barrier heights.

More recently, it has been found that other metal complexes are readily involved in oxidative addition reactions with alkanes.[7—12] The Ermakov—Basset system, *viz.*,[8] silica-supported highly coordinatively unsaturated transition metal (Ti and Zr) compounds, is one of systems in which C—H bond activation and C—C bond cleavage in alkanes (olefin polymerization and depolymerization) were experimentally observed. The mechanisms of a series of catalytic processes were studied and the nature of the active centers in the Ermakov—Basset system was established by simulating the reactions of methane and propane with the model compounds $(\equiv Si{-}O{-})_3M^{IV}H$, $(\equiv Si{-}O{-})_2M^{III}H$, and $(\equiv Si{-}O{-})_2M^{IV}H_2$ (M = Zr or Ti) by the DFT/PBE method.[9,10] The study of the reactions of methane with hydrides $(\equiv Si{-}O{-})_3M^{IV}H$ and dihydrides $(\equiv Si{-}O{-})_2M^{IV}H_2$ (M = Zr or Ti) demonstrated that they occur in one step as bimolecular processes without the formation of intermediate complexes. The reactions are characterized by four-center transition states, dihydrides and hydrides of trivalent compounds, *viz.*, $(\equiv Si{-}O{-})_2M^{IV}H_2$ and $(\equiv Si{-}O{-})_2M^{III}H$, respectively, being more reactive with respect to C—H bonds of alkanes. The energy barriers of the transformations of the centers in $(\equiv Si{-}O{-})_3M^{IV}H$ (18.9—24.1 kcal mol^{-1}) are substantially higher than those for the centers of two other types ($(\equiv Si{-}O{-})_2M^{IV}H_2$, 6.4—12.3 kcal mol^{-1}; $(\equiv Si{-}O{-})_2M^{III}H$, 4.2—7.2 kcal mol^{-1}).

Rhodium(III) complexes can catalyze various reactions, including methane oxidation.[11,12] For example, various oxidation products of methane, including methanol and formic acid, were obtained by passing a mixture of methane, CO_2, and O_2 over the $RhCl_3Cu^{II}Cl$ system.[12] The rhodium chloride—potassium iodide—sodium chloride system is also suitable for this purpose. Presumably, these processes occur with the involvement of rhodium oxo complexes.

The Au^{III} ion is an analog of Pt^{II} possessing the d^8 electronic configuration, and square-planar Au^{III} and Pt^{II} chloride complexes have similar electronic characteristics.[13] In addition, it is known[14] that auration of aromatic compounds with $AuCl_3$ occurs at lower temperature than platination with $[PtCl_6]^{2-}$.[15] This brings up the question as to whether gold complexes can activate the C—H bonds in alkanes analogously to platinum compounds. Catalytic systems for alkane functionalization in the presence of gold complexes are unknown, although coupled oxidation of methane and the hydrated form of nicotinamide adenine dinucleotide (NADH) with the Au—rutin complex in the presence of oxygen has been recently documented for the first time.[16] Gold complexes, like other transition metal complexes, can initiate radical reactions of alkanes.[17] However, these processes do not involve the step of C—H bond activation by metal complexes.

Therefore, it is of interest to study the reactivity of Au^{III} complexes, in particular, of aqua chloride complexes, toward methane. For this purpose, we carried out simulation of the C—H bond activation in methane by gold(III) aqua chloride complexes with the general formula $[AuCl_x(H_2O)_{4-x}]^{3-x}$ (x = 2, 3, and 4).

Calculation procedure

All calculations were carried out by density functional theory with the use of the nonempirical local PBE (Perdew—Burke—Ernzerhof) functional,[18] which we have used earlier in the study of gold complexes.[19] Calculations were performed with the use of the PRIRODA program.[20]

The basis set with the SBK pseudopotential[21] was used. In this pseudopotential, the outer electron shells are described by the following basis sets: H [311/1], C [311/311/11], O [311/311/11], Cl [311/311/11], and Au [51111/51111/5111]. The types of stationary points on potential energy surfaces were determined from analysis of Hessians; the second derivatives were calculated analytically. The character of transition states was confirmed by calculations of the intrinsic reaction coordinate.[22] The zero-point energy was calculated in the harmonic approximation.

Results and Discussion

Simulation of the reaction of the $[AuCl_4]^-$ complex with methane. The first step of C—H bond activation in methane can occur by one of two mechanisms, as electrophilic substitution (1) or oxidative addition (2).

$$[AuCl_4]^- + CH_4 = [Au(CH_3)Cl_3]^- + HCl \qquad (1)$$

$$[AuCl_4]^- + CH_4 = [AuH(CH_3)Cl_4]^- \qquad (2)$$

To reveal the most probable mechanism, we calculated the energies and the structures of the starting compounds, reaction products, and transition states (TS).

The $[AuCl_4]^-$ anion in the ground ($^1A_{1g}$) state, like other d^8 transition metal complexes, have square-planar

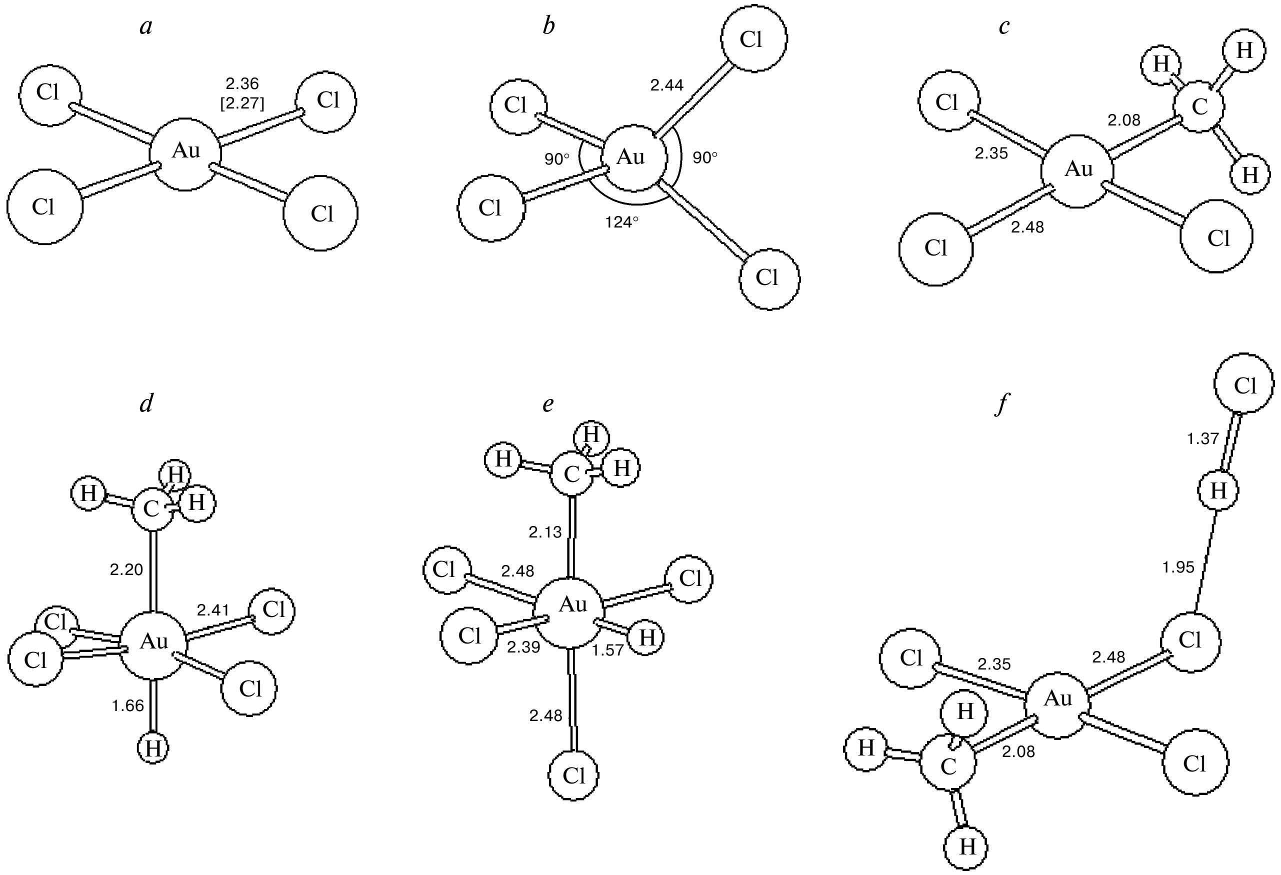

Fig. 1. Structures of the $[AuCl_4]^-$ anion in the $^1A_{1g}$ ground state (D_{4h} symmetry) (*a*) and the $^3A_1$ first excited state (D_{2d} symmetry) (*b*), the substitution products $[Au(CH_3)Cl_3]^-$ (*c*) and $[Au(CH_3)Cl_3](HCl)^-$ (*f*), and the addition product $[AuH(CH_3)Cl_4]^-$ (*d*, *e*) and the calculated bond lengths (Å). X-ray data[17] are given in square brackets.

structures (Fig. 1, *a*). The calculated Au—Cl distance (2.36 Å) is slightly larger than the average Au—Cl bond length in the $[AuCl_4]^-$ anions in 24 structures[23] (2.27 Å). Calculations[24] performed earlier by different methods (B3LYP and MP2 with the aug-cc-PVTZ basis set) gave similar values (2.33—2.36 Å). Since all calculations were carried out for isolated complexes, a small discrepancy between the results of calculations and X-ray diffraction data are admissible.

In the tetrahedral $[AuCl_4]^-$ anion, 5d electrons at the upper t_z orbital become unpaired giving rise to the orbital-degenerate electronic state with spin 1. The Jahn—Teller effect causes the D_2 distortion of the ideal tetrahedral structure of the first excited state ($^3A_1$) (see Fig. 1, *b*), the energy gap between the $^3A_1$ state and the $^1A_{1g}$ ground state remaining large (34.6 kcal mol^{-1}). Therefore, all subsequent calculations were performed only for the singlet ground state.

The calculated structure of the $[Au(CH_3)Cl_3]^-$ complex produced in reaction (1) is shown in Fig. 1, *c*. All Au, Cl, and C atoms are in one plane. The distance between the Au atom and the Cl atom in the *trans* position to the CH_3 group is 0.13 Å larger than two other equivalent Au—Cl bond lengths. This is associated with the *trans* effect of the methyl group, which appears when the ligands present in the *trans* positions to each other differ substantially in the donor ability. In subsequent calculations, we observed this effect for other complexes. The energy of the Au—CH_3 bond in the substitution product is 48.1 kcal mol^{-1}, which is 20% lower than the Au—Cl bond energy in the starting anion (60.3 kcal mol^{-1}, Table 1).

Of two possible products of the addition reaction (2) (see Fig. 1, *d*, *e*), the symmetric structure containing four equatorial chloride ligands and the axial methyl and hydride ligands is less stable (see Fig. 1, *d*). The energy of the structure with an asymmetric arrangement of the Cl atoms (see Fig. 1, *e*) is lower than that of the symmetric structure by 22.9 kcal mol^{-1}. It is this less stable *cis* structure (see Fig. 1, *e*) that can be formed in one oxidative addition step. A comparison of the structures (see Fig. 1, *e* and *d*) shows that the *trans* effect of the hydride ligand is stronger than that of the methyl ligand. This leads to a more substantial elongation of the Au—Cl

Table 1. Calculated bond energies in gold complexes

Complex	Cleaved bond	E*
$[AuCl_4]^-$	Au—Cl	60.3
$[Au(CH_3)Cl_3]^-$	Au—C	48.1
$[Au(H_2O)Cl_3]$	Au—Cl	53.7
	Au—O	26.8
trans-$[Au(CH_3)(H_2O)Cl_2]$	Au—C	61.3
	Au—O	17.5
cis-$[Au(CH_3)(H_2O)Cl_2]$	Au—C	48.6
	Au—O	14.8
cis-$[Au(H_2O)_2Cl_2]^+$	Au—Cl	52.0
	Au—O	39.5
trans-$[Au(H_2O)_2Cl_2]^+$	Au—Cl	45.6
	Au—O	33.1
cis-$[Au(CH_3)(H_2O)Cl(HCl)](H_2O)^+$	Au—C	33.5
cis-$[Au(CH_4)(H_2O)Cl_2](H_2O)^+$	Au—(H_2O)	24.2
cis-$[Au(CH_4)(H_2O)Cl_2]^+$	Au—(CH_4)	16.3
trans-$[Au(CH_4)(H_2O)Cl_2](H_2O)^+$	Au—(H_2O)	25.5
trans-$[Au(CH_4)(H_2O)Cl_2]^+$	Au—(CH_4)	11.7
$[Au(CH_4)Cl_3]$	Au—(CH_4)	5.5
cis-$[Au(CH_4)(OH)Cl_2](HCl)$	Au—(HCl)	9.3
cis-$[Au(CH_4)(OH)Cl_2]$	Au—(CH_4)	5.6

* Bond dissociation energy/kcal mol^{-1}.

bond in the *trans* position to H$^-$ compared to that in the *trans* position to CH_3^-.

The transition state of substitution reaction (1), TS_1, is shown in Fig. 2, *a*. This transition state can be classified as the early state because the distance between the C atom and the leaving H atom (1.19 Å) is only slightly longer than the C—H bond in methane (1.10 Å). Consequently, the methyl ligand is incompletely bound to the Au atom, and the Au—C distance (2.50 Å) is substantially longer than that in the product (2.08 Å). Because of this, the methyl ligand has no effect on the *trans*-arranged chloride ligand. The H—Cl distance (2.05 Å) is also substantially longer than that (1.37 Å) in the product (see Fig. 1, *f*). At the same time, a substantial elongation of the Au—Cl bond with the leaving Cl atom (3.12 Å) better corresponds to the late transition state. A strong Au—H interaction, which is evident from the rather short Au—H distance (2.04 Å), indicates that the central Au atom plays an important role in the proton transfer from CH_3^- to Cl$^-$. After completion of the formation of the HCl molecule, the H atom in the latter is oriented toward the Cl ligand (see Fig. 1, *f*) due hydrogen bonding (14.0 kcal mol^{-1}).

The transition state of addition reaction (2), TS_2, (see Fig. 2, *b*) is structurally similar to the $[AuH(CH_3)Cl_4]^-$ product (see Fig. 1, *e*) and is the late transition state. The Au—C and Au—H distances are only 0.1 Å longer than those in the product due to which the *trans* effects of the hydride and methyl ligands manifest themselves in almost full measure. The leaving H atom in TS_2 is virtually not bound to the C atom (C—H, 1.64 Å), the Au—H distance being substantially shorter than that in TS_1.

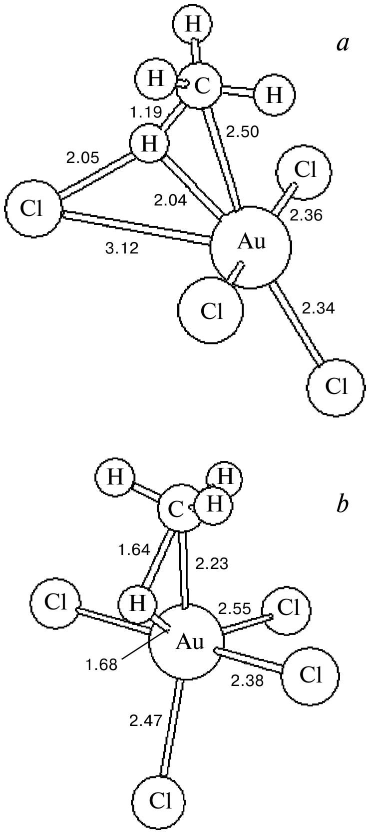

Fig. 2. Structures of the transition states of reactions (1) (*a*) and (2) (*b*) (TS_1 and TS_2, respectively) and the calculated bond lengths (Å).

The results of quantum chemical simulation of reactions (1) and (2) are presented in the energy diagram (Fig. 3). The sum of the energies of $[AuCl_4]^-$ and CH_4 was

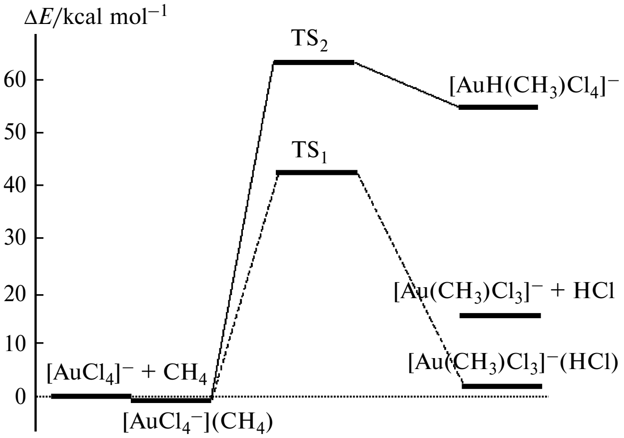

Fig. 3. Energy diagram for reactions (1) (dashed line) and (2) (solid line).

taken as the zero level. The prereaction $[AuCl_4]^-$—CH_4 complex is van der Waals in character, and has a low bond energy (1.1 kcal mol^{-1}). Both reactions are endothermic (16.3 and 50.5 kcal mol^{-1}, respectively) and are accompanied by an increase in the free energy by 13.3 and 60.8 kcal mol^{-1}, respectively. This is, apparently, responsible for a substantial difference in the energy barriers for TS_1 and TS_2 (42.2 and 63.9 kcal mol^{-1}, respectively). It should be noted that the energy barrier of reverse reaction (2) is low, which is indicative of instability of the $[AuH(CH_3)Cl_4]^-$ compound. Although reaction (2) formally proceeds as oxidative addition (Au^V state is known[25]), it is unlikely that gold in the complex has the oxidation state of +5 (see Fig. 1, *e*). Since the hydride ion is a stong donor, the Au^V center characterized by strong electron-withdrawing properties will accept the electron pair of the hydride ligand. This is also evidenced by the the charge on the H atom (0.007) in the structure of the product (see Fig. 1, *e*). This charge is similar to that in the AuH molecule (0.008). Due to a high electron affinity (2.3 eV), gold has a high electronegativity comparable with that of selenium.[26] Hence, the bond in the AuH molecule is polarized (Au^-H^+) rather than covalent. Therefore, the six-coordinate $[AuH(CH_3)Cl_4]^-$ complexes can be considered as protonation products of the $[Au^{III}(CH_3)Cl_4]^{2-}$ complexes. In this case, reaction (2) occurs as the electrophilic substitution, where the proton binds a rather weak base, *viz*., the Au^{III} center in the coordinatively unsaturated anionic complex. The same is true for the addition reaction in the CH_4—$[Au(H_2O)Cl_3]$ system, where the metal atom is even more electrophilic.

Therefore, the reaction of $[AuCl_4]^-$ with methane is unlikely to occur under mild conditions because of a high activation energy. It should be noted that of all the Pt^{II} aqua chloride complexes, the $[PtCl_4]^{2-}$ complex is the least active catalyst for the H—D exchange of alkanes with solvents.[4]

Simulation of the reaction of the $[Au(H_2O)Cl_3]$ complex with methane. Two reactions of methane with the neutral $[Au(H_2O)Cl_3]$ complex can proceed (Fig. 4, *a*):

$$[Au(H_2O)Cl_3] + CH_4 = [Au(CH_3)(H_2O)Cl_2] + HCl, \qquad (3)$$

$$[Au(H_2O)Cl_3] + CH_4 = [AuH(CH_3)(H_2O)Cl_3]. \qquad (4)$$

Due to a lower symmetry of the structure of the starting complex compared to the $[AuCl_4]^-$ anion, the following several pathways are possible depending on the spatial arrangement of the attacking methane molecule with respect to the aqua ligand: *cis*- and *trans*-substitution (reactions (3a) and (3b)) and *cis*- and *trans*-addition (reactions (4a) and (4b)). We will consider these two types of reactions separately.

trans-Substitution and trans-addition. The neutral $[Au(H_2O)Cl_3]$ complex is planar (see Fig. 4, *a*). A comparison of the geometry of this complex and the $[AuCl_4]^-$

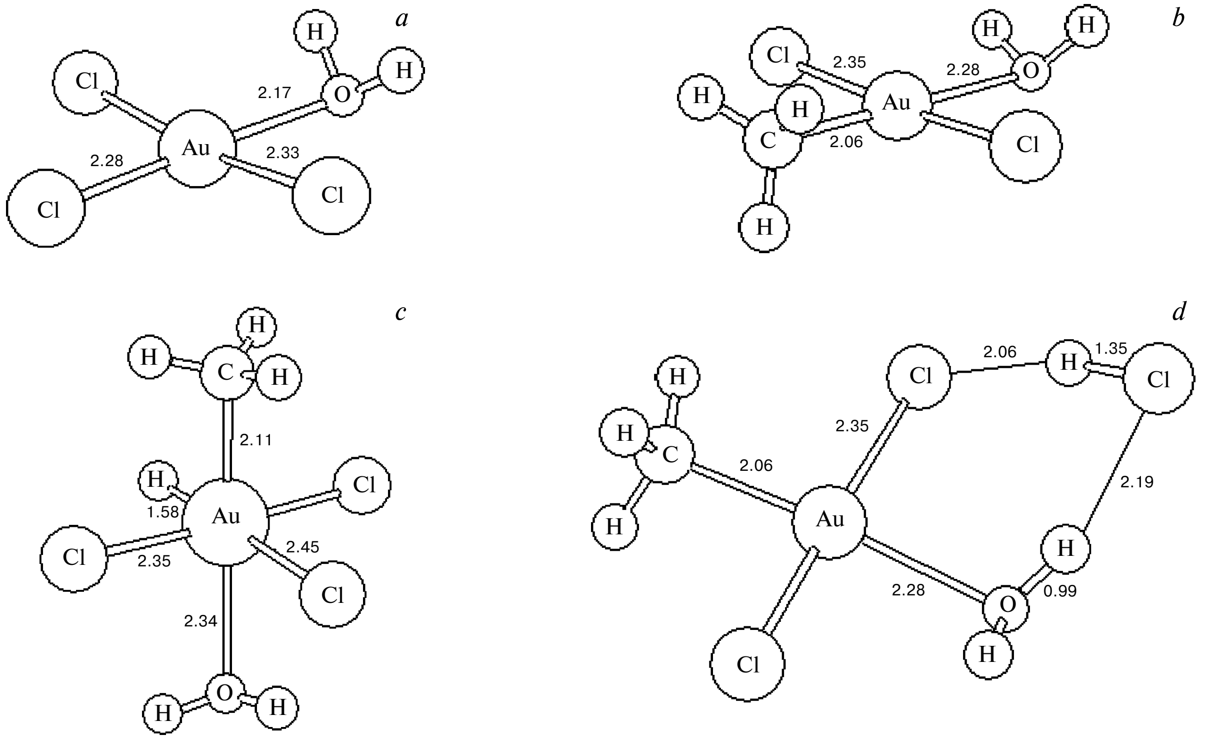

Fig. 4. Structures of the $[Au(H_2O)Cl_3]$ (*a*), *trans*-$[Au(CH_3)(H_2O)Cl_2]$ (*b*), *trans*-$[AuH(CH_3)(H_2O)Cl_3]$ (*c*), and $[Au(H_2O)(HCl)Cl_3]$ (*d*) complexes and the calculated bond lengths (Å).

anion shows that the replacement of the chloride ligand by water leads to a shortening of all Au—Cl distances. The shortest Au—Cl bond is observed for the Cl ligand in the *trans* position to H_2O due to the mutual *trans* effect of the ligands. The weaker *trans* effect of H_2O compared to that of Cl^- is also evidenced by a shortening of the Au—C distance in the *trans*-product of the substitution reaction $[Au(CH_3)(H_2O)Cl_2]$ (see Fig. 4, *b*) compared to the corresponding distance in the $[Au(CH_3)Cl_3]^-$ complex.

The structure of the substitution product, *viz.*, *trans*-$[Au(CH_3)(H_2O)Cl_2]$, is shown in Fig. 4, *b*. The Au—C bond (2.06 Å) is even shorter than that in $[Au(CH_3)Cl_3]^-$. This is also due to the *trans* effect of the CH_3 group, resulting in an increase in the Au—O bond length from 2.17 Å to 2.28 Å. As in the substitution reaction for $[AuCl_4]^-$, the HCl molecule forms a hydrogen bond (the H—Cl distance (2.06 Å; see Fig. 4, *d*) is similar to that in the complex presented in Fig. 1, *f*). In spite of the formation of the second weaker HO—H...Cl—H hydrogen bond (2.19 Å), the binding energy of the HCl molecule is lower (9.9 kcal mol^{-1}) due to the disappearance of the negative charge of the complex.

In the substitution product, the Au—C bond is stronger than that in $[Au(CH_3)Cl_3]^-$. Its energy is 61.3 kcal mol^{-1}, whereas the bond energies of the chloride and aqua ligands in the starting $[Au(H_2O)Cl_3]$ complex are 53.7 and 26.8 kcal mol^{-1}, respectively. These results are also indicative of the strong *trans* effect of the methyl ligand, which is larger than the *trans* effects of the chloride and aqua ligands. Due to a strengthening of the Au—C bond in the neutral complex, reaction (3) is thermodynamically more favorable than reaction (1). An analogous effect is observed for reactions (2) and (4).

The addition product *trans*-$[AuH(CH_3)(H_2O)Cl_3]$, (see Fig. 4, *c*) is structurally similar to $[AuH(CH_3)Cl_4]^-$ (see Fig. 1, *e*) with the only difference that an elongation of the Au—O bond is more substantial than that of the Au—Cl bond due to the stronger *trans* effect of the methyl ligand compared to the chloride ligand.

The structures of the corresponding transition states of the reaction of methane with $[Au(H_2O)Cl_3]$ (TS_{3a} and TS_{4a}) are shown in Fig. 5. The transition state of the substitution reaction is analogous to TS_1, and it is, apparently, the late transition state because the Au—C and H—Cl bonds are shorter (by 0.11 and 0.05 Å, respectively) and the C—H bond is elonagated by 0.03 Å. However, the Au—Cl bond is 0.20 Å shorter. This is more likely to be a consequence of the shorter Au—Cl bond in the *trans* position to H_2O in the starting complex than an evidence of the early transition state. An increase in the Au—O distance by 0.07 Å (which is 60% of its total increase by 0.11 Å in the product (see Fig. 4, *c*)) is, apparently, responsible for a shortening of the Au—H distance by 0.11 Å (in TS_1, the *trans*-Au—Cl bond length remains virtually unchanged; on the contrary, it even decreases by 0.02 Å).

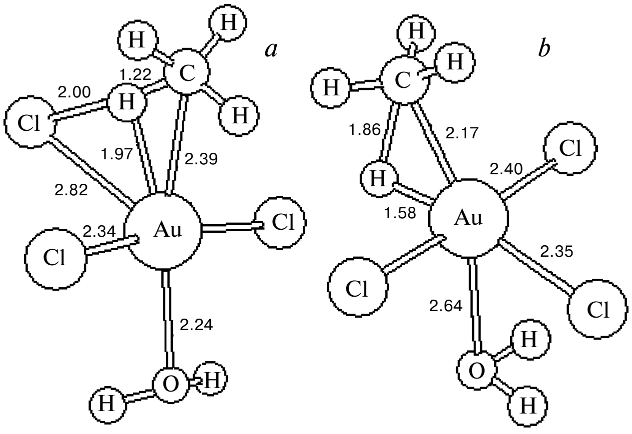

Fig. 5. Structures of the transition states of reactions (3a) (*a*) and (4a) (*b*) (TS_{3a} and TS_{4a}, respectively) and the calculated bond lengths (Å).

The transition state of the addition reaction, TS_{4a}, is also structurally similar to *trans*-$[AuH(CH_3)(H_2O)Cl_3]$ (as in TS_2). The character of changes in the Au—H, Au—C, and C—H distances in TS_{4a} compared to TS_2 indicates that TS_{4a} is a late transition state. As a result, the almost completely bound methyl and hydride ligands simultaneously have the *trans* effect on the aqua ligand, due to which the Au—O distance is substantially elongated (2.64 Å). The elongation of this distance compared to the corresponding distance in the starting $[Au(H_2O)Cl_3]$ complex is 0.47 Å, which is twice as large as that in the product (0.17 Å).

The results of quantum chemical simulation of reactions (3a) and (4a) are presented in the energy diagram

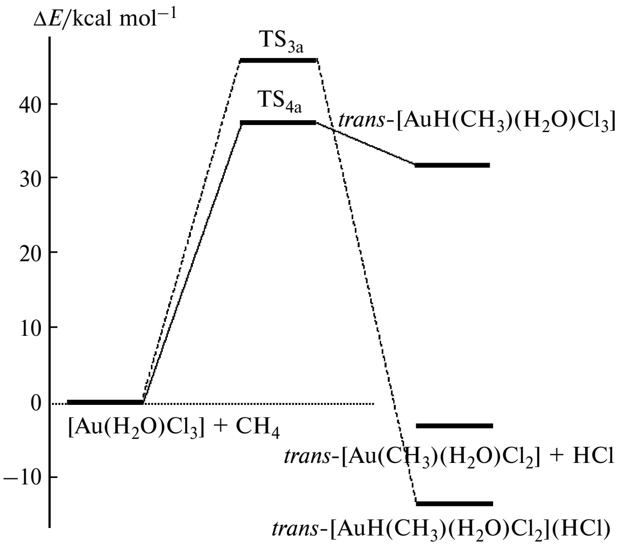

Fig. 6. Energy diagram for reactions (3a) (dashed line) and (4a) (solid line).

(Fig. 6). As mentioned above, the relative energies of the products obtained in the reactions with the involvement of the neutral complex are lower than those in the case of $[AuCl_4]^-$. The substitution reaction is accompanied by an energy gain of 13.3 kcal mol^{-1} and a decrease in the free energy by 5.2 kcal mol^{-1}, but has a higher energy barrier (46.6 kcal mol^{-1}). Addition reaction (4a) is endothermic (like reaction (2)) and is accompanied by an increase in the free energy by 41.9 kcal mol^{-1}. In the case of the smaller endothermic effect (32.1 kcal mol^{-1}), the energy barrier is lower (37.8 kcal mol^{-1}). As mentioned above, both reactions with the use of the neutral $[Au(H_2O)Cl_3]$ complex have later transition states. As a result, the activation energy of the addition reaction is lower due to the fact that TS_{4a} is very structurally similar to the lower-energy product. To the contrary, the activation energy of the early transition state of the substitution reaction with the involvement of the neutral complex is slightly lower (by 4.4 kcal mol^{-1}) than that of the late transition state in spite of a decrease in the energy of the product by 20 kcal mol^{-1}. This is qualitatively evident from the lower lability of the chloride ligand in the *trans* position to the aqua ligand due to a shortening of the Au—Cl distance.

cis-Substitution and cis-addition. The structures of the reaction products for the second direction of the attack of methane on the *cis* position to the aqua ligand ((3b) and (4b)) are shown in Fig. 7. In the substitution product, *viz*., the *cis*-$[Au(CH_3)(H_2O)Cl_2]$ complex (see Fig. 7, *a*), the Au—C bond length (2.08 Å) is equal to that in $[Au(CH_3)Cl_3]$ and is only slightly larger than that in the *trans*-$[Au(CH_3)(H_2O)Cl_2]$ complex due to the stronger *trans* effect of Cl^- compared to H_2O. The Au—Cl and Au—O distances with the *trans* ligands remain virtually unchanged in the course of the substitution reaction. The energy of the *cis*-$[Au(CH_3)(H_2O)Cl_2]$ complex is 12.7 kcal mol^{-1} higher than that of *trans*-$[Au(CH_3)(H_2O)Cl_2]$.

In the addition product *cis*-$[AuH(CH_3)(H_2O)Cl_3]$, the lengths of the Au—Cl bonds in the *trans* positions and the Au—H and Au—CH_3 bond lengths are similar to the corresponding bond lengths in the analogous *trans*-$[AuH(CH_3)(H_2O)Cl_3]$ and $[AuH(CH_3)(Cl_4)]^-$ complexes. Like the substitution product, *cis*-$[AuH(CH_3)(H_2O)Cl_3]$ is less stable than *trans*-$[AuH(CH_3)(H_2O)Cl_3]$ (by 12.4 kcal mol^{-1}), and its formation from the starting neutral aqua chloride complex is accompanied by a slight increase in the free energy (by 8.1 kcal mol^{-1}).

The structures of the transition states of reactions (3b) and (4b), which are denoted by TS_{3b} and TS_{4b}, respectively, are shown in Fig. 8. The structure of the transition state corresponding to reaction (3b) differs substantially from the above-described TS of the substitution reactions in that the leaving Cl atom in this state is located between the H atom of the methane ligand and the aqua ligand. The relaxation of TS_{3b} along the reaction coordinate in the direction of its formation revealed the presence of the intermediate methane complex $[Au(CH_4)(OH)Cl_2](HCl)$ (see Fig. 7, *c*), which is energetically less stable (by 28.8 kcal mol^{-1}) than the starting $[Au(H_2O)Cl_3]$—HCl system (the formation of the former complex is accompanied by an increase in the free energy by 35.1 kcal mol^{-1}). In fact, this complex is formed as a result of displacement of the chloride ligand to the outer sphere with the simultaneous proton transfer to this ligand from the aqua ligand. The presence of a strong hydrogen bond between the HCl molecule and the hydroxo ligand decreases the energy consumption for its formation. For comparison, the replacement of Cl^- in the $[AuCl_4]^-$ complex, in which this stabilization is impossible, the energy consumption for the formation of the methane complex is 28.8 kcal mol^{-1}.

$$CH_4 + [AuCl_4]^- = [AuCH_4Cl_3] + Cl^-$$

Undoubtedly, a particular energy barrier must be overcome to displace HCl from the complex with methane.

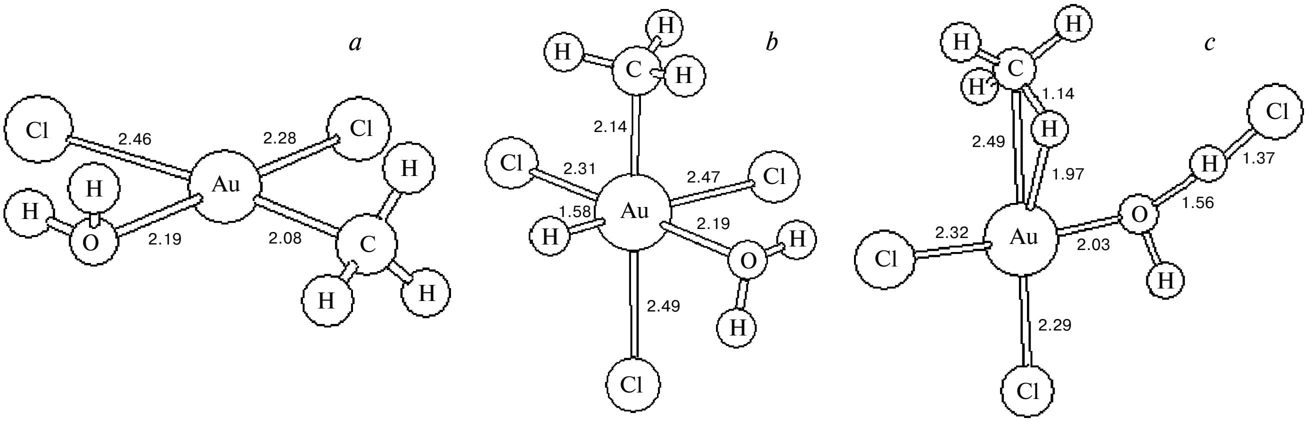

Fig. 7. Structures of *cis*-$[Au(CH_3)(H_2O)Cl_2]$ (*a*), *cis*-$[AuH(CH_3)(H_2O)Cl_3]$ (*b*), and the methane complex *cis*-$[Au(CH_4)(OH)Cl_2](HCl)$ obtained by relaxation of TS_{3b} (*c*) and the calculated bond lengths (Å).

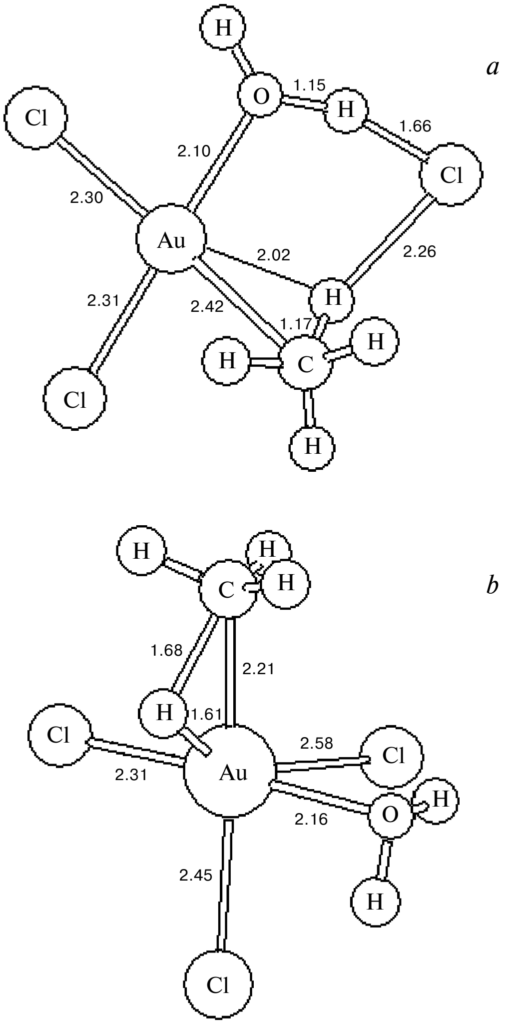

Fig. 8. Structures of the transition states of reactions (3b) (*a*) and (4b) (*b*) (TS_{3b} and TS_{4b}, respectively) and the calculated bond lengths (Å).

However, the corresponding transition state was not localized.

The transition state of the addition reaction is structurally similar to TS_2 and TS_{4a}, but TS_{4b} is more similar to TS_2 in the position on the reaction coordinate. This is an expected result because the effect of the H_2O molecule in the *cis* position is minimum.

As can be seen from the energy diagram (Fig. 9), the *cis*-substitution and *cis*-addition of methane to the $[Au(H_2O)Cl_3]$ complex are energetically slightly more favorable than those for the $[AuCl_4]^-$ anion in spite of destabilization of the products compared to those with the *trans* ligands (see Fig. 6). The *cis*-addition reaction is characterized by a larger endothermic effect (43.8 kcal mol^{-1}), a higher free energy (by 54.3 kcal mol^{-1}), and late TS_{4b} compared to the *trans*-addition reaction. The activation energy increases from 37.8 to 54.6 kcal mol^{-1}. To the contrary, the energy barrier of the *cis*-substitution reaction decreases from 46.6 to 30.6 kcal mol^{-1}, but the character of TS differs from that observed in the *trans*-substitution reaction due to the formation of an intermediate complex. A comparison of the energy profiles for two different directions of the attack of methane shows that the *trans* substitution is thermodynamically more favorable, but the lowest energy barrier was obtained for the *cis* substitution.

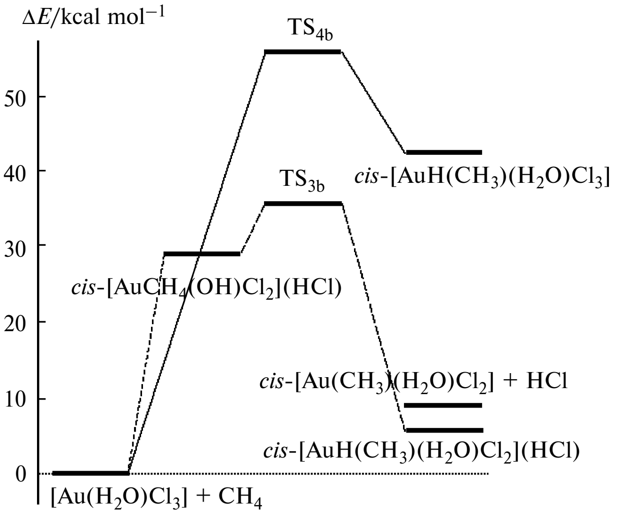

Fig. 9. Energy diagram for reactions (3b) (dashed line) and (4b) (solid line).

Simulation of the reaction of the $[Au(H_2O)_2Cl_2]^+$ complex with methane. The cationic diaqua dichloride complex $[Au(H_2O)_2Cl_2]^+$ can exist as two isomers, *viz.*, *trans*-$[Au(H_2O)_2Cl_2]^+$ and *cis*-$[Au(H_2O)_2Cl_2]^+$, which differ in the arrangement of the aqua and chloride ligands (Fig. 10, *a*, *b*). This leads to an increase in the number of the pathways of the reaction with methane. The reactions of the complexes under consideration with methane would also be expected to proceed as either electrophilic substitution or oxidative addition. The structures of the substitution products *trans*- and *cis*-$[Au(CH_3)(H_2O)(HCl)Cl](H_2O)^+$ are shown in Fig. 10, *c* and *d*. However, we failed to localize the six-coordinate addition products. Taking into account the above-mentioned features of the electronic structures of the addition products of methane and Au^{III} complexes, it can be concluded that the acidic character of the formally hydride bond in the hypothetical cationic addition products hinders the existence of the latter as equilibrium structures. In the *trans* structure, water has no effect on the Au—Cl bond length. A shortening of the Au—O bond to 2.05 Å provides an indirect estimate of the *trans* effect of Cl in the *cis* complex (0.12). In the *cis* complex, the metal—ligand bond lengths are virtually equal to those in the *trans*-Cl—Au—OH_2 group. The *cis*-$[Au(H_2O)_2Cl_2]^+$ complex is more stable (by 6.5 kcal mol^{-1}) than the *trans* complex.

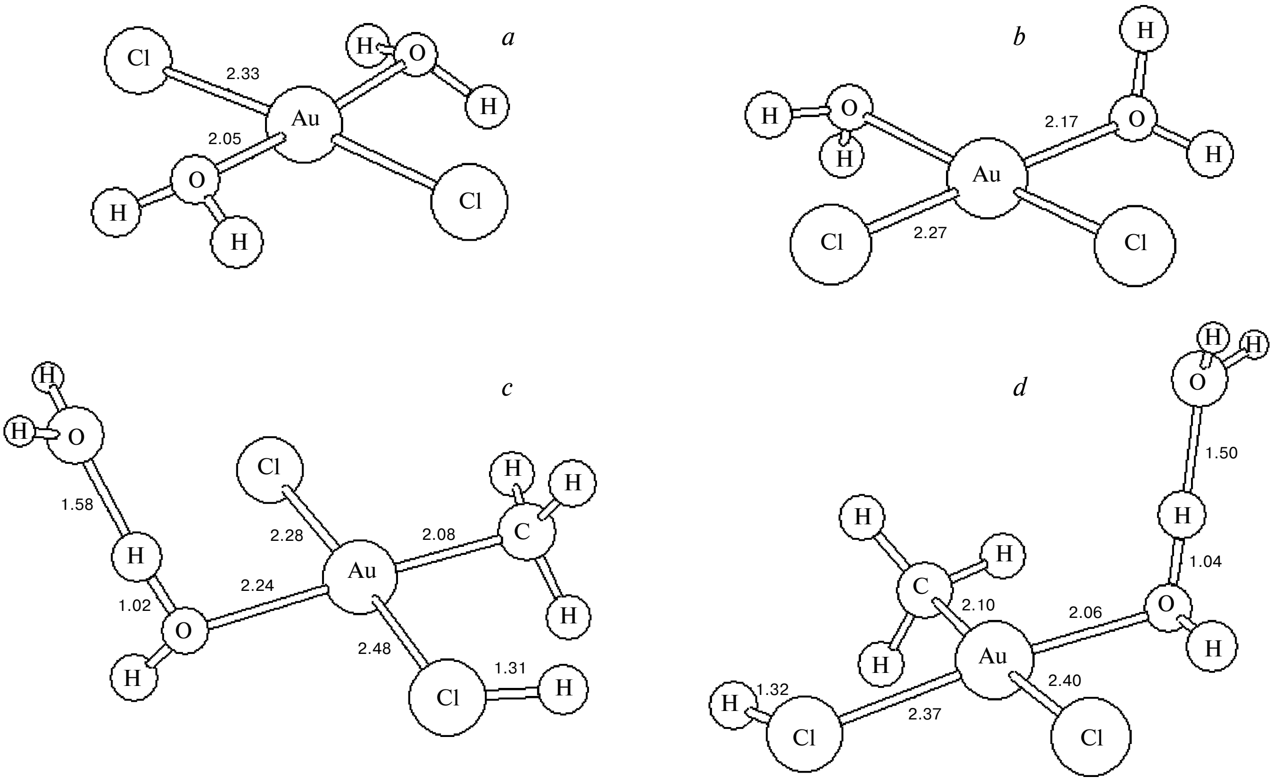

Fig. 10. Structures of the *trans*- (*a*) and *cis*-$[Au(H_2O)_2Cl_2]^+$ (*b*) complexes and the *trans*- (*c*) and *cis*-$[Au(CH_3)(H_2O)(HCl)Cl](H_2O)^+$ (*d*) complexes obtained by relaxation of TS_{5a} and TS_{5b}, respectively, and the calculated bond lengths (Å).

Location of the transition states of the reactions of methane with the *trans*-$[Au(H_2O)_2Cl_2]^+$ (TS_{5a}) and *cis*-$[Au(H_2O)_2Cl_2]^+$ (TS_{5b}) complexes (Fig. 11) demonstrated that they are structurally similar to the transition states of the substitution reaction (see Fig. 8, *a*), but water rather than the chloride ligand is displaced to the outer coordination sphere.

The structures of the corresponding methane complexes (Fig. 12) were determined by performing relaxation of TS_{5a} and TS_{5b} along the reaction coordinates toward the starting compounds. The formation of these complexes is accompanied by a slight increase in the free energy (by 7.43 and 3.6 kcal mol^{-1} for *cis*- and *trans*-$[Au(CH_4)(H_2O)Cl_2](H_2O)^+$, respectively). As in the above-considered case, the common structural unit remains unchanged upon relaxation toward the reaction products. This unit consists of the outer-sphere water molecule linked to the aqua ligands in the *cis* or *trans* position with respect to the methyl group by a strong hydrogen bond. The structure of the H_2O---HOH fragment remains virtually unchanged. The Au—O distances in the products change in accordance with the above-considered *trans* effect. The transition states of the reactions occurring as *trans* and *cis* substitution with respect to the H—Cl and H—C bonds should most likely be assigned to the early and late states, respectively. These structures can be correlated to the structures of the methane complexes, which are characterized by the longer H—Au (by 0.17 Å) and C—Au (by 0.14 Å) distances and a smaller elongation of the C—H bond (by 0.04 Å) in the case of the *trans* arrangement. In the complex, the Au—O bond length varies within a narrow range (from 2.04 to 2.13 Å). This indicates that the *trans* effect of the methane ligand is smaller than that of the methyl ligand. Based on a shortening of the Au—O bond in the *trans*-$[Au(CH_4)(H_2O)Cl_2](H_2O)^+$ complex (see Fig. 12, *a*) by 0.01 Å compared to this bond in the *trans*-$[Au(H_2O)_2Cl_2]^+$ complex, it can be concluded that the *trans* effect of methane is smaller than that of water. This explains why the distance between the methane ligand and the gold atom in the *cis* complex (see Fig. 12, *b*) is longer, and the formation of the methane complex is accompanied by the minimum energy gain. It should be noted that the energy of the reaction product, *viz.*, the *trans*-$[Au(CH_3)(H_2O)(HCl)Cl](H_2O)^+$ complex, is lower than that of the *cis*-$[Au(CH_3)(H_2O)(HCl)Cl](H_2O)^+$ complex by 15.6 kcal mol^{-1}, although the relation between the energies of the starting *trans*- and *cis*-$[Au(H_2O)_2Cl_2]^+$ compounds was reverse. This is, apparently, attributed to the replacement of the Cl^- ligand by HCl due to displace-

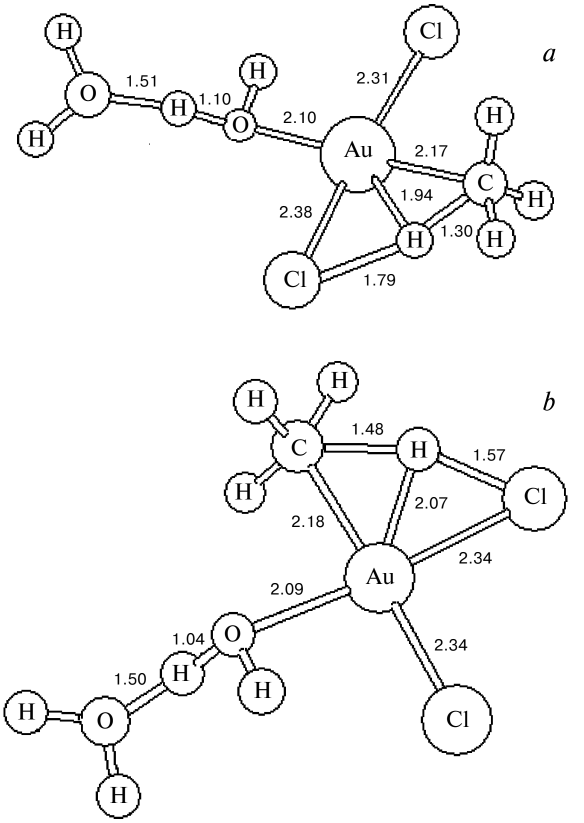

Fig. 11. Structures of the transition states of the C—H bond activation in *trans*-$[Au(H_2O)_2Cl_2]^+$ (TS_{5a}) (*a*) and *cis*-$[Au(H_2O)_2Cl_2]^+$ (TS_{5b}) (*b*) and the calculated bond lengths (Å).

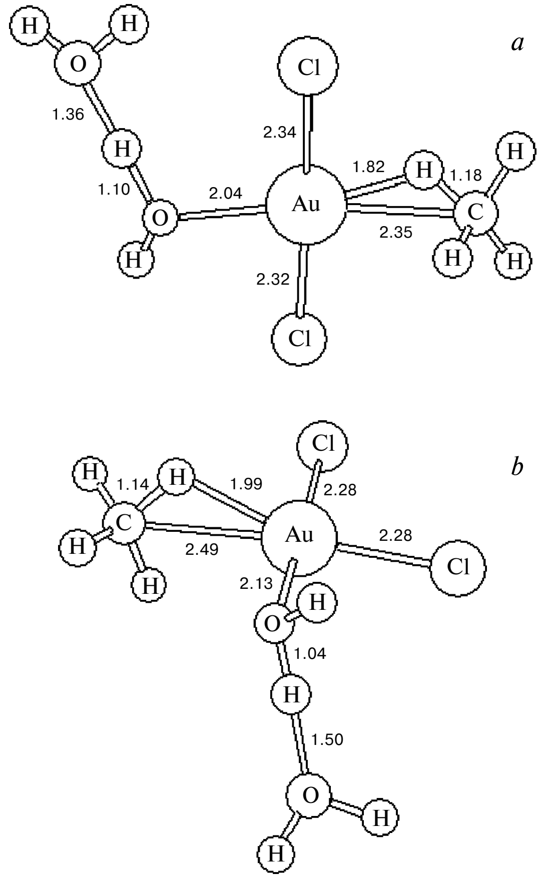

Fig. 12. Structures of the methane complexes *trans*- (*a*) and *cis*-$[Au(CH_4)(H_2O)Cl_2](H_2O)^+$ (*b*) obtained by relaxation of TS_{5a} and TS_{5b}, respectively, and the calculated bond lengths (Å).

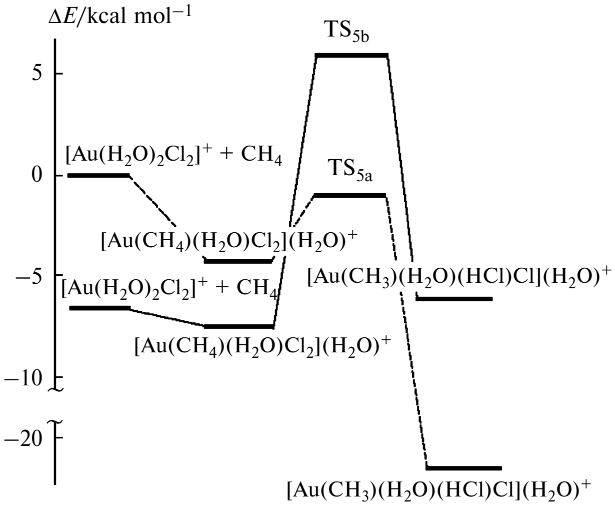

Fig. 13. Energy diagram for methane activation by the *trans*- (dashed line) and *cis*-$[Au(H_2O)_2Cl_2]^+$ (solid line) complexes.

ment of the water molecule to the outer sphere in the case of formation of the methane complex, in which the proton is bound to the chloride ligand. In this respect, the mechanism of the reaction of the $[Au(H_2O)_2Cl_2]^+$ complex differs from that observed for $[Au(H_2O)Cl_3]$ and $[AuCl_4]^-$. It should be noted that the formation of *trans*-$[Au(CH_3)(H_2O)(HCl)Cl](H_2O)^+$ from the corresponding complex is accompanied by a decrease in the free energy by 14.2 kcal mol^{-1}, whereas the formation of *cis*-$[Au(CH_3)(H_2O)(HCl)Cl](H_2O)^+$ leads to an increase in the energy by 8.1 kcal mol^{-1}.

The calculated Au—C bond energy in the *cis* product (38 kcal mol^{-1}) shows that this bond is weaker than the corresponding bonds in the substitution products for the anionic and neutral complexes. This value is similar to the Au—O bond energies in the *cis*- and *trans*-$[Au(H_2O)_2Cl_2]^+$ complexes (39.5 and 33.1 kcal mol^{-1}, respectively).

The energy diagram for the reaction of methane with the cationic $[Au(H_2O)_2Cl_2]^+$ complex is shown in Fig. 13. We failed to localize the transition states for the reactions giving rise to the methane complexes. However, the corresponding activation energies are, presumably, lower than 23 kcal mol^{-1}. This upper estimate was obtained from the calculated bond energies (see Table 1) for the dissociation mechanism. Depending on the activation energy for *cis—trans* isomerization, which, to a first approximation, can be considered to be equal for the starting gold complex and the methane complex, auration of methane can follow different pathways. If this activation energy is high, the higher-energy *trans* complex is kinetically stable, and its reaction with methane directly affords the major product. In the case of easy isomerization, the lower-energy *cis* complex will react with methane. Then the *cis—trans* isomerization of the methane complex will lead to the fast formation of the main substitution product.

Therefore, the calculations demonstrated that methane can react with $[Au(H_2O)_2Cl_2]^+$ under mild conditions. Unlike the anionic and neutral systems, the smoother energy profile of this reaction is atrributed to the fact that the formation of the methane complex is thermodynamically favorable. This is promoted by an increase in the electrophilic properties of the center, because the Au—CH_4 bond energy increases in the series of the $[Au(CH_4)Cl_3]$, *cis*-$[Au(CH_4)(OH)Cl_2](HCl)$, *trans*-$[Au(CH_4)(H_2O)Cl_2](H_2O)^+$ (see Fig. 12, *a*), and *cis*-$[Au(CH_4)(H_2O)Cl_2](H_2O)^+$ (see Fig. 12, *b*) complexes (5.5, 5.6, 11.7, and 16.3 kcal mol^{-1}, respectively). Taking into account the Au—O bond energies in the *cis*-$[Au(CH_4)(OH)Cl_2](HCl)$ and *trans*-$[Au(CH_4)(H_2O)Cl_2](H_2O)^+$ complexes (24.2 and 25.5 kcal mol^{-1}, respectively) and the formation of a hydrogen bond with the water molecule displaced to the second coordination sphere, the formation of the cationic methane complexes is accompanied by an exothermic effect. In the neutral system, the chloride ligand, which has a much higher bond energy, is displaced to the outer coordination sphere, due to which the formation of the methane complex is thermodynamically unfavorable.

In conclusion, let us compare the results of calculations for the gold(III) aqua chloride complexes with the published data on methane activation by other transition metal complexes. As mentioned above, the quantum chemical study of the reaction of methane with the platinum(II) aqua chloride complex *trans*-$[PtCl_2(H_2O)_2]$[6] demonstrated that this reaction proceeds through the formation of the methane complex accompanied by the displacement of the water molecule to the second coordination sphere and is characterized by the energy barrier of 16.5 kcal mol^{-1}. A similar situation is observed for its analog, *viz*., the gold(III) *trans*-diaqua dichloride complex. The formation of the methane complex is accompanied by an exothermic effect, the energy barrier decreases to 3.5 kcal mol^{-1}, and the energy effect of the product formation is 21.5 kcal mol^{-1}.

Most of the known catalytic systems, which activate the C—H bond in methane, have particular drawbacks. Hence, it is of interest to design new catalysts. The results of the present study show that gold complexes offer promise in this respect.

To summarize, we performed quantum chemical simulation of the C—H bond activation by the $[AuCl_4]^-$, $[Au(H_2O)Cl_3]$, and *trans*- and *cis*-$[Au(H_2O)_2Cl_2]^+$ complexes. Based on the calculated structures of the substitution and addition reaction products and the transition states, high activation energies (higher than 35 kcal mol^{-1}) were found for the reactions of methane with the anionic and neutral complexes, because of which these processes cannot occur under mild conditions.

For cationic complexes, the replacement of the aqua ligand by the methane ligand is thermodynamically favorable. As a result, a new pathway of electrophilic substitution through the transformation of intermediate methane complexes into the corresponding methyl complexes with a rather low energy barrier becomes possible.

In our opinion, the studies of the methane activation by gold complexes opens new avenue for the design of systems for functionalization of alkanes.

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