

Quantum Chemical Simulation of the Reaction of Methane with Gold(I) Acetylacetone and Aquaacetylacetone Complexes

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Abstract—The interaction between methane and gold(I) acetylacetone via electrophilic substitution (reaction (I)) and oxidative addition (reaction (II)) is simulated. In both cases, the formation of the products is thermodynamically favorable: the decrease in energy is 31 kcal/mol for reaction (I) and 26 kcal/mol for reaction (II). The product of reaction (II) is additionally stabilized by Au–H interaction. Both reactions have a low activation barrier and proceed via the formation of structurally different methane complexes reducing the energy of the system by 9.3 kcal/mol for reaction (I) and by 10.9 kcal/mol for reaction (II). The complex $[\text{Au}(\text{H}_2\text{O})(\text{acac})]$ is also capable of forming methane complexes. These complexes result from a thermally neutral reaction and turn into products after overcoming a low energy barrier. The structure of the complex activating methane in the gold–rutin system is deduced from the data obtained.

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The reactivity of transition metal complexes toward methane is of both theoretical and applied interest. It has attracted attention from researchers developing new methods of functionalization of saturated hydrocarbons under mild conditions, as well as from those who are looking for an explanation for a variety of chemical processes occurring in biosystems [1]. Of special interest are gold complexes that catalyze methane oxidation with atmospheric oxygen in the presence of rutin and NADH (protonated form of nicotinamide adenine dinucleotide) [2, 3].

The activation of the C–H bond by gold compounds is a poorly explored area of metal complex catalysis: there have been only sparse theoretical publications dealing with the reactivity of gold complexes toward alkanes [4, 5]. In a recent DFT study of the interaction between methane and homoleptic gold complexes, very high energy barriers were found for anionic ($[\text{AuCl}_4]^-$, $[\text{AuBr}_4]^-$, $[\text{AuI}_4]^-$, $[\text{AuH}_4]^+$, $[\text{Au}(\text{CN})_4]^-$, $[\text{Au}(\text{OH})_4]^-$, $[\text{Au}(\text{OCH}_3)_4]^-$, $[\text{Au}(\text{O}(\text{CO})_2\text{O})_2]^-$, $[\text{Au}(\text{NH}_2)_4]^-$, $[\text{Au}(\text{SH})_4]^-$, and $[\text{Au}(\text{S}(\text{CH}_2)\text{S})_2]^-$) and neutral (Au_2Cl_6) gold(III) complexes [4]. At the same time, for cationic complexes, such as $[\text{Au}(\text{H}_2\text{O})_2\text{Cl}_2]^+$ and $[\text{Au}(\text{COOR})_2]^+$, which form intermediate complexes with methane, subsequent activation by the electrophilic substitution mechanism is characterized by a much lower energy barrier and can take place under mild conditions [5].

Rutin (Rut, 5,7,3',4'-tetrahydroxyflavone; see Fig. 1a) can form transition metal complexes with various structures and compositions [6–9]. Since its molecule has several chelating sites with donor oxygen atoms, it is believed that rutin will coordinate to the

gold atom in a bidentate mode, as in its identified complexes. In a catalytic system investigated by Levchenko et al. [3], the starting compound was $[\text{AuCl}_4]^-$ in the presence of excess rutin. Since rutin is a readily oxidizable compound and the redox potential of trivalent gold is fairly high, the most likely oxidation state of gold in the active complex is +1.

For gold(I) complexes, the most typical coordination number is 2 and the most typical ligand arrangement is linear; therefore, the composition of the gold–rutin complex should be assumed to be 1 : 1. Of the two possible bidentate coordination modes, namely, coordination through the pyrocatechin fragment and coordination through the carbonyl group and the oxy group, the latter is more likely. With this coordination mode, the complex is neutral and the O–Au–O fragment is closer to the linear geometry [4]. The transformation of the pyrocatechin fragment into dianionic form, which would be favorable for the first coordination mode, would require high pH values unfeasible in the experiment considered [3]. Moreover, the dianionic form of rutin is unstable and undergoes spontaneous oxidation in air [10]. In addition, according to an earlier theoretical analysis [4], the dianionic complex is less active.

For simpler calculations, the most likely gold complex was modeled as an acetylacetone complex. The known gold(I) acetylacetone complexes contain one or two extra phosphine ligands (Figs. 1b, 1c) [11, 12]. The increase in the coordination number is due to the noticeable nonlinear distortion of the O–Au–O fragment. In view of this, a gold(I) acetylacetone complex

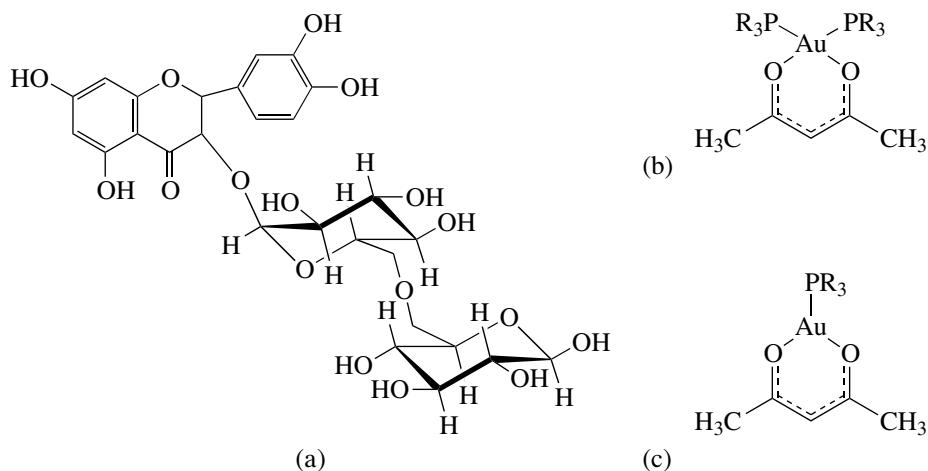


Fig. 1. (a) Rutin [6] and (b, c) gold(I) acetylacetonate complexes [11, 12].

containing a solvent (water) molecule was also considered.

Here, we report a quantum chemical study of the reactivity of the gold(I) acetylacetonate complexes $[\text{Au}(\text{acac})]$ and $[\text{Au}(\text{H}_2\text{O})(\text{acac})]$ toward methane. The main purpose of this study is to elucidate the primary reactions taking place in the model biomimetic system. Obviously, this study will not answer all possible questions about the mechanism of catalytic methane oxidation in the presence of the gold–rutin system. This process should be the subject of further experimental and theoretical studies. Since Au(I) acetylacetonate complexes do exist, these studies would be of independent significance.

COMPUTATIONAL PROCEDURE

The computational method was DFT with the Perdew–Burke–Ernzerhof (PBE) ab initio local-orbital density functional [13], which was applied earlier to other gold complexes [4, 5, 14]. The calculations were carried out using the PRIRODA program [15].

The gold nucleus bears a rather large electric charge; therefore, relativistic effects are significant for gold. The most significant scalar relativistic effects can be taken into account effectively within the nonrelativistic approach by using an appropriate pseudopotential. To do this, we employed an SBK pseudopotential basis set [16] in which the outer electron shells are described by the following basis functions: H [311/1], C [311/311/11], O [311/311/11], Cl [311/311/11], and Au [51111/51111/51111]. The types of stationary points on the potential-energy surface were determined by considering Hessians with analytical second derivatives. The reaction coordinates were constructed using the intrinsic reaction coordinate method [17]. The contribution from the zero-point energy was calculated in the

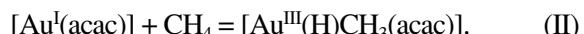
harmonic approximation. According to previous tests [14], this computational method reproduces well the structure and energy properties of few-atom gold-containing molecules and ions.

RESULTS AND DISCUSSION

Acetylacetonate Complex

The structure of the initial complex $[\text{Au}(\text{acac})]$ (**R₁**) (Fig. 2a) contains a symmetric square metallocycle in which the Au–O distance is 2.18 Å and the O–Au–O angle is 102.2°. The C–C–C angle, which is 134.7°, is noticeably different from the angle ideal for the sp^2 -hybridized carbon atom (120°), and the C–O bonds are far from parallel. This is a consequence of the flexibility of the carbon chain and probably will not take place if the acetylacetonate coordination fragment is part of a rigid polycyclic system.

There are two possible routes for the first step of methane activation by the $[\text{Au}(\text{acac})]$ complex:



Reaction (I) is methane addition at the Au–O bond without a change in the valence or coordination number of the gold atom. This reaction can be viewed as electrophilic substitution with proton transfer to the ligand. Reaction (II) is classical oxidative addition increasing the coordination number to 4. The energy effect of reaction (I) was calculated to be 29.1 kcal/mol, and the Gibbs energy of this reaction is –19.3 kcal/mol. The high stability of the product **P₁** (Fig. 2), which results from the cleavage of a strong C–H bond, is explained by the formation of a strong O–H bond and by the Au–H extra interaction (Au–H 2.05 Å). In the conformational isomer **P₂** (Fig. 2), because the OH fragment is rotated by 180° about the C–O bond, there is no

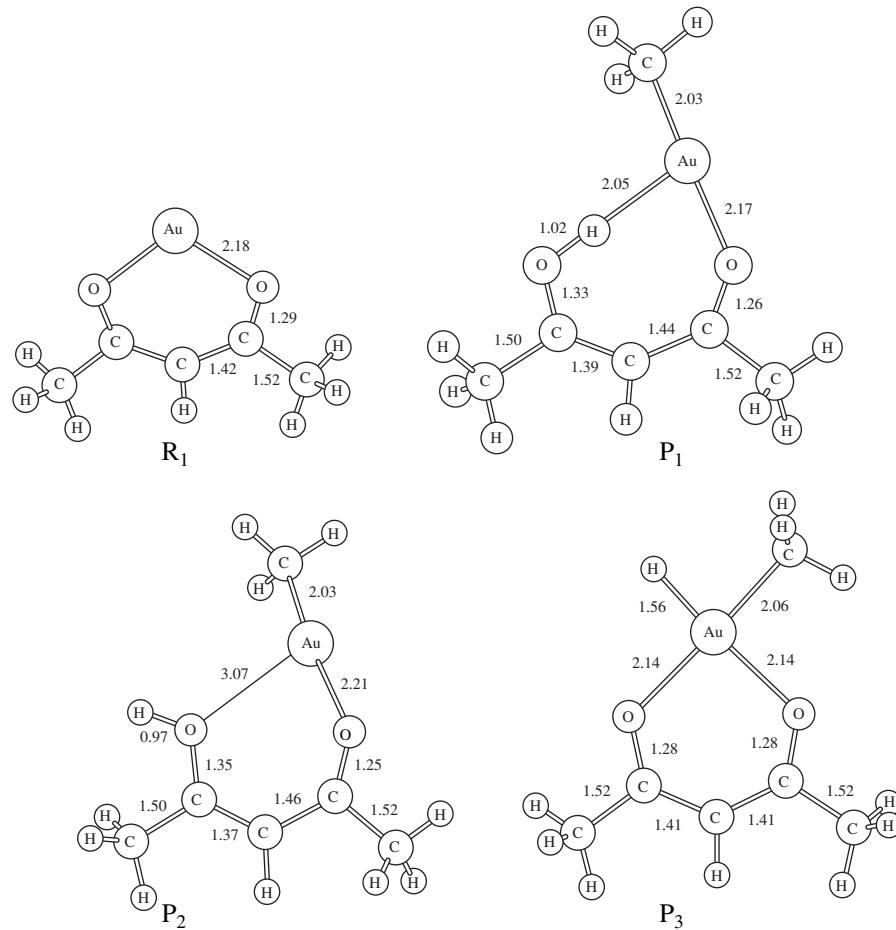


Fig. 2. Structures of the $[\text{Au}(\text{acac})]$ complex in the ground state (R_1), the product of reaction (I) (P_1) and its isomer (P_2), and the product of reaction (II) (P_3). The calculated bond lengths are given in Å.

Au–H interaction and the structure is nonplanar: the Au–CH₃ fragment is off the acetylacetone ligand plane and the torsion angles are C–C–O–H = 170° and C–C–O–Au = 23.3°. The $\text{P}_1 \rightarrow \text{P}_2$ transition implies a 12.1-kcal/mol increase in energy, which can be attributed to the energy of the hydrogen bond Au–H.

The energy of the product of the oxidative addition of methane to the Au center (P_3 in Fig. 2) is 4.5 kcal/mol higher than the energy of the electrophilic substitution product P_1 . The formation of P_3 is accompanied by a 13.2-kcal/mol decrease in the free energy of the system. The calculation of the charge on the main atoms and groups of P_3 (Table 1) demonstrated that the oxidative addition reaction increases the charge on the gold atom from 0.18 (in R_1) to 0.24, while the electrophilic substitution reaction decreases this charge because of the appearance of the strongly donating ligand CH₃[–]. The O–H distance in the transition state of reaction (I) (TS₁) is 2.07 Å (versus 1.02 Å in the product), and, therefore, this transition state can be classified as early (Fig. 3). However, the Au–C distance in TS₁ is only 0.04 Å longer than the same distance in the product, and the Au–H distance is as short as 1.53 Å. With the zero-

point energy taken into account, the energy barrier of reaction (I) is as low as 4.2 kcal/mol relative to the energy of the initial system $[\text{Au}(\text{acac})] + \text{CH}_4$. The transition state in reaction (II) (TS₂ in Fig. 3) is similar to TS₁ in terms of the Au–C, Au–H, and C–H bond lengths, but its energy is 10.8 kcal/mol lower than the total energy of the initial compounds. Analysis of the TS₁ and TS₂ structures suggests that the products P_1 and P_3 result from preformed methane complexes rather than the free reactants.

Indeed, examination of the descents from the transition states along the reaction coordinate demonstrated that both reactions between methane and $[\text{Au}(\text{acac})]$ yield an intermediate methane complex (Fig. 4) (I₁, I₂) and that the energy of the system is thus reduced by 9.3 kcal/mol for reaction (I) and by 10.9 kcal/mol for reaction (II). As calculated from standard Gibbs energies, the equilibrium constants of the formation of I₁ and I₂ are 2.29 and 6.40, respectively. The structures of these methane complexes differ in terms of the position of the activated C–H bond relative to the oxygen atom of the acetylacetone ligand. Another distinction is that coordinated methane forms one extra Au–H contact in

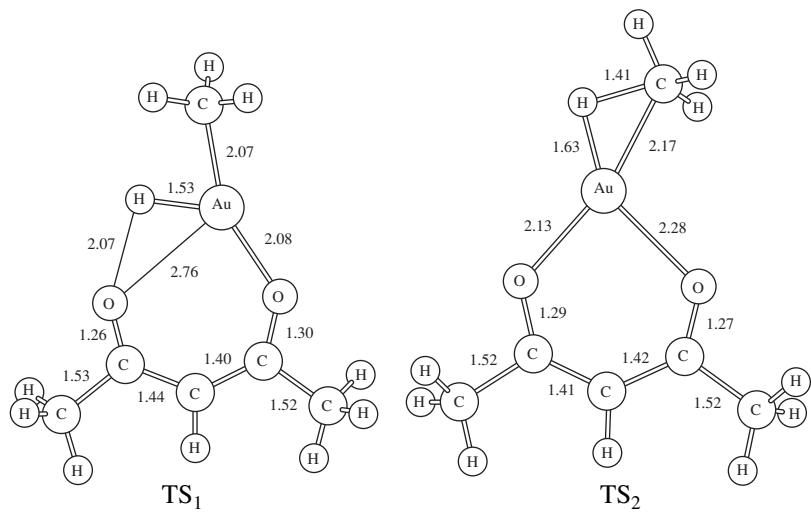
Table 1. Calculated charges on the main atoms and groups in $[\text{Au}(\text{acac})]$, $[\text{Au}(\text{H}_2\text{O})(\text{acac})]$, the products of their interaction with methane, and the corresponding transition states

Structure	Au	O ₁	O ₂	CH ₄	H ₂ O	CH ₃	H
R ₁	0.18	-0.19	-0.19	-	-	-	-
R ₂	0.17	-0.25	-0.18	0.13	-	-	-
I ₁	0.17	-0.19	-0.24	0.12	-	-	-
I ₂	0.08	-0.25	-0.17	-	0.18	-	-
I ₃	0.18	-0.20	-0.18	0.10	-0.07	-	-
I ₄	0.18	-0.16	-0.24	0.13	-0.10	-	-
P ₁	0.04	-0.13	-0.18	-	-	-0.13	0.09
P ₂	-0.06	-0.12	-0.17	-	-	-0.16	0.19
P ₃	0.24	-0.19	-0.19	-	-	-0.05	-0.02
P ₄	0.07	-0.13	-0.18	-	-0.08	-0.12	0.10
P ₅	0.25	-0.16	-0.19	-	-0.08	-0.05	-0.02
P ₆	0.01	-0.15	-0.18	-	-0.17	-0.15	0.12
TS ₁	0.27	-0.24	-0.22	-	-	-0.03	0.07
TS ₂	0.19	-0.20	-0.23	-	-	0.05	0.03
TS ₃	0.23	-0.20	-0.21	-	0.02	-0.09	0.06
TS ₄	0.14	-0.22	-0.20	-	-0.08	-0.03	0.07
TS ₅	0.20	-0.17	-0.22	-	-0.10	0.06	0.04

Note: O₁ and O₂ are the oxygen atoms of the acetylacetone ligand, of which O₁ is the oxygen atom nearest to the water molecule or its structural analogue in the absence of water. H is the hydrogen atom participating in the reaction.

I₁ and two such contacts in I₂. As compared to complex I₁, with a *trans*-O–Au–H fragment, complex I₂, which has a *trans*-O–Au–C fragment and is more stable, has a

0.05 Å longer C–H bond in the methane molecule and 0.08 Å shorter Au–H and Au–C bonds. Atomic charge calculations (Table 1) demonstrated that methane in the



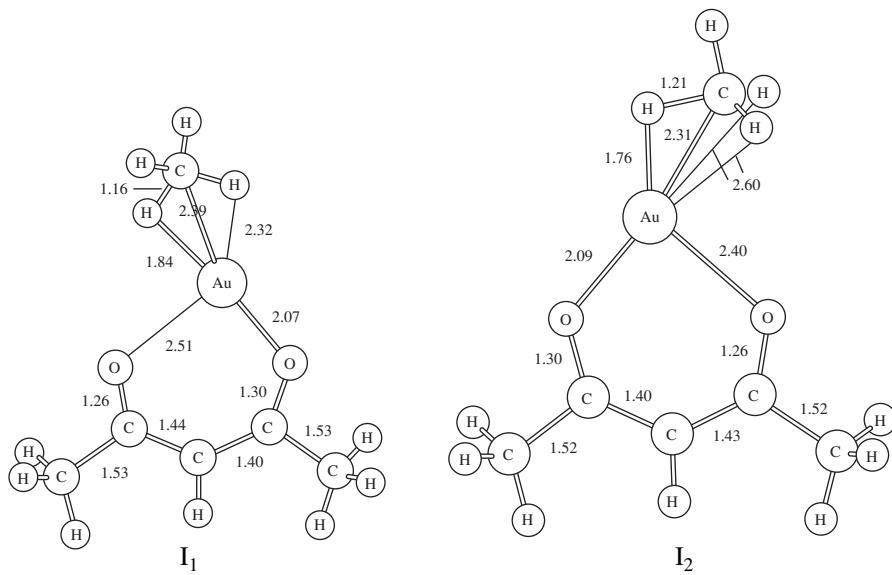


Fig. 4. Structures of the methane complexes obtained by the relaxation of TS_1 (I_1) and TS_2 (I_2) along the reaction coordinate toward the initial compounds. The geometric parameters are given in Å.

methane complexes is an electron donor. However, the charge on the gold atom is almost invariable and the charge donated by methane is accepted by the ligand. As a result, the structure of the ligand loses its symmetry, the uninvolved carbonyl group is 0.2–0.3 Å farther from the gold atom as compared to the same group in R_1 , and the Au–O bond length for the alcoholic oxygen atom is 0.1 Å shorter. Thus, methane coordination causes the acetylacetone ligand to switch to the monodentate coordination mode, resulting in the energetically most favorable, linear CH_4 –Au–O arrangement.

The energy diagram for the interaction between methane and $[\text{Au}(\text{acac})]$ is shown in Fig. 5. In view of the formation of the methane complexes, the energy barriers for reactions (I) and (II) are 13.4 and 1.1 kcal/mol, respectively. This difference likely arises from the fact that, in the former case, a hydrogen atom is transferred to the ligand, eliminating the $\text{Au}-\text{H}$ interaction. Thus, the electrophilic substitution not affecting the coordination number of the gold atom is thermodynamically favorable. However, the oxidative addition reaction is characterized by a much lower activation energy.

In order to verify these calculated data, we performed additional calculations taking into account the correlation effects in the framework of MP2 and MP3 perturbation theories (Table 2). In these calculations, we employed the same basis set and SBK pseudopotential. The calculations were carried out using the Gaussian 98 program [18]. For all participants of the reaction, both the MP2 and MP3 calculations led to nearly the same relative energies as the simpler procedure. Low energy barriers were again obtained for reactions (I) and (II). Thus, the use of the perturbation methods, which imply a much more complicated computational

procedure and a larger computational burden, does not lead to any significant changes in the overall reaction profile. For this reason, the above DFT method was used in further calculations.

Aquaacetylacetoneate Complex

Since real chemical reactions take place in a solution, it is necessary to calculate the solvation energy for each participant of reactions (I) and (II). This was done for the polarized continuum (overlapping spheres) model using the DFT method with a B3LYP functional

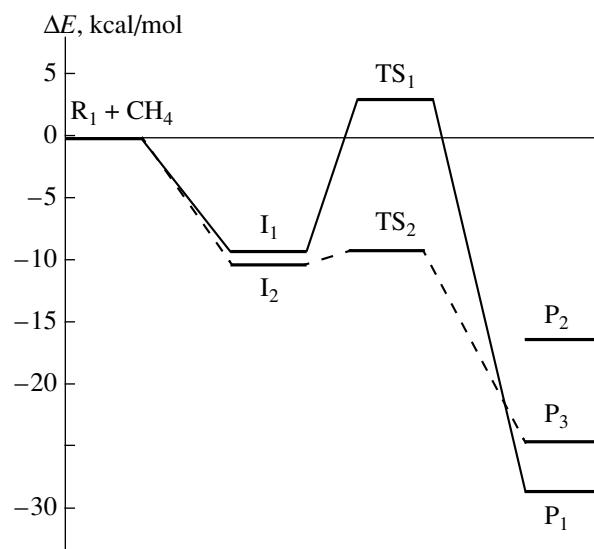


Fig. 5. Energy diagrams for reaction (I) (solid line) and reaction (II) (dashed line).

Table 2. Relative energies of the initial complexes, products, and transition states calculated by different methods and the solvation energies of these compounds calculated using the polarized continuum (overlapping spheres) model and the B3LYP approach

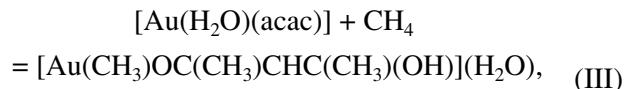
Complex	<i>E</i> (DFT/PBE), kcal/mol	<i>E</i> (MP2), kcal/mol	<i>E</i> (MP3), kcal/mol	<i>Es</i> , kcal/mol
R ₁ + CH ₄	0	0	0	-4.14; 1.80
P ₁	-29.1	-30.2	-28.3	1.58
P ₂	-17	-25.0	-25.4	-3.73
P ₃	-24.6	-32.7	-25.6	1.80
I ₁	-9.3	-12.6	-11.4	-2.49
I ₂	-10.9	-14.9	-12.8	-2.35
TS ₁	4.1	1.1	7.8	-7.62
TS ₂	-10.8	-13.7	-7.6	-3.03

and the Gaussian 98 program [18]. For most of the compounds and transition states, the corrections (Table 2) thus calculated are small positive or negative values, apparently because the reactants and products are uncharged.

In the presence of water as the external medium, a solvent molecule binds to a vacant coordination site. Note that, for the gold–rutin complex, the role of the water molecule as an extra ligand can likely be played by one of the hydroxyl groups of the disaccharide residue, which is very close to the acetylacetone coordinating site (Fig. 1a). The formation of [Au(H₂O)(acac)] from [Au(acac)] and water is energetically favorable to the extent of 19.2 kcal/mol, an energy close to the methane binding energy. The addition of another water molecule yields only a weak outer-sphere complex; that is, the second water molecule does not enter the coordina-

tion sphere of the gold atom. The optimized structure of the [Au(H₂O)(acac)](H₂O) complex is shown in Fig. 6. Comparing this structure with the structure of [Au(H₂O)(acac)] (Fig. 7) suggests that the second water molecule exerts only a slight effect on the geometry of the main part of the molecule. Considering that the effect of the second water molecule is weak, we believe that the further solvent addition effects on the energy profiles of reactions (I) and (II) will be insignificant.

In order to determine the strongest solvent effect associated with water coordination, we carried out quantum chemical simulation of the following reactions between the aquaacetylacetone complex and methane:



The structure of the initial complex R₂ is asymmetric (Fig. 7). The addition of a water molecule causes the acetylacetone ligand to switch to the asymmetric monodentate coordination mode, as in the case of the methane complexes. The Au–O distance in this structure is 2.61 Å and is longer than the same distance in [Au(acac)] (2.18 Å), and the distance between the gold atom and the other oxygen atom is shortened to 2.03 Å. A well-defined hydrogen bond with an O–H distance of 1.90 Å appears between the water molecule and the carbonyl oxygen atom. This bond causes a nonlinear distortion of the O–Au–O fragment. The fact that the C–O and C–C bond lengths are not equivalent indicates that the acetylacetone structure is shifted to the enol form. This weakens the interaction between the gold atom and the carbonyl oxygen atom and strengthens the

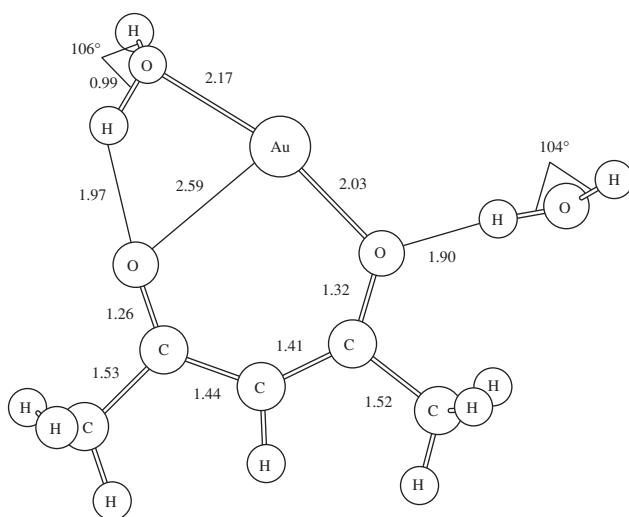


Fig. 6. Structure of the [Au(H₂O)₂(acac)] complex and calculated bond lengths (in Å).

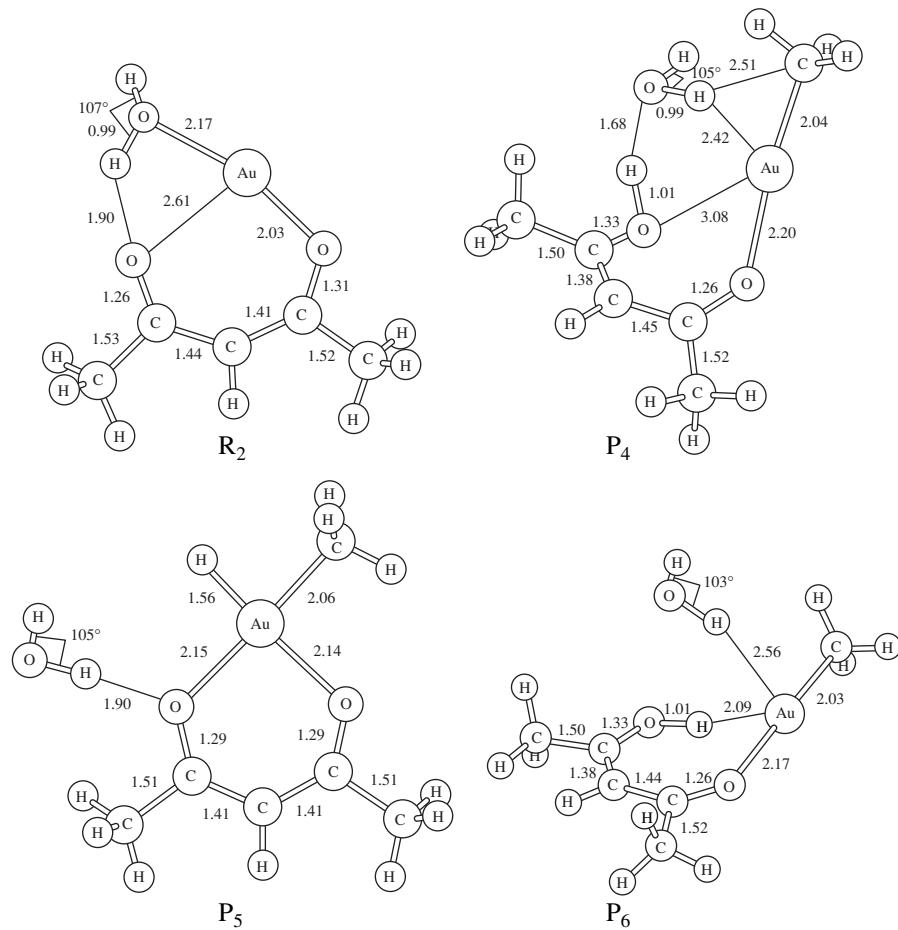


Fig. 7. Structures of the $[\text{Au}(\text{H}_2\text{O})(\text{acac})]$ complex (R_2), the product of reaction (III) (P_4), the product of reaction (IV) (P_5), and the isomer of P_3 (P_6). The calculated bond lengths are given in Å.

interaction between the gold atom and the oxygen atom of the oxy group.

The products of reactions (III) and (IV) are structurally similar to the products of reactions (I) and (II), respectively (Fig. 7). In both cases, the water molecule is displaced into the second coordination sphere. In the electrophilic substitution product P_4 , the ligand is coordinated to the gold atom through its carbonyl group and the $\text{Au}-\text{O}$ bond length is 2.20 Å. The structure of $\text{H}_2\text{O}-[\text{Au}(\text{CH}_3)\text{OC}(\text{CH}_3)\text{CHC}(\text{CH}_3)(\text{OH})]$ is 12.1 kcal/mol more stable than the structure of the initial system and forms with an energy gain of 6.0 kcal/mol. The oxidative addition product P_5 forms with an energy gain of 10.4 kcal/mol, but the gain in free energy in this case is only 1.5 kcal/mol. In the complex P_4 , the water molecule forms a strong hydrogen bond with the hydroxyl group of the ligand ($\text{O}-\text{H}$ 1.68 Å) and its hydrogen atom is in contact with the central (gold) atom ($\text{Au}-\text{H}$ 2.42 Å). Nevertheless, the binding energy of the water molecule is as low as 2.2 kcal/mol. Although the water molecule in the oxidative addition product P_5 (which is geometrically similar to P_3) has a substantially higher

binding energy (5.1 kcal/mol), it forms a weaker hydrogen bond with the oxygen atom of the ligand ($\text{O}-\text{H}$ 1.90 Å). This distinction is likely due to the fact that the elimination of the water molecule from P_4 causes the reorientation of the hydroxyl hydrogen atom toward the gold atom, implying a gain in energy. The intermediate complex in this pathway is P_6 , which is geometrically very similar to P_1 and is 1.6 kcal/mol lower on the energy scale than P_4 . The water molecule in P_6 is weakly coordinated to the gold atom through a hydrogen atom ($\text{Au}-\text{H}$ 2.56 Å). The energy of this bond is 3.8 kcal/mol.

The transition state in the isomerization process $\text{P}_4 \rightarrow \text{P}_6$ (TS_3) is depicted in Fig. 8. It is surprising that this transition state involves a hydride hydrogen atom ($\text{Au}-\text{H}$ 1.60 Å) and that the energy barrier is as high as 15 kcal/mol. This value is rather large for the rotation of the OH group. In order to understand this situation, we examined the coordinate of the reaction $\text{P}_4 \rightarrow \text{P}_6$ (Fig. 9). It was found that this reaction is not trivial rotation. The mechanism of this process includes the concerted cyclic transfer of two hydrogen atoms

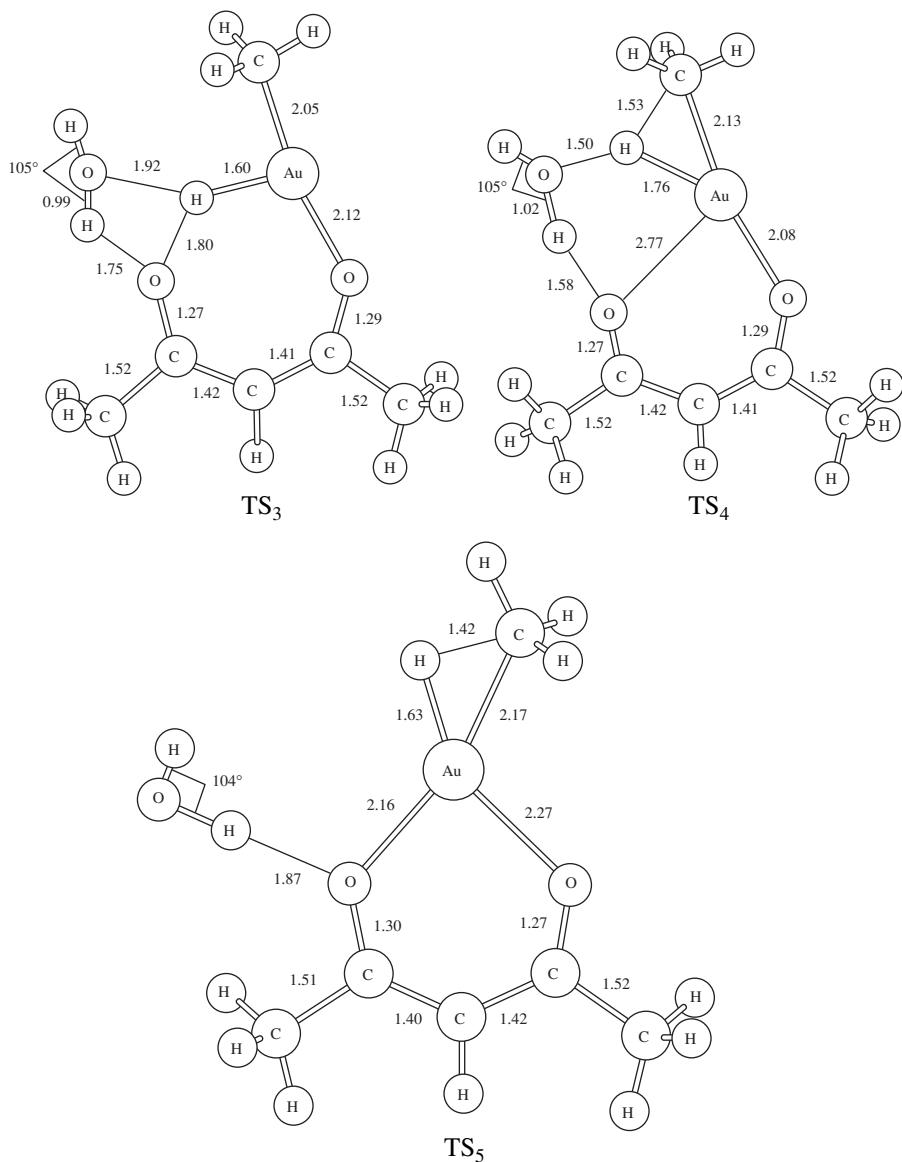


Fig. 8. Structures of the transition states of the isomerization reaction $P_4 \longrightarrow P_6$ (TS₃), reaction (III) (TS₄), and reaction (IV) (TS₅). The geometric parameters are given in Å.

involving the gold atom. No transition state was deduced for the $P_4 \rightarrow P_6$ isomerization reaction of $[\text{Au}(\text{acac})]$.

The transition states in reactions (III) and (IV) (TS_4 and TS_5 in Fig. 8) are structurally similar to TS_1 and TS_2 and are associated with low energy barriers (6.1 and 2.3 kcal/mol, respectively). Examination of the descents from TS_4 and TS_5 along the reaction coordinate toward the reactants again suggested the formation of intermediate methane complexes (Fig. 10).

The methane complexes I_3 and I_4 result from near-thermoneutral reactions, I_3 with an energy gain of 0.3 kcal/mol and I_4 with an energy loss of 2.9 kcal/mol, although the methane affinity of the complex R_1 is almost 10 kcal/mol lower than its water affinity. This is

explained by the fact that the water molecule stays in the second coordination sphere, being strongly hydrogen-bonded to the carbonyl oxygen atom ($O-H$ 1.8 Å). The calculated equilibrium constants of the I_3 and I_4 formation reactions are much smaller than the same constants for I_1 and I_2 and are 5×10^{-3} and 1.8×10^{-7} , respectively. These values refer to the gas phase. The equilibrium constants for the same reactions in solution are expected to be somewhat larger because of the lower translational entropy of CH_4 .

The energy diagram for the reaction between methane and the aquaacetylacetone complex is presented in Fig. 11. With the formation of the methane complex taken into account, the energy barrier for the electrophilic substitution reaction is reduced to 6.4 kcal/mol

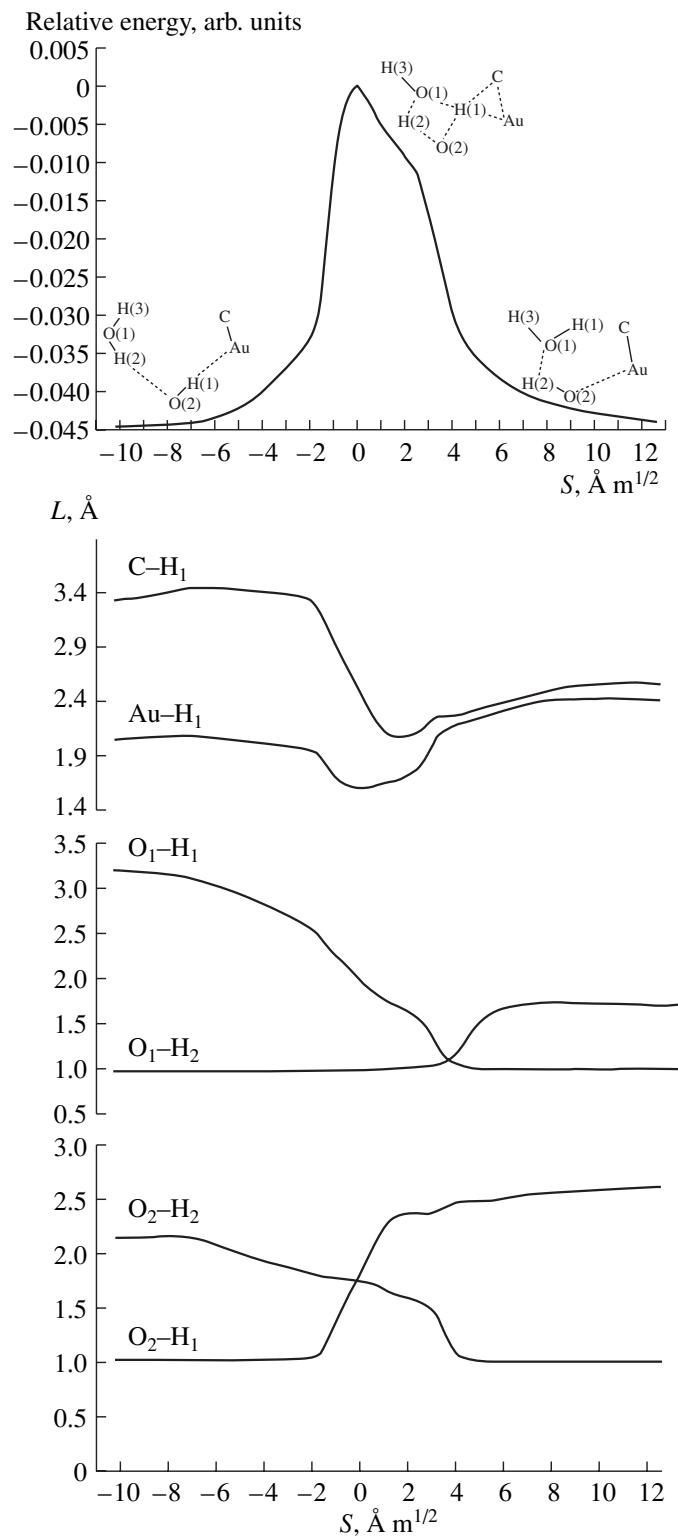


Fig. 9. Energy profile along the coordinate of the reaction $P_4 \longrightarrow TS_3 \longrightarrow P_6$ and the corresponding changes in bond lengths.

and the energy barrier for the oxidative addition reaction is as low as 0.1 kcal/mol.

Thus, both complexes are very reactive toward methane. The highest activation barrier is found for the

replacement of the water molecule by a methane molecule. This reaction step was not studied in detail. Based on the data obtained, the activation energy of this step can roughly be estimated at 10 kcal/mol, the value that

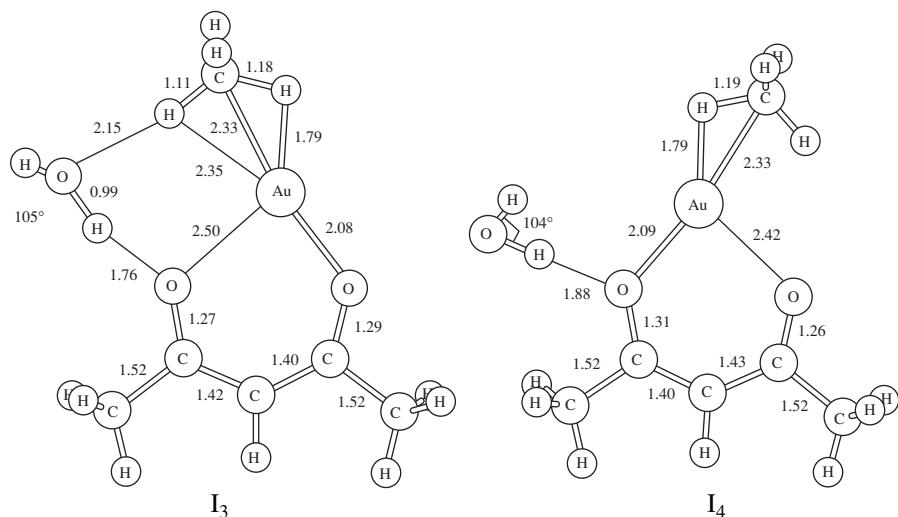


Fig. 10. Structures of the methane complexes I_3 and I_4 obtained by the relaxation of TS_4 and TS_5 . The geometric parameters are given in Å.

is the difference between the binding energies of the water molecule in R_1 and I_3 or I_4 . In view of this, methane activation can take place under mild conditions. The presence of a more strongly binding base in the reaction mixture would hamper this reaction. This follows, for example, from the fact that the bond energy of the phosphine ligand in $[\text{Au}(\text{PH}_3)\text{acac}]$ has a much higher value of 45.6 kcal/mol. On the one hand, the coordinative unsaturation of the gold atom in $[\text{Au}(\text{acac})]$ is favorable for methane activation. On the other hand, it has an adverse effect, because it favors Au–Au bonding due to “aurophilic” attraction. This may give rise to inactivation processes, including the formation of colloidal gold. Therefore, it is quite necessary that the reaction system contain an appropriate ligand that does not bind very strongly to the gold atom but can serve as a protector.

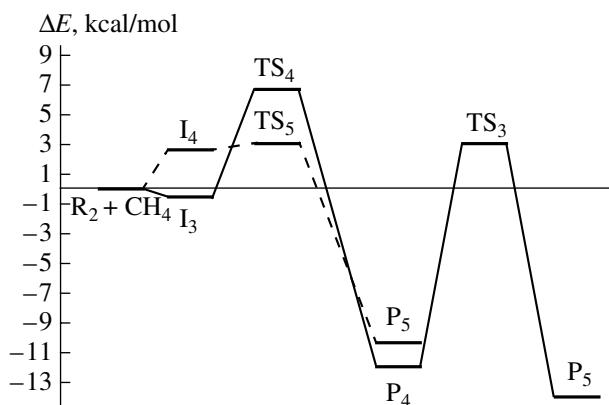


Fig. 11. Energy diagrams for reaction (III) (solid line) and reaction (IV) (dashed line).

CONCLUSIONS

The DFT calculations carried out in this study indicate that the $[\text{Au}(\text{acac})]$ and $[\text{Au}(\text{H}_2\text{O})\text{acac}]$ complexes can react with methane via two routes, both with low activation barriers, forming intermediate methane complexes. These reactions yield methane derivatives of gold(I) and gold(III) with a gain in energy. The Au–H₂O bond energy in $[\text{Au}(\text{H}_2\text{O})\text{acac}]$ is 22.2 kcal/mol and is comparable with the formation energy of the methane complex (~10 kcal/mol), but this energy is too low for the methyl derivative to be formed under mild conditions.

Assuming that the acetylacetone complexes are adequate models of the gold–rutin complex in the catalytic methane-oxidizing system, one can infer that the activation of a C–H bond in the CH_4 molecule involves a 1 : 1 $\text{Au}^{\text{I}}\text{–Rut}$ complex.

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