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Adducts of hydrogen and methane with Os(II) and Os(IV) complexes: Theoretical analysis of (η^2-H_2)$OsCl_2(PH_3)_2$ and (η-CH_4)$OsCl_2(PH_3)_2$ molecular complexes by RHF, MP2 and DFT methods

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Abstract

A theoretical study of model $OsCl_2(PH_3)_2$ complex and its adducts with hydrogen and methane is reported. Geometry of two isomers of $OsCl_2(PH_3)_2$ complex and structures of possible σ complexes (η^2-H_2)$OsCl_2(PH_3)_2$, (η^2-CH_4)$OsCl_2(PH_3)_2$ have been calculated using density functional theory and MP2-method. It was shown that some isomers of weakly bonded hydrogen σ-complex $OsH_2Cl_2(PH_3)_2$ can form stable methane adducts followed by reductive elimination of hydrogen. Calculations of the reaction pathways for methane oxidative addition to isomers of 14-electron intermediate $OsCl_2(PH_3)_2$ have been performed. For the isomer active in this reaction, structures of the transition state and methylhydride product were calculated. Frequencies of vibrations of stable σ-complex (η^2-CH_4)$OsCl_2(PH_3)_2$ along with its deuterated form (η^2-CD_4)$OsCl_2(PH_3)_2$ have been computed in the MP2/LAN1DZ approximation. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Complexes of Osmium; Adducts of methane and hydrogen; Oxidative addition of methane; Quantum chemical calculations

1. Introduction

More than 25 years ago Malin and Taube [1] have shown that reduction of $[OsO_2(en)_2]^{2+}$ (en – ethylene diamine) ion to Os(II) in acid solutions results in the formation of a novel 16-electron complex $[OsH_2(en)_2]^{2+}$ with H_2 in *cis*-configuration. The authors [1] described it as a six-coordinate dihydride complex, in which each H^- ligand independently coordinates the metal site with its electron pair. Only significantly later [2] this complex was shown to be a representative of a new wide class of the so-called "nonclassic" molecular complexes, in which H_2 molecule acts as one ligand. Hence, this complex should be considered as five-coordinate unsaturated complex. Kubas et al. [3,4] were the first to identify and describe complexes of molecular hydrogen with transition metals (M). Afterwards the number of such nonclassic hydrogen complexes grew rapidly (see reviews [5,6]), and some of them [7], including molecular polyhydride complexes of osmium [8–12], became the subject of detailed theoretical analysis.

Almost simultaneously with this discovery, intramolecular interaction of a C–H bond of saturated

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hydrocarbons in complexes with metal center was reported [13,14]. The authors have called this interaction by a mysterious word "agostic", what means "holding some object", in a free translation from Greek. The formation of an agostic bond is a consequence of an interaction between an electron pair of the σ(C–H) bond of a coordinatively bonded alkyl ligand with a vacant d orbital of a metal. Such interaction results in an additional stabilization of the metal–alkyl bond. Thus, these bonds have a similar origin as electron-deficient bonds in carbocations, which were known before [15]. Therefore, their mystery is purely historic, but the term "agostic" was preserved with respect to weak two-electron three-center bifurcated [η^2-(R–H)]M bonds of large alkyl ligands.

A natural question arises whether pure agostic interaction can result in the formation of a metal–alkane bond in the case of an intermolecular interaction. In other words, is the formation of stable molecular σ complexes of the (η^2-CH_4)M type, which are analogous to (η^2-H_2)M complexes of molecular hydrogen [5,6], possible? It is natural to suppose that an intermolecular interaction of a σ(C–H) bond with an acceptor d orbital of metal center could also result in the formation of a non-classic molecular complex [η^2-(C–H)]M. However, as a saturated C–H bond in alkanes is a very weak base and Lewis acidity of an ML_n complex is usually weak as well, a priori it was difficult to hope that relatively stable adducts of saturated hydrocarbons with such complexes can exist. Nevertheless, subsequent experimental data [16–20] make it possible to believe that C–H bonds in alkanes can act as σ-donor ligands to form adducts with metallocomplexes via the formation of three-center two-electron bonds:

$$\mathrm{C{-}H} + \mathrm{ML}_n \rightarrow \eta^2(\mathrm{C{-}H})\mathrm{ML}_n \qquad (1)$$

Now the formation of a molecular σ complex according to reaction (1) is accepted as a possible stage in some mechanisms of activation of saturated hydrocarbons by transition metal complexes [21–24]. Usually such active complexes are prepared by a photodissociative or thermal reductive elimination of one or more ligands from an initial stable 18-electron complex. Under certain conditions such intermediate ML_n complex can be stabilized and characterized by physicochemical methods. Only few such complexes are capable of activating the C–H bond. First of all, these are 14-electron $ClML_2$ and 16-electron C_pML complexes of rhodium and iridium (C_p=C_5H_5, C_5R_5, C_5Ph_5; L=CO, PH_3, PR_3, PPh_3). Among complexes of other metals, Shilov's [21–24] complexes $[PtCl_4]^{2-}$ should be mentioned. These complexes were the first to be successfully applied for the C–H bond activation in alkanes [25–27], including methane [28,29].

Appropriate position of a vacant d orbital of metal relative to the occupied σ orbital of methane is an important condition for the stabilization of the σ complex. The promotion energy $E(\sigma\rightarrow d)$ is a measure of efficiency of the electron transfer from the C–H bond to the metal. For the same metal and geometry of the complex, $E(\sigma\rightarrow d)$ is determined by the position of the first occupied σ(C–H) orbital and is proportional to the first hydrocarbon ionization potential. A correlation between the alkane ionization potentials and their adduct formation enthalpies with $W(CO)_5$ was indeed observed [19]. The $E(\sigma\rightarrow d)$ value depends on the structure of the ML_n intermediate rather than on the nature of the metal and ligands. The reason is that σ(C–H) bonds are spatially localized (sp^3 hybridization in methane). Therefore, a vacant d orbital has to rearrange to make the overlap between σ and d orbitals maximal. This is possible for labile ML_n intermediates having free coordination sites in the first coordination sphere of the complex. For square planar complexes (n=4), the formation of σ complexes can be realized in two ways: Either via dissociative substitution of one of the L ligands for CH_4. In this case the resulting (η^2-CH_4)ML_{n-1} complex have a square planar structure; or else via shifting one of the ligands from the complex plane to an axial position (to the fifth coordination site). In this case methane coordination at the sixth coordination site is possible. The resulting (η^2-CH_4)ML_n complex has an octahedral structure with one vacancy in the equatorial plane.

For Pt(II)-complexes (d^8 electron configuration), only the first pathway is realized [30]. The second one is energetically very expensive. However, the second reaction pathway may appear very effective for metals with the d^6 configuration due to stabilization of four-coordinate stereoisomers with a nonplanar structure. From this point of view, Os(II) complexes of the $Os(Cl)_2(PH_3)_2$ type, for which the second variant of the σ-complex formation is realized, are of special interest.

Werner and co-workers [32] have shown that 16-electron diamagnetic complexes $OsH_2Cl_2(P^iPr_3)_2$(**1**) (^{i}Pr-isopropyl) catalyze many reactions of hydrocarbons. Several important reactions with participation of osmium complexes with the composition similar to **1** were studied by Gusev et al. [33,34], Esterualas and co-workers [35–38], Heinekey and Luther [39]. Some of these complexes could serve as stable models of reactive center or catalyst precursor for many catalytic transformations with participation of saturated hydrocarbons and probably display somewhat different reactivity from that of their Rh and Ir counterparts. From this viewpoint it is interesting to determine theoretically possible structures of alkylhydridoosmium intermediates.

Hydride complex **1** can be considered as a product of hydrogen oxidative addition to a 14-electron intermediate $OsCl_2(P^iPr_3)_2$ (**2**). Complex **1** can easily add one more hydrogen molecule to form an 18-electron stable complex $OsH_4Cl_2(P^iPr_3)_2$ [33,34]. One can expect that complexes **1** and **2** form adducts not only with hydrogen but with methane as well

$$OsCl_2(PR_3)_2 + (H_2) \rightarrow (\eta^2\text{-}H_2)OsCl_2(PR_3)_2 \quad (2)$$

$$OsCl_2(PR_3)_2 + CH_4 \rightarrow (\eta^2\text{-}CH_4)OsCl_2(PR_3)_2 \quad (3)$$

$$H_2OsCl_2(PR_3)_2 + CH_4 \rightarrow (\eta^2\text{-}CH_4)H_2OsCl_2(PR_3)_2 \quad (4)$$

Several recent papers are devoted to computational analysis of unusual properties of osmium hydride complexes [8–12], including complexes of type **1** [33–39]. However, only few reports on theoretical calculations of the methane interaction with osmium complexes have been published. Paper [40] should be mentioned here. Its authors have performed DFT computations of the reaction enthalpies, adduct formation energies and energy profile for the methane addition to 16-electron complex $Os(CO)_4$ (d^8 electron configuration). The adduct formation energy for the $(\eta^2\text{-}CH_4)Os(CO)_4$ intermediate has a very low value $\Delta H(Os)=-0.48$ kcal/mol. The computations show that in contrast to Rh and Ir complexes (having d^8 electron configuration) this osmium compound does not form σ complex with methane. In [41] the dependence of stability of methane σ complexes for several d^0–d^2 metals on the nature of metal, ligand and d-orbital population are determined. For a 20-electron imido-complex $Os(NH)_3$ a very high activation energy (~50 kcal/mol) for [2s+2p] C–H methane activation is predicted. In contrast to this, a 16-electron intermediate $Os(NH)_2$ is probably more reactive and could form a stable adduct with methane.

In the present study structures of several isomers of model complexes of types **1** and **2** have been determined using ab initio quantum chemical calculations. Two isomers of the square pyramidal (Str1) and tetrahedral (Str2) structures have been obtained for the basic intermediate **2**. Relative stability of hydrogen and methane adducts with isomers Str1 and Str2: $(\eta^2\text{-}H_2)$-Str(n), $(\eta^2\text{-}CH_4)$-Str(n), $(H)(CH_3)$-Str(n), $(\eta^2\text{-}H_2)(\eta^2\text{-}CH_4)$-Str($n$), ($n$=1, 2) have been calculated. This paper also analyses methane activation. Methane oxidative addition to isomers Str1 and Str2 have been performed. Structures of the $(CH_4)OsCl_2(PR_3)_2$ complex were calculated in stationary points of reaction CH_4+Str1→$(\eta^2\text{-}CH_4)$-Str1→$(H)(CH_3)$-Str1. Fundamental vibrational frequencies have been analyzed for stable complex of methane, $(\eta^2\text{-}CH_4)$-Str2, and its deuterated form $(\eta^2\text{-}CD_4)$-Str2.

2. Computational methods and theoretical details

For analysis of the electronic structure of systems based on Os(II), three theoretical approaches were used: restricted Hartree–Fock (RHF) method, second order Moller–Plesset perturbation theory (MP2) [42] and density functional theory (DFT) [43,44]. In the DFT approximation a Hartree–Fock exchange term is replaced by a more general expression for the exchange correlation potential, including electron correlation term, which is not presented in the traditional RHF method. For the exchange correlation potential, we used Beck's hybrid three-parameter functional [45,46] with a nonlocal correlation by Lee et al. [47] (B3LYP method).

The Os, P and Cl core electrons were replaced by an effective core potential and all calculations were performed in LANL1DZ basis [48] as in previous communications [30,31]. Corrections for the zero-point vibration energy were not taken into account for the hydrogen and methane adducts of complexes **1** and **2**. For hydrogen and carbon, all electrons were taken into account with double-ξ basic functions C(9s,5p)→C[4s,2p], H(4s)→H[2s] [49]. The PH_3 ligands were assumed to have trigonal symmetry and rotation around the Os–PH_3 bond was frozen. All calculations were carried out using the GAUSSIAN92/DFT package [50].

Let us mention several methodic aspects of the calculations. Taking the correlation energy into consideration results in a dramatic change of the reaction pathway. This is caused by the fact that the electron correlation energy determines the formation of Os–C and Os–H bonds. The RHF approximation is completely unsatisfactory in this case. However, the computations show that in some points of the reaction pathway structures optimized in the MP2 approximation are not very different from those determined in the RHF one. This made it possible to compute the reaction pathways in two stages. First, the RHF approximation was used to determine an optimized structure at several points along the reaction coordinate. Then, energy at these points was calculated in the MP2 approximation. This combined approach was called MP2/RHF. Such a method has an important drawback: there is a chance to jump to a different energetic surface while moving from one point to another. To make sure that the starting reagents (R) and the reaction products (P) belong to the same energetic surface with the transition state (TS), the following simple algorithm was applied. The reaction pathway was passed twice: in the P→TS→R direction in one set of points and in the R→TS→P direction using intermediate points. A coincidence of energy in the stationary points R, TS and P served as a criterion of the procedure correctness. Calculations of optimized structures and relative stability of isomers were performed only by the MP2 and DFT methods.

3. Computational results and discussion

3.1. *Structure of* $OsCl_2(PH_3)_2$ *stereoisomers*

Werner and co-workers [32] have shown that under certain conditions complex **1** can form an intermediate reactive towards two-electron donor ligands via reductive hydrogen elimination. Some such reactions, including the formation of (η^2-H_2) complexes, have been studied experimentally in detail [33–39]. Let us discuss the electronic structure of a 14-electron complex **2** as a model of such a catalytic active site. The model complex $OsCl_2(PH_3)_2$ discussed here differs from **2** only due to the substitution of a bulky P^iPr_3 ligand for the simplest phosphine ligand PH_3. Unless steric factors, which can significantly alter the energy [33,34], are taken into account, such a substitution is energetically worth only 1–2 kcal/mol [7].

Depending on the number of d electrons and the nature of ligands, four-coordinate complexes of transition metals can have either planar or tetrahedral structure. For Os(II) complexes (d^6 configuration), which have two vacant d orbitals, a strong distortion of the planar structure is possible with the stabilization of a square pyramidal structure with the Os atom on top of the pyramid. Fig. 1 presents structural parameters of $OsCl_2(PH_3)_2$ complex obtained with full geometry optimization in the MP2 and DFT approximations.

The computations show that though Str1 is less stable than the tetrahedral structure Str2 by 4.2 kcal/mol, both structures can coexist as they are separated by a relatively high energetic barrier. Generally, a planar structure is also possible, but the computations show that it is unstable and is converted into Str1 or Str2. Both MP2 and DFT approximations yield similar results for the structural parameters. However, the DFT method overestimates the ZOsCl angle in Str1. It is noted that POsP angles in Str1 and Str2 are radically different: POsP(Str1)=176.8°/175.0°; POsP(Str2)=93.4°/94.4°. The Os–P bond length, and correspondingly, its strength also significantly depend on the isomer structure. The Os–P bond in Str1 is longer than in Str2, however, for the latter the Os–Cl bond is shorter (and stronger).

There are no experimental data on the structure of 14-electron complexes of the $OsCl_2(PR_3)_2$ type, but some comparable structural data can be extracted from the structures of the 16-electron complex $OsH_2Cl_2(PR_3)_2$ [32] and 18-electron complexes: $OsH_4Cl_2(PR_3)_2$ [33,34], $OsH_6(PR_3)_2$ [51], $OsCl_3(PR_3)_3$ and $OsCl_4(PR_3)_2$ [52]. For Os–P bond reported lengths are 2.29–2.30 Å [32], 2.41–2.42 Å [33,34], 2.34–2.35 Å [51], and 2.35–2.45 Å [52]; the Os–Cl bond lengths are 2.37–2.38 Å [32], 2.44–2.45 Å [33,34], and 2.32–2.44 Å [52]; the POsP angles are 112.2° [32], 155.2° [51], and 176.9° [33,34].

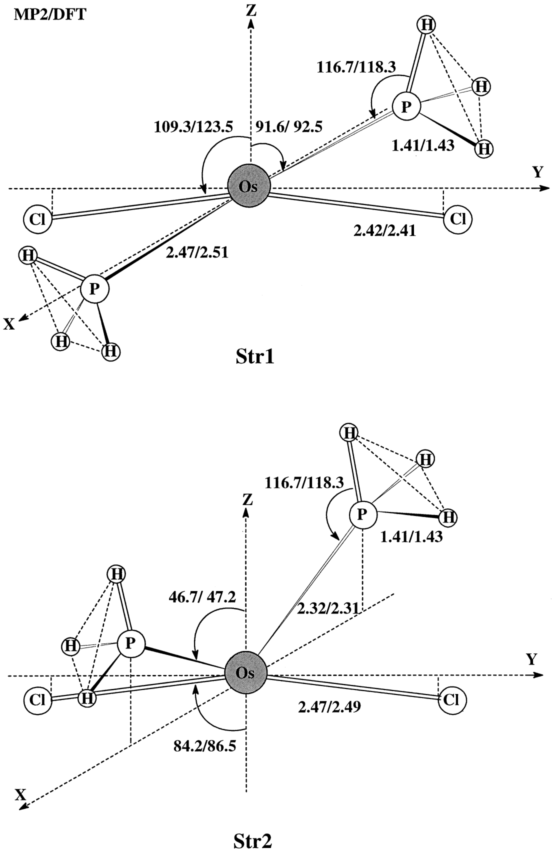

Fig. 1. Optimized structures (in Å and degree) at the MP2 and DFT levels (MP2/DFT) for stereoisomers of the original $OsCl_2(PH_3)_2$ complex. Str1 is an isomer with a square pyramid structure, Str2 is an isomer with a tetrahedral type structure.

In [52] it was shown that an increase in the osmium oxidation state results in an increase in the Os–P distance, whereas a substitution of chlorine ligands for hydride ones with preservation of the oxidation state facilitates an increase of the POsP angle: 112.2° for $OsH_2Cl_2(PR_3)_2$ [32] and 176.9° for $OsH_4(PR_3)_2$ [33,34]. Thus, there is an obvious experimental tendency towards stretching the Os–P bond with an increase of the POsP angle. In [33,34] it was noted that osmium polyhydride complexes exhibit a definite trend to avoid the highest possible oxidation states and accept nonclassic structures in the presence of strong acceptor ligands such as Cl. But this does not exclude a possibility to form stable methane adducts and methylhydride products from them with a wide range of different intermediates based on Os(II). The two isomers Str1 and Str2 of complex **2** predicted theoretically are two limiting cases in this row. The Str1 isomer has more favorable conditions for stabilization of alkylhydride complex increasing the oxidation state, whereas the Str2 isomer favors the formation of molecular complexes. It is impossible to obtain Str2 from Str1 via a gradual structural deformation as these isomers correspond to singlet states of two different electronic configurations. Below we will show that Srt1 and Str2 isomers act in principally different ways in the methane oxidative addition reaction.

3.2. *Hydrogen adducts with* $OsCl_2(PH_3)_2$

Both molecular σ complexes (η^2-H_2)-**2** and dihydride complexes (H)(H)-**2** can form from the hydrogen reaction with isomers Str1 and Str2 of complex **2**. Figs. 2–4 present optimized structures of possible intermediates. Relative stability (ΔE) of hydride complexes ($X=H_2$) calculated from the following equation is also shown:

$$\Delta E(X) = E[OsXCl_2(PH_3)_2] - E[X] - E[OsCl_2(PH_3)_2]. \quad (5)$$

As for the initial complexes Str1 and Str2, MP2 and DFT approximations give similar values of their structural parameters. However, the DFT method (B3LYP variant) underestimates stability of the complex. This is caused by its overestimation of H_2 dissociation energy, whereas the MP2 method underestimates it.[2] The most stable isomer is shown in Fig. 2(1). The computations give an equilibrium length r(H–H)=1.59/1.48 Å for (η^2-H_2)-Str1 complex. It substantially exceeds corresponding values known for hydrogen molecular σ complexes with transition metals, where average r(H–H) is 0.8–0.85 Å [5].

This distance is usually considered to be a direct characteristic of the type of such complexes. According to [7], dihydride compounds with r(H–H)<1.0 Å belong to nonclassic complexes. Complexes with r(H–H)>1.5 Å are usually related to classic hydrogen complexes, whereas complexes with 1.0 Å<r(H–H)<1.5 Å are called intermediate hydride complexes. According to this classification, the complex shown in

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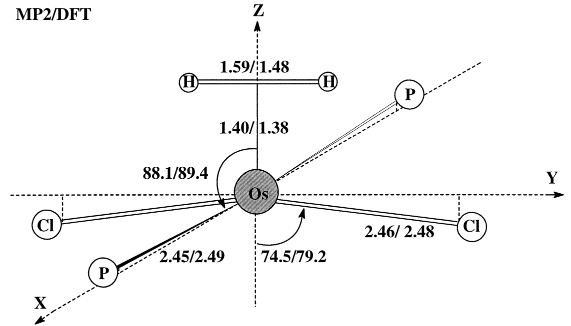
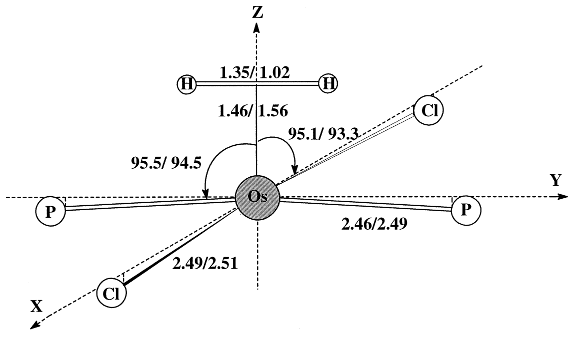
[2] Hydrogen dissociation energy $D_0(H_2)$ is 109.5 kcal/mol in the B3LYP/LANL1DZ approximation and 90.3 kcal/mol in the MP2/LANL1DZ approximation.

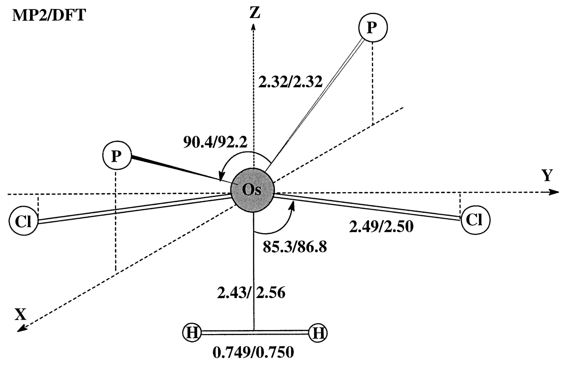


1. (η^2-H$_2$)-Str1: ΔE = -35.4/-17.1 (kcal/mol)

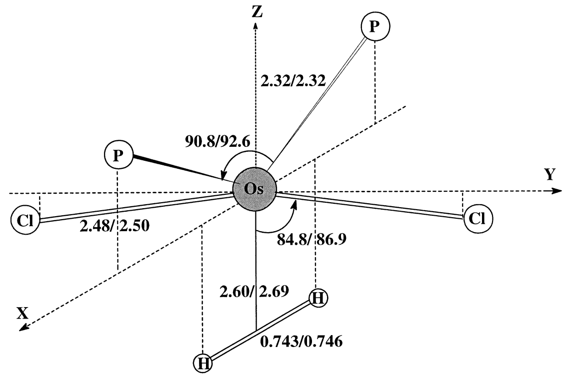


2. (η^2-H$_2$)-Str1: ΔE = -18.5/-8.1 (kcal/mol)

Fig. 2. Optimized structures for two hydrogen adducts with the Str1 complex. ΔE are the stereoisomer energies relative to the Str1 and H_2 reactants.



1. (η^2-H$_2$)-Str2: ΔE = -3.5/-1.6 (kcal/mol)

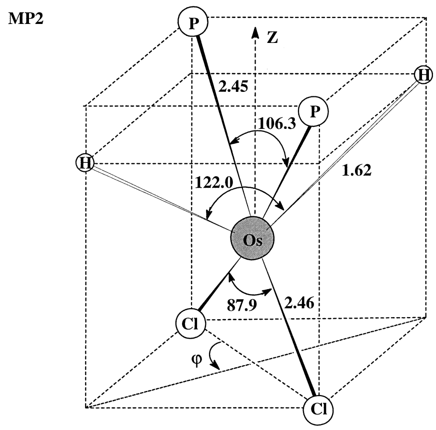


2. (η^2-H$_2$)-Str2: ΔE = -1.5/-0.3 (kcal/mol)

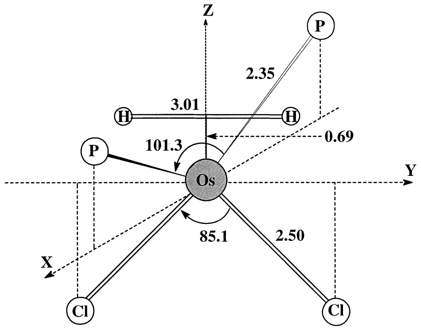
Fig. 3. Optimized structures for two hydrogen adducts with the Str2 complex. ΔE are the energies to the Str2 and H_2 reactants.

Fig. 2 should belong to the classic type. However, an analysis of the electron energy distribution over the bonds shows that here the hydrogen molecule acts as a σ-donor ligand with its electron pair. The Os–(H_2) bond is realized via an electron density transfer from the σ(H–H) bond to the osmium empty d orbital. Therefore, we attribute the (η^2-H$_2$)-Str1 isomer (Fig. 2(1)) to a molecular hydrogen σ complex. Due to a high π donor ability of chlorine, the electron density is partially transferred from Cl to the σ^*(H–H) orbital resulting in a complex with unusually high r(H–H) values. Rotation of the hydrogen molecule around axis Z by 90° in the isomer as shown in Fig. 2(1) transforms it into a new isomer (Fig. 2(2)). In this structure the electron density transfer from Cl to the σ^*(H–H) orbital is partly blocked, and the H–H bond length decreases to 1.35/1.02 Å, with the stability slightly decreasing as well. Thus, the (η^2-H$_2$)-Str1 isomer is a molecular hydrogen σ complex with a square pyramidal structure.

In the hydrogen adduct formation the Str2 isomer behaves in a completely different way. Fig. 3 presents two possible isomers. The (η^2-H$_2$)-Str2 isomer differs from (η^2-H$_2$)-Str1 only by the POsP angle, the other structural parameters being similar. As phosphine ligands are stronger σ donors than molecular hydrogen and are in *trans*-position relative to the Os–H_2 bond, the electron transfer from the σ(H–H) orbital to Os is partly hindered due to the *trans*-influence. Therefore, (η^2-H$_2$)-Str2 isomers form weak σ complexes with hydrogen. But the situation is principally changed if the H–H bond is completely broken and a six-coordinate dihydride complex is formed. Computational results obtained for two such complexes by the MP2 method are shown in Fig. 4. The first isomer



1. (H)(H)-Str2: ΔE = -25.1 (kcal/mol)



2. (H)(H)-Str2 : ΔE = -2.9 (kcal/mol)

Fig. 4. Optimized structures for two classic hydride complexes on the base of the Str2 isomer.

(H)(H)-Str2 (Fig. 4(1)) is the most stable among classic complexes of type **1**. This complex has an unusual structure due to the deformation of the Str2 fragment from the tetrahedral to a planar structure. Hydrogen atoms are localized along a line perpendicular to the POsP plane. Formally a similar structure can be obtained by rotation of the ClOsCl plane in Str2 around axis Z by $\varphi=90^\circ$. A pure tetrahedral structure has a significantly lower stability (Fig. 4(2)).

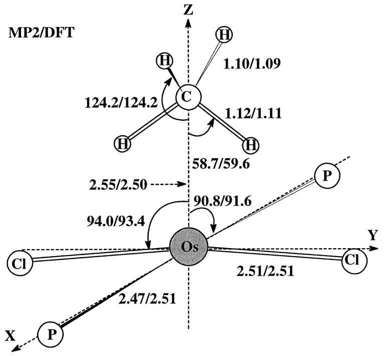
Thus, the calculations predict that a hydride complex of type **1** has two stable isomers, one of which (Fig. 2(1)) is a typical σ complex with the bond length r(H–H) ∼1.5 Å and second one (Fig. 4(1)) is a typical example of classic hydride complex with a distorted octahedral structure. These two isomers can coexist in solution without mutual conversion as both correspond to deep minima on two different energetic surfaces.

The structure of complex **1** in the solid phase was experimentally determined in [32]. The structure was described as a square antiprism with a two-fold axis passing through the metal and the midpoint of P–P and Cl–Cl segments. The experimental values of angles (POsP=112.2°, ClOsCl=83.4°) and bond lengths (Os–P=2.30, Os–Cl=2.38, Os–H=1.66 Å) can be compared with the theoretical values obtained for the isomer in Fig. 4(1). The theoretical value for the dihedral angle φ is still 90°, whereas for the solid-state structure of complex **1** the experimental value φ is about 45°. This discrepancy might be caused by a steric effect between bulky phosphine and chlorine ligands. Such a contingency is discussed in [33,34].

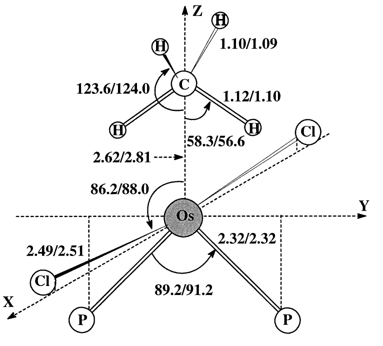
3.3. *Methane adducts with* $\mathrm{OsCl_2(Pr_3)_2}$

No calculations of the intermolecular interaction of methane with Os(II) complexes have been reported to date. Based on the electronic structure and properties of isomers Str1 and Str2 presented above, the reaction with methane with subsequent stabilization of the adduct can be proposed to be more preferable for Str2 as the formation of the molecular complex (η^2-CH_4)-Str2 does not require changing of the metal oxidation state. Nonetheless, for the Str1 isomer, as it will be shown below, the formation of both molecular (η^2-CH_4)-Str1 and stable methylhydride (H)(CH_3)-Str1 complexes is possible. Fig. 5 presents optimized structures of methane adducts with the isomers Str1 and Str2.

As one could expect, molecular complex (η^2-CH_4)-Str2 of C_{2V} symmetry is most stable. The MP2 calculations show that the methane bond energy for Str2 (without consideration of zero vibrations) is substantially higher compared to Str1 (E(Str2)=11.4 and E(Str1)=4 kcal/mol). In the adduct formation process, the structure of Str2 changes insignificantly but the deformation of Str1 is noticeable. The initial tetrahedral HCH angle and C–H bond length in methane increase, making the carbon atom more accessible to interaction with the metal. The Os–C bond length of 2.55 Å (Str1), and 2.62 Å (Str2) is typical for molecular agostic interaction of the C–H bond with the transition metal.



1. (η^2-CH_4)-Str1: $\Delta E = -4.0/-3.7$ (kcal/mol)



2. (η^2-CH_4)-Str2: $\Delta E = -11.4/-6.0$ (kcal/mol)

Fig. 5. Optimized structures of the σ methane complexes with Str1, Str2 isomers. ΔE are the energies relative to the Str1, Str2 and CH_4 reactants. The PH_3 ligand structure parameters are $P{-}H$=1.41 Å, (MP2), 1.43 Å (DFT) and OsPH=116.5° (MP2), 117.0° (DFT).

Rare experimental estimations show that the formation enthalpy of σ complexes [η^2-(H-C)]M varies in the range of $\Delta H = -(5{-}12)$ kcal/mol for a wide selection of saturated hydrocarbons. Bergman and co-workers [16–18] have experimentally identified molecular complex $(CH_4)RhC_p(CO)$ and determined $\Delta H = -10$ kcal/mol. Coordinatively unsaturated 16-electron complex $W(CO)_5$ gives $\Delta H = -(5{-}11)$ kcal/mol for a number of hydrocarbons (including methane). For the cationic complex $[(CH_4)Re(C_p)_2]^+$, experimental value is −6 kcal/mol [20]. Moreover, a number of indirect evidences, for example, H/D isotope exchange, also confirm the feasibility of methane adduct formation [53–55].

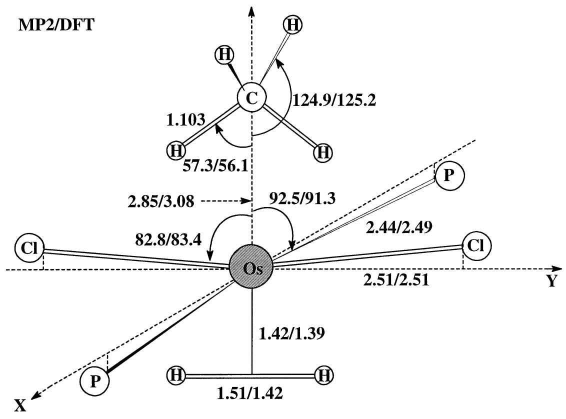
As to theoretic estimates, they have been mostly devoted to the mentioned rhodium and iridium complexes of the XML_n type (X=Cl; L=CO, PH_3). For $(CH_4)C_pRh(CO)$ the calculations give correlating formation enthalpy values: $\Delta H = -6.9$ [40], −7.7 [56,57], −14.8 [58], −2.3 kcal/mol [59]. The discrepancy of the values is caused by the use of different computational methods (RHF, MP2–4, DFT, etc.). For $(CH_4)C_pIr(CO)$ the calculations predict $\Delta H = -14.1$ [40], −17.6 kcal/mol [59]. For $(CH_4)RhCl(PH_3)_2$ the MP2 theoretical estimates give $\Delta H = -13.9$ [59], −17.7 [60], −12.0 kcal/mol [61]. For $(CH_4)IrCl(PH_3)_2$, ΔH is −15.6 kcal/mol in the same approximation [62].

3.4. Methane adducts with $OsH_2Cl_2(Pr_3)_2$

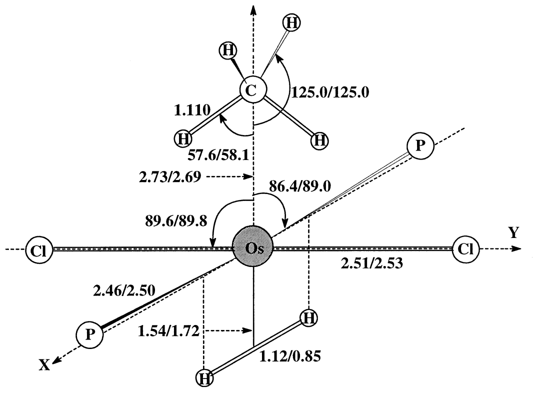
The analysis of the electronic structure of complex **1** isomers allows to propose that the isomers which form weakly bonded molecular hydrogen σ complexes (Figs. 2 and 3) can form rather stable methane adducts. The resulting 18-electron complex of type (η^2-CH_4)-**1** is interesting as a possible intermediate of a catalytic cycle with methane participation. Figs. 6 and Fig. 7 present two types of such intermediates, in which H_2 and CH_4 molecules are in *trans*- (Fig. 6) and *cis*- (Fig. 7) positions. Stability of methane adducts was calculated according to Eq. (5) relative to hydrogen σ complexes shown in Figs. 2 and 3. Though *trans*-isomers have similar structures, their stability is very different. A weakly bonded σ complex with methane (Fig. 6(1)) is formed on the basis of the stable hydrogen complex (η^2-H_2)-Str1 (Fig. 2(1)). A decrease in the hydrogen σ-complex stability (Fig. 2(2)) leads to an increase in the stability of the methane σ complex (Fig. 6(2)). This trend is more vividly expressed for *cis*-isomers (Fig. 7). In this case weakly bonded molecular hydrogen σ complexes (Fig. 3) lead to the most stable methane adducts.

Thus, the computations predict a very important result. Methane reaction with complexes of type **1** results in a reductive elimination of hydrogen and formation of a catalytic site of type **2** based on Os(II) capable of methane activation. Hence, it seems important to make an analysis of the reactivity of the starting isomers Str1 and Str2.

However, as shown below, the most stable σ complexes with methane are not necessarily the most active in the C–H bond activation. The formation of a molecular adduct with methane is a necessary but not



1. t-(η^2-CH4)(η^2-H2)-Str1: ΔE = -5.3/-2.1 (kcal/mol)



2. t-(η^2-CH4)(η^2-H2)-Str1: ΔE = -10.7/-7.6 (kcal/mol)

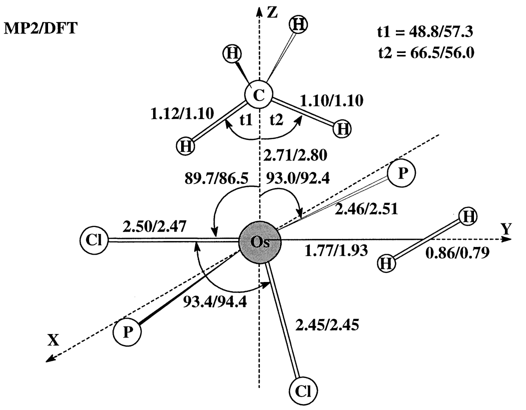
Fig. 6. The most active moleclar σ complexes in the reaction of methane oxidative addition.

sufficient condition. For the activation energy to be low, the reaction has to be highly exothermic. Consequently, there is one more necessary condition – formation of a stable methylhydride complex. To exhibit different reactivity of the isomers Str1 and Str2 in the methane activation, reaction pathways of the methane oxidative addition to the isomers Str1 and Str2 were calculated.

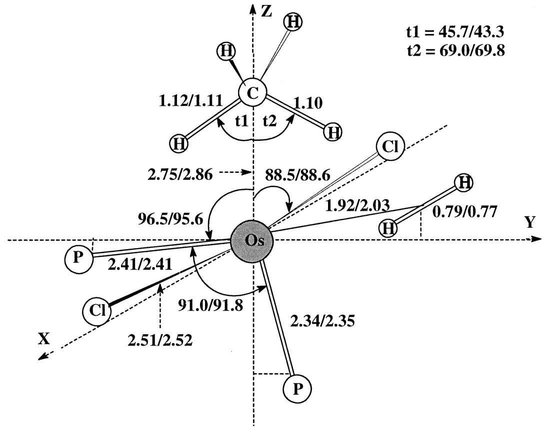
3.5. *Reaction pathway*

$$\mathrm{Str}(n) + \mathrm{CH_4} \rightarrow \mathrm{TS} \rightarrow (\mathrm{CH_3})(\mathrm{H})\text{-}\mathrm{Str}(n)$$

In Fig. 8 the initial part of the reaction pathway of methane reaction with Str1 is marked with an arrow. This direction is fixed in such a way that a methane molecule from the gas phase could approach the metal atom at a distance shorter than the sum of Van der Waals radii of the metal and carbon atoms with minimal steric difficulties. Angle *b* between the methane attack direction (Fig. 8) and the newly formed Os–H bond was chosen as a reaction coordinate. During a synchronous formation of Os–C and Os–H bonds, an increase of *b* corresponds to the movement along the energetic surface towards the reaction products. The alkylhydride product (P) corresponds to a minimum on the reaction pathway at b=60°, the transition state (TS) corresponding to a maximum at b=35°.



1. c-(η^2-CH4)(η^2-H2)-Str2: ΔE = -20.5/-8.3 (kcal/mol)



2. c-(η^2-CH4)(η^2-H2)-Str2: ΔE = -23.3/-12.5 (kcal/mol)

Fig. 7. Optimized structures of the most stable σ methane–hydrogen complexes with Str2-isomer. ΔE are the energies compared to structures in Fig. 3.

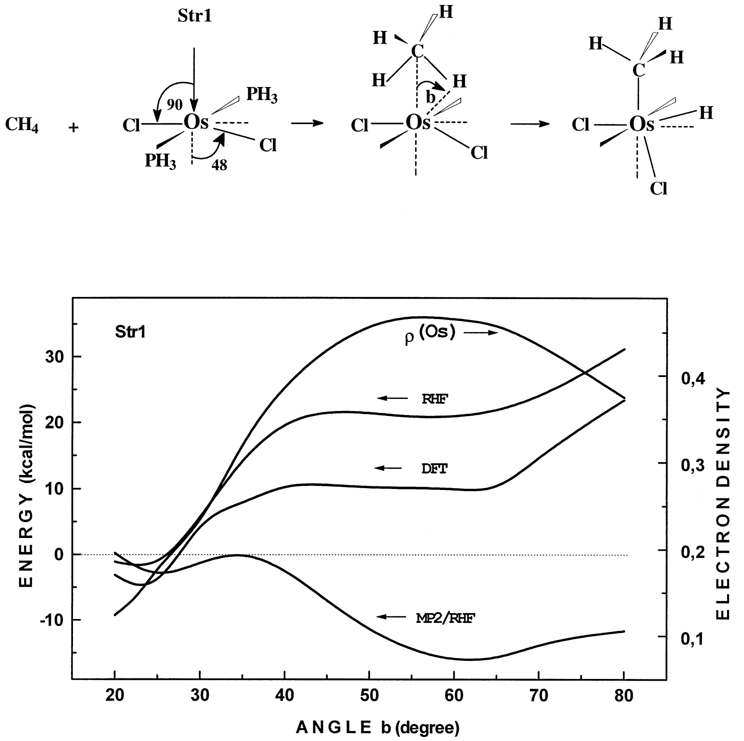


Fig. 8. The reaction path of the Str1+CH_4→TS→(H)(CH_3)-Str1 reaction along *b* coordination at the RHF, DFT and MP2/RHF approximations. Energies of starting reactants are accepted as zero. Electron density of osmium ρ(Os) is calculated from the Malliken standard population analysis. The angle between the direction of attack (shown on top figure) and the Os–Cl bond is fimex at 90°.

As one can see from Fig. 8, the RHF approximation does not adequately describe the TS→P region of the reaction pathway. In this region, where a C–H bond is broken and a new Os–H and Os–C bonds are formed, the electron correlation is very important. The cause of an obvious discrepancy between the results of MP2 and DFT computations is not clear so far. Similar facts have already been noted in literature [55]. During analysis of the methane activation with C_pRh(CO), it was noted that the MP2 method predicts the reaction enthalpy $H=-18.8$ kcal/mol correlating well with the experimental value $\Delta H=-15$ kcal/mol. Meanwhile, the B3LYP approximation gave an extremely low value $\Delta H=-5.8$ kcal/mol [55]. Correspondingly, the MP2-calculated TS energy $E^{*}=-6.2$ kcal/mol is in accordance with the experimental value $E^{*}=-4.5$ kcal/mol. In its turn, DFT predicts $E^{*}=3.1$ kcal/mol that is above the energy of the starting reactants (positive value). That is why we used only the MP2 method for comparison of the reactivity of the isomers (Fig. 10).

Let us note the main properties of the reaction pathway shown in Fig. 8. Stability of the molecular complex (η^2-CH_4)-Str1 is significantly lower than that of (η^2-CH_4)-Str2, but the reaction goes through TS with an energy below that of the initial reactants until the methylhydride product is stabilized. Changes in the electron density on osmium ρ(Os) along the reaction coordinate *b* are also shown in Fig. 8. At $b=0$ (it corresponds to the methane removal out of the first coordination sphere of the complex) $\rho(\mathrm{Os})=0$. A formally two-electron oxidative addition increases the metal oxidation state by +2, in this case Os(II)→Os(IV). But the calculations show that the electron density ρ(Os) does not decrease in the direction of the reaction products. On the contrary, it increases. Furthermore, for Str1 the electron density reaches a maximum in P, where the C–H bond is

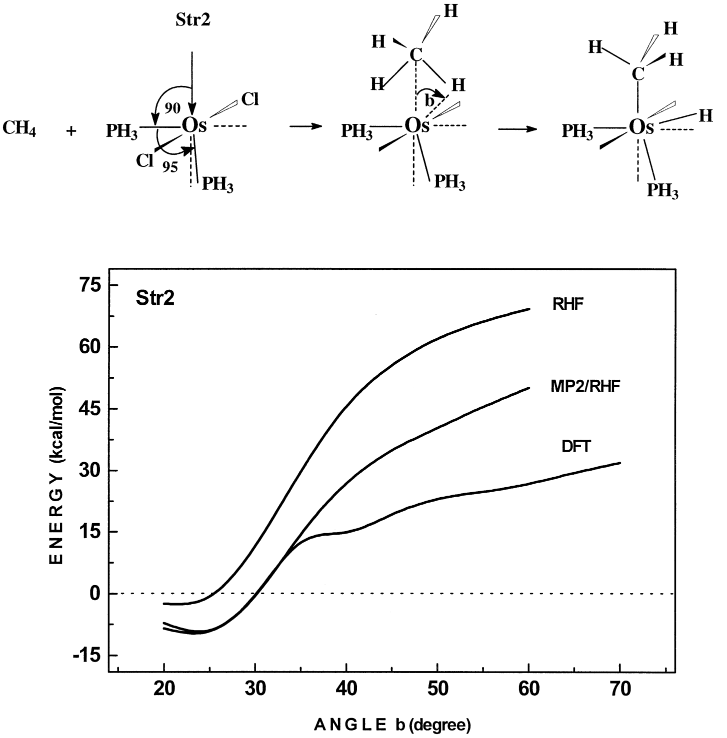


Fig. 9. The reaction path of the Str2+CH_4→(η^2-CH_4)-Str2 reaction along *b* coordination. The angle between the direction of attack (shown on top figure) and the Os–P bond is 90°.</fig

completely broken and two new bonds Os–C and Os–H are formed. This result shows how provisional the term "oxidation state" is for organometallic compounds. A redistribution of the electron density takes place so that a total electron stream is directed towards the metal.

The other isomer Str2 behaves in a completely different way in the methane oxidative addition reaction. The direction of the initial attack relative to the POsP plane in Str2 and the corresponding energetic profile as a function of *b* are shown in Fig. 9>. The starting region of the reaction pathway calculated in the MP2 and DFT approximations are close to each other or coincide. Stability of the molecular complex (η^2-CH_4)-Str2 in the MP2/RHF approximation is $\Delta E=-9.0$ kcal/mol. Full MP2 optimization gives $\Delta E=-12.0$ kcal/mol. As one can see from Fig. 9, the reaction pathway does not lead to methylhydride products. Thus, Str2 is inert to the C–H bond rupture.

Fig. 10 shows optimized structures of intermediates in stationary points (η^2-R), TS and P for methane oxidative addition to Str1. When comparing the reaction pathways of the two isomers, energy *E*(Str1)+*E*(CH_4) was set to be zero. A comparative characterization shows two clearly defined peculiarities. First, the isomer Strl is more active in the methane activation via two-electron oxidative addition. The other isomer Str2 forms a stable molecular complex (η^2-CH_4)-Str2 which is inert in this reaction. Thus, there is no direct correlation between the strength of the bifurcation bond [η^2-(C–H)]ML_n and the reactivity of the complex. Second, the mentioned reactivity of complexes Str1 and Str2 is an obstacle for experimental identification of methane σ complexes. Indeed, intermediates of type Str1 and Str2 are usually obtained by irradiation of stable complexes with high-energy photons. In this case it is difficult to realize the reaction Str2+CH_4 along the reaction pathway shown in Fig. 10 as an inevitable energy excess transforms σ-complex (η^2-CH_4)-Str2 into (η^2-CH_4)-Str1 with subsequent stabilization of the methylhydride product. We believe that this is the reason why methane σ

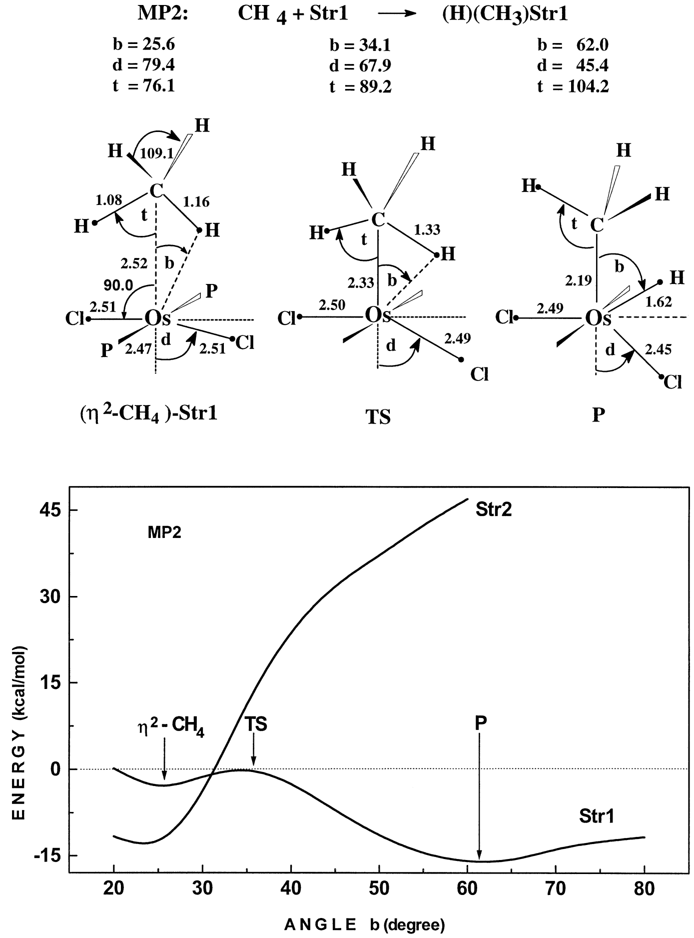


Fig. 10. Relative reaction ability of the Str1 and Str2 isomers in the reaction of *cis*-methane oxidative addition with the optimized structures in the (η^2-CH_4), TS and P stationary points for Str1 isomer at the MP2-approximation.

complexes with intermediates based on Os(η^2-arene) failed to be identified [63].

Nevertheless, the formation of a σ complex with methane is a necessary step in the initiation of the reaction along a synchronous reaction pathway. Results presented in Fig. 10 show that a synchronous reaction path (6) is energetically favorable for Str1:

$$\mathrm{Str1} + \mathrm{CH_4} \rightarrow (\eta^2\text{-}\mathrm{CH_4})\mathrm{Str1} \rightarrow \mathrm{TS} \rightarrow \mathrm{P} \qquad (6)$$

Four parameters – three angles *b*, *d* and *t* and Os–C bond – are subjected to the largest changes during reaction (6). The importance of σ-complex (η^2-CH_4)-M in the oxidative addition reaction is determined by the feasibility to localize one C–H bond of methane rather than by its stability. Such a localization is required for the following synchronization of two processes: C–H bond rupture and formation of two new bonds Os–H and Os–C on the same energetic surface. This energetic compensation effect is well illustrated by the TS structure. An increase of the C–H bond length to 1.33 Å is accompanied by the formation of the Os–C bond in TS with the bond length Os–C=2.33 Å. This results in a decrement of the *d* angle releasing the *cis*-site for the formation of another bond with Os–H=1.67 Å. The energetic compensation is almost complete so that the TS energy is lower ($E^*=-1.5$ kcal/mol) than that of the initial reactants. Reaction (6) results in the formation of a stable product with the reaction heat $\Delta Q=-16.6$ kcal/mol. In this product, angle $t=104.2°$ is close to tetrahedral,

CH_3 and H act as independent ligands forming a six-coordinate methylhydride complex $(H)(CH_3)OsCl_2(PH_3)_2$ with bond lengths of Os–C=2.19 Å and Os–H=1.62 Å.

Recently Ziegler and co-workers [64] have performed a DFT analysis of the methane carbonylation catalytic cycle. They found that *trans*-$RhCl(PH_3)_2$, which is less stable than *cis*-$RhCl(PH_3)_2$, is more active in the C–H bond activation. On the other hand, these 14-electron intermediates are more active than their 16-electron analog $Rh(CO)Cl(PH_3)_2$. The latter intermediate does not form a σ complex with methane. A RHF/MP2 calculation of the reaction pathway for methane oxidative addition to $Rh(CO)Cl(PH_3)_2$ gives activation energy $E^*=27$ kcal/mol and reaction heat $Q=+20$ kcal/mol [65]. The advantages of 14-electron complexes in the formation of σ complexes and the necessity for stable methylhydride complexes have been already noted [66,67].

Literature lacks reports about stable $(\eta^2\text{-}CH_4)$-Str2 type complexes. For their experimental identification, spectral characteristics of this complex and its deuterated forms may be useful. Table 1 summarizes computed vibrational frequencies of CH_4 and CD_4 adducts with Str2. During formation of a molecular σ-complex $(\eta^2\text{-}CH_4)$-Str2, three translational degrees of freedom of a gas phase methane molecule are transformed into a stretching vibration $\nu_z(Os\text{–}CH_4)$ and intermolecular deformational vibrations (ρ_x and ρ_y) of the molecule relative to POsP and ClOsCl planes. It can be seen from Table 1 that frequency ν(Os–C) of 249 cm^{-1} is in the region where one can speculate about a direct interaction of the carbon atom of methane with Os(II). Hence, the ν(Os–C) frequency is a direct characteristic of the methane σ-complex formation. Deuteration results in an insignificant decrease of the corresponding frequencies. Accordingly, in the complex three rotational degrees of freedom of gas phase methane are transformed into frozen rotational vibrations of the molecule. The corresponding frequencies in the deuterated state are lower by a factor of {$\sqrt{}$}2. As to fundamental frequencies, atten-

Table 1
Some frequencies (in cm^{-1}) of the σ methane complex $(\eta^2\text{-}CH_4)OsCl_2(PH_3)_2$ and its deuterated form in the MP2/LAN1DZ approximation

	$(\eta^2\text{-}CH_4)$-Str2	CH_4	$(\eta^2\text{-}CD_4)$-Str2	CD_4
$\delta_y(C\text{–}Os{<}Cl_2)$	66	Translation	69	Translation
$\delta_x(C\text{–}Os{<}P_2)$	160		128	
$\nu_z(Os\text{–}C)$	249		222	
$\rho_z(t,CH_4)$	357	Rotation	253	Rotation
$\rho_y(\omega,CH_4)$	360		253	
$\rho_x(\omega,CH_4)$	774		556	
$\delta_{as}(HCH)$	1284	1442	978	1091
$\delta_{as}(HCH)$	1426		1071	
$\delta_{as}(HCH)$	1521		1076	
$\delta_s(HCH)$	1525	1620	1137	1146
$\delta_s(HCH)$	1649		1169	
$\nu_s(C\text{–}H)$	2887	3063	2060	2167
$\nu_{as}(C\text{–}H)$	3004	3194	2226	2363
$\nu_{as}(C\text{–}H)$	3151		2306	
$\nu_{as}(C\text{–}H)$	3226		2392	

Symmetric (s) and asymmetric (as) stretch modes (ν) and intramolecular modes (δ) are classified relative to the $Os(Cl)_2$ plane. For types of intermolecular modes (ρ) the following definitions are used: ω – fan rotation; t – rotation and deformation of molecule. Polarization of frequencies corresponding to rotational and translational degrees of freedom of the isolated gas phase methane are designated as x, y and z.

tion should be paid to a significant decrease in the ν_s(C–H) frequency of the symmetric stretching vibration of a C–H bond in the σ complex. This is caused by an electron transfer from methane σ(C–H) bond to Os(II) during the (η^2-CH_4)-Str2 formation.

4. Conclusion

The results obtained bring us to a conclusion that either a methylhydride complex with a structure similar to hydride complexes of $OsH_2Cl_2(PR_3)_2$ type [32] or a molecular σ-complex (η^2-CH_4)-Str2 with a structure as shown in Fig. 5(2) is the most stable product of methane reaction with complex **2**. Methane adduct formation with transition metal complexes is necessary, first of all, for initiation of a synchronous reaction. But stability of the complex (η^2-CH_4)–M should not be used as a reactivity characteristic of the corresponding intermediate. The calculations show an exceptional importance of a theoretical analysis of isomeric structures for determination of the catalytically active site.

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