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Structure of methane comlexes according to the data of experimental and theoretical investigations

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Abstract. The results of experimental and theoretical studies of the structures of methane complexes with neutral metal atoms, metal ions M^+ and molecular fragments ML_n are considered and generalised. The influence of the charge and electronic configuration of the central atom and the nature of stabilising ligands L on the mode of coordination of methane in the complexes is analysed. The data from theoretical calculations of the structures of methane complexes are compared with the results of structural studies of some classes of model compounds, namely, borane complexes $M(CO)_5 \cdot BH_3L$ (M = Cr, Mo, W) and tetrahydroborate complexes $ML_n(BH_4)_m$ containing BH_4^- anions as ligands. Some rules determining the mode of methane coordination in the complexes are elucidated and assumptions concerning the dependence of the mode of methane coordination on the electronic configuration of the central atom are made. The bibliography includes 173 references.

I. Introduction

The development of methods for mild selective catalytic functionalisation of saturated hydrocarbons (alkanes) is a highly important problem having great potential in organometallic chemistry. As D R H Barton said figuratively,[1] the solution of this problem is the dearest chemists' wish of the last few decades, as desired and unattainable as the Holy Grail for medieval knights. The key stage in alkane functionalisation is the activation of the chemically inert C – H or C – C bonds by metal complexes. Experimental data on the reactions of metal complexes with hydrocarbons have been considered in detail in a number of reviews and monographs (see, for example, Refs 2–12).

Numerous spectroscopic and kinetic data indicate that the addition of metal complexes to C – H bonds in saturated hydrocarbons as well as the reverse elimination of alkanes give intermediate alkane complexes of the corresponding metals containing one or several alkane molecules.[13–15] The existence of such complexes is now beyond doubt. Some of them have been detected by spectroscopy [for example, $M(CO)_5$(alkane) complexes, where M = Cr, Mo, W].[3] Recently, the intermediate formation of alkane complexes has been observed directly by femtosecond IR spectroscopy during activation of the C – H bonds in alkanes both in low-temperature matrices[16] and in solutions at usual temperatures.[17] The first example of direct NMR monitoring of the formation of an alkane complex of a transition metal, $CpRe(CO)_2(C_5H_{10}$-cyclo), in solution at $-80\,^{\circ}C$ was reported.[18] Similar methane complexes have not been detected experimentally in solutions.[5]

Those involved in experimental investigations of the structures of metal complexes with alkanes are faced with considerable difficulties because these complexes have not been isolated in a pure state. The existing data on these structures were mainly deduced from the results of quantum-chemical calculations.

Methane complexes attract particular attention of researchers because methane is the most naturally abundant hydrocarbon widely applied as an energy carrier and is promising as a cheap, readily available potential raw material for the chemical industry. Catalytic reforming of methane to methanol has been mentioned recently among the ten most important goals of catalysis.[19] Meanwhile, methane is the least reactive hydrocarbon; therefore, its functionalisation is a particularly difficult task.

Of great theoretical interest are items concerning the modes of methane coordination in metal complexes and factors dictating the predominance of one or another coordination mode. A large number of publications have been devoted to the structures of methane complexes with neutral metal atoms, metal ions M^+ and molecular fragments ML_n. According to quantum-chemical calculations, there exist a diversity of possible modes of methane coordination and the difference between the energies of various structures is slight, which is indicative of structurally non-rigid compounds. Therefore, determination of the most stable structure is ambiguous and depends on the particular system (complex) as well as on the calculation method and the basis set of functions used. This ambiguity is inherent in the calculations for any of the three modes of methane complexes, *i.e.*, those with neutral metal atoms, cations and molecular fragments. The lack of uniqueness of calculation results hampers elucidation of the regular structural features of methane complexes. In this connection, there appears to be a need to compare the theoretical data for methane complexes with experimental data obtained for complexes of some species structurally similar and isoelectronic to methane.

This review considers the results of experimental and theoretical studies of the structures of methane complexes with neutral metal atoms, cations M^+ and molecular fragments ML_n. The effects of the charge and the electronic configuration of the central atom and the nature of the stabilising ligands L on the mode of methane coordination in the complexes are analysed. The calcu-

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lated data on the structures of methane complexes are compared with the results of structural investigations of some classes of model compounds — borane complexes $M(CO)_5 \cdot BH_3L$ (M = Cr, Mo, W) and tetrahydroborate complexes $ML_n(BH_4)_m$ in which the ligands are represented by the BH_4^- anions isoelectronic to methane and resembling methane in geometry. Some features determining the mode of methane coordination in the complexes are elucidated and suggestions concerning the dependence of the methane coordination mode on the electronic configuration of the central atom are made. The review covers papers published up to 2001 inclusively and some publications of 2002.

The following designations are used for the modes of methane coordination in the complexes. Compounds in which methane is linked to the central metal atom through one hydrogen bridge [$MHCH_3$ (**A**), the $M-H_b-C$ angle is $\sim 180^\circ$, the CH_4 tetrahedron is coordinated by a vertex] are designated as η^1-complexes (Fig. 1). Compounds where methane is bound to the central atom by two [MH_2CH_2 (**B**), the CH_4 tetrahedron is coordinated by an edge] or three [MH_3CH (**C**), the $M-C-H_t$ angle is $\sim 180^\circ$, the CH_4 is coordinated by a face] hydrogen bridges are designated as η^2- and η^3-complexes, respectively. Compounds with one bent hydrogen bridge [$MHCH_3$ (**D** and **E**), the $M-H_b-C$ angle is much smaller than 180°] are referred to as η^1_2- and η^1_3-complexes. The complexes **D** and **E** are often designated in the literature by η^2-C,H; however, this designation does not provide a strict description of the structure, because these complexes can be formed upon distortion of either the η^2- or η^3-structure. Therefore, for more exact descriptions of the structures of these complexes, here we call them η^1_2 and η^1_3.

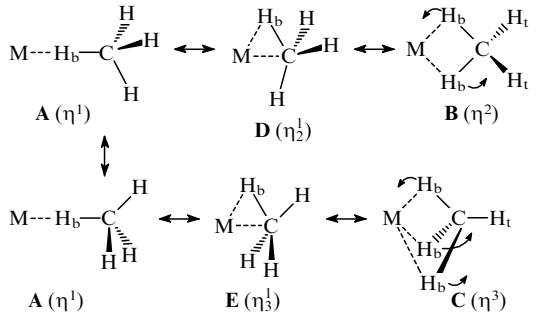


Figure 1. Types of methane coordination in the complexes; η^1 is mono-; η^2 is bi-; and η^3 is tridentate coordination of methane; η^1_2 and η^1_3 are intermediate modes of coordination; H_b and H_t are bridging and terminal hydrogen atoms, respectively.

The accepted notation for the quantum-chemical methods and the software used is given in the Supplement.

II. Methane complexes with neutral metal atoms

The data on the structures of methane complexes with neutral metal atoms are relatively scarce. The formation of the $Co(CH_4)$ complex was detected experimentally by IR spectroscopy upon irradiation of the CH_3CoH complex with light with $\lambda > 400$ nm in a low-temperature argon matrix. This reaction is reversible; on exposure to UV radiation, the $Co(CH_4)$ complex is converted again into CH_3CoH. After the formation of the $Co(CH_4)$ complex, the triply degenerate absorption band of methane $\nu_4(f_2)$ located at 1305.3 cm^{-1} was split into two peaks. This allowed the authors to suggest that this complex has C_{3v} symmetry. The most likely coordination of methane in this complex is tridentate — $Co(\eta^3\text{-}CH_4)$.[20]

Similar complexes have also been obtained for iron atoms in a methane matrix.[21] Molecular orbital calculations using the effective Hamiltonian proposed by Anderson (see Ref. 22 and references therein) have shown that Fe atoms in the ground state ($^5D,3d^64s^2$) are able to form complexes with methane. A tridentate coordination of methane is most probable for these complexes. The energy of the Fe—C bond is 11 kcal mol^{-1} and the Fe–C distance is 3.4 Å. The oxidative addition of methane to an iron atom is hampered due to the mutual repulsion of the closed electron shells of the methane C—H bonds and the 4s electrons of iron atoms.[22]

Experimental studies showed that none of the neutral atoms of 3d metals in the ground state reacts with alkanes in the gas phase at 300 K. In the case of 4d-metal atoms, only palladium atoms in the ground state ($^1S,4d^{10}$) form complexes with higher alkanes with a binding energy of not less than 8 kcal mol^{-1} (see Ref. 23). However, a palladium complex with methane is not formed under these conditions, which points to a lower energy of the Pd–C bond. The results of *ab initio* self-consistent field (SCF)[24] calculations of the interaction between a palladium atom and methane, which were carried out using the minimum basis set of gaussian orbitals (LCGO) before the relevant experiments, are at variance with experimental data.[23] According to calculations,[24] the palladium atom forms a methane complex with monodentate coordination of the methane ligand, $Pd(\eta^1\text{-}CH_4)$; the bond energy is 7–8 kcal mol^{-1}.

In a series of publications,[25–30] Blomberg and coworkers studied theoretically the activation of the C—H bonds in methane by 3d-, 4d- and 5d-metal atoms.† A modified coupled pair functional (MCPF) study of the reaction of methane with 4d metals ranging from yttrium to palladium showed[27] that only palladium in the ground state ($^1S,4d^{10}$) is able to be complexed with methane to give a $Pd(\eta^2\text{-}CH_4)$ type complex. The stabilisation energy of this complex with respect to the initial reactants is 4 kcal mol^{-1}. Ruthenium and rhodium form complexes with methane only in the low-spin excited state ($^3F,4d^75s^1$ and $^2D,4d^9$, respectively), the stabilisation energies of these complexes relative to the excited metal atoms being 12 and 9 kcal mol^{-1}, respectively. It was noted[27] that the potential energy surface (PES) minima corresponding to metal complexes with methane can also be found for other 4d-metal atoms, but the metal···carbon distances in these complexes are very long (stabilisation energies do not exceed 2 kcal mol^{-1}). A MCPF study of the interaction of rhodium and niobium atoms with methane showed that rhodium in the low-spin excited state ($^2D,4d^9$) is inserted almost without a barrier into a C—H bond of methane to give the $HRhCH_3$ complex.[31] The $Rh(\eta^2\text{-}CH_4)$ complex is formed as an intermediate. Unlike rhodium, niobium does not react with methane.[26]

Experimental and theoretical investigations of the reactions of alkanes with transition metal atoms in the ground electronic state have shown that rhodium and palladium‡ are the only 4d metals able to react with ethane and higher alkanes at 300 K.[28]

According to experimental results, among the transition 5d metals in the ground electronic state, only neutral platinum atoms can activate methane in the gas phase at 300 K.[29] The results of theoretical investigations [using the density functional theory (DFT) with Becke's exchange functional and the Lee–Yang–Parr correlation functional (B3LYP) with parametrised configuration interactions (PCI-80) and *ab initio* calculations][30] of the activation of methane C—H bonds by transition 3d-, 4d- and 5d-metal atoms are consistent with experimental data. The calculations showed that platinum and rhodium atoms are capable of activating the C—H bonds in methane but only platinum can participate in the further formation of the $Pt=CH_2$ carbene, which is needed for experimental monitoring of the reaction.[29]

† It is noteworthy that calculations of the M—C bond energies for all metals were carried out using the geometric parameters optimised for the rhodium complex $Rh(\eta^2\text{-}CH_4)$, *i.e.*, the influence of the electronic configuration of the central atom on the mode of coordination of the methane ligand was not taken into account.

‡ Palladium is unique due to its ability to form η^2-complexes with linear alkanes (except for methane), while rhodium is able to dehydrate higher alkanes (but not methane).

Experimental and theoretical (MCPF technique) research of gas-phase reactions of iridium and platinum with n-alkanes C_nH_{2n+2} (n = 3, 4) demonstrated that the potential barrier to the reaction between a platinum atom and propane or butane does not exceed 1–2 kcal mol^{-1}, while iridium atoms are inert towards these alkanes.[29] Thus, the chemical behaviour of atomic iridium in the gas phase differs appreciably from the behaviour of iridium complexes in solutions; many of these complexes are able to react with alkanes.[5]

Density functional theory calculations in the PCI-80 approximation have shown [30] that the inertness of iridium atoms is due to the great promotion energy between the chemically inert ground state ($5d^76s^2$) and the excited state ($5d^86s^1$). In the excited state the iridium atom reacts with methane to give a molecular adduct with a bond energy of 2 kcal mol^{-1}. Attempts to calculate the geometric parameters of the complex formed by the iridium atom with methane by *ab initio* SCF methods in the MCPF approximation and by the second-order Møller–Plesset perturbation theory (MP2) have not met with success.

The platinum atom in the ground state (^{3}D,$5d^96s^1$) forms a weak complex with methane (the Pt–C distance is 3.61 Å, the bond energy is 2.1 kcal mol^{-1}).[30] The mode of coordination of methane in this complex was not indicated. In the case of the low-spin excited state of platinum (^{1}S,$5d^{10}$), MP2 calculations predict the formation of an η^2-complex with a Pt–C distance of 2.38 Å and a binding energy of 19.1 kcal mol^{-1}. However, when the geometry of the singlet Pt(η^2-CH_4) complex was optimised by more effective methods, no minimum was found on the PES.[30]

The activation of methane by 5d-metal atoms (Re, Os, Ir and Pt) has been studied by *ab initio* methods using the relativistic effective core potentials (RECP) and taking into account electron correlation.[32] It was found that rhenium atoms in the ground state (^{6}S,$5d^56s^2$) are highly inert with respect to methane, compared with other transition 5d metals, due to the presence of a half-filled 5d shell. Osmium in the ground state (^{5}D,$5d^66s^2$) is also inert toward methane; however, the energy barrier to the reaction is much lower for osmium than for rhenium. Iridium atoms in the excited state (^{2}P), like platinum atoms in the ground (^{3}D,$5d^96s^1$) and low-spin (^{1}S,$5d^{10}$) states, are inserted into the C–H bond of methane to give $HMCH_3$ complexes.

III. Methane complexes with bare metal ions

It was found in 1979 that transition metal cations (Ti^+, Fe^+, Co^+, Ni^+) are able to react with alkanes (butane and isobutane) in the gas phase.[33] This discovery has triggered intensive research into gas-phase reactions of transition metal cations M^+ with alkanes and the carbene complexes MCH_2^+ with hydrogen, which is still being continued. The purpose of the researches mentioned above is to elucidate the mechanism of activation of the H–H, C–H, and C–C bonds by metal cations. According to the obtained results, metal ions are markedly more reactive toward alkanes than neutral atoms. A typical gas-phase reaction of metal ions not stabilised by ligands is the dehydrogenation of alkanes C_nH_{2n+2} ($n \geqslant 2$). Methane dehydrogenation has been much less studied. None of the 3d transition metal ions in the ground state is able to perform exothermic dehydrogenation of methane. Of the 4d-metal ions, only Zr^+ exhibits capacity for methane dehydrogenation in the ground state. As regards 5d-metal ions, the fast successive reactions

$$M^+ \xrightarrow[-H_2]{CH_4} MCH_2^+ \xrightarrow[-H_2]{CH_4} \cdots \xrightarrow[-H_2]{CH_4} MC_nH_{2n}^+$$

have been observed for Ta^+, W^+, Os^+, Ir^+, and Pt^+ (iridium and platinum atoms are most reactive in this reaction); La^+, Hf^+, Re^+ and Au^+ ions did not dehydrogenate methane under similar conditions.[34] The reactivity of these ions depends on both the electronic configuration and the spin state.

Meanwhile, many ions of both transition and non-transition metals are able to form ion–molecular complexes $M(CH_4)_n^+$ with methane. The properties of these complexes, resulting from association of metal cations with one or more CH_4 molecules, have been studied experimentally using various methods, in particular, electron impact, photoionisation, photoelectron-photoion coincidence spectroscopy, standard or quadrupole mass spectrometry, *etc*. The $Mg(CH_4)^+$, $V(CH_4)^+$, $Fe(CH_4)_n^+$, $Co(CH_4)_n^+$ (n = 1–4), and $Pt(CH_4)_n^+$ (n = 1, 2) complexes have been studied experimentally. Under multicollision conditions at 300 K and a helium pressure of 0.75 mmHg, 3d-metal ions react with methane to form complexes with the composition $M(CH_4)_n^+$ [M = Sc^+ (n = 1–3), Ti^+ (n = 1–5), V^+ (n = 1–4), Cr^+ (n = 1, 2), Fe^+ (n = 1–3), Co^+ (n = 1–3), Ni^+ (n = 1, 2), Cu^+ (n = 1, 2), and Zn^+ (n = 1)], the structures of which have not been determined.[35] According to experimental results,[35] the energy of methane binding in these complexes exceeds 10 kcal mol^{-1}. An exception is the manganese ion, which does not form complexes with methane under these conditions.

The alkane complexes of alkali metal cations (sodium and potassium), which are similar in size to transition metal ions, have not been observed experimentally. This attests to an important role of d orbitals in the stabilisation of metal complexes of alkanes. The geometric parameters and bond energies of complexes formed by methane with lithium, sodium, magnesium, scandium, titanium, vanadium, chromium, iron, cobalt, copper, 4d metals, tantalum, iridium and platinum were calculated by quantum-chemical methods. Some of the results of experimental and theoretical investigations of the ion–molecular $M(CH_4)^+$ complexes are considered below.

1. Non-transition metal ions

The interaction of methane with the lithium cation has been studied theoretically.[36–38] The geometry of the $Li(CH_4)^+$ complex was optimised by the restricted Hartree–Fock (RHF) method using the SKBJ effective core potential (relativistic compact effective core potential and the Stevens, Basch, Krauss and Jasien shared-exponent basis set). The complex Li(η^3-CH_4)$^+$ with C_{3v} symmetry was found to correspond to the minimum on the PES. The ion–ligand interaction in this complex was assumed to be mainly of the ion–dipole nature.[36]

The potential energy surface of the $Li(CH_4)^+$ complex was studied within the framework of the *ab initio* Hartree–Fock method.[37] The tridentate coordination of methane in the Li(η^3-CH_4)$^+$ complex with a binding energy of 8.2 kcal mol^{-1} was found to be energetically the most favourable. The researchers believe [37] that this binding energy is large enough to enable the existence of this ion in an isolated state in molecular beams or inert matrices. The potential barrier to the transition from the η^3- to η^2-complex is low (0.5 kcal mol^{-1}), indicating structural non-rigidity of the $Li(CH_4)^+$ complex. Analysis of the Mulliken populations showed that the Li^+ cation perturbs only slightly the electron density of the CH_4 ligand. The electron density (expressed in fractions of the electron charge) on hydrogen atoms decreases upon coordination by 0.06 (H_b) and 0.13 e (H_t), and that on the C atom increases by 0.17 e. The overlap populations Q(Li–H_b) and Q(Li–C) are fairly low (0.03 and 0.16 e, respectively), pointing to weak covalent interaction of the Li^+ ion with the ligand. It should be noted that in the study cited,[37] the calculations were carried out in the approximation of a rigid tetrahedral CH_4 core with a fixed C–H distance (1.096 Å).

Charkin *et al*.[38] used the *ab initio* QCISD(T)/6-31G**//MP2/6-31G* + ZPE(MP2/6-31G*) calculation methods § to represent

§ Here QCISD(T) means the single and double quadratic configuration interaction with an estimation of triple excitations by a perturbation method; 6-31G** is the Pople basis set extended by d- and p-polarisation functions with the 1s-AO being approximated by six and the 2s,2p-AO, by four gaussian type functions grouped in the (3,1) form; ZPE is the zero-point energy.

fragments of the potential energy surfaces for the $Li(CH_4)^+$ and $Na(CH_4)^+$ ion–molecular complexes in the vicinity of formation of mono-, bi- and tridentate structures. It was found that the global minimum on the $M(CH_4)^+$ PES (M = Li, Na) corresponds to a tridentate structure, whereas a bidentate structure is matched by a maximum connecting the two nearest minima in the potential curve. The calculated energies for cation elimination from $M(CH_4)^+$ complexes (M = Li, Na) do not exceed 10–12 kcal mol^{-1}. However, they are sufficiently high to ensure the existence of these complexes in the isolated state or in inert matrices. The $Li(\eta^2\text{-}CH_4)^+$ and $Li(\eta^1\text{-}CH_4)^+$ complexes are 1.6 and 6.5 kcal mol^{-1} less stable than $Li(\eta^3\text{-}CH_4)^+$, while the corresponding complexes $Na(\eta^2\text{-}CH_4)^+$ and $Na(\eta^1\text{-}CH_4)^+$ are 0.6 and 3.4 kcal mol^{-1} less stable than $Na(\eta^3\text{-}CH_4)^+$.

For the $Mg(CH_4)^+$ complex, the geometric parameters and the energies of binding of the Mg^+ ion in the ground and excited electronic states to the methane ligand were calculated theoretically. The tridentate coordination of methane to form $Mg(\eta^3\text{-}CH_4)^+$ was found to be energetically the most favourable for the Mg^+ ion in the ground state (^{2}S,3s^1); the same geometric configuration corresponds to a minimum on the system PES. The Mg–CH_4 binding energy in this complex is 4.0–7.6 kcal mol^{-1} (see Ref. 39). The Mg^+ and CH_4 species in this complex are weakly bound by electrostatic forces. The methane ligand differs slightly from non-coordinated methane in geometric parameters, in particular, the H–C–H angles change by about 0.5° and the C–H distances, by less than 0.01 Å. Analysis showed that in the case of the Mg^+ ion, η^3-coordination is preferred for methane over η^2- or η^1-coordination, as this decreases the repulsion between the 3s^1 electron of the magnesium ion and the C–H-bond electrons of the methane molecule. This results in a shorter M–C bond and, hence, enhances the electrostatic interaction between the species. When the Mg^+ s electron passes to the pσ orbital of the complex, the methane ligand in $Mg(CH_4)^+$ retains the η^3-coordination, while upon transition of the s electron to the pπ orbital, the coordination of the methane ligand changes to a bidentate one. The structure of the $Mg(CH_4)^+$ complex has been studied experimentally using photoelectron spectroscopy with a reflectron time-of-flight mass spectrometer.[40] The results of calculations [39] are in good agreement with the experimental data.

2. Transition metal ions

Mass-spectrometric studies of the interaction of the Sc^+ ion with alkanes in the gas phase have shown unique properties of this ion compared to other 3d-metal ions. With butane or higher alkanes, this ion forms $Sc(C_nH_{2n+2})_m^+$ complexes (presumably, dialkylscandium ions), which have not been detected for other 3d-metal ions.[41] The reaction of Sc^+ with methane has been studied theoretically.[42,43] The $Sc^+ + CH_4$ and $ScCH_2^+ + H_2$ reactions were investigated by the complete active space self-consistent field (CASSCF) method and by the multideterminant configuration interaction method with single and double excitations using the wave function obtained by CASSCF (MR-SDCI-CASSCF).[42] The Sc^+ ion in the ground state (^{3}D,3d^{1}4s^1) reacts with methane to form the $Sc(\eta^3\text{-}CH_4)^+$ complex with a tridentate methane coordination and with an Sc–CH_4 binding energy of 15.1 kcal mol^{-1}. After the formation of this complex, the reaction is terminated due to the high energy barrier to its conversion into other isomeric complexes. In the case of the Sc^+ ion in the first excited state (^{1}D,3d^{1}4s^1), the bidentate coordination of methane is preferred. The stabilisation energy relative to the reactants is 13.3 kcal mol^{-1} (the stabilisation energy with respect to the ground state of the Sc^+ ion is 5 kcal mol^{-1}).[42] The reaction of methane with the Sc^+ cation was also studied by the density functional approach in the B3LYP approximation.[43] It was found that the Sc^+ cation both in the ground (^{3}D,3d^{1}4s^1) and the first excited state (^{1}D,3d^{1}4s^1) forms tridentate methane complexes $Sc(\eta^3\text{-}CH_4)^+$ due to the ion–dipole interaction. The Sc–CH_4 bond energies in these complexes are 15.7 and 8.4 kcal mol^{-1}, respectively (relative to the starting reactants).

A mass-spectrometric study [44] of the reaction of titanium ions with excess methane in the gas phase at 300 K has shown that under these conditions, the Ti^+ ion in the ground state (^{4}F,3d^{2}4s^1) is able to add up to three methane molecules. The binding energy for the first two methane molecules is ~17 kcal mol^{-1}, while that for the third molecule is 6.6 kcal mol^{-1} (see Ref. 44). After the addition of two methane molecules, activation of C–H bonds starts to compete with the addition reaction; in this case, the gas phase contains simultaneously the $Ti(CH_4)_3^+$, $(CH_4)_2Ti(H).(CH_3)^+$ and $(CH_4)_2Ti^+{=}CH_2$ ions. In the researchers' opinion,[44] the increase in the methane binding energy in the insertion products with respect to its binding energy in the corresponding $Ti(CH_4)_n^+$ complexes is the driving force of activation. The discovered reaction mechanism was called 'cluster-assisted σ-bond activation'.

The reaction of the excited titanium ion Ti^+(^{2}F,3d^{2}4s^1) with CH_4 has been studied by the MP2/6-31G** method taking account of electron correlation and using the Hay–Wadt effective core potentials.[45] It was found that the first stage represents the formation of the intermediate $Ti(CH_4)^+$ complex, which is followed by hydrogen migration from methane to Ti^+ giving rise to an insertion product, $HTiCH_3^+$. The calculation showed that the tridentate (η^3, C_{3v}) coordination of methane with a binding energy of 73.1 kcal mol^{-1} is most favourable for the Ti^+(^{2}F,3d^{2}4s^1) ion. The $Ti(\eta^3\text{-}CH_4)^+$ complex corresponds to a deep energy minimum on the PES with respect to the starting reactants and to the transition state of the oxidative addition.[45]

More recent calculations [46] by the DFT method in the B3LYP approximation also confirm the predominance of the tridentate coordination of methane to the excited Ti^+(^{2}F,3d^{2}4s^1) ion; however, according to these results, the binding energy of methane to the titanium ion is only 21.81 kcal mol^{-1} relative to the reactants (8.89 kcal mol^{-1} with respect to the ground state of the Ti^+ ion). The reaction of methane with the Ti^+ ion in the ground state (^{4}F,3d^{2}4s^1) also yields the $Ti(\eta^3\text{-}CH_4)^+$ complex,[46] the Ti–CH_4 bond energy (22.21 kcal mol^{-1}) being roughly equal to that in a similar complex with the excited Ti^+(^{2}F,3d^{2}4s^1) ion. These data are more consistent with the results of experimental studies [44] than the data obtained earlier.[45]

Study of the gas-phase reaction between vanadium ions and methane by mass spectrometry [47] has shown that V^+ ions in the ground quintet state (^{5}D,3d^4) do not react with methane. Transition of the V^+ ion into the triplet excited state (^{3}F,3d^{3}4s^1) results in a substantial increase in its reactivity. The weakly bound $V(CH_4)^+$ complex was prepared by ultrasonic expansion of the vanadium ion plasma generated by laser radiation with the use of helium containing 1% of methane as the carrier gas. The isolated $V(CH_4)^+$ ion was studied by resonance single-photon photodissociation spectroscopy.[48] The $3d^4 \rightarrow 3d^34s^1$ electron transition corresponding to the excitation of the central metal atom in the electrostatically bound $V(CH_4)^+$ complex was observed in this experiment. The binding energy between the V^+ ion in the ground state (^{5}D,3d^4) and methane is ~15 kcal mol^{-1}. This differs little from the calculated Nb–C bond energy (11.8 kcal mol^{-1}) in the $Nb(\eta^2\text{-}CH_4)^+$ complex.[49] However, the researchers note that C_{2v} symmetry cannot be reliably ascribed to the $V(CH_4)^+$ complex in the ground state without full analysis of the rotation spectrum. The binding energy between the excited V^+(3d^{3}4s^1) ion and methane amounts to 8.3 kcal mol^{-1}. The decrease in the V^+–CH_4 binding energy taking place as vanadium passes from the ground state to the excited state is assumed [48] to be due to the mutual repulsion of the electron in the 4s shell of the excited ion and the electrons of the methane ligand.

The results of density functional calculations in the B3LYP approximation for the $V(CH_4)^+$ complex are consistent with the assumed bidentate coordination of methane by the V^+ ion in the ground state (^{5}D,3d^4). The calculated energy of the bond between methane and V^+ in this complex (15.09 kcal mol^{-1}) is in good agreement with the experimental value (~15 kcal mol^{-1}). The

excited vanadium ion $V^+(^3F,3d^34s^1)$ was found [46] to form a complex with tridentate coordination of the methane ligand.

Ab initio quantum-chemical calculations with allowance for electron correlation (MCPF method) of the insertion of single-charged 4d-metal ions into a methane C–H bond have shown [49] that all these ions are capable of forming complexes with methane, the ion–ligand binding energy being lower for ions with an outer s shell or d^5 shell than for d^4, d^7, d^8 and d^9 ions.[49] It should be noted that these calculations were carried out for a fixed η^2-geometry of methane complexes, *i.e.*, the influence of the electronic configuration of a particular ion on the geometry of the complex was neglected.[49] As far as we know, experimental data concerning the binding energies in the methane complexes with 4d-metal ions are missing.

The activation of the methane C–H bonds by the Ta^+ cation observed experimentally in the gas phase [2, 50, 51] has been studied by the density functional approach in the B3LYP approximation.[52] This process was found to consist of several steps. The first step is the formation of the $Ta(CH_4)^+$ complex with electrostatic binding; this is followed by Ta^+ insertion into the C–H bond to give the dihydride $H_2TaCH_2^+$. A slightly distorted η^3-coordination of methane is preferred for the Ta^+ ion in the ground state ($^5F,5d^36s^1$); the Ta^+-CH_4 binding energy is 12 kcal mol^{-1}. The interaction between Ta^+ and methane is mainly electrostatic. The methane ligand almost retains the geometry of the free molecule (the length of one C–H_b bridging bond is increased by 0.003 Å). The Ta^+ ion does not lie on the C–H_t axis but is shifted somewhat toward one of the H_b atoms (the Ta–C–H_{1b} angle equals 73.02°).[52]

Recent results obtained by density functional calculations in the B3LYP approximation for the reaction of methane with the Cr^+ ion in the ground ($^6S,3d^5$) and excited ($^4D,3d^44s^1$) states attest to a tridentate methane coordination in the resulting complexes.[46] The binding energies between methane and chromium ions in the ground and excited states are equal to 13.1 and 29.31 kcal mol^{-1}, respectively, relative to the reactants.

The reaction of methane with the Fe^+ ion (in the gas phase) has been studied in more detail.[53–56] The ion–ligand binding energy for the $Fe(CH_4)^+$ complex was determined experimentally and calculated theoretically. The collision-induced dissociation (CID) of $Fe(CH_4)_n^+$ ions ($n = 1-4$) was studied by mass spectrometry.[53] The dissociation energy of the $Fe(CH_4)^+$ complex was found to be 13.7 ± 0.8 kcal mol^{-1}. These results prompted the conclusion that the Fe^+ ion in $Fe(CH_4)^+$ has a sextet ground state ($^6D,3d^64s^1$).[53] In a mass-spectrometric investigation [54] of the $FeCH_2^+ + D_2$ and $Fe^+(^6D,^4F) + CD_4$ reactions, the bond dissociation energy was found to be $D_0(Fe^+-CH_4) = 13.62$ kcal mol^{-1}; this is consistent with the value $D_e(Fe^+-CH_4) = 13 \pm 1$ kcal mol^{-1}, determined by the MCPF calculations.[54]

The CASSCF and MR-SDCI-CASSCF methods were employed to study the PES of the $FeCH_2^+ + H_2$ reaction; the formation of the ion–molecular $Fe(CH_4)^+$ complex was established.[55] The $Fe(CH_4)^+$ complex with a binding energy of ~16 kcal mol^{-1} is stable with respect to dissociation into $Fe^+(^6D,3d^64s^1)$ and CH_4. The back reaction, $Fe^+ + CH_4$, gives only one product, $Fe(CH_4)^+$, at moderate temperatures. The calculations showed that the structures with C_{2v} (η^2) and C_{3v} (η^3) symmetry for $Fe(CH_4)^+$ are almost degenerate (the energy difference between these two complexes is equal to 0.05–0.17 kcal mol^{-1}). Thus, $Fe(CH_4)^+$ can be considered to be a structurally non-rigid system in which the Fe^+ ion is almost free to migrate around the CH_4 molecule giving structures with the symmetry

$$C_{2v} \rightleftharpoons C_{3v} \rightleftharpoons C_{2v} \rightleftharpoons C_{3v} \ldots$$

The main forces that stabilise the $Fe(CH_4)^+$ complex are the dispersion interaction and the 'ion–induced dipole' interaction. Study of the back reaction $Fe^+ + CH_4$ demonstrated that Fe^+ in the ground state ($^6D,3d^64s^1$) forms the ion–molecular $Fe(CH_4)^+$ complex in the sextet state ($^6A_2$) with a binding energy of 15.5 kcal mol^{-1}, which does not participate in subsequent transformations.

The structure in which methane is coordinated to Fe^+ by only one hydrogen atom (η^1) is energetically less favorable than the η^2- or η^3-structures.[55] More recent calculations [56] by the DFT method in the B3LYP approximation point to a η^2-coordination of methane in the $Fe(CH_4)^+$ complex; however, the values for the Fe^+-CH_4 binding energy obtained in this study do not correspond to experimental results.

Of all the methane–bare metal ion systems studied in the gas phase, the CH_4-Co^+ system has been studied in most detail.[57–62] The temperature-dependent equilibria of gas-phase reactions were investigated by mass spectrometry; the ion–ligand binding energies in the $Co(CH_4)_n^+$ complexes ($n = 1-4$) were determined. In the case of $Co(CH_4)^+$, the dissociation energy is equal to 22.9 ± 0.7 kcal mol^{-1} (see Ref. 57).

According to MCPF calculations with electron correlation,[58] methane is coordinated by the Co^+ ion through two or three hydrogen atoms, the complex with η^2-coordination being 1.3 kcal mol^{-1} more stable than the complex with η^3-coordination. The dissociation energy of the $Co(\eta^2\text{-}CH_4)^+$ complex found by these calculations is 21.4 kcal mol^{-1}. The Co^+ ion in this complex has a d^8 electron configuration. The researchers noted a substantial change in the methane geometry in the η^2-complex compared to free methane, in particular, the C–H_b bond lengths increase by 0.016 Å and the Co–H_b–C angle increases by 10.3°. The C–H_t bond lengths change slightly. This change in the methane geometry diminishes the energy of the complex by 2.9 kcal mol^{-1}. In the η^3-complex, the methane geometry changes to a lesser extent; consequently, the bond strength increases by only 1.1 kcal mol^{-1} (see Ref. 58). In the researchers' opinion,[58] the strength of the Co^+-CH_4 bond is mainly determined by the charge-induced polarisation. However, if the contribution of only this effect is taken into account, the η^3-conformation should be somewhat more stable than the η^2-conformation (18.2 and 17.7 kcal mol^{-1}, respectively). When other factors such as electron repulsion according to the Pauli principle, charge transfer from methane to Co^+, and polarisation of metal non-bonding orbitals are also taken into account, the order of stability for these two conformations is reversed.[58]

The mechanism of the reaction

$$CoCH_2^+ + H_2 \longrightarrow Co^+ + CH_4$$

has been studied by the CASSCF and MR-SDCI-CASSCF methods.[59, 60] It was found that cleavage of the H–H bond is the first to occur; this is followed by the formation of the ion–molecular $Co(CH_4)^+$ complex with a stabilisation energy of 19–22 kcal mol^{-1}. The back reaction $Co^+ + CH_4$ gives only one product, $Co(CH_4)^+$, at moderate temperatures. The researchers calculated the metal–ligand binding energies in the $Co(CH_4)^+$ complexes with C_{2v} and C_{3v} symmetry. The C–H_b and C–H_t bond lengths are nearly equal in the complexes with both types of symmetry, whereas the Co–H_b bond is much longer in the C_{3v} than in the C_{2v} structure. The calculations using the Hay–Wadt effective potential have shown that the two structures are nearly degenerate and it is difficult to choose which of them is more favourable. However, the calculations by the above-mentioned methods in the SKBJ approximation have shown that the C_{2v} structure is much more favourable (by 6.5 kcal mol^{-1}) than the C_{3v}-symmetric structure. The η^1-structure in which Co^+ is coordinated to one hydrogen atom is 15–16 kcal mol^{-1} less favourable than η^2- or η^3-structures.[59, 60]

The energies of successive elimination of the ligands from the $Co(CH_4)_n^+$ ($n = 1-4$) complexes have been determined both experimentally and theoretically.[61] Study of the collision-induced dissociation of $Co(CH_4)_n^+$ complexes gave a dissociation energy of the $Co-CH_4^+$ bond $D_0(Co-CH_4)^+ = 21.45 \pm 1.38$ kcal mol^{-1}, which is close to the value found previously.[57] These results are in good agreement with the results of *ab initio* calculations (MCPF method), which gave the value $D_e(Co-CH_4)^+ = 21.45$ kcal

mol^{-1}. According to calculations,[61] the methane ligands in the Co(η^2-CH$_4$)$_n^+$ complexes ($n = 1-4$) are bound electrostatically to the Co$^+$ ion in the ground state (^{3}F,3d^8). The structures with η^3-coordination of the methane ligand are energetically somewhat less favourable.[61]

Study of the reactions

$$MCH_2^+ + H_2 \longrightarrow M^+ + CH_4,$$

M = Co, Rh

by the density functional method with Becke's exchange potential and Perdew's correlation potential (B3P86)[62] led to the conclusion that the reaction $CoCH_2^+ + H_2$ proceeds by a four-centre mechanism in the triplet state. In the complex formed upon the addition of hydrogen, methane is coordinated to cobalt in the bidentate manner. According to these calculations, the Co(η^2-CH$_4$)$^+$ complex corresponds to a global minimum on the PES, and its dissociation to give Co$^+$ and CH$_4$ requires 22.4 kcal mol^{-1}.

The reaction of Rh$^+$ with CH$_4$ was studied by guided-ion beams mass spectrometry (GIBMS).[63] This endothermic reaction was found to give ionic products, RhH$^+$ and $RhCH_x^+$ ($x = 0-3$). For low energies of the reactants, methane dehydrogenation is the predominant process

$$Rh^+ + CH_4 \longrightarrow RhCH_2^+ + H_2. \quad (1)$$

However, direct experimental data on the mechanism of the Rh$^+$ + CH$_4$ reaction are missing because the method used is unable to disclose mechanistic details. Therefore, considerable attention was devoted to quantum-chemical studies of methane activation by the Rh$^+$ ion.[49, 60, 62, 64, 65] The PES of the reaction

$$RhCH_2^+ + H_2 \longrightarrow Rh^+ + CH_4 \quad (2)$$

was studied by the CASSCF and MR-SDCI-CASSCF methods.[60, 64]

It was found that the first stage of the reaction gives the ion–molecular (H$_2$)RhCH$_2^+$ complex, which is then converted into $HRhCH_3^+$ upon cleavage of the H–H bond. The latter complex rearranges into Rh(η^2-CH$_4$)$^+$, probably, without a barrier. This complex is more stable than the products of its dissociation, Rh$^+$(^{3}F) and CH$_4$, by 16.8 kcal mol^{-1}. The Rh(CH$_4$)$^+$ structures with η^2- and η^3-coordination of methane differ little in energy but the C_{2v}-symmetric structure is more stable. The C–H$_b$ bond lengths in Rh(η^2-CH$_4$)$^+$ are longer than C–H$_t$ by 0.01–0.02 Å.[60, 64] Modified coupled pair functional calculations[49] also demonstrated that the η^2-coordination of methane in the Rh(CH$_4$)$^+$ complex is most favourable (the Rh–CH$_4$ binding energy is ~13 kcal mol^{-1}).[49]

The potential energy surface of reaction (2) has been studied by the DFT approach in the B3P86 approximation.[62] The Rh$^+$ cation occurs in the ground state ^{3}F,4d^8, and the initial steps of the $RhCH_2^+ + H_2$ reaction take place on a triplet potential surface. It was found that the $HRhCH_3^+$ intermediate formed in this reaction is unstable and rearranges without a barrier into Rh(η^2-CH$_4$)$^+$. The final complex corresponds to an absolute minimum on the PES with respect to any other critical point of the PES for both the triplet and singlet states of the Rh$^+$ ion. Dissociation of the Rh(η^2-CH$_4$)$^+$ complex to give Rh$^+$ and CH$_4$ requires 13.9 kcal mol^{-1} (see Ref. 62). The researchers cited[62] note that the results of PES calculations they obtained for this reaction are in good agreement with experimental data, unlike the results obtained in another study.[64]

The potential energy surface for endothermic reaction (1) was studied by the density functional approach in the B3LYP approximation using the Hay–Wadt effective potential and by the MCPF method in the PCI-80 approximation.[65] The first stage gives the Rh(CH$_4$)$^+$ complex with electrostatic binding. The triplet state of this complex is more stable than the ground states of the reactants by 14.2 (PCI-80) or 11.5 kcal mol^{-1} (B3LYP). The calculated[65] values for the Rh–CH$_4$ binding energy in Rh(CH$_4$)$^+$ are consistent with the results of calculations carried out by other researchers.[62, 64] However, in Ref. 65 considering the Rh(CH$_4$)$^+$ molecular complex with C_s symmetry, methane was assumed to have a distorted η^3-coordination, which was found to be more stable than the η^2-coordination by 0.9 kcal mol^{-1}. Meanwhile, the latter was proposed as the coordination of choice in the other two studies.[62, 64]

It has been noted above that the Ir$^+$ ion is most efficient, among transition metal ions, in the gas-phase methane dehydrogenation.[34] A theoretical investigation [Hartree–Fock method with singly and doubly excited configurations (HFSD)][66] of the reaction profile for

$$Ir^+ + CH_4 \longrightarrow IrCH_2^+ + H_2$$

has shown that the reaction of the Ir$^+$ ion in the ground state (^{5}F,5d^{7}6s^1) with methane yields initially an ion–molecular complex Ir(η^2-CH$_4$)$^+$ with weak binding. However, due to the intersection of PES for the triplet and quintet states, the spin state of iridium changes, which results in the formation of a triplet ion–molecular complex Ir(η^2-CH$_4$)$^+$ with stronger bonds (^{3}B$_2$, C_{2v}). The stabilisation energy of this complex with respect to the ground states of the reactants [Ir$^+$(^{5}F,5d^{7}6s^1) + CH$_4$] amounts to 20.4 kcal mol^{-1}. The energy of the triplet η^3-complex (^{3}E, C_{3v}) is 4 kcal mol^{-1} higher than the energy of the η^2-complex.[66]

The CASSCF and MR-SDCI-CASSCF methods were used[60] to study the PES of the reaction

$$IrCH_2^+(^3A_2) + H_2 \longrightarrow Ir(CH_4)^+(^3A_2) \longrightarrow Ir^+(^5F,5d^76s^1) + CH_4.$$

Unlike the exothermic reactions of the carbene complexes of cobalt and rhodium with hydrogen, this reaction with iridium is endothermic. The Ir(CH$_4$)$^+$(^{3}A$_2$) complex is ~15.7 (26.4) kcal mol^{-1} more stable than the products of its dissociation, Ir$^+$(^{5}F,5d^{7}6s^1) and CH$_4$. The structures of Ir(CH$_4$)$^+$ with C_{2v} and C_{3v} symmetry are rather similar in energy. The back reaction Ir$^+$ + CH$_4$ yields initially the Ir(CH$_4$)$^+$ complex and then the $HIrCH_3^+$ methyl hydride complex and the $(H)_2IrCH_2^+$ bis(hydrido)carbene complex.[60]

The Pt$^+$ cation is only slightly inferior to Ir$^+$ regarding the efficiency of methane dehydrogenation.[34] Several studies dealing with reactions of methane with this cation have been reported.[67–70] One publication presents a theoretical and experimental (guided ion beam tandem mass spectrometry, GIBTMS) study of the activation of methane by the Pt$^+$ ion.[67] The dehydrogenation of CH$_4$ by thermalised Pt$^+$ cations ($Pt^+ + CH_4 \longrightarrow PtCH_2^+ + H_2$) proceeds on a doublet PES of the ground state of the ion. The reaction is reversible under conditions of ion–cyclotron mass spectrometry (FTICR-MS). The insertion of the Pt$^+$ cation in the ground state (^{2}D,5d^9) into the methane C–H bond occurs *via* the formation of the Pt(η_3^1-CH$_4$)$^+$ complex, which is transformed with a negligibly low activation barrier (1.3 kcal mol^{-1}) to give the methyl hydride $HPtCH_3^+$ complex. This complex corresponds to a global energy minimum on the PES. The Pt(η^2-CH$_4$)$^+$ and Pt(η^3-CH$_4$)$^+$ complexes are transition states; they are matched by saddle points on the reaction PES. According to calculations,[67] the ion–ligand binding energy in the Pt(η_3^1-CH$_4$)$^+$ complex is equal to 28.3 kcal mol^{-1}. In the researchers' opinion,[67] no structures of this type have been considered previously in theoretical investigations of M(CH$_4$)$^+$ complexes.

An experimental and theoretical study of the oxidation of methane by oxygen in the presence of the Pt$^+$ cation as the catalyst has been reported.[68] The first step of the process is the formation of electrostatically bound complex Pt(η_3^1-CH$_4$)$^+$ with C_s symmetry. The ion–ligand binding energy is equal to 19.2 (B3LYP) and 25.4 kcal mol^{-1} (PCI-80). Calculations[68] using a fuller basis set than those reported in the publication discussed above[67] also showed the presence of a C_{2v}-symmetric structure very close in energy to the C_s structure. Unfortunately, no energetic or geometric parameters for the Pt(η^2-CH$_4$)$^+$ complex are given in the publication.[68]

The reactions of argon complexes of platinum ions $PtAr_m^+$ ($m = 1-6$) with CH_4 and CD_4 were studied experimentally by the FTICR-MS method and theoretically by the density functional approach in the B3LYP approximation.[69] The $PtAr_m^+$ complexes ($m = 2-6$) enter into ligand exchange reactions in which up to four argon atoms can be replaced by methane molecules. Conversely, the bare Pt^+ ion and the $PtAr^+$ complex react with methane to give $PtCH_2^+$. The intermediate formation of the $Pt(CH_4)^+$ complexes in the $Pt^+ + CH_4$ and $PtAr^+ + CH_4$ reactions is confirmed by peaks of these complexes observed experimentally in the mass spectra. It was noted [69] that the results of calculations of the geometric and energetic parameters of the $Pt(CH_4)^+$ complexes with predominating 'ion–induced dipole' interaction depend appreciably on the basis set chosen. As expected, the geometric parameters of these complexes calculated using polarisation functions and without these functions are substantially different.[69]

The results of a combined experimental (GIBMS) and theoretical (DFT/B3LYP) investigation of the $Pt^+ + CH_4$ and $PtCH_2^+ + H_2$ reactions and collision-induced dissociation of $Pt(CH_4)^+$ upon the reaction with xenon have been reported.[70] For the $Pt^+ + CH_4$ system, it was found that the only process observed at low temperatures is effective exothermic dehydrogenation of methane giving rise to $PtCH_2^+ + H_2$. The reaction starts with the formation of the $Pt(CH_4)^+$ complex due to the 'ion–induced dipole' interaction. The depth of the potential well for the $Pt(CH_4)^+$ adduct with respect to the reactants is $\sim$20 kcal mol^{-1} (0.9 eV). The geometric parameters of the $Pt(CH_4)^+$ complex were not reported.

A number of publications [71–74] report a theoretical study of the methane adduct with the Cu^+ cation with the filled d-electron shell. This adduct is of interest because it involves interaction of two species having filled electron shells, namely, the Cu^+ ion with a formal d^{10} configuration and a fully saturated hydrocarbon (CH_4). The *ab initio* SCF method with different basis sets was used [71] to calculate the geometry and the relative energetic characteristics for various structures of $Cu(CH_4)^+$. This complex was shown to be stable against unimolecular decomposition. It was suggested that it can exist in the isolated state in inert matrices. At the given theoretical level, the tridentate coordination of the CH_4 molecule, characterised by a $Cu-CH_4$ binding energy of 9.8 kcal mol^{-1}, was shown to be the most favourable for the $Cu(CH_4)^+$ ion. The complexes with bi- and monodentate types of coordination of methane are higher in energy than the η^3-complex by 3.8 and 5 kcal mol^{-1}, respectively. At moderately high temperatures, the Cu^+ cation can migrate quasi-freely around the methane molecule.[71]

The electronic structure and the geometric parameters of the $Cu(CH_4)^+$ adduct were also calculated by the SCF method in the approximation of linear combination of gaussian orbitals (LCGO-SCF) and by the MP2 method.[72] The $Cu(CH_4)^+$ complex was found to be stable with respect to the reactants. The metal–ligand binding is mainly due to electrostatic interactions. The geometry optimisation for $Cu(CH_4)^+$ resulted in a C_{3v}-symmetric structure with a rotation axis. In the $Cu(\eta^3\text{-}CH_4)^+$ complex, the Cu, C and H_t atoms are located on the rotation axis, while the other three hydrogen atoms are arranged to form an 'umbrella' pointing towards the copper ion. The dissociation energy of this complex is 9.3 kcal mol^{-1} (SCF) or 16.6 kcal mol^{-1} (MP2).[72]

The full optimisation of the complex geometry at the SCF level with the use of analytical methods to calculate the first and second derivatives (the GRADSCF method) has also led to an η^3-structure.[73] It was noted that metal–ligand binding in $Cu(CH_4)^+$ is mainly electrostatic; therefore, it is not surprising that the geometric structure of the methane ligand differs little from the structure of free methane. The C–H distances in methane change by not more than 0.01 Å upon complexation. Other geometric parameters of the complex were not reported. The energy of the $Cu-CH_4$ bond for this structure determined by MCPF calculations is equal to 14.8 kcal mol^{-1}. It was suggested [73] that this value is understated by $\sim$5 kcal mol^{-1} due to the limited basis set and incomplete allowance made for the correlation interaction.

In another study,[74] where the geometry of $Cu(CH_4)^+$ was optimised by the MP2 method with fuller basis sets, a structure with bidentate coordination was found to be most stable; in particular, more stable than the η^3-structure by 0.3–1.2 kcal mol^{-1}. Comparison of these results [74] with the results of earlier calculations [71–73] provides the conclusion that with the extension of the basis set and more perfect allowance for the electron correlation for the $Cu^+(d^{10})$ ion, the η^2-coordination of methane to Cu^+ would prove to be preferred. The researchers believe that the electrostatic interaction promotes η^3-coordination to the Cu^+ ion, whereas the dative interaction is favourable for the formation of the η^2-complex.[74]

The dissociation energies of the $M(CH_4)^+$ complexes determined experimentally and the calculated geometric parameters

Table 1. Results of experimental and theoretical studies of the $M(CH_4)^+$ complexes.

Complex	Electronic state and term of the ion	Symmetry	Bond lengths /Å			The M–C–H_b angle /deg	E_{bd} [a] /kcal mol^{-1}	Calculation techniques (programs); investigation methods	Ref.
			M···C	M–H_b	C–H_b (C–H_t)				
$Li(\eta^3\text{-}CH_4)^+$	$^1S,1s^2$	C_{3v}	2.25	–	–	–	–	RHF/SKBJ (GAMESS)	36
$Li(\eta^3\text{-}CH_4)^+$	$^1S,1s^2$	C_{3v}	2.33	[2.27]	1.096	–	8.2	*ab initio* Hartree–Fock method	37
$Li(\eta^3\text{-}CH_4)^+$	$^1S,1s^2$	C_{3v}	2.195	2.165	1.098	–	<10–12	QCISD(T)/MP2 (GAUSSIAN92, 94)	38
$Na(\eta^3\text{-}CH_4)^+$	$^1S,2p^6$	C_{3v}	2.631	2.541	1.095	–	<10–12		
$Mg(\eta^3\text{-}CH_4)^+$ (see [b])	$^2S,3s^1$	C_{3v}	2.65	–	–	–	4.0 (SCF)	photoelectron spectroscopy; SCF, MP2 (GAUSSIAN90); MCPF (MOLECULE-SWEDEN)	39, 40
			2.54	–	–	–	7.6 (MP2)		
$Sc(\eta^3\text{-}CH_4)^+$	$^3D,3d^14s^1$	C_{3v}	2.785	[2.691]	1.087	73.72	15.1	CASSCF (GAMESS, MOLPRO), MR-SDCI-CASSCF (MOLPRO)	42
$Sc(\eta^2\text{-}CH_4)^+$	$^1D,3d^14s^1$	C_{2v}	4.281	[3.776]	1.085	55.59	13.1		
$Sc(\eta^3\text{-}CH_4)^+$	$^3D,3d^14s^1$	C_{3v}	2.025	–	–	–	15.7	DFT/B3LYP (GAUSSIAN94/DFT)	43
$Sc(\eta^3\text{-}CH_4)^+$	$^1D,3d^14s^1$	C_{3v}	2.411	–	–	–	8.4 (3.8 rel. to ^3D)		
$Ti(\eta^3\text{-}CH_4)^+$	$^2F,3d^24s^1$	C_{3v}	2.751	[2.526]	1.093	74.1	73.1	MP2/6-31G** (GAUSSIAN92W)	45

Table 1 (continued).

Complex	Electronic state and term of the ion	Sym-metry	Bond lengths /Å			The $M-C-H_b$ angle /deg	E_{bd} [a] /kcal mol^{-1}	Calculation techniques (programs); investigation methods	Ref.
			M···C	M−H_b	C−H_b (C−H_t)				
Ti(η^3-CH_4)$^+$	^{2}F,3d^{2}4s^1	C_{3v}	2.354	–	–	75.0	21.81	DFT/B3LYP	46
Ti(η^3-CH_4)$^+$	^{4}F,3d^{2}4s^1	C_{3v}	2.350	–	–	74.0	22.21	(GAUSSIAN94/DFT)	
V(CH_4)$^+$	^{5}D,3d^4	–	–	–	–	–	(15.0)(for ^{5}D,3d^4)	resonance single-photon photodissociation spectroscopy	48
	$^5P_2$,3d^{3}4s^1	–	–	–	–	–	(8.3)(for $^5P_2$,3d^{3}4s^1)		
V(η^2-CH_4)$^+$	^{5}D,3d^4	C_{2v}	2.485	–	–	59.0	15.09	DFT/B3LYP	46
V(η^3-CH_4)$^+$	^{3}F, 3d^{3}4s^1	C_{3v}	2.259	–	–	88.6	16.68	(GAUSSIAN94/DFT)	
Nb(η^2-CH_4)$^+$ (see [b])	^{5}D,4d^4	C_{2v}	2.65	–	–	–	11.8	SCF/MCPF (GAMESS)	49
Ta(η^3-CH_4)$^+$ (see [b])	^{5}F,5d^{3}6s^1	C_s	3.199	[2.924]	1.096 (1.093)	73.02	12	DFT/B3LYP (GAUSSIAN94)	52
Cr(η^3-CH_4)$^+$	^{6}S,3d^5	C_{3v}	2.361	–	–	75.8	13.1	DFT/B3LYP	46
Cr(η^3-CH_4)$^+$	^{4}D,3d^{4}4s^1	C_{3v}	2.296	–	–	75.5	29.31	(GAUSSIAN94/DFT)	
Fe(CH_4)$^+$, Fe(CH_4)$_n^+$ ($n = 1-4$)	^{6}D,3d^{6}4s^1	–	–	–	–	–	(13.7 ± 0.8)	mass spectrometry	53
Fe(CH_4)$^+$	–	–	–	–	–	–	(13.6 ± 0.9)	mass spectrometry	54
Fe(η^2-CH_4)$^+$	^{6}D,3d^{6}4s^1	C_{2v}	3.433	[2.871]	1.088 (1.080)	56.4	15.5	CASSCF (GAMESS), MR-SDCI-CASSCF (MOLPRO)	55
Fe(η^3-CH_4)$^+$	^{6}D,3d^{6}4s^1	C_{3v}	3.12	[2.88]	1.086 (1.081)	74.72 {180 (Fe−C−H_t)}	~15.5		
Fe(η^2-CH_4)$^+$	^{4}F,3d^7	C_{2v}	2.373	–	–	58	[24.5]	DFT/B3LYP	56
	^{6}D,3d^{6}4s^1	C_{2v}	2.780	–	–	58	[5.9]	(GAUSSIAN94)	
Co(CH_4)$^+$, Co(CH_4)$_n^+$ ($n = 1-3$)	–	–	–	–	–	–	(22.9 ± 0.7)	mass spectrometry	57
Co(η^2-CH_4)$^+$	^{3}F,3d^8	C_{2v}	2.24	1.94	[1.109]	[~60]	21.4	MCPF (GVB, MOLECULE-SWEDEN)	58
Co(η^3-CH_4)$^+$	^{3}F,3d^8	C_{3v}	2.11	2.11	–	–	20.1		
Co(η^2-CH_4)$^+$	^{3}F,3d^8	C_{2v}	2.608	2.229	1.093 (1.078)	57.9	19 – 22	CASSCF (GAMESS),	59, 60
Co(η^3-CH_4)$^+$	^{3}F,3d^8	C_{3v}	2.370	2.313	1.092 (1.078)	73.6	15.5 – 22.3	MR-SDCI-CASSCF (MOLPRO)	
Co(η^2-CH_4)$^+$ (see [b])	^{3}F,3d^8	C_{2v}	2.24	–	–	–	(21.4 ± 1.4) 17.3	mass spectrometry, MCPF (GVB, MOLECULE-SWEDEN)	61
Co(η^2-CH_4)$^+$	^{3}F,3d^8	C_{2v}	2.034	1.810	1.152 (1.101)	62.1	22.4	DFT/B3P86 (Dgauss)	62
Rh(η^2-CH_4)$^+$	^{3}F,4d^8	C_{2v}	2.829	2.427	1.092 (1.078)	57.65	16.8	CASSCF (GAMESS), MR-SDCI-CASSCF (MOLPRO)	60, 64
Rh(η^3-CH_4)$^+$	^{3}F,4d^8	C_{3v}	2.515	2.440	1.085 (1.076)	73.52	13.8 – 13.9		
Rh(η^2-CH_4)$^+$	^{3}F,4d^8	C_{2v}	2.65	–	–	–	13	SCF/MCPF (GAMESS); GRADSCF,	49
Rh(η^2-CH_4)$^+$	^{3}F,4d^8	C_{2v}	2.347	2.083	1.132 (1.101)	62.6	13.9	DFT/B3P86 (Dgauss)	62
Rh(η_3^1-CH_4)$^+$	–	C_s	2.536	[< 2.33]	1.132 (1.098)	–	11.5 (B3LYP) 14.2 (MCPF)	DFT/B3LYP, MCPF (STOCKHOLM)	65
Ir(η^2-CH_4)$^+$	see text	C_{2v}	2.47	[2.016]	–	59.15 {112.3 (H_t−C−H_t)}	20.4	HFSD, MCPF (GVB, MOLECULE-SWEDEN)	66
Ir(η^2-CH_4)$^+$	see text	C_{2v}	2.754	2.370	1.095 (1.079)	58.33	6.0; 18.2	CASSCF (GAMESS), MR-SDCI-CASSCF (MOLPRO)	60
Ir(η^3-CH_4)$^+$	see text	C_{3v}	2.794	2.705	1.087 (1.084)	74.44	–		
Pt(η_3^1-CH_4)$^+$	^{2}D,5d^9	C_s	2.258	1.700	1.229	[53.25]	28.3	DFT/B3LYP (GAUSSIAN92)	67
Pt(η_3^1-CH_4)$^+$	–	C_s	2.36	1.83	1.19	[53.24]	25.4 (PCI-80) 19.2 (B3LYP)	mass spectrometry, MCPF (STOCKHOLM),	68
Pt(η^2-CH_4)$^+$	–	C_{2v}	–	–	–	–	–	DFT/B3LYP (GAUSSIAN94)	

Table 1 (continued).

Complex	Electronic state and term of the ion	Symmetry	Bond lengths /Å			The $M-C-H_b$ angle /deg	E_{bd} [a] /kcal mol^{-1}	Calculation techniques (programs); investigation methods	Ref.
			M···C	M−H_b	C−H_b (C−H_t)				
Pt(η^1_3-CH_4)$^+$	–	–	2.28	1.71	1.22	[52.71]	30.12	mass spectrometry, DFT/B3LYP (GAUSSIAN94)	69
Pt(CH_4)$^+$	–	–	–	–		–	(19.67–21.06)	mass spectrometry, DFT/B3LYP (GAUSSIAN98)	70
Cu(η^3-CH_4)$^+$ (see [b])	^{1}S,3d^{10}	C_{3v}	2.44	[2.37]	1.10 (1.09)	73.5	9.8	SCF (GAUSSIAN80)	71
Cu(η^3-CH_4)$^+$ (see [b])	^{1}S,3d^{10}	C_{3v}	4.489	[4.186]	1.077 (1.065)	74.36	9.3 (SCF) 16.6 (MP2)	SCF-CI, MP2	72
Cu(η^3-CH_4)$^+$ (see [b])	^{1}S,3d^{10}	C_{3v}	–	–	–	–	14.8 (MCPF)	MCPF, GRADSCF (MOLECULE-SWEDEN)	73
Cu(η^2-CH_4)$^+$	^{1}S,3d^{10}	C_{2v}	[2.41]	1.944	1.108	58.9	16.8–21.43	MP2, CCSD(T) (GAUSSIAN90)	74

Note. The values in brackets are the distances and the angles calculated by the author of the review using data from the cited publications.
[a] The methane–cation bond energy in the complex. The values in parentheses are experimental data. [b] The complex is formed due to weak electrostatic interactions. The CH_4 ligand is slightly distorted with respect to non-coordinated methane.

Li $\overline{\eta^3}$	**Be**											**B**
Na $\overline{\eta^3}$	**Mg** $\overline{\eta^3}$											**Al**
K	**Ca**	**Sc** $\overline{\eta^3}$	**Ti** $\overline{\eta^3}$	**V** $\overline{\eta^2}$, η^3	**Cr** $\overline{\eta^3}$	**Mn**	**Fe** η^3 ($Fe^0d^6s^2$) $\eta^2 \sim \eta^3$	**Co** η^3 ($Co^0d^7s^2$) η^2	**Ni**	**Cu** $\overline{\eta^2}$	**Zn**	**Ga**
Rb	**Sr**	**Y**	**Zr**	**Nb** $\overline{\eta^2}$	**Mo**	**Tc**	**Ru**	**Rh** η^2 (Rh^0d^9) η^2, η^1_3	**Pd** η^2 (Pd^0d^{10}) η^2	**Ag**	**Cd**	**In**
Cs	**Ba**	**Lu**	**Hf**	**Ta** $\overline{\eta^3}$	**W**	**Re**	**Os**	**Ir** $\overline{\eta^2}$	**Pt** η^2 (Pt^0d^{10}) $\eta^1_3 \sim \eta^2$	**Au**	**Hg**	**Tl**

Figure 2. Dependence of the modes of coordination of the CH_4 ligands in the complexes $M^0(CH_4)$ and $M^+(CH_4)$ on the nature of the complexing metal (the upper line gives the data for complexes of neutral atoms and the lower line, for cation complexes).

and M−CH_4 binding energies are summarised in Table 1. The dependence of the mode of coordination of CH_4 ligands on the nature of the complexing metal in the $M(CH_4)^0$ and $M(CH_4)^+$ complexes is shown in Fig. 2.

IV. Methane complexes with the molecular fragments ML_n

Complexes of many transition metals are able to react with saturated hydrocarbons under certain conditions in solutions, thus activating the C−H bonds. The activation of alkanes can follow different mechanisms. Complexes containing metals in high oxidation states with a d^0 electron configuration tend to undergo cycloaddition of alkanes to a single or multiple metal–ligand bond (σ-bond metathesis and 1,2-addition, respectively). Transition metal complexes with a d^n electron configuration of the metal are prone to enter into electrophilic substitution or oxidative addition of alkane to the central atom of the complex.[2–12] The activation of alkanes by complexes of platinum group metals, especially rhodium and iridium, has been studied most comprehensively. Presumably, complexes with alkane molecules as ligands are formed as intermediates in these reactions.[13–18] Apart from experimental studies, considerable attention has been devoted to the theoretical investigation of the mechanisms of these reactions, in particular, by quantum-chemical methods.

1. Complexes with the d^0 electron configuration of the complex-forming ion

It was found experimentally that organometallic compounds of early transition metals (lanthanides, actinides) in higher oxidation states are able to activate the C−H bonds in alkanes according to the mechanism of σ-bond metathesis. The first example of this type of reaction was described by Patricia Watson in 1983.[75]

$$Cp^*_2M-CH_3 + {}^{13}CH_4 \longrightarrow Cp^*_2M-{}^{13}CH_3 + CH_4$$

M = Y, Lu; Cp* = η^5-C_5Me_5.

Subsequently, other similar systems have been found and studied in detail.[11,76–79] Metathesis of σ-bonds is highly selective with respect to the sterically least hindered C−H bonds at the primary carbon atom. The selectivity is so high that it is possible to use cyclohexane as an inert solvent to study these reactions.[5,7]

A number of publications[80–82] have been devoted to quantum-chemical investigations of the mechanism of σ-bond metathesis. The activation of the H−H and C−H bonds in the

$X_2LuCH_3 + H_2$ and $X_2LuCH_3 + CH_4$ systems was studied by the density functional approach with different potentials.[80]

$$X_2Lu-CH_3 + H_2 \longrightarrow X_2Lu-H + CH_4,$$

$$X_2Lu-CH_3 + CH_4 \longrightarrow X_2Lu-CH_3 + CH_4.$$

In this study, the Cp^*_2Lu fragment of the $Cp^*_2LuCH_3$ complex used in experiments, was modelled by the Cl_2Lu species. It was found that both reactions involve the formation of a highly ordered four-centre transition state with a negative activation entropy. The weakly bound methane adduct $Cl_2LuH(\eta^1_3\text{-}CH_4)$ with a binding energy of 1.96 kcal mol^{-1} with respect to the final products, Cl_2LuH and CH_4, is formed as the intermediate compound in hydrogenolysis.

The exchange reaction

$$Cl_2Lu-CH_3 + CH_4 \longrightarrow Cl_2Lu-CH_3 + CH_4$$

has a high activation barrier and proceeds *via* the adduct $Cl_2Lu(CH_3)(\eta^1_2\text{-}CH_4)$, which is 4.64 kcal mol^{-1} less stable than the initial reactants (Cl_2LuCH_3 and CH_4). The methane fragments in the η^1_3 and η^1_2 adducts are distorted only slightly compared to free methane.

The density functional approach in the B3P86 approximation has been used [81] to study the energy profiles of hydrogenolysis and methyl-group exchange for the Cp_2ScCH_3 complex.

$$Cp_2Sc-CH_3 + H_2 \longrightarrow Cp_2Sc-H + CH_4,$$

$$Cp_2Sc-CH_3 + CH_4 \longrightarrow Cp_2Sc-CH_3 + CH_4.$$

After the initial formation of the Cp_2ScCH_3 adduct with H_2, the energetic profile of hydrogenolysis leads, *via* a transition state, to the $Cp_2ScH(\eta^1_3\text{-}CH_4)$ adduct. The methane ligand in this complex has a distorted tridentate coordination. The bridging $C-H_b$ bonds (1.14 and 1.11 Å) are elongated compared to the C–H bonds in free methane. The binding energy of methane in the $Cp_2ScH(\eta^1_3\text{-}CH_4)$ complex is 4.78 kcal mol^{-1} relative to the products (Cp_2ScH and CH_4). The exchange by methyl groups proceeds *via* the adduct $Cp_2Sc(CH_3)(\eta^2\text{-}CH_4)$ with a binding energy of 5.97 kcal mol^{-1}. Comparison of the hydrogenolysis and methyl exchange processes for scandium and lutetium complexes shows that the replacement of hydrogen in X_2M-Y (M = Sc, Lu; X = Cp, Cl; Y = H, CH_3) by a bulkier CH_3 group entails a change in the mode of coordination of the methane ligand from the tridentate (or distorted tridentate) coordination found in the $X_2MH(CH_4)$ complex to a bidentate one in the $X_2M(CH_3)(CH_4)$ complex. This replacement also results in a longer $M-CH_4$ bond, apparently, due to steric factors (the geometric parameters of the complexes were optimised without non-local corrections).

The activation of methane by model compounds Cl_2LnZ (Z = H, CH_3) has been studied for the whole lanthanide row [82] by the density functional method using the hybrid B3PW91 functional. These compounds were assumed to be rather good models for bis(pentamethylcyclopentadienyl) complexes Cp^*_2LnZ. The obtained results appear to cast doubt on the possibility of intermediate formation of the $Cp^*_2LnZ(CH_4)$ complexes in these reactions. The researchers believe that the process of methane activation can be represented in this case as proton transfer between two anionic groups coordinated to Ln atoms.

It is well-known that Ziegler–Natta catalysts and metallocene catalysts for polymerisation of α-olefins can react with methane and that methane can be used to terminate the growth of polymer chains to control the molecular mass of polymers.[83] To elucidate the mechanism of methane activation by metallocene catalysts, the PES for model reactions between methane and $Cp_2M(CH_3)^+$ cations (M = Ti, Zr) (σ-bond metathesis) have been studied in detail by the density functional method in the generalised gradient approximation (GGA) using the Perdew, Burke and Ernzerhof (PBE) density functional.[84,85] The calculations showed that the first stage gives the intermediate σ-complex $Cp_2M(CH_3).(\eta^2\text{-}CH_4)^+$. The complexation energy for the zirconium cation is 9.4 kcal mol^{-1} and that for the titanium cation is 4.2 kcal mol^{-1}. It was noted that the free energies of complexation (ΔG_{298}) at room temperature are positive with respect to the initial components due to a great entropy contribution; they are 1.5 kcal mol^{-1} for zirconium and 8.3 kcal mol^{-1} for titanium.

The reactions of $Cp_2MCH^+_3$ cations with H_2 result directly in the $Cp_2MH(\eta^2\text{-}CH_4)^+$ σ-complexes without an activation barrier. The back reaction $Cp_2MH^+ + CH_4$ also includes the intermediate formation of $Cp_2MH(\eta^2\text{-}CH_4)^+$ in which the electrons of two $C-H_b$ bridging bonds are involved in binding of the CH_4 molecule to the central metal atom.

Density functional theory calculations in the PBE approximation for the model reaction

$$Cp_2MCH^+_3 + RH \rightleftharpoons Cp_2MR^+ + CH_4,$$

M = Ti(IV), Zr(IV); R = Me, Et, Pr^n, Pr^i

showed that the reaction of $Cp_2MCH^+_3$ with alkanes proceeds *via* the stage of formation of $Cp_2M(RH)(CH_3)^+$ complexes, which are subsequently isomerised into $Cp_2MR(CH_4)^+$.[86] The energy of the $M-CH_4$ bond in the $Cp_2MR(CH_4)^+$ complexes decreases on passing from R = Me to R = Et, Pr^n or Pr^i. This sequence of variation of the bond energy was attributed to the influence of steric factors. In the case of isopropyl ligands, the minima corresponding to the $Cp_2MPr^i(CH_4)^+$ complexes (M = Ti, Zr) could not be found on the PES, as these complexes undergo barrier-free dissociation to give methane and $Cp_2M(Pr^i)^+$. In zirconium complexes, methane is coordinated according to the η^2 mode; in the case of the titanium ion, which is smaller in diameter, according to the η^1_2 mode (R = Pr^n, Pr^i), apparently, also due to steric factors. The geometric parameters of methane ligands in these complexes were not reported.[86]

Yet another type of complexes formed by high-valence transition metals able to activate the C–H bonds in alkanes includes compounds with metal–ligand multiple bonds. It has been found experimentally that the imido complexes $L_nM=NR$ formed by transition d^0 metals (M = Ti, Zr, Ta, V, W) are able to activate various hydrocarbons including methane.[87–94] The reaction results in alkane (R′H) addition to the highly polarised $M^{\delta+}=N^{\delta-}$ double bond of the complex giving rise to $L_nM(R')(NHR)$. The addition of alkanes to the $M^{\delta+}=N^{\delta-}$ multiple bonds, like the metathesis of σ-bonds, is distinguished by a high degree of selectivity with respect to the primary C–H bonds. It was suggested that high polarity of the metal–imide ligand bond is important for this reaction, as it promotes the subsequent cleavage of the activated C–H bond in the alkane.[87] Data obtained by isotope labelling are consistent with the intermediate formation of alkane complexes assumed for these reactions.[91,93,94]

A series of publications have been devoted to theoretical investigation of the mechanism of methane addition to the M=NR multiple bonds.[36,95–100]

The activation of methane by the imido complexes $H_2M=NH$ (M = Ti, Zr, Hf) has been studied by *ab initio* (RHF, MP2) methods.[95] Methane is coordinated by the metal in the η^3 mode to give the $H_2M(=NH)(\eta^3\text{-}CH_4)$ charge transfer complex. The hydrogen atoms bound to the metal occur in an eclipsed conformation relative to the $H_2M=NH$ complex. In this complex, the activated C–H bond lies in the same plane as the M=N bond. The geometric parameters of fragments in the $H_2M(=NH).(\eta^3\text{-}CH_4)$ complexes are virtually identical to those calculated for free reactants. The calculation results support the hypothesis of an important role of the highly polar M=N bond in this reaction and demonstrate that the formation of the alkane complex increases the polarity of the $C^{\delta-}-H^{\delta+}$ bond. In the free methane molecule, the charge on the carbon atom is −0.24 e, while that on the hydrogen atoms is +0.06 e. On complexation, the polarity of the C–H bonds increases and the charge on carbon becomes equal to -0.48 ± 0.02 e, and that on hydrogen is $+0.15 \pm 0.01$ e. Due to the reaction, the negatively charged

methyl group is transferred to the central metal atom and the positively charged hydrogen atom migrates to the imide nitrogen atom carrying a negative charge. Thus, the overall process can be regarded as proton transfer between two anionic centres. The calculated energy barriers to the elimination of methane from the $H_2M(CH_3)(NH_2)$ complexes (M = Ti, Zr, Hf) are in good agreement with the values found experimentally regarding both the absolute magnitude and the pattern of variation of the magnitude depending on the nature of the central atom.

The structures of methane complexes with monoimides of Group IV metals, bisimides of Group V metals, and trisimides of Group VI metals with a d^0 electron configuration and the $M-CH_4$ binding energies in these compounds have been determined by RHF and MP2 calculations.[96] It was found that methane adducts with pyramidal bisimides $(NH_2)M(=NH)_2$ (M = Nb, Ta) and trisimides $M(=NH)_3$ (M = Mo, W) are characterised by rather high bond enthalpies (11–16 kcal mol^{-1}), comparable to those for dihydrogen complexes (Kubas complexes). Meanwhile, the enthalpy of binding of the methane ligand to Group IV metal monoimides is much lower. The coordination of methane is accompanied by the transfer of 0.1–0.3 e from methane to the central metal atom, which results in elongation and polarisation of the $C^{\delta-}-H^{\delta+}$ bond. These data are indicative of the important role of the methane adduct in the subsequent cleavage of the C–H bond.

The charges on the central metal atoms (Z) in the starting imido complexes have been calculated.[96] According to this calculation, the enthalpy of the $M-CH_4$ bond in Group IV–VI metal imido complexes varies in proportion to the variation of the Z/r^2 ratio, where r is the M–C distance (Table 2). In our opinion, this correlation implies a predominant contribution of electrostatic interaction to the formation of the methane–imido complex bond. In the case of imido complexes of metals with a d^2 electron configuration, no correlation of this type is found; they cannot form adducts with methane due to repulsion between the free electron pair in the metal d orbital and the electrons of the C–H σ-bond.

Table 2. Dependence of the stabilisation enthalpy of methane complexes with metal imides on the charge on the central metal atom and the M–C distance (from the data of Ref. 96).

Complex	Electronic state of M	M–C /Å	Z(M)[a]	Z/r^2	H_{add} (see[b])
$Ti(OH)_2(=NH)(\eta^1_2\text{-}CH_4)$	d^0	2.84	+1.36	0.169	6.6
$Ti(NH_2)_2(=NH)(\eta^1_2\text{-}CH_4)$	d^0	3.10	+1.08	0.112	4.4
$Zr(NH_2)_2(=NH)(\eta^1_2\text{-}CH_4)$	d^0	3.05	+1.62	0.174	6.3
$Nb(NH_2)(=NH)_2(\eta^2\text{-}CH_4)$	d^0	2.84	+1.48	0.183	11.1
$Ta(NH_2)(=NH)_2(\eta^2\text{-}CH_4)$	d^0	2.79	+1.55	0.199	13.6
$Mo(=NH)_3(\eta^1_2\text{-}CH_4)$	d^0	2.77	+1.2	0.19	13.7
$W(=NH)_3(\eta^1_2\text{-}CH_4)$	d^0	2.72	+1.48	0.224	15.6
$W(OH)_2(=NH)(CH_4)$	d^2	–	+1.54	–	<0
$Os(=NH)_3(CH_4)$	d^2	–	+1.19	–	<0

[a] Calculated (Mulliken) charges on the metal atoms in the reactants. [b] In kcal mol^{-1}.

The mechanism of methane activation by Group V metal bisimido complexes has been studied.[98] Methane adducts with the $(NH_2)M(=NH)_2$ complexes (M = V, Nb, Ta) have C_s symmetry; one C–H bond of the methane ligand is arranged above the bisector of the N=M=N angle. The geometric parameters of the fragments in the adducts differ little from those of free molecules. In the Group V metal adducts, methane is considered to be coordinated by an edge, because the $M-H_b$ distances for the two bridging hydrogen atoms are nearly equivalent. The complexes formed by Group V metals, $M(NH_2)(=NH)_2(\eta^2\text{-}CH_4)$, differ in the mode of methane coordination from similar complexes derived from Group IV and VI metals, which should rather be regarded as monodentate complexes with a bent M–H–C bridge, $M(NH_2)_2(=NH)(\eta^1_2\text{-}CH_4)$ (M = Ti, Zr, Hf) and $M(=NH)_3(\eta^1_2\text{-}CH_4)$ (M = Mo, W), because in this case, the lengths of the $M-H_b$ bonds for two bridging H atoms markedly (by more than 0.2 Å) differ from each other.

The activation of methane by the trisimido complexes formed by d^0 metals, $M(=NH)_3$ (M = Mo, W), $Ta(=NH)_3^-$, $M(=NH)_3^+$ (M = Tc, Re), and d^2 metals, $Tc(=NH)_3^-$, $Os(=NH)_3$, has been studied by RHF calculations with the effective core potential and by molecular mechanics.[36] It was found that the energy of methane binding to imido complexes is more sensitive to the type of electronic configuration of the central atom (d^0 or d^2) than to the nature of the metal or the charge of the complex. According to calculations, methane reacts with d^0-metal complexes irrespective of their charge (neutral, anionic, or cationic) but does not react with d^2-metal imides.

In the complexes formed by d^0 metals, the energy of binding of methane to the metal increases on passing from anionic to neutral and cationic complexes in the series $Ta(=NH)_3^- < W(=NH)_3 < Re(=NH)_3^+$, being equal to 8.3, 15.6 and 26.3 kcal mol^{-1}, respectively. The methane binding energy increases on passing from Group III metal amides to Group IV metal monoimides, Group V metal bisimides, and Group VI metal trisimides

$$M(NH_2)_3 < M(=NH)(NH_2)_2 < M(=NH)_2(NH_2) < M(=NH)_3 .$$

It was suggested that complexes of alkanes with $M(=NAr)_3^+$ (M = Tc, Re) can be sufficiently stable to be studied experimentally.

The changes in the geometry of the reactants upon complexation are insignificant. The angle between the $C-H_b$ bridging bonds somewhat increases, from 109.5° (in free methane) to 113° [in the anionic complex of tantalum $Ta(=NH)_3^-$] and to 119° [in the cationic complex of rhenium $Re(=H)_3^+$]. The lengths of uncoordinated C–H bonds are similar to the C–H bond lengths in free methane. The length of the $C-H_b$ bridging bond increases with an increase in the $M-CH_4$ binding energy from 1.10 (in the anionic tantalum complex) to 1.14 Å (in the cationic rhenium complex).[36, 98]

The above theoretical data dealing with the activation of methane C–H bonds by two types of complexes based on metal ions in high oxidation states with a formal d^0 electron configuration (cyclopentadienyl complexes of Group III, IV metals and Group IV–VI metal imides) show that methane is coordinated in these compounds *via* either a face (η^3 and η^1_3 modes of coordination) or an edge (η^2 and η^1_2 modes of coordination). The mode of methane coordination is appreciably affected by steric (the size of stabilising ligands) and electronic factors (high polarity of the metal–ligand bond). The activation of methane C–H bonds by complexes of this type can be represented as proton transfer between two anionic centres in the coordination sphere of a highly charged d^0 metal.

2. Complexes with a d^n electron configuration of the complexing ion

A much larger number of papers have been devoted to methane activation by complexes formed by transition metals with d^n electron configurations. Sixteen-electron molybdenum and tungsten metallocenes Cp_2M (d^4 configuration) are well-known to be highly reactive intermediates which readily enter into oxidative addition reactions to give 18-electron derivatives. In particular, these complexes are able to activate the C–H bonds of alkanes. The reactions of methane with metallocene derivatives of molybdenum and tungsten have been studied by the density functional method in the B3P86 and B3LYP/LANL2DZ approximations.[101–103]

Study of the intramolecular hydrogen exchange in the $Cp_2W(CH_3)H$ and $[CH_2(C_5H_4)_2]W(CH_3)H$ complexes showed that in both cases, hydrogen exchange proceeds *via* the intermediate formation of the methane complex with η^1_2-coordination of

methane. In these complexes, two C–H bonds of the methane ligand pointing toward the tungsten atom are located in the equatorial plane of the metallocene fragment.[101]

Density functional theory calculations in the B3LYP approximation were used to study the oxidative addition of methane to molybdenum and tungsten 16-electron [*n*]-metallocenophanes.[102] According to the results of calculations, these [*n*]-metallocenophanes react with methane to form σ-complexes with a binding energy of 1.3–7.6 kcal mol^{-1}. In these σ-complexes, methane is bound to the central metal atom according to the η^1_2 type, the bridging C–H_b bonds being located in the equatorial plane of the metallocene fragment.[102]

Poli and coworkers [103] have studied the addition of methane to various types of metallocenes formed by Group VI metals, namely, Cp_2M, $[CH_2(C_5H_4)_2]M$, and Cp^*_2M (M = Mo, W), by density functional theory calculations in the B3LYP/LANL2DZ approximation. It was found that these compounds in the singlet excited state form asymmetric η^1-complexes with methane, in which the M–H_b–C hydrogen bridge is situated in the equatorial plane of the metallocene fragment. The C–H_b bridging bond is much longer than the other C–H bonds of the methane ligand, whose average length is 1.088 Å. This elongation is more pronounced in tungsten complexes (1.138–1.156 Å) than in molybdenum complexes (1.122–1.126 Å), indicating that the M–CH_4 interaction is stronger in the case of tungsten. The W···H_b distance is 0.1 Å shorter than Mo···H_b. The binding energy of methane in cyclopentadienyl and *ansa*-metallocene complexes is equal to 3.4–6 kcal mol^{-1} relative to the excited (singlet) state of the corresponding metallocenes. The reaction of Cp^*_2M with methane is energetically unfavourable even for the singlet state of these complexes due to the influence of steric factors.[103]

To elucidate the reason for the experimentally observed difference between the reactivities of the $Cp^*W(NO)(CH_2Bu^t)_2$ and $Cp^*Mo(NO)(CH_2Bu^t)_2$ complexes towards alkanes,[104] the reactions of model compounds $CpM(NO)(=CH_2)$ (M = W, Mo) were studied by density functional theory calculations in the B3LYP/LANL2DZ approximation.[105] It was found that the reaction of methane with the model compound $CpW(NO)(=CH_2)$ is more exothermic and has a lower activation barrier than the reaction with $CpMo(NO)(=CH_2)$. The calculations attest to the formation of intermediate $CpM(NO)(=CH_2)(CH_4)$ complexes for both molybdenum and tungsten. The methane ligands in both complexes are coordinated according to the η^1_2 pattern, one M···H_b bridging bond being 0.4 Å shorter than the other. One of the C–H_b bonds in the methane ligand is somewhat elongated (1.119 Å for Mo and 1.12 Å for W) compared to the other C–H bonds (each $\leqslant$1.10 Å). In addition, the H–C–H angle between the two hydrogen atoms directed toward the metal is also increased to 116.5° for Mo and to 117.2° for W. The energy of methane binding in the complexes is 6.5 (for Mo) and 7.7 kcal mol^{-1} (for W). The $CpM(NO)(=CH_2)(CH_4)$ complexes can participate in two competing processes, namely, activation of the C–H bonds to give $CpM(NO)(CH_3)_2$ and dissociation with the loss of methane. The calculations showed that for the tungsten complex, the heights of the energy barriers to both reactions are almost equal, whereas in the case of the molybdenum complex, the formation of $CpM(NO)(CH_3)_2$ is energetically rather unfavourable.[105]

Fast time-resolved infrared spectroscopy (TRIS) has been used to study the reactions of a number of alkanes and fluoroalkanes with the 16-electron species $W(CO)_5$ in the gas phase.[106] It was found that $W(CO)_5$ is reversibly complexed with unsubstituted alkanes, except for CH_4. The binding energies of alkanes in the complexes are in the range 7–11 kcal mol^{-1}; they increase with an increase in the alkane size. Since no complex with CH_4 was detected experimentally, it was concluded [106] that the binding energy in this complex is less than 5 kcal mol^{-1}.

For comparison with experimental data, the energies of binding of alkanes to $W(CO)_5$ were found by *ab initio* calculations using various basis sets and methods for taking into account the electron correlation.[107] The Hartree–Fock (HF) optimisation of the geometric parameters of the $W(CO)_5(RH)$ complexes showed that the η^1_2-coordination is energetically the most favourable for methane, although two transition states with η^1_3 and η^2 modes of coordination do not differ much from it in energy. When the geometry of $W(CO)_5(CH_4)$ was optimised by the MP2 methods, all three structures were found to correspond to energy minima, the energy difference between them being less than 1 kcal mol^{-1} and the order of their stability being dependent on the basis set and the calculation method used. Excellent agreement with experimental data was attained only when the MP2 binding energies in the largest basis set were corrected for the basis set superposition error (BSSE), the zero point energy (ZPE), and the temperature; the difference between the results of MP2 and QCISD calculations was also taken into account.[107]

In a recent publication,[18] the alkane complex $CpRe(CO)_2.(C_5H_{10}$-cyclo) was observed directly by NMR spectroscopy in a solution at −80 °C. According to NMR data, the cyclopentane ligand in this complex is bound to rhenium according to the η^2 or η^1_2 pattern.[18] Unfortunately, to the best of our knowledge, no theoretical calculations of a similar rhenium complex with methane have been reported.

The oxidative addition of methane to model 14-electron complexes, *cis*- and *trans*-$[OsCl_2(PH_3)_2]$, was studied theoretically by the RHF method with subsequent correction for electron correlation by the MP2 and the density functional theory techniques. It was concluded that isomeric σ-complexes can be formed, namely, *cis*- and *trans*-$[OsCl_2(PH_3)_2(\eta^2\text{-}CH_4)]$.[108] According to the calculations, the complex of methane with *cis*-$[OsCl_2(PH_3)_2]$ is much more stable than that with *trans*-$[OsCl_2(PH_3)_2]$. Oxidative addition giving rise to $OsCl_2(PH_3)_2(CH_3)(H)$ was found to be energetically favourable for the *trans*-$[OsCl_2(PH_3)_2(\eta^2\text{-}CH_4)]$ complex.

The coordination of methane by the Cp_2M complexes (M = Ti–Ni) was studied by semiempirical SCF MO LCAO calculations in the INDO (intermediate neglect of differential overlap) valence approximation using the unrestricted Hartree–Fock (UHF) formalism.[109] The results of calculations attest to the possible formation of weak complexes of methane with these metallocenes. In the researchers' opinion,[109] the coordination of a methane molecule by titanium, vanadium, manganese or nickel derivatives is likely to be accompanied by oxidative addition resulting in $Cp_2M(H)(CH_3)$. In all of these complexes, methane is coordinated according to the η^1_2 pattern. It should be noted that the calculation method used leads to an unusually great value for the length of the C–H_b bridging bond (1.2–1.35 Å) in these complexes compared to the values obtained by other researchers (1.11–1.16 Å). The unusually high bond energies of methane in the complexes with ferrocene, cobaltocene and nickelocene (14–21 kcal mol^{-1}) also raise doubts.

A number of papers are devoted to the theoretical investigation of carbonylation of alkanes with carbonyl chloride rhodium complexes $Rh(PR_3)_2Cl(CO)$, which was discovered experimentally and studied by Sakakura and Tanaka.[110] An *ab initio* investigation of the PES for the oxidative addition of methane to the model 14-electron $RhCl(PH_3)_2$ complex has shown [111] that the reaction proceeds *via* the formation of the *trans*-$[RhCl(PH_3)_2(\eta^2\text{-}CH_4)]$ complex and a three-centre transition state. According to these calculations, the bond energy of methane in $RhCl(PH_3)_2(\eta^2\text{-}CH_4)$ is 16.7–17.2 kcal mol^{-1}. However, a repeated (MP2) study of this system carried out by the same researchers [112] gave somewhat different results. The authors noted that C–H-bond activation proceeds *via* the *trans*-$[RhCl(PH_3)_2(\eta^1_2\text{-}CH_4)]$ complex with C_s symmetry rather than *via* the *trans*-$[RhCl(PH_3)_2(\eta^2\text{-}CH_4)]$ complex, as they had established previously. One Rh···H_b distance in the η^1_2 complex is much shorter than the other (by 0.4 Å). Both C–H_b bridging bonds are elongated relative to the C–H bonds in free methane, although to different extents. The energy of methane binding in this complex is 13.7 kcal mol^{-1}. The energy of the structure with C_{2v} symmetry is

higher by 0.1 kcal mol^{-1} than the energy of the C_s-symmetric structure. The former is not an equilibrium structure but a transition state between two C_s structures. The Rh—C distances are nearly equal for both structures ($\sim$2.53 Å). The C—H_b bond length in the C_{2v} structure is 1.119 Å. According to more recent density functional theory calculations,[113] the activation of methane by the $RhCl(PH_3)_2$ complex proceeds *via* a η^2-adduct with C_{2v} symmetry, $RhCl(PH_3)_2(\eta^2\text{-}CH_4)$. The stabilisation energy of the *cis*-isomer with respect to the reactants is 6.4 kcal mol^{-1}, while that of the *trans*-isomer is 13.9 kcal mol^{-1}. Comparison of the results of two publications [112, 113] concerning the structures of the $RhCl(PH_3)_2(CH_4)$ complex determined using different calculation techniques attests to a higher stability of the *trans*-isomer [the bond energies are similar, 13.7 (Ref. 112) and 13.9 kcal mol^{-1} (Ref. 113)] relative to the *cis*-isomer. However, the modes of methane coordination found in the two studies are dissimilar.

The intermediate complexes formed in the reactions of methane with rhodium compounds, RhCl(CO), RhH(CO) and $RhH(NH_3)$, have been studied theoretically.[114] The presence of a ground or low-lying singlet state of the central metal atom was found to favour the formation of a stable methane complex, while the presence of a ground or low-lying triplet state contributes to the decrease in the energy barrier to oxidative addition. The geometric parameters of methane complexes were found by SCF and MP2 calculations. In these complexes, methane was assumed to have a distorted η^3-coordination [114] with one of the three Rh—H_b bonds being substantially shorter than the other bonds. This difference increases in the sequence $RhCl(CO)(CH_4)$–$RhH(CO)(CH_4)$–$RhH(NH_3)(CH_4)$.

Numerous experimental data have been obtained indicating that the 16-electron intermediates Cp*ML (M = Rh, Ir; L = PR_3, CO) are able to activate C—H bonds in alkanes according to the oxidative addition mechanism (see a review [115] and references therein). This initiated several theoretical studies dealing with methane interaction with the CpMX fragments (M = Co, Rh, Ir; X = CO, CH_2, PH_3, SH_2).[116–119] Ziegler *et al.*[116] used the density functional method to find out that a σ-adduct of methane with CpMX (M = Rh, Ir; X = CO, PH_3) is formed in an early step. The energy of formation of the adduct varies from 5.7–6.9 kcal mol^{-1} for rhodium complexes to 12.2–14.1 kcal mol^{-1} for iridium complexes. In the $CpRh(CO)(CH_4)$ complex, methane is coordinated to rhodium in the η^1 mode (the Rh—H_b—C angle is close to 180°). The C—H_b bond (1.15 Å) is somewhat longer than the C—H_t bonds (1.09 Å).[116]

Song and Hall [117] studied the oxidative addition of methane to CpRh(CO) by the RHF and MP2 methods. The reaction PES was found to contain two local energy minima, one corresponding to the $CpRh(CO)(CH_4)$ complex and the other, to the oxidative addition product, $CpRh(CO)(CH_3)(H)$. The methane binding energy in $CpRh(CO)(CH_4)$ is 2.2 (RHF) or 14.8 kcal mol^{-1} (MP2). The experimental value for the binding energy of alkanes in such complexes was estimated to be $\sim$10 kcal mol^{-1} (see Ref. 120). According to Song and Hall,[117] the methane ligand in the $CpRh(CO)(CH_4)$ intermediate is coordinated in the η^1_2 mode (the Rh—H_b—C fragment is markedly bent, the corresponding angle being 114.9°). The C—H_b bond is somewhat elongated (1.128 Å) with respect to the C—H bonds in free methane.[117]

Musaev and Morokuma,[118] who studied the PES of the $CpRh(CO) + CH_4$ reaction by the MP2 method with the effective Hay–Wadt potential for the Rh atom and with different basis sets, have found that the first step of the reaction gives $CpRh(CO)(\eta^1\text{-}CH_4)$ (the Rh—H_b—C angle is 179.3°) with a stabilisation energy of 7.7 kcal mol^{-1} with respect to the reactants. The formation energies of the structures with two or three bridging hydrogen atoms are only 1 kcal mol^{-1} higher than the energy of the monodentate structure but they do not correspond to local minima on the PES and, hence, they rearrange spontaneously to a monodentate complex. The C—H_b bridging bond in the methane ligand is 0.02 Å longer than the C—H_t bonds. The charge on the bridging hydrogen atom changes under the influence of the electronically unsaturated rhodium atom from +0.12 e in free CH_4 to −0.13 e in $CpRh(CO)(\eta^1\text{-}CH_4)$.

More recently,[119] the reactions of the 16-electron complexes CpM(CO) (M = Ru^-, Os^-, Rh, Ir, Pd^+, Pt^+) with methane have been studied by the MP2, MP4SDTQ (fourth-order Møller–Plesset perturbation theory with single, double, triple and quadruple excitations) and by the density functional method in the B3LYP approximation. Each of these complexes was found to form the compounds $CpM(CO)(CH_4)$ with η^2- or slightly distorted η^2-coordination of methane. The equilibrium geometries of the intermediate methane complexes were determined without any symmetry restrictions by the MP2 method with the LANL1DZ basis set and by the density functional method in the B3LYP approximation. It was found that the central atoms with a high electron density (Ru^-, Os^-) or with a large atomic mass (Pd^+, Pt^+) readily enter into oxidative addition reactions with methane, while electronically unsaturated light central metal atoms tend to undergo reductive elimination reactions to give C—H bonds.[119] The results of calculations attest to η^1_2-coordination of CH_4 in the $CpRh(CO)(CH_4)$ complex and they are in better agreement with the data obtained by Song and Hall [117] than with Ziegler's [116] and Musaev and Morokuma's results.[118]

The binding energies of methane in the complexes with CpML (M = Co, Rh, Ir; L = CO, CH_2, SH_2, PH_3) have been determined in terms of the perturbation theory in the PCI-80 approximation and by the density functional method in the B3LYPB approximation.[121, 122]

The mechanism of activation of methane C—H bonds by coordinatively unsaturated rhodium and iridium complexes $CpM(PH_3)(CH_3)^+$ has been studied by the MP2 method with the LANLD2DZ basis set and the QCISD method.[123] The iridium complex tends to undergo oxidative addition, whereas in the case of rhodium, σ-bond metathesis with a four-centre transition state is a more probable mechanism. The $CpM(PH_3)(CH_3)(\eta^1_2\text{-}CH_4)^+$ complexes (the M—CH_4 binding energy is 9.5 kcal mol^{-1} for Rh and 7.09 kcal mol^{-1} for Ir) are formed intermediately in these reactions.

A number of studies [124–127] have been devoted to experimental and theoretical investigations of the reactions of alkanes with pyrazolylborate rhodium complexes.

$$L_{n+1}M \underset{}{\overset{-L}{\rightleftharpoons}} L_nM \overset{R-H}{\rightleftharpoons} L_nM(R-H) \rightleftharpoons L_nM\begin{matrix}R\\H\end{matrix}$$

Experimental data [124, 125] indicate that alkane σ-complexes are involved in the reductive elimination of alkanes from the pyrazolylborate rhodium complexes Tp′Rh(L)(R)(H) [Tp′ is tris(3,5-dimethylpyrazolyl)borate, L = $CNCH_2Bu^t$; R = CH_3, CH_2D, CD_3]. The results of a study of the photoinitiated activation of alkanes by the $Tp'Rh(CO)_2$ complexes by fast time-resolved infrared spectroscopy point to successive formation of two different complexes along the pathway to the oxidative addition product, Tp′Rh(CO)(R)(H).[126] To elucidate the nature of these complexes, density functional theory calculations in the B3P86 and LANL2DZ approximations were carried out for the PES of the reaction between the model TpRh(CO) compound [Tp is tris(pyrazolyl)borate] and methane.[127] Two minima corresponding to the $(\eta^3\text{-Tp})Rh(CO)(\eta^1\text{-}CH_4)$ and $(\eta^2\text{-Tp})Rh(CO)(\eta^1_2\text{-}CH_4)$ complexes were found on the PES. Parameters of the methane–rhodium bonds (bond length and energy) in these complexes are substantially different, which is consistent with the results of experimental studies.

Generally, different calculation methods give different results concerning the mode of coordination of the methane ligand in rhodium complexes. Structures with one linear (η^1-coordination) or bent (η^1_2- or η^1_3-coordination) Rh—H_b—C bridge or with two bridges (η^2-coordination) are presumably formed.

Parallel supercomputer calculations have been performed to study the methane activation by 14-electron $Ir(PH_3)_2X$ fragments (X = H, Cl).[128] This study demonstrated that the formation of σ-complexes with an η_2^1-coordination of methane is energetically the most favourable for $Ir(PH_3)_2H$. The geometric parameters of the products were determined by the RHF method. The energy of the complex with η_2^1-coordinated methane is only 0.1 kcal mol^{-1} lower than the energy of the transition state with η^2-coordination. In the author's opinion, the $Ir(PH_3)_2(H)(CH_4)$ methane adduct should exhibit structural non-rigidity at ambient temperatures. The replacement of hydrogen by chlorine in $Ir(PH_3)_2X$ results in a substantial decrease in the Ir···C and Ir···H distances and an increase in the stabilisation energy of the $Ir(PH_3)_2Cl(\eta_2^1\text{-}CH_4)$ complex.

Strout *et al.*[129] carried out a density functional theory study (B3LYP approximations) of the mechanism of the low-temperature activation of C−H bonds in alkanes by the cationic iridium complex $Cp^*Ir(PMe_3)(CH_3)^+$ in perfluoropyridine. Earlier, this reaction was found experimentally.[130] This reaction is formally similar to the metathesis of σ-bonds typical of electron-deficient complexes of early transition metals. Therefore, it was suggested in the experimental study [130] that this reaction was a new example of σ-bond metathesis involving a complex of a late transition metal. Since the two possible mechanisms (oxidative addition or σ-bond metathesis) cannot be distinguished experimentally, it was of interest to perform a theoretical study of this system. Quantum-chemical calculations for the model $CpIr(PH_3)(CH_3)^+ - CH_4$ system showed the intermediate formation of the $CpIr(PH_3).(CH_3)(\eta_2^1\text{-}CH_4)^+$ complex in which methane is weakly bound to iridium by the bent Ir−H_b−C bridge (the Ir−H_b−C angle is 134°). The results of density functional theory calculations of the coordination mode of methane in this complex [129] are consistent with the results obtained by the MP2 method with the LAND2DZ basis set.[123] According to the calculations, the low-temperature reaction of $CpIr(PH_3)(CH_3)^+$ with CH_4 occurs as oxidative addition of methane to the central metal atom. The pathway involving a four-centre transition state (metathesis of σ-bonds) is energetically unfavourable.

Thus, the results obtained by various methods point to the η_2^1-coordination of the methane ligand as energetically the most favourable for all the iridium complexes studied, namely, $CpIr(CO)(CH_4)$, $Ir(PH_3)_2(H)(CH_4)$, $Ir(PH_3)_2Cl(CH_4)$ and $CpIr(PH_3)(CH_3)(CH_4)^+$.

Density functional theory calculations have been carried out[131] to study the mechanism of the recently discovered dehydrogenation of alkanes by the $[\eta^3\text{-}C_6H_3(CH_2PBu^t_2)_2\text{-}1,3]IrH_2$ complex.[132] It was shown that the formation of a σ-complex with methane is endothermic in this case.[131]

The energy characteristics and the mechanism of oxidative addition of methane to the zerovalent 14-electron $Ni(PH_3)_2$ fragment has been studied by the RHF method.[133] It was shown that the formation of the $Ni(PH_3)_2(CH_4)$ σ-complex is energetically favourable and that the pseudo-tetrahedral η^2-coordination of the methane ligand with two hydrogen atoms pointing towards the nickel atom is the most stable.

The MP2 and the density functional (B3LYP) approaches were used to study the PES for two model systems — CH_4 – *trans*-$[PdCl_2(PH_3)_2]$ and CH_4 – *trans*-$[PtCl_2(PH_3)_2]$.[134] According to the results,[134] the palladium and, especially, platinum complexes $MCl_2(PH_3)_2$ (M = Pd, Pt) are more active in stepwise methane activation according to the oxidative addition pattern with preliminary forced abstraction of the phosphine ligand than in the metathesis of the C−H and M−Cl bonds. The 14-electron $MCl_2(PH_3)$ fragments resulting from the removal of one phosphine ligand react with methane to give the σ-complexes $MCl_2(PH_3)(\eta^2\text{-}CH_4)$.

The elementary steps of the recently described [135] activation of methane by a cationic platinum(II) complex with a bidentate N-donor ligand [*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda)]

$$[(tmeda)Pt(CH_3)(NC_5F_5)]^+[BAr_f]^- + {}^{13}CH_4 \longrightarrow$$
$$\longrightarrow [(tmeda)Pt({}^{13}CH_3)(NC_5F_5)]^+[BAr_f]^-,$$

$BAr_f = B[C_6H_3(CF_3)_2\text{-}3,5]_4$

have been studied by the density functional technique in the B3P86 approximation.[136] The theoretical results are consistent with the mechanism comprising the formation of a σ-complex and subsequent oxidative addition. In the model σ-complex $[(en)Pt(CH_3)(CH_4)]^+$ (en is ethylenediamine), methane is bound according to the η_2^1 type. The C−H_b bridging bond is elongated by 0.08 Å compared to the C−H bonds in free methane. The energy of the Pt−CH_4 bond amounts to 21.9 kcal mol^{-1}. In order to compare the calculated bond energy with that obtained experimentally (for the reaction in solution), the energy of methane solvation by the solvent has to be subtracted from the calculated value.

Calculations by the MP4SDQ method for the reaction of $(PH_3)_2Pt$ with CH_4 indicate the formation of the $(PH_3)_2Pt(\eta^2\text{-}CH_4)$ complex having C_{2v} symmetry and a very small stabilisation energy (0.6 kcal mol^{-1}).[137] In line with the small stabilisation energy, the geometric parameters of the methane fragment in this complex change only slightly with respect to those in free methane.

The reductive elimination of methane from a model complex of divalent platinum, $(PH_3)_2Pt(H)(CH_3)$, has been investigated by the density functional approach in the B3LYP approximation.[138] Unlike the results cited above,[137] the results of these calculations showed that the process includes the formation of the $(PH_3)_2Pt(\eta^1\text{-}CH_4)$ σ-complex with a straight bridge (the Pt−H_b−C angle is close to 180°). The length of the C−H_b bond directed towards the metal is virtually the same as the lengths of the other three C−H_t bonds. The stabilisation energy of this complex with respect to free reactants is close to zero.

The reductive elimination of methane from the $(PH_3)Pt(H).(CH_3)$ complex gives the σ-complex $(PH_3)Pt(\eta^2\text{-}CH_4)$ as an intermediate in which two C−H bonds of the methane ligand undergo equally strong interactions with the platinum atom (the corresponding Pt−H bonds are 2.065 and 2.066 Å). Both these bonds are almost 1 Å shorter than the Pt−H agostic bond in $(PH_3)_2Pt(\eta_2^1\text{-}CH_4)$, which is indicative of a stronger binding of methane in this complex. Indeed, the enthalpy of methane binding in $(PH_3)Pt(\eta^2\text{-}CH_4)$ is 10.8 kcal mol^{-1}, whereas this value for $(PH_3)_2Pt(\eta^1\text{-}CH_4)$ is negligibly small. The reductive elimination of methane from *trans*-$[(PH_3)PtCl_2(H)(CH_3)]$ proceeds *via* the complex *trans*-$[(PH_3)PtCl_2(\eta^2\text{-}CH_4)]$ (C_{2v} symmetry) in which the enthalpy of methane binding is equal to 3.6 kcal mol^{-1}.

The reductive elimination of methane from the cationic *cis*-$[(PH_3)_2PtCl(H)(CH_3)]^+$ complex yields *cis*-$[(PH_3)_2PtCl(\eta_2^1\text{-}CH_4)]^+$ in which the lengths of the two Pt−H_b bonds are different. The enthalpy of methane binding in *cis*-$[(PH_3)_2PtCl(\eta_2^1\text{-}CH_4)]^+$ is 9.5 kcal mol^{-1}, which is much higher than that in *cis*-$[(PH_3)PtCl_2(\eta^2\text{-}CH_4)]$. Apparently, the stronger binding of methane in $(PH_3)_2PtCl(\eta_2^1\text{-}CH_4)^+$ is due to the fact that methane is attached to the positively charged $(PH_3)_2PtCl^+$ fragment, unlike the neutral $(PH_3)PtCl_2$ fragment in the other complex.[138]

The results of calculations of geometric parameters of the $ML_n(CH_4)$ complexes and the binding energies of the methane ligand in these complexes are listed in Table 3, and the modes of coordination of the CH_4 ligand in these complexes, depending on the nature of the complexing ion, are shown in Fig. 3.

The results of calculations considered above demonstrate that in methane complexes with ML_n molecular fragments whose central atoms have a d^n electron configuration, the methane ligand is typically coordinated along the edge (η^2 and η_2^1 modes of coordination). The η_2^1-coordination where one bridging bond is much shorter than the other is found most often. A somewhat less frequently encountered mode of methane coordination to the metal is η^2-coordination due to two bridging hydrogen atoms, which results in elongation of the C−H_b bonds compared to those

Table 3. Data of calculation of the geometric structure and the bond energy for the $ML_n(CH_4)$ complexes containing stabilising ligands.

Complex	Bond lengths /Å			The M−C−H_b angle /deg	E_{bd} [a] /kcal mol^{-1}	Calculation techniques (programs)	Ref.
	M···C	M−H_b	C−H_b				
$Cl_2LuH(\eta^1_3\text{-}CH_4)$	2.535	–	1.118	–	1.96	DFT (A-MOL)	80
$Cl_2Lu(CH_3)(\eta^1_2\text{-}CH_4)$	2.625	2.277	1.117	[59.75]	−4.64		
$Cp_2ScH(\eta^1_3\text{-}CH_4)$	2.51	2.31; 2.50	1.14; 1.11	[66.7; 76.7]	[4.78]	DFT/B3P86 (A-MOL)	81
$Cp_2Sc(CH_3)(\eta^2\text{-}CH_4)$	2.72	2.34; 2.36	1.11; 1.11	[58.5; 59.5]	[5.97]		
$Cp_2TiH(\eta^2\text{-}CH_4)^+$	2.53	2.09; 2.24	1.12; 1.11	55; 62	0.8	DFT/PBE, GGA (Laikov)	84
$Cp_2ZrH(\eta^2\text{-}CH_4)^+$	2.70	2.27; 2.39	1.12; 1.11	56; 62	12.0		
$Cp_2Ti(CH_3)(\eta^2\text{-}CH_4)^+$	2.66	2.23; 2.31	1.11	56; 60	4.2	DFT/PBE, GGA (Laikov)	85
$Cp_2Zr(CH_3)(\eta^2\text{-}CH_4)^+$	2.77	2.40; 2.37	1.11	59; 58	9.4		
$Cp_2TiEt(\eta^2\text{-}CH_4)^+$	–	–	–	–	2.0	DFT/PBE, GGA (Laikov)	86
$Cp_2ZrEt(\eta^2\text{-}CH_4)^+$	–	–	–	–	7.3		
$Cp_2TiPr^n(\eta^1_2\text{-}CH_4)^+$	–	2.19; 2.33	–	–	2.5		
$Cp_2ZrPr^n(\eta^2\text{-}CH_4)^+$	–	2.42; 2.37	–	–	7.8		
$Cp_2TiPr^i(\eta^1_2\text{-}CH_4)^+$	–	2.13; 2.41	–	–	−4		
$Cp_2ZrPr^i(\eta^2\text{-}CH_4)^+$	–	2.34; 2.39	–	–	2		
$H_2Ti(=NH)(\eta^3\text{-}CH_4)$	2.63	–	–	–	8.9	RHF/MP2, SKBJ (GAMESS)	95
$H_2Zr(=NH)(\eta^3\text{-}CH_4)$	2.80	–	–	–	8.7		
$H_2Hf(=NH)(\eta^3\text{-}CH_4)$	2.79	–	–	–	9.3		
$Ti(OH)_2(=NH)(\eta^1_2\text{-}CH_4)$	2.84	2.32; 2.60	1.11; 1.10	–	6.6	RHF/MP2 (GAMESS)	96
$Ti(NH_2)_2(=NH)(\eta^1_2\text{-}CH_4)$	3.10	2.52; 2.79	1.10; 1.10	[56.5]	4.4		
$Zr(NH_2)_2(=NH)(\eta^1_2\text{-}CH_4)$	3.05	2.55; 2.69	1.10; 1.10	[57]	6.3		
$Nb(NH_2)(=NH)_2(\eta^2\text{-}CH_4)$	2.84	2.44; 2.43	1.10; 1.10	[57.5]	11.1		
$Ta(NH_2)(=NH)_2(\eta^2\text{-}CH_4)$	2.79	2.37; 2.41	1.11; 1.11	[58]	13.6		
$Mo(=NH)_3(\eta^1_2\text{-}CH_4)$	2.77	2.25; 2.51	1.11; 1.10	[58]	13.7		
$W(=NH)_3(\eta^1_2\text{-}CH_4)$	2.72	2.22; 2.46	1.12; 1.10	[58.5]	15.6		
$Hf(NH_2)_2(=NH)(\eta^1_2\text{-}CH_4)$	–	–	–	–	8.6	RHF/MP2 (GAMESS)	98
$V(NH_2)(=NH)_2(\eta^2\text{-}CH_4)$	2.76	2.31; 2.39	1.104; 1.10	–	13.2		
$Ta(=NH)_3(\eta^1_2\text{-}CH_4)^-$	3.03	2.51; [2.67]	1.10	[52; 61]	8.3 [b]	RHF/MP2, SKBJ (GAMESS)	36
$Tc(=NH)_3(\eta^1_2\text{-}CH_4)^+$	2.66	2.06; [2.51]	1.13	[46.8; 70]	25.7 [b]		
$Re(=NH)_3(\eta^1_2\text{-}CH_4)^+$	2.64	2.05; [2.46]	1.14	[47.5; 68.5]	26.3 [b]		
$Cp_2Ti(\eta^1_2\text{-}CH_4)$	3.32	–	1.32	–	2	MO LCAO SCF/INDO	109
$Cp_2V(\eta^1_2\text{-}CH_4)$	2.84	–	1.35	–	6		
$Cp_2Cr(\eta^1_2\text{-}CH_4)$	2.66	–	1.35	–	7 [b]		
$^1[Cp_2W(\eta^1_2\text{-}CH_4)]$	2.925	2.224; 2.804	1.14; 1.099	[42.6; 72.8]	–	DFT/B3P86 (ADF)	101
$^1[CH_2(C_5H_4)_2W(\eta^1_2\text{-}CH_4)]$	2.895	2.196; 2.786	1.144; 1.096	[42.7; 73.3]	–		
$^1[Cp_2Mo(\eta^1_2\text{-}CH_4)]$	2.940	2.185	1.122	38.96	2.55	DFT/B3LYP, LANL2DZ (GAUSSIAN94)	102
$^1[S(CH_2C_5H_4)_2Mo(\eta^1_2\text{-}CH_4)]$	2.975	2.202	1.120	37.96	1.86		
$^1[(CH_2C_5H_4)_2Mo(\eta^1_2\text{-}CH_4)]$	2.937	2.203	1.121	40.24	3.48		
$^1[CH_2(C_5H_4)_2Mo(\eta^1_2\text{-}CH_4)]$	2.891	2.178	1.123	41.31	4.52		
$^1[Cp_2W(\eta^1_2\text{-}CH_4)]$	2.884	2.093	1.138	37.16	4.70	DFT/B3LYP, LANL2DZ (GAUSSIAN94)	102
$^1[S(CH_2C_5H_4)_2W(\eta^1_2\text{-}CH_4)]$	2.944	2.128	1.133	35.64	7.57		
$^1[(CH_2C_5H_4)_2W(\eta^1_2\text{-}CH_4)]$	2.901	2.111	1.137	37.24	1.61		
$^1[CH_2(C_5H_4)_2W(\eta^1_2\text{-}CH_4)]$	2.827	2.057	1.143	38.35	1.28		
$^1[Cp_2Mo(\eta^1_2\text{-}CH_4)]$	2.842	2.215	1.122	[46]	3.56	DFT/B3LYP, LANL2DZ (GAUSSIAN98, Jaguar 4.0)	103
$^1[CH_2(C_5H_4)_2Mo(\eta^1_2\text{-}CH_4)]$	2.867	2.162	1.126	[41.8]	4.47		
$^1[Cp^*_2Mo(\eta^1_2\text{-}CH_4)]$	2.981	2.200	1.122	[37.5]	−2.17		
$^1[Cp_2W(\eta^1_2\text{-}CH_4)]$	2.752	2.120	1.138	[45.7]	3.42		
$^1[CH_2(C_5H_4)_2W(\eta^1_2\text{-}CH_4)]$	2.729	2.022	1.156	[41.9]	6.14		
$^1[Cp^*_2W(\eta^1_2\text{-}CH_4)]$	(2.797)	(2.040)	(1.150)	[39.2]	−7.3		
$CpMo(NO)(=CH_2)(\eta^1_2\text{-}CH_4)$	2.76	2.17; [2.58]	1.119; 1.10	[47.6]	6.5	DFT/B3LYP, LANL2DZ (GAUSSIAN94)	105
$CpW(NO)(=CH_2)(\eta^1_2\text{-}CH_4)$	2.74	2.14; [2.67]	1.12; 1.10	[44.75]	7.7		
$W(CO)_5(\eta^1_2\text{-}CH_4)$	2.804	2.096	1.147	[42]	7.07 – 8.88	HF, MP2 – MP4 (GAUSSIAN92,94; GAMESS-UK)	107
$W(CO)_5(\eta^2\text{-}CH_4)$	2.764	2.350	1.129	[57]	6.09 – 8.51		
$Cp_2Fe(\eta^1_2\text{-}CH_4)$	2.44	–	1.20	–	14 [b]	MO LCAO SCF/INDO	109
$CpRu(CO)(\eta^2\text{-}CH_4)^-$	2.617	[2.315]	1.108	62.07	6.87 (B3LYP)	MP2, MP4SDTQ, DFT/B3LYP (GAUSSIAN94)	119
	2.533	[2.143]	1.129	57.21	13.2 (MP2)		
$CpOs(CO)(\eta^2\text{-}CH_4)^-$	2.558	[2.155]	1.127	56.65	10.1 (B3LYP)	MP2, MP4SDTQ, DFT/B3LYP (GAUSSIAN94)	119
	2.253	[2.164]	1.135	57.39	19.4 (MP2)		
cis-$[(PH_3)_2Cl_2Os(\eta^2\text{-}CH_4)]$	2.62	[2.24]	1.118	58.3	12 (MP2)	RHF, MP2, DFT/B3LYP (GAUSSIAN92)	108
	2.81	[2.39]	1.103	56.6	– (DFT)		
trans-$[(PH_3)_2Cl_2Os(\eta^2\text{-}CH_4)]$	2.55	[2.19]	1.118	58.7	4 (MP2)		
	2.50	[2.16]	1.112	59.6	– (DFT)		

Table 3 (continued).

Complex	Bond lengths /Å			The M – C – H_b angle /deg	E_{bd} [a] /kcal mol^{-1}	Calculation techniques (programs)	Ref.
	M···C	M – H_b	C – H_b				
$Cp_2Co(\eta^1_2\text{-}CH_4)$	3.40	–	1.23	–	16 [b]	MO LCAO SCF/INDO	109
$RhCl(PH_3)_2(\eta^2\text{-}CH_4)$ (C_{2v})	2.395	2.046	1.094	[58.4]	16.7 – 17.2	RHF/MP2, MP4SDTQ (GAUSSIAN82, MELD)	111
$RhCl(PH_3)_2(\eta^1_2\text{-}CH_4)$ (C_s)	2.533	1.994; 2.356	1.136; 1.105	[47; 68.1]	13.7	MP2 – MP4, QCISD (GAUSSIAN90)	112
trans-$[RhCl(PH_3)_2(\eta^2\text{-}CH_4)]$ (C_{2v})	2.427	2.038	1.127	56.6	13.9	DFT/B3P86 (ADF)	113
cis-$[RhCl(PH_3)_2(\eta^2\text{-}CH_4)]$ (C_{2v})	2.562	2.167	1.113	56.9	6.4		
$RhCl(CO)(\eta^1_3\text{-}CH_4)$	2.58	2.20; 2.66	1.115; 1.104	[57.9]	3.4 (MP2)	SCF (GAMESS); MCPF (STOCKHOLM); MP2 (GAUSSIAN92)	114
	2.87	2.37; 2.94	1.089; 1.083	[52.5]	– 3.8 (SCF)		
$RhH(CO)(\eta^1_3\text{-}CH_4)$	2.47	2.12; 2.55	1.122; 1.105	[58.9]	10.8 (MP2)	SCF (GAMESS); MCPF (STOCKHOLM); MP2 (GAUSSIAN92)	114
	2.80	2.24; 2.90	1.093; 1.083	[49.0]	8.6 (SCF)		
$RhH(NH_3)(\eta^1_3\text{-}CH_4)$	2.49	1.88; 2.71	1.138; 1.102	[46.0]	14.5 (MP2)	SCF (GAMESS); MCPF (STOCKHOLM); MP2 (GAUSSIAN92)	114
	2.91	2.26; 3.05	1.090; 1.082	[44.2]	7.1 (SCF)		
$CpRh(CO)(\eta^1\text{-}CH_4)$	3.16	2.01	1.15	(180)	6.9	HFS-LCAO (A -MOL)	116
$CpRh(CO)(\eta^1\text{-}CH_4)$	2.494	1.799	1.128	[40.8]	2.2 (RHF)	RHF (GAMESS), MP2 (GAUSSIAN90)	117
				(114.9)	14.8 (MP2)		
$CpRh(CO)(\eta^1\text{-}CH_4)$	3.003	1.893	1.110	[0.45] (179.3)	7.7	MP2 (GAUSSIAN92/DFT)	118
$CpRh(CO)(\eta^1_2\text{-}CH_4)$	2.676	[2.058]	1.122	[45.85] [(111.1)]	6.37 (B3LYP)	MP2, MP4SDTQ, DFT/B3LYP (GAUSSIAN94)	119
	2.542	[1.969]	1.135	[47.86] [(106.9)]	13.6 (MP2)		
$\eta^3\text{-}TpRh(CO)(\eta^1\text{-}CH_4)$	3.538	2.436	1.103	[2] (177.6)	1.70	DFT/B3P86, LANL2DZ, (GAUSSIAN94)	127
$\eta^2\text{-}TpRh(CO)(\eta^1_2\text{-}CH_4)$	2.450	1.902	1.139	[48.7] (104.6)	9.39		
$CpRh(PH_3)(CH_3)(\eta^1_2\text{-}CH_4)^+$	2.689	2.014; 2.598	1.128	42.88	12 (MP2)	MP2/LANL2DZ, QCISD (GAUSSIAN94)	123
					9.5 (QCISD)		
$Ir(PH_3)_2H(\eta^1_2\text{-}CH_4)$	2.95	2.25	1.10	[41.6] (119)	6.8	RHF/MP2, SKBJ (GAMESS)	128
$Ir(PH_3)_2H(\eta^2\text{-}CH_4)$	–	–	–	–	6.7		
$Ir(PH_3)_2Cl(\eta^1_2\text{-}CH_4)$	2.67	1.97	1.13	[41.4] (116)	15.6		
$CpIr(PH_3)(CH_3)(\eta^1_2\text{-}CH_4)^+$	2.905	2.007	1.129	[29.9] [(133.8)]	1	DFT/B3LYP (GAUSSIAN94)	129
$CpIr(PH_3)(CH_3)(\eta^1_2\text{-}CH_4)^+$	2.653	1.909; 2.699	1.152	39.43	10 (MP2)	MP2/LANL2DZ, QCISD (GAUSSIAN94)	123
					7.09 (QCISD)		
$CpIr(CO)(\eta^1_2\text{-}CH_4)$	2.588	[1.891]	1.160	41.94	9.64 (B3LYP)	MP2, MP4SDTQ, DFT/B3LYP (GAUSSIAN94)	119
	2.609	[1.945]	1.114	42.79	16.4 (MP2)		
$Cp_2Ni(\eta^1_2\text{-}CH_4)$	3.28	–	1.25	–	21 [b]	MO LCAO SCF/INDO	109
$(PH_3)_2Ni(\eta^2\text{-}CH_4)$	2.49	2.07	–	[55.2]	3.5	SCF-SDCI (GAMESS)	133
$CpPd(CO)(\eta^2\text{-}CH_4)^+$	2.641	[2.211]	1.112	55.53	9.96 (B3LYP)	MP2, MP4SDTQ, DFT/B3LYP (GAUSSIAN94)	119
	2.527	[2.133]	1.118	56.91	12.2 (MP2)		
trans-$[(PH_3)Cl_2Pd(\eta^2\text{-}CH_4)]$	2.55	2.17	–	[57.6]	8.8 (MP2)	MP2, DFT/B3LYP, CCSD(T), SBK (GAMESS, GAUSSIAN94)	134
trans-$[(PH_3)Cl_2Pt(\eta^2\text{-}CH_4)]$	2.66	2.37	–	[63]	– (HF)		
	2.51	2.14	–	[58]	8.6 (B3LYP)		
	2.47	2.10	–	[58]	11.9 (MP2)		
$(En)PtCH_3(\eta^1_2\text{-}CH_4)^+$	2.36	1.73	1.18	[44.5] (29)	21.9	DFT/B3P86 (ADF)	136
$(PH_3)_2Pt(\eta^2\text{-}CH_4)$	4.644	–	–	–	0.6 (HF)	HF; MO/MP4SDQ (GAUSSIAN82)	137
					0.4 (MP4)		
$(PH_3)_2Pt(\eta^1\text{-}CH_4)$	4.4	3.308	1.095	0 (180)	~0	DFT/B3LYP, CCSD(T) (GAUSSIAN98)	138
$(PH_3)Pt(\eta^2\text{-}CH_4)$	2.43	2.065; 2.066	1.119; 1.118	[58]	10.8		
trans-$[(PH_3)Cl_2Pt(\eta^2\text{-}CH_4)]$	2.562	2.188; 2.188	1.108; 1.108	[58]	3.6		
cis-$[(PH_3)_2ClPt(\eta^2\text{-}CH_4)]^+$	2.543	2.082; 2.296	1.121; 1.105	[53.5; 64.6]	9.5		
$CpPt(CO)(\eta^1_2\text{-}CH_4)^+$	2.674	[2.019]	1.137	44.11	10.9 (B3LYP)	MP2, MP4SDTQ, DFT/B3LYP (GAUSSIAN94)	119
	2.611	[1.928]	1.116	41.78	17.4 (MP2)		

Note. The values in brackets have been calculated by the author of the review using data from the cited publications.
[a] The M – CH_4 bond energy in the complex. [b] The enthalpy of formation of the complex.

Li	**Be**											**B**
Na	**Mg**											**Al**
K	**Ca**	**Sc** η^1_3, η^2	**Ti** $\eta^1_2, \eta^1_3, \eta^2, \eta^3$	**V** η^1_2, η^2	**Cr** η^1_2	**Mn**	**Fe** η^1_2	**Co** η^1_2	**Ni** η^1_2, η^2	**Cu**	**Zn**	**Ga**
Rb	**Sr**	**Y**	**Zr** η^1_2, η^2, η^3	**Nb** η^1_2, η^2	**Mo** η^1_2	**Tc** η^1_2	**Ru** η^2	**Rh** $\eta^1_2, \eta^1_3, \eta^1, \eta^2$	**Pd** η^2	**Ag**	**Cd**	**In**
Cs	**Ba**	**Lu** η^1_3, η^2	**Hf** η^3	**Ta** η^1_2, η^2	**W** η^1_2	**Re** η^1_2	**Os** η^2	**Ir** η^1_2, η_2	**Pt** η^1_2, η^1, η^2	**Au**	**Hg**	**Tl**

Figure 3. Dependence of the modes of coordination of the CH_4 ligands in the complexes $ML_n(CH_4)$ on the nature of the complexing ion.

in free methane. Examples of methane coordination along a face (η^3 and η^1_3) by d^n-ion complexes are rare; this mode of coordination was mentioned only in one study.[114] The η^1-coordination of methane (by a tetrahedron vertex) is equally unusual.[116, 118]

V. Some structural features of methane complexes

The data considered above demonstrate that the results of quantum-chemical calculations of methane complexes with neutral metal atoms, metal ions and molecular fragments ML_n predict a diversity of modes of methane coordination in these complexes and small energy differences between various structures, which is typical of structurally non-rigid compounds. In complexes with neutral atoms or metal ions without stabilising ligands, η^2 and η^3 modes of coordination are energetically preferred for methane. No complexes with linear η^1-coordination have been found for these species. In rare cases, calculations predict the η^1_3-coordination of methane as the most stable [for example, in $Rh(\eta^1_3\text{-}CH_4)^+$ and $Pt(\eta^1_3\text{-}CH_4)^+$];[65, 67] however, the use of other calculation methods or higher-level theories shows that for Rh^+ and Pt^+ complexes, too, η^2-coordination is the most stable.[62, 68]

Complexes with η^3-coordination of methane are mainly typical of non-transition metal ions M^+ and for transition metal ions of the beginning of the row (Li^+, Mg^+, Sc^+, Ti^+, Cr^+, Ta^+), while transition metal ions of the end of the row (Co^+, Rh^+, Ir^+, Cu^+) tend to form complexes with η^2-coordination of methane. The $Fe(CH_4)^+$ structures with C_{2v} (η^2) and C_{3v} (η^3) symmetry are nearly degenerate, the energy difference between them being 0.05–0.17 kcal mol^{-1} (see Ref. 55).

The results of calculations of the geometric structure of $Mg(CH_4)^+$ and $V(CH_4)^+$ show that it depends appreciably on the electronic state of the central atom.[39, 46] The energy of binding of the methane ligand to the metal increases on passing from non-transition to transition metals. For neutral metal atoms in the ground state, the energy of methane binding in the complexes is relatively low, as a rule, less than 4 kcal mol^{-1} (see, for example, Ref. 29). Of transition metal ions in the ground state, the lowest binding energy of the methane ligand was found for Mn^+ and Zn^+ ($\sim$10 kcal mol^{-1}),[35] while the highest energy was found for the Pt^+ ion ($\sim$30 kcal mol^{-1}).[69]

Some discussion has been devoted to the dependence of the mode of methane coordination on the nature of the complexing ion. According to Yoshizawa,[56] η^2-coordination is most probable for low-spin states of ions and η^3-coordination is most likely for high-spin ions. Bauschlicher and coworkers,[74] while considering the structure of the $Cu(CH_4)^+$ complex, suggested that electrostatic interaction is favourable for the formation of a η^3-structure, and dative interaction promotes η^2-coordination.

Other modes of coordination are typical of methane complexes with ML_n molecular fragments. Only a few examples of complexes where η^3-coordination of methane should be preferred according to calculations are known [derivatives of d^0 ions: Cl_2LuH,[80] $H_2M{=}NH$ (M = Ti, Zr, Hf)[95]]. Complexes with η^1_3-coordination of the methane ligand are also represented by single examples [RhHCl, RhH(CO), $RhH(NH_3)$[114]]. It is noteworthy that η^1_3-coordination of methane has not been found for platinum complexes containing stabilising ligands, whereas this mode of coordination has been reported[67] to be preferred for complexes of the Pt^+ ion without ligands. In most cases, calculations point to monodentate methane coordination with a bent M–H–C bridge (η^1_2-coordination) as the most energetically favourable for complexes with ML_n molecular fragments. η^2-Coordination is also often found for these complexes (however, not as often as η^1_2). In both cases, methane is coordinated to the metal by the tetrahedron edge. The difference between these modes of coordination is that in the case of η^1_2-coordination, two bridging $M{-}H_b$ bonds have markedly different lengths. The energy of methane binding is much lower in complexes containing stabilising ligands than in complexes with bare ions; in most cases, the former does not exceed 10 kcal mol^{-1}.

It is obvious that this difference in the structures and binding energies between complexes with bare ions and with ML_n molecular fragments is due to the stabilising ligands. In particular, a substantial influence of steric factors on the structure of methane complexes has been noted in an early publication[139] devoted to this problem and in a number of subsequent studies.[81, 86]

It should be noted that the results of calculations of the geometric structures of methane complexes obtained by different researchers differ markedly from one another. Quantum-chemical calculations point to an insignificant energy difference between complexes that differ only in the mode of methane coordination. Therefore, determination of the most stable structure is ambiguous and depends on both the system under study (the complex) and the calculation methods and basis sets used.[107] This ambiguity is observed both for complexes containing stabilising ligands and for complexes formed by bare ions.

Currently it is impossible to verify experimentally the calculation results for methane complexes, because, unlike complexes formed by molecular N_2 or H_2, which have been isolated in the crystalline state, no metal complexes with an alkane molecule as a ligand have been isolated so far. In view of the ambiguity of calculation results and the impossibility of their experimental verification, it would be useful to compare the results of calculations of the structures of methane complexes with experimental data for some existing systems that resemble methane complexes in electronic and geometric structures.

Several systems have been proposed to model various steps of alkane activation. For example, structural data for alkyl complexes with intramolecular C–H···M agostic bonds were used by Crabtree *et al.*[140] to model the trajectory of addition of the C–H bond to the central atom. However, this model does not allow one to identify the mode of methane coordination in the complexes.

Recently, adducts of metal carbonyls with phosphine and amine boranes, $M(CO)_4 \cdot H_3BL$ (M = Cr, Mo, W; L = PMe_3,

PPh_3, NMe_3), have been considered as structural models of methane complexes.[141, 142] Presumably, these complexes are fairly important as model systems because H_3BL molecules are isoelectronic to methane and, like methane, they are electrically neutral. According to X-ray diffraction data, the borane ligand in the considered complexes is attached to the metal according to the η^1_3 pattern through one bent hydrogen bridge.[141] This mode of coordination is apparently due to steric reasons because it allows the bulky substituent L in the borane ligand to be located far from the $M(CO)_4$ fragment. According to NMR data, the three hydrogen atoms of the borane ligands are equivalent in solutions; this is indicative of structural non-rigidity of the complexes on the NMR time scale. Examples of η^2-complexes formed by boranes are also known.[143]

The η^1_3-coordination of phosphine or amine boranes to Group VI metal carbonyls, found experimentally, is not quite consistent with the results of calculations for $M(CO)_5 \cdot CH_4$, according to which the η^1_2-coordination of methane is preferred for these complexes from the energy standpoint.[107] The data presented in this review demonstrate (see Tables 1 and 3) that η^1_3-coordination is unusual for methane and seldom corresponds to an energy minimum. Apparently, this difference between the two systems being compared is due to steric factors, in particular, the presence of bulky substituents L in phosphine or amine boranes and the absence of such groups in the methane molecule. Unfortunately, the scope of applicability of this model is limited due to the limited selection of stabilising ligands (mainly, these are carbonyl or phosphine ligands) and complexing ions (Group VI – VIII metals). The number of structurally studied complexes of this type is small. Therefore, this model does not permit a systematic investigation of the dependence of the structure of complexes on the nature of the ligands and the complexing metal. It is also evident that due to steric factors, these complexes are not quite suitable for the modelling of methane complexes.

It has been assumed repeatedly that tetrahydroborates of various metals, whose structures have been studied rather extensively, could serve as structural models of methane complexes.[144, 145] Indeed, the BH_4^- anion is isoelectronic to the methane molecule. The BH_4^- and CH_4 species are very similar in size and geometry (tetrahedron), which is rather important in view of the considerable influence of the steric factor on the mode of coordination of these ligands. The BH_4^- anion forms a rather large number of complexes, sufficiently stable to be studied experimentally, with metal ions of almost all Groups (with diverse modes of ligand coordination). However, the use of these compounds as models for comparison with methane complexes was precluded by the lack of knowledge of particular factors determining the structural and dynamic properties of tetrahydroborates themselves.

Recently, some previously unknown features of the structures of tetrahydroborate complexes have been elucidated.[146] It was shown that tetrahydroborate complexes can be subdivided into two large groups which differ appreciably in the structural (the mode of coordination of the tetrahydroborate ligand) and dynamic (structural rigidity or non-rigidity) properties.[146] The main factor determining the difference between the structures and dynamic properties of tetrahydroborate complexes is the difference between the electronic configurations of the central metal atom.

Derivatives of transition metals in high oxidation states [as a rule, these are Group III and IV metals having no outer d electrons — d^0-electron configuration or d^1-configuration in the case of Ti(III) complexes] and alkali and alkaline earth metals tend to form structurally non-rigid complexes with tridentate BH_4 ligands. Other modes of coordination (η^2 and η^1) in these complexes usually arise due to the presence of stabilising ligands (*e.g.*, as a result of steric hindrance), *i.e.*, they are forced.[147]

Tetrahydroborate complexes of monovalent metals with the s^1 configuration have not been isolated in a pure state and no structural data for these compounds are available. However, gas-phase studies have shown that the tetrahydroborate ligand in the monovalent calcium complex $Ca(BH_4)$ is coordinated according to the η^3 type (C_{3v} symmetry).[148] These data are consistent with the results of *ab initio* calculations.[149]

Tetrahydroborate η^3-complexes with $d^2 - d^{10}$ central metal atoms are unknown. Even in the absence of steric hindrance, the BH_4 ligand in these complexes is coordinated according to the η^2 type (in a few cases, according to the η^1 type).

The data presented in this review demonstrate that a similar pattern of dependence of the structure of complexes on the electronic configuration of the central atom is also observed for methane complexes with neutral metal atoms and bare metal ions. Indeed, according to quantum-chemical calculations, a tridentate methane coordination is assumed for $Li^+(1s^2)$, $Na^+(2p^6)$, $Mg^+(3s^1)$, $Sc^+(3d^14s^1)$, $Ti^+(3d^24s^1)$, $V^+(3d^34s^1)$, $Ta^+(5d^36s^1)$, $Cr^+(^4D,3d^34s^1)$, $Fe^+(3d^64s^1)$, $Fe^0(3d^64s^2)$ and $Co^0(3d^74s^2)$ ions having no d electrons in the outer shell. In the case of d^n ions ($n = 2-10$) and neutral atoms with a d^n-type shell — $Nb^+(^5D,4d^4)$, $Co^+(^3F,3d^8)$, $Rh^+(^3F,4d^8)$, $Ir^+(^3F,5d^8)$, $Cu^+(^1S,3d^{10})$, $Rh^0(^2D,4d^9)$, $Pd^0(^1S,4d^{10})$ and $Pt^0(^1S,5d^{10})$ — a bidentate methane coordination predominates. Due to the scarcity of experimental data and the results of calculations of methane complexes with multicharged M^{n+} ions, it is impossible to draw any general conclusions concerning their structure. However, the dependence of the mode of methane coordination on the electronic configuration of the complexing ion, observed for single-charged ions M^+, might also hold for multicharged ions M^{n+}.

Similar regularities, that is, the tendency for the formation of η^3-complexes for d^0 ions and $\eta^2(\eta^1_2)$-complexes for d^n-ion derivatives, are also observed for complexes containing stabilising ligands. However, in this case, the mode of methane coordination is determined not only by the electronic configuration of the central metal atom but also by the electronic and steric properties of the ligands. Thus the bidentate coordination of the methane ligand in the complexes formed by d^0 ions, in particular, $Cp_2Sc(CH_3)(\eta^2\text{-}CH_4)$[81] and $Cp_2MR(\eta^2\text{-}CH_4)^+$ (M = Ti, Zr; R = CH_3, C_2H_5, C_3H_7),[86] corresponds to the coordination of the BH_4 groups in similar tetrahydroborates, namely, $Cp^*_2Sc(\eta^2\text{-}BH_4)$, $Cp_2Ti(\eta^2\text{-}BH_4)$ and $Cp_2Zr(\eta^2\text{-}BH_4)_2$, where this mode of coordination is due to the influence of steric factors.[147]

There are only a few exceptions to this regularity. The results of calculations predict a tridentate coordination of methane to the Cr^+ ion in the ground ($^6S,3d^5$) state[46] and η^1_3-coordination to the $Pt^+(^2D,5d^9)$ ion,[67] instead of the expected η^2-coordination. Currently, it is impossible to find out whether this discrepancy in the calculation results is caused by the difference in the coordination properties of methane and the tetrahydroborate anion or is related to inaccuracy of the calculation techniques. An extension of the basis set and the use of higher-level theory for these calculations might bring the calculated data in correspondence with those we predict in terms of the tetrahydroborate model, as was the case for the $Cu^+(^1S,3d^{10})$ ion.

Unfortunately, direct comparison of the structure of methane complexes with similar tetrahydroborate complexes can seldom be carried out. The prevalence of monodentate coordination for methane complexes can be explained by the lower strength of the bond between the methane ligand and the metal compared to that in the case of tetrahydroborate; this makes methane more susceptible to the influence of the ligands.

In our opinion, the analogy found in the dependences of the mode of coordination of methane and the tetrahydroborate anion on the electronic configuration of the central atom for these two types of complexes is not accidental. This is due, apparently, to high accuracy of modern quantum-chemical calculations, which often allow one to predict properly the relative stabilities of various conformations of methane complexes, and to the existence of some common features in the structures of complexes formed by tetrahedral species, BH_4^- and CH_4.

Probably, the discovered dependence of the structure of the BH_4^- and CH_4 complexes on the nature of the central metal atom is related to the difference between the coordination properties of d^0 and d^n ions, well-known in coordination chemistry.[150] The d^0-metal ions tend to undergo ion–ion or ion–dipole electrostatic interactions with formation of weak complexes, while d^n-metal ions are more prone to covalent interactions to give strong metal–ligand bonds. Thus, these two types of complexes differ in the nature of the metal–ligand interaction. The results of studies of the electronic structure of the methane ligand in complexes formed by d^0 and d^n ions are in line with this assumption.

In d^0-ion complexes [Cl_2LuH,[80] Cl_2LnZ (Z = H, CH_3),[82] $H_2M{=}NH$ (M = Ti, Zr, Hf)[95]], methane coordination is accompanied by an increase in the negative charge on the carbon atom and the positive charge on the bridging hydrogen atoms ($C^{\delta-}-H_b^{\delta+}$). Therefore, metathesis of σ-bonds in the series of lanthanide complexes and methane addition to imide complexes can be interpreted as hydrogen transfer between two anionic CH_3 groups in the coordination sphere of the positively charged central atom.[82,96] When methane reacts with CpRh(CO), polarisation of the C–H bonds switches to the opposite one: $C^{\delta+}-H_b^{\delta-}$ (see Ref. 118). Unfortunately, data on C–H bond polarisation in other d^n-ion complexes are missing, but one can assume that polarisation of the methane C–H bonds in these complexes would be similar to that found in CpRh(CO)(CH_4). Apparently, the difference in the polarisation of C–H bonds of the methane ligand is responsible for the different mechanisms of activation of these bonds by d^0- and d^n-ion complexes, namely, proton transfer between two carbanions for d^0-ion complexes and oxidative addition of the hydride ion and the carbocation for d^n complexes.

The observed dependence of the ligand denticity on the nature of the complexing ion can be explained qualitatively in the following way. In the case of spherically symmetrical ions with an $s(s^1,s^2)$ or s^2p^6 outer electronic shell where the ion–ion or ion–dipole interaction predominates, the highest bond energy is provided by the shortest distance between the components, which is attained in the case of η^3-coordination. As noted above, this entails only a slight change in the geometric parameters of the methane ligand. In the case of d^n ions, the predominant contribution is made by directional covalent interaction with one or two E–H bonds of the EH_4 species (E = B, C), resulting in η^2- or η^1_2-coordination, higher bond energy and more pronounced distortion of the ligand geometry.

It should be noted that the differences between the properties of d^0 and d^n transition metal complexes can also be followed in systems with intramolecular M···H–C agostic bonds. Indeed, the figure, reported previously,[140] which describes the dependence of the M···H–C angle (α) in complexes with an agostic bond on the radius r_{bp} ($r_{bp} = d_{bp} - r_M$, where d_{bp} is the distance from the metal to the electron pair of the C–H agostic bond, r_M is the covalent radius of the metal, and bp is the bonding pair), shows that any point for d^0 complexes lies below the curve characteristic of d^n complexes (Fig. 4).

Thus, of all the structural models of methane complexes considered above, the tetrahydroborate model describes most adequately the available results of structural studies of methane complexes. In terms of this model, one is not only able to make assumptions concerning the influence of the electronic configuration of the central atom on the mode of coordination of the methane ligand but can also attack the problem of the possible difference between structural properties of M···C–H agostic bonds in d^0 and d^n transition metal complexes.

One may hope that further studies of the structure of tetrahydroborate complexes would throw light on some structural features of methane complexes. For instance, information concerning monodentate tetrahydroborate complexes, little studied at present, could be useful for the understanding of factors that determine the prevalence of η^1_2 methane coordination in the complexes containing stabilising ligands. Systematic research into structurally rigid tetrahydroborates could be helpful in the search for compounds that would hold methane most firmly in the coordination sphere.

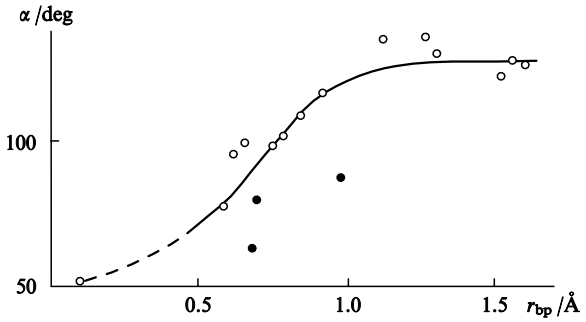


Figure 4. Dependence of the M···H–C angle in complexes with agostic bonds on the radius r_{bp} (according to Ref. 140).
The light dots are the M···H–C angles in d^n-complexes and the dark dots correspond to d^0-complexes.

* * *

The considered experimental and theoretical data on the structures of complexes containing methane as a ligand and comparison of these data with the structural information concerning tetrahydroborate complexes provide the following conclusions:

— methane as a ligand is characterised by diverse modes of coordination to central metal atoms. The mode of coordination of the methane ligand depends appreciably on the electronic configuration of the central metal atom and the nature of stabilising ligands;

— neutral atoms M^0 and bare ions M^+ tend to form $M(\eta^2\text{-}CH_4)^+$ or $M(\eta^3\text{-}CH_4)^+$ complexes. The geometry of these complexes is determined by the electronic configuration of the central atom: ions and neutral atoms with either s or s^2p^6 outer shell form complexes with tridentate coordination of methane. In the case of d^n ions ($n = 2-10$), bidentate methane coordination predominates. Apparently, similar regularities are to be expected for multicharged M^{n+} ions;

— for ML_n fragments containing stabilising L ligands, calculations point to a similar dependence of the structure of methane complexes on the electronic configuration of the central atom (η^3-complexes are formed for derivatives of d^0 ions and are not formed for complexes of d^n ions). However, the presence of stabilising ligands results in η^2 and η^1_2 modes of methane coordination becoming more energetically favourable for these complexes, apparently, due to the electronic and steric influence of the ligands. Factors determining the preference of the η^1_2 methane coordination over η^2-coordination have not yet been elucidated.

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VI. Supplement

Below we present the accepted abbreviations for calculation techniques and software
SCF — self-consistent field method;
LCGO — linear combination of gaussian orbitals;
MCPF — modified coupled pair functional method;
DFT — density functional theory;
PCI-80 — parametrised configuration interaction method with an 80% parameter (in the general case, PCI-X);[151]
RECP — relativistic effective core potential;
B3LYP — Becke's gradient-corrected three-parameter non-local exchange functional[152,153] and Lee–Yang–Parr gradient-corrected non-local correlation functional;[154]

B3P86 — Becke's gradient-corrected three-parameter non-local exchange functional combined with Perdew's gradient-corrected correlation functional;[155]
B3PW91 — the same with the Perdew *et al*. correlation functional;[156]
RHF — restricted Hartree – Fock method;
UHF — unrestricted Hartree – Fock method;
HFSD — Hartree – Fock method with singly and doubly excited configurations;
SKBJ — relativistic compact effective core potential and the Stevens, Basch, Krauss and Jasien shared-exponent basis set;[157]
DZVP — a basis set proposed by Wimmer and coworkers;[158]
6-31G — Pople basis set with the 1s-AO being approximated by six and the 2s,2p-AO, by four gaussian functions grouped in (3,1);
6-31G** — the 6-31G basis set extended by d- and p-polarisation functions;
6-31G + — the 6-31G basis set extended by diffusive functions;
QCI — quadratic configuration interaction method;
QCISD — single and double quadratic configuration interaction method;
QCISD(T) — the same with an estimation of triple excitations by a perturbation method;
MP2(3,4) — second- (third-, fourth) order Møller – Plesset perturbation theory;
MP4SDTQ — fourth-order Møller – Plesset perturbation theory with single, double, triple and quadruple excitations;
CASSCF — complete active space self-consistent field method;
MR-SDCI-CASSCF — multideterminant configuration interaction method with single and double excitations using the wave function obtained by CASSCF;
GRADSCF — a vectorised SCF method with the first and second derivatives;
SCF-CI — self-consistent field configuration interaction method;
SCF-SDCI — self-consistent field with single and double configuration interactions ;
CCSD(T) — coupled-cluster theory with singles and doubles and non-iterative estimation of triple excitations;
GGA — generalised gradient approximation;[159]
PBE — Perdew, Burke and Ernzerhof density functional;[159]
INDO — intermediate neglect of differential overlap;
SBK — relativistic compact effective potential and the Stevens, Basch and Krauss basis set;[160]
LANL1DZ, LANL2DZ — effective core potentials and basis sets developed by Hay and Wadt at the Los-Alamos National Laboratory;[161 – 163]
GVB (General Valence Bond) — a quantum-chemical program package developed at the California Institute of Technology under the direction of W A Goddard III;
GAMESS (General Atomic and Molecular Electronic Structure System) — a quantum-chemical program package (M Dupuis, D Spangler, J Wendolowski. NRCC Software Catalog. Vol. 1, Program No. QG01);[164]
GAMESS-UK — a quantum-chemical program package (F M Guest, P Fantucci, R J Harison, J Kendrick, J H Van Lenthe, K Schoeffel, P Sherwood. CFS Ltd., Darensbury, UK, 1993);
GAUSSIAN80 – 98 — various versions of a quantum-chemical program package developed by the GAUSSIAN corporation (Gaussian Inc., Pittsburgh, PA, 1998);
MOLECULE-SWEDEN — a quantum-chemical program package (J Almlof, C W Bauschlicher Jr., M R A Blomberg, D P Chong, A Heiberg, S R Langhoff, P-A Malmqvist, A P Rendell, B O Roos, P E M Siegbahn, P R Taylor);
MOLPRO — a quantum-chemical program package developed at the Sussex University;[165 – 168]
Dgauss — a quantum-chemical program package;[169]
STOCKHOLM — a quantum-chemical program package for general purposes (P E M Siegbahn, M R A Blomberg, L G M Petersson, B O Roos, J Almlof);
A-MOL — a program system developed by Baerends *et al*.[170] and vectorised by Ravenek;[171]
Laikov — is the program package developed by Laikov;[172]
ADF — the Amsterdam density functional program system;[173]
Jaguar 4.0 — a quantum-chemical program package of the Schrödinger corporation (Schrödinger Inc., Portland, Oregon, 1991 – 2000;
MELD — a quantum-chemical program package (E R Davidson, L E McMurchie, S T Elbert, S R Langhoff, D Rawlings, D Feller. Computer Centre Library Program No 030).

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