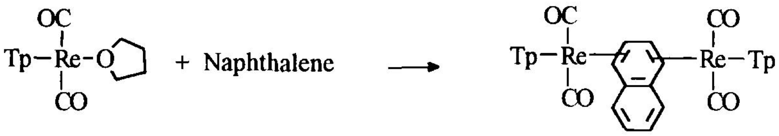
CHAPTER VI

MECHANISMS OF C–H BOND SPLITTING BY LOW-VALENT METAL COMPLEXES

Reactions of metal complexes with saturated hydrocarbons are very important not only from the standpoint of applications but are also extremely interesting for theoretical chemistry. So it is not surprising that many papers devoted to the theoretical aspects of C–H bond activation and especially oxidative addition of C–H compounds to metal complexes (as well as ions and atoms), have been published in recent decades. Some of their results are summarized in books [1] and reviews [2].

VI.1. WEAK COORDINATION OF METAL IONS WITH H-H AND C-H BONDS

Reactions between metal complexes and organic substrates in the condensed phase usually begin with the coordination of these reactants. Due to π- and *n*-electrons present in the molecules of substances frequently employed in catalytic processes (such as olefins, acetylenes, carbon monoxide) they are capable of forming rather stable complexes with transition metals. For example, the complex $TpRe(CO)_2(THF)$ (Tp = hydridotris(pyrazolyl)borate; THF = tetrahydrofuran) reacts with a variety of aromatic molecules to form stable binuclear complexes of the form $\{TpRe(CO)_2\}_2(\mu\text{-}\eta^2\text{-}\eta^{2'}\text{-L})$, where L = furan, *N*-methylpyrrole, or naphthalene [3a]:



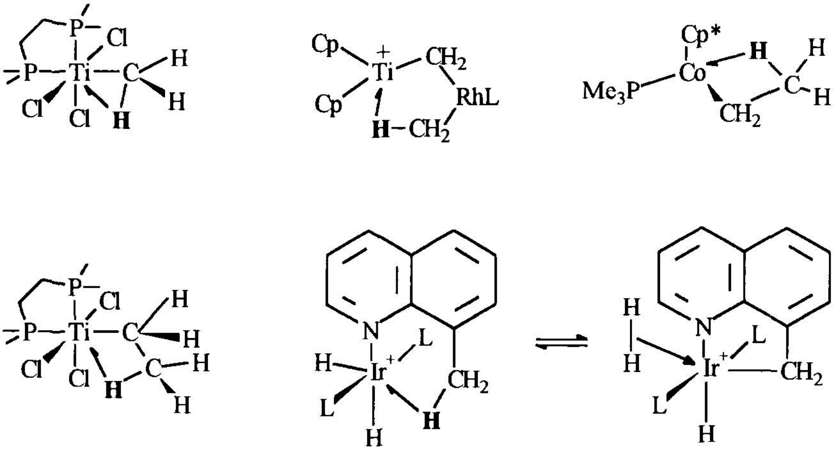
The pentaammineosmium(II) fragment $[(NH_3)_5Os]^{2+}$ is also known to coordinate easily to double bonds in arenes thereby activating them to various transformations[3b].

From a classical viewpoint, the formation of any complexes of saturated hydrocarbons is still difficult to imagine due to the lack of π- or *n*-electrons in their molecules. However, compounds containing hydrogen and other three-center bonds, for example $B\cdots H\cdots B$ or $Al\cdots CH_3\cdots Al$, are known (see discussions of hydrogen and other "nonclassical" bonds [4]). Fairly stable complexes of molecular hydrogen have been prepared and thoroughly investigated recently (see, for example, [5]). If these data are taken into account, one can foresee the possibility of the existence of complexes of alkanes.

On the other hand, bearing in mind that saturated hydrocarbons are extremely weak electron donors and poor electron acceptors, one can postulate that alkane adducts with metal-containing species should be extremely unstable. Thus, a quantum-chemical calculation for one of the most simple metal-free systems (CH_4–O_2) showed that if the C–H σ-bond is located along the axis of the π orbital of oxygen in such a way that the $O\cdots H$ distance is 2.05 Å, a minimum corresponding to a bond energy between the components of ~ 0.5 kcal mol^{-1} appears on the potential curve [6]. According to the calculation for another model system ($CH_3H\cdots ONH_2$) by the INDO method, the stabilization energy of the adduct for a O H distance of ~2.0 Å does not exceed 1 kcal mol^{-1}

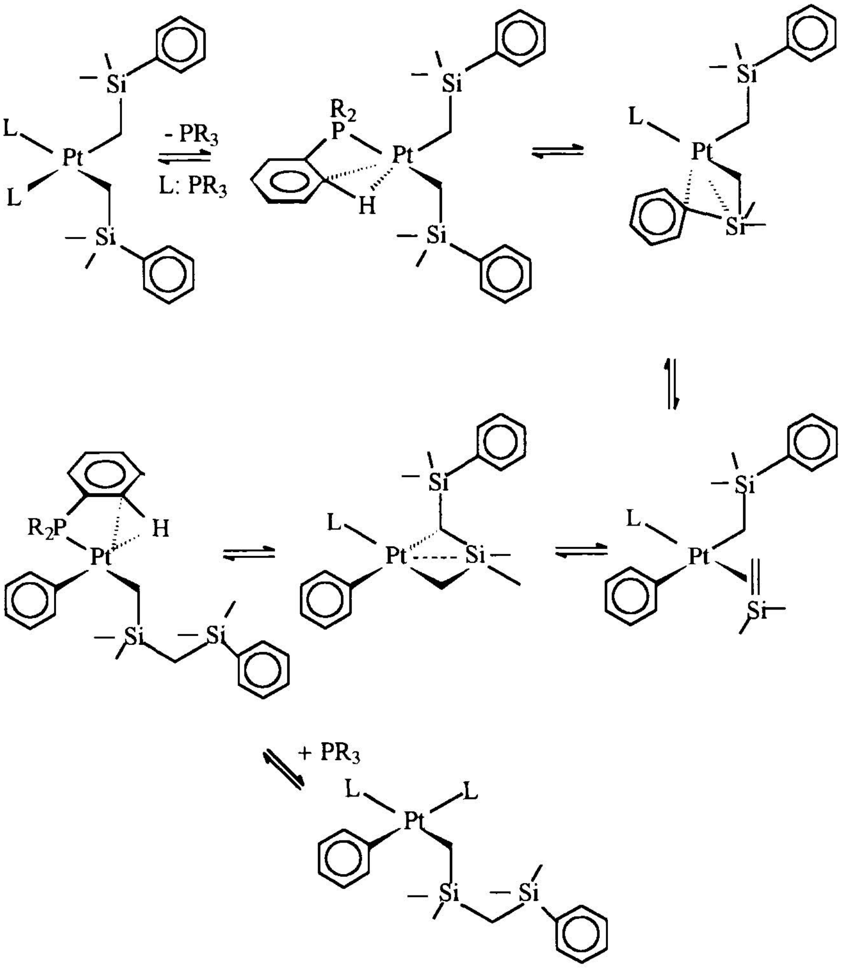
VI 1. A. FORMATION OF "AGOSTIC" BONDS

Complexes in which there is an intermolecular bond between the metal atom and one of the C–H groups of the ligand, according to X-ray diffraction data and confirmed by IR and NMR spectra, have been discovered in recent decades [7], The bonds formed by saturated hydrocarbon fragments, especially methyl groups, are of special interest. It has been suggested that such a bond be referred to as "agostic" and to designate it by a half arrow: $C–H \rightharpoonup M$. Thus the term "agostic" bond refers to the case where the hydrogen atom is simultaneously bound covalently by a three-center two-electron bond to carbon and the transition metal atom. When the agostic bond is formed, the C–H bond usually lengthens by 5–10%, but in the case where it is formed by the $C(sp^3)$–H fragment virtually no increase in length is observed. The M–H bond is also somewhat longer (by 15–20%) than in the usual hydride. The M–C bond length is always appreciably smaller than the sum of the van der Waals radii of M and C. The appearance of the agostic bond is reflected in the NMR spectra (upfield shift of the ^{1}H and ^{13}C signals) and IR spectra (decrease of the stretching vibration frequency of the C–H bond to 2700-2350 cm^{-1}). A few examples of complexes with agostic bonds are presented in Scheme VI. 1.



Scheme VI.1. Examples of complexes containing agostic C–H ⇀ M bonds.

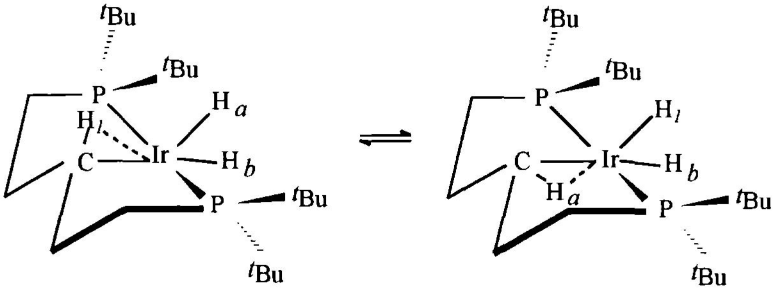
Thus, a system with a C–H ⇀ M agostic bond is, as it were, on the reaction pathway between the C–H + M system and the alkyl hydride derivative C–M–H. In recent years, compounds containing agostic bonds have been proposed as intermediates in reactions that involve C–H bond activation. For example, in the thermolytic rearrangement of *cis*-bis(silylmethyl)platinum(II) complexes, a mechanism is proposed which involves preliminary dissociation of one Pt–P bond compensated by an agostic interaction between the coordinatively unsaturated metal and a phosphine substituent (VI.2) [8].



Scheme VI.2. The mechanism of the rearrangement of *cis*-bis(silylmethyl)platinum(II).

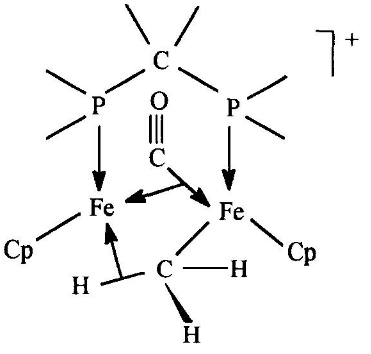
A dynamic motion of the metalated C–H bond and/or exchange of the agostic hydrogen atom in the iridium complex is reflected in the ^{13}C NMR equivalence of the tertiary butyl group quaternary carbon atoms. In the proposed [9] slow exchange that H_l undergoes with iridium atom in the equilibrium **VI-1**

$\rightleftharpoons$ **VI-2** the agostic atom **H_l** moves to the iridium while one of the iridium hydrogen atoms moves to **C_l**.



VI-1 **VI-2**

Reversible on/off switching of C–H $\rightarrow$ Rh interactions in rhodathiaboranes has been decribed [10]. Theoretical investigations of complexes containing agostic bonds have been carried out [11]. The conclusion that formula **VI-3** (in comparison with **VI-4**) describes more precisely the "true" structure of the complex $[Fe_2(CH_3)(CO)(Ph_2PCH_2PPh_2)Cp_2]^+$ has been made on the basis of calculations by the INDO method [12].



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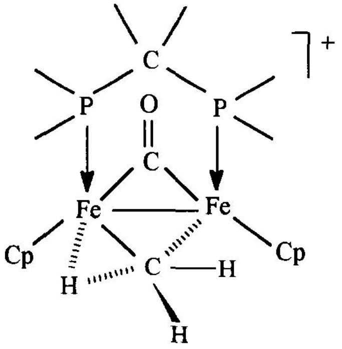


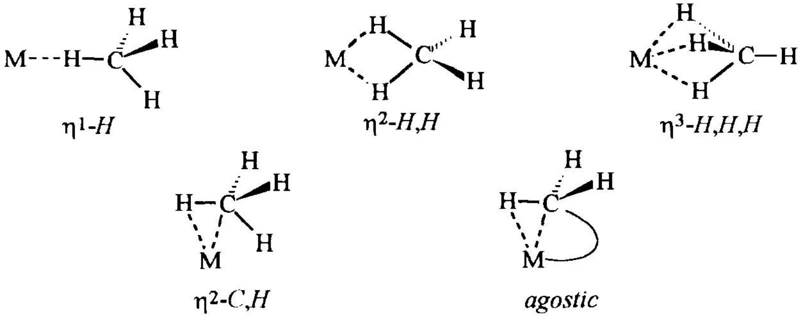
VI-4

Ab initio calculations on the complex $IrH_2[P(Et)H_2]_2^+$ showed that the methyl group of the phosphine ligand does not form any agostic bond with the strongly electron-deficient metal, while the analogous complex $Ir(H_2)(PtBu_2Ph)_2^+$, containing bulky substituents, has two agostic *tert*-butyl groups [13].

VI.1.B. UNSTABLE ADDUCTS BETWEEN ALKANES AND METAL COMPLEXES

Weak adducts of alkanes and metal derivatives (the alkane molecules play the role of "token" ligands in these complexes) have been detected and even isolated using a number of methods [14]. These complexes are unstable at room temperature. Matrix isolation is one of the best established methods for the stabilization and characterization of intermediates. Complexes of alkanes with metal atoms and ions have been detected in the gas phase. All these adducts belong to the larger class of σ-complexes, which has been defined as complexes where the donor is a σ-bond [14c]. Dihydrogen and silane complexes are also from this class.

The following nomenclature has been proposed in review [14c] and publication [15]. If the alkane is bound in an end-on fashion through one, two, or three hydrogen atoms, the complexes are termed η^1-*H*, η^2-*H,H*, and η^3-*H,H,H*, respectively (see Scheme VI.3). The η^2-*H,H* and η^3-*H,H,H* structures involve close contact between the metal and carbon. An alkane may also bind side-on through a single C–H σ-bond: η^2-*C,H* mode. This mode is distinguishable from an end-on η^1-*H* interaction.

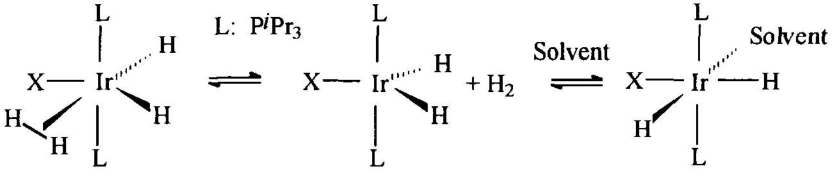


Scheme VI.3. Coordination modes of methane to metal atoms.

Weak adducts of alkanes with metal complexes have been detected by ^{13}C NMR. Dissolution of chromium *tris*-acetylacetonate in 1-chlorobutane entails a paramagnetic shift of the ^{13}C signals of the solvent in the NMR spectrum [16a]. It is of interest that the shift ($\Delta\delta$) along the chain initially diminishes and then again increases for the terminal CH_3 group; the ratio of $\Delta\delta$ is C(1) : C(2): C(3) : C(4) = 1.00 : 0.30 : 0.14 : 0.62. These results indicate the transfer of electron spin density from the complex to the methyl group of the chlorobutane coordinated to it and, since the complex is coordinatively saturated, the interaction apparently takes place via the acetonylacetonate ligand of the complex (outer-sphere coordination). Acetylacetonate complexes of chromi-um(III) and iron(III) also induce changes of chemical shifts in ^{13}C NMR spectra of various alkanes [16b]. The application of the NMR method led to the detection of the short-lived adducts of *bis*[hydro*tris*(pyrazolyl)borato]cobalt with alkanes in solutions [16c,d].

Complexation of a free alkane has been stabilized by creating a binding cavity in the vicinity of a vacant coordination site. This has been seen in the interaction of *n*-heptane with iron(II) in a crystalline complex with the double A-frame porphyrin at room temperature, as confirmed by X-ray analysis [16e].

It has been shown that solid samples of the complex $IrXH_2(H_2)(P^iPr_3)_2$, which are dissolved in hydrocarbons, liberate hydrogen [17a]. The following equilibrium has been proposed for this reaction:



The values of ΔH and ΔS, determined for the chloride and bromide analogs, were higher in alkane solvents than in toluene (Table VI. 1). On the basis of these results it has been concluded that Cl and Br complexes lose an H_2 molecule with little or no complexation of the alkane, and that solvent coordination to the resulting five-coordinate complex occurs in toluene solution. The low values obtained for the iodo complex's thermodynamic parameters indicate that this five-coordinate complex adds a solvent molecule to produce the adduct **$IrIH_2(P^iPr_3)_2$**(Alkane). Influence of arene and alkane coordination on reversible hydrogen elimination from these complexes has been also investigated [17b].

Table VI.1. Thermodynamic parameters for the loss of H_2 from $IrXH_2(H_2)(P^iPr_3)_2$.

X	Solvent	ΔH, kcal mol^{-1}	ΔS, e.u.
Cl	Toluene-d_8	8.6	15
	Methylcyclohexane-d_{14}	12.4	35
	n-Hexane-d_{14}	12.3	36
Br	Toluene-d_8	8.0	10
	Methylcyclohexane-d_{14}	12.1	31
	n-Hexane-d_{14}	12.0	32
I	Toluene-d_8	[a]	[a]
	Methylcyclohexane-d_{14}	10.5	22
	n-Hexane-d_{14}	10.2	22

[a] Equilibrium shifted too far toward $IrIH_2(H_2)(P^iPr_3)_2$ for accurate determination of the equilibrium constants.

The adducts of alkanes with various metal complexes formed at low temperature can be detected by IR spectroscopy [18]. EPR spectroscopy has revealed that the **RhH_2** molecule is strongly complexed with methane in argon matrices at 4K[19].

The investigation [20a] of the photoinitiated reaction of **Cp*$Rh(CO)_2$** with neopentane in liquid krypton by low-temperature IR flash kinetic spectroscopy gave the results that are consistent with a pre-equilibrium mechanism. According to this mechanism, an initially formed transient krypton complex **Cp*Rh(CO)(Kr)** is in rapid equilibrium with a transient (uninserted) alkane complex

$Cp^*Rh(CO)(Me_4C)$. The last complex forms the neopentyl hydride in a unimolecular step. It is interesting that rhodium is bound an order of magnitude more strongly to $(CD_3)_4C$ than to $(CH_3)_4C$. Recently, the reactive intermediate in a cyclohexane C–H bond activation reaction with $CpRh(CO)_2$ has been identified as the cyclohexane solvate η^5-$CpRh(CO)(c\text{-}C_6H_{12})$ by sub-picosecond IR spectroscopy [20b].

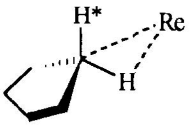
The reaction between cobalt atoms and diazomethane proceeds spontaneously to yield methane and MeCoH when these reactants and dihydrogen are co-condensed with argon onto a rhodium-plated copper surface at 12 K. Wavelength-dependent photolysis of this reaction gave evidence for a cobalt–methane complex formation [15]:

$$CH_3CoH \underset{UV}{\overset{\lambda > 400\ \mathrm{nm}}{\rightleftharpoons}} Co(CH_4)$$

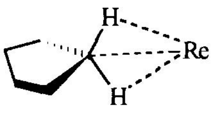
Intermediates (Alkane)$M(CO)_5$ are produced in predominant concentration in solution after flash photolysis of the metal carbonyls $M(CO)_6$ (M = Cr, Mo, W). It has been proposed that the alkane (used as a solvent) is coordinated to the metal via a $C{-}H \rightarrow M$ agostic interaction [21a,b]:

$$M(CO)_6 \xrightarrow{h\nu} [M(CO)_5] \xrightarrow{\text{Alkane}} (\text{Alkane})M(CO)_5$$

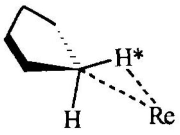
The complex $CpRe(CO)_2(n\text{-heptane})$ has been characterized at or above room temperature in *n*-heptane by fast time-resolved infrared (**TRIR**) spectroscopy [21c]. The reactivity of this complex with carbon monoxide ($k = 2.1 \times 10^3\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$) demonstrates that $CpRe(CO)_2(n\text{-heptane})$ is the least reactive of the reported organometallic alkane complexes. It is interesting that an analogous xenone derivative $CpRe(CO)_2(Xe)$ is less reactive toward CO than all of the reported alkane complexes except $CpRe(CO)_2(n\text{-heptane})$ [21c], More recently, direct observation of a transition metal alkane complex using **NMR** spectroscopy has been reported [21d], When a supersaturated solution of the complex $CpRe(CO)_3$ ($\sim 4 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$) in neat cyclopentane was cooled to –80 °C or below and photolyzed, a new singlet peak at δ 4.92 in the Cp region of the ^{1}H NMR spectrum, as well as another resonance at δ –2.32, appeared at the expense of the peak at δ 5.23 due to the starting complex. The authors attributed these new peaks to the alkane complex $CpRe(CO)_2$(cyclopentane) with the peak at δ –2.32 apparently due to one methylene unit of the cyclopentane ring being coordinated to the metal center:



η^2-*C,H*



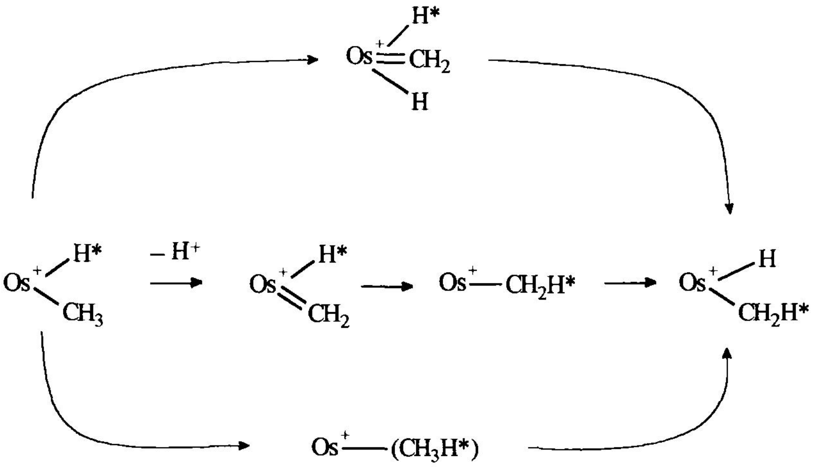
η^2-*H,H*



η^2-*C,H**

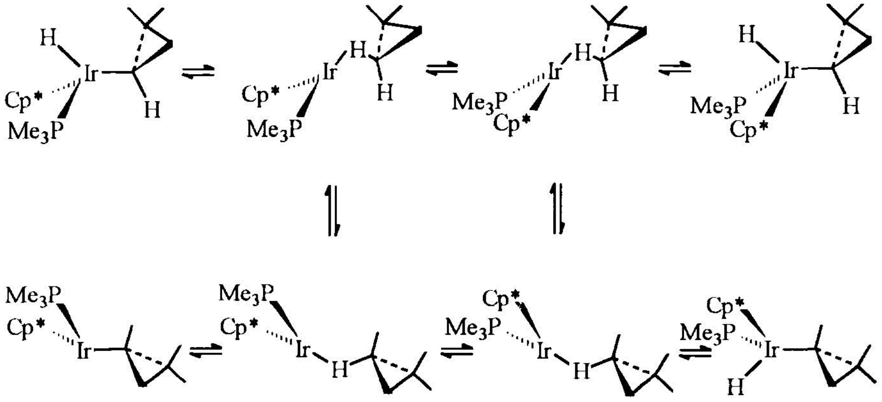
Results of nanosecond and microsecond transient absorption spectroscopic experiments on the photolysis of the complex (η^2-dfepe)$Cr(CO)_4$ [dfepe = $(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$] in hexane and cyclohexane solvents indicated the formation of alkane complexes of the type (η^2-dfepe)$Cr(CO)_3$(Alkane) and (η^1-dfepe)$Cr(CO)_4$(Alkane) [22]. The rearrangement of the silane complex $CpMn(CO)_2(HSiEt_3)$ has been studied by photoacoustic calorimetry [23].

It has been established that methane inhibits the reaction chain free-radical autooxidation of dialkylcadmium [24a] and the reaction of butyllithium with butyl iodide [24b]. It has been proposed that in the second case this effect is due to the coordination of methane to the lithium alkyl in the reaction or to the prereaction complex. The investigation [25] of the kinetics of the reductive elimination of methane from the complex $Cp^*_2W(CH_3)H$ or $Cp_2W(CH_3)H$ led to the proposal of the formation of the so called methane "σ-complex", i.e., a complex with η^2-coordination of the C–H σ bond. The existence of an analogous intermediate has been postulated in the reaction involving the elimination of CH_4 from the methylrhenium hydride derivative [26a]. Rapid exchange of hydrogen atoms between hydride and methyl ligands in the complex $[Cp^*Os(dmpm)\text{-}(CH_3)H^+]$, where dmpm is bis(dimethylphosphino)methane, can proceed by means of α-hydrogen elimination to form an osmium methylene dihydride intermediate or via reversible deprotonation of the Os–CH_3 group by the $HC(SO_2CF_3)_2^-$ anion present in the solution. However, the authors' opinion suggests that this reaction most likely takes place by formation of a coordinated methane ligand (Scheme VI.) [26b].



Scheme VI.4. Possible intermediates in the exchange of hydrogen atoms between hydride and methyl ligands in [Cp*Os(dmpm)(CH_3)H.

In the literature [25, 26a,c–g], inverse kinetic isotope effects for the reductive elimination of alkanes from metal centers, which is the microscopic reverse of alkane activation by oxidative addition, have been explained by the presence of an σ alkane intermediate. Recently, thermolysis of the diastereomerically pure complexes (*RS*),(*SR*)-[2,2-dimethylcyclopropyl) **(Cp*)-(PMe$_3$)IrH]** and (*RR*),(*SS*)-[2,2-dimethylcyclopropyl)**(Cp*)(PMe$_3$)IrH]** (see Scheme VI.5) in C_6D_6 has been shown [26h] to result in its interconversion to the other diastereomer. The analogous reaction of the deuterium-labeled complexes resulted additionally in scrambling of the deuterium from the α-position of the dimethylcyclopropyl ring to the metal hydride position. Diastereomer interconversion and isotopic scrambling occurred at similar rates and have been discussed in terms of a common intermediate mechanism involving a metal alkane complex (Scheme VI.5).



Scheme VI.5. The alkane-complex intermediate mechanism proposed for deuterium-scrambling and diastereomer interconversion in the iridium complexes.

Alkane σ-complexes have also been detected in the gas phase. The study by time-resolved IR spectroscopy of the interaction of a range of open-chain and cyclic alkanes with the 16-electron species $W(CO)_5$ has shown that reversible complexes with all the unsubstituted alkanes, L, are formed except with methane [27a]. The equilibrium constant

$$K_p = \frac{[W(CO)_3L]}{[W(CO)_3]p(L)}$$

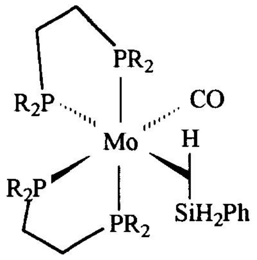
at 300 K, increases with carbon number from 610 atm^{-1} in ethane to 5200 atm^{-1} in *n*-hexane, and from 1300 atm^{-1} in cyclopropane to 7300 atm^{-1} in cyclohexane. Binding energies are in the range of 7–11 kcal mol^{-1}, again increasing with the size of the alkane. The kinetic and activation parameters have been determined for the reactions of complexes $(\eta^6\text{-arene})Mo(CO)_2(Sol)$ and $M(CO)_5(Sol)$ (M = Cr, Mo, W) with CO [27b]; for M = Cr the $\Delta H^\ddagger$ is constant (~ 5 kcal mol^{-1}), while the $\Delta S^\ddagger$ term becomes less negative as the alkane chain length increases. In high-pressure mass spectrometry studies of organometallic species, a $[\mathrm{Mn, C_6, O_5, H_4}]^+$ ion was observed when $\mathrm{Mn_2(CO)_{10}}$ was used as a precursor and methane as a chemical ionization agent [28a]. The authors proposed that this ion is a $\mathrm{(OC)_5Mn^+{-}CH_4}$ complex formed in the high-pressure ion source by the interaction between $\mathrm{(OC)_5Mn^+}$ and methane.

Reacting mass-selected species $\mathrm{Fe(CO_2)^+}$ with the mixtures $\mathrm{N_2{-}CH_4}$, $\mathrm{CO_2{-}CH_4}$ and others provided an internally consistent set of equilibrium constants and free energies $\Delta\Delta G$ (298 K) (Table VI.2) [28b].

Table VI.2. Equilibrium constants for ligand-exchange reactions with $\mathrm{Fe(L)^+}$ and $\Delta\Delta G$ (298 K) values.

No	Reaction	K_{eq}	$\Delta\Delta G_R$ kcal mol^{-1}
1	$\mathrm{Fe(N_2)^+ + CH_4 \longrightarrow Fe(CH_4)^+ + N_2}$	5.4±0.7	- 1.0±0.1
2	$\mathrm{Fe(CO_2)^+ + CH_4 \longrightarrow Fe(CH_4)^+ + CO_2}$	1.5±0.3	- 0.2±0.1
3	$\mathrm{Fe(Xe)^+ + CO_2 \longrightarrow Fe(CO_2)^+ + Xe}$	2.7±1.3	- 0.6±0.4
4	$\mathrm{Fe(N_2)^+ + CO_2 \longrightarrow Fe(CO_2)^+ + N_2}$	3.8±0.8	- 0.8±0.2
5	$\mathrm{Fe(N_2)^+ + Xe \longrightarrow Fe(Xe)^+ + N_2}$	1.5±0.3	- 0.2±0.1

The η^2-coordination of the Si-H bond in complexes **VI-5** [29a] and **VI-6** [29b] and the C–H bonds of the *meso*-octaethyltetraoxaporphyrinogen [29c] has been confirmed by X-ray analysis.



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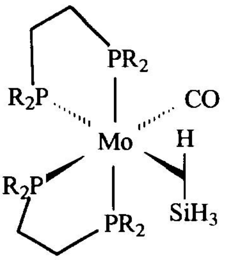


VI-6

The concept of the transient formation of a carbon–hydrogen σ bond complex has been used in the discussion [30] of the possible mechanism of equilibration between diastereomeric chiral rhenium alkene complexes $[CpRe(NO)(PPh_3)(H_2C{=}CHR)]^+$

Quantum-Chemical Calculations

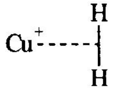
The problem of the coordination of alkanes to metal atoms, ions and complexes has attracted the attention of theoretical chemists. It has been suggested that the interaction of saturated C–H bonds with transition metals is due to the overlap of the diffuse outer orbitals of the transition metal with the localized orbitals of the saturated bond [31].

The simplest system for modeling the interaction of the C–H bond with an unoccupied diffuse orbital of the metal is a methane molecule coordinated to a palladium atom. A calculation has been carried out for this system by the nonempirical SCF MO method [32]. Three possible symmetrical structures of $Pd \cdot CH_4$, differing in the number of hydrogen atoms coordinated directly to the palladium atom, were examined: two structures with C_{3v} symmetry (η^1-*H* and η^3-*H,H,H* coordination, see Scheme VI.3) and one with the C_{2v} symmetry (η^2-*H,H* coordination). The calculated $CH_4 \cdot Pd$ bond energies decrease in the sequence η^1-*H* > η^2-*H,H* > η^3-*H,H,H*, although they are similar for all three structures (8.4 and 7.3 kcal mol^{-1} for η^1-*H* and η^3-*H,H,H*, respectively).

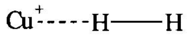
Coordination leads to a slight transfer of electron density from methane (mainly from the hydrogen atoms) to the 5s and 5p orbitals of palladium via a donor–acceptor mechanism; this entails some redistribution of electron density in the individual AO of both components. Thus, the electron density in the $4d_{z^2}$ AO of the palladium atom decreases in all three structures. There is a simultaneous increase of electron density in the 5s, $5p_\pi$, and $5p_\sigma$ AOs, but the overall negative effective charge on palladium increases. Changes in the populations of the AOs of methane (much smaller) show that the electron density is to some extent transferred also via a dative mechanism. Since a carbon and not a hydrogen atom plays the main role in the structure with η^3-*H,H,H* coordination, where the methane molecule is oriented towards the palladium atom via three hydrogen atoms (the equilibrium $Pd \cdot H$ distance in this structure is 2.2 Å against 1.7 Å in the η^1-*H* structure), the dative transfer of electron density from palladium mainly to the carbon atom is most clearly expressed precisely in this structure.

It is of interest that the bond energy in the $Pd\cdots H_2$ system, calculated by the same method, is almost twice as high as the bond energy in the methane complex. The donor–acceptor transfer in the alkane complex is much smaller than in the complex with dihydrogen. On the other hand, in general, since the HOMO energy in methane is higher than in hydrogen (the ionization potentials are 12.7 and 15.4 eV respectively), methane should be a better electron donor. However, according to the calculation, the opposite behavior takes place. One can therefore conclude that the interaction is in this instance determined by the overlap of the corresponding orbitals and not by the difference between the energy levels.

The non-empirical MO method has been also used for the calculation of complexing copper(I) ion with molecules of hydrogen, methane and ethane [33]. The potential surfaces for the addition reactions of H_2, CH_4 and C_2H_6 from infinity up to the equilibrium state are of bonding character. There is only one minimum on these surfaces corresponding to the complexes Cu^+H_2 (energy of complexing ~ 17 kcal mol^{-1}), Cu^+CH_4 (~ 10 kcal mol^{-1}) and $Cu^+C_2H_6$ (~ 13 kcal mol^{-1}). The H_2 molecule is more strongly coordinated to the central Cu^+ ion by an η^2 mode.



η^2



η^1

The structure with η^1 coordination lies 3.7 kcal mol^{-1} higher and transforms into the η^2 configuration without any barrier.

In the case of methane, the tridentate coordination η^3-*H,H,H* to the Cu^+ ion is more advantageous. Bidentate (η^2-*H,H*) and monodentate (η^1-*H*) coordination structures are situated 3–4 kcal mol^{-1} higher than the tridentate configuration. These differences are small and at low temperatures, the Cu^+ cation may apparently migrate around the CH_4 molecule, i.e., all possible modes of coordination can alternate. It is important that the geometrical parameters of CH_4 when it coordinates to the Cu^+ ion change only negligibly, so the rupture of the C–H bond in methane by this cation seems to be impossible. Two modes of motion can be discussed for the complex $Cu^+\cdot C_2H_6$: migration (Cu^+ around C_2H_6)

and rotation (CH_3 groups around the C–C bond). There are two minimums on the potential surface corresponding to isomers σ and π (Figure VI. 1). All complexes of the Cu^+ ion are stable in respect to any channel of monomolecular decay and can exist in the gas phase or in matrices of inert gases.

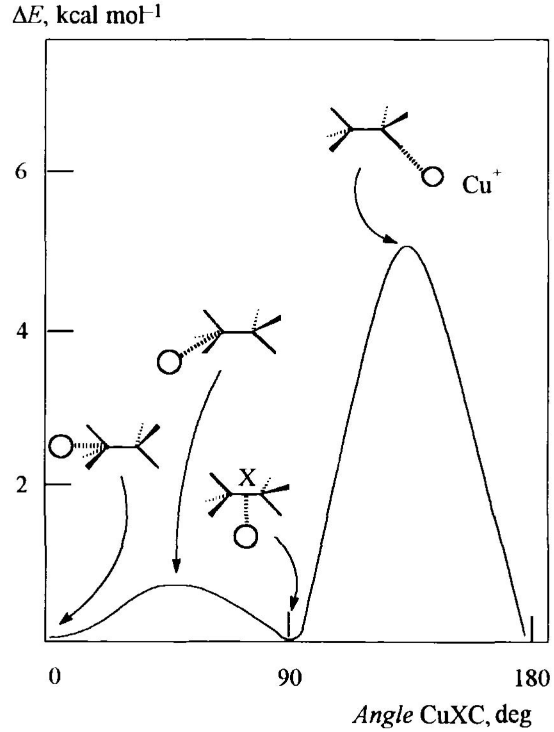


Figure VI. 1. Coordination of the ethane molecule with ion Cu^+ according to the nonempirical MO caclulations.

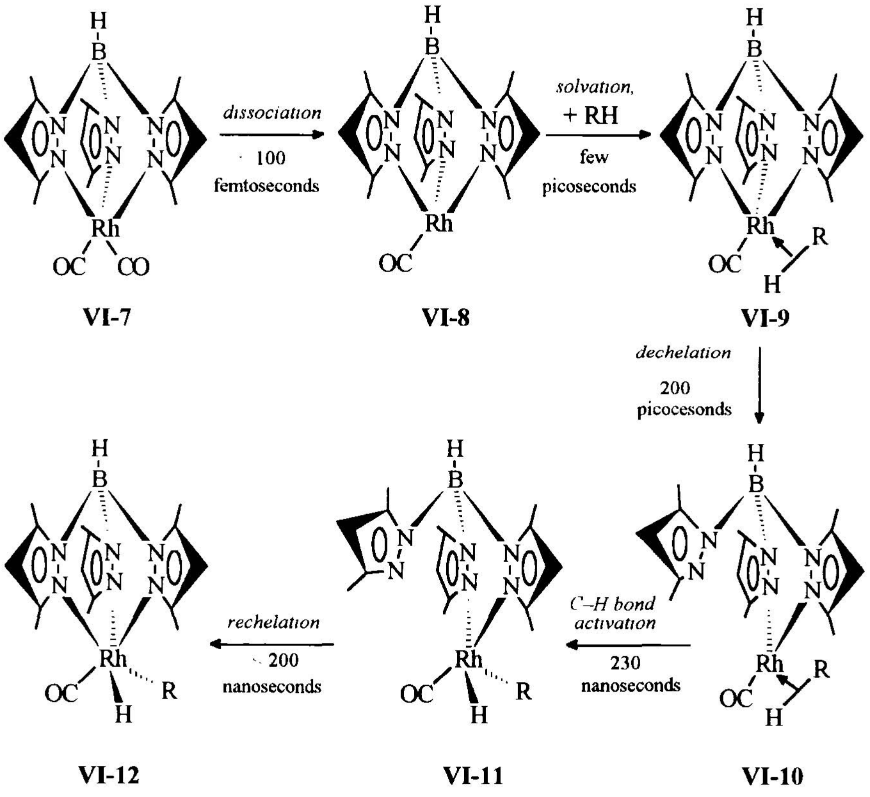
Ab initio considerations [34a] of methane adducts of pyramidal complexes $M(NH_2)(=NH)_2$ (where M = Nb, Ta) and $M(=NH)_3$ (where M = Mo, W) have shown that these adducts have appreciable calculated binding enthalpies (~ 11–16 kcal mol^{-1}) (see, however, [34b]). Planar imidos $(NH_2)_2M=NH$, where M = Ti, Zr, and $(HO)_2Ti=NH$ have much smaller binding enthalpies. A significant covalent contribution to the bonding between the substrate and the formally d^0 complex has been evaluated by the calculations. Upon coordination there is a weakening of a methane C–H bond, charge transfer from methane to metal, and increased $C^{\delta-}$–$H^{\delta+}$ polarization; all indicative of a role for the adduct in the all-important C–H scission step to follow. In a recent publication, it has been shown that the reactivity of primary alkyl halides with $[(^tBu_3SiN=)_3WH]K$ provides evidence of alkane complexation and d^0 alkane complexes $(^tBu_3SiN=)_3W(RH)$ precede C–H activation [34c]. Although the results obtained were also consistent with a solvent cage comprised of $(^tBu_3SiN=)_3W$ and **RH**, calculational studies strongly supported the proposed alkane adducts (also see [34d]).

Calculations of high accuracy were used for the theoretical consideration of molecular precursor complexes for the reaction between methane and a selected set of second-row transition metal complexes [35]. It turned out that the electronic structure requirements are quite different to form a strong precursor and to obtain a low barrier for the oxidative addition reaction. Thus for the formation of a strong precursor, a ground state singlet is important and the precursor binding energy will be larger if the complex does not have π-bonding ligands. For example, the precursor binding energy for the complex RhH(CO) (10.8 kcal mol^{-1}) is smaller than the precursor binding energy for the complex $RhH(NH_3)$ (14.5 kcal mol^{-1}). A low barrier for the oxidative addition reaction with methane requires a low-lying triplet state of the reactant. Complexes of this type are RhCl(CO) and RuH_2, which are ground state triplets.

An *ab initio* study [36a] demonstrated that the complexes *cis*-$Mo(CO)(PH_3)_4(HSiH_3)$ (compare to structure **VI-6**) and $CpMn(CO)_2(HSiR_3)$ can be regarded as pseudooctahedral d^6-ML_6, which defines a particularly stable class of complexes. Finally, theoretical analysis of the molecular complexes $(\eta^2\text{-}H_2)OsCl_2(PH_3)_2$ and $(\eta\text{-}CH_4)OsCl_2(PH_3)_2$ by RHF, MP2 and DFT methods has been recently reported [36b].

VI.2. MECHANISTIC STUDIES

In a series of recent publications, Bergman, Harris, Frei, Bromberg and their co-workers investigated the mechanism of alkane activation by complexes of rhodium and iridium [37, 38]. The study of ultrafast (femtosecond–picosecond)



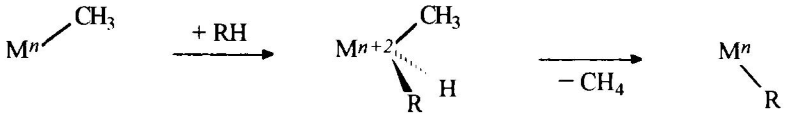
Scheme VI.6. Proposed mechanism for the C–H activation reaction of Tp*Rh(CO)$_2$ in alkane solution.

excited state dynamics of the complexes Cp*M(CO)$_2$, where M = Rh, Ir, and Tp*Rh(CO)$_2$, where Tp* is H-tris(3,5-dimethylpyrazolyl)borate, in alkane solutions led to the conclusion that the primary photoprocess of the highly photoactive Tp*Rh(CO)$_2$ is the dissociation of one carbon monoxide ligand to generate the vibrationally excited coordinatively unsaturated species Tp*Rh(CO). After the formation of solvated Tp*Rh(CO), activation of the C–H bonds in the alkanes occurs.

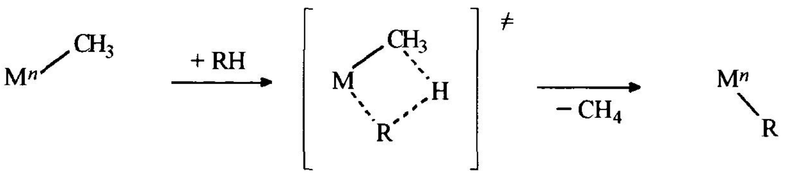
The authors established directly the time scale for activation of C–H bonds in solutions at room temperature by monitoring the C–H bond activation reaction in the nanosecond regime with infrared detection. In the first stage of the process, loss of one carbon monoxide ligand (reaction **VI-7** ⟶ **VI-8** in Scheme VI.6) substantially reduces back-bonding from the rhodium ion and increases the electron density at the metal center. Formed after the solvation stage, complex **VI-9** traverses a 4.2 kcal mol^{-1} barrier ($k = 5.0 \times 10^9\ s^{-1}$) and forms the η^2-Tp* complex **VI-10** which is more reactive toward C–H oxidative addition.

The bond-breaking stage occurs with a barrier of ~ 8.3 kcal mol^{-1} and produces the unstable η^2 C–H activated complex **VI-11** containing the metal center in a formal oxidation state of III. After rechelation, which reduces the electron density on the metal center, the final product, **VI-12,** is formed.

Bergman *et al.* have suggested [39a,b] two mechanisms for the σ-bond metathesis reaction by cationic iridium (III) complexes (see review [39c], i.e., a two-step addition-elimination mechanism:

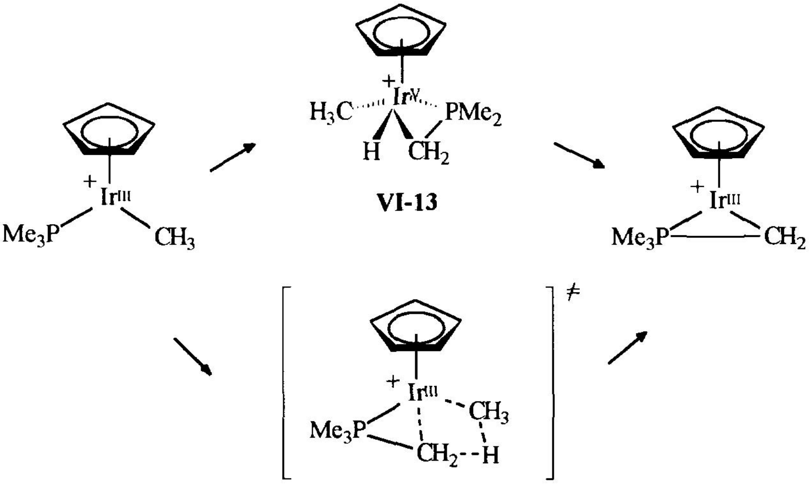


and concerted σ-bond metathesis mechanism:



A similar pattern of reactivity has been reported for platinum(II) complexes [39d]. *Ab initio* calculations demonstrated that an oxidative addition–reductive elimination mechanism is more likely than the concerted metathesis [39e].

The C–H activation reactions of complexes $Cp^*(PMe_3)Ir(CH_3)^+$ and $Cp(PMe_3)Ir(CH_3)^+$ has been studied by a combination of electrospray ionization MS/MS techniques, isotopic labeling experiments in the gas phase and in solution, and by *ab initio* calculations [40a,b]. The authors concluded that their experimental and computational results demonstrate the C–H activation in the gas phase proceeds by a third mechanism, namely the elimination of a methane molecule with the formation of an intermediate metallaphosphacyclopropane. Although the experimental results obtained did not distinguish decisively between the two possibilities shown in Scheme VI.7, the *ab initio* calculations found structure **VI-13** to be a minimum.



Scheme VI.7. Two possible mechanisms of C–H activation by the complex $Cp(PMe_3)Ir(CH_3)^+$.

A further investigation of C–H activation reactions of cyclometalated complexes of iridium(III) showed that the complex $Cp^*(PMe_3)Ir(CH_3)^+$ does not undergo intermolecular C–H activation in solution via a cyclometalated intermediate [40c] (see also below).

In a work which is relative to the problem of C–H bond addition, Goldman and coworkers have investigated the thermolysis of *trans*-$Ir(^iPr_3)_2(CO)Cl(H)(C_6H_5)$ affording benzene and the Vaska-type complex $IrL_2(CO)Cl$ [41]. Two pathways for the elimination have been elucidated with no evidence for a direct elimination pathway (estimated upper limit for direct elimination, 1.5 × 10^{-6} s^{-1} at 120 °C, corresponds to a high kinetic barrier, $\Delta G^{\ddagger} \geq 34$ kcal mol^{-1}). The first pathway involves a catalysis by molecular hydrogen, and the authors assumed that it may be possible to use H_2 to catalyze oxidative addition of C–H bonds when such additions are thermodynamically favorable. The second pathway involves an isomerization proceeding via reversible loss of carbon monoxide.

VI.3. THERMODYNAMICS OF OXIDATIVE ADDITION

Thermodynamics of C–H oxidative addition to various metal complexes, as well as to metal ions and atoms, have been considered in a number of experimental and theoretical works (see, e.g., [42]). The energy of the oxidative addition of hydrocarbons, RH, to complexes L_nM is determined by the equation [43]:

$$E(\text{M–R}) + E(\text{M–H}) - E(\text{R–H}) \approx E(\text{M–M})$$

and hence can be estimated from E(M–M). The highest value of E(M–M) has been obtained for platinum and in addition it has been shown that the reaction involving Group VIII and I transition metals is energetically favorable.

An estimation [44a] of the heat of oxidative addition via the mechanism

$$L_nM + \text{R–H} \longrightarrow \text{R–}L_nM\text{–H}$$

demonstrated that this reaction is in many cases endothermic with $\Delta H \cong +10$ kcal mol^{-1}. Oxidative addition with cleavage of the C–C bond via the mechanism

$$L_nM + \text{R–R} \longrightarrow \text{R–}L_nM\text{–R}$$

should be thermodynamically even less favorable. The above considerations refer to complexes of the first transition series of metals. The alkyl-metal bonds can be stronger in the case of heavy metals, although, for example, the values $D(\text{M–CH}_3)$ for the M^+–CH_3 ions in the gas phase do not support this trend when passing from light to heavy metals within a given Group. The calculated [44b] values D(Pt–C) = 36 kcal mol^{-1} and D(Pt–H) = 60 kcal mol^{-1}made it possible to estimate the enthalpies of the oxidative addition to $Pt(PH_3)_2$ of dihydrogen (–16 kcal mol^{-1}; exothermic reaction), methane via the CH_3–H bond (+9 kcal mol^{-1}; endothermic reaction), and ethane via the CH_3–CH_3 bond (+19 kcal mol^{-1}; strongly endothermic reaction). The complex *cis*-$OsHMe(CO)_4$ is apparently thermodynamically stable and does not exhibit a tendency towards intermolecular reductive elimination of CH_4. It has been suggested [44a] that the $Os(CO)_4$ species, generated photochemically, is capable of combining oxidatively with alkanes, this addition process being thermodynamically favorable. Thus the kinetic barrier to the oxidative addition of RH to low-valent metal complexes is fairly low and the inability of many 16-electron complexes to activate alkanes can be associated with the thermodynamic causes. Indeed, the rate of addition of methane to Cp*IrCO depends only very slightly on temperature [45]. The nature of ligand L has little influence on the reactivity of the complexes Cp*IrL in relation to alkanes, which can also indicate that the activation barrier is low.

Calculated (B3LYP) enthalpies of addition and the effects of phosphine methylation (substitution of PMe_3 for PH_3) in reactions of some iridium complexes with C–H compounds (as well as with molecular hydrogen) are summarized in Table VI.3 [46], It can be seen that the addition of aryl and especially acetylene C–H bonds is thermodynamically more favorable than the addition of simple alkyl C–H bonds. Addition of an aryl C–H bond has been found to be at least 16 kcal mol^{-1} less exothermic than H_2 addition. However, on the basis of the Bryndza–Bercaw relationship [47]

$$\mathrm{BDE(M{-}X)} - \mathrm{BDE(M{-}Y)} = \mathrm{BDE(H{-}X)} - \mathrm{BDE(H{-}Y)}$$

(where BDE's are bond dissociation enthalpies), the enthalpy of H–C_6H_5 addition is predicted to be equal to that of H_2 addition.

The insertion of a neutral transition metal atom, M, into methane according to the equation

$$\mathrm{M} + \mathrm{CH_4} \longrightarrow \mathrm{H{-}M{-}CH_3}$$

is exothermic for a number of ground state transition metal atoms [48]. Decay to $MH+CH_3$ or MCH_3+H is highly endothermic ($\Delta H \sim + 60$ kcal mol^{-1}) and cannot occur [49]. It is important that elimination of H_2 with formation of a metal carbene

$$M + CH_4 \longrightarrow H\text{-}M\text{-}CH_3 \longrightarrow M{=}CH_2 + H_2$$

is thermodynamically possible for several metals [48a]. We will also be concerned with the thermodynamics of oxidative addition in the next section while considering quantum-chemical calculations.

Table VI.3. Addition of some compounds to iridium complexes.

Metal center	C–H Compound	ΔH, kcal mol^{-1}	
		L = PH_3	L = PMe_3
IrL_2Cl	H–H	– 51.2	– 57.2
	H–CH_3	– 27.2	– 37.6
	H–C_6H_5	– 32.9 [a]	– 47.5 [a]
	H–CCH	– 49.8	– 64.4
$IrL_2Cl(CO)$	H–H	– 3.8	– 11.1
	H–CH_3	+ 20.4	+ 14.9
	H–C_6H_5	+ 15.1 [a]	+ 7.8 [a]
	H–CCH	+ 0.7	– 7.5

[a] ΔE value (ΔE were used in lieu of ΔH for the H–C_6H_5 additions).

VI.4. QUANTUM-CHEMICAL CALCULATIONS

Processes involving the oxidative addition of saturated H–H or C–H bonds to metal complexes or metal atoms as well as the reductive elimination of RH have been investigated by quantum-chemical methods and published in numerous articles (see, for example, recent papers [50]). Some of the recent theoretical works have been used in the previous sections, others will be discussed below.

VI.4.A. ACTIVATION BY BARE METAL IONS AND ATOMS

The reaction of Ta^+ with methane in the gas phase has been computationally investigated using approximate density functional theory [51]. The overall reaction sequence

$$Ta^+ + CH_4 \longrightarrow Ta{=}CH_2^+ + H_2$$

is exothermic by ca. 14 kcal mol^{-1} and the Ta–C binding energy in the carbene complex is 119 kcal mol^{-1}. The bond activation process consists of several steps, commencing with the formation of an electrostatically bound encounter complex. Then the insertion of the Ta^+ ion into a C–H bond and the generation of a $H_2TaCH_2^+$ dihydrido species occur. The latter intermediate rearranges into a complex between molecular hydrogen and a carbene cation, which eliminates H_2 in the final step.

Theoretical studies [52] of the complete reaction profile for the dehydrogenation of methane by gaseous iridium ions have shown that three salient factors are responsible for the high reactivity of these ions: the ability of Ir^+ to change spin easily, the strength of the Ir–C and Ir–H bonds, and the ability of Ir^+ to form up to four covalent bonds. Iridium ions are unique in possessing all three characteristics. The reaction steps for the reaction are as follows:

(a) initial formation of an η^2-molecular complex, $Ir(CH_4)^+$;

(b) oxidative addition of a single C–H bond to form the hydridomethyliridium complex, $Ir(H)(CH_3)^+$;

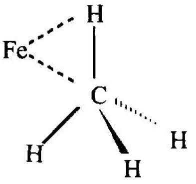
(c) insertion into a second C–H bond to form the pyramidal dihydridomethylideneiridium complex, $Ir(H)_2(CH_2)^+$;

(d) coupling of the H–H bond to form the planar (dihydrogen)methylideneiridium complex, $Ir(H_2)(CH_2)^+$;

(e) elimination of H_2.

There is a global minimum (~ 63 kcal mol^{-1}) for the singlet $Ir(H)_2(CH_2)^+$ structure, which plays an important role in the activation. The overall exothermicity of the reaction is calculated to be 3 kcal mol^{-1}. On the basis of these calculations, the authors suggested solution-phase analogues that may also activate methane. Indeed, in order to obtain a solution-phase complex with chemistry analogous to the gas-phase iridium ion, it is necessary to remove two electrons. This suggests Re^+ in the form of complex $XReL_3$.

Calculations for the oxidative addition reactions between methane and the whole sequence of second row transition metal atoms from yttrium to palladium have been carried out [53]. The lowest barrier for the C–H insertion has been found for the rhodium atom. Palladium has the lowest methane elimination barrier. In another paper [54], the formation of complexes $[CH_4–Fe]^q$ ($q = +1, 0, -1$) and the oxidative addition of methane to Fe^q has been studied by using the MINDO/SR-UHF method. The potential energy curves for the oxidative addition were calculated for a C_S symmetry (structure **VI-14**).



VI-14

It turned out that the formation of alkane complexes and oxidative addition were favored as the system became negatively charged, suggesting that an electronic transfer from the metal to the methane molecule promotes the C–H bond activation. An increase in the *p* character of the metal center favors the C–H bond splitting.

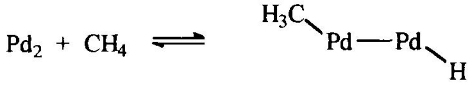
Both the C–C and C–H bond activation branches of the potential energy surface for the reaction between Fe^+ and ethane (calculations by B3LYP method) are characterized by a low barrier for the first step (the insertion of the Fe^+ into a C–C or C–H bond) [55]. The second step is the rate determining one. In the C–C bond activation this is a [1,3]-H shift leading to a complex between $Fe{=}CH_2^+$ and methane. Calculations using high-accuracy quantum chemical methods (B3LYP and PCI-80) for the endothermic reaction

$$Rh^+ + CH_4 \longrightarrow RhCH_2^+ + H_2$$

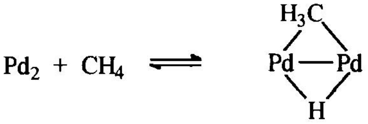
have demonstrated [56] that there is no barrier in excess of the endothermicity of the H_2 elimination reaction.

An investigation of the oxidative addition of CH_4 and CD_4 [57a], as well as ethane [57b], to a bare palladium atom has demonstrated that quantum tunneling plays a very important role in the process. The barrier of insertion of different transition metal atoms into a C–C bond has been found to be 14–20 kcal mol^{-1} higher than the barrier for insertion into a C–H bond [57c]. Calculations for the activation of the C–H bond in ethylene by second row transition metal atoms showed that the oxidative addition barrier is lowest for the atoms to the right (for rhodium there is no barrier and for palladium the barrier is almost zero) [57d]. The activation energy for B_2 insertion into methane has been predicted to be 4.1 kcal mol^{-1}, while this value increases to 16.2 kcal mol^{-1} for insertion of B [58].

Two mechanisms have been considered by the SCF CNDO/S method for the oxidative addition of methane to the palladium cluster Pd_2 [59a]. In the first possible reaction, the C–H bond oxidatively adds to different palladium atoms:



The second mechanism involves the transition state with simultaneous coordination of the methyl group and hydrogen atom to both palladium atoms:



The calculations have elucidated the higher catalytic activity of the cluster compared to a bare palladium atom.

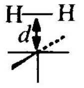
In the reaction of molecular hydrogen or methane with the platinum cluster Pt_2, activation of H–H or C–H bonds takes place first on one metal atom via structures far from planar [59b]. Then one of the hydrogen atoms migrates to the other platinum atom with a negligible activation barrier. In the system "Pd_3+H_2", Pd_3, like Pd_2, activates molecular hydrogen without an activation barrier [59c]. For the activation of the C–H bond in methane, the activation barriers on Pd_3 are much higher than those on Pd_2. Systems "Pt_3+H_2" and "Pt_3+CH_4" are similar to analogous systems containing Pt_2 clusters.

VI.4.B. OXIDATIVE ADDITION OF C–H AND C–C BONDS TO METAL COMPLEXES

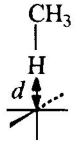
In the most simple system “metal complex $(ML_n) + H_2$”, when the bonding σ orbitals of hydrogen interact with the unoccupied acceptor orbital of the complex and with the antibonding σ^* orbital at the occupied donor orbital, four orbitals of a new hydride derivative are generated [60]. The two low-lying orbitals are filled with electrons, one being symmetrical and the other antisymmetrical relative to the twofold axis or the mirror symmetry plane. A symmetrical combination is formed, for the M–H bond generated, from the occupied orbital of the hydrogen molecule and such electron transfer from $\sigma_g(H_2)$ to ML_n weakens the H–H bond and strengthens the M–H bond. The electron transfer in the opposite direction, namely “donor orbital $\rightarrow \sigma_u^*$”, also weakens the H–H bond and strengthens the M–H bond. One can assume that the occupied a_1-orbitals and the three degenerate t_2-orbitals in the methane molecule correspond to the σ_g orbital of the hydrogen molecule. Since the energy of the t_2-orbital is greater by 2 eV than the energy of the $\sigma_g(H_2)$ orbitals, the methane molecule is a somewhat stronger donor.

The total energy of the system $H_2\cdots Cr(CO)_5$ has been calculated by the extended Hückel method [60]. The interaction energy is negative for both the perpendicular orientation (structure **VI-15**) and the parallel orientation (structure **VI-16**) of the H_2 molecule approaching the $Cr(CO)_5$ fragment, which has the C_{4v} symmetry.

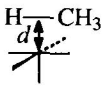
VI-15



VI-16

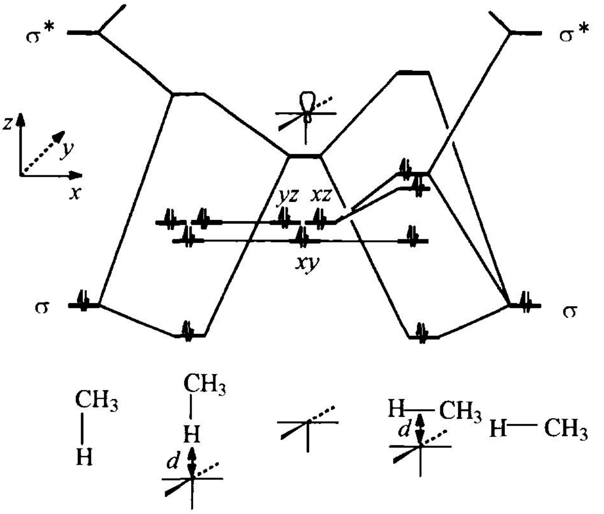


VI-17



VI-18

However, in the case of the parallel approach of H_2, the energy of the system has a much more distinct minimum. When H_2 is replaced by CH_4, the curve for the perpendicular approach (structure **VI-17**) has the same form but the parallel approach (structure **VI-18**) becomes extremely unfavorable. Whereas the d_{xz}-orbital (which functions as the donor orbital in the complex) is lowered for **VI-16**, in the case of CH_4 (structure **VI-18**) the energies of both d_{xz}- and d_{yz}-orbitals increase (Figure VI.2). If the methane molecule approaches $Cr(CO)_5$ in such a way that the $H–CH_3$ axis forms an angle θ with the height of the pyramid, the structure is stable for $d(M–H) = 2.0$ Å and $\theta \leq 130°$. However, the perpendicular orientation ($\theta = 180°$) remains the most favorable.



VI-17 **VI-18**

Figure VI.2. Diagram for the oxidative addition of $H–CH_3$ to the fragment $Cr(CO)_5$.

The reactions involving the oxidative addition of dihydrogen and methane to the fragment $Rh(CO)_4^+$, or the corresponding isolobal complex CpRh(CO), or to the metallic surfaces of nickel and titanium have also been analyzed [60].

When an η^2-C–H coordinated adduct $X(PH_3)Ir\cdots HCH_3$ is formed, considerable weakening of the coordinated methane C–H bond occurs [61a]. The calculated enthalpy for the reaction

$$Ir(PH_3)_2H + CH_4 \longrightarrow Ir(PH_3)_2(H)_2CH_3$$

is −12.8 kcal mol^{-1}. It has been shown in this work that although donation of electron density from methane to the metal is essential for adduct formation, it is not until back donation to the σ^*_{CH} increases that the C–H bond is activated and cleaved. Calculations [61b] by the *ab initio* restricted Hartree-Fock method of the reaction.

$$\text{“}(H_3P)_2Ni\text{”} + CH_4 \longrightarrow (H_3P)_2NiH(CH_3)$$

showed that the oxidative addition is endothermic by 7.0 kcal mol^{-1} and the planar *trans* product is the most stable, being lower in energy than the *cis* isomer by 3.4 kcal mol^{-1}.

The oxidative addition reactions of C–H and Si–H σ-bonds of CH_4 and $HSiR_3$ to $Pt(PH_3)_2$ occur through a planar transition state structure, but the reactions of CH_3–CH_3 and SiH_3–CH_3 take place through a nonplanar transition state [62a]. The oxidative addition of a σ-C–H bond to $Pt(PH_3)_2$ and $Pd(PH_3)_2$ requires a considerably high activation energy (30 and 37 kcal mol^{-1} for Pt and Pd complexes, respectively) [62b]. It is interesting that if two monodentate phosphine ligands are replaced by one chelate phosphine, the reaction proceeds with a much lower activation energy (20.0 and 3.8 kcal mol^{-1} for Pd and Pt complexes with diphosphinomethane, respectively).

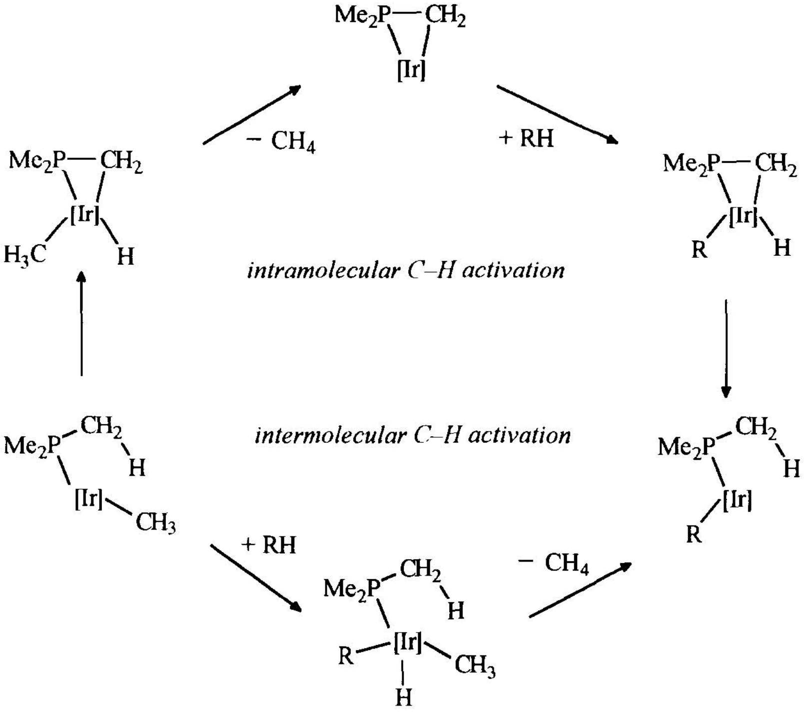
A theoretical study of the reactions between methane and ML_2 complexes (where M = Pd, Pt; L = PH_3, CO, L_2 = $PH'_2CH_2CH_2PH_2$), led to the conclusion that for 14-electron ML_2 complexes, a smaller L–M–L angle, a better electron-donating ligand, and a heavier transition metal center should be a potential model for the oxidative addition of C–H bonds [63a].

The theoretical calculations using density functional theory showed that the intermolecular C–H activation of alkanes by the complex $CpIr(PMe_3)(CH_3)^+$ (described by Bergman, *vide supra*) is a lower-energy process and that both *inter*- and *intra*molecular C–H activation proceed only through an oxidative-addition mechanism (Scheme VI.8) [64] (compare Scheme VI.7).

Calculations [65] carried out with the MP2 technique predicted that for the reaction

$$CH_4 + CpRh(CO) \longrightarrow CH_4 \cdot RhCp(CO) \longrightarrow CH_3Rh(H)Cp(CO)$$

the intermediate alkane complex is stabilized by 14.8 kcal mol^{-1}, a transition state lies 4.1 kcal mol^{-1} higher than the intermediate and the reaction is exothermic (30.6 kcal mol^{-1})



Scheme VI.8. Intra- and intermolecular C–H activation by the complex $Cp(PMe_3)Ir(CH_3)^+$

The effects of ligands in the activation of C–H bonds by transition metal complexes were discussed in certain works. It has been suggested [66a] that a combination of hydride and lone-pair ligands with a minimum of π-bonding should be an optimal combination for the reaction between methane and some model Rh(I) and Ru(II) complexes. For example, it should be advantageous to have methyl and lone-pair ligands with as little covalent bonding as possible. As for the methane activation by a Ru(II) complex, which has not yet been done experimentally, halide ligands and lone-pair ligands with strong π-bonding should be avoided. Only one ligand is needed to improve the exothermicity of the reaction of Rh^+ with methane and the position of this ligand is critical [66b]. Covalent ligand effects in the oxidative addition of methane to second-row transition-metal complexes have been evaluated [66c]. The theoretical study of methane activation by complexes $M(=NH)_2(NH_2)$ (M = V, Nb and Ta) demonstrated that an activation pathway involving C–H addition across the metal-amido bond (σ-bond metathesis) is disfavored relative to a pathway involving C–H addition across the metal-imido bond ($[2_\sigma+2_\pi]$ addition) [67].

A comparison of the activation of C–H and Si–H bonds has been carried out. It has been shown that while C–H bond activation by the complex $RhCl(PH_3)_2$ passes through an η^2-CH_4 adduct and a three-centered transition state, Si–H bond activation is downhill and the η^2-SiH_4 complex is a transition state for intramolecular rearrangement connecting two silyl hydride complexes [68]. The *ab initio* MO study of the mechanism of activation by transient species CpRh(CO) not only of C–H but also H–H, N–H, O–H and Si–H bonds has also been carried out [69].

VI.4.C. OTHER PROCESSES

Bare Ta^+ cations induce the coupling of methane and carbon dioxide in the gas phase [70a] according to the sequence:

$$Ta^+ + CH_4 \longrightarrow TaCH_2^+ + H_2$$

$$TaCH_2^+ + CO_2 \longrightarrow O{=}TaCH_2^+ + CO$$

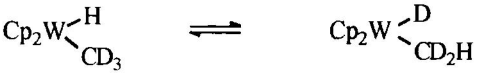
$$O{=}TaCH_2^+ + CO_2 \longrightarrow TaO_2^+ + O{=}C{=}CH_2$$

The overall reaction equation is as follows:

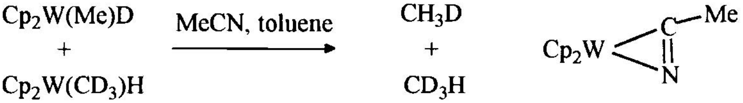
$$Ta^+ + CH_4 + 2\,CO_2 \longrightarrow TaO_2^+ + H_2 + CO + O{=}C{=}CH_2$$

Density functional calculations employing the B3LYP hybrid functional method combined with an adequate one-particle description [70b] gave an overall computed exothermicity of –55.9 kcal mol^{-1} (experimental value is –53 kcal mol^{-1}). The formation of the final products, TaO_2^+ and the ketene $O{=}C{=}CH_2$, proceeds as a concerted metathesis reaction in which Ta–CH_2 and a C–O bond are broken while simultaneously a Ta–O and C–C bond are newly formed.

Calculations have been carried out using density functional theory [71a] on the hydrogen exchange



and methane elimination



reactions of the complex $Cp_2W(Me)H$ [71b,c]. The hydrogen exchange proceeds along a reaction path on which lies a η^1-*H* σ-complex. The midpoint of the reaction is an η^2-*H,H* σ-complex and the transition state lies 19.5 kcal mol^{-1} above the ground state. Elimination of methane is calculated to have an overall reaction energy of 4.7 kcal mol^{-1} and an activation energy of ca. 19 kcal mol^{-1}.

A computational study of ethane dehydrogenation by the 14-electron complex $Ir(PH_3)_2H$ has been carried out [72]. The first step of the reaction is the formation of the ethane adduct

$$(H_3P)_2(H)Ir + H{-}CH_2{-}CH_3 \longrightarrow (H_3P)_2(H)Ir(H{-}CH_2{-}CH_3)$$

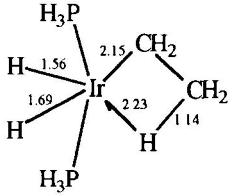
and oxidative addition of ethane to the catalyst:

$$(H_3P)_2(H)Ir(H{-}CH_2{-}CH_3) \longrightarrow (H_3P)_2(H)Ir(H)(CH_2{-}CH_3)$$

The oxidative addition transition state has a three-centered M···H···C geometry with an Ir–H–C angle of 93°. The activation barrier to C–H oxidative addition starting from the ethane adduct is only 1 kcal mol^{-1} and $\Delta H_{rxn} = -18$ kcal mol^{-1}. The ethyl(hydride) is then converted to an olefin complex through β-hydrogen transfer:

$$(H_3P)_2(H)Ir(H)(CH_2{-}CH_2{-}H) \longrightarrow (H_3P)_2(H)_3Ir(CH_2{=}CH_2)$$

Calculations of the intrinsic reaction coordinate showed the reactant in β-H transfer to be the agostic ethyl complex:



Ir–H–C = 97°
Ir–C–C = 89°
C–C = 1.55

with an activation barrier for β-H transfer of 12 kcal mol^{-1}. Then olefin dissociation occurs (47 kcal mol^{-1} uphill):

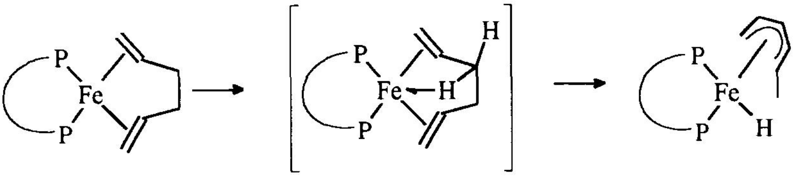
$$(H_3P)_2(H)_3Ir(CH_2{=}CH_2) \longrightarrow (H_3P)_2(H)_3Ir + CH_2{=}CH_2$$

and the Ir-trihydride regenerates the catalyst through reductive elimination of dihydrogen:

$$(H_3P)_2(H)_3Ir \longrightarrow (H_3P)_2(H)Ir + H_2$$

A dynamic density functional study of methane photo-carbonylation by the $Rh(PH_3)_2Cl$ catalyst has been reported [73]. It involves C–H bond activation to produce $Rh(PH_3)_2Cl(H)(CH_3)(CO)$ followed by migratory insertion of CO into the Rh–CH_3 bond to generate $Rh(PH_3)_2Cl(H)(CH_3CO)$ and, finally, the elimination of acetaldehyde to form $Rh(PH_3)_2Cl(CO)(H)(CO)(CH_3CO)$.

The following reaction has been recently studied by molecular modeling methods [74]:



It has been concluded that sterically demanding ligands in the fragment $[R_2P(CH_2)_nPR_2]Fe$ lead to a small accessible molecular surface at the metal atom and further reaction of the coordinated hexadiene is hindered. On the contrary, less demanding ligands lead to a larger accessible molecular surface, which enables the metals atom to interact with a methylenic hydrogen atom with resulting hydrogen transfer and formation of a hydride species.

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