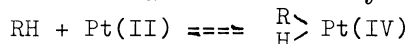# ACTIVATION OF ALKANES BY TRANSITION METAL COMPLEXES

A.E.Shilov

Institute of Chemical Physics, USSR Academy of Sciences,
Chernogolovka, Moscowskaja oblast, (USSR)

Abstract - The data are presented for catalytic H-D exchange
of alkanes with protic solvents and some other reactions of
alkanes in the presence of transition metal complexes, par-
ticularly Pt(II). In Pt(II) chloride solutions the activi-
ty of Pt-containing species towards alkanes is in the order
$S_2PtCl_2 > SPtCl_3^- > PtCl_4^{2-}$ (S-solvent). Ligands with properties
of soft bases (CN^-, CNS^-, PPh_3 etc.) decrease the rate of
H-D exchange. There is a strong evidence that alkyl deri-
vatives and carbene complexes are the intermediates in
reactions of alkanes catalyzed by Pt(II). The first step
of the reaction is likely to be an oxidative addition

$$RH + Pt(II) \rightleftharpoons \begin{array}{c} R \\ H \end{array}\!\!> Pt(IV)$$

INTRODUCTION

Activation of C-C or C-H bonds in alkanes by transition metal complexes is,
as J.Halpern put it in 1968 (1), one of the most important and challenging
problems in the entire field of homogeneous catalysis.

Creation of new selective catalytic processes of alkanes as a substitute
for poorly selective radical chain reactions is particularly important now
since the shortage of traditional sources of alkanes such as oil and natu-
ral gas is becoming a real problem.

The well known inertness of alkanes is reflected in their other names such
as "paraffins" (from Latin: parum affinis - without affinity), and "satu-
rated hydrocarbons" (from their inability to enter any addition reactions).
However in respect of cleavage of strong covalent C-H bonds the problem
looks similar to that of H-H bond activation in molecular hydrogen which
was successfully solved in coordination catalysis.

Activation of H_2 by metal complexes is known to involve oxidative addition
as a primary step in a number of catalytic systems:

$$M + H_2 \rightleftharpoons M\!\!<\begin{array}{c} H \\ H \end{array}$$
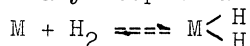
(M - here and further is a metal atom or ion in a metal complex).
If a similar reaction takes place in case of alkanes:

$$M + RH \rightleftharpoons M\!\!<\begin{array}{c} R \\ H \end{array}$$
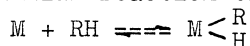
it could give rise to consequent reactions, the simplest being H-D exchange
with solvent's exchangeable deuterium provided the alkyl hydride formed
has acidic properties:

$$M\!\!<\begin{array}{c} R \\ H \end{array} \rightleftharpoons M - R^- + H^+$$
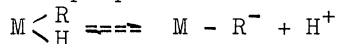
Another possibility is the isotope exchange of RH with D_2 if reversible
decomposition of trihydride MH_3 occurs in the presence of hydrocarbon and
deuterium

$$MH_3 \rightleftharpoons H_2 + MH$$

$$MH + D_2 \rightleftharpoons MHD_2 \rightleftharpoons MD + HD$$

$$MD + RH \rightleftharpoons M\!\!<\begin{array}{c} R \\ H \\ D \end{array} \rightleftharpoons RD + MH \qquad \text{etc.}$$
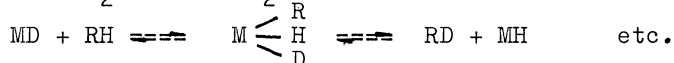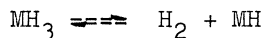
Procceding from the above assumed mechanisms we observed in 1969 the isotope exchange between alkanes and $D_2O + CH_3CO_2D$ in the presence of Pt(II) and also between alkanes and D_2 in the presence of $(Ph_3P)_3CoH_3$ (2).

Afterwards other platinum as well as non-platinum metal complexes were found by several groups of workers to be active towards alkanes, and some other reactions of alkanes catalyzed by metal complexes were discovered besides isotope exchange.

It should be noted that though the first observation of C-H bond activation in alkanes in the presence of metal complexes in solution was made in 1969, other reactions involving C-H activation by transition metals had been known before which may now be compared with homogeneous activation of alkanes, e.g.,

  i. heterogeneous activation of alkanes at metal surface
  ii. homogeneous activation of C-H bond in aromatic compounds
     and some molecules with "activated" C-H bond
  iii. intramolecular insertion of metal in ligands with aliphatic
     and aromatic C-H bonds in some coordination compounds
     ("cyclometallation reaction")

H-D EXCHANGE

When methane and ethane are heated to 100°C in sealed ampouls containing solutions of K_2PtCl_4 in D_2O - CH_3COOD mixture deuteration of the alkanes molecules is observed (2). In the absence of a catalyst this reaction is known to be possible only at about 1000°C, i.e., at temperatures of alkane pyrolysis.

In later studies a homogeneous exchange catalyzed by platinum (II) salts was observed for a whole series of simple alkanes including also iso-alkanes and cyclo-alkanes, the latter being particularly reactive (3). The isotope exchange may serve as an effective way of deuteroalkanes preparation. Substituted derivatives of alkanes (haloidoalkyls, alcohols, acids etc.) are also capable to H-D exchange with a solvent, which is often facilitated in the substituent's presence. However, in the case of some of these compounds the exchange is complicated by side processes such as oxidation, hydrolysis etc. Ethylene does not exchange its hydrogen atoms with solvent's protons in platinum (II) solutions, while at the same time it inhibits exchange in alkanes probably due to the formation of strong π-complexes with Pt(II) (4). Alkanes of the $RC(CH_3)_2$ - $CH = CH_2$ type, containing a quaternary carbon atom in the vicinity of the double bond, exchange their hydrogen atoms in the presence of platinum salts in the alkyl part of the molecule and almost exclusively in C_5 (5)
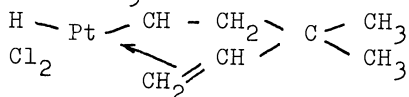
Investigation into selectivity of the attack of Pt(II) on C-H bond in alkanes revealed importance of steric hindrances, which is even more pronounced than that of C-H bond energy changes. Thus the ratio of selectivity of primary, secondary and tertiary C-H bonds was found to be 1: 1 : 0 , e.g., for isobutane 9 atoms out of 10 turned out to be exchangable, the tertiary C-H bond being unaffected.

In 1973 Garnett found that Na_3IrCl_6 can catalyze H-D exchange of alkanes with CH_3CO_2D - D_2O (6). Recently $RhCl_3$ was found to be able to catalyze similar exchange as well (7) Ir(I) and Rh(I) isoelectronic with Pt(II) (d^8) were assumed to be active in the isotope exchange, Pt(II) being the most active out of the three.

Some isotope exchange in the presence of non-platinum metal complexes besides $(Ph_3P)_3CoH_3$ mentioned above has been also studied. Activation of methane to H-D exchange in the presence of Ziegler catalysis based on Ti and V was reported in (8), and in recent work ($\pi-C_5H_5)_2$ V was found to catalyze isotope exchange of methane and ethylene (9).

In 1977 Cu(II) in water solution was found to be the first non-platinum metal catalyzing H-D exchange of alkanes with protic solvent (10).

OTHER CATALYTIC REACTIONS OF ALKANES

Transition metal compounds have been often used to initiate radical chain reactions of hydrocarbons, e.g., oxidation by molecular oxygen, the role of initiator being to form free radicals.

At present, however, there is some evidence for possibility of catalytic transformations of alkanes directly in coordination sphere of complexes(II). Thus in the presence of Pt(II) complexes Pt(IV) is reduced by alkanes including methane and ethane in aqueous solutions at 100-120°C to Pt(II), the latter being the catalyst (12). The main products of alkanes transformation are chlorohydrocarbons, whereas alcohols, esters and some other compounds are the by-products. Benzene is the main product in the case of cyclohexane. (Table 1) Kinetic results show that chlorohydrocarbons are intermediates for other products including benzene.

TABLE 1. Products of Oxidation of Hydrocarbons in Aqueous Solution of H_2PtCl_6 - Na_2PtCl_4

No.	Alkane	t°C/time(h)	Products(relative yield, %)
1	Methane, 50atm	120/4	Methyl chloride
2	Ethane, 20atm	120/4	Ethyl chloride
3	Propane, 6atm	120/4	$n-C_3H_7Cl(75)$, $iso-C_3H_7Cl(25)$
4	Pentane	120/0.25	$n-C_5H_{11}Cl(56)$, $sec-C_5H_{11}(44)$
5	Isopentane	120/0.25	$prim-C_5H_{11}Cl(78)$, $sec-C_5H_{11}Cl(22)$
6	Hexane	110/5	$n-C_6H_{11}Cl(40)$, $n-C_6H_{13}OCOCF_3(30,5)$, $C_4H_9COCH_3(23,9)$, $sec-C_6H_{13}OCOCF_3$, $sec-C_6H_{13}Cl(1,4)$
7	Cyclohexane	110/5	$C_6H_6(77,6)$,$C_6H_5Cl(11)$,$C_6H_{11}Cl(5,4)$, $C_6H_{11}OCOCF_3(5)$,cyclohexanone,traces of alcohol and dichloride
8	Methyl cyclohexane	110/5	Toluene (61,6), n-chlorotoluene (11,2), $CH_3C_6H_{10}Cl(9,1)$, $CH_3C_6H_{10}OCOCF_3(8,2)$, $C_6H_{11}CH_2Cl$ (4,1), ketone (4,1)
9	Decalin	110/5	Naphthalene

Note. Experiments (1-5)-in H_2O, 0.5M Pt(IV), 0.05M Pt(II); (6-9)-in 8.7M CF_3COOH, 0.18M Pt(IV), 0.02M Pt(II).

The selectivity of the reaction is similar to H-D exchange and distinctly different from that of radical chain reactions, e.g., chlorination. Thus the yield if $n-C_3H_7Cl$ is considerably higher than of $iso-C_3H_7Cl$ again indicating importance of steric factors.

Though Pd(II) complexes do not catalyze H-D exchange of alkanes with the solvent, solutions of $PdSO_4$ in sulfuric acid were shown (13) to absorb alkanes at 90°C. The reaction is accompanied by formation of SO_2 and palladium metal. Presumably olefines are formed first which are then subject to fast reaction of sulfonation, oxidation and dehydrogenation. Benzene and benzene sulfonic acid are formed in the case of cyclohexane. As distinct from Pt(II) catalyzed reaction "normal" order of selectivity of attacking C-H bonds (tert>sec>prim) was found for palladium induced oxidation.

It was found later (4) that alkanes (n-hexane and cyclohexane) reduce Pd(II) trifluoroacetate at 90°C in trifluoroacetate acid to Pd(0). The stoichiometry for cyclohexane is

$$3 \; Pd(CF_3CO_2)_2 + C_6H_{12} \longrightarrow 3 \; Pd(0) + C_6H_6 + 6 \; CF_3CO_2H$$
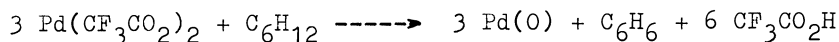
Chloride complexes of Ru(IV) substantially accelerate the oxidation of al-
kanes in aqueous solutions of chromic acid, alkyl chlorides being the prima-
ry products of alkanes transformation (15). Alkyl chlorides were found to
be also formed in solution of Cu(II) chlorides, which undergo reduction to
Cu(I) (10). Activation of alkanes by Cu(II) complexes to oxidation as well
as to H-D exchange with the solvent is of particular interest since its me-
chanism may be similar to alkanes activation by certain monooxygenases in
bacteria. It was found recently (16) that the enzyme isolated from methane
oxidyzing bacteria Methylosinus trichoporium contain copper.

Table 2 summarises the metals, which in their complexes are able to activate
aliphatic C-H bond in free alkanes (circles) and in ligands bound to metal
in complexes (squares)

TABLE 2. Metals Activating Alkanes

| IV	V	VI	VII	VIII			I
(Ti)	(V)	Cr	Mn	[Fe]	(Co)	Ni	(Cu)
Zr	Nb	Mo	Tc	[(Ru)]	(Rh)	[(Pd)]	Ag
Hf	Ta	(W)	Re	[Os]	(Ir)	[(Pt)]	Au

It is seen that there are now a number of metals in their complexes able to
C-H bond activation, and one can expect that the list will continue to grow.

MECHANISM OF ALKANES ACTIVATION

a. The Nature of Active Centre
The mechanism of alkanes activation by various transition metal complexes is
by no means certain and probably not the same for different systems. The
most detailed mechanistic information has been obtained from the investiga-
tions of H-D exchange with the solvent and oxidation of alkanes in the pre-
sence of Pt(II) complexes (17-25).

The reaction of H-D exchange at 80-120°C is about 30 times as fast in 50%
deuterated acetic acid as in D_2O. Thus is indicative of a specific solva-
tion of the active particle with acetic acid molecule, probably with forma-
tion of a weak chelate complex of $PtCl_2$

$$Cl_2Pt \underset{O}{\overset{O}{<}} \!\!\!\!\!> C - CH_3$$
                        D
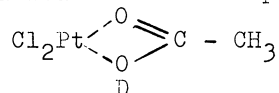
H-D exchange is of the first order with respect to hydrocarbon concentration,
the reaction rate being virtually independent on ionic strength and the aci-
dity in the range of 0.2 to 1.0M.

The order of the reaction with respect to a chloride ion changes from 0 to
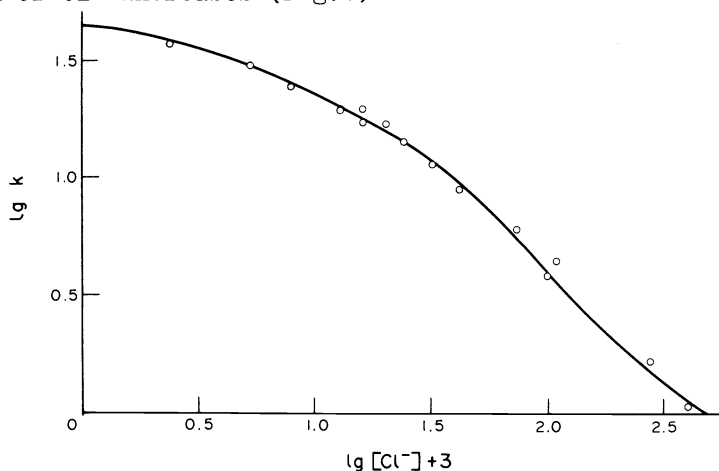-1 as the concentration of Cl^- increases (Fig.1)

Figure 1.

Investigation of the dependence of the rate on Cl⁻ concentration shows
(17,18,21) that S_2PtCl_2 are the most active species in platinum(II) chloride
solution in equilibrium with $SPtCl_3^-$ and $PtCl_4^{2-}$ (S–solvent molecule). The
line in Fig. 1 corresponds to the formula

$$k = \frac{(k_1 + k_2K_2[Cl^-] + k_3k_{12}[Cl^-]^2)\,[PtCl_2]_0}{1 + K_2[Cl^-] + K_{12}[Cl^-]^2}$$

k_1, k_2, k_3 being the rate constants for S_2PtCl_2, $SPtCl_3^-$ and $PtCl_4^{2-}$ respecti-
vely, $K_{12} = K_1K_2$, and K_1 and K_2 are equilibrium constants for reactions

$$PtCl_4^{2-} \xrightleftharpoons{S} SPtCl_3^- + Cl^-$$

$$SPtCl_3^- \xrightleftharpoons{S} S_2PtCl_2 + Cl^-$$
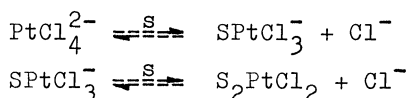
respectively.
For cyclohexane at 100°C

$$k_1 : k_2 : k_3 = 100 : 14 : 0.6$$

From the temperature dependence of k_1 in the range from 81 to 112°C it fol-
lows that

$$k_1 = 2.5 \times 10^8 \exp(-18.\ 200/RT) \quad M^{-1}\ sec^{-1}$$

To elucidate the nature of activation of alkanes the effect of ligands was
studied (21) on the rate of H-D exchange catalyzed in $PtLCl_3^-$
(L = H_2O, Cl^-, NO_2^-, DMSO, NH_3, Py) and $PtCl_2L_2$ (L = H_2O, Cl^-, Br^-, I^-,
NO_2, CN^-, Ph_3P). As can be seen from Table 3 the exchange rate constant
changes by three orders of magnitude depending on ligands decreasing to-
wards more basic as well as softer (more polarizable) ligands with a growing
tendency for double bonding

TABLE 3. Deuterium exchange of cyclohexane in the presence of
Pt(II) complexes   Pt = 0.0043M (1-2); 0.02M (3-12);
$HClO_4$ = 0.1M; C_6H_{12} = 0.15M;   100°C

d_i is the percentage of a deuterated alkane containing
i atoms of D

No	Complex	Time (hrs)	$\sum d_i\%$	$kx10^3$ (1 mol⁻¹ sec⁻¹)	$M = \dfrac{\sum i d_i}{\sum d_i}$
1	$PtCl_2S_2$	2	0.230	7.42	1.93
2	$KPtCl_3S$	2	0.154	4.97	1.74
3	K_2PtCl_4	1.66	0.333	2.78	1.75
4	$K_2Pt(NO_2)Cl_3$	7	0.185	0.366	1.52
5	$KPt(NH_3)Cl_3$	2.5	0.140	0.777	1.65
6	$KPt(py)Cl_3$	12	0.0268	0.025	1.46
7	$KPt(DMSO)Cl_3$	12.5	0.0549	0.056	1.60
8	$Pt(DMSO)Cl(NO_3)$	4	0.0242	0.083	1.62
9	$K_2Pt(NO_2Cl)_2$	7	0.0584	0.115	1.41
10	$Pt(PPh_3)_2Cl_2$	16.5	0.0078	0.007	1.34
11	$Pt(acac)_2$	7.5	0.0511	0.094	1.57
12*	$Pt(CF_3COO)_2$	0.3	0.0158	0.732	1.34

*Experiment carried out in CF_3COOD at 91°C

The rate changes in parallel with a multiplicity factor M (average number of
D atoms entering an alkane molecule during its contact with Pt(II) complex).
All the ligands tested can be arranged as to their effect on the rate of
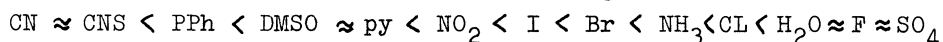deuterium exchange of cyclohexane in the following order

$$CN \approx CNS < PPh < DMSO \approx py < NO_2 < I < Br < NH_3 < CL < H_2O \approx F \approx SO_4$$

TABLE 4.   Distributions of d-methanes formed in methylation Pt(II)
           by CH_3HgBr and direct H-D exchange of CH_4 and D_2O

Conditions	$D=\sum d_i$	$\alpha_i = d_i / \sum d_i$				M
		α_1	α_2	α_3	α_4	
K_2PtCl_4 : $HgCl_2$: DCl= 1:1:3; P_{CH_4} = 760torr	0.915					1.4
100°C; 9 hours		0.650	0.251	0.0735	0.0296	
K_2PtCl_4 : CH_3HgBr : DCl= 1:1:3; 100°C; 0.3 hour	35.0	0.630	0.268	0.0815	0.0212	1.49

c. Mechanism of Multiple Exchange in the Presence of Pt(II). Carbene Complexes and Organometallic Cycles as Intermediates.

The distribution of deuteroalkanes formed in multiple exchange does not depend on the time at the initial stages of the reaction. Thus all the deuterated species are formed in parallel as a result of a single elementary reaction of an alkane molecule with Pt(II) centre (17,18).

For methane the phenomenon may be explained assuming reversible formation of a complex of methylene with platinum Pt - CH_2 alongside with methyl platinum compound. The distribution of deuterohydrocarbons can be calculated by the stationary state method from the scheme:
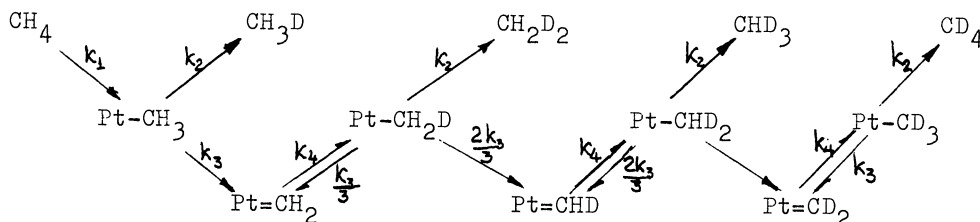
The part of each deuteromethane present in the mixture $\alpha_i = d_i / \sum d_i$ may be calculated from the factor $p=k_3/k_2$. The calculation of the distribution (i.e., values α_i) of deuterohydrocarbons for the exchange of methane and ethane in $CH_3CO_2D-D_2O$ (1:1) indicates that this scheme adequately represents the experimental results. For ethane and other alkanes the multiple exchange can be explained assuming ethylene and olefines intermediates forming π-complexes with Pt(II) (23). However, experiments with ethane exchange in water solution revealed (24) an unusual stepped distribution including two groups $\alpha_1 -\alpha_3$ and $\alpha_4 -\alpha_6$, the distribution in each of these groups being ascending (Fig.3)
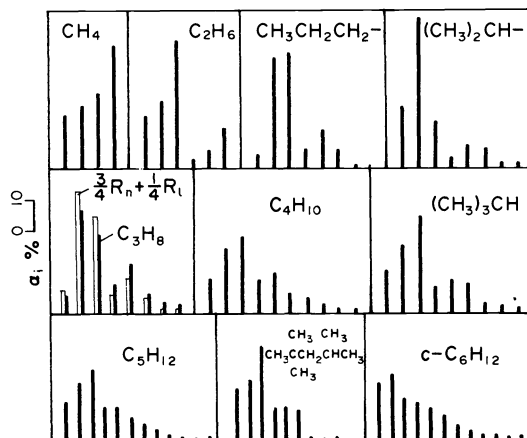

Figure 3. Distribution of deuteroalkanes in products of H-D exchange. $CH_3CH_2CH_2$- and $(CH_3)_2CH$- the distribution in alkanes formed in hydrolysis of corresponding RHgBr. Open lines for C_3H_8 corresponds to a distribution constructed using the 1:1 selectivity ratio for prim.:sec. C-H bonds.

It may be noted that the order is opposite to that of trans-effect of li-gands in substitution reactions in square Pt(II) complexes.

Decrease of activity with the increase of basic properties of ligands indicate that acceptor properties of Pt(II) are important in reaction with alkane molecule which behaves as a donor.

The support for this conclusion was found in a study of the dependence of exchange rate on the nature of substituents in methane and ethane derivatives (20). It turned out that two-parameter Taft equation holds (Fig. 2)

$$\log \frac{k_s}{k_o} = \rho^* \sigma^* + n\psi$$

The value of ρ^*(-1.4) corresponds to moderate electron accepting properties of Pt(II) with respect of hydrocarbon molecule. In addition to the polar parameter σ^* the reaction rate depends on resonance term $n\psi$. ψ characterizes the conjugation of the α-substituent in transition state, n-being equal to the number of substituents capable of such a conjugation.

The effect of π-accepting ligands (inverse trans-effect) apparently correlates with changes in Pt-R and Pt-H bond energies)
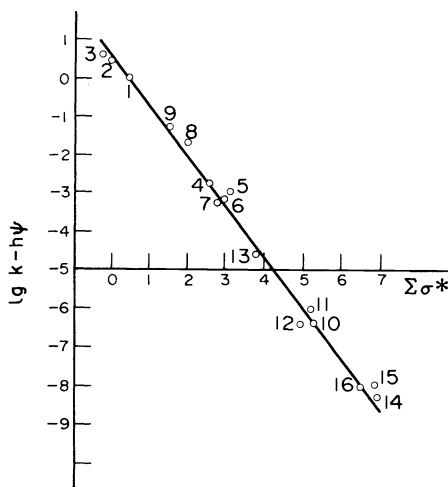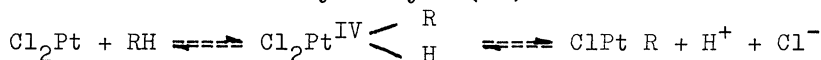

Figure 2.

b. Alkyl Platinum Compounds as Intermediates in Homogeneous Activation of Alkanes.

According to the assumed mechanism of oxidative addition, alkyl derivatives of Pt(IV) and Pt(II) have to be formed as intermediates in both H-D exchange and oxidation of alkanes catalyzed by Pt(II):

$$Cl_2Pt + RH \rightleftharpoons Cl_2Pt^{IV} \diagup \begin{array}{c} R \\ H \end{array} \rightleftharpoons ClPt\ R + H^+ + Cl^-$$

Although the isolation of alkylated intermediates has been so far difficult some evidence for such intermediates was obtained from comparison of distribution of deuterated alkanes obtained in H-D exchange and those formed in reaction of $PtCl_2$ with RHgBr where primary alkylation of Pt is very likely (22). It was mentioned already that polydeuterated alkanes are formed together with monodeutero-alkanes as a result of multiple exchange. The nature of this will be discussed later but independently of its mechanism the distribution of isotope substituted alkanes can be used as a "fingerprint" indicating the source of alkanes formed in the exchange.
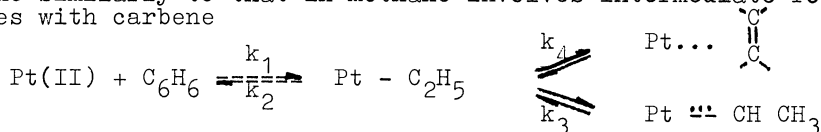
In interaction of K_2PtCl_4 with organomercuric compounds in D_2O deuteroalkanes are formed showing the multiple exchange pattern similar to that for alkanes exchange.

Tabulated below are the distributions of deuteroalkanes in the reaction of CH_3HgBr with K_2PtCl_4 and in direct H-D exchange of CH_4 catalyzed by K_2PtCl_4 under identical conditions.

Close agreement of both distributions is a convincing evidence for the formation of alkyl compounds of platinum in homogeneous activation of alkanes.

Kinetic results for chlorination of alkanes and their derivatives by Pt(IV) catalyzed by Pt(II) show that this reaction involves the same intermediates as for H-D exchange, thus alkylated Pt compounds are also formed in catalyzed chlorination and other oxidation reactions (26-29).

The pattern of stepped distribution suggests that the exchange takes place first in one methyl group of ethane, and then, after the molecule turns round, in the other. Obviously such a distribution is inconsistent with the π-complex alone as an intermediate and can be explained if the reaction of ethane similarly to that in methane involves intermediate formation of complexes with carbene

$$\text{Pt(II)} + C_6H_6 \;\underset{k_2}{\overset{k_1}{\rightleftharpoons}}\; \text{Pt} - C_2H_5 \;\underset{k_3}{\overset{k_4}{\rightleftharpoons}}\; \begin{array}{l} \text{Pt} \ldots \;\overset{\displaystyle C}{\underset{\displaystyle C}{\|}} \\[4pt] \text{Pt} \doteq \text{CH } CH_3 \end{array}$$

The "turning round" might be performed via π-complex, this reaction being slower than carbene complex formation. The ratio of rate constants k_3/k_4 apparently depends on medium composition and is responsible for the shape of multiple exchange pattern.

For higher alkanes stepped distribution was also observed (Fig. 3). Analysis of products mass-spectra suggests cyclic intermediates formation alongside with carbene- and π-complexes as most plausble explanation for the distribution (25).

d. Nature of Transition State.
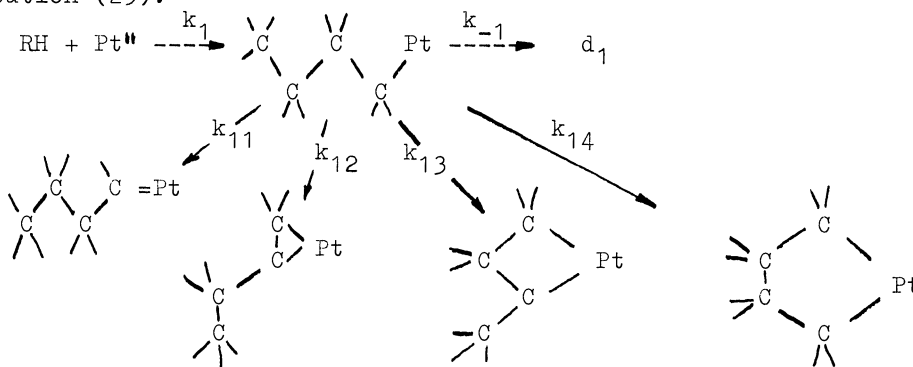
There is much experimental evidence that oxidative addition of alkane molecule to Pt(II) is in fact the primary step of alkane activation.

In particular the order of activities of the ligands (reverse trans-effect) and the effect of substituents (importance of non-polar conjugation) is consistent with oxidative addition and difficult to reconcile with an alternative mechanism of electrophylic substitution which would also explain alkylation of Pt by alkanes

$$\text{Pt}^{2+} + RH \longrightarrow PtR^+ + H^+$$
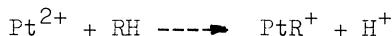
It should be noted that formation of alkyl hydrides was directly observed in some cases of intramolecular cleavage of C-H bond in ligands bound to transition metal, the reaction bearing much similarity with behaviour of free alkanes.

The dependence of the reaction rate on Pt(II) concentration also agrees with intermediate alkyl hydride formation rather than with direct substitution of H^+ by Pt^{2+}.

The transition state of the Pt(II) + RH reaction seems to be similar to that of the reaction of insertion of a singlet carbene (e.g., CH_2) in C-H bond

$$CH_2 + CH_4 \longrightarrow C_2H_6$$
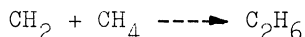
Calculation of potential energy surface made by Hoffmann (30) by means of extended Hückel method as well as by Dewar (31) by means of MINDO/2 method show that the insertion is a concert reaction with CH_2 attacking CH_4 first almost along C-H axis similarly to H atom abstraction by free radicals. The final stage of the reaction is close to free CH_3 radicals recombination in radical pair formed
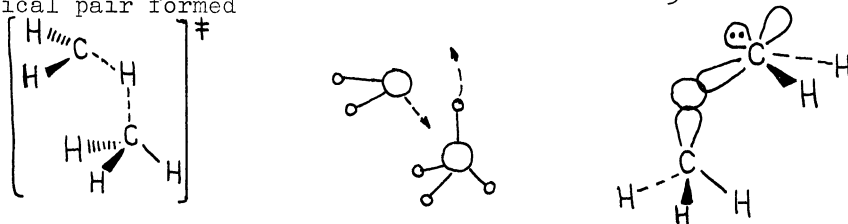
Similarly the first step of alkanes activation by square Pt(II) complexes can be visualized as alkane approaching Pt atom along its p_z-orbital, followed by H atom abstraction forming Pt(III) in a radical pair with alkyl radical R. The process terminates in a recombination of R and Pt(III) to form an octahedral alkyl hydride of Pt(IV). Multiple exchange of alkanes reveals a tendency of Pt(II) to covalent double bonding which is an indication of Pt(II) "carbenoid" properties. The transition state agrees with the order of reactivity of complexes with various ligands (note that multiple exchange factor changes in parallel with exchange rate constant) and also with the effect of substituents (stabilization by R in radical pair by conjugation in ligands).

There is a growing experimental evidence of covalent C-H bond interaction of organic ligands with metal atoms in coordination compounds forming some kind of "soft" hydrogen bonding indicative of low potential barrier for C-H...M interaction.

Thus C-H bond activation by transition metal complexes is a general phenomenon and form a new and a very promising field of homogeneous catalysis. One may expect an important development for the future with new catalytic processes including those for alkanes.

REFERENCES.

1. J.Halpern, Disc. Farad. Soc. 47, 7 (1968).
2. N.F.Goldshleger, M.B.Tyabin, A.E.Silov and A.A.Shteinman, Zhur. Fiz. Khim. 43, 2174 (1969).
3. R.J.Hodges, D.E.Webster and P.B.Wells, Chem. Commun. 462, (1971); J. Chem. Soc. Dalton, 2577 (1972).
4. A.I.Mustafin, A.A.Shteinman, Kinetika i Kataliz 16, 953 (1975).
5. C.Masters, Chem. Commun. 1258 (1972); P.A.Kramer and C.Masters, J. Chem. Soc. Dalton, 849 (1975).
6. J.L.Garnett, M.A Long and K.B.Peterson, Austr. J.Chem. 27, 1823 (1974).
7. M.R.Blake, J.R.Garnett, I.K.Gregor, W.Hannan, K.Hoa and M.A.Long, Chem. Commun. 930 (1975).
8. E.A.Grigorian, F.S.Dyachkovsky and I.R.Mullagaliev, Dokl. AN SSSR, 224, 859 (1975).
9. E.A.Grigorian, F.S.Dyachkovsky, Dokl. AN SSSR, in press.
10. Yu.A.Dorfman, V.S.Emeljanova, V.V.Lavrushko, A.G.Strukovsky, A.E.Shilov and A.A.Shteinman, Kinetika i Kataliz, 18, 1077 (1977).
11. A.E.Shilov and A.A.Shteinman, Kinetika i Kataliz, 14, 149 (1973).
12. N.F.Goldshleger, V.V.Eskova, A.E.Shilov and A.A.Shteinman, Zhur. Fiz. Khim. 46, 1353 (1972); V.V.Eskova, A.E.Shilov and A.A.Shteinman, Kinetika i Kataliz, 13, 534 (1972).
13. E.S.Rudakov, V.V.Zamashchikov, N.P.Belyaeva and R.I.Rudakova, Zhur. Fiz. Khim. 47, 2732 (1973).
14. N.F.Golshleger, M.L.Khidekel, A.E.Shilov and A.A.Shteinman, Kinetika i Kataliz, 15, 261 (1974).
15. V.P.Tretyakov, L.N.Arzamaskova and Yu.I.Yermakov, Kinetika i Kataliz, 15,538 (1974).
16. C.M.Tonge, E.F.Harrison and I.J.Higgins, Biochem. J. 161, 281 (1977).
17. M.B.Tyabin, A.E.Shilov and A.A.Shteinman, Dokl. AN SSSR, 198, 380 (1971).
18. R.J.Hodges, D.E.Webster and P.B.Wells, J. Chem. Soc.(A), 3230 (1971).
19. R.J.Hodges, D.E.Webster and P.B.Wells, J. Chem. Soc. Dalton, 257 (1977).
20. L.F.Repka and A.A.Shteinman, Kinetika i Kataliz, 15, 805 (1974).
21. N.F.Goldshleger and A.A.Shteinman, React. Kinet. Catal.Lett. 43, 6 (1977)
22. N.F.Goldshleger, I.I.Moiseev, M.L.Khidekel and A.A.Shteinman, Dokl. AN SSSR, 198, 380 (1971).
23. E.S.Rudakov and A.A.Shteinman, Kinetika i Kataliz, 14, 1346 (1973).
24. A.I.Mustafin, E.S.Rudakov, A.E.Shilov and A.A.Shteinman, Kinetika i Kataliz, 16, 1173 (1975).
25. A.I.Mustafin and A.A.Shteinman, Reac. Kinet.Catal.Lett. 6, 153 (1977).
26. V.V.Eskova, A.E.Shilov and A.A.Shteinman, Kinetika i Kataliz,13,534(1972)
27. V.V.Lavrushko, A.E.Shilov and A.A.Shteinman, Kinetika i Kataliz, 16, No. 6 (1975).
28. V.P.Tretyakov, E.S.Rudakov, A.A.Galenin and R.I.Rudakova, Dokl. AN SSSR, 225, 583 (1975).
29. V.P.Tretyakov and L.I.Arzamaskova, Kinetika i Kataliz, 17, 119 (1976).
30. R.C.Dobson, D.M.Hayes and R.Hoffman, J.Am.Chem.Soc. 93, 6188 (1971).
31. N.Bodor, M.J.S.Dewar and J.S.Wasson, J.Am.Chem.Soc. 94, 9095 (1972).