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Reactions of Transition Metal Polyhydride Complexes with Hydrocarbons

V.D.Makhaev and A.P.Borisov

The literature data on the interaction of transition metal polyhydride complexes with hydrocarbons are surveyed and analysed. Attention is concentrated on the examination of reactions with participation of the C-H bonds of hydrocarbons, i.e. on the activation of C-H bonds. The principal features of these reactions—the influence of the central atom of the complex, the nature of the stabilising ligands, the structure of the hydrocarbon, the reaction conditions, the solvent, and thermodynamic and kinetic factors—are examined. The possibility of increasing the catalytic activity of systems based on transition metal polyhydride complexes is discussed.
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I. INTRODUCTION

The term "activation of the C—H bond" in metal complex catalysis denotes processes in which a more reactive carbon—metal bond is formed from a C—H bond at least as an intermediate stage in some kind of process (isomerisation, isotope exchange, dehydrogenation, etc.).[1] In many compounds, the C—H bonds are sufficiently reactive to interact with the active centres of metal complexes. Many examples of reactions with participation of reactive C—H bonds, such as cyclometallation, isomerisation of olefins, isotope exchange in aromatic hydrocarbons, etc. are known.

About two decades ago, Shilov and co-workers[2] showed that in the presence of platinum(II) compounds isotope exchange takes place in solution between saturated hydrocarbons and deuterium. This discovery altered significantly the established ideas about the reactivity of alkanes and influenced greatly the further development of research into the activation of the C-H bond of hydrocarbons. However, for a long time it was impossible to discover new homogeneous systems capable of activating the C—H bonds of unstrained saturated hydrocarbons under mild conditions.

The beginning of the 1980s was marked by considerable advances in this field of research: the first examples of reactions involving the oxidative addition of saturated hydrocarbons to metal complexes with formation of stable alkyl hydride derivatives were discovered and investigated and the possibility of the selective homogeneous catalytic dehydrogenation of alkanes and cycloalkanes was demonstrated. An important step was made on the way to the creation of homogeneous catalytic systems capable of converting saturated hydrocarbons into their functional derivatives under mild conditions. The current interest in this problem is evident—after all, a considerable proportion of the organic raw material resources in fact comprise saturated hydrocarbons, whose low chemical reactivity prevents their widescale employment in chemical industry. The thermal and free-radical reactions used to synthesise functional derivatives of alkanes require a large expenditure of energy and are distinguished by a low selectivity. The need for the creation of new highly selective ways of processing hydrocarbons is the reason for the ever increasing interest in the study of the reactions of alkanes and cycloalkanes with transition metal complexes.[3,4]

Three main types of metal complex systems capable of activating the C—H bond of saturated hydrocarbons under mild homogeneous conditions are known at present—platinum(II) salts in an acid medium, biscyclopentadienyl derivatives of the lanthanides and actinides, and also transition metal polyhydride complexes and their derivatives. There exist a number of reviews on the first two types of activating systems, for example, those of Shilov and Shteinman[5] and Rothwell.[6]

The present review deals with the available literature data at the beginning of 1987 on the interaction of hydrocarbons with transition metal polyhydride complexes (PC)—compounds containing four and more hydride ligands linked to one transition metal atom. The types of PC known at present, the methods for their synthesis, and their chemical and physicochemical properties have been examined in detail in existing reviews.[7,8] The high reactivity of PC with respect to the C—H bonds is explained by the relative ease, characteristic of these compounds, with which they lose some of the ligands (the splitting off of hydrogen or phosphine). This involves the formation of coordination-unsaturated intermediates which tend to fill the coordination sphere by forming metal—hydrogen bonds and which are capable of abstracting a hydrogen atom from the molecules of compounds of different classes—alcohols, ethers, and saturated and unsaturated hydrocarbons.

The studies on the reactions of transition metal PC with hydrocarbons are developing vigorously. We therefore thought it useful to examine initially the available data, in some cases still inadequate, on the reactions of various PC with hydrocarbons and then to discuss the principal features of the processes considered and the factors influencing the reactivity of PC.

II. INTERACTION OF TRANSITION METAL POLYHYDRIDE COMPLEXES WITH HYDROCARBONS

1. Group VB Metal Complexes

The niobium pentahydride $NbH_5(DMPE)_2$, where DMPE = 1,2-bis(dimethylphosphino)ethane, forms an ethylene complex on interaction with ethylene, whereupon hydrogen and traces of ethane are evolved:

$$NbH_5(DMPE)_2 + C_2H_4 \xrightarrow[16\ h,\ 1\ atm]{pentane,\ 25\ ^\circ C} NbH(C_2H_4)_2(DMPE)_2 + 1{,}8H_2 + C_2H_6\ (traces).$$

When the reaction is carried out with deuterioethylene ($Nb:C_2D_4 = 1:6$), isotope exchange of ethylenic and hydride hydrogen atoms is observed; the hydrogen evolved consists of a mixture of isotopes (21% H_2, 44% HD, and 35% D_2). The exchange is slow and does not lead to the broadening of the ^1H NMR signals even at 95 °C in toluene-d_8.[9] The insertion of deuterium in the alkyl groups of the phosphine ligands was not observed.

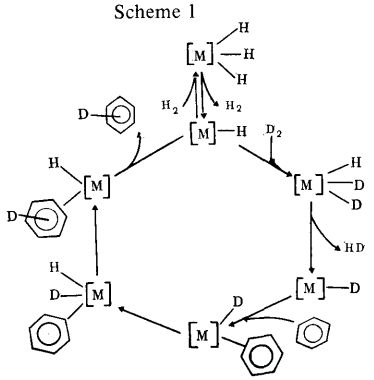
In contrast to the niobium complex, its tantalum analogue is much less reactive in relation to ethylene.[9] According to patent data, niobium and tantalum pentahydrides catalyse the dimerisation and hydrogenation of ethylene at an elevated temperature and pressure.[10]

The polyhydride complexes of the metals in the third transition row, having an odd number of valence electrons (TaH_5L_4,[11,12] ReH_7L_2,[13] ReH_5L_3, and IrH_5L_2,[14,15] where L is a tertiary organic phosphine), are active catalysts of isotope exchange between molecular hydrogen and aromatic hydrocarbons. $TaH_5(DMPE)_2$ proved to be the most active among these catalysts. The isotope exchange reaction has the following characteristic features:[12] (1) only the aromatic C–H bonds participate in the isotope exchange (in contrast to the exchange catalysed by metallic platinum or $PtCl_4^{2-}$, deuterium does not enter into the methyl groups of toluene or xylene); (2) the exchange takes place in stages—one C–H bond is involved in the exchange in each cycle of the reaction; (3) the reaction is sensitive to the steric effects of the substituents (deuterium exchange in the *ortho*-positions relative to the methyl or trifluoromethyl group takes place to an insignificant extent; the introduction of a second substituent in the *para*-position relative to the first retards the reaction sharply; electron-accepting substituents accelerate the reaction but the differences between the rates of reaction for monosubstituted arenes are small regardless of the type of substituent); (4) the presence of the isotope effect $k_H/k_D = 2-3$ shows that the C–H bond is dissociated in the rate-determining stage.

When triphenylphosphine is added to the reaction mixture, the hydrogen atoms in the *meta*- and *para*-positions in the benzene rings of phosphine participate exclusively in the isotope exchange, while in the presence of the $RuHCl(PPh_3)_2$ catalyst, the hydrogen atoms in the *ortho*-positions are exchanged. It has been suggested that, in the system considered, the phosphorus atom of triphenylphosphine is not coordinated to the tantalum atom and the polyhydride reacts with PPh_3 in the same way as with a substituted benzene having bulky PPh_2 substituents hindering the exchange in the *ortho*-position.

A mechanism has been proposed for the isotope exchange, including alternating stages involving the reductive elimination of H_2, the coordination of the arene, and oxidative addition:

Scheme 1



The weak influence of substituents is explained by the fact that both the oxidative addition and the coordination of the arene influence the rate of the reaction. It has been suggested that substituents exert the opposite influence on the rates of these stages, which in fact leads to the observed variation.

The absence of the deuteriation of the more acid hydrogen atoms in the methyl groups of toluene and anisole shows that only the hydrogen of the double bond coordinated to the metal is exchanged.[12]

The interaction of $Cp^*TaH_4L_2$ ($Cp^* = \eta^5$-C_5Me_5) with ethylene leads to a mixture of tantalum-containing products, ethane, but-1-ene, and free phosphine. Depending on the nature of the ligands L, the rate of reaction diminishes in the sequence $PMe_2Pb > PMe_3 > P(OMe)_3 > Me_2PCH_2CH_2PMe_3$, which is correlated with the decrease in the ease of elimination of the phosphine ligands from the complex. The addition of an excess of the phosphine to the reaction mixture inhibits the reaction. It has been concluded that the interaction of ethylene is preceded by the stage involving the reversible elimination of the phosphine ligand.[16] The complexes $Cp^*TaH_4L_2$, where L are monodentate ligands, form the butadiene complex $Cp^*TaCH_2CH_2CH_2CH_2(C_4H_6)$ in a high yield as a result of the reaction with ethylene. The tetrahydride stabilised by trimethylphosphine catalyses the dimerisation of ethylene to but-1-ene.

The photolysis of the benzene solution of $Cp^*TaH_4(DMPE)$ in an atmosphere of ethylene (2 atm) leads to the complex $Cp^*TaH_2 \cdot (C_2H_4)(DMPE)$ and the stoichiometric amount of ethane. When the ethylene complex is acted upon by hydrogen, the initial tetrahydride and ethane are produced.[16] The photochemical reaction probably proceeds, via a hydrogen elimination stage, in contrast to the thermal reaction.

2. Group VIB Metal Complexes

The interaction of PC of Group VIB metal complexes with hydrocarbons has been studied mainly in relation to the complexes $MH_4 \cdot (DPPE)_2$ [DPPE = 1,2-bis(diphenylphosphino)ethane] and $MH_4 \cdot (PMePh_2)_4$ (M = Mo or W). At 25 °C, the above compounds do not interact with alkenes in solution. Heating of toluene solutions of alk-1-enes and $MH_4(DPPE)_2$ to 100 °C leads to the stoichiometric reduction of the alkenes.[17,18]

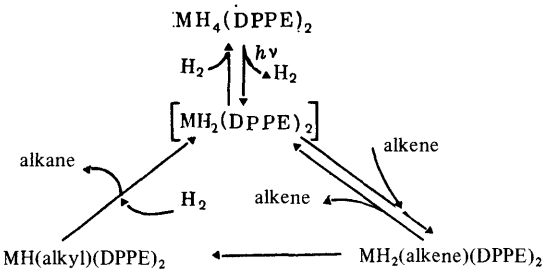
Irradiation of toluene solutions of pent-1-ene and $MH_4(DPPE)_2$ (λ = 355 nm) at room temperature leads to the stoichiometric reduction of the pentene, isomerisation with formation of pent-2-ene not being observed even after prolonged irradiation. Under analogous conditions, *cis*-pent-2-ene, 3,3-dimethylpent-1-ene, and cyclopentene are also reduced.

The photochemical reduction of $MoH_4(DPPE)_2$ with ethylene entails the formation, apart from ethane, of the diethylene complex $Mo(\eta^2$-$C_2H_4)_2(DPPE)_2$, which was isolated from the reaction mixture. The reaction with propene takes place differently and affords the π-allyl complex $MoH(\eta^3$-$C_3H_5)(DPPE)_2$.

It has been suggested that analogous products, containing η^2- or η^3-ligands depending on the structure of the initial olefin, are formed also in the interaction of $MH_4(DPPE)_2$ with other alkenes, but these products could not be isolated. The quantum yield of the pent-1-ene reduction reaction is 0.09 for $MoH_4(DPPE)_2$ and 0.006 for $WH_4(DPPE)_2$. When solutions of molybdenum (or tungsten) tetrahydride and pent-1-ene are irradiated in an atmosphere of hydrogen, the catalytic reduction of the pentene to pentane, unaccompanied by the formation of isomerisation products, is

observed (after 15 h, which corresponds to 150 catalytic cycles, only 1% of pent-2-ene is obtained). Internal olefins and olefins without an allylic hydrogen atom are reduced analogously. Photochemical reduction requires constant irradiation, i.e. long-lived catalytically active species are not formed. When a 0.1 M solution of pent-1-ene is reduced, the quantum yield is approximately equal to the yield in a stoichiometric reaction. On raising the pent-1-ene concentration to 5 M, the quantum yield also increases by an order of magnitude, which agrees with the process mechanism presented below:

Scheme 2



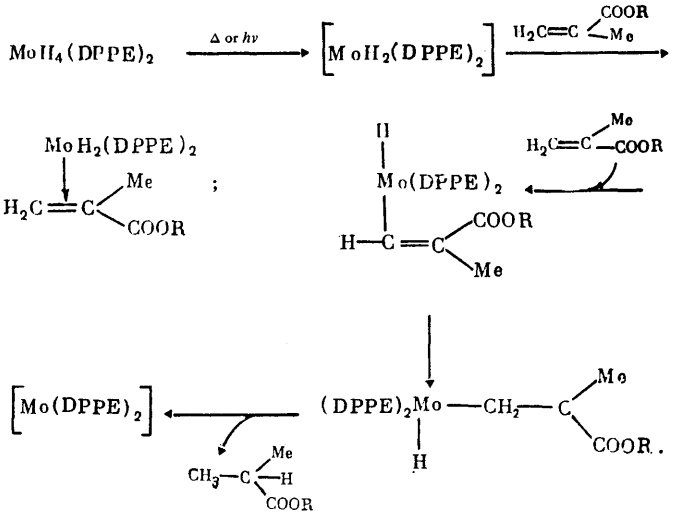
As can be seen from the Scheme, the irradiation of $MH_4(DPPE)_2$ leads to the elimination of a hydrogen molecule with formation of the dihydride, which either interacts with the alkene or again reacts with H_2.

The relative rates of photochemical reduction of alkenes correspond to those expected for reactions with participation of the sterically hindered species $MH_2(DPPE)_2$: pent-1-ene > 3,3-dimethylpent-1-ene > cyclopentene > *cis*-pent-2-ene. The hydrogenation proceeds without the isomerisation of the alkenes, in contrast to many other photocatalytic systems investigated previously.[19] In the reduction of pent-1-ene by deuterium, deuterium atoms add stereospecifically to the double bond and are not distributed statistically among various positions in the molecule, which would have been observed on isomerisation. It is believed[18] that the absence of isomerisation is associated with the steric hindrance due to the two bulky bisphosphine ligands. However, one should note that data concerning the stereospecific addition of deuterium do not agree with the authors' hypothesis of the intermediate formation of π-allyl complexes by alkenes having allylic hydrogen atoms.

The introduction of an aryl substituent into the alkene influences appreciably the composition of the reaction products. The reduction of 4-phenylbut-1-ene under the conditions indicated above also leads to the addition of deuterium in the 1,2-positions. However, this entails the formation of an appreciable amount of isomerisation products; the absence of deuterium from these products shows that structurally different photogenerated species are responsible for reduction and isomerisation.

At 80–100 °C, the complex $MoH_4(DPPE)_2$ interacts with alkyl methacrylates, forming one mole of H_2, one mole of alkyl isobutyrate, and a certain amount of the corresponding hydrido-σ-alkenyl complex $MoH[CH=C(Me)C(O)(OR)](DPPE)_2$ [R = Et, iso-Pr, Bu, or Cy (cyclohexyl); yield 15–80%]. On irradiation, the reaction takes place at room temperature resulting in the insertion of the intermediate coordination-unsaturated species in the C–H bond of the unsaturated compound:[20]

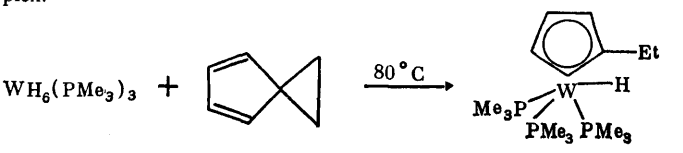
Scheme 3



Under the conditions of the photochemical reaction, molybdenum and tungsten PC are capable of interacting also with benzene and saturated hydrocarbons.[21] When solutions of MH_4L_4 in benzene-d_6 or cyclohexane-d_{12} are irradiated (254 nm), deuterium molecules are present in the gas phase after the reaction and in the case of cyclohexane-d_{12} much more deuterium is evolved than in the reaction in deuteriobenzene. The complex with methyldiphenylphosphine is much more active in this reaction than the complex with bis-(diphenylphosphino)ethane. The composition of the products of the reaction of the metal complexes and hydrocarbons has not been investigated. It has been suggested that the reaction proceeds via a stage involving the oxidative addition of a photogenerated active species to a C–H bond of the hydrocarbon. The cyclometallation reaction is a competing process, which is indicated by the appearance of deuterium in the gas phase on irradiation of $WH_4[P(CD_3)_2Ph_2]_4$ and $WH_4[P(CD_2CD_3)Ph_2]_4$ in benzene or cyclohexane.[22] The dependence of the composition of the gas phase on the irradiation wavelength (deuterium is not observed in the gas phase at λ = 366 nm) and on the nature of the phosphine ligands suggests that, with increase in the irradiation frequency, not only hydrogen but also some of the phosphine ligands are split off (see the reactions with participation of ReH_5L_3).

An interesting feature of the study of Pivovarov et al.[21] is the observation of a higher reactivity of cyclohexane compared with benzene. It may be that a change in the ligand environment and in the reaction conditions will make it possible to devise a system manifesting a still higher activity in relation to alkanes than to arenes.

The reactions of the molybdenum and tungsten hexahydrides MH_6L_3 (M = Mo or W) with hydrocarbons have been scarcely investigated. It has been reported that, when a benzene solution of $WH_6(PMe_3)_3$ is refluxed in the presence of cyclopenta-2,4-dienespirocyclopropane, the cyclopropane ring is rapidly opened, which results in the formation of an ethylcyclopentadienyltungsten complex:[23]



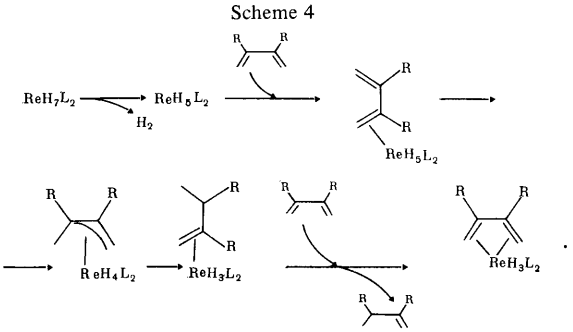
3. Rhenium Complexes

Perhaps the greatest number of different polyhydride complexes are now known for a Group VII metal—rhenium. The interaction of PC with hydrocarbons has in fact been studied in greatest detail in relation to the rhenium complexes. Technetium, an analogue of rhenium, is a radioactive element and studies on the chemical properties of technetium PC have not so far been reported.

The rhenium heptahydrides ReH_7L_2 react under mild conditions with phosphines, amines, and arsines to form the pentahydride ReH_5L_2L'. Further substitution of hydrogen, leading to trihydrides, requires much more severe conditions.[13,24] However, the interaction of ReH_7L_2 with various dienes proceeds readily under mild conditions and is accompanied by the conversion of the heptahydride into the trihydride.[25,26]

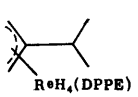
The reaction of $ReH_7(PPh_3)_2$ with buta-1,3-diene and its alkyl derivatives in boiling tetrahydrofuran (THF) ends after several minutes. The trihydrodiene complexes $ReH_3(diene)(PPh_3)_2$ are pale-yellow crystalline substances stable in air. The interaction of $ReH_7 \cdot (PPh_3)_2$ with an excess of cyclopentadiene at 25 °C results in the formation of the diene complex $(\eta^4\text{-}C_5H_6)ReH_3(PPh_3)_2$. However, with increase in the amount of the heptahydride, the complex is dehydrogenated catalytically with formation of $CpReH_2L_2$.[27] The interaction of equimolar amounts of ReH_7L_2 and cyclopentadiene in THF at 60 °C leads directly to $CpReH_2L_2$.[25] Cyclohexa-1,3-diene or cyclohexa-1,4-diene afford $(\eta^4\text{-}1,3\text{-}C_6H_8)ReH_3(PPh_3)_2$, the heating of which leads to the arene complex $ReH(\eta^6\text{-}C_6H_6)(PPh_3)_2$. Baudry et al.[26] described the following scheme for the interaction of rhenium heptahydride with dienes:

Scheme 4

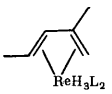


As a consequence of its low thermal stability in solution, the heptahydride loses a hydrogen molecule and is converted into the pentahydride, which interacts with the diene. The diene ligand promotes further reaction, acting as a hydrogen acceptor, and the complexes $ReH_5(\eta^2\text{-diene})L_2$ are therefore unstable and have not been isolated. The proposed mechanism is supported by the finding that only one mole of hydrogen per mole of the complex is evolved during the reaction and that part of the diene is hydrogenated to a mono-olefin.

The reaction conditions and the composition of the product depend on the properties of the ligands. Thus $ReH_7(DPPE)$, containing the bidentate phosphine ligand, is more thermally stable and does not react with dienes under the conditions indicated. Subsequent treatment of this PC with potassium t-butoxide and dimethyl sulphate in the presence of 2,3-dimethylbutadiene yielded the first example of a PC with an allyl ligand:[28]



On refluxing in THF, the complexes ReH_7L_2 react with propene to form complexes containing the propene dimerisation product—2-methylpenta-1,3-diene—as the ligand:

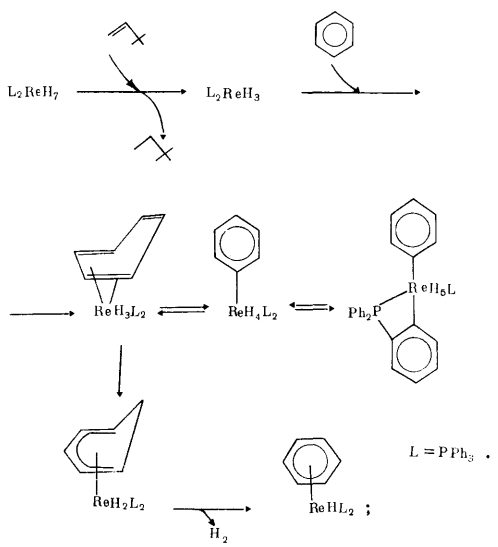


The photochemical reaction of this compound or of the initial heptahydride with an excess of propene affords $(\eta^3\text{-}C_3H_5)_2ReHL_2$, which permits the conclusion that rhenium heptahydride is successively converted initially into the diene complex $ReH_3(\eta^4\text{-}C_6H_{10})L_2$ and then into the π-allyl complex $(\eta^3\text{-}C_3H_5)_2ReHL_2$.[29]

Using the activating effect of olefins on the rhenium PC, a series of unusual reactions have been carried out.[25,26] 3,3-Dimethylbut-1-ene [t-butylethylene (TBE)], which has been shown[30] to be the most convenient dehydrogenating agent in such reactions, was used as the hydrogen acceptor.

In the presence of TBE, rhenium heptahydride reacts with benzene on refluxing, giving rise to $(\eta^5\text{-}C_6H_7)ReH_2(PPh_3)_2$. During the reaction, one mole of H_2 is evolved and 1.1 mole of 2,2-dimethylbutane is formed. When benzene-d_6 is employed, the rhenium complex containing a 50% deuteriated cyclohexadienyl ring, 25% deuteriated hydride ligands, and triphenylphosphine ligands (deuteriated in the *ortho*-position to the extent of 10—15%) is formed. The hydrogen evolved contains hardly any deuterium. Heating of the product *in vacuo* affords the η^6-arene complex:[31]

Scheme 5



The reactions with toluene, *p*-xylene, and mesitylene proceed analogously. This results in the formation of the corresponding dihydrocyclohexadienylrhenium complexes.[32]

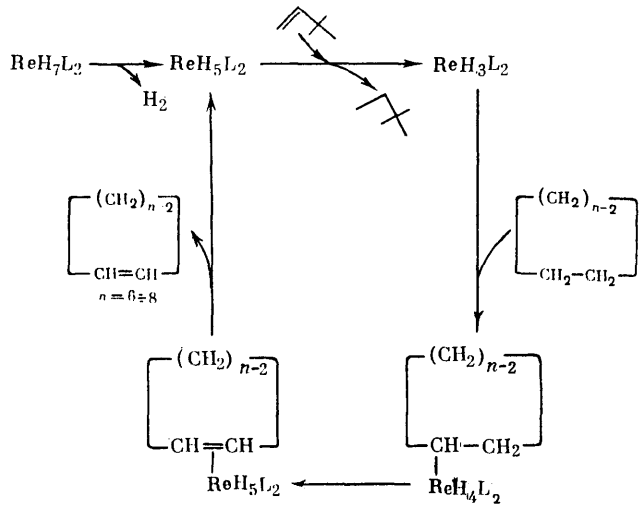
In the presence of TBE, rhenium heptahydride is capable of dehydrogenating saturated hydrocarbons—both cyclic and acyclic.[33-35] The reaction is carried out by refluxing rhenium heptahydride in the corresponding hydrocarbon in the presence of an excess of TBE in an inert atmosphere.

The reaction of ReH_7L_2 (L = PPh_3 or PEt_2Ph) with cyclopentane gives rise to $CpReH_2L_2$. The reaction terminates after 10 min, the entire hydrogen (both from the rhenium hydride and from cyclopentane) being consumed in the hydrogenation of TBE.[33]

The interaction of ReH_7L_2 with higher cycloalkane homologues (cyclohexane, cycloheptane, and cyclo-octane) leads to the corresponding cycloalkenes. It has been noted that the dehydrogenation of cycloalkanes takes place even when air or pure oxygen is passed through the reaction mixture.[34] The yield of the dehydrogenation products increases with enhancement of the electron-donating properties of the phosphine ligands forming part of the composition of the rhenium complex: $P(C_6H_4F\text{-}p)_3 < PPh_3 < P(C_6H_4Me\text{-}p)_3$.

The decrease in the ReH_7L_2 concentration from 5×10^{-2} to 3×10^{-3} M made it possible to achieve the dehydrogenation of cycloalkanes under catalytic conditions. The nature of the PR_3 ligands in ReH_7L_2 has a decisive influence on the course of the catalytic process. Best results have been obtained using $ReH_7.[P(C_6H_4F\text{-}p)_3]_2$, which reacts with cyclo-octane even at 30 °C, giving rise to 1.6 conversion cycles after 10 min. At 80 °C, nine moles of cyclo-octene are formed per mole of the PC. Cyclo-hexene may be used instead of TBE as the hydrogen acceptor in the dehydrogenation of cyclo-octane. The reaction is highly selective: no dehydrogenation products other than cycloalkenes have been observed. Rhenium heptahydrides with more electron-donating triarylphosphine ligands are less active in the catalytic process in contrast to the non-catalytic reaction. Presumably, the electron-donating substituents in the benzene ring of the ligand promote *ortho*-metallation and thereby deactivate the intermediate catalytically active species. Electron-accepting substituents hinder this reaction and therefore promote a higher yield of products. The catalytic process is described by the scheme:

Scheme 6



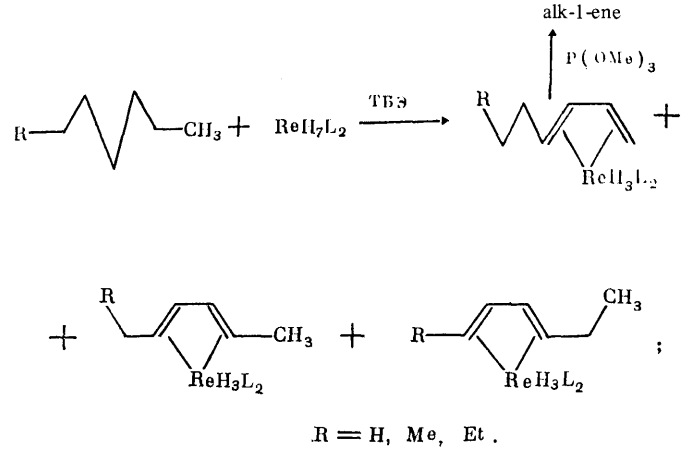
Under the conditions of this reaction, methylcyclohexane affords a mixture of isomeric olefins,[36] the thermodynamically most stable 1-methylcyclohexene being present only in trace amounts, and the main products are 3- and 4-methylcyclohexenes, which indicates the absence of radical intermediates in the dehydrogenation process. The isomeric composition of the olefins formed depends on the properties of the stabilising phosphine ligands (see Table).

The feasibility of the selective non-radical catalytic conversion of sterically unstrained saturated hydrocarbons into their functional derivatives by treatment with soluble transition metal complexes has been demonstrated[36] in relation to the catalytic dehydrogenation of cycloalkanes in the presence of rhenium hydride complexes.

Composition of the products of the dehydrogenation of methylcyclohexane catalysed by rhenium and iridium PC in the presence of an excess of TBE.[36,37]

Catalyst	Reaction conditions		Number of catalytic cycles	Reaction products, %			
				methylene-cyclohexane	methylcyclohexenes		
	T, °C	t, h			3-Me	4-Me	1-Me
$ReH_7[P(C_6H_4F\text{-}p)_3]_2$	80	1/6	3	6	29	65	1
$ReH_7(PPh_3)_2$	80	1/6	1	9	28	63	1
$ReH_7(PEt_3)_2$	80	2	0.2	28	27	45	1
$IrH_5[P(Pr\text{-}iso)_3]_2$	100	1/4	3	64	10	16	9
	100	1	3.5	55	12	18	15
	150	65	10	1	13	24	62

In the presence of TBE, rhenium heptahydrides are capable of dehydrogenating also normal alkanes.[35] Heating of ReH_7L_2 with an excess of TBE in pentane in a sealed tube (80 °C, 30 min) leads to the pentadiene complex $ReH_3(\eta^4\text{-}C_5H_8)L_2$. The yield of this complex increases on passing from L = PPh_3 to L = $P(C_6H_4Me\text{-}p)_3$. With increase in the rhenium heptahydride concentration, the yield of the complex $ReH_3(\eta^4\text{-}C_5H_8)L_2$ diminishes as a result of the competing formation of $ReH_2(\eta^5\text{-}C_5H_7)L_2$ (cf. with the results of Jones and Maguire[27]). When $ReH_3(\eta^4\text{-}C_5H_8)L_2$ is treated with trimethyl phosphite, pent-1-ene is formed in a high yield and with a high selectivity, while treatment with triethyl or triphenyl phosphite produces a mixture of pentane and pent-1-ene.[38] Treatment of the same compound with benzylisonitrile† leads to the selective formation of *cis*-pent-2-ene. Normal alkanes with 6–8 carbon atoms also react with $ReH_7(PPh_3)_2$ in the presence of TBE. This results in the formation of a mixture of isomeric trihydridodienerhenium complexes, whose treatment with trimethyl phosphite leads to alk-1-enes in a high yield and with a high selectivity:



R = H, Me, Et.

† T.Burchard and H.Felkin, New J. Chem., 1986, **10**(12), 673.

Since the isomeric rhenium complexes are in a dynamic equilibrium under the reaction conditions, the data obtained do not allow one to determine which of the C–H bonds of the alkanes is attacked in the initial stage of the process. It has been suggested that the C–H bonds of the methyl groups are the first to be attacked. In contrast to the reactions with cycloalkanes, which lead to catalytic dehydrogenation products, in the interaction of ReH_7L_2 with n-alkanes, the loss of olefins from the coordination sphere of the complex takes place to an insignificant extent, which makes it impossible to carry out the reaction under catalytic conditions.

The alkanes used in the reaction must be completely free of admixtures of olefins, because even an insignificant amount of such compounds fully inhibits the interaction of rhenium heptahydrides with alkanes.[35]

Rhenium heptahydride stabilised by tricyclohexylphosphine ligands proved to be thermally more stable‡ than the complexes with triarylphosphines, which permitted a more detailed study of certain stages of the activation of C–H bonds by rhenium PC.[39,40] At 60–80 °C, $ReH_7(PCy_3)_2$ reacts with benzene-d_6, deuterium substituting not only the hydride ligands but also the hydrogen atoms at the C(2) and C(3) carbon atoms of the cyclohexyl rings. The regioselectivity of the isotope exchange indicates an intramolecular process mechanism. The higher rate of isotope exchange at the C(3) atom agrees with the intramolecular metallation mechanism, for which the preferential formation of the less strained five-membered ring compared with the four-membered ring should be observed. Acenaphthylene $C_{12}H_8$ is hydrogenated in the inner sphere of the complex with formation of $(\eta^4\text{-}C_{12}H_{10})ReH_3L_2$. The reaction with anthracene does not occur, which indicates the ineffectiveness of the rhenium PC in radical hydrogen transfer processes leading to the hydrogenation of the 9,10-positions in anthracene.

The study of the isotope exchange between ReH_7L_2 and deuterium and of its interactions with acenaphthylene, olefins, and other compounds showed that all these reactions proceed via a stage involving the formation of the intermediate ReH_5L_2 species.

The interaction of rhenium pentahydride $ReH_5(PMe_2Ph)_3$ with hydrocarbons under the conditions of the photochemical reaction has also been investigated.[43–46] Irradiation of a solution of this complex in benzene-d_6 leads to the exchange of the solvent deuterium atoms with the hydrogen atoms in the *meta*- and *para*-positions in the benzene rings of the ligands.[43] the presence of naphthalene in the reaction mixture results in the extensive deuteriation of naphthalene, mainly in the 2,3,6,7-positions.[44]

The photochemical hydrogenation of hex-1-ene by molecular hydrogen has been achieved. The reaction is catalytic with respect to rhenium but requires constant irradiation, as in the case of molybdenum and tungsten PC: when the reaction mixture is kept in the dark for 12 h after irradiation for 10 min, there is no appreciable increase in the yield of hydrogenation products.[44]

‡ The thermal stability of rhenium heptahydrides increases with enhancement of the electron-donating properties of the ligands. Thus, $ReH_7(PMe_3)_2$, stabilised by trimethylphosphine which is a powerful electron-donating ligand with a small bulk, sublimes *in vacuo* at 40 °C and decomposes at 102 °C.[41] The conversion of ReH_7L_2 into $Re_2H_8L_4$ on heating in solution is retarded on passing from the triphenylphosphine ligand to the more electron-donating ligands PMe_2Ph and PEt_2Ph,[39] although their bulk is in fact smaller.[42] The higher stability of $ReH_7(PCy_3)_2$ can also be explained by the powerful electron-donating properties of tricyclohexylphosphine and not by its small bulk.

Reaction with internal olefins leads to the formation of hydrido-olefinrhenium complexes. When a solution of rhenium pentahydride and cyclopentene in benzene is irradiated, $(\eta^2\text{-}C_5H_8)ReH_3.(PMe_2Ph)_3$ is formed almost quantitatively. The hydrogenation of the olefin is not then observed.[44] Photolysis of the compound obtained leads to coupled hydrogenation-dehydrogenation of the coordinated olefin, which results in the formation of cyclopentane and a mixture of the complexes $CpReH_2L_2$ and $CpReH_4L$.

In the photochemical interaction of ReH_5L_3 with cyclopentadiene, the tetra-hydride complex $CpReH_4L$ (L = PMe_2Ph) was mainly formed, while the thermal interaction afforded the dihydride $CpReH_2L_2$ (L = PPh_3).[25] The interaction of ReH_5L_3 with cyclo-octatetraene under irradiation gives rise to the cyclo-octatriene complex $(\eta^4\text{-}C_8H_{10})ReH_3L_2$.[45] The same compound has been obtained on refluxing $ReH_7(PMe_2Ph)_2$ with cyclo-octa-1,5-diene in hexane, which confirms the hypothesis of the intermediate formation of ReH_5L_2 both in the photochemical activation of ReH_5L_3 and in the thermal activation of ReH_7L_2. On standing for 12 h, the compound $(\eta^4\text{-}C_8H_{10})ReH_3L_2$ is fully converted into the cyclo-octa-1,5-dienyl complex $(\eta^5\text{-}C_8H_{11})ReH_2L_2$. Cyclo-octatetraene is converted into the cyclo-octadienyl ligand regiospecifically: all three hydrogen atoms transferred from rhenium to the hydrocarbon are in the *endo*-positions relative to the rhenium atom, which indicates the intramolecular character of the process.

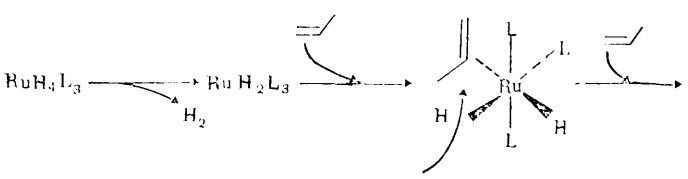
Irradiation of ReH_5L_3 in cyclopentane in the presence of TBE results in the formation of the complex $CpReH_2L_2$ in a low yield, while in the absence of TBE only the dimeric complex $Re_2H_6L_5$—the product of the interaction of ReH_5L_2 with ReH_5L_3—is formed.[47] If ReH_5L_3 (L = PMe_2Ph) is irradiated in the presence of TBE in benzene under nitrogen pressure, a mixture of products is obtained. One of them—the η^6-arene complex—contains the TBE residue, i.e. $(\eta^6\text{-}C_6H_6)ReL_2(CH_2CH_2Bu\text{-}t)$, while the other contains the *ortho*-metallated phosphine and coordinated nitrogen—$\overline{ReL_3(PMe_2C_6H_4\text{-}o)}.(N_2)$.[44]

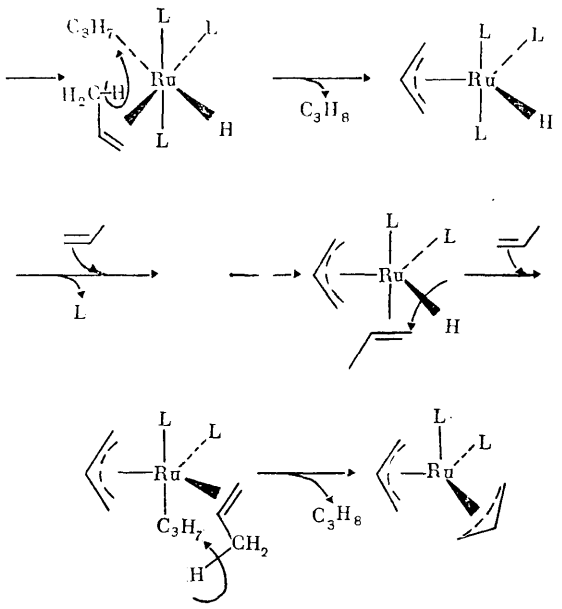
4. Iron Subgroup Metal Polyhydride Complexes

The iron tetrahydride complex $FeH_4(PEtPh_2)_3$ reacts in THF with cyclohexene, affording $FeH(C_6H_{11})(PEtPh_2)_2$ (THF). It has been suggested that an η^2-olefin iron complex is formed as an intermediate.[48]

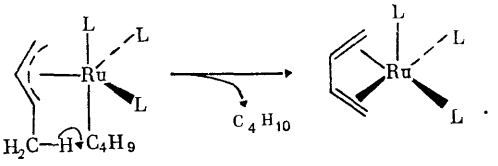
The solid ruthenium tetrahydride $RuH_4(PPh_3)_3$ catalyses the hydrogenation of ethylene but at room temperature the reaction is very slow (ten catalytic cycles in a week[49]). However, if the reaction is carried out in toluene, it is completed after 10 min with formation of $\overline{RuH(PPh_2C_6H_4\text{-}o)}(PPh_3)_2(C_2H_4)$, one mole of hydrogen and one mole of ethane being evolved.[50,51] The reaction of $RuH_4(PPh_3)_3$ with propene at 100 °C takes place in 30 min, affording bis(η^3-allyl)bis(triphenylphosphine)ruthenium:

Scheme 7





The main product of the interaction of $RuH_4(PPh_3)_3$ with an excess of but-1-ene is the butadiene complex $Ru(\eta^4\text{-}C_4H_6)(PPh_3)_3$, the same complex being formed also in the reaction of ruthenium tetrahydride with buta-1,3-diene at room temperature. It is suggested that the butadiene ligand is formed from but-1-ene also via Scheme 7, but in the last stage the hydrogen atom is split off from the methyl group of the 1-methyl-allyl ligand:



Solutions of $RuH_4(PPh_3)_3$ in toluene catalyse the isomerisation of alk-1-enes to alk-2-enes at 25 °C.[52-54] It has been shown in relation to pent-1-ene that *trans*-pent-2-ene is formed preferentially in the isomerisation process in amounts greatly exceeding the equilibrium values for the *cis*-pent-2-ene—*trans*-pent-2-ene system. The reaction is carried out in an argon atmosphere. It takes place initially very rapidly but after a few minutes it begins to slow down and then follows first-order kinetics. The rate of reaction diminishes also when argon is replaced by nitrogen. In the first rapid stage, the isomerisation is accompanied by the hydrogenation of two moles of pent-1-ene per mole of the PC, which corresponds to the utilisation of all the hydride ligands in RuH_4L_3 and, according to the author,[54] indicates the formation of a complex of zerovalent ruthenium with the olefin. The rate of isomerisation is 250 times higher than the rate of hydrogenation. In the second stage of the reaction, only traces of pentane are formed, but, if the reaction mixture is allowed to stand for 24 h or more, yet another mole of pentane per mole of the catalyst is formed. The catalyst then loses its activity, which, however, is restored on treatment with hydrogen. The catalytic activity is apparently lost as a result of the slow *ortho*-metallation reaction.

Subsequent investigations[51] failed to confirm data indicating the formation of alkene complexes in reactions with pentenes. The product of the reaction of RuH_4L_3 with pent-1-ene is RuH_4L_4 for the stoichiometric reactant ratio. The interaction with an excess of pent-1-ene produced the diene complex $Ru(\eta^4\text{-}C_5H_8)L_3$, which is apparently formed from but-1-ene similarly to the butadiene complex. This hypothesis agrees with data demonstrating the formation of two moles of pentane per mole of the catalyst and explains the evolution of one mole of H_2 in the initial stage of the reaction.

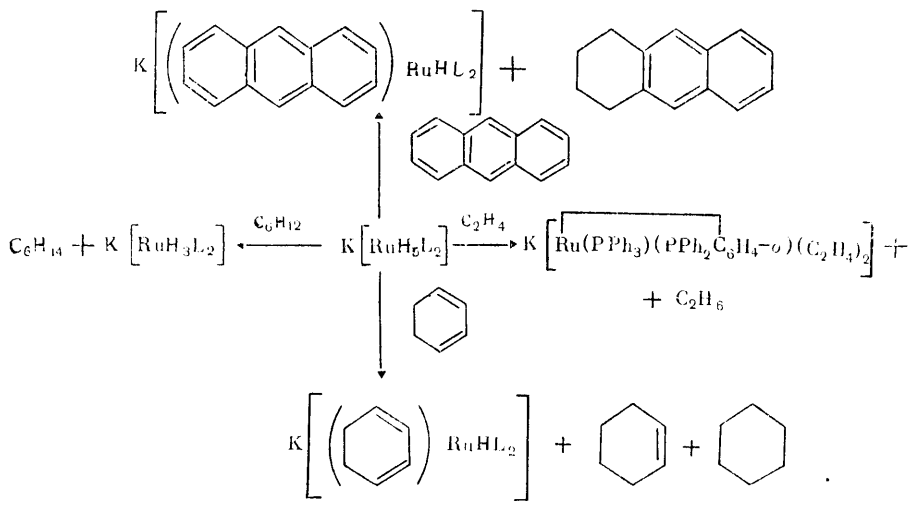
The complex $RuH_4(PPh_3)_3$ reacts with the non-conjugated chelating cyclo-octa-1,5-diene (toluene, 100 °C, 5 h) with formation of one mole of cyclo-octane and $Ru(PPh_2C_6H_4\text{-}o)(PPh_3)(\eta^5\text{-}C_8H_{11})$. RuH_4L_3 does not interact with isobutene, cyclohexene and cyclo-octene even at 100 °C.[51]

The complexes RuH_4L_3 [L = $P(Pr\text{-}iso)_3$, PCy_3, or $P(NEt_2)_3$] activate the C—H bonds of aromatic hydrocarbons and the alkyl groups in phosphine ligands at room temperature in the dark.[55,56] When the above compounds are dissolved in deuteriobenzene, a rapid disappearance of the signals of the hydride protons and the appearance of signals due to $C_6D_{6-x}H_x$ ($x > 1$) are observed. The products formed catalyse the slower deuterium exchange reaction between the solvent and the phosphine ligand. Triisopropylphosphine is deuteriated to the extent of 70—76%, tricyclohexylphosphine is 25% deuteriated and tris(diethylamino)phosphine is 40% deuteriated. The process mechanism includes stages involving the elimination of the phosphine ligand, the coordination of the arene, and the subsequent activation of the C—H bond of benzene and the phosphine ligand. Analogous reactions take place also in toluene but much more slowly. In the reaction with deuteriotoluene, an increase in temperature to 110 °C results in a sharp acceleration of the process, which indicates a change in the reaction mechanism. According to the authors,[55,56] solutions of ruthenium tetrahydride in aromatic solvents constitute the first example of a system capable of catalysing spontaneously (in the dark without heating or irradiation) the deuterium exchange between the hydrogen atoms of the phosphine ligands and the deuterium atoms of the solvent. Ruthenium polyhydride complexes are apparently much more active catalysts of the activation of the C—H bonds in arenes than the PC of 5*d* metals (tantalum, rhenium, and iridium) investigated previously.[12]

In the presence of TBE, ruthenium tetrahydrides catalyse the dehydrogenation of cyclo-octane. When $RuH_4[P(C_6H_4F\text{-}p)_3]_3$ is heated in cyclo-octane to 150 °C in the presence of TBE, 45—55 moles of cyclo-octene are formed per mole of the catalyst. The complex of ruthenium tetrahydride with triphenylphosphine ligands is less active in this reaction.[57]

The anionic ruthenium complex $K[RuH_5(PPh_3)_2]$ hydrogenates alkenes (ethylene, hex-1-ene), dienes (cyclohexa-1,3-diene), and anthracene (Scheme 8) at room temperature. Two hydride ligands participate in the reaction with hex-1-ene, four hydride ligands are involved in the reaction with cyclohexa-1,3-diene, and six hydride ligands react with ethylene, one of them being formed as a result of the *ortho*-metallation reaction. Anthracene may be hydrogenated under catalytic conditions, whereupon 1,2,3,4-tetra-hydroanthracene is formed with a high selectivity[58,59] (Scheme 8).

Scheme 8



The interaction of $RuH_6(PCy_3)_2$ with ethylene at room temperature leads to $Ru\overline{H[C_6H_{10}PCy_2]}(PCy_3)(C_2H_4)_2$. It has been suggested that the hydride ligands are displaced by the excess ethylene and that intramolecular metallation of one of the cyclohexyl groups takes place in the unstable zerovalent ruthenium complex $Ru(C_2H_4)_2 \cdot (PCy_3)_2$ formed.[56]

The reaction of $RuH_6(PCy_3)_2$ with an excess of cyclopentene in pentane at room temperature affords a mixture of the products $RuH_2(PCy_3)_2(C_5H_6)$ and $RuH(PCy_3)_2Cp$. $RuH(PCy_3)_2Cp$ is formed quantitatively in the presence of TBE. At 120 °C in the presence of TBE, ruthenium hexahydride reacts with cyclopentane to form hydridocyclopentadienyl complexes, which, however, could not be identified.[60]

Osmium tetrahydrides are much less active in relation to olefins than their ruthenium analogues.[61] The interaction of $OsH_4 \cdot (PEt_2Ph)_3$ with four moles of cyclo-octa-1,5-diene (COD) (toluene, 100 °C, 65 h) produces, after treatment with ethanol, cyclo-octene (50 % yield), the unreacted cyclo-octadiene, and $Os(COD)(PEt_2Ph)_3 \cdot EtOH$. The reaction with 12 moles of oct-1-ene under the same conditions gives rise to two moles of octane, a mixture of various octenes (isomerisation products), and an uncharacterised olefin complex of osmium. The catalytic hydrogenation of oct-1-ene, accompanied by the formation of isomerisation products, takes place in the presence of hydrogen. At the end of the reaction, the osmium PC can be regenerated from the reaction mixture. The selectivity of the hydrogenation and isomerisation of olefins has been noted: predominantly terminal alkenes are hydrogenated, while isomerisation leads mainly to internal olefins.

The irradiation of $OsH_4(PMe_2Ph)_3$ in benzene-d_6 leads to isotope exchange. After irradiation for 1 h, the initial tetrahydride is 90% converted into the deuteride $OsD_4(PMe_2Ph)_3$.[62]

It has been noted that the hexahydrides OsH_6L_2 dehydrogenate saturated hydrocarbons in the presence of TBE.[63]

5. Iridium Complexes

Like other PC of metals with an odd number of valence electrons (see subsection 1), the complexes IrH_5L_2 catalyse the deuterium exchange between gaseous deuterium and aromatic hydrocarbons.[14,15]

The iridium pentahydrides IrH_5L_2 interact with alkenes similarly to ruthenium tetrahydride: the reaction with ethylene at 45 °C in benzene affords ethane and complexes with metallated phosphines, while the reaction with propene gives rise to the π-allyl complexes $Ir(\eta^3\text{-}C_3H_5)L_2$.[64]

In the reactions with linear mono-olefins C_nH_{2n} ($n > 3$), iridium pentahydrides catalyse the intermolecular transfer of hydrogen atoms with formation of the corresponding alkane and diene. Ethylene, may be used as the hydrogen acceptor, which is reduced to ethane; a higher olefin is converted to a diene under these conditions:

$$\text{Alkene(1)} + \text{alkene(2)} \xrightarrow[2\text{-}25 \text{ cat. cycles}]{25\text{-}130\ ^\circ\text{C},\ 3\text{-}40\ \text{h}} \text{alkane(1)} + \text{diene(2)}.$$

The linear conjugated dienes formed have predominantly the *trans,trans*-configuration. The interaction of IrH_5L_2 with *cis*-but-2-ene at 60 °C yielded the butadiene complexes $IrH(\eta^4\text{-}C_4H_6)L_2$; after the reactions with pent-1-ene, hex-1-ene, and hex-2-ene, it was not possible to isolate any hydride or olefin complexes. A decrease in the catalytic activity of IrH_5L_2 is observed during the reaction. Depending on the nature of the ligands L, the catalytic activity of iridium pentahydride diminishes in the sequence $IrH_5[P(Pr\text{-}iso)_3]_2$ » $IrH_5(PPh_3)_2$ > $IrH_5(PMe_3)_2$ » $IrH_5(PCy_3)_2$.[64] The mechanism of the disproportionation reaction is probably similar to that described above for the interaction of ruthenium tetrahydride with olefins (see Scheme 7). The possibility of carrying out the reaction under catalytic conditions indicates the great lability of the coordination sphere of iridium complexes, because the reactions involving ruthenium stop

at the stage in which stable diene complexes are formed, while in the case of iridium the diene ligand is displaced from the coordination sphere by the alkene.

At 35 °C, $IrH_5[P(Pr\text{-}iso)_3]_2$ catalyses the deuterium exchange between the vinyl hydrogen atoms of TBE and the deuterium atoms of deuteriobenzene.[65] The rate of exchange of hydrogen atoms in the *trans*-positions relative to the t-butyl group is approximately an order of magnitude higher than for the *cis*-atoms. These results show that the activation of the vinyl C–H bonds can occur for certain types of olefins at a higher rate than the reaction involving the addition-elimination of the metal hydride at the double bond. The competition between the processes involving oxidative addition to the C–H bond and the formation of a π-complex has also been observed in the reaction of ethylene with the pentamethylcyclopentadienyliridium complex $[Cp^*Ir(PMe_3)]$.[66]

At a higher temperature, $IrH_5[P(Pr\text{-}iso)_3]_2$ catalyses the deuterium exchange between the hydrogen atoms of methane and the deuterium atoms of deuteriobenzene in the presence of two equivalents of TBE. Approximately 13 catalytic cycles take place after 7 days and approximately 40 cycles take place after 53 days at 80 °C. The main reaction product is CH_3D. It has been noted[67] that, in contrast to isotope exchange catalysed by transition metal halides in an acid medium,[5] in the system considered the contribution of multiple exchange is insignificant. In the absence of TBE, the deuterium exchange takes place between deuteriobenzene and the hydride ligands and also the hydrogen atoms of the phosphine ligands. An excess of TBE (> 10 equivalents) prevents the deuterium exchange with methane. In this case, small amounts of ethane, toluene, biphenyl, and propane were detected among the reaction products. It has been suggested that the first three products are formed via the reductive elimination of R–R′ from the intermediate LL′IrRR′ [R = Me, R′ = Ph, L = $P(Pr\text{-}iso)_3$, L′ = $P(Pr\text{-}iso)_2CHMeCH_2$)]. Propane is formed as a result of the degradation of the phosphine ligand.[67]

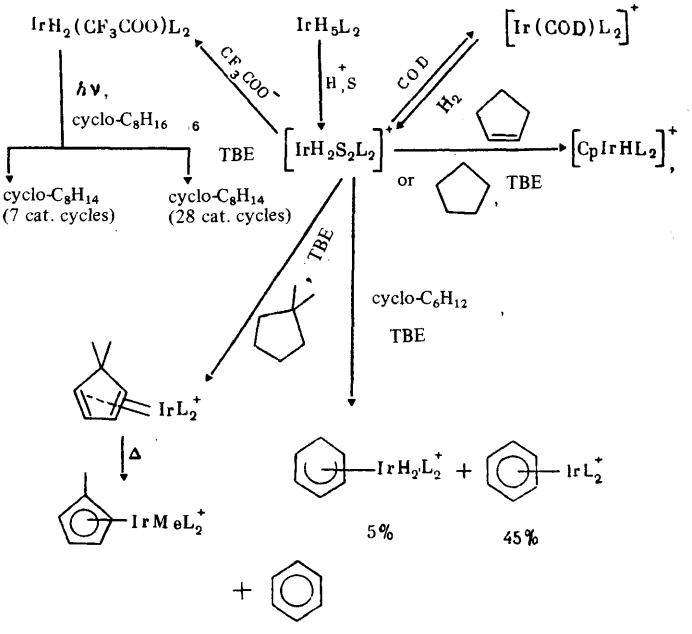
Iridium pentahydride exhibits a higher catalytic activity in catalytic reactions involving the dehydrogenation of cycloalkanes to cycloalkenes than the rhenium or ruthenium PC. Heating of $IrH_5[P(Pr\text{-}iso)_3]_2$ with an excess of TBE in cyclo-octane at 150 °C for 5 days leads to 70 moles of cyclo-octene per mole of the PC, while the best result for ruthenium tetrahydride was 45–55 moles after 10 days and that for rhenium heptahydride was 9 moles. It has been noted that compounds capable of forming 14-electron intermediates on elimination of two molecules of hydrogen, like the iridium PC, are effective catalysts of processes leading to the activation of C–H bonds in hydrocarbons.[57]

In the dehydrogenation of methylcyclohexane under the influence of $IrH_5(PPr^i_3)_2$, the main primary reaction product is methylenecyclohexane, which gradually isomerises under the reaction conditions, affording the thermodynamically more stable 1-methylcyclohexene (see Table). Iridium pentahydrides are capable of dehydrogenating catalytically not only cycloalkanes but also n-alkanes, in contrast to the rhenium PC, which forms stable diene complexes in their reactions with alkanes. The primary product of the reaction of IrH_5L_2 with n-hexane is hex-1-ene (45 °C, 5 min, 0.3 of a catalytic cycle, selectivity 78%), which isomerises rapidly, giving rise to a mixture of *cis*- and *trans*-hex-2-enes (80 °C, 30 min, 9 catalytic cycles, selectivity 75%).

The reactivity of the test systems in relation to different types of C–H bonds has been determined by the method of competing reactions: CH_2 (in cyclohexane) : CH_3 (in methylcyclohexane) : CH_3 (in n-hexane) = 1 : 8 : 60. Despite the fact that the primary C–H bonds are much stronger than the secondary and tertiary bonds, when IrH_5L_2 is used the methyl groups are in fact attacked preferentially probably under the influence of steric factors. Thus the iridium PC catalyse the selective catalytic introduction of functional groups into saturated hydrocarbons. After active and stably operating catalysts have been created, such a process might be useful, for example, for the selective preparation of functional derivatives of higher n-alkanes containing many identical methylene groups but only two methyl groups.[37,63,68]

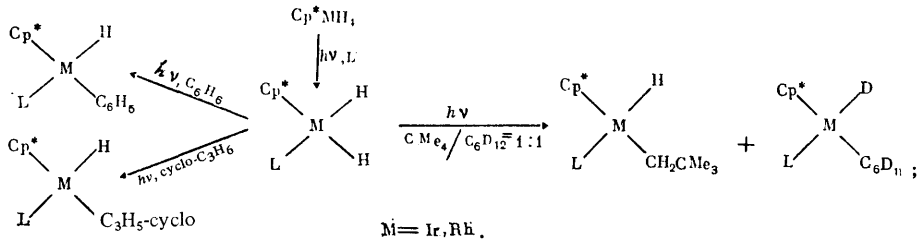
In an acid medium, $IrH_5(PPh_3)_2$ catalyses the ionic hydrogenation of olefins, surpassing in its activity systems such as $PtL_2(CF_3COO)_2$ and $Ru(CF_3COO)_3$ in CF_3COOH.[69,70] On treatment with acids, iridium pentahydrides form the complexes $[IrH_2(Solv)_2L_2]^{x+}$, where Solv is the solvating solvent (acetone, methylene chloride, etc.), an acid anion, H_2 molecule, etc., capable of entering into the C–H bond activation reactions. Like the Cp^*IrH_4 derivatives examined below, these compounds are not polyhydrides but they can be regarded as derivatives of the corresponding PC. In the present review, the properties of these compounds are examined only in terms of the aspects which are necessary for the discussion of the reactivities of the PC. We may note that it was in fact in the study of the interaction of $[IrH_2(Solv)_2L_2]BF_4$ (Solv = acetone, L = PPh_3) with cycloalkanes (cyclopentane, cycloheptane, and cyclooctane) in dichloroethane that the first stable organometallic compounds, with ligands formed as a result of the reactions of a saturated hydrocarbon in the coordination sphere of the complex, were obtained.[71] The results of a study of the reactions of these complexes with hydrocarbons[71–75] are presented in Scheme 9:

Scheme 9



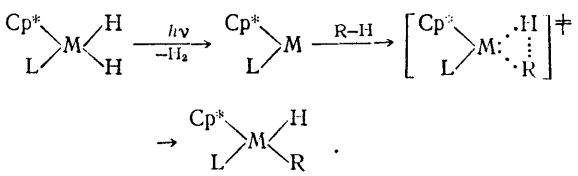
Irradiation of the polyhydride complex Cp^*IrH_4 ($Cp^* = C_5Me_5$) in the presence of trimethylphosphine leads to the dihydride complex $Cp^*Ir(PMe_3)H_2$ capable of interacting photochemically with a wide variety of hydrocarbons—alkanes, cycloalkanes, alkenes, and arenes—to form the products resulting from insertion in a C–H bond (Scheme 10).[76,78]

Scheme 10

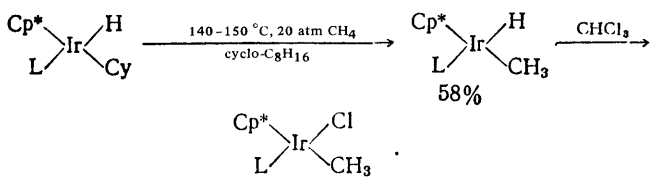


The rhodium analogue $Cp^*Rh(PMe_3)H_2$ also has analogous properties. The product of the interaction of the rhodium complex with cyclopropane has been isolated in the form of the bromo-derivative which has been characterised by X-ray diffraction.[78] The study of the selectivities of the iridium and rhodium complexes examined in relation to different types of C–H bonds in saturated hydrocarbons showed that the insertion takes place predominantly in primary C–H bonds. The secondary C–H bonds are less active and the products of insertion in tertiary C–H bonds have not been observed.

Irradiation of the iridium complex in a mixture of neopentane and cyclohexane-d_{12} leads to the formation of the hydridoneopentyl and deuteridocyclohexyl complexes. These data, together with the study of the selectivity of the insertion reaction, led the authors to the conclusion that the reaction proceeds via a mechanism involving direct insertion in a C–H bond and not via a free radical formation stage:



Alkyl hydride complexes with secondary alkyl groups are thermally less stable than those with primary alkyl radicals, regenerating the reactive intermediate on heating, which leads to the possibility of the thermal activation of alkanes. At an elevated temperature, alkyliridium hydrides are capable of entering into the oxidative addition reaction with methane. The methyliridium complex formed under these conditions has been isolated on a preparative scale in the form of the chloro-derivative:[78]



III. FACTORS INFLUENCING THE REACTIVITY OF TRANSITION METAL POLYHYDRIDE COMPLEXES IN REACTIONS WITH HYDROCARBONS

The data examined shows that the transition metal PC are capable of entering into a wide variety of reactions with hydrocarbons: of forming π-complexes with unsaturated compounds, of hydrogenating, dehydrogenating, and isomerising olefins, of catalysing hydrogen isotope exchange, dimerisation, and polymerisation reactions, of dehydrogenating alkanes and cycloalkanes, etc. Involvement in coupled hydrogenation-dehydrogenation reactions is characteristic of transition metal PC, which makes it possible to carry out such reactions under conditions catalytic with respect to the PC. The formation of π-complexes by metal polyhydrides with unsaturated compounds promotes in many instances the occurrence of further reactions of the latter.

In most cases the reactions of metal PC with hydrocarbons proceed via a stage involving the C–H bonds of the hydrocarbons. For olefins, such reactions lead to the isomerisation or dehydrogenation of the initial compound, which results in an increase of the strength of the bond between the hydrocarbon ligand and the metal ($\eta^2 \rightarrow \eta^3 \rightarrow \eta^4$, etc.). It has been shown recently that a C–H bond in olefins can be dissociated via the oxidative addition mechanism and that the formation of a π-complex is in this case a competing process. The activation of the C–H bonds of arenes or alkanes by metal polyhydrides also takes place via the stage involving the oxidative addition of the hydrocarbon to the metal complex. The relative reactivities of the C–H bonds in alkanes in oxidative addition (primary > secondary > tertiary) form a sequence which is the opposite of that for the free-radical reactions. Whereas in radical processes the dissociation of the weakest tertiary bond is energetically preferable, in oxidative addition reactions, thermodynamic and kinetic factors (the stronger the metal–primary alkyl bond, the smaller steric hindrance to attack on the primary carbon atom) favour the insertion of metal polyhydrides in a primary C–H bond. The characteristics of the oxidative addition of the C–H bonds of hydrocarbons to metal complexes are being at present vigorously investigated.

It is noteworthy that metal polyhydride complexes as such are relatively inactive in reactions with hydrocarbons, because the majority of PC are electron-saturated stable compounds obeying the effective atomic number rule.[7,8] In order to involve these compounds in the reaction, a definite influence is necessary—thermal, photochemical, or chemical (for example, by a hydride ligand acceptor—a proton, a carbonium ion, or an olefin), leading to the loss of some of the hydride or phosphine ligands and the formation of highly reactive electron- and coordination-unsaturated intermediates. The molecular hydrogen or the free phosphine formed in this process can inhibit further reaction. Therefore, substitution of some of the hydride ligands in the PC can also increase the reactivity, as shown in relation to the iridium complex Cp^*IrH_4.[78,79]§

§A series of previously unknown transition metal PC with cyclopentadienyl and alkylcyclopentadienyl ligands $CpMH_mL_n$ (M = Ta, W, Re, or Ir), whose chemical properties have been studied inadequately, have been synthesised in recent years. However, studies by Bergman[78] and Jones[79] have shown that compounds of this type merit very close attention as starting materials for the creation of systems activating C–H bonds.

Compounds formed on protolysis of certain PC are highly reactive in reactions with hydrocarbons. These are complexes in which coordination sites liberated as a result of the loss of hydride ligands are occupied by molecules (acetone, dichloromethane, etc.—solvento-complexes) or anions weakly bound to the central atom.[80]

It is noteworthy that the protolysis of transition metal PC can lead to the formation of compounds with molecular hydrogen as the ligand (hydrogen complexes). For example, on treatment with acids, IrH_5L_2 is converted under certain conditions into $[IrH_2(H_2)_2.L_2]^+$.[81] Transition metal complexes of molecular hydrogen as the ligand were first described in 1980.[82] It has been suggested that compounds of this type are more common than is known at the present time. One of the most active compounds in C—H bond activation reactions, namely ReH_7L_2, is also a complex of molecular hydrogen—$ReH_5(H_2)L_2$.[83] Molecular hydrogen complexes can probably play an important role in reactions leading to the activation of C—H bonds.[83]

The 16-electron intermediates formed on thermal or photochemical treatment exhibit a high reactivity and rapidly enter into intramolecular and intermolecular reactions. However, the formation of 14-electron intermediates is necessary for the catalytic process, which can be achieved, for example, by specially selecting hydrogen acceptors. An effective hydrogen acceptor in reactions with transition metal PC is TBE.[30] This olefin is fairly reactive, has a high heat of hydrogenation, and the 2,2-dimethylbutane formed when it is reduced is readily split off, liberating a coordination site, as a result of which a 14-electron intermediate is produced. The use of TBE made it possible to carry out the dehydrogenation reactions of cyclic and acyclic alkanes, which are catalytic as regards the PC. The dehydrogenation of an alkane to the alkene with liberation of hydrogen is an endothermic process ($\Delta H \simeq 140$ kJ mol^{-1}). Under normal conditions, the equilibrium is almost wholly displaced towards the formation of the alkane. The coupled TBE hydrogenation reaction compensates for the energy expenditure and the dehydrogenation of the alkane becomes thermodynamically feasible. However, for industrial processes involving the synthesis of functional derivatives from alkanes, reagents more readily available than TBE (for example, oxygen), interaction with which would compensate for the energy expended on the dissociation of the C—H bond, are necessary. It has not yet been possible to achieve such processes. Photochemical dehydrogenation, in which the driving force of the process would be ensured by supplying energy from outside in the form of radiation, is attractive from the technological point of view. The possibility of such a process¶ has been demonstrated in relation to the homogeneous catalytic dehydrogenation of cyclooctane by an iridium complex under irradiation.[75]

The nature of the central atom has a marked influence on the reactivity of PC. The PC of 5*d* metals are the most stable and their involvement in reactions with hydrocarbons requires comparatively severe conditions. The PC of 4*d* metals are much more reactive. Since the PC of 3*d* metals have been studied inadequately, it is impossible to compare their properties with those of other PC.

The results of the investigation of the PC-catalysed isotope exchange of deuterium with arenes have shown that compounds of 5*d* metals, having an odd number of valence electrons, are much more reactive than complexes of metals with an even number of valence electrons. The coordination sphere of the former is probably more labile, its lability increasing along the Period from left to right (cf. the reactions of rhenium and iridium PC with alkenes[35,64] and alkanes[38,68]). According to the data available at the present time, Group VIII metal compounds with an odd number of valence electrons (rhodium and iridium) do in fact have the highest activity in reactions including a stage involving oxidative addition with participation of a C—H bond.

Many transition metal PC contain tertiary organic phosphines as ligands, whose electronic and steric properties have a decisive influence on the reactivity of the PC. An increase in the number of phosphine ligands increases the strength of the metal—hydrogen bond, as a result of which more severe conditions are required for the involvement of the PC in the reaction. The role of steric factors also becomes more pronounced under these conditions. For complexes of a specific type (for example, MH_4L_4), the lability of the metal—phosphorus bond increases with increase in the bulk of the ligands.[85] The use of very bulky ligands such as PCy_3 and P(Pr-iso-)$_3$ ($\theta = 160-180°$ [42]) can be regarded as one of the methods for increasing the reactivity of the complexes. Electron-deficient complexes containing such bulky ligands and exhibiting a high reactivity in reactions with small molecules have been obtained.[86] As the electron-donating properties of the ligand become more pronounced, the thermal stability of the PC increases but so also does the reactivity of the intermediates formed both in reactions with hydrocarbons and in intramolecular processes, leading to their deactivation. One of these processes is cyclometallation for the suppression of which one uses ligands with a comparatively low reactivity in this reaction—trimethylphosphine and the pentamethylcyclopentadienyl anion. However, the best result is not always achieved by using these ligands. Thus the highest reactivity in the catalytic dehydrogenation of cycloalkanes has been observed for the iridium complex with triisopropylphosphine and not with trimethylphosphine.[57] The ratio of the rates of the target and side processes apparently depends not only on the electronic but also on the steric properties of the ligand and on the nature of the complex-forming metal. The data available at the present time are insufficient to make a well-founded choice of the metal, stabilising ligands, and the type of complex for the attainment of the best result in the reactions considered.

The properties of the solvent and the purity of the reactants play an important role in the reactions of transition metal PC with hydrocarbons. For example, the dehydrogenation of n-alkanes by rhenium heptahydrides and of cycloalkanes by solvento-complexes of iridium is suppressed by unsaturated compounds or solvents capable of forming stable complexes with the intermediate. Stable complexes of transition metals with saturated hydrocarbons are at present unknown. Unstable complexes, for example, $Cr(CO)_5.(C_6H_{12}$-cyclo), have been obtained.[87] An excess of the alkane or perfluorohydrocarbons are therefore used as solvents for the reactions of PC with alkanes. However, the question of which compounds are capable of inhibiting the reactions of PC with alkanes has not yet been solved. In certain cases, the PC interact with saturated hydrocarbons also in the presence of reactive compounds. Thus iridium complexes solvated by the highly reactive acetone dehydrogenate cycloalkanes in solvents such as chlorinated hydrocarbons, while the complexes ReH_7L_2 are capable of dehydrogenating cycloalkanes even in air. All this gives rise to the hope that

¶ In our country, studies on the introduction of functional groups into alkanes in the presence of transition metal complexes under the influence of radiation are being prosecuted by Shilov and co-workers.[84]

further investigations will create catalytic systems for the activation of alkanes which operate successfully in the usual solvents and which do not impose extremely rigorous conditions on the purity of the reactants.

Thus the results of the study of the interaction of transition metal PC with hydrocarbons have made a definite contribution to the investigation of the homogeneous activation of the C–H bonds of hydrocarbons. However, the creation of industrial methods for the selective synthesis of functional derivatives from alkanes still requires a large amount of fundamental research. It may be hoped that further investigations of the reactions of transition metal PC with hydrocarbons will prove useful for the solution of this problem, which is important from both theoretical and practical points of view.

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