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Hydrogen Transfer from Organic Compounds Catalysed by Transition Metal Complexes

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The review deals with the new rapidly developing field of homogeneous catalysis and coordination chemistry, namely with reactions involving hydrogen transfer from organic compounds to transition metal complexes accompanied by the dissociation of a C-H bond and the formation of a metal-hydrogen bond. Particular attention has been devoted to catalytic reactions in which transition metal compounds serve as catalysts of hydrogen transfer and of the reduction of organic compounds by the C-H bonds of other organic molecules.
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I. INTRODUCTION

The homogeneous hydrogenation of organic compounds catalysed by transition metal complexes is one of the most thoroughly investigated fields of homogeneous coordination catalysis (see the relevant reviews[1-17]). The most important stage in the mechanism of homogeneous hydrogenation reactions is the activation of the H_2 molecule and the dissociation of the H-H bond. Recently we witnessed the growth of interest in extremely similar processes—the activation and dissociation of a C-H bond by transition metal compounds. Reactions of this kind are being increasingly used to transfer hydrogen and (or) an organic residue to different molecules.

This review deals with the part of the problem concerning hydrogen transfer from one organic molecule to another with the aid of transition metal compounds. These reactions have not so far been reviewed and are only mentioned in studies on homogeneous hydrogenation (see, for example, Ugo[13] and Kwiatek[14]).

Hydrogen transfer reactions are of significant interest both from the standpoint of the search for new methods of activating C-H bonds and in the preparative sense, since they lead to new ways of achieving hydrogenation and dehydrogenation reactions under mild conditions. It should also be noted that reactions of this type have attracted attention from the standpoint of the simulation of biochemical hydrogen and electron transfer processes (cf. Zelenin and Khidekel'[18]).

In the present review we consider only those catalytic hydrogen transfer reactions which are accompanied by the dissociation of C-H bonds. We are not concerned with the large field of reactions accompanied by the oxidation of C-H bonds, which results in electron transfer to a molecule of oxygen or another oxidant. Thus we are dealing primarily with processes where one can speak with greater or lesser certainty of hydrogen transfer from one organic molecule to another, catalysed by transition metal compounds.

Catalytic hydrogen transfer from organic compounds has much in common with homogeneous hydrogenation by molecular hydrogen. Like homogeneous hydrogenation, it includes two fundamental stages.

1. Dissociation of the C-H bond and hydrogen transfer to the metal (M):

$$R{-}H + M \rightarrow R{+}MH \quad \text{or} \quad R\!\!<\!\!\begin{matrix}H\\H\end{matrix} + M \rightarrow MH_2 + R\,.$$

2. Hydrogen transfer from the metal to an unsaturated substrate (S):

$$M{-}H + S \rightarrow S{-}H + M \quad \text{or} \quad MH_2 + S \rightarrow SH_2 + M\,.$$

The second stage is evidently the same as the analogous stage in homogeneous hydrogenation. Thus the specific features of hydrogen transfer processes are fundamentally related to the specific features of the first reaction stage. In this connection we shall consider separately the first, most important reaction stage and shall then return to the problem of the catalysis of hydrogen transfer, which includes the simultaneous occurrence of both processes.

II. DISSOCIATION OF THE C-H BOND AND HYDROGEN TRANSFER TO THE TRANSITION METAL

As in the dissociation of the H-H bond, the dissociation of the C-H bond with the aid of transition metal compounds can occur in principle via several different mechanisms (M is the transition metal atom in the complex).

1. With proton transfer:

$$R{-}H + M \longrightarrow R^- + (M{-}H)^+\,.$$

2. With hydride hydrogen transfer:

$$R{-}H + M \longrightarrow R^+ + (M{-}H)^-\,.$$

3. With homolytic dissociation of the C-H bond:

$$R{-}H + 2M \longrightarrow M{-}H + M{-}R\,.$$

4. Via reactions of the oxidative addition type:

$$R{-}H + M \rightarrow M\!\!<\!\!\begin{matrix}H\\R\end{matrix}\,.$$

The nature of the process occurring will of course depend not only on the transition metal compounds but to

no less an extent on the nature of the C–H bond in the reacting organic compounds, the properties of which can vary within extremely wide limits.

Reactions of Type (1)

These involve the acid dissociation of the C–H bond and protonation of the transition metal compounds. They are not of interest for the present problem, since such hydrogen transfer cannot lead to the reduction of the substrate. However, one should note that the analogous process—the dissociation of the C–H bond as a result of electrophilic substitution,

$$R{-}H + M^+ \longrightarrow RM + H^+ , \qquad (1a)$$

is the first stage of a number of important catalytic processes. The metal–carbon σ bond formed in this reaction can undergo further transformations and in the first place can give rise to oxidative dimerisation products[19]. A reaction of this type is, for example, the first stage of the conversion of benzene into biphenyl under the influence of palladium and platinum compounds[20–23]:

$$ArH + Pd^{2+} \rightarrow ArPd^+ + H^+ ,$$
$$2ArPd^+ \rightarrow ArAr + 2Pd^+ .$$

Possibly the oxidative dimerisation of olefins under the influence of palladium salts takes place analogously[24–27]:

$$2CH_2{=}CR_2 + Pd^{2+} \rightarrow R_2C{=}CHCH{=}CR_2 + 2H^+ + Pd^0 ,$$

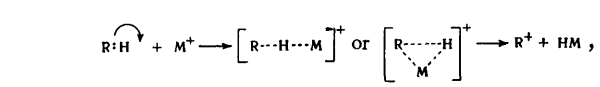
as well as the oxidative coupling of aromatic hydrocarbons to olefins[28]†:

$$ArH + Ar'CH{=}CH_2 + Pd^{2+} \rightarrow Ar'CH{=}CHAr + 2H^+ + Pd .$$

We shall examine in somewhat greater detail reactions of types (2), (3), and (4), which are of greatest interest from the standpoint of hydrogen transfer to unsaturated substrates.

Reaction (2)

This can be regarded as the transfer of the hydride ion H^- from carbon to the metal (the hydride shifts in organic chemistry have been reviewed[29]). Reactions of this type can occur either as a synchronous transfer of hydrogen and an electron pair via a transition state of a linear or π-type,



or as a result of a one-electron transfer followed by the transfer of hydrogen in the form of a proton (or radical):

$$R{:}H + M^+ \rightarrow \begin{matrix}[RH^{+\cdot} + \cdot M] \rightarrow R^+ + HM \\ \searrow [R^+ + H^+ + :M^-] \nearrow\end{matrix} .$$

However, regardless of the nature of these "intimate" mechanisms of the hydride shift, the latter should be favoured by factors such as a positive (not unduly large) charge at the metal atom and the presence of π-ligands, which stabilise the metal–hydrogen bond.

The hydride mobility of the C–H bond in the organic compound which behaves as the donor of the hydride ion is particularly important for the occurrence of such reactions. The ease of the elimination of the hydride ion is paralleled by the stability of the carbonium ion formed as a result—the more stable the carbonium ion under the given conditions the greater the ease with which the hydride ion is split off from the initial C–H bond. The stability of carbonium ions is known to be determined to a considerable degree by the nature of the substituents at the carbonium carbon atom.

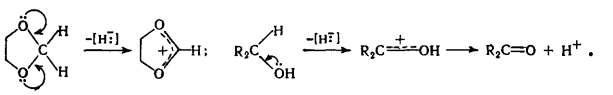
The resulting carbonium ions are stabilised and the hydride shifts via mechanism (2) are thus facilitated by electron-donating substituents of the following kinds.

a. Alkyl groups; the ease of elimination of hydride hydrogen increases in the sequence Me–H < Me_2CH–H < Me_3C–H.

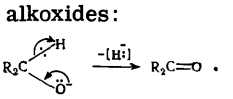
b. Substituents containing multiple bonds (in the first place carbon–carbon bonds) coupled with the carbonium centre and giving rise thereby to the possibility of the delocalisation of the positive charge. The accumulation of such aryl or vinyl substituents at the carbon atom significantly facilitates the elimination of the hydride ion from the latter; an example is provided by triphenylmethane, which is readily converted into the triphenylmethyl cation:

$$Ph_3CH \xrightarrow{-[H^-:]} Ph_3C^+ .$$

c. Substituents containing a free pair of *p* electrons ($-\ddot{N}R_2$, $\ddot{O}R$, $\ddot{S}R$, etc.). Such substituents stabilise the carbonium centre with formation of much more stable conjugate cations:



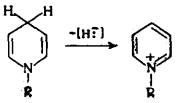
Groups bearing not only an electron pair but also a negative charge facilitate the elimination of the hydride ion even more. In particular this accounts for the high reducing capacity of alkoxides:



d. The hydride ion elimination reaction is significantly facilitated when it results in the formation of molecules with enhanced stability. This factor accounts for the particularly great ease of elimination of the hydride ion from cyclopropene and cycloheptatriene (including cases where the process takes place under the influence of transition metal compounds), leading to the formation of non-benzenoid aromatic cyclopropenylium and tropylium cations:



Another example is provided by the dihydropyridine-nucleotide coenzyme (reduced nicotinamide-adenine dinucleotide NADH), which is an active hydride ion donor (cf. Zelenin and Khidekel'[18]):



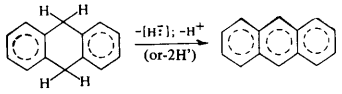
This reaction, which is biochemically important, is facilitated both by the presence of the free electron pair

† However, one cannot rule out the possibility that in the dimerisation of olefins the first stage is the dissociation of the C–H bond via mechanisms (2), (3), or (4). Thus reversible homolytic dissociation of the vinyl C–H bond has been suggested[27] for the oxidative coupling of acrylonitrile under the influence of ruthenium(III) salts:

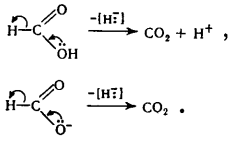
$$2L_nRu + 2CH_2{=}CHCN \rightleftarrows 2L_nRuH(CH{=}CHCN) \rightarrow NCCH{=}CH{-}CH{=}CHCN .$$

of nitrogen and by the formation of the aromatic pyridinium system.

In certain cases the stabilisation of the products of the hydride shift reaction is accompanied by rapid elimination of a proton. The elimination of the hydride ion from dihydroanthracene, which leads to the formation of the aromatic anthracene system, takes place in this way:



The ease of elimination of the hydride ion from formic acid and formates can be explained not only by the influence of the free electron pair of the adjacent oxygen atom but also by the considerable stability of the resulting carbon dioxide molecule:



Reaction (3)

We shall now turn to the mechanism of reactions (3), which involves the homolytic dissociation of the C–H bond. The energy of the homolytic dissociation of the C–H bond (R–H → R· + H·) is 103 ± 2 kcal mole^{-1} (at 298°K) for the methane molecule and has similar values for other saturated hydrocarbons and for benzene. It differs very little from the dissociation energy of the H–H bond, which is 104.2 kcal mole^{-1} (at 298°K)‡. Thus comparison of reaction (3) with the analogous homolytic dissociation reaction of the H_2 molecule,

$$H_2 + 2M\cdot \rightarrow 2MH \ ,$$

shows that the differences between the free energies of these two reactions must be determined primarily by the differences between the stabilities of the metal–carbon and metal–hydrogen bonds.

Reaction (4)

The same considerations apply also to the occurrence of the oxidative addition reactions of type (4). As in the analogous reaction of H_2,[30] the energy of this reaction can be deduced from the following qualitative considerations. If in the course of the dissociation of the C–H bond the metal is oxidised as a result of oxidative addition via mechanism (4) and passes from the square d^8 configuration to the octahedral d^3 configuration [d^6 configuration (Ed. of Translation)], the energy of the reaction will be approximately described by the equation

$$\Delta E = E_{M\text{-}H} + E_{M\text{-}C} - (E_{C\text{-}H} + P) \ ,$$

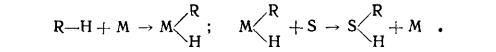
where $E_{M\text{-}H}$ is the energy of the hydrogen–metal bond, $E_{M\text{-}C}$ the energy of the carbon–metal bond, $E_{C\text{-}H}$ the dissociation energy of the C–H bond, and P the promotion energy of electron transfer in the ligand field to a higher orbital (for example from the $5d_{z^2}$ orbital to the $6p_z$ orbital). As stated above, $E_{C\text{-}H}$ changes within fairly narrow limits and ΔE will thus depend primarily on P and $E_{M\text{-}C}$. P will decrease (and hence ΔE will increase) following the introduction of electron-donating ligands (promoting the transfer of non-bonding electrons to higher orbitals) and on passing to metals of the lower Periods. On the other hand, electron-accepting ligands should hinder the reaction. One should of course note that, for hydrogen transfer catalysts, P must not be very small either, since otherwise the hydride formed will be unduly stable and will be unable to give up its hydrogen to the substrate.

It is as yet not completely clear how the $E_{M\text{-}C}$ depend on different factors. However, one should note that previous ideas concerning the low thermodynamic stability of the transition metal–carbon bond proved to be incorrect and that the role of the ligands in the stabilisation of these bonds is related in the first place to kinetic factors[31,32]. Electron-donating, strongly nucleophilic ligands should probably exhibit a powerful stabilising effect[31]. The available thermodynamic data are very scanty, but they do show that the transition metal–aryl bond is much more stable than the transition metal–alkyl bond. Thus the energy of the Pt–Ph bond in $(Et_3P)_2PtPh_2$ is approximately 250 kJ mole^{-1},[33] while the Pt–Me bond in $CpPtMe_3$ has an energy of only about 164 kJ mole^{-1}.[34] Similarly the energies of the Ti–Ph and Ti–Me bonds in Cp_2TiPh_2 and Cp_2TiMe_2 are respectively 350 and 250 kJ mole^{-1}.[35]

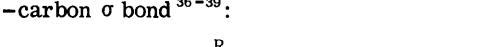
Thus, other conditions being equal, the reactions involving the oxidative addition of the C–H bond to a transition metal atom should occur much more readily for aromatic compounds than for aliphatic compounds. Indeed the experimental data quoted below confirm this conclusion.

Furthermore, in oxidative addition reactions occurring with the formation of a metal–carbon bond the entropy component will presumably make a large contribution to $E_{M\text{-}C}$ (in contrast to the M–H bond). For this reason, such reactions should be favoured by a low coordination number of the initial complex (which is frequently associated also with a low oxidation state of the metal) and a small size of the ligands present and of the organic group R introduced.

It is noteworthy that reactions of type (3) and (4) give rise to the possibility not only of hydrogen transfer but also of the transfer of various organic groups R to substrates S with the aid of transition metal complexes, for example:



It has been shown recently that the dissociation of C–C bonds can sometimes take place analogously to the dissociation of C–H bonds with formation of products containing a metal–carbon σ bond[36–39]:



In certain cases these reactions, in which the metal is inserted into the C–C bond, constitute intermediate stages in skeletal rearrangements[40,41]. However, examination of these interesting reactions is outside the scope of the present review.

The data available at present by no means make it always possible to decide which of the mechanisms (1)–(4)

‡ In those cases where the radical R· is stabilised by conjugation, the dissociation energy is appreciably lower: 77 kcal mole^{-1} for the allyl–H bond and 78 kcal mole^{-1} for the benzyl–H bond. This accounts for the greater ease of dissociation of these bonds.

governs the activation of the C–H bond; usually this has to be inferred solely on the basis of the structure of the resulting transition metal hydride complexes.

Fairly extensive experimental data on the use of various organic hydrogen donors for the synthesis of hydride complexes have accumulated in the coordination chemistry of transition metals (see reviews [42-44]). We shall examine these experimental results from the standpoint of the ideas formulated above concerning the dissociation of C–H bonds. We shall consider first reactions where a hydride mechanism of type (2) can be postulated.

The formation of ruthenium, osmium, rhodium, and iridium hydride complexes using alcohols as hydrogen donors has been most widely investigated. This reaction is promoted by alkaline agents, i.e. the C–H bond in alcohols is activated as a result of the formation of the alkoxide ion and in the course of the reaction the alcohols themselves are converted into aldehydes and ketones; reactions of this type probably take place with a hydride ion shift via mechanism (2).

Thus, when the complex $PtCl_2(PEt_3)_2$ is refluxed in an ethanol solution of potassium hydroxide, the hydride complex of platinum and acetaldehyde are obtained [45,46]:

$$PtCl_2(PEt_3)_2 + KOH + EtOH \rightarrow PtHCl(PEt_3)_2 + Me-C\overset{O}{\underset{H}{<}} + KCl + H_2O ,$$

$$Ru_2Cl_5(PEt_2Ph)_6Cl + 2EtOH + 2KOH \rightarrow 2RuHCl(CO)(PEt_2Ph)_3 + 2CH_4 + 2KCl + 2H_2O .$$

The rhodium hydride complex $HRh(PPh_3)_4$ is formed when $(Ph_3P)_3RhCl$ interacts with triphenylphosphine in n-propyl alcohol in the presence of alkaline agents [47]. In certain cases hydride complexes can be obtained from alcohols also in the absence of alkalis. Thus, when $(Ph_3P)_3IrCl$ reacts with ethanol (in the absence of a base), the hydride complex $(Ph_3P)_3IrH_2Cl$ and acetaldehyde are obtained [48]. The question of which hydrogen atom in the alcohol passes to the metal was elucidated for the formation of iridium hydride complexes in the presence of deuteriated alcohols [49]:

$$K_2IrCl_6 + Ph_3P \begin{cases} + CH_3CH_2OH + H_2O \rightarrow IrHCl_2(Ph_3P)_3 , & (1) \\ + CH_3CH_2OH + D_2O \rightarrow IrHCl_2(Ph_3P)_3 , & (2) \\ + CH_3CH_2OD + D_2O \rightarrow IrHCl_2(Ph_3P)_3 , & (3) \\ + CH_3CD_2OH + H_2O \rightarrow IrDCl_2(Ph_3P)_3 . & (4) \end{cases}$$

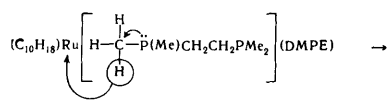
The mechanism shows that the interaction of the iridium salt and triphenylphosphine with both aqueous ethanol and with EtOD in the presence of D_2O [reactions (1)–(3)] leads to the formation of the iridium hydride complex $IrHCl_2(PPh_3)_3$, i.e. neither water nor the hydrogen atom of the alcoholic hydroxy-group behave as hydrogen donors in this reaction. On the other hand, the use of an alcohol with deuterium atoms at the 1-C atom [reaction (4)] leads to the formation of the deuteriated complex $IrDCl_2(Ph_3P)_3$. The experimental data show convincingly that the formation of hydride complexes from alcohols takes place as a result of the elimination of a hydrogen atom from the 1-C carbon atom of the alcohol, which exhibits the greatest hydride mobility. The fact that the addition of a base facilitates the removal of hydrogen from the alcohol as a result of the enhancement of the effect of p, σ conjugation in alkoxides becomes understandable from the same point of view.

One should note that alcohols can behave not only as hydrogen donors but also simultaneously as donors of the carbonyl group. For example, when triphenylphosphine is refluxed with $(NH_4)_2OsCl_6$ in the monomethyl ether of diethylene glycol, the mixed hydridocarbonyl complex $HOsCl(CO)(Ph_3P)_3$ is obtained [50]. When [^{14}C]ethylene glycol was used, it was shown that the glycol in fact behaves as the carbonylating agent in this reaction.

The formation of iridium, ruthenium, rhodium, and osmium hydride complexes in the reaction with alcohols has been described also in a number of other studies [51-58].

When transition metal complexes react with alcohols, it is not always possible to isolate and identify the hydride complex, although its formation is indirectly confirmed by the identification of the alcohol dehydrogenation products. For example, when allyl alcohol was refluxed with $RuCl_3 \cdot 3H_2O$, propene, acrolein, and propionaldehyde were found in the reaction products, although the hydride complex was not identified [59]. The study of the effect of phosphines on the capacity of rhodium complexes to eliminate hydride hydrogen from alcohols showed that the more basic the phosphine the greater the ease of this reaction [60].

It is noteworthy that the ligands coordinated to the metal atom can themselves behave as hydride donors in the formation of transition metal hydride complexes. In this case the hydride complex is formed as a result of hydrogen transfer from the organic component of the ligand molecule to the metal atom with dissociation of the C–H bond. Thus in the ruthenium complex $(C_{10}H_{18})Ru(DMPE)$, where DMPE = $Me_2P(CH_2)_2PMe_2$, hydrogen transfer from the methyl group of the phosphine ligand leads to the formation of a ruthenium hydride complex [61]:



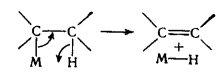
$$\rightarrow C_{10}H_{18} + RuH[CH_2{=}P(Me)CH_2CH_2PMe_2](DMPE) .$$

According to the authors' data, the hydride complex is in tautomeric equilibrium with a zerovalent ruthenium complex:

$$RuH\left[\begin{matrix}H\\H\end{matrix}\!\!>C{=}P(Me)CH_2CH_2P(Me_2)\right](DMPE) \rightleftarrows Ru(DMPE)_2 .$$

The dissociation of the C–H bond of the methyl group is observed also for the rhodium complex coordinated to the $(o\text{-tolyl})_3P$ ligand [62].

Reactions involving the intramolecular transfer of hydride hydrogen from the β-position of σ-alkyl ligands, leading to the formation of hydride complexes, are very common in the chemistry of organic derivatives of transition metals (they have been reviewed [63]):



Reactions of this type take place readily when organolithium, organomagnesium, and organoaluminium compounds act on salts and complexes of transition metals. As an example of reactions involving individual σ-alkyl derivatives, we may quote the reaction of the platinum complex $PtCl(Et)(PEt_3)_2$, which eliminates ethylene on heating and forms a hydride complex via the mechanism [64,65]

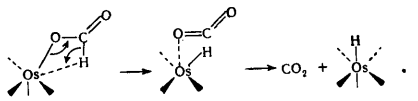
$$(Et_3P)_2ClPt-CH_2CH_3 \rightarrow (Et_3P)_2ClPt \leftarrow \begin{matrix}CH_2\\\|\\CH_2\end{matrix} \rightarrow (Et_3P)_2ClPt-H + CH_2{=}CH_2 .$$

That β-elimination does in fact take place has been demonstrated, in particular for the n-butylcopper complex [66]:

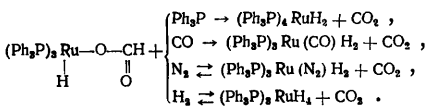
$$(Bu_3P)CuCH_2CD_2CH_2CH_3 \rightarrow (Bu_3P)CuD + CH_2{=}CDCH_2CH_3 .$$

Coordinated formate ligands can also readily give up hydrogen with formation of hydride complexes. For example, the osmium formate complex $Os(OOCH)_2(CO)_2 \cdot (PPh_3)_2$ is converted on refluxing in benzene into the

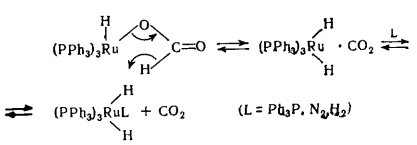
hydride $H_2Os(CO)_2(Ph_3P)_2$ with evolution of carbon dioxide via the mechanism [67]



The migration of hydrogen from carbon to the transition metal was observed very easily in the ruthenium formate complex $(Ph_3P)_3Ru(H)OOCH$. [68-70] This complex eliminates carbon dioxide unusually readily under the influence of various agents with formation of a hydride complex:

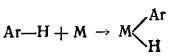


These unusual properties of the ruthenium formate complex can be accounted for by the exceptional ease of the migration of the hydride hydrogen of the formate group to the metal, accompanied by the formation of an unstable ruthenium hydride complex with carbon dioxide via the mechanism

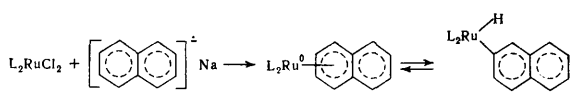


All the examples described above concerned reactions leading to the formation of a metal–hydrogen bond via mechanism (2), i.e. with formal transfer of a hydride ion from the C–H bond. Reactions involving the dissociation of the C–H bond via mechanisms (3) and (4), accompanied by the simultaneous formation of metal–carbon and metal–hydrogen bonds, constitute another group.

In contrast to hydride addition reactions, processes of this type are most typical for the dissociation of aromatic C–H bonds and the majority of examples known at present concern reactions of the type

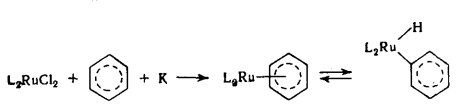


These reactions, which occur under the influence of low-valence transition metal derivatives, are frequently accompanied by the intermediate formation of π-arene complexes and their isomerisation to σ-aryl derivatives. According to the data of Chatt and Davidson [71], dichlorodi-(1,2-bisdimethylphosphinoethane)ruthenium is converted on treatment with sodionaphthalene in tetrahydrofuran (THF) into a π-arene complex of ruthenium which is in equilibrium with the σ-naphthylruthenium hydride complex:

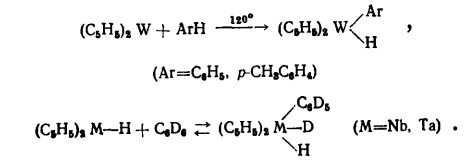


$(L = Me_2PCH_2CH_2PMe_2)$

The radical-anions of other aromatic hydrocarbons react similarly. In the case of benzene one can employ a mixture of benzene and metallic potassium instead of the radical-anions:



Similar reactions with aromatic radical-anions have been observed for cyclopentadienyl complexes of tungsten, tantalum, platinum, and other transition metals [72-75], for example:



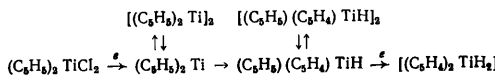
$(Ar = C_6H_5,\ p\text{-}CH_3C_6H_4)$

Titanium, vanadium, and chromium complexes give rise to reactions of the same type, with dissociation of the aromatic C–H bond [76,77].

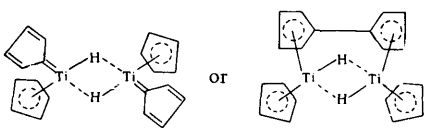
It has been shown by X-ray diffraction [78] that the product of the reaction of naphthalene with the 1,2-bisdimethylphosphinoethane complex of ruthenium is indeed a σ-naphthyl derivative of ruthenium.

It is noteworthy that hydrogen isotope exchange in benzene, catalysed by platinum salts, proceeds via an analogous mechanism with preliminary dissociation of the C–H bond [79,80].

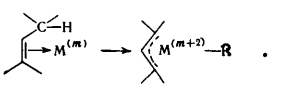
Not only aromatic hydrocarbons of the benzene type but also cyclopentadienyl ligands can serve as a source of hydrogen for the formation of the metal–hydrogen bond. Thus, in the reduction of titanocene derivatives by sodium, magnesium, sodionaphthalene, and other reducing agents, extremely ready migration of hydrogen from the ligand to the metal takes place [81-84]:



These reactions are also accompanied by the π, σ rearrangement of the ligand. Thus the following structural formulae have been proposed for the hydride form of titanocene $[(C_5H_5)(C_5H_4)TiH]_2$:

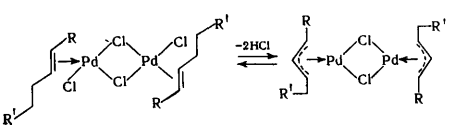


Finally the formation of hydride–allyl complexes from olefinic π complexes can be included among reactions of the type occurring with homolytic dissociation of the C–H bond via a mechanism close to oxidative addition:



(m = degree of oxidation)

Thus ruthenium hydride–allyl complexes $HRu(CO)_9(C_{12}H_{15})$, $HRu_3(CO)_9(C_{12}H_{17})$, and $HRu_3(CO)(C_{24}H_{33})$ are formed when cyclododecatriene reacts with ruthenium carbonyl $Ru_3(CO)_{12}$. [85] In the formation of π-allyl complexes of palladium, allyl hydrogen is also split off with intermediate formation of the Pd–H bond [86-91]:



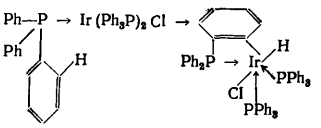
Dienes are formed in the decomposition of allyl complexes at an elevated temperature; a reaction of this

kind in the presence of oxidising agents (for example $CuCl_2$) can be achieved catalytically[92,93]:

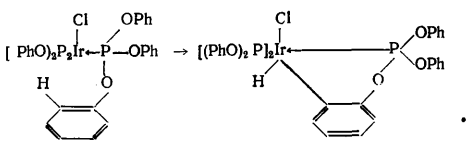
$$ROOCCH_2CH{=}CHCH_2COOR + 2CuCl_2 \xrightarrow{PdCl_2} \rightarrow ROOCCH{=}CHCH{=}CHCOOR + 2CuCl + 2HCl\ .$$

Another group of reactions occurring with insertion of the metal in an aromatic C–H bond comprises intramolecular hydrogen transfer from the *ortho*-position in the aromatic rings of phenylphosphine and phenyl phosphite ligands. Thus, on heating a solution of $(Ph_3P)_3IrCl$ in benzene, a hydride complex is formed[94]. The migration of the hydrogen atom from the phenyl ring was demonstrated using a fully deuteriated initial complex. On heating of $[P(C_6D_5)_3]_3IrCl$ in benzene, the product is a complex whose infrared spectrum indicates the presence of the Ir–D bond and the absence of the Ir–H bond.

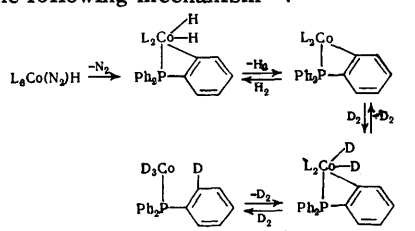
Evidently this reaction is a type of oxidative addition [reaction (4)]:



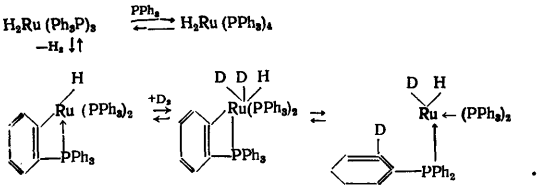
The interaction of IrCl(1,5-cyclo-octadiene) with triphenyl phosphite in acetone also leads to the formation of a hydride complex as a result of the migration of the *ortho*-hydrogen from the ligand[95]:



In many instances reactions of this kind are reversible and lead to the exchange of the *ortho*-hydrogen atoms of the benzene rings with the hydride hydrogen linked to the metal. For example, the exchange of hydrogen for deuterium in the *ortho*-positions of the benzene ring of the triphenylphosphine ligands in the cobalt complex proceeds via the following mechanism[96]:

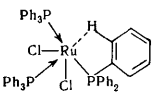


The deuterium exchange reactions take place similarly with the phosphine complexes of ruthenium[97–99]. For example, when the ruthenium complex $H_2Ru(Ph_3P)_4$ was allowed to react with D_2 in benzene and this was followed by the decomposition of the resulting complex with hydrogen peroxide, deuterium was identified in the benzene ring[99]. On the basis of these results, the authors concluded that in the course of the reaction there is a rapid reversible interaction of the ruthenium atom with the *o*-C–H bond:



A similar hydrogen transfer to the ruthenium atom with formation of a hydride complex occurs also in the case of the triphenyl phosphite ligand[100].

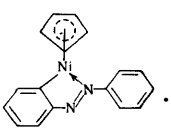
It is noteworthy that the ease of migration of hydrogen from the *ortho*-position of the benzene ring is probably related not only to the nature of the metal but also to the structure of the complex. X-Ray diffraction analysis of the triphenylphosphine complex of ruthenium $(Ph_3P)_3RuCl_2$ showed that the hydrogen atom in the *ortho*-position in the benzene ring is at a very short distance from the ruthenium atom[101]:



This accounts for the ease of migration of the hydrogen atom to ruthenium in such complexes.

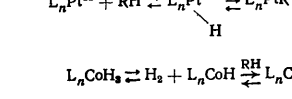
The formation of hydride complexes as a result of hydrogen transfer from the phenyl group and the coordinated phosphine ligand was also observed for cobalt and iron complexes. Thus the interaction of $HCo(N_2)[P(C_6D_5)_3]_3$ with bis-(1,2-diphenylphosphinoethane) results in the formation of a mixture of $HCo(DPPE)_2$ and $DCo(DPPE)_2$, where DPPE is diphenylphosphinoethane[102], while irradiation of $Fe(C_2H_4)(DPPE)_2$ in benzene solution leads to the formation of ethylene and the hydride complex $HFe(o\text{-}C_6H_4)(PC_6H_5)CH_2CH_2P(C_6H_5)_2(DPPE)$, the phosphine ligand behaving as the source of hydrogen in both instances[103,104]. A similar reaction has been observed also for ruthenium complexes with triphenylphosphine[105,106].

It is noteworthy that the cleavage of the *o*-C–H bonds of the benzene ring in the ligands proceeds so readily that in many cases they yield products with a stable transition metal–carbon bond. Certain transition metal complexes of azobenzene[107,108] and Schiff bases[109,110] have this structure, for example:



In the course of formation of such complexes the metal is apparently inserted in the *o*-C–H bond with subsequent elimination of hydrogen (as a proton or a hydrogen atom).

The examples examined above concern the insertion of the metal in an aromatic C–H bond. However, recent findings show that transition metal compounds are capable of being inserted also in an aliphatic C–H bond in saturated hydrocarbons. Shilov, Shteinman, and coworkers[111–113] and then also other workers[114,115] observed deuterium exchange involving methane, ethane, and other saturated hydrocarbons under the influence of platinum and cobalt. The results can be accounted for by reversible oxidative addition with dissociation of an aliphatic C–H bond and the intermediate formation of hydride–alkyl derivatives:



Analysis of kinetic data for deuterium exchange with water in aqueous acetic acid solutions of platinum(II) salts showed that the activity of the platinum compounds decreases in the sequence $PtX_2 > PtX_3^- > PtX_4^{2-}$ and in the

following sequence of the ligands X: Cl > Br > I. However, this reaction can occur also without the formation of a hydride via the elimination of a proton and the formation of an alkylplatinum derivative[116]:

$$PtCl_4^{2-} + RH \rightleftarrows PtCl_3R^{2-} + H^+ + Cl^- .$$

Thus fairly numerous organic substrates can behave as hydrogen donors in reactions with transition metal complexes leading to hydride complexes. However, the formation of hydride complexes alone is insufficient for the reduction of organic substrates. The hydrogen atom in the hydride complex must be sufficiently labile for the complex to be capable of participating in hydrogen transfer reactions. Moreover, as in homogeneous hydrogenation, the resulting hydride complex must be able to coordinate and activate the unsaturated substrate.

III. CATALYTIC HYDROGEN TRANSFER

The range of catalytic reactions involving hydrogen transfer from organic compounds to unsaturated substrates (olefins, aldehydes, ketones, etc.) known at present is much narrower than that of hydrogen reduction reactions. However, the number of known reactions of this kind is rapidly increasing and some of them have already assumed preparative importance.

1. Reduction by Alcohols, Alkoxides, and Ethers

Alcohols and alkoxides are most widely used as hydrogen donors. One of the first studies in this field was carried out by Italian workers[47,117], who found that unsaturated compounds can be reduced in the presence of rhodium, complexes using benzyl alcohol as the hydrogen donor. In the presence of rhodium complexes of the type $L_3Rh(CO)H$, where L = Et_3P, Bu_3P, Ph_2MeP, etc., the reduction of oct-1-ene by benzyl alcohol in the presence of potassium benzyloxide (with formation of PhCOOK) was observed. However, this reaction was fairly slow even at an elevated temperature (130°C), the maximum yield of the hydrogenation product (octane) amounting to only 35% after 4 h (Table 1).

Table 1. Catalytic activities of the phosphine complexes of rhodium in hydrogen transfer from benzyl alcohol to oct-1-ene (0.06 mole of benzyl alcohol, 0.035 mole of oct-1-ene, 0.006 mole of potassium benzyloxide, and 0.0003 mole of the catalyst, 130°C, time 4 h).

Catalyst	Conversion of benzyloxide into benzoate, %	Conversion of oct-1-ene into octane, %
$HRh(CO)(PEt_3)_3$	50	35
$HRh(CO)(PBu_3)_3$	25	6
$HRh(CO)(PEt_2Ph)_3$	15	3
$HRh(CO)(PMePh_2)_3$	2	traces
$HRh(CO)(PEt_3)_3$	4	6

The reduction of unsaturated compounds with hydrogen transfer from alcohols can occur also in the presence of certain transition metal salts[118]. Thus rhodium and ruthenium chlorides catalyse at 100°C the reduction by ethanol of hex-3-yne to hex-3-ene, of cyclopentadiene to cyclopentene, and of 5-vinylbicyclo[2,2,1]hept-2-ene to 2-vinylbicyclo[2,2,1]heptane, the ruthenium salt proving to be more active than the rhodium salt.

The authors of this investigation suggest that in the course of the reduction process an intermediate complex with an Rh–H bond is formed and is responsible for the reduction. The study[119] where it was shown that rhodium salts catalyse the dehydrogenation of 2-propanol is interesting in this connection. It is suggested that the dehydrogenation of the alcohol proceeds via an intermediate hydride according to the mechanism

$$Me_2CHOH + [Rh^{III} - Cl] \rightleftarrows Me_2CO + [Rh^{III} - H] + HCl ,$$

$$[Rh^{III}H] + HCl \rightarrow [Rh^{III}Cl] + H_2 .$$

The alcohol dehydrogenation reaction has also been described in the presence of cobalt carbonyl as a process which is the converse of the hydrogenation of aldehydes in the hydroformylation reaction[120–123].

There are literature data concerning the transfer of hydrogen from alcohols to unsaturated compounds under the influence of transition metal acetylacetonates (for example, nickel acetylacetonate)[124]. The reaction proceeds under fairly severe conditions at a temperature of 200–220°C. Methyl linoleate and methyl octadecadienoate, which have conjugated double bonds, were reduced under these conditions with the aid of different alcohols (isopropyl, n-propyl, ethyl, s-butyl, n-butyl, s-pentyl, and n-tentyl). In the hydrogenation of methyl linoleate the reaction products contain an appreciable proportion of *trans*-octadecenoate. The authors did not observe an appreciable difference between the rates of hydrogenation of *cis*-octadecenoate and its *trans*-isomer, but, owing to steric hindrance, *trans,trans*-octadecadienoate is reduced much more slowly than the *cis,trans*-isomer.

Other examples of hydrogen transfer from alcohols to the unsaturated soya-bean oil esters, to linoleic and linolenic acid esters, and to other polyenes have also been described[125,126]. The reactions proceed at 100°C and lead mainly to the formation of mono-olefins. Complexes of the type $Cl_2M(PPh_3)_2$, where M = Pt or Pd, in combination with $SnCl_2$ behave as catalysts of these hydrogen transfer reactions.

The double bonds activated by functional groups can be selectively reduced by alcohols. Thus a study has been made of the catalytic hydrogen transfer from 2-propanol to $\alpha\beta$-unsaturated ketones in the presence of iridium compounds[127,128]. The reduction of the double bond is catalysed by the complex $H[IrCl_4(Me_2SO)_2].2Me_2SO$, which on refluxing forms the hydride $HIrCl_2(Me_2SO)_3$.

The C=C double bond in benzylideneacetophenone and in other similar compounds has been reduced with the aid of the same catalytic system:

$$PhCOCH{=}CHPh \rightarrow PhCOCH_2CH_2Ph ,$$

$$Me_3CCOCH{=}CHPh \rightarrow Me_3CCOCH_2CH_2Ph ,$$

$$PhCO(CH{=}CH)_2Ph \rightarrow PhCO(CH_2CH_2)_2Ph .$$

The reduction of $\alpha\beta$-unsaturated ketones to saturated ketones by benzyl alcohol is catalysed effectively by the ruthenium complex $(Ph_3P)_3RuCl_2$.[129] For example, when 1-phenylbut-1-en-3-one is heated in benzyl alcohol in the presence of a catalytic amount of the ruthenium complex at 200°C, the product is 92% of 1-phenylbutan-3-one. Together with benzyl alcohol, other alcohols were also employed as hydrogen donors in this reaction: $PhCH_2CH_2OH$, $PhCH(OH)CH_3$, and $CH_3(CH_2)_6CH_2OH$ (Table 2). The same investigators showed that the aromatic aldehydes α-$C_{10}H_7CHO$, β-$C_{10}H_7CHO$, and others can also function as hydrogen donors[130] (Table 3).

Reports have been published recently concerning the reduction of the double bond in cyclo-olefins with the aid of dihydric phenols[131,132]§. Thus when cyclo-octa-1,3-diene and cyclo-octa-1,5-diene react with hydroquinone in dioxane in the presence of triphenylphosphine complexes of iron(II), cobalt(II), and nickel(II) at 200°C the cyclo-octadienes are reduced catalytically to cyclo-octene and cyclo-octane. According to the authors, these reactions take place as a result of an intramolecular hydrogen transfer, since the pressure in the reaction vessel remained unchanged in the course of the reactions, i.e. the evolution of molecular hydrogen was not observed. Apart from cyclo-octene and cyclo-octane, isomerisation products were detected at the end of the reaction: cyclo-octa-1,4-diene and cyclo-octa-1,3-diene. The efficiency of various compounds as reducing agents under the conditions investigated decreases in the sequence pyrogallol > catechol > hydroquinone > n-dodecanethiol > 1-octanol > cyclohexene > 2-octanol > 1-dodecanol > n-dodecylamine.

Table 2. Hydrogen transfer from alcohols to $\alpha\beta$-unsaturated carbonyl compounds in the presence of $(Ph_3P)_3RuCl_2$ (Sasson and Blum[129]).

Hydrogen donor (weight, g)	Hydrogen acceptor (weight, g)	Reaction temp., °C	Yield of saturated carbonyl compound after 4 h, %
$PhCH_2OH$ (1.08)	PhCH = CHCOMe (1.46)	200	94
$PhCH_2CH_2OH$ (1.22)	PhCH = CHCOMe (1.46)	200	94
PhCH(OH)Me (1.22)	PhCH = CHCOMe (1.46)	200	93
$Me(CH_2)_6CH_2OH$ (1.30)	PhCH = CHCOMe (1.46)	190	82
$PhCH_2OH$ (1.08)	PhCH = CHCOPh (2.08)	200	98
$PhCH_2OH$ (1.08)	$CH_2CMe_2CH_2CMe = CHCO$ (1.38)	200	41
$PhCH_2OH$ (1.08)	PhCH = $CHCOCMe_3$ (1.88)	200	89
$PhCH_2OH$ (1.08)	PhCH = CMeCHO (1.46)	200	61
$PhCH_2OH$ (1.08)	PhCH = CHCOOEt (1.76)	200	53

The reduction of the multiple bond in unsaturated compounds with the aid of dihydroxybenzene derivatives can occur also in aqueous solutions[133], for example in aqueous alkaline solutions of vanadium(III) in the presence of a number of di- and trihydroxy-derivatives of benzene and naphthalene (catechol, pyrogallol, and 2,3-dihydroxynaphthalene). Acetylene is reduced to ethylene at room temperature.

Together with alcohols, cyclic ethers can also be used as hydrogen donors for the reduction of unsaturated compounds. For example, when tetrahydrofuran is employed as the solvent in the presence of catalysts of the type $Cl_2M(PPh_3)_2$, where M = Ni, Pd, or Pt, the olefins are reduced[125,126,134]. It is interesting that the nickel catalyst is active also in a benzene medium, but it is not clear what the hydrogen source is in this case.

Japanese workers[135] described the reduction of olefins with the aid of dioxane in the presence of a rhodium catalyst. When cyclopentene is heated at 180°C in dioxane solution in the presence of $(Ph_3P)_3RhCl$, 0.43 mole of dioxene and 0.42 mole of cyclopentane are formed. After the reaction the individual complex $(Ph_3P)_2RhCl(C_4H_8O_2)$, formed as a result of the displacement of one phosphine group from the initial complex by dioxane, was isolated.

§ These reactions proceed with the dissociation of O–H bonds only. However, the similarity of the catalysts and conditions employed make it useful to examine them in this section.

By analogy with hydrogenation by molecular hydrogen and the isomerisation of olefins, the authors suggest the following reaction mechanism:

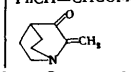
$$RhCl(PPh_3)_2(C_4H_8O_2) \rightleftarrows RhClH(C_4H_7O_2)(PPh_3)_2 \rightleftarrows RhClH_2(PPh_3)_2(C_4H_6O_2) \xrightleftharpoons{+olefin}$$

$$\rightleftarrows RhClH_2(PPh_3)_2(\text{olefin I}) \rightleftarrows RhClH(\text{alkyl})(PPh_3)_2 \xrightleftharpoons{+dioxane}$$

$$\rightleftarrows RhCl(PPh_3)_2(C_4H_8O_2) + \text{paraffin}$$

There is convincing evidence showing that rhodium monohydride complexes are formed via the oxidative addition of dioxane with dissociation of the C–H bond (kinetic data, isotope effect data, etc.). With the aid of organic hydrogen donors, primarily alcohols, it is possible to reduce not only carbon–carbon multiple bonds in unsaturated compounds but also functional groups such as the carbonyl and nitro-groups.

Table 3. Hydrogen transfer to $\alpha\beta$-unsaturated quitones in the presence of ruthenium, rhodium, and iridium complexes[130] (donor : acceptor : catalyst = 1 : [?] : 5×10^{-2} for Nos. 1–8 and 1 : 20 : 5×10^{-3} for Nos. 9–16).

No.	Hydrogen donor	Hydrogen acceptor	Catalyst*	Temp., °C	Reaction time, h	Yield of saturated ketone, %
1	α-$C_{10}H_7CHO$	PhCH=CHCOPh	1	285	2,5	60
2	α-$C_{10}H_7CHO$	PhCH=CHCOPh	2	285	2,5	21
3	α-$C_{10}H_7CHO$	PhCH=CHCOPh	3	285	2.5	34
4	α-$C_{10}H_7CHO$	PhCH=CHCOC(Me_3)	1	285	2.5	60
5	β-$C_{10}H_7CHO$	PhCH=CHCOPh	1	285	2.5	28
6	p-$CH_3C_6H_4CHO$	PhCH=CHCOPh	1	200	14	50
7	p-$CH_3C_6H_4CHO$	p-$MeOC_6H_4CH$=CHCOPh	1	200	14	68
8	p-ClC_6H_4CHO	PhCH=CHCOPh	1	210	14	31
9	HCONHMe	PhCH=CHCOMe	1	180	2.5	25
10	HCONHMe	PhCH=CHCOPh	1	180	2.5	30
11	HCOOH	PhCH=CHCOMe	1	97	24	90
12	HCOOH	PhCH=CHCOMe	2	97	24	16
13	HCOOH	PhCH=CHCOMe	3	97	24	94
14	HCOOH	PhCH=CHCOPh	3	97	24	95
15	HCOOH	PhCH=$CHCOMe_3$	3	97	24	96
16	HCOOH		1	97	24	90

* 1. L_3RuCl_2. 2. L_3RhCl. 3. $L_2Ir(CO)Cl$, L = Ph_3P.

Thus the reaction of substituted cyclic ketones with solutions of chloroiridic acid in aqueous isopropyl alcohol containing different ligands (dimethyl sulphoxide, trimethyl phosphite, or phosphorous acid) leads to the formation of axial alcohols in high yields[127]. For example, 4-t-butylcyclohexanol is formed from 4-t-butylcyclohexanone under these conditions. When the reaction was carried out in the presence of dimethyl sulphoxide, a number of iridium complexes, which catalyse hydrogen transfer reactions, were isolated[128].

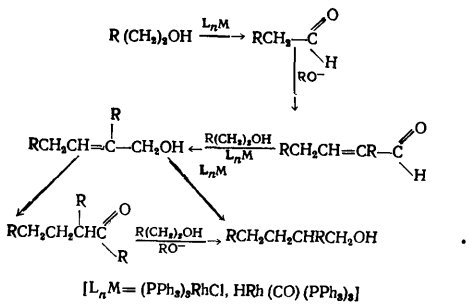
Hydrogen transfer and reduction of carbonyl group are observed also when isopropyl alcohol is refluxed with cyclohexanone in the presence of catalytic amounts of the complexes $IrH_3(PPh_3)_3$, $IrH_3(PPh_3)_2$, $ReH_7(Ph_3P)_2$, and $RuHBr(CO)(PEt_2Ph)_3$.[136] It is interesting that, when 4-substituted cyclohexanones are employed, equatorial alcohols are formed as the main reduction products[137].

An active ruthenium catalyst of hydrogen transfer from primary and secondary alcohols to ketones [$RuCl_2(PPh_3)_3$] was proposed by Freidlin and coworkers[138–141]. The addition of bases accelerates this reaction. The reaction rate depends on the structure of the alkyl substituents in the alcohol molecule and falls sharply following the introduction of bulky tertiary groups. Alkylphenylmethanols reduce ketones at a much higher rate than 2-alkanols. The structure of the ketone has also a significant influence

on the rate of reaction, which decreases in the sequence cyclohexanone > acetophenone > cyclopentanone > 2-hexanone > cycloheptanone > cyclo-octanone.

It is interesting that the univalent rhodium complex $(PPh_3)_3RhCl$, which is an active catalyst of homogeneous hydrogenation, is also active in hydrogen transfer from alcohols[138,139]. Its activity in this reaction is higher approximately by a power of ten than the activity of the ruthenium complex $(PPh_3)_3RhCl_2$ and depends little on the structure of the alcohol and ketone.

Catalytic reduction of aldehydes by alcohols was observed also in the course of the condensation of alcohols catalysed by rhodium compounds[142]. In this reaction the rhodium catalyst dehydrogenates the primary alcohol to the aldehyde with simultaneous formation of a carbonyl–phosphine–hydride complex (in this complex the carbonyl group of the aldehyde formed serves as a source of CO). In an alkaline medium two aldehyde molecules condense with formation of an $\alpha\beta$-unsaturated aldehyde, which is reduced by the rhodium hydride complex to a saturated aldehyde and to a higher alcohol:



$[L_nM = (PPh_3)_3RhCl, HRh(CO)(PPh_3)_3]$

Studies on the catalytic reduction of the carbonyl group in complex natural products are interesting. Thus steroid ketones can be reduced by isopropyl alcohol in the presence of tris(triphenylphosphine)rhodium chloride[143]. Under these conditions, the reduction of ketones to axial alcohols is to some extent stereospecific. The rate of reduction in the presence of the rhodium catalyst did not increase appreciably following the addition of alkali.

A study has also been made of the reduction by alcohols of a wide range of steroids in the presence of the $H_2IrCl[P(OMe)_3]_3$ catalyst[144]. This system is fully selective in the reduction of the 3-oxo-group in the presence of oxo-groups in other positions. Thus the oxo-groups in the 6-, 7-, 11-, 12-, 17-, 17α-, and 20-positions are hardly reduced (Table 4).

The reduction of other functional groups, in particular of the nitro-group, by alcohols in the presence of transition metal complexes has been described[145]. Thus a methanol solution of $Fe_3(CO)_{12}$ reduces specifically the aromatic nitro-group to a primary amino-group. The nitro-group is reduced with relatively high yields also in the presence of different substituents in the benzene ring (*p*-Cl, *o*-Cl, *o*-Me, *p*-OMe, *p*-OH, *p*-COOEt, *p*-COMe, *p*-HCOMe, *p*-CH=CH–CH=CH_2, *m*-NO_2, *p*-NH_2, and others).

It is noteworthy that the hydrogen transfer from alcohols to unsaturated substrates occurs under somewhat more severe conditions (temperature 80—130°C) than in homogeneous hydrogenation under the influence of analogous catalysts (usually at room temperature). This can be accounted for by the greater difficulty of the dissociation of the C–H bond compared with the H–H bond.

2. Reduction by Formic Acid and Formates

One of the interesting and extremely effective hydrogen donors for the reduction of organic compounds is formic acid and its derivatives. It is well known that formic acid and its salts are powerful reducing agents. This is usually attributed to the presence of the "aldehyde-like" hydrogen at the carbon atom which exhibits an appreciable hydride mobility (see above). In 1967 Coffey reported that, in the presence of phosphine complexes of platinum, ruthenium, and iridium, formic acid undergoes catalytic decomposition with formation of hydrogen and carbon dioxide[146]. He also stated that, following the introduction into this catalytic system [in the presence of the complex $H_3Ir(PPh_3)_3$] of butyraldehyde, the latter is reduced to the corresponding alcohol. Further results obtained in the reduction of the carbonyl group by formic acid were published by the same author in a patent[147].

Table 4. Reduction of 3-oxosteroids in the presence of the Henbest reagent [H_2IrCl_6, $(MeO)_3P$, and 90% aqueous 2-propanol]*.

Steroid	Amount of initial ketone after 24 h, %	Reaction time [h ?]	Yield of axial 3-OH, %	Yield of equatorial 3-OH, %	Yield of other products, %
5α-Series					
5α-Androstan-3-one	74	131	90	10	–
17β-Hydroxy-5α-androstan-3-one	45	128	95	2	–
5α-Androstane-3,17-dione	71	94	94	2	3-oxo-derivative (3%)
5α-Androstane, 3,11,17-trione	40	72	94	5	–
5α-Cholestane-3,6-dione	73	175	68	29	3-oxo-derivative (3%)
5α-Pregnane-3,20-dione	67	94	78	6-7	3-oxo-derivative (3%), 17-isoproducts (11%)
20α-Hydroxy-5α-pregnan-3-one	88	131	59	4	3-oxo-derivative (34%)
20β-Hydroxy-5α-pregnan-3-one	87	131	15	5	3-oxo-derivative (75%), unidentified products (5%)
5α-Pregnane-3,11,20-trione	61	92	63	9	3-oxo-derivative (3%), 17-isoproducts (24%)
5β-Series					
5β-Androstane-3,17-dione	42	72	98	2	–
17β-Hydroxy-5β-androstan-3-one	78	209	98	2	–
5β-Pregnane-3,2-dione	76	94	72	1	3-oxo-derivative (2%), 17-isoproducts (25%)
20α-Hydroxy-5β-pregnan-3-one	90	232	98	2	–
5β-Pregnane-3,11,20-trione	33	94	72	1	17-isoproducts (27%)
5β-Pregnane-3,12,20-trione	21	72	88	4	17-isoproducts (8%)

* The reaction is carried out in boiling isopropyl alcohol.

It was found recently that formic acid can readily reduce carbon–carbon multiple bonds in the presence of various transition metal complexes as catalysts[148-151].

The study of a wide range of phosphine complexes in this reaction showed that the principal relations observed in hydrogenation by molecular hydrogen are retained also in the reduction of olefins by formic acid. The influence of ligands, the valence of the transition metal, the nature of the substrate, etc. is similar. However, in contrast to hydrogenation by hydrogen, the reduction of olefins by formic acid is significantly affected by the solvent. The reduction hardly occurs in non-polar solvents (benzene, toluene, etc.) even under severe conditions, but proceeds extremely readily in dimethylformamide (DMF) and

dimethylacetamide. It is extremely significant that molecular hydrogen does not hydrogenate olefins in these solvents and under these conditions, which is evidence of intramolecular hydrogen transfer from HCOOH. That the hydride hydrogen from formic acid is involved in the reduction of the olefins has been demonstrated by separate experiments with DCOOH.

Olefins are reduced by formic acid usually at a higher temperature (60–100°C) than in the hydrogenation by molecular hydrogen in the presence of the same complexes. This is due in all probability to the greater difficulty of the dissociation of the C–H bond in formic acid. There are several ways of increasing the catalytic activity of the systems in which formic acid functions as a source of hydrogen.

1. By employing a combination of catalysts instead of individual complexes. Thus combination of the catalysts $(PPh_3)_2Rh(CO)Cl$ and $(PPh_3)_2Ir(CO)Cl$ is more active than each complex separately.

2. By employing a combination of transition metal complexes one of which is incapable of reducing the olefin but behaves under mild conditions as a catalyst of the decomposition of formic acid and the other can transfer hydrogen to the olefin. Such a system can be achieved, for example, by combining the complex $(Ph_3P)_3Co(N_2)H$, which can catalyse the decomposition of formic acid at room temperature, and any catalyst of homogeneous hydrogenation which can give rise to hydrogen transfer [for example, $(PPh_3)_3RhCl$].

3. By adding formate salts. In this case the formate anion presumably serves as an efficient donor of the hydride ion and formic acid behaves as a proton donor:

$$H\text{—}COO^- + M \longrightarrow (MH)^- + CO_2 ,$$

$$(MH)^- + HCOOH \longrightarrow MH_2 + HCOO^- ,$$

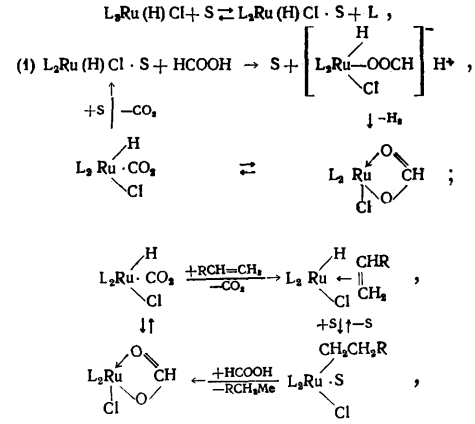
$$MH_2 + RCH{=}CH_2 \longrightarrow M + RCH_2CH_3 .$$

Indeed the employment of a mixture of formic acid and its salt made it possible in a number of cases to increase appreciably the degree of reduction and to lower the reaction temperature. For example, a mixture of formic acid with its salt in the presence of the complex $(Ph_3P)_3RhCl$ reduces quantitatively oct-1-ene and oct-4-ene, while the degree of their reduction by formic acid alone under the same conditions does not exceed 15%. In many instances a mixture of formates and formic acid reduces olefins even at room temperature.

It is interesting that formates themselves are also capable of reducing olefins and acetylenes in the presence of transition metals and in some cases the reduction by alkali metal formates proceeds more readily than by formic acid. Water behaves as the source of protons in such systems. The nature of the cation linked to the formate has hardly any effect on the activity of the reducing agent.

Comparison of the catalytic activities of various transition metal complexes in the reduction of olefins by formic acid showed that ruthenium complexes are the most active and among these the highest activity is shown by $(Ph_3P)_3Ru(H)Cl$. This complex catalyses the reduction of terminal olefins at room temperature in high yields. This behaviour of the ruthenium complex can be explained by the exceptional ease of the dissociation of the C–H bond of the formate group at the ruthenium atom with transfer of the hydride ion to ruthenium (see above). It is noteworthy that the ruthenium formate complex $(PPh_3)_3RuH(OOCH)$ is itself an effective catalyst of the decomposition of formic acid and of the reduction of olefins by formic acid at room temperature.

Kinetic studies and studies on model reactions suggest the following general mechanism of the decomposition of formic acid and the reduction of olefins [in the presence of the complex $(Ph_3P)_3Ru(H)Cl$]:



where S is a solvent molecule.

The decomposition of formic acid under the influence of transition metals can probably proceed not only via the formation of a formate complex with subsequent hydride transfer from the C–H bond to the metal in accordance with the mechanism

$$M + HCOOH \rightarrow HCOOM^- + H^+ \rightarrow HM^- + CO_2 + H^+ \rightarrow MH_2 + CO_2 ,$$

but also by the insertion of the metal in the carbon–hydrogen bond with the initial formation of the hydride of the metallocarboxylic acid:

$$M + HCOOH \rightarrow \overset{H}{\underset{COOH}{M}} \rightarrow MH_2 + CO_2 .$$

Indeed, when formic acid is refluxed with iridium complexes of the type L_3IrCl_3 (where L = Me_2PhP or Et_2PhP), the product is a complex, which has the structure $L_2Ir(CO)H(COOH)Cl$ according to infrared spectroscopic data and its chemical properties[152]. This reaction is of interest not only from the standpoint of the understanding of the mechanism of the decomposition of formic acid but also from the standpoint of the possible transfer of fragments of the metallocarboxylic acid to olefins via a mechanism involving a kind of reductive carboxylation[153]:

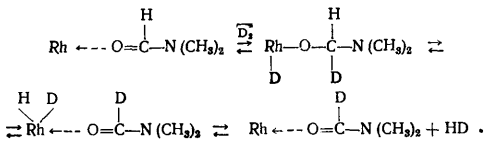
$$M + HCOOH \rightarrow \overset{H}{\underset{COOH}{M}} \xrightarrow{>C=C<} H\text{—}\overset{|}{C}\text{—}\overset{|}{C}\text{—}COOH .$$

The possibility of such addition of the elements of formic acid and also of its esters to cyclohexene and other olefins has been demonstrated in catalysis by rhodium, ruthenium, osmium, and platinum complexes[68]. The complexes $(PPh_3)_3RhCl$, $(PPh_2)_3RhCl$, $(PPh_3)_2Ir(CO)Cl$, and $(PPh_3)Rh(CO)_2Cl$ proved to be the most active catalysts. However, the yields of the carboxylic acid are low and do not exceed 40 mole per mole of the catalyst; the process is complicated by side reactions involving the decomposition of formic acid, the reduction of the olefin, etc.

This reaction is an example of an interesting type of C–H bond dissociation and of the transfer of both hydrogen and of an organic group to the substrate. Such reactions can in many instances lead to new ways of obtaining valuable substances.

In conclusion of the section devoted to formic acid as a reducing agent, mention should be made of the fact that in

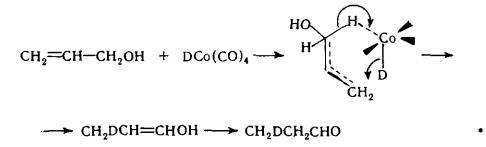
the presence of ruthenium and rhodium complexes the acid is capable of the selective reduction of $\alpha\beta$-unsaturated ketones to saturated ketones[130] (Table 3). It is interesting that, when the complex $(PPh_3)_3RuCl_2$ is used as a catalyst, not only formic acid but also DMF can serve as a source of hydride hydrogen. The study on the exchange of hydrogen in the C–H bond in DMF with molecular deuterium catalysed by rhodium complexes[154,155] is interesting in this connection. The authors propose the following possible mechanism for the exchange process:



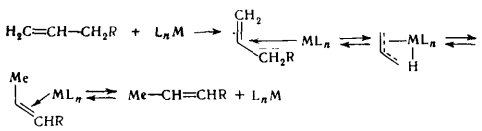
3. Disproportionation Reactions

Catalytic reactions where the same substrate molecule can behave both as a donor and as an acceptor of hydrogen are of great interest. This results either in the isomerisation of the initial molecule (with intramolecular hydrogen migration) or disproportionation (with intermolecular hydrogen migration).

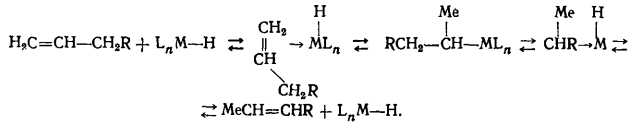
The isomerisation of allyl alcohol to propionaldehyde catalysed by cobalt hydrocarbonyl[156], iron[157], ruthenium[158], and palladium[159] complexes can serve as an example of such intramolecular hydrogen transfer. When allyl alcohol is acted upon by deuteriated cobalt hydrocarbonyl, the entire deuterium is bound in the methyl group of propionaldehyde, which suggests the following mechanism for this reaction[156]:



Numerous olefin isomerisation reactions under the influence of transition metal compounds also constitute essentially intramolecular hydrogen migrations. They occur either with activation of the allylic C–H bond of the olefin (which is most readily dissociated):

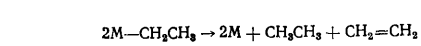


or they involve the metal–hydrogen hydridic bond already present via an intermediate σ-alkyl derivative:

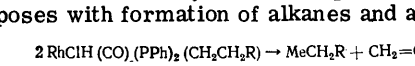


The isomerisation reactions have been discussed in greater detail in numerous reviews, for example that of Orchin[89].

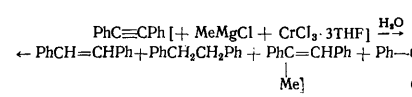
σ-Alkyl derivatives of transition metals, which are in many instances intermediates in the catalytic migration of hydrogen in olefins, are also capable of undergoing very readily intermolecular hydrogen exchange in the course of the dissociation of the metal–carbon bond via the mechanism



For example, the decomposition of pentacyano(2-butenyl)-cobaltate(III) results in the formation of butenes and butadienes[160]. The alkylcarbonylrhodium hydride complex (formed in the decarbonylation of aliphatic aldehydes) decomposes with formation of alkanes and alkenes[161–163]:

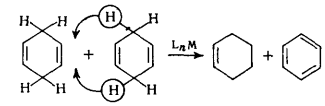


The number of examples of this kind could be greatly extended. It is noteworthy that σ-alkyl groups can behave also as reductants for an "external" substrate (an unsaturated compound), but this reaction does not have preparative value. For example, when tolane reacts at room temperature with σ-methyl derivatives of chromium, tolane reduction products were identified after hydrolysis[164]:

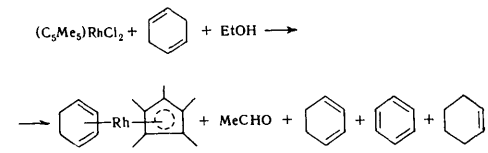


When a deuteriated Grignard reagent was employed it was shown that the methyl group is in fact the hydrogen donor[165].

The olefin disproportionation reactions in the presence of complex catalysts discovered recently are interesting. It was found that cyclohexe-1,4-diene can disproportionate in a homogeneous medium in the presence of $(Ph_3P)_2Ir(CO)Cl$ with formation of benzene and cyclohexane[166]. In this case, as in N.D. Zelinskii's classical irreversible catalysis, one cyclohexadiene molecule behaves as the donor and the other as the acceptor of hydrogen:



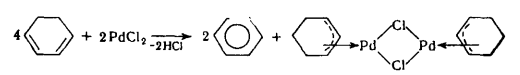
The complex $Ph(\pi\text{-}C_5Me_5)C_6H_8$ also catalyses the disproportionation of cyclohexa-1,3-diene and cyclohexa-1,4-diene to cyclohexene and benzene[167]. This involves the formation of a rhodium complex accompanied by the isomerisation of the 1,4-diene to the 1,3-diene with subsequent disproportionation:



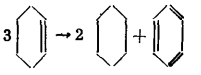
The formation of the rhodium complex from the 1,3-diene is accompanied only by disproportionation without isomerisation.

The reaction of cyclohexa-1,3-diene with $RuCl_3$ in ethanol results in the formation of a π-benzene complex of ruthenium[168]. This reaction probably proceeds via the catalytic disproportionation of cyclohexadiene.

In the presence of palladium salts cyclohexa-1,3-diene is converted into benzene and an allyl complex of palladium[169]:

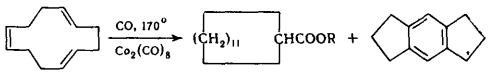


The disproportionation reactions of cyclohexene catalysed by palladium salts[170,171] probably belong to the same type. For example, on heating with $Pd(CN)_2$ at 130°C, cyclohexene gives rise to a mixture of cyclohexanes and benzene [yields of 479 and 212% relative to $Pd(CN)_2$][170]:



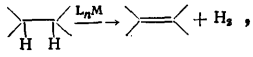
When acted upon by $PdCl_2$, 1-methylcyclohex-1-ene forms similarly methylcyclohexane and toluene even at room temperature[170]; this entails the simultaneous oxidation of the olefin and the formation of metallic palladium. However, the authors believe that palladium complexes and not metallic palladium catalyse this reaction.

An interesting disproportionation reaction was discovered by Rüll[172], who established that, in the presence of $Co_2(CO)_8$ under the conditions of the Reppe synthesis, cyclododeca-1,5,9-triene is converted into the methyl ester of cyclododecanecarboxylic acid. In addition it was found that the corresponding aldehyde is formed in the course of the reaction. Hydrogen required for this reaction is formed as a result of the conversion of cyclododeca-1,5,9-triene into the symmetrical hydrindacene, which was detected in the reaction products:

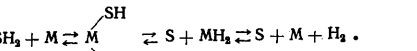


4. Direct Dehydrogenation Reactions

The problem of the possible occurrence of direct dehydrogenation reactions under the influence of complex catalysts, i.e. reactions which are the converse of hydrogenation, for example



has attracted particular attention. Such reactions could in principle be catalysed by the same complexes as hydrogenation and the reaction mechanism might include the activation of the C–H bond:



However, under mild conditions all these reactions are as a rule thermodynamically unfavourable and the equilibrium is displaced wholly towards the formation of the hydrogenation products.

The few examples in which processes of this kind are known involve the formation of products which are thermodynamically the most stable. Thus, as already stated above, formic acid decomposes extremely readily when acted upon by various transition metal complexes via the mechanism

$$HCOOH \rightarrow CO_2 + H_2 .$$

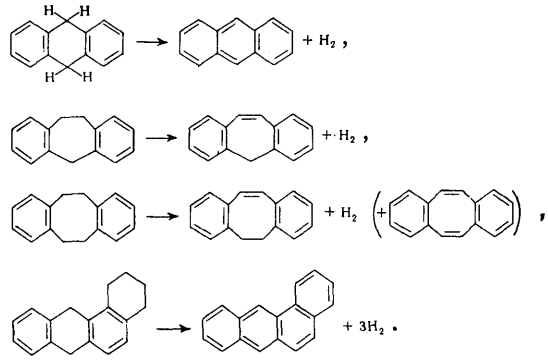
Here the "driving force" of the reaction, which is completely displaced to the right, is the high thermodynamic stability of the CO_2 molecule ($\Delta H_{298} \simeq 264$ kcal mole^{-1}).

Direct dehydrogenation with formation of a C=C double bond was observed in a few instances and only for compounds where the double bond is stabilised by conjugation. Thus it has been stated[173] that cyclohexane is dehydrogenated to benzene on interaction with $IrCl(PPh_3)_3$. However, the yield of benzene was small and it was not clear whether hydrogen was evolved or an iridium hydride complex was formed. (Experiments with a deuteriated substrate showed that hydrogen is transferred to iridium from the phosphine ligands and not from the substrate.) There are also data for the dehydrogenation of cyclohexane by palladium(II) salts[174].

Extremely interesting examples of catalytic dehydrogenation were observed by Blum and Biger[175] for compounds whose dehydrogenation results in the formation of a double bond between two benzene rings. For example, on heating with a catalytic amount of $(Ph_3P)_3RhCl$, $(AsPh_3)_3RhCl$, $(Ph_3P)_2Ir(CO)Cl$, or $(PPh_3)_3RuCl_2$ at 260°C, bibenzyl gives rise to *trans*-stilbene:

$$PhCH_2—CH_2Ph \rightarrow PhCH=CHPh + H_2 .$$

Other dehydrogenation reactions proceed similarly:

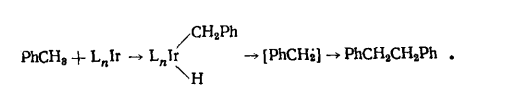


It is interesting that the rates of these reactions are close to those of dehydrogenation at a heterogeneous palladium catalyst, but the reactions in the presence of the complexes are more selective. Thus, on heating with $(Ph_3P)_3RhCl$ (at 225°C for 15 h), 9,10-dihydroanthracene gives a quantitative yield of anthracene (without the formation of tetrahydroanthracenes). Transition metal hydride complexes are probably formed as intermediates in this reaction. Indeed the hydride was isolated in the case of the ruthenium complex.

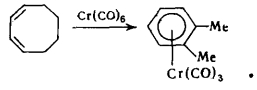
There has been a brief communication[176] concerning the catalytic dehydrogenation of toluene in the presence of $(PPh_3)_3IrCl$:

$$PhCH_3 \xrightarrow{(PPh_3)_3IrCl} PhCH_2CH_2Ph + PhCH=CHPh + PhC\equiv CPh .$$

Presumably the occurrence of this reaction is related primarily to the great ease of the dissociation of the benzyl–hydrogen bond and subsequent dimerisation of the benzyl radicals:



Finally mention may be made of the reaction in the course of which cyclo-octa-1,3-diene is dehydrogenated under the influence of chromium carbonyl with simultaneous ring contraction and aromatisation. The chromium carbonyl complex of *o*-xylene was isolated in a low yield[177]:



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The present review has dealt with a wide variety of reactions involving the dissociation of C–H bonds with subsequent hydrogen transfer to unsaturated compounds. Transition metal complexes are effective catalysts of these reactions and make it possible to carry them out under comparatively mild conditions and fairly selectively.

Alcohols, alkoxides, aldehydes, dihydric phenols, cyclic ethers, etc. can be used as hydrogen donors. Formic acid and formates are particularly convenient reducing agents.

Carbon–carbon double and triple bonds, the carbonyl group, and the nitro-group have been hydrogenated with the aid of these reducing agents. In many instances it proved possible to demonstrate the high selectivity of the reactions and their stereospecificity. It is noteworthy that the ease and selectivity of the hydrogen transfer processes and the availability of the reducing agents and catalysts used make the reactions very convenient in many instances on a preparative scale.

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