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Metal Complex Catalysts for the Hydrogenation of Aromatic and Heterocyclic Compounds

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The application of metal complex catalysts (in homogeneous and heterogenised forms) to the hydrogenation of aromatic and heterocyclic compounds is examined.
The bibliography includes 128 references.

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I. INTRODUCTION

The study of the hydrogenation of aromatic and heterocyclic compounds constitutes an important (from both practical and theoretical standpoint) and at the same time a complex problem. There are numerous literature data on the hydrogenation of the above compounds (see, for example, Smith,[1] Bel'skii and Shostakovskii,[2] Kreile et al.,[3] and Mashkina[4]), but these concern mainly only heterogeneous-catalytic reactions, requiring as a rule the use of fairly severe conditions, which entails in its turn a decrease in the selectivity of the processes.

A much smaller number of studies have been devoted to the hydrogenation of aromatic and heterocyclic compounds in the presence of metal complex catalysts apparently owing to the difficulty of selecting metal complexes capable of activating aromatic and heterocyclic compounds and at the same time remaining resistant to the poisoning activity of the latter. Nevertheless the synthesis and employment of metal complexes as hydrogenation catalysts (homogeneous and particularly heterogenised catalysts which possess simultaneously the advantages of homogeneous and traditional heterogeneous catalysts) is extremely promising, since it permits the process to be carried out under mild conditions, which significantly increases the yield of products and the reaction selectivity.

The advantages and disadvantages of metallic and metal complex catalysts combined with the theoretical development of a general approach to the investigation of the characteristic features of catalytic reactions of organic compounds in the presence of these systems in the course of various processes (deuterium–hydrogen exchange, hydrogenation, oxidation, etc.) have been considered in a number of publications (see, for example, Refs.5–17).

Hydrogenation is one of the first reactions carried out using metal complex catalysts. A number of reviews have been devoted to this question (for example, those of James,[18] Coffy,[19] and McQuillin,[20] in which mainly the hydrogenation of compounds containing bonds of the olefinic type is discussed. This review deals with the available literature data for the hydrogenation of aromatic and heterocyclic compounds in the presence of metal complex catalysts—both homogeneous and heterogenised. Instances of the hydrogenation of unsaturated substituents are excluded from consideration if such hydrogenation does not entail the hydrogenation of the aromatic or heterocyclic ring.

II. CATALYSTS FOR THE HYDROGENATION OF AROMATIC HYDROCARBONS

1. Catalysts Active under Hydroformylation Conditions

Dicobalt octacarbonyl was the first metal complex catalyst used for the hydrogenation of aromatic and heterocyclic compounds.[21] However, its use requires the reaction to be carried out in the presence of an excess carbon monoxide pressure and hydrocarbonylation can therefore occur to a greater or lesser extent together with the hydrogenation reaction.

Benzene and its alkyl-derivatives are hardly hydrogenated under hydroformylation conditions.[22,23] For example, only a slight degree of conversion of benzene into hydroxymethylcyclohexane has been noted[22] to occur at 200 °C and an initial pressure of the $CO : H_2 = 1 : 1$ mixture of 300 atm.†

Hydrogenation under hydroformylation conditions has been studied in greatest detail for condensed polycyclic aromatic hydrocarbons[21,23–26] (Table 1). Overall, the hydrogenation of polycyclic aromatic hydrocarbons proceeds more readily than the hydrogenation of benzene and the rings condensed with two or several other aromatic rings are mainly hydrogenated. Thus anthracene is readily converted into 9,10-dihydroanthracene (Table 1).

The low activity of dicobalt octacarbonyl in the hydrogenation of naphthalene and phenanthrene should also be noted. In addition, the naphthalene and phenanthrene system formed in the hydrogenation of polynuclear aromatic compounds are as a rule fairly resistant to further reduction[23] (Table 1).

The absence of stereoselectivity in the hydrogenation reactions under hydroformylation conditions has been demonstrated for 9,10-dimethylanthracene;[24] *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracenes are formed in approximately equal amounts. The addition of tributyl phosphite does not increase the selectivity but lowers the activity of the catalyst and *cis–trans* isomerisation is not observed.

The deuteriation of polycyclic aromatic compounds in the presence of the $D_2 : CO = 1 : 1$ mixture at approximately

† Here and henceforth the initial pressure at room temperature before heating the reaction mixture is quoted.

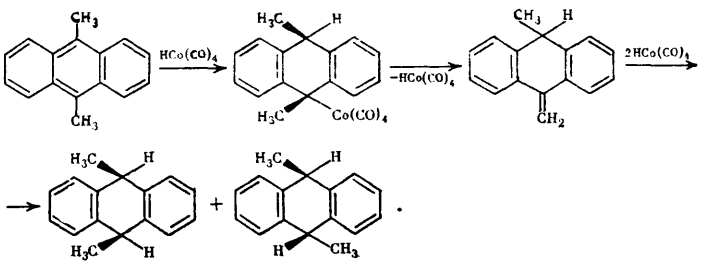
200 °C, which is catalysed by $Co_2(CO)_8$, has been investigated.[27] Anthracene and anthraquinone are converted into 9,9,10,10-tetradeuterio-9,10-dihydroanthracene, pyrene undergoes reduction and H–C exchange in the 4- and 5-positions, while phenanthrene does not react.

Table 1. Hydrogenation of condensed polycyclic aromatic hydrocarbons under hydroformylation conditions*.

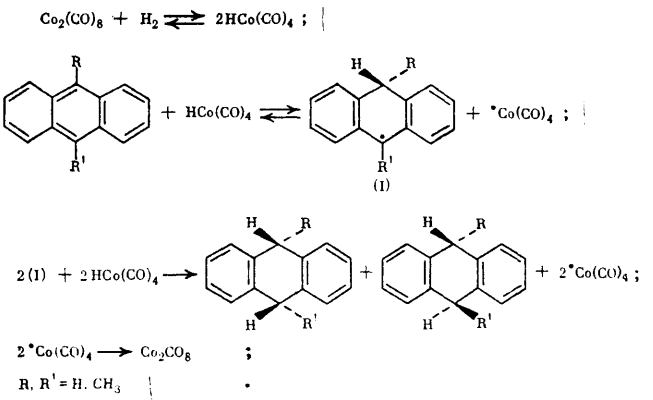
Substrate	Hydrogenation products (yield, %)
Phenanthrene**	9,10-Dihydrophenanthrene (7); 1,2,3,4-tetrahydrophenanthrene (1)
Naphthalene	Tetralin (16)
2-Methylnaphthalene	Methyltetralins (43)
1,1-Binaphthyl	Is not hydrogenated
Acenaphthene	2a,3,4,5-Tetrahydroacenaphthene (45)
Fluorene	Is not hydrogenated
Anthracene	9,10-Dihydroanthracene (99)
Naphthacene	5,12-Dihydronaphthacene (70)
Chrysene	5,6-Dihydrochrysene (24)
Fluoranthrene	1,2,3,10c-Tetrahydrofluoranthrene (54)
Triphenylene	Is not hydrogenated
Pyrene	4,5-Dihydropyrene (69)
Perylene	1,2,3,10,11,12-Hexahydraperylene (72)
Coronene	Is not hydrogenated

*Catalyst—dicobalt octacarbonyl, 1–5 mole %, 150–200 °C, 200 atm pressure of $H_2 : CO = 1 : 1$ mixture (2 : 1 in the case of phenanthrene).
**According to the results of Wender et al.;[21] in the remaining cases the data of Freedman et al.[23] were used.

In order to establish the mechanism of the hydrogenation reaction, a study has also been made of the reduction of anthracene and 9,10-dimethylanthracene by the stoichiometric amount of $HCo(CO)_4$.[24] It has been shown that anthracene is hydrogenated to 9,10-dihydroanthracene to the extent of 25% at 25 °C, while 9,10-dimethylanthracene is 99% hydrogenated with formation of 35% of the *cis*-isomer and 65% of the *trans*-isomer of 9,10-dihydro-9,10-dimethylanthracene. The following reaction mechanism, which explains the formation of the *cis*- and *trans*-products, has been put forward:



At the same time, it is believed[28] that organometallic intermediates are not formed in the hydroformylation of polycyclic aromatic compounds. This conclusion is based on the analysis of data for the deuteriation of anthracene and pyrene under deuterioformylation conditions[27] as well as the following facts: (1) the absence of hydroxymethylation products from the reaction mixture after the hydrogenation of polycyclic aromatic compounds under hydroformylation conditions and (2) the easier hydrogenation of 2-methylnaphthalene or acenaphthene compared with naphthalene[23] and of 9,10-dimethylanthracene compared with anthracene[24] despite the steric hindrance. A radical reaction mechanism has therefore been put forward:[28]



2. Catalysts of the Ziegler Type

A number of studies on the hydrogenation of aromatic hydrocarbons in the presence of Ziegler catalysts have been described in the literature.[31–41] It is noteworthy that data[29] concerning the catalytic activity of a number of transition metal salts in the course of the hydrogenation of aromatic compounds have been refuted in another study.[30] The addition of aluminium alkyls or aluminium hydrides to the reaction mixture containing transition metal ions increases sharply the activity of the catalyst. Overall, catalysts of the Ziegler type make it possible to carry out the hydrogenation under much milder conditions than in the presence of $Co_2(CO)_8$. Thus the addition of aluminium alkyls or aluminium hydrides to cobalt and nickel carboxylates makes it possible to obtain catalysts for the hydrogenation of benzene which are active at temperatures of approximately 50 °C and pressures of approximately 30 atm.[31]

The hydrogenation of benzene under mild conditions (30 °C, 2 atm) has been studied using the triethylaluminium–cobalt acetylacetonate system.[32] On the basis of EPR studies, it has been suggested that the zerovalent cobalt complex decomposes with formation of clusters which directly propagate the hydrogenation reaction.

The reduction of iron, cobalt, and nickel acetylacetonates with sodium and lithium tetrahydroborates and lithium tetrahydroaluminate makes it possible to obtain benzene hydrogenation catalysts which are active at 30 °C and 1 atm.[33] Catalysts for the hydrogenation of benzene, toluene, and xylene have been obtained by the reduction of cobalt, nickel, and copper complexes of salicylaldehyde with $LiAlH_4$ using metal : aluminium ratios ranging from 1 : 1 to 1 : 7.[34]

The addition of triethylaluminium to transition metal 2-ethylhexanoates or naphthenates yields active catalysts for the hydrogenation of aromatic compounds.[35,36] The catalysts are prepared in solvents which show no tendency towards complex formation, such as heptane, benzene, etc.; this is accompanied by the evolution of a gas containing 95% of ethane. The maximum catalytic activity in the case of nickel is attained for the Al : Si = 3 : 1–4 : 1 ratios. The activity in the hydrogenation of benzene diminishes in the sequence Ni ≥ Co > Fe > Cr > Cu. In mixtures containing 0.3–0.5 mole % of nickel 2-ethylhexanoate for an initial hydrogen pressure of approximately 70 atm and temperatures in the range 150–200 °C, fairly rapid and quantitative reduction of benzene to cyclohexane, of phenol to cyclohexanol, and of dimethyl phthalate to dimethyl hexahydrophthalate takes place. The hydrogenation of pyridine to piperidine, of

dimethyl terephthalate to dimethyl hexahydroterephthalate, and of naphthalene to tetralin and decalin proceeds less actively.[35]

The stereoselectivity of the hydrogenation reaction in the presence of a system containing nickel has been pointed out.[37] o-Xylene has been hydrogenated to 66% of *cis*-1,2-dimethylcyclohexane and 34% of *trans*-1,2-dimethylcyclohexane. It has been possible to hydrogenate polystyrene to a product with a 15% content of cyclohexane rings by weight at 150 °C and an H_2 pressure of 100 atm. Physicochemical investigation has demonstrated that the nickel in the catalyst is reduced to the zerovalent diamagnetic state.[37]

Table 2. Hydrogenation of aromatic hydrocarbons in the presence of the cobalt 2-ethylhexanoate/$AlEt_3$ catalyst.[38]

Substrate	a *	Al:Co	τ, h	α **, %	Products (composition, %)
Benzene	0.25	2	30	63	Cyclohexane (100)
o-Xylene	0.2	2	15	50	1,2-Dimethylcyclohexane (*cis*-70, *trans*-26)
m-Xylene	0.2	2	22	40	1,3-Dimethylcyclohexane (*cis*-63, *trans*-37)
p-Xylene	0.1	2	24	55	1,4-Dimethylcyclohexane (*cis*-63, *trans*-37)
Biphenyl	0.05	2	20	100	Bicyclohexyl (81); phenylcyclohexane (19)
Naphthalene	0.05	2	18	100	Decalin (*cis*-43, *trans*-11), tetralin (37)
Tetralin	0.1	2	66	100	Decalin (*cis*-66, *trans*-34)

*Substrate: catalyst molar ratio.
**Degree of conversion.

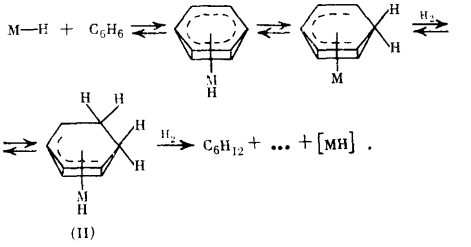
The analogous system based on cobalt 2-ethylhexanoate has been investigated[38] (Table 2). The hydrogenation was carried out at 20–30 °C at a hydrogen pressure of 65 atm. In addition a study has been made of the hydrogenation of a number of polar compounds at an initial hydrogen pressure of 50–60 atm. Phenol is 25% hydrogenated at 45 °C in the course of 20 h to give a mixture of 98% of cyclohexanol and 2% of cyclohexanone. Diethyl phthalate has been 95% hydrogenated at 20 °C during 16 h and the products were found to contain 83% of diethyl *cis*-hexahydrophthalate and 17% of the *trans*-isomer. The same workers[38] showed in a study of competitive hydrogenation that olefins and naphthalene prevent the hydrogenation of benzene.

The hydrogenation of benzene and its alkyl derivatives in the presence of acetylacetonate, cyclopentadienyl, and dimethylglyoximate complexes reduced with trialkylaluminium has been studied.[39,40] The relative activities of different complexes in the benzene hydrogenation reaction[40] vary in the following sequence:

$$Ni(C_5H_7O_2)_2 > Co(C_5H_7O_2)_2 \geqslant Cu(C_5H_7N_2O_2)_2 > Fe(C_5H_7O_2)_3 > Fe(C_5H_5)_2 > > Mn(C_5H_7O_2)_2 > VO(C_5H_7O_2)_2 > Ni(C_5H_7N_2O_2)_2 > (C_5H_5)_2TiCl_2 > Cr(C_6H_7O_2)_3 .$$

Here C_5H_5 = cyclopentadienyl, $C_5H_7O_2$ = acetylacetonate, and $C_5H_7N_2O_2$ = dimethyl glyoximate. The apparent activation energy for the hydrogenation of benzene in the presence of iron and nickel acetylacetonates does not vary with the Al : metal ratio; consequently the number of active complexes and not the "energy relations" of the process vary. The experimental activation energy for the hydrogenation of benzene in the presence of acetylacetonate complexes diminishes in the sequence[41] Cu > Ni > Fe > Cr > Mo when the Al : metal ratio is 8 : 1 for Cr, Fe, and Ni and 6 : 1 for Cu and Mo. In the hydrogenation of benzene, toluene, *o*-xylene, and mesitylene in the presence of nickel and iron acetylacetonates the activation energy diminishes with increase of the number of alkyl substituents, while in the presence of chromium and molybdenum acetylacetonates it increases.[41]

At 150 °C in the presence of nickel acetylacetonate the hydrogenation reaction is of first order with respect to hydrogen, while the order with respect to benzene varies from a fraction less than unity to zero; in the presence of chromium acetylacetonate the reaction order with respect to hydrogen is less than unity.[41] On the basis of their results, the authors[39] proposed the following mechanism for the benzene hydrogenation reaction assuming that the metal hydride is the active catalytic species:



(II)

It has been suggested that the rate-limiting stage is the activation of the hydrogen molecule involving the formation of the hydride (II).

3. Metal Complexes Containing Unsaturated and Aromatic Hydrocarbons as Ligands

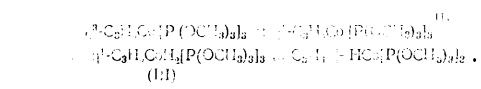
A large number of studies have been devoted to the hydrogenation of aromatic hydrocarbons in the presence of complexes containing unsaturated hydrocarbons as ligands.

The catalytic activity of pentamethylcyclopentadienyl complexes has been investigated in the hydrogenation of olefins and aromatic hydrocarbons.[42–45] Di-μ-chlorobis[chloro(pentamethylcyclopentadienyl)rhodium] $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ is an active catalyst of the hydrogenation of aromatic hydrocarbons; its iridium analogue is much less active. A heterolytic mechanism has been proposed for the activation of hydrogen, since the catalyst is active in the presence of 15 moles of NEt_3 per mole of the catalyst. The base is required to bind the HCl evolved in the activation of H_2 and to promote the formation of rhodium hydride.[44] The intermediate formation of partial reduction products has not been observed in the hydrogenation of benzene.

Table 3 presents the results of the hydrogenation of a number of aromatic compounds in the presence of $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ at 50 °C and a hydrogen pressure of 50 atm. A fairly high stereoselectivity has been noted in the hydrogenation of xylenes. The ratio of the *cis*- and *trans*-isomers in the hydrogenation products is 6.2 : 1.0 for *o*-xylene, 3.8 : 1.0 for *m*-xylene, and 2.0 : 1.0 for *p*-xylene. An increase in the number of alkyl substituents hinders the hydrogenation of the aromatic ring. In terms of the relative rates of hydrogenation alkylbenzenes can be arranged in the following sequence:[45] benzene (1.00) > toluene (0.94) > *o*-xylene (0.70) > ethylbenzene (0.58) > mesitylene (0.35) > s-butylbenzene (0.25) > durene (0).

Extensive studies have been carried out on the hydrogenation of various aromatic compounds in the presence of $\eta^3\text{-}C_3H_5Co[P(OCH_3)_3]_3$ and related catalysts.[46–53] The possibility of the hydrogenation of benzene under mild conditions has been demonstrated: 25 °C, p_{H_2} = 1 atm, $\eta^3\text{-}C_3H_5Co$.

.$[P(OCH_3)_3]_3$ catalyst.[47] The complex is stable in approximately 20 benzene hydrogenation cycles and then decomposes into inactive species. Even at low partial hydrogen pressures and in the initial stages of the reaction, partially hydrogenated benzenes were not detected. During 24 h from the start of the reaction, a visible decomposition of the complex, accompanied by the breakdown of homogeneity, is not observed. On decomposition of the complex, phosphite and $HCo[P(OCH_3)_3]_4$ are detected in solution. It has been suggested[48] that the π-allyl ligand is eliminated when the complex decomposes:

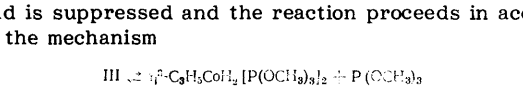


(III)

Table 3. Hydrogenation of aromatic compounds in the presence of the di-μ-chlorobis[chloro(pentamethylcyclopentadienyl)rhodium] catalyst.[44]

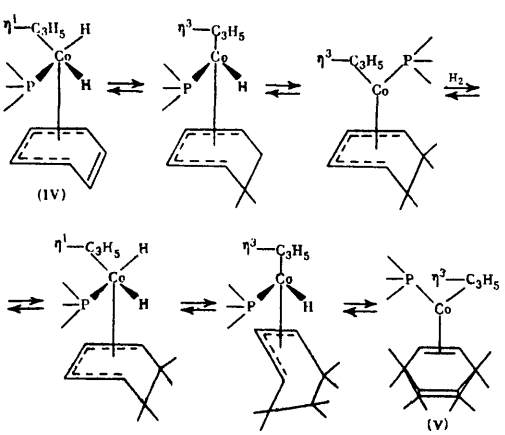
Substrate	Reaction products (yield, %)
Styrene	Ethylbenzene (97); ethylcyclohexane (3)
Phenylacetylene	Styrene (7)
Anisole	Methoxycyclohexene (19); methylcyclohexane (6)
Phenol	Cyclohexanone (1); cyclohexene (0.5)
Methyl benzoate	Methyl cyclohexanoate (75); toluene (8)
Acetophenone	Cyclohexyl methyl ketone (100)
Benzophenone	Dicyclohexyl ketone (50); cyclohexyl phenyl ketone (15); dicyclohexylmethanol (10)
NN'-Dimethylaniline	*NN*'-Dimethylcyclohexylamine (73)
Nitrobenzene	Aniline (96); cyclohexane (4)
Fluorobenzene	Fluorocyclohexane (14); cyclohexane (38)
Bromobenzene	Cyclohexane (10)
Iodobenzene	Cyclohexane (2); benzene (3)
Anthracene	Tetrahydroanthracene (70); octahydroanthracene (22), perhydroanthracene (3)

In the presence of an arene, the *cis*-elimination of the ligand is suppressed and the reaction proceeds in accordance with the mechanism

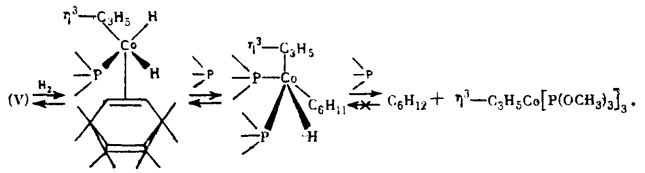


(IV)

Benzene is hydrogenated in the intermediate complex (IV) in accordance with the mechanism:[48]



(V)



The above scheme accounts for the absence of the products of the partial reduction of the aromatic benzene ring from the reaction mixture and for the high *cis*-stereoselectivity of the hydrogenation of substituted benzene derivatives. It has been noted[48] that the rate of hydrogenation of benzene is much higher than that of cyclohexene.

Table 4. Hydrogenation of aromatic compounds in the presence of η^3-$C_3H_5Co[P(OCH_3)_3]_3$.*[49]

Substrate	a**	τ, h	Reaction products (yield, %)
Benzene	1:100	24	Cyclohexane (16)
Benzene	1:100	24	Cyclohexane (16.4)
Benzene	1:100	10	Cyclohexane (5)
Benzene + D_2	1:100	10	*cis*-$C_6H_6D_6$ (5)
Perdeuteriobenzene	1:100	15	*cis*-$C_6H_6D_6$ (8)
Toluene	1:100	10	Methylcyclohexane (5)
o-Xylene	1:100	10	*cis*-1,2-Dimethylcyclohexane (3)
o-Xylene	1:100	48	*cis*-1,2-Dimethylcyclohexane (15)
m-Xylene	1:100	10	*cis*-1,3-Dimethylcyclohexane (3)
m-Xylene	1:100	48	*cis*-1,3-Dimethylcyclohexane (7)
p-Xylene	1:100	10	*cis*-1,4-Dimethylcyclohexane (3)
p-Xylene	1:100	49	*cis*-1,4-Dimethylcyclohexane (7)
Mesitylene	1:100	15	*cis,cis*-1,3,5-Trimethylcyclohexane (1)
1,2,3-Trimethylbenzene	1:10	65	*cis,cis*-1,2,3-Trimethylcyclohexane (2)
1,2,4,5-Tetramethylbenzene	1:10	72	*cis,cis,cis*-1,2,4,5-Tetramethylcyclohexane (9)
Naphthalene	1:10	168	*cis*-Decalin (99); tetralin (1)
Anthracene	1:10	49	*cis,syn,cis*-Perhydroanthracene (76); mixture of products (14)
Furan	1:100	15	Tetrahydrofuran (14)
Benzofuran	1:100	96	Perhydrobenzofuran (19); C_8H_8O (12); $C_8H_{12}O$ (1.5)
Anisole	1:100	10	Cyclohexyl methyl ether (5)
NN'-Dimethylaniline	1:100	48	*NN*'-Dimethylcyclohexylamine (3)
Ethyl benzoate	1:13	24	Ethyl cyclohexanecarboxylate (2); ethyl cyclohex-1-enecarboxylate (13)
NN'-Dimethylbenzamide	1:10	68	*NN*'-Dimethylcyclohexanecarboxamine (54); benzyl alcohol (4)
Acetophenone	1:50	24	Cyclohexyl methyl ketone (1)
Cyclohex-2-en-1-one	1:47	42	Cyclohexanone (3)
Styrene	1:41	24	Vinylcyclohexane (5); ethylbenzene (6); ethylcyclohexane (4)
1-Phenylpropyne	1:23	43	Propenylcyclohexane (2); propylbenzene (3); allylbenzene (1); *cis*-propenylbenzene (1); *trans*-propenylbenzene (1)
Propylbenzene	1:34	25	Propylcyclohexane (15)
Allylbenzene	1:36	30	Allylcyclohexane (2); propylcyclohexane (3); propylcyclohexene (5); propylbenzene (4)
Cyclo-octa-1,5-diene	1:32	37	Cyclo-octene (50); cyclo-octane (26)

*Reaction conditions: 20 °C, 1 atm H_2, 0.112 mmol of catalyst.
**Catalyst : substrate molar ratio.

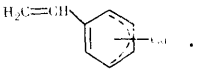
The results of the study of hydrogenation in the presence of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ have been surveyed[49] (Table 4). In the presence of this system, polycyclic hydrocarbons are hydrogenated less effectively than benzene. Electron-accepting substituents deactivate the aromatic ring: fluorobenzene and nitrobenzene were not hydrogenated, since the reaction requires a high π-donor capacity of the aromatic ring. Nucleophilic substituents are in their turn bound preferentially to the metal atom, preventing the hydrogenation of the aromatic ring, as happens, for example, in the case of phenylacetonitrile, triphenylphosphine, and benzonitrile. The oxidation-reduction interaction of the catalyst with

chlorobenzene prevents the hydrogenation of the latter. Protonation of the catalyst leads to the unstable complex η^3-$C_3H_5CoH[P(OCH_3)_3]_3^+$, which decomposes with evolution of propene. For this reason, it has not been possible to hydrogenate phenol and benzoic acid.

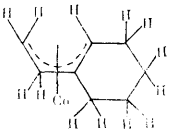
The influence of steric hindrance following the introduction of alkyl substituents into the benzene ring and the consequent resistance of 1,2,3,4-tetramethylbenzene and hexamethylbenzene to hydrogenation have been noted.[49]

When the competitive hydrogenation of a mixture of benzene and hex-1-ene is carried out,[49] the ratio of the hydrogenated aromatic hydrocarbon and hexane is 7 : 10 and appreciable amounts of cyclohexene are formed. Thus alkenes are bound to the catalyst less strongly than aromatic hydrocarbons and the alkene which has failed to react can competitively displace the products of the partial reduction of aromatic hydrocarbons.

The hydrogenation of styrene leads to the formation of approximately equal amounts of vinylcyclohexane, ethylbenzene, and ethylcyclohexene for a low degree of conversion. This composition of the reaction products can be accounted for by the competitive displacement of the partly hydrogenated products. On the other hand, there is a possibility (by virture of steric factors) of the following type of interaction with the catalyst:



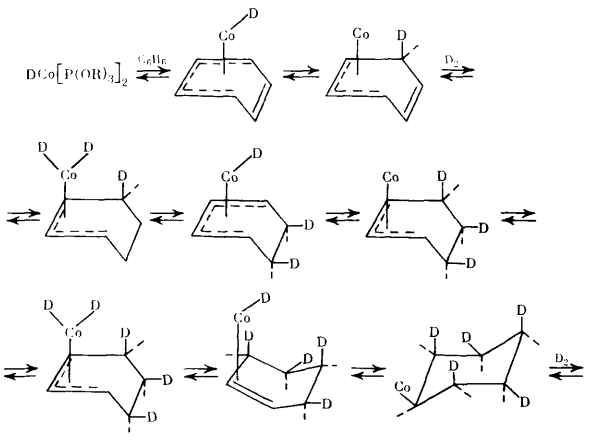
After the addition of four hydrogen atoms, the intermediate

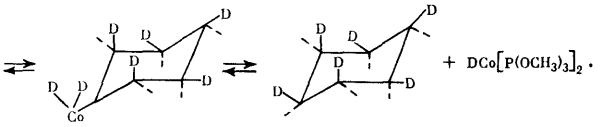


is formed and, after combining with a further two hydrogen atoms, the latter can give rise to vinylcyclohexane and cyclohexenylethane.

Experiments on the deuteriation of benzene using perdeuteriobenzene[49] demonstrated the absence of H–D exchange involving the aromatic ring; thus the hydrogen addition stage is irreversible. The absence of deuterium from the propene evolved after the decomposition of the complex indicates the irreversibility of the decomposition of the latter. Deuteriation of benzene and hydrogenation of C_6D_6 lead to the formation of *cis*-stereoisomers. The deuteriation of the side chain in alkylbenzenes has also been observed.[49,50]

A mechanism has been proposed for the *cis*-deuteriation reaction:[51]

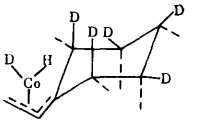




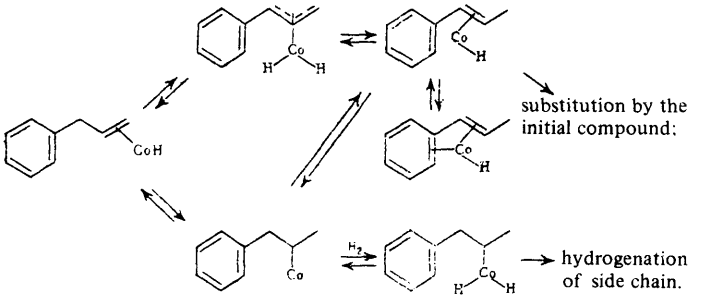
It has been shown that the 14-electron complex, capable of interacting with arenes as η^4-ligands, is catalytically active.

The hydrogenation and deuteriation of aromatic alkyl derivatives in the presence of η^3-$C_3H_5Co[P(OCH_3)_3]_3$ has also been studied.[52] The occurrence of *cis*-deuteriation and of the H–D exchange involving the n-alkyl substituents has been noted; the t-butyl substituent is not deuteriated. Alkyl- and alkenyl-cyclohexenes are formed in the presence of hexene.

The deuteriation of the side chain in substituted benzenes proceeds via the formation of the intermediate complex



according to Bleeke and Muetterties.[52] The same workers[52] explained the complex composition of the allylbenzene hydrogenation products by competing reactions involving the isomerisation of the intermediates and their displacement by the starting material in accordance with the following mechanism:



It has been shown[52] that η^3-$C_8H_{13}Co[P(OCH_3)_3]_3$ also catalyses the hydrogenation of benzene and a rapid stage involving the elimination of η^3-cyclo-octenyl ligand is observed. The hydrogenation mechanism proposed by Hirsecorn et al.[48] has been revised on the basis of the study of the intermediates in the hydrogenation of toluene in the presence of this complex.

According to Bleeke and Muetterties,[52] the catalytically active species is formed via the mechanism

$$\eta^3\text{-}C_8H_{13}Co[P(OCH_3)_3]_3 \rightleftarrows \underset{\text{(VI)}}{\eta^3\text{-}C_8H_{13}Co[P(OR)_3]_2} + P(OR)_3 ;$$

$$\text{(VI)} \xrightarrow{H_2} \underset{\text{(VII)}}{HCo[P(OR)_3]_2} + C_8H_8 ;$$

$$\text{(VII)} \xrightarrow{P(OR)_3} \underset{\text{(VIII)}}{HCo[P(OR)_3]_3} \overset{H_2}{\rightleftarrows} \underset{\text{(IX)}}{H_2Co[P(OR)_3]_3} ;$$

$$\text{(VIII)} \xrightarrow{P(OR)_3} \underset{\text{(X)}}{HCo[P(OR)_3]_4} .$$

In the absence of the arene, the inactive complexes (IX) and (X) are obtained, while in its presence hydrogenation takes place via the mechanism

$$HCo[P(OR)_3]_2(\eta^4\text{-}C_8H_8) \rightleftarrows \eta^3\text{-}C_8H_{13}Co[P(OR)_3]_2 \overset{H_2}{\rightleftarrows}$$
$$\rightleftarrows \eta^3\text{-}C_8H_{13}CoH_2[P(OR)_3]_2 \rightleftarrows HCo[P(OR)_3]_2(\eta^4\text{-}C_8H_8) \text{ etc.}$$

The main disadvantages of the η^3-$C_3H_5Co[P(OCH_3)_3]_3$ catalyst are its low stability and low activity.

Attempts have been made[53] to increase the stability and activity of the complexes by varying the ligand environment. The relative rates of hydrogenation of benzene in the presence of a series of phosphine and phosphite complexes are as follows:

η^3-$C_3H_5Co[P(OCH_3)_3]_3$ (1), η^3-$C_3H_5Co[P(OC_2H_5)_3]_3$ (2),
η^3-$C_3H_5Co[P(OCH_3)_3]_2P(OC_3H_7\text{-iso})_3$(4),
η^3-$C_3H_5Co[P(CH_3)_3]_3$ (5), η^3-$C_3H_5Co[P(OC_3H_7\text{-iso})_3]_3$ (30),
η^3-$C_3H_5Co(CO)_3$ (0), $ONCo[P(OC_3H_7)_3]_3$ (0).

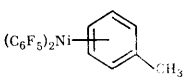
The increase of the activity of the complex was accompanied by a decrease of its stability. The complexes investigated contain the allyl ligand, which reacts readily ($\eta^x \rightleftarrows \eta^{x-2}$) as well as phosphine or phosphite ligands, which ensure a high electron density at the metal atom promoting the activation of H_2, and dissociate with a low activation energy.

However, the suggested intermediate $C_3H_5CoH_2L_3$ decomposes readily to an inactive hydride. Therefore a more stable catalyst would be one containing an η^x-ligand or a redox-ligand, which has either undergone ready conversion into the η^{x-2}-form or has been involved in electron transfer between the metal and the ligand; these transformations must not be accompanied by the elimination of the H ligand. The ON ligand, for example, is of this type but the complex containing it proved to be inactive in hydrogenation.[53]

It has been possible to synthesise the stable complex[54] η^6-$C_6(CH_3)_6$Ru-η^4-$C_6(CH_3)_6$, which is capable of catalysing the hydrogenation of benzene at 90 °C and a pressure of 2–3 atm. The hexamethylbenzene ligand proved to be resistant to both hydrogenation and competitive displacement by the substrate and the reaction products. The stereoselectivity of the complex was found to be lower than that of η^3-$C_3H_5Co[P(OCH_3)_3]_3$. The ratio of the *cis*- and *trans*-isomers is 9 : 1 and 9 : 2 respectively after the hydrogenation of *o*- and *p*-xylenes. In the hydrogenation of benzene and xylenes considerable amounts of cyclo-olefins were detected. For benzene, *o*-xylene, and *p*-xylene, the amounts are 5, 40, and 55% respectively. In the presence of η^6-$C_6(CH_3)_6$Ru-η^4-$C_6(CH_3)_6$, intense H–D exchange takes place. The hydrogenation of C_6D_6 and the deuteriation of C_6H_6 involve the formation of cyclohexanes containing between zero and 12 deuterium atoms, $C_6H_6D_6$ predominating. The catalyst ligands are also deuteriated. The deuteriation of the alkyl substituent predominates in toluene.[54]

The stability of the complex is determined by the resistance of the ligands to reduction by hydrogen. The transition of the arene to the η^4-state in bis(hexamethylbenzene)ruthenium(0) requires a low activation energy (16 kcal mole^{-1}).[55] In complexes where the activation energy for this process is higher, the hydrogenation of benzene is difficult, as happens for example, in the case of $CH_3C_6H_5TiAl_2Cl_8$.[55]

η^6-Toluenebis(pentafluorophenyl)nickel(II) proved to be a catalyst capable of hydrogenating benzene and toluene at 100 atm at 25 °C:[56]



It is fairly unstable and decomposes with formation of nickel and C_6F_5H.

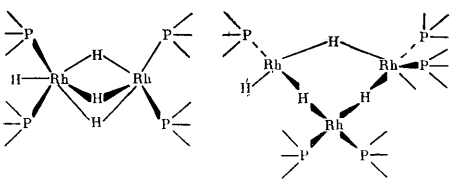
The reduction of the complex $RuCl_2(C_6Me_6)(PPh_3)$ with sodium tetrahydroborate, lithium tetrahydroaluminate, or an isopropyl alcohol solution of sodium carbonate leads to the formation of $RuHCl(C_6Me_6)(PPh_3)$, which is capable of hydrogenating benzene even at room temperature.

Treatment of the complex $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ with a solution of sodium carbonate in isopropyl alcohol makes it possible to obtain the complex $[(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}H_2)(\mu\text{-}Cl)Ru(\eta^6\text{-}C_6Me_6)]Cl$. Benzene is hydrogenated to cyclohexane in the presence of this catalyst, the turnover number of the reaction amounting to 4.1 min^{-1}. At 50 °C and a pressure of 50 atm in the course of 36 h, the catalyst effects the quantitative hydrogenation of styrene to ethylcyclohexane, of anisole to methoxycyclohexane, of methyl benzoate to methyl cyclohexanoate, and of acetophenone and benzophenone to the corresponding cyclohexyl ketones. The hydrogenation of phenol to cyclohexanol, of nitrobenzene to aniline, of dimethylaniline to cyclohexylamine, and of phenylacetylene to ethylbenzene and styrene proceeded less vigorously.[58] Halogenobenzenes were converted into cyclohexane. The halogeno-substituent was retained in the cyclohexane ring only in the case of fluorobenzene.[58]

The complex η^3-$C_3H_5RhL_2$, where L = $P(OC_3H_7\text{-iso})_3$, is an extremely short-lived catalyst of the hydrogenation of aromatic hydrocarbons.[59] The complexes where L = $P(OEt)_3$ and $P(OMe)_3$ are inactive. The above complexes interact with hydrogen in accordance with the mechanism

$$6H_2 + 3\eta^3\text{-}C_3H_5RhL_2 \rightarrow 3C_3H_8 + (HRhL_2)_3;$$
$$7H_2 + 3\eta^3\text{-}C_3H_5RhL'_2 \rightarrow 3C_3H_8 + H_3RhL'_4 + (HRhL'_2)_2.$$

The clusters formed under these conditions are capable of catalysing the hydrogenation of benzene and alkylbenzenes to the corresponding cyclohexanes. The hydrogenation of *p*-xylene proceeds with the intermediate formation of *cis*-1,4-dimethylcyclohexane, while *o*-xylene is hydrogenated more slowly, the *cis*- and *trans*-isomers being formed in equimolar amounts. In the hydrogenation of benzene derivatives containing unsaturated substituents of the olefinic type, both the aromatic ring and the substituent are reduced. It is of interest to note that the above compounds prevent the hydrogenation of benzene when they are introduced jointly into the reaction mixture.[60] Deuteriation in the presence of these complexes involves vigorous deuterium–hydrogen exchange. According to Sivak and Muetterties,[60] the bridged hydrides



function as the catalytic species.

The *p*-tolyl complexes $(p\text{-tol})_4Cu_2Rh_2$ and $(p\text{-tol})_4Au_2Rh_2$ are active in the hydrogenation of benzene and naphthalene at 1 atm at 20 °C.[61]

$(RhCl.cyclo\text{-}octadiene)_2$, reduced with an equimolar amount of n-butyl-lithium, catalyses the hydrogenation of benzene to cyclohexane and of naphthalene to *cis*- and *trans*-decalins under normal conditions; styrene and phenylacetylene are reduced to ethylcyclohexane, while stilbene is reduced to 1,2-dicyclohexylethane.[62]

A complex of analogous activity has been obtained by the reaction[63]

$$RhCl(H_2C{=}CH_2)_2 + \text{n-BuAuLiEt}_2O \rightarrow Au^0/Rh^0.$$

Hydrogenation catalysts which incorporate unsaturated hydrocarbon ligands in the coordination sphere during the reaction or after appropriate treatment have been described in a number of investigations.[64–68]

The coupled hydrogenation of arenes together with alkenes or dienes has been achieved in the presence of the system $AlR_3 + Co(C_5H_7O_2)_2 + P(C_4H_9)_3$, where $C_5H_7O_2$ = acetylacetonate.[64] The hydrogenation of benzene is ten times faster than that of cyclohexene, which is formed in apreciable amounts together with cyclohexane in the benzene hydrogenation reaction. After the complete conversion of alkenes or dienes into saturated hydrocarbons, the hydrogenation of arenes ceases. The activity of the catalyst increases as the temperature is reduced from 30° to 5 °C. $H_3Co[P(C_4H_9)_3]_3$ also catalyses the joint hydrogenation of arenes and alkenes, but its activity is lower. σ-Alkylcobalt, containing one or two phosphite ligands and an arene, has been suggested as the catalytically active species.[64]

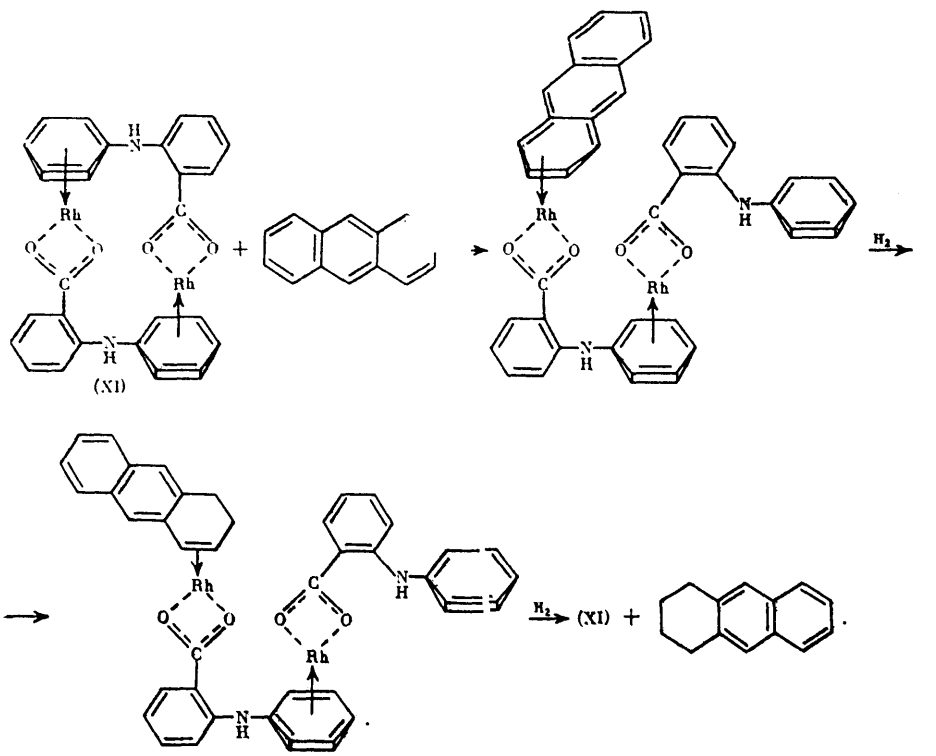
The complexes $(Al)(MR)Co(ML)_2$ (where Ar = aromatic hydrocarbons, R = alkyl, M = Li, MgBr, or AlR_2, and L = chelating ligands with carbonyl or imino-groups), $Co(PR_3)(RCH{=}CH_2)_2(AlEt_3)$ (where R = alkyl or aryl), and $Co(1,5,9\text{-}trans,trans,cis\text{-}C_{12}H_{18})(AlEt_3)$ are also capable of effecting the coupled hydrogenation of arenes and alkenes under mild conditions, benzene being hydrogenated to cyclohexene with a selectivity of 25–30%.[65]

Chlorotris(triphenylphosphine)rhodium (Wilkinson's complex) is incapable of catalysing the hydrogenation of aromatic compounds because of the presence of ligands with a tendency towards a dative interaction. However, the hydrogenation of benzene has been observed in the presence of Wilkinson's complex subjected to preliminary oxidation in a benzene solution. Cyclohexane is apparently formed as a result of the reduction of the aryl ligand in the intermediate oxidised complex.[66]

4. Metal Complexes with Ligands of the Aminoacid Type

The possibility of hydroxylating polycyclic aromatic compounds in the presence of rhodium complexes with strong π-donor systems such as naphthacene and *N*-phenylanthranilic acid has been demonstrated.[69] The rhodium complex of naphthacene makes it possible to hydrogenate the latter at 80 °C and a hydrogen pressure of 50 atm in dimethylformamide solution with formation of 1,2,3,4-tetrahydronaphthacene and a small amount of *sym*-octahydronaphthacene. Anthracene is hydrogenated to 1,2,3,4-tetrahydroanthracene under the same conditions in the presence of the rhodium complex of *N*-phenylanthranilic acid; the yields are fairly high also at room temperature and atmospheric pressure.[69]

The rhodium complexes of *N*-phenylanthranilic acid, other aminoacids, and aromatic carboxylic acids are active in the hydrogenation of naphthalene, phenol, and other aromatic hydrocarbons as well as their derivatives.[70–72] Experiments were performed at 20 °C and atmospheric pressure using a dimethylformamide solution of the catalyst. The initial rates of hydrogenation in the rhodium–*N*-phenylanthranilic acid system[72] decrease in the sequence anthracene > fluorene > fluoranthrene > naphthalene > pyrene > chrysene > benzene. Naphthalene is hydrogenated successfully to tetralin and decalin, benzene is hydrogenated to cyclohexane, and anthracene is hydrogenated to 1,2,3,4-tetrahydroanthracene. The structure of the complex was investigated by a wide variety of physicochemical methods.[73,74] A mechanism for the hydrogenation of anthracene has been proposed on the basis of investigations of the H–D exchange reaction of anthracene:[72]



In conclusion of the Sections devoted to the metal complex catalysts for the hydrogenation of aromatic hydrocarbons, it is necessary to consider catalytic systems of a kind which strictly speaking do not form part of any of the types examined.

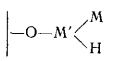
The chlorobishexa-1,5-dienerhodium complex has been used for the hydrogenation of arenes under conditions of catalysis with phase transfer.[75] The hydrogenation of a number of phenyl and benzyl ketones, benzene, phenol, and naphthalene has been investigated under mild conditions. The selectivity of the reaction was not always sufficiently high.

A system containing a hydrogen activator and a catalyst for the transfer of the activated hydrogen to the substrate has been proposed.[76,77] The use of Adams platinum as the hydrogen activator and titanium chloride complexes with various ethers as hydrogen transferring agents made it possible to hydrogenate benzene at room temperature and atmospheric pressure. Apart from cyclohexane, appreciable amounts of cyclohexene and cyclohexadiene are formed in the mixture and their relative amounts are not influenced by the duration of the hydrogenation process. Catalytically active species $[HTiL_{4-n}Cl^{+}_{n-1}]Pt$ arises in the reduction of the complex cation $TiL_{4-n}Cl^{+}_{n-1}$ by molecular hydrogen in the presence of PtO_2. The insertion of benzene in the Ti–H bond and the subsequent hydrogenation of the complex formed led to the formation of the reaction products.[76]

5. Polymer-containing Catalysts

The attempts to eliminate certain disadvantages of the homogeneous metal complex catalysts which limit their industrial application led to the creation of complexes containing organic and mineral polymers and macroligands. Whereas the mineral polymers are mainly used as heterogenising supports bound chemically to the metal complex, two applications are possible for organic polymers: either for the heterogenisation of the complex or for the synthesis of metal complexes with monodentate and polydentate macroligands whose solubility can often be varied reversibly depending on the stage of the process. A description of the properties of the metal-polymer complexes and the applications of catalysts can be found in other reviews.[78,79] The hydrogenation of aromatic hydrocarbons in the presence of these systems has been vigorously studied recently.

Systems which are tentatively similar to Ziegler catalysts and are capable of hydrogenating C_6–C_{30} aromatic hydrocarbons have been obtained by impregnating a suitable inorganic carrier having surface hydroxy-groups with a transition metal salt and subsequent treatment with trialkylaluminium or a similar compound.[80–82] A mechanism has been proposed[82] for the formation of intermediate active species of the type



where M = Fe, Ni, Co, or Cu and M′ is a Group I–III metal atom. Although the authors do not quote experimental data confirming rigorously the formation of such species, their hypothesis agrees with data obtained in a study[79] devoted to analogous catalysts.

In the interaction of polystyrene with (η^6-cyclo-octa-1,3,5-triene)(η^4-cyclo-octa-1,5-diene)ruthenium(0) the ligands are substituted by the benzene rings of polystyrene.[83,84] The resulting complex is an active catalyst of the hydrogenation of aromatic compounds (Table 5). Ru_2-1,3-diphenylpropane, obtained by a similar procedure from diphenylpropane, exhibits an analogous activity.[84] The increase of the number of benzene rings to more than two per metal atom lowers the activity of the catalyst.

Table 5. Hydrogenation of aromatic compounds in the presence of the Ru(0)–polystyrene catalyst.[83]

Substrate	a*	p_{H_2}, atm	t, °C	τ, h	Product**
Benzene	135	59	20	6	Cyclohexane
Benzene***	135	50	20	6	Cyclohexane
Toluene	90	50	20	6	Methylcyclohexane
Hexamethylbenzene	37	70	140	10	Hexamethylbenzene
Naphthalene	37	70	140	10	Naphthalene
Phenol	135	50	80	7	Cyclohexanol
Nitrobenzene	185	50	80	10	Cyclohexylamine

*Substrate : catalyst molar ratio.
**The content of the product or the substrate which failed to react is close to 100%.
***Re-use of the catalyst.

Table 6. Hydrogenation of aromatic compounds in the presence of the rhodium–anthranilic acid–polystyrene catalyst[90]).

Substrate (content, mmol)	K*, mmol	τ, h	p_{H_2}, atm	t, °C	Product (yield, %)
Benzene (230)	3	18	3.4	20	Cyclohexane (99)
Benzene (230)	0.35	18	68	20	Cyclohexane (12)
Benzene (230)	0.35	5	68	100	Cyclohexane (25)
Benzene (230)	0.35	3	68	180	Cyclohexane (10)
Benzene (115)	0.044**	6	41	70	Cyclohexane (9)
Toluene (90)	0.2	18	3.4	20	Methylcyclohexane (15)
p-Xylene (160)	0.2	14	68	100	***
Ethyl benzoate (90)	0.2	20	68	100	****
Naphthalene (70) + benzene (110)	0.2	3	68	70	1,2,3,4-Tetrahydronaphthalene (100); cyclohexane (80)

*Amount of catalyst.
Catalyst stored in air for 1.5 years.
***Hydrogenation takes place to the extent of 10%.
Traces of hydrogenation.

A number of studies have been devoted to catalysts based on complexes of anthranilic and *N*-phenylanthranilic acid using polymeric macroligands. The rhodium and ruthenium complexes of *N*-phenylanthranilic acid, bound to phosphinated polystyrene or an inorganic carrier, catalyse the hydrogenation of benzene, anthracene, and 6-ethylchrysene.[85] The catalyst is obtained by the interaction of the finished complex with the carrier.

Another approach to the synthesis of the deposited complex is possible, namely by treating chloromethylated polystyrene with anthranilic or *N*-phenylanthranilic acid and then with a metal salt, this being followed by the reduction of the intermediate complex.[86–89] The catalyst prepared using *N*-phenylanthranilic acid did not show catalytic activity; an active catalyst was obtained from anthranilic acid. The rhodium and ruthenium catalysts effect the hydrogenation of benzene

at room temperature and a hydrogen pressure of approximately 2 atm. Under more severe conditions (100 °C, 20 atm H_2) the palladium catalyst permits the hydrogenation of benzene and *p*-xylene.

The rhodium complex of anthranilic acid bound to chlormethylated polystyrene has been studied in detail[90] (Table 6). According to the results of elemental analysis, the molar ratio of the anthranilate anions and rhodium in the catalyst is 3 : 1. The metal atoms are mainly distributed on the surface of the carrier. Only 3% of the chloromethylated groups of the initial polymer react with anthranilic acid. Analysis by X-ray electron spectroscopy (AXES) shows that the oxidation state of rhodium in the complex is +1. It is of interest that the nickel analogues are inactive in the hydrogenation of aromatic compounds.[91]

Table 7. Hydrogenation of aromatic compounds in the presence of rhodium complexes of carboxyl-containing polymers.[92,93,126]

Substrate	Polymer*	t, °C	n**, h^{-1}	Reaction products (yield, %)
Benzene	STMC	30	51	Cyclohexane (100)
Benzene	PAA	30	85	Cyclohexane (100)
Toluene	PAA	20	19	Methylcyclohexane (100)
Nitrobenzene	STMC	30	11	Aniline (58)
Nitrobenzene	PAA	30	23	Aniline (77)
Phenol	STMC	50	34	Cyclohexanol (100)

*Here and henceforth PAA = polyacrylic acid and STMC = styrene–maleic acid copolymer.
**Turnover number of reaction.

Effective catalysts for the hydrogenation of the aromatic ring of benzene and its derivatives[92,93,126] (Table 7) have been obtained from rhodium complexes of carboxyl-containing polymers—such as polyacrylic acid and the styrene—maleic acid copolymer. The catalyst is prepared by adding rhodium tetrahydroborate to a solution containing the polymer and a rhodium salt. Under mild conditions (atmospheric pressure, 30 °C), it has been possible to hydrogenate benzene quantitatively to cyclohexane with a selectivity of 100%. The catalysts are extremely active in the hydrogenation of phenol to cyclohexanol and cyclohexanone. Apart from the reactions listed in Table 7, these catalysts are active in the hydrogenation of benzaldehyde, benzyl alcohol, and t-butylbenzene.

Treatment with hydrogen of the complex $Rh_2Cl_2(C_2H_4)_2$ deposited on chlormethylated and phosphinated cross-linked polystyrene[94] or of $Rh_2Cl_2(CO)_4$ deposited on the same polymer,[95] on SiO_2, or on polyphenylsiloxane, with both supports modified by phosphine groups,[96] leads to the formation of finely dispersed metallic rhodium which is active in the hydrogenation of benzene. Wilkinson's complex on modified SiO_2 and polyphenylsiloxane is not reduced and does not effect the hydrogenation of benzene.[96]

The formation of rhodium clusters has been detected in benzene solution following the interaction of $Rh_6(CO)_{16}$ with a film of cross-linked phosphinated polystyrene. At 80 °C and 1 atm the resulting catalyst reduces benzene with a low degree of conversion.[97] Aggregation of the clusters leads to an increase of the activity of the catalyst. The relation between the degree of aggregation of the hexa-atomic rhodium clusters and the catalytic activity has been studied.[98] The catalyst was prepared by impregnating silica gel with an $Rh_6(CO)_8$ solution and drying. Benzene was hydrogenated in a flow system. It has been shown[98] that particles with diameters less than 1.4 nm, consisting of six rhodium atoms, are catalytically inactive. The most active particles are 1.4–2.0 nm in size and contain 2–3 hexa-atomic clusters.

Catalysts having the general formula

$$\left[\left(\begin{array}{c}-CH_2-CH_2-N- \\ \\ R\end{array}\right)_n MX_q\right]_m$$

$R = H$; C_{1-7}^{alkyl}, $C_6H_5CH_2CH_2$, $(CH_3)_3SiCH_2CH_2$, CH_3CO, C_6H_5CO; $n = 2, 4, 8, 16$, $m = 4$–200; $X = Cl, Br$; $q = 2, 4$; $M = Pt(IV)$, $Pd(II)$, $Ni(II)$, $Co(II)$, $Fe(III)$.

(the metal : nitrogen ratio varies from 1 : 2 to 1 : 16) are capable of effecting the quantitative hydrogenation of benzene to cyclohexane at 50 °C and a 100 atm pressure.[99]

The hydrogenation of *p*-nitrophenol at room temperature and atmospheric pressure with formation of 4-aminocyclohexanol has been described.[100] A catalyst prepared on the basis of rhodium, ruthenium, or iridium and polyvinylpyrrolidinone was used for this purpose.

Numerous studies have been devoted to the hydrogenation of aromatic compounds in the presence of metal complexes of polyamides. The first investigations in this field refer to the hydrogenation of benzene in the presence of a platinum–polyamide catalyst prepared on the basis of polymers obtained from caprolactam, hexamethylenediamine, and the β-lactam of β-aminosebacic acid.[101] A high yield of cyclohexene has been noted in some instances. The occurrence of two-point adsorption of benzene on the active centres has been suggested.

Dini et al.[102] also noted the selectivity of platinum–polyamide catalysts in the hydrogenation of benzene to cyclohexene. The reaction was carried out in a pulse apparatus at 140–190 °C. The authors explained the low degree of adsorption of hydrogen on the catalyst by the fact that the catalytically active species are compounds of platinum in which the degree of oxidation is non-zero.

The metal–nylon complexes catalysing the hydrogenation of benzene have been investigated.[103–106] Detailed study of the platinum–nylon complex[104] has shown that the optimum composition of the catalyst is attained when there are eight peptide groups per platinum atom. The authors suggest that it is unlikely that stable eight-membered chelate complexes are formed under the reaction conditions[104] and the complex apparently contains one peptide group. It has been shown that, when halogen substituents are introduced into the benzene ring, the rate of hydrogenation diminishes, which has been attributed to a decrease of the ionisation potential and the formation of an unduly stable substrate–catalyst complex.[102] Apart from the change in the ionisation potential of the substrate, steric hindrance plays a significant role in the hydrogenation of alkylbenzenes.

The hydrogenating activities of various metals in the nylon complexes have been examined.[105,106] It has been shown that the capacity for the formation of complexes with nylon varies in the sequence Pt > Pd > Rh > Ir, while the activities of the nylon complexes in the hydrogenation of benzene vary in the sequence Ir > Pt > Rh > Pd. The optimum ratio of the number of polyamide units to that of the metal atoms is four for rhodium and palladium, in contrast to platinum, the activity of the palladium complex proving very low in the hydrogenation of benzene. However, one should note that sufficiently rigorous evidence has not been presented[102–106] for the existence of complexes in the course of the reaction; one cannot rule out the possibility that the metallic phase is active.[107,108]

The hydrogenation of benzene on atomically dispersed platinum on nylon has been investigated[107,109] and the influence of the specific surface on the activity has been demonstrated.[107] The unusually high selectivity of the platinum–nylon catalyst with respect to cyclohexene has been explained by the weak adsorption of benzene on the catalyst.[109] It has been suggested that benzene forms a π-bond with only one metal atom. In this case hydrogen does not add as a result of a surface reaction (as in the metal) but involves the bonds conjugated with those participating in the formation of the π-complex. The double bond which has not been hydrogenated remains unavailable for the addition of hydrogen.

III. HYDROGENATION OF HETEROCYCLIC COMPOUNDS

Many fewer studies have been made of the hydrogenation of heterocyclic compounds on metal complex catalysts. The reason for this is apparently the risk that the formation of stable complexes of heterocycles with the metal ion might deactivate the complex. Since hydrogenation under severe hydroformylation conditions makes it possible to avoid the poisoning effect of even sulphur-containing heterocycles, this reaction has been studied to the greatest extent. Thus the hydrogenation of furan derivatives has been described.[21] At 180 °C and pressures of the H_2 + CO (2 : 1) mixture of about 200 atm in the presence of $Co_2(CO)_8$ furan is converted in the course of 4 h into 2-tetrahydrofurfuryl alcohol to the extent of 35%, while 2,5-dimethylfuran is converted into 2,5-dimethyltetrahydrofurfuryl alcohol to the extent of 23%.

The hydroformylation of 5,6-dihydro-4*H*-pyrans is accompanied by the saturation of the pyran ring.[110] The product consisted of 78% of 2-hydroxymethyltetrahydropyran, 8% of 3-hydroxymethyltetrahydropyran, and 3% of tetrahydropyran. In addition, reactions of other dihydropyrans have been investigated at a pressure of the mixture of equimolar amounts of carbon monoxide and hydrogen of 300 atm and a temperature of 190 °C in the presence of dicobalt octacarbonyl.[110]

Table 8. Hydrogenation of thiophen and its derivatives under hydroformylation conditions*.[111]

Substrate	a**	τ, h	Reaction product (yield, %)
Thiophen	14.7	5	Thiophan (50)
Thiophen	5.9	4	Thiophan (66)
2-Methylthiophen	22.7	5	2-Methylthiophan (77)
2-Ethylthiophen	9.1	3	2-Ethylthiophan (82)
2,5-Dimethylthiophen	18.3	5	2,5-Dimethylthiophan
2-Thenyl alcohol	15.0	4	2-Methylthiophen (24); 2-methylthiophan (57)
2-Acetylthiophen	15.6	9	2-Ethylthiophen (52); 2-ethylthiophan (26)

*Temperature 180 °C, pressure of H_2 : CO = 2 : 1 mixture 22 atm, catalyst–dicobalt octacarbonyl.
**Substrate : catalyst molar ratio calculated per metal atom.

The reduction of thiophen derivatives under hydroformylation conditions has been described[111] (Table 8). Sometimes cobalt is introduced in the form of the carbonate instead of the octacarbonyl, but in all cases the active species is cobalt hydrocarbonyl. It is especially interesting that substituted thiophens are reduced more readily than thiophen itself. It has been shown that the hydrogenation is irreversible, this being indicated by the stability of thiophan under the reaction conditions.[111]

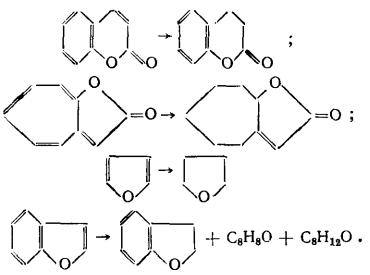
The hydrogenation of nitrogen-containing heterocycles has been investigated in the presence of various metal carbonyls and carbonyl phosphite complexes.[22,26,112–115] Pyridine is converted into a mixture of *N*-formyl- and methyl-pyridines at 200 °C under a pressure of an equimolar mixture of carbon monoxide and hydrogen of 410 atm.[112] At a lower pressure (213 atm), dihydro-derivatives of 2-methyl- and 2-phenylindoles have been obtained[113]. In both cases cobalt was introduced into the reaction mixture in the form of the metal or salts.

It has been shown[25,26,114,115] that the carbonyl and carbonyl phosphine complexes promote the preferential hydrogenation of the heteroring in bicyclic and polycyclic nitrogen-containing heterocycles.

Catalysts of the Ziegler type, which are also frequently used under severe conditions, have been used mainly for the hydrogenation of pyridine heterocycles. Thus the hydrogenation of pyridine to piperidine has been described.[32,34] Quinoline[116] is hydrogenated in the presence of cobalt acetylacetonate activated with AlR_3 (where R = alkyl or alkoxy-group) with formation of 78% of 1,2,3,4-tetrahydroquinoline, 9% of 5,6,7,8-tetrahydroquinoline, and 2% of decahydroquinoline (cobalt : aluminium = 10, H_2 pressure 68 atm, 90–100 °C). Only 17% of 1,2,3,4-tetrahydroquinoline is formed under the same conditions in the presence of diethyl sulphide.

The catalyst based on cobalt 2-ethylhexanoate makes it possible to hydrogenate furan to tetrahydrofuran to the extent of 95% at 20 °C and an H_2 pressure of 50–60 atm in the course of 4 h.[35]

Table 4 shows that the catalyst η^3-$C_3H_5Co[P(OCH_3)_3]_3$ is capable of hydrogenating oxygen-containing heterocycles under mild conditions.[49] The following reactions have been carried out using this catalyst:[49]

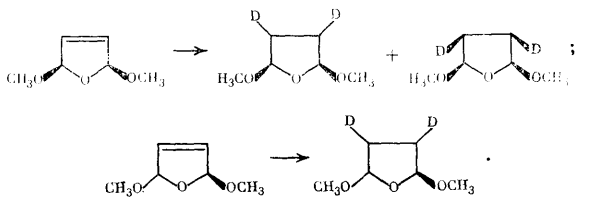


Overall, the hydrogenation is slow and the yields of reaction products are low.

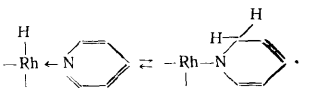
It has been stated[71,117] that the rhodium complexes of anthranilic and *N*-phenylanthranilic acids, L-tyrosine, aspartic acid, and α-piperidinoacetophenone oxime catalyse the hydrogenation of pyridine, quinoline, pyrrole, furan, dibenzofuran, and thiophen.

Chlorotris(triphenylphosphine)rhodium, which is known to be inactive in the hydrogenation of benzene, has been used for the stereoselective deuteriation of the double bond in

substituted 2,5-dihydrofurans.[118] 2,5-Dimethoxy-2,5-dihydrofurans are deuteriated in the *cis*-positions, the *cis*-isomer giving rise to a mixture of products:



Treatment of the complex $RhCl_3Py_3$ (where Py = pyridine) with sodium tetrahydroborate in dimethylformamide leads to the formation of $Py_2DMF.RhCl_2BH_4$.[119,120] The complex is capable of catalysing the reduction of pyridine to piperidine and of quinoline to 1,2,3,4-tetrahydroquinoline; the reaction proceeds under mild conditions at low rates. Isoquinoline and indole are not reduced. It is believed that the hydrogenation begins with hydrogen transfer:[20]



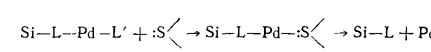
This is followed by the addition of hydrogen to the hydropyridine complex.

The hydrogenation of quinoline using metallophthalocyanine catalysts at temperatures in the range 300–400 °C and pressures up to 200 atm takes place selectively with formation of 1,2,3,4-tetrahydroquinoline.[121] The hydrogenation of thiophen and sulpholene in the presence of mononuclear and polynuclear palladium complexes containing ligands of different types linked to silica gel has been investigated.[122–124] Sulpholene is readily reduced to sulpholan, while thiophen is reduced with much more difficulty to thiophan (1 atm H_2, 20 °C, in isopropyl alcohol). The activation of H_2 has been suggested as the rate-limiting stage for the mononuclear complexes. Enhancement of the electron-donating properties of the ligand lowers the instability constant of the complex and the equilibrium concentration of the hydride formed in accordance with the equation

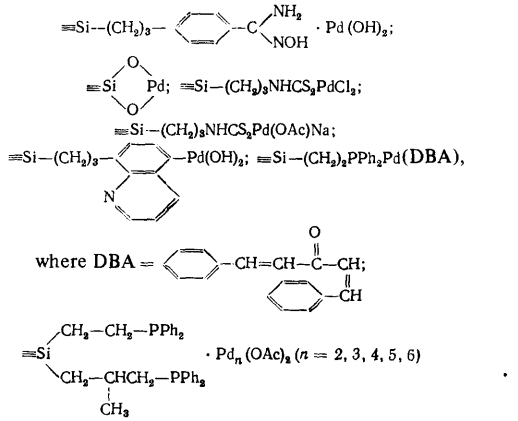
$$\equiv Si-L-Pd^{II} + H_2 \rightleftarrows [\equiv Si-L-Pd^{II}-H]^- + H^+.$$

The rate of hydrogenation of sulpholene is reduced as a consequence.

With increase of the number of palladium atoms in the cluster complex from 2 to 6, its activity in the hydrogenation of sulpholene also rises, but the activity in the hydrogenation of thiophen changes only slightly. The low activity of the catalysts in the hydrogenation of thiophen can be explained by the difficulty of activating the substrate and the poisoning of the catalyst by the reaction product, the complex being decomposed in certain instances in accordance with the mechanism



In the hydrogenation reaction in dimethylformamide, which is capable of entering into a complex formation reaction in competition with the metal, the catalysts are more stable. Enhancement of the electron-donating properties of the ligands in the mononuclear complexes promotes an increase of the stability of the complexes in the hydrogenation of thiophen, since the ability of the metal ion to coordinate to the sulphur heteroatom is then reduced.[122–124] The following compounds have been used as catalysts:



The catalysts prepared from carboxyl-containing polymers and platinum-group metal salts, which exhibited an activity in the hydrogenation of benzene, proved to be extremely active and selective in the hydrogenation of oxygen-containing compounds[92,93,125–128] (Table 9).

Table 9. Hydrogenation of heterocyclic compounds in the presence of catalysts prepared from carboxyl-containing polymers.[92,93,125–128]

Substrate	Catalyst*	t, °C	n**, h^{-1}	Reaction product (yield, %)
Furan	Rh-STMC	30	52	Tetrahydrofuran (100)
2-Methylfuran	Rh-STMC	30	113	2-Methyltetrahydrofuran (100)
Benzofuran	Pd-STMC	30	53	2,3-Dihydrobenzofuran (100)
1,4-Benzodioxan	Rh-PAA	30	7	Hexahydro-1,4-benzodioxan (32)
6-Nitro-1,3-benzodioxan	Rh-PAA	20	4	5-Amino-1,3-benzodioxan (75)
Furfural	Rh-PAA	20	44	Tetrahydrofurfuryl alcohol (96)

*For the significance of the abbreviations, see Table 7.
**The turnover number of the reaction.

Mention should also be made of the hydrogenation of pyridine, quinoline, and furan derivatives under the conditions of catalysis with phase transfer in the presence of rhodium complexes.[75] Fairly high yields of the hydrogenation products were then achieved.

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The above analysis of data for the hydrogenation of aromatic compounds in the presence of metal complex catalysts shows that, despite the large amount of experimental data available, the possibilities for the selection of effective catalysts for the hydrogenation of aromatic hydrocarbons are small. The point is that the rational employment of metal complex catalysts requires the use of comparatively mild conditions, whereupon their ability to propagate processes at high rates is most fully realised, the process being at the same time highly selective and involving a small expenditure of energy. However, the use of active catalysts for the hydrogenation of the above compounds, such as the hydroformylation Ziegler catalysts and some of the complexes

with unsaturated hydrocarbon ligands, requires fairly severe reaction conditions. On the other hand, complexes active under mild conditions are frequently relatively unstable.

In the case of heterocyclic compounds the choice of metal complex hydrogenation catalysts is still more limited apparently owing to the low stability of the majority of the metal complexes investigated and acted upon by heterocycles. The successful solution of this problem involves the selection of a suitable ligand environment for the metal ion, which would stabilise it in the catalytically active state and would thus counteract the poisoning effect of the heterocycle; such stabilising activity of certain ligands can be demonstrated in the deuterium–hydrogen exchange involving thiophen and its derivatives.[15]

Overall, among the catalysts considered in this review, the most stable and effective under mild conditions and sufficiently universal is the rhodium complex of *N*-phenylanthranilic acid. Effective and "technological" catalysts on a polymer carrier have been based on it and it has been established reliably that the metal in such catalysts is in fact present in the form of a complex.

Catalysts based on carboxyl-containing polymers have also exhibited a high activity in the hydrogenation of aromatic and heterocyclic compounds under mild conditions.

The instances quoted above of the successful application of polymer-containing complexes in the hydrogenation of aromatic and heteroaromatic compounds show that the most promising procedure is the creation of effective metal complex catalysts on the basis of polymer-containing complexes, particularly with organic polymers and copolymers, which not only make it possible to heterogenise the catalyst when this is necessary but also can ensure its high stability by functioning as polydentate macroligands.

REFERENCES

1. H.A.Smith, "Catalytic Hydrogenation of Aromatic Compounds", in "Catalysis in the Petrochemical and Petroleum Industry" (Edited by P.Emmett) (Translated into Russian), Gostoptekhizdat, Moscow, 1959, p.184.
2. I.F.Bel'skii and V.M.Shostakovskii, "Kataliz v Khimii Furana" (Catalysis in the Chemistry of Furan), Izd. Nauka, Moscow, 1972.
3. D.Kreile, V.A.Slavinskaya, L.Kruminia, A.Gutmanis, K.Ziemelis, and U.Tomsons, Izv.Akad.Nauk Latv.SSR, 1980, No.10(399), 93.
4. A.V.Mashkina, "Geterogennyi Kataliz v Khimii Organicheskikh Soedinenii Sery" (Heterogeneous Catalysis in the Organic Chemistry of Sulphur Compounds), Izd. Nauka, Novosibirsk, 1977.
5. J.L.Garnett, Catalysis Reviews, 1971, **5**, 229.
6. M.A.Long, R.B.Moyes, P.B.Wells, and J.L.Garnett, J.Catalysis, 1978, **52**, 206.
7. K.Davis, J.L.Garnett, K.Hoa, R.S.Keynon, and M.Long, Proc.V.Int.Congr.on Catalysis, Palm Beach, Florida, 1973, Paper No.31.
8. P.Keith, D.Garnett, and J.Garnett, Austral.J.Chem., 1975, **28**, 1699.
9. I.I.Moiseev, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1977, **22**, 30.
10. I.I.Moiseev, "Problemy Kinetiki i Kataliza" (Problems of Kinetics and Catalysis), Izd.Nauka, Moscow, 1968, Vol.13, p.36.
11. I.I.Moiseev, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1982, **27**, 309.
12. M.E.Vol'pin, I.I.Moiseev, and A.E.Shilov, Zhur.Vses. Khim.Obshch.im.Mendeleeva, 1980, **25**, 515.
13. E.A.Karakhanov, A.G.Dedov, and A.S.Loktev, Khim. Geterotsikl.Soed., 1981, 1332.
14. E.A.Karakhanov and A.G.Dedov, Khim.Geterotsikl. Soed., 1982, 1011.
15. E.A.Karakhanov, A.G.Dedov, A.S.Loktev, L.V.Popov, P.A.Sharbatyan, and I.V.Arkhangel'skii, Khim.Geterotsikl.Soed., 1983, 754.
16. E.L.Muetterties, Science, 1977, **196**, 839.
17. A.K.Smith and J.M.Basset, J.Mol.Catalysis, 1972, 2, 229.
18. B.James, "Homogeneous Hydrogenation" (Translated into Russian), Izd.Mir, Moscow, 1976, 570 pp.
19. R.S.Coffy, "Latest Advances in the Homogeneous Hydrogenation of Carbon–Carbon Multiple Bonds" in "Aspects of Homogeneous Catalysis" (Edited by R.Ugo) (Translated into Russian), Izd.Mir, Moscow, 1973, p.7.
20. F.J.McQuillin, "Homogeneous Hydrogenation in Organic Chemistry" (Translated into Russian), Izd. Khimiya, Moscow, 1980.
21. I.Wender, R.Lewine, and M.Orchin, J.Amer.Chem. Soc., 1950, **72**, 4375.
22. J.W.Rathke and H.M.Feder, J.Amer.Chem.Soc., 1978, **100**, 3623.
23. S.Freedman, S.Metlin, A.Svedi, and I.Wender, J.Org. Chem., 1959, **24**, 1287.
24. P.D.Taylor and M.Orchin, J.Org.Chem., 1972, **37**, 3913.
25. R.H.Fish, A.D.Thormodsen, and G.A.Cremer, J.Amer.Chem.Soc., 1982, **104**, 5234.
26. R.Sweany, S.G.Butler, and J.Halpern, J.Organometal. Chem., 1981, **213**, 487.
27. T.A.Weil, J.Org.Chem., 1974, **39**, 48.
28. H.M.Feder and J.Halpern, J.Amer.Chem.Soc., 1975, **97**, 7186.
29. V.A.Tulupov, Zhur.Fiz.Khim., 1957, **31**, 519.
30. J.W.Larsen and L.W.Chang, J.Org.Chem., 1976, **41**, 3332.
31. Dutch Appl.7 714 290, 1978; Chem.Abs., 1979, **90**, 71 820.
32. V.V.Saraev, F.K.Shmidt, Yu.S.Levkovskii, V.A.Gruznykh, G.M.Larin, and N.D.Malakhova, Koord.Khim., 1979, **5**, 1190.
33. N.Murugesan and S.Sarkar, Indian J.Chem., Sect.A, 1976, **14A**(2), 107.
34. P.Pradyot and S.Sarkar, Tetrahedron Letters, 1977, 2531.
35. S.J.Lapporte and W.R.Shuett, J.Org.Chem., 1963, **28**, 1947.
36. US P.3 205 278, 1965.
37. S.J.Lapporte, Ann.New York Sci., 1969, **158**, 510; Chem.Abs., 1969, **71**, 60 281.
38. G.Bressan and R.Broggi, Chim.Ind.(Milan), 1968, **50**, 1194.
39. I.V.Kalechits, V.G.Lipovich, and F.K.Shmidt, "IV Mezhdunarodnyi Kongress po Katalizu. Simpozium 'Mikhanizm i Kinetika Slozhnykh Kataliticheskhikh Reaktsii'" (The IVth International Congress on Catalysis. Symposium 'The Mechanism and Kinetics of Complex Catalytic Reactions'), Moscow, 1968, Preprint of Report No.25.
40. V.G.Lipovich, F.K.Shmidt, and I.V.Kalechits, Kinetika i Kataliz, 1967, **8**, 939.
41. V.G.Lipovich, F.K.Shmidt, and I.V.Kalechits, Kinetika i Kataliz, 1967, **8**, 1300.
42. Canadian P.915 697, 1972; Chem.Abs., 1973, **78**, 76 413.
43. P.M.Maitlis, Acc.Chem.Res., 1978, **11**, 301.

44. M.J.Russel, C.White, and P.M.Maitlis, Chem.Comm., 1977, 427.
45. P.M.Maitlis, "Inorganic Compounds with Unusual Properties. II Chem.Symp.(Athens, 1978)", Washington, 1979, p.31.
46. E.L.Muetterties and J.R.Bleeke, Acc.Chem.Res., 1979, 12, 324.
47. E.L.Muetterties and F.J.Hirsecorn, J.Amer.Chem.Soc., 1974, **96**, 4063.
48. F.J.Hirsecorn, M.C.Racowski, and E.L.Muetterties, J.Amer.Chem.Soc., 1975, **97**, 237.
49. L.S.Stuhl, M.Du Bois Racowski, F.J.Hirsekorn, J.K.Bleeke, A.E.Stevens, and E.L.Muetterties, J.Amer.Chem.Soc., 1978, **100**, 2405.
50. E.L.Muetterties, M.C.Racowski, F.J.Hirsecorn, W.D.Larson, V.J.Basus, and F.A.L.Anet, J.Amer. Chem.Soc., 1975, **97**, 1266.
51. E.L.Muetterties, Inorg.Chim.Acta, 1981, **51**, 1.
52. J.R.Bleeke and E.L.Muetterties, J.Amer.Chem.Soc., 1981, **103**, 556.
53. M.C.Racowski, F.J.Hirsecorn, L.S.Stuhl, and E.L.Muetterties, Inorg.Chem., 1976, **15**, 2379.
54. J.W.Johnson and E.L.Muetterties, J.Amer.Chem.Soc., 1977, **99**, 7395.
55. E.L.Muetterties, H.Schaffer, R.I.Mink, M.J.Darensbourg, M.Millar, T.Groshens, and K.Klabunde, Inorg. Chem., 1979, **18**, 883.
56. K.J.Klabunde, B.B.Anderson, M.Bader, and L.J.Radnovich, J.Amer.Chem.Soc., 1978, **100**, 1313.
57. M.A.Bennett, T.-N.Huang, A.K.Smith, and T.W.Turney, Chem.Comm., 1978, 582.
58. M.A.Bennett, T.-N.Huang, and T.W.Turney, Chem. Comm., 1979, 312.
59. V.W.Day, M.F.Fredrich, G.S.Reddy, A.J.Sivak, W.R.Pretzer, and E.L.Muetterties, J.Amer.Chem.Soc., 1977, **99**, 8091.
60. A.J.Sivak and E.L.Muetterties, J.Amer.Chem.Soc., 1979, 101, 4878.
61. US P.4 152 303, 1979; Chem.Abs., 1979, **91**, 1 404 227.
62. US P.4 207 213, 1980.
63. US P.4 222 898, 1980.
64. F.K.Schmidt, J.S.Leukowskii, V.V.Saraev, N.M.Ryutina, O.L.Kosinskii, and T.J.Bakunina, React.Kinet.Catal.Letters, 1977, 7, 445.
65. F.K.Schmidt, V.V.Saraev, V.A.Gruznykh, Yu.S.Levkovskii, and G.M.Larin, "Tezisy Dokladov XIII Vsesoyuznogo Chugaevskogo Soveshchaniya po Khimii Kompleksnykh Soedinenii" (Abstracts of Reports at the XIIIth All-Union Chugaev Conference on the Chemistry of Complex Compounds), Moscow, 1978, p.458.
66. R.L.Augustine and J.F.Van Peppen, Chem.Comm., 1970, 571.
67. C.R.Landis and J.Halpern, Organometallics, 1983, 2, 840.
68. F.Pruchnik and A.Litewka, Wiadomosci chemiczne, 1982, **36**, 525.
69. USSR P.271 501, 1870; Byul.Izobret., 1970, No.18.
70. USSR P.891 609, 1981; Byul.Izobret., 1981, No.47.
71. I.Rajca, Pol.J.Chem., 1981, **55**, 775.
72. O.N.Efimov, O.N.Eremenko, A.G.Ovcharenko, M.L.Khidekel', and P.S.Chekrii, Izv.Akad.Nauk SSSR, Ser.Khim., 1969, 855.
73. O.N.Efimov, M.L.Khidekel', V.A.Avilov, P.S.Chekrii, O.N.Eremenko, and A.G.Ovcharenko, Zhur.Obshch. Khim., 1968, **38**, 2668.
74. V.A.Avilov, Yu.G.Borod'ko, V.P.Panov, M.L.Khidekel', and P.S.Chekrii, Kinetika i Kataliz, 1968, 9, 698.
75. K.R.Januszkewicz and H.Alper, Organometallics, 1983, **2**, 1055.
76. T.G.Vaistub, L.I.Samokhvalova, and M.L.Khidekel', Symposium, "Issledovaniya v Oblasti Sinteza i Kataliza Organicheskikh Soedinenii" (Studies in the Synthesis and Catalysis of Organic Compounds), Izd.Saratov Gos.Univ., 1975, p.52.
77. V.V.Abalyaeva, T.G.Vaistub, I.V.Kalechits, L.N.Samokhvalova, Yu.N.Usov, and M.L.Khidekel', in "Kataliticheskie Reaktsii v Zhidkoi Faze. Materialy IV Vsesoyuznoi Konferentsii po Kataliticheskim Reaktsiyam v Zhidkoi Faze" (Catalytic Liquid Phase Reactions. Proceedings of the IVth All-Union Conference on Catalytic Reactions in the Liquid Phase), Alma-Ata, 1974, Part 3, p.680.
78. G.Chauwin, D.Commereuc, and F.Davans, Progr. Polymer Science, 1977, **5**, 95.
79. G.V.Lisichkin and A.Ya.Yuffa, "Geterogennye Metallokompleksnye Katalizatory" (Heterogeneous Metal Complex Catalysts), Izd.Khimiya, Moscow, 1981.
80. Yu.I.Ermakov, A.M.Lazutkin, E.A.Demin, V.A.Zakharov, and Yu.P.Grabovskii, Kinetika i Kataliz, 1972, **13**, 1442.
81. Yu.I.Ermakov, Izv.Sibir.Otd.Akad.Nauk SSSR, Ser. Khim.Nauk, 1976, No.4, 2, 58.
82. US P.3 932 547, 1976; Chem.Abs., 1976, **84**, 7411.
83. S.Cambi, C.Carlini, P.Pertini, and G.Vitulli, XIII Congresso Nationale di Chimia Inorganica, Camerino Universita Degli Studi, Pisa, 1980, E7, p.317.
84. P.Pertini, G.Vitulli, C.Carlini, and F.Ciardelli, J.Mol.Catalysis, 1981, 11, 353.
85. B.P.1 408 013, 1976; Chem.Abs., 1976, **84**, 9429.
86. N.L.Holy, Tetrahedron Letters, 1977, 3703.
87. N.L.Holy, J.Org.Chem., 1978, **43**, 4686.
88. BRD Appl.2 816 321, 1978; Chem.Abs., 1979, **90**, 71 239.
89. N.L.Holy, "Fundamental Research on Homogeneous Catalysis. Proc.I.Int.Conf.on Homogeneous Catalysis" (Corpus Christi, 1978), New York–London, 1979, Vol.3, p.691.
90. N.L.Holy, J.Org.Chem., 1979, **44**, 239.
91. N.L.Holy, J.Org.Chem., 1980, **45**, 1418.
92. USSR P.1 034 761, 1983; Byul.Izobret., 1983, No.3.
93. E.A.Karakhanov, A.G.Dedov, A.S.Loktev, V.S.Pshezhetskii, and T.S.Lebedeva, Dokl.Akad.Nauk SSSR, 1984, **275**, 1098.
94. A.Guyot, C.Graillat, and M.Bartholin, J.Mol.Catalysis, 1977, 3(1–3), 39.
95. M.Bartholin, C.Graillat, and A.Guyot, J.Mol.Catalysis, 1981, **10**, 361.
96. M.Bartholin, C.Graillati, A.Guyot, G.Coudurier, J.Baudiera, and C.Naccahe, J.Mol.Catalysis, 1977, 3(1–3), 17.
97. M.S.Jarrell, B.C.Gates, and E.D.Nicolson, J.Amer. Chem.Soc., 1978, **100**, 5727.
98. W.F.Graydon and M.D.Lagnan, J.Catalysis, 1981, **69**(1), 180.
99. USSR P.611 908, 1978; Byul.Izobret., 1978, No.23.
100. BRD Appl.2 835 943, 1980; Chem.Abs., 1980, **93**, 81 265.
101. D.P.Harrison and H.F.Rase, Ind.Eng.Chem.Fundam., 1967, **6**(2), 161.
102. P.Dini, D.Dones, S.Montelatici, and N.Giordano, J.Catalysis, 1973, **30**(1), 1.
103. E.N.Rasadkina, A.T.Telesheva, I.D.Rozhdestvenskaya, and I.V.Kalechits, Kinetika i Kataliz, 1973, **14**, 1214.

104. E.N.Rasadkina, T.S.Kukhareva, I.D.Rozhdestvenskaya, and I.V.Kalechits, Kinetika i Kataliz, 1965, **26**, 1465.
105. E.N.Rasadkina, T.V.Kuznetsova, A.T.Telesheva, I.D.Rozhdestvenskaya, and I.V.Kalechits, Kinetika i Kataliz, 1974, **25**, 969.
106. E.N.Rasadkina, I.D.Rozhdestvenskaya, and I.V.Kalechits, in "Kataliticheskie Reaktsii v Zhidkoi Faze. Materialy IV Simpoziuma po Kataliticheskim Reaktsiyam v Zhidkoi Faze" (Catalytic Liquid Phase Reactions. Proceedings of the IVth Symposium on Catalytic Reactions in the Liquid Phase), Alma-Ata, 1974, Part 3, p.658.
107. C.Michel, C.V.Hoang, and S.J.Teichner, J.chim. phys.phys.chim.biol., 1978, **75**, 819.
108. S.Galvagno, P.Staiti, P.Antonicci, A.Giannetto, and N.Giordano, React.Kinet.Catal.Letters, 1982, **21**, 157.
109. N.G.McDuffie, J.Catalysis, 1979, **57**, 193.
110. J.Falbe and F.Korte, Chem.Ber., 1974, **97**, 1104.
111. H.Greenfeld, S.Metlin, M.Orchin, and I.Wender, J.Org.Chem., 1958, **23**, 1054.
112. P.Pino and R.Ercoli, Ric.Sci., 1953, **23**, 1231.
113. J.T.Shaw and F.T.Tyson, J.Amer.Chem.Soc., 1956, **78**, 2538.
114. T.T.Derencsenyi and T. Vermeulen, Energy Res. Abstr., 1980, **5**(13), 19 901; Chem.Abs., 1980, **93**, 188 929.
115. R.M.Laine, D.W.Thomas, and L.W.Cary, J.Org. Chem., 1979, **44**, 4964.
116. US P.3 412 174, 1968; Chem.Abs., 1968, **69**, 106 002.
117. I.Rajca, A.Borowski, and A.Rajca, "Rhodium Homogeneous Catalysis. (Proc.)", Veszpre (Hungary), 1978, p.58.
118. D.Gagnaire and P.Vottero, Bull.Soc.chim.France, 1970, 164.
119. P.Abley, J.Jardine, and F.J.McQuillin, J.Chem.Soc.C, 1971, 840.
120. J.Jardine and F.J.McQuillin, Chem.Comm., 1970, 626.
121. L.J.Boucher, N.L.Holy, and B.H.Davis, Amer.Chem. Soc.Symp.Ser., 1981, 169 (New Approaches to Coal Chem.); Chem.Abs., 1982, **96**, 9167.
122. T.P.Voskresenskaya, V.A.Semikolenov, V.A.Likholobov, A.I.Trofimchuk, A.P.Shekelin, P.A.Zhdan, and A.V.Mashkina, Symposium, "Katalizatory Soderzhashchie Nanesennye Kompleksy. Materialy Simpoziuma" (Catalysts Containing Deposited Complexes. Symposium Proceedings), Novosibirsk, 1980, Part 2, p.22.
123. T.P.Voskresenskaya, V.A.Semikolenov, V.A.Kuznetsov, V.A.Likholobov, A.K.Trofimchuk, Yu.I.Ermakov, and A.V.Mashkina, Symposium, "Katalizatory Protsessov Polucheniya i Prevrashcheniya Sernistykh Soedinenii" (Catalysts of the Synthesis and Reactions of Sulphur Compounds), Novosibirsk, 1979, p.74.
124. T.P.Voskresenskaya, V.N.Yakovleva, V.A.Semikolenov, V.A.Likholobov, and A.V.Mashkina, "Tezisy III Vsesoyuznogo Simpoziuma 'Geterogennyi Kataliz v Khimii Geterotsiklicheskikh Soedinenii'" (Abstracts of Reports at the IIIrd All-Union Symposium 'Heterogeneous Catalysis in the Chemistry of Heterocyclic Compounds'), Izd.Zinatne, Riga, 1981, p.94.
125. USSR P.1 002 292, 1983; Byul.Izobret., 1983, No.9.
126. E.A.Karakhanov, A.S.Loktev, V.S.Pshezhetskii, E.P.Neimerovets, and A.G.Dedov, "Trudy IV Mezhdunarodnogo Simpoziuma po Gomogennomu Katalizu" (Proceedings of the IVth International Symposium on Homogeneous Catalysis), Leningrad, 1984, Vol.4, p.79.
127. E.A.Karakhanov, E.B.Neimerovets, and A.G.Dedov, Vestnik Moskov.Gos.Univ., Khim. (in the Press).
128. E.A.Karakhanov, A.S.Loktev, V.S.Pshezhetskii, I.P.Stepanova, and A.G.Dedov, Khim.Geterotsikl. Soed., 1984, 1032.

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