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Catalysis as an important tool of green chemistry

I P Beletskaya, L M Kustov

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Abstract. The major advances of the last decade in the catalytic synthesis of organic compounds from the standpoint of the green chemistry principles are surveyed. It is shown that among the most promising approaches to such processes, one should distinguish the use of new catalysts (including nanosized ones) and solvents (water, ionic liquids and fluorous compounds), microwave technologies, supercritical and biphasic media as well as heterogenized catalytic metal complex systems. The major application areas of the metal complex systems comprising hydrogenation, partial oxidation and cross-coupling inlcuding enantioselective reactions are addressed. The bibliography includes 248 references.

I. Introduction

Chemistry occupies a special place in the development of civilization, and its role in industrial world is particularly important. It is chemistry that bears on the development of alternative energy sources (in particular, hydrogen energy) and new fuel types, synthesis of pharmaceuticals, new material design, sustainable harvests in agriculture and many others. However, there is also 'the other side of the coin' of chemicalization, it is not without reason that chemsitry is accused of environmental pollution including air, water and soil pollutions. One can endlessly criticize chemical industry, however it is clear to everybody that mankind already cannot do without drugs, crop protection chemicals, dyes, photo materials, polymers and fibres, and many other chemical products. Is it possible to propose a compromise? A way out is offered by green chemistry, albeit, naturally, it would be naive to expect a solution to all the problems within the framework of one concept. The authors of this concept, Anastas and Warner,[1, 2] developed 12 principles of green chemistry in 1998 by relying on a motto that is spiritually close to the physician maxim 'Primum non nocere' — 'Seek prevention, not cure'. One of the most important principles is the replacement of stoichiometric reactions with catalytic ones. It is clearly evident that a catalytic process allows one to reduce reactor volume, shorten reaction time, reduce reaction temperature, avoid unnecessary waste and, therefore, significantly decrease environmental foot print.

There are many types of catalysis — acid and base, catalysis by metal oxides and metal salts, catalysis by organic and inorganic polymers, catalysis by transition metal complexes, biocatalysis. It is impossible to examine all the types of catalysis within one review, hence we had to restrict ourselves to only one area. We decided to focus our attention on the field that is the most environmentally problematic and requires the use of solvents and other expensive auxiliary substances, *viz*., on the catalytic synthesis of organic compounds with the use of metal complex catalysts. Indeed, as follows from the already repeatedly quoted comparison of environmental pollution in different chemical industries that has been made by Sheldon,[3] it is the production of complex organic compounds and pharmaceuticals that is the most harmful to the environment due to a low efficiency of such processes.

Industry	Production volume /tonne per year	Ratio /kg of waste (kg of product)$^{-1}$ (*E*-factor)
Oil refining	$10^6 – 10^8$	< 0.1
Synthesis of basic organic chemicals	$10^4 – 10^6$	$< 1 – 5$
Synthesis of fine organic chemicals	$10^2 – 10^4$	5 to > 50
Drug synthesis	$10 – 10^3$	25 to > 100

Meanwhile, all these industrial branches are essential for the modern society. We shall concentrate our attention on

I P Beletskaya Department of Chemistry, M V Lomonosov Moscow State University, Leninskie Gory, 119992 Moscow, Russian Federation. Fax (7-495) 932 88 46, tel. (7-495) 939 36 18, e-mail: beletska@org.chem.msu.ru
L M Kustov N D Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky prosp. 47, 119991 Moscow, Russian Federation, Fax (7-499) 135 53 28, tel. (7-499) 137 29 35, e-mail: lmk@ioc.ac.ru

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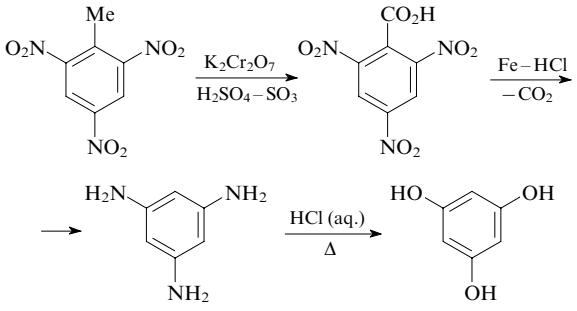
the use of homogeneous and heterogenized (supported) metal complex systems, since this field is characterized by the highest degree of novelty of development and the broadest scope of various reaction types. We are constrained to leave studies reporting the use of supported metal catalysts with metal particles containing 6–13 (subnanoparticles) to hundreds of metal atoms beyond the scope of our work.

We shall demonstrate advantages of the use of metal complexes for the synthesis of organic compounds, since the processes they are involved in often comply with several green chemistry principles rather than one. For example, good results can be achieved by combining metal complex catalysis with the absence of solvents or the presence of such green solvents as water, ionic liquids, supercritical media and fluorous biphasic systems as well as the exposure to microwave radiation which allows reduction of power consumption. Preference will be given to those examples that demonstrate the possibility of catalyst turnover and a decrease in catalyst leaching, although frequently it is the transfer of the complex to solution that contributes to catalytic activity. However, the same effect can lead to a loss of catalytic activity.

The principles of green chemistry have been in detail discussed in the literature (see, for example, the monographs[4–6] and a review[7]), they are also listed in the introductory article in this issue of the journal, hence only note that the use of highly selective catalytic systems is an essential principle included in the concept of green chemistry.

Let us cite an illustrative example that typifies the problems arising when synthesizing fine organic chemicals. The synthesis of phloroglucinol (**1**) is normally carried out by the oxidation of TNT according to Scheme 1.[8]

Scheme 1



1

The atom efficiency of this process is by far lower than 5%, and the *E*-factor is around 40, *i.e.*, the production of 1 kg of phloroglucinol results in 40 kg of wastes [$Cr_2(SO_4)_3$, NH_4Cl, $FeCl_2$ and $KHSO_4$] (excluding sewage), thus, the necessity to seek for new catalysts is evident.

The catalytic processes making allowance for green chemistry demands are being actively developed. Attempts are undertaken to replace toxic reagents by less harmful and more efficient ones or those resulting in a lesser amount of by-products or yielding by-products that are easier to dispose. For instance, it is recommended to use dimethyl carbonate [$(MeO)_2C(O)$] as a carbonylating agent instead of phosgene ($COCl_2$). The former is also employed as a methylating agent alternative to methyl chloride and dimethyl sulfate.

For the reduction of organic compounds it is environmentally more justified to use hydrogen rather than $LiAlH_4$, $NaBH_4$, formic acid and other reductants that give by-products to dispose.

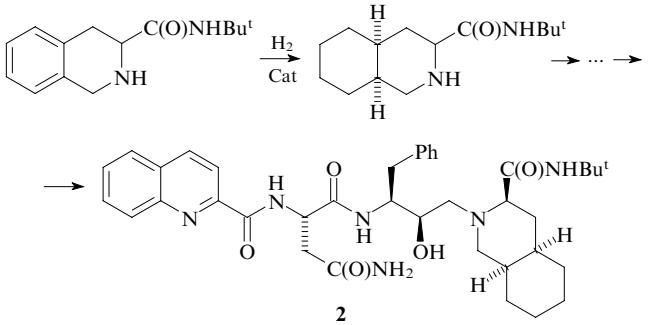
An analogous situation is characteristic also of oxidation processes. Apparently, the use of such reagents as $KMnO_4$, CrO_3, K_2CrO_4, $K_2Cr_2O_7$, $NaClO_3$, NaClO, organic hydroperoxides, *etc.*, as oxidants in stoichiometric processes is less attractive than of hydrogen peroxide, nitrogen(I) oxide or air (oxygen).† The replacement of chromates and permanganates by sodium hypochlorite in the oxidation of steroid alcohol groups to carbonyls exemplifies again the application of green chemsitry principles, because hypochlorite produces innocuous sodium chloride as the by-product. Below examples of catalytic processes using such green reductants and oxidants will be discussed.

One of the most promising approaches to the synthesis of organic compounds is the use of catalytic metal complex systems including nanosized catalysts in combination with microwave technologies, supercritical media, novel solvents (ionic liquids, fluorous solvents) as well as the employment of heterogenized catalytic metal complex systems combining the advantages of homogeneous and heterogeneous catalysts — high activity, selectivity, stability and recyclability. The present review explores major applications of metal complex systems in catalysis: 1) hydrogenation reactions; 2) partial oxidation reactions including some examples of enantioselective hydrogenation and oxidation, which are particularly important in drug design; 3) cross-coupling reactions to form the carbon–carbon and carbon–heteroatom bonds.

II. Hydrogenation

Numerous examples of the use of organometallic complexes in hydrogenation processes including the production of useful products and intermediates are cited in the books[4,9] and review.[10] Since the most conventional application of metal complex catalysts is hydrogenation, we consider catalysts exploited in important industrial processes, above all in manufacturing drugs and crop protection chemicals. According to the study[11], hydrogenation steps performed on metal complex catalysts take ~10%–20% in the synthesis of vitamins. Let us consider for example the synthesis of Saquinavir (**2**) — a protease inhibitor (Scheme 2), — which includes an enantioselective hydrogenation step.

Scheme 2



2

To date, considerable experience has been accumulated in heterogenization of metal complex catalysts on the surface of inorganic and polymeric supports.[12] The use of a polymeric matrix with proper functional groups in many

† Unfortunately, air as the oxidant does not always give the desired product.

cases provides stronger immobilization of a complex on the matrix, more homogeneous surface distribution of active sites, higher grafting density and higher solubility of catalytic systems. However, due to relative flexibility of polymeric chains, part of active sites can be blocked and, thus, become inaccessible to reagent molecules.

The inorganic matrices (supports) used for the development of heterogenized systems of this type are oxides [particularly SiO_2 (Refs 13, 14) as well as TiO_2,[15] Al_2O_3 (Ref. 16)], zeolites [17] and other materials with the properties of molecular sieve (aluminophosphates of the AlPO-5 type,[18] silicalites, *i.e.*, zeolites containing no aluminium,[19] and titanosilicates of the TS-1 [20] type), mesoporous systems of the MCM-41 [21] and SBA-15 types,[22] carbon supports, especially with functional groups involved in interaction with ligands of the complex.[23] Such superficial functional groups can, for example, be represented by carboxyl groups on the surface of a carbon material obtained by partial oxidation of the surface on treatment with hydrogen peroxide or nitric acid.[24] Systems based on silica in a variety of its modifications are studied in most detail. The advantages of SiO_2 are its high chemical and thermal stability and inertness along with a significant concentration of surface silanol groups, which by virtue of their amphoteric character are readily modified, particularly with the use of organoelement (for instance, organosilicon, organotin, *etc.*) compounds in order to create specific centres and functional groups on the SiO_2 surface. Systems containing aminopropyl groups on the SiO_2 surface have been studied in most detail. A terminal amino group in such modified matrices serves as a complexing agent for numerous complexes bearing interesting catalytic properties.

In the general case, a heterogenized metal complex system comprises a support, an anchor (a functional group that attaches metal complexes to the support surface), a spacer (an aliphatic, aromatic or more complex atom chain required to separate an active site from the support surface and make it flexible) and the active complex itself (Fig. 1).

Of a host of hydrogenation processes using metal complexes, alkene hydrogenation is studied in most detail. Thus ruthenium complexes of the $[Ru^{II}Cl_2(bpea)(PPh_3)]$ [bpea is *N*,*N*-bis(2-pyridylmethyl)ethylamine] type were tested in hydgrogenation of unsaturated model compounds (hex-1-ene, styrene, cyclohexene, *etc.*).[25] The catalyst activity did not decrease in 25 hydrogenation cycles. Analogous properties are also manifested by systems based on Rh, Pd, Ni.[26, 27]

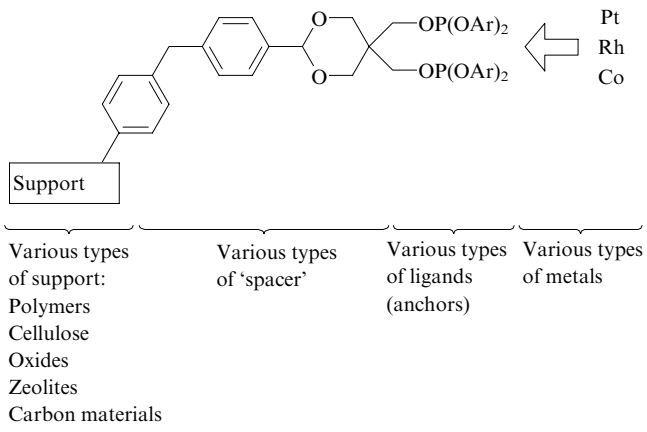


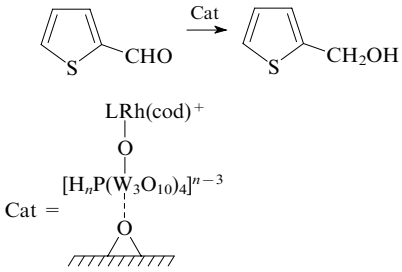
Figure 1. The structure of heterogenized metal complex catalysts.

Hydrogenation of aromatic hydrocarbons on the complexes $[Rh(cod)Cl]_2$ and $Na[HRu_3(CO)_{11}]$ (cod is cycloocta-1,5-diene) immobilized on an oxide support was explored.[28] It was shown that unlike the hydrogenation of aliphatic substrates (alkenes and alkynes), which require higher temperature (near 120 °C), the hydrogenation of alkylaromatic hydrocarbons occurs at room temperature and is not accompanied by the formation of reduced metal particles. Among other carbonyl precursors employed for the heterogenization of metal complexes on a support surface, $[Rh_2Co_2(CO)_{12}]$ is also prominent.[29]

The work,[30] which reports on the heterogenization of cationic ruthenium complexes $[\eta^5\text{-}MeC_5H_4)Ru.(\eta^3\text{-}PPh_2CHCH_2)(\eta^1\text{-}PPh_2CHCH_2)]^+$ in the mesopores of the HMS aluminosilicate support having a hexagonal structure by ion exchange, also deserves attention. These catalysts proved quite active in the hydrogenation of phenylacetylene. SiO_2-supported rhodium complexes with phenylphosphine ligands bearing terminal $Si(OMe)_3$ groups were successfully employed for the hydrogenation of aromatic substrates as well as for the hydroformylation of hex-1-ene.[31]

Hydrogenation of styrene and other aromatic compounds was efficiently carried out on Pd(II) complexes with Schiff bases, including those polymer-supported.[32]

Yet another example demonstating the efficiency of heterogenized metal complexes in chemoselective hydrogenation is offered by the hydrogenation of an aldehyde group in the thiophene ring.‡ For this process, a heterogenized catalyst composed of rhodium complex immobilized on the surface of a solid support with the aid of the tungstophosphoric heteropolyacid anion was developed. Such a catalyst withstood several hydrogenation cycles without loss of activity.

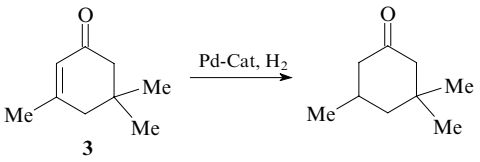


Hydrogenation of imines using heterogenized palladium and nickel salen complexes has been reported.[33] This process can also be performed on rhodium and iridium complexes immobilized on clays.[34]

1. The use of green solvents and supercritical media for hydrogenation

Green solvents and supercritical media proved very promising in hydrogenation processes. By using supercritical CO_2 an industrial process was developed for the hydrogenation of isophorone (**3**) to trimethylcyclohexanone (around 1000 tonnes per year).[35]

‡ Thiophenes, as a rule, poison catalyst active sites during hydrogenation.



3

Attractive are catalytic processes in which the starting reactant, the substrate of a catalytic reaction, is in the supercritical conditions. Such substrates can be hydrocarbons (alkenes, alkanes, aromatic hydrocarbons) for which critical conditions are reached at comparatively low pressures and temperatures (up to 40–80 atm and up to 200–300 °C).§

Supercritical fluids exhibit a favourable combination of the useful properties of a gas and a liquid: low viscosity and a high diffusivity of a gas and high density of a liquid. They are capable of dissolving non-polar substances including solid ones as well as hydrogen and other non-polar gases, the solubility being a function of pressure. Given exceptionally environmentally clean and economical processes invlolved, straightforward apparatus and chemically inert media used, an assumption can be made that catalytic processes in supercritical media will find wide application in the future.¶

Lately catalytic reactions involving metal complexes in ionic liquids have been actively investigated. The number of ionic liquids reported to date is very large (nearly 300). The majority of ionic liquids contain heterocyclic derivatives as cations. They are both already well-known ionic liquids, such as pyridinium, imidazolium, polyalkylammonium and recently synthesized — guanidinium, piperidinium, pyrrolium, pyrrolidinium, morpholinium, cholinium, piperazinium, thiazolium, polycyclic ones, ionic liquids with bridged structures, binuclear or polynuclear, zwitterionic, hydrophobic (fluorinated), and chiral ones.[36]

The starting compounds in hydrogenation reactions in ionic liquids were cyclohexene, cyclohexadiene, pent-1-ene, aromatic hydrocarbons including styrene and phenylacetylene, sorbic acid, copolymers of acrylonitrile and butadiene and many other including compounds of complex structure.[37–39] It is known that these reactions proceed efficiently enough in conventional solvents. It would seem that ionic liquids can hardly improve any parameters of the process. Nevertheless, there is a number of examples in the literature that demonstrate advantages of ionic liquids over conventional solvents, as a minimum it is the possibility of their recycling and re-use.[37,39]

The most impressive example is offered by the hydrogenation of cyclohexadiene to cyclohexene in an ionic liquid, 1-ethyl-3-methylimidazolium hexafluoroantimonate ($[EMIM]^+[SbF_6]^-$), with the use of the complex $[Rh(nbd)PPh_3]PF_6$ (nbd is norbornadiene).[40] In this case, very high selectivity was achieved (98% at a conversion of 96%) with respect to cyclohexene. This reaction in virtually all classical systems does not stop after the cyclohexene formation and goes up to the end resulting in cyclohexane. For the hydrogenation of pent-1-ene in the ionic liquid $[BMIM]^+[SbF_6]^-$ (BMIM is 1-n-butyl-3-methylimidazolium) the catalyst activity was 5 times higher than that for this reaction in acetone, whereas the rhodium leaching was below the detection limit (below 0.02%).

Data on the hydrogenation of other unsaturated and aromatic substrates[41] as well as acrylonitrile copolymers with butadiene,[42] styrene[43] and phenylacetylene[44] confirm the high efficiency of ionic liquids in these processes. In particular, in hydrogenation of styrene the activity of metal complexes (osmium, ruthenium and iron carbonyl complexes) in ionic liquids is 3–6 times as high as that in organic solvents.

Palladium complexes dissolved in the ionic liquid $[BMIM]^+[BF_4]^-$ exhibit activity in the hydrodimerization of buta-1,3-diene.[45]

In order to solve the problem of solubility and separation, mixed 'green' solvents can be employed that made it possible to switch from complete solubility to limited solubility or insolubility of reaction medium components. In the case of a combination of an ionic liquid with supercritical CO_2, an extra opportunity emerges to extract the products and recycle the catalyst.[46,47]

The hydrogenation of dec-1-ene in the presence of the Wilkinson catalyst $[RhCl(PPh_3)_3]$ in the system supercritical CO_2–$[BMIM]^+[PF_6]^-$ proceeded in a biphasic system by 98% (the turnover frequency, TOF, was 410 h^{-1}).[48] Decane was readily separated from CO_2, which permitted multiple recycling of the system. The catalyst was readily soluble in the ionic liquid and practically insoluble in supercritical CO_2.

Further advances in the hydrogenation area when using ruthenium complexes as catalysts and ionic liquids as solvents pertain to stereoselective processes. For example, sorbic acid was selectively hydrogenated to *cis*-hex-3-enoic acid.[49] In this case, a three-fold increase in catalyst activity was observed in ionic liquid as compared to conventional solvents. This justifies the conclusion that an ionic liquid has multifunctional role in catalytic processes, and it should be regarded as a catalytic medium rather than just a solvent.

Among few but continuosly increasing number of instances of asymmetric catalysis in ionic liquids, there are also hydrogenation reactions. The review[50] summarizes virtually all avalaible data on enantioselective hydrogenation and oxidation reactions in low-temperature salt melts.

Asymmetric synthesis reactions require the presence of chiral centres in the system, which, in the case of ionic liquids, can be created by one of the following means:

— the use of a chiral catalyst or a metal complex with chiral ligands, as a rule, phosphines (BINAP, DIPAMP, *etc.*, see the formulas below);

— the introduction of a chiral modifier in the system as is done in the case of heterogeneous systems (for example, natural or synthetic optically active alkaloids such as cinchonine and cinchonidine);

— the use of a chiral support or medium (in our case, a chiral ionic liquid). The latter approach rarely provides good results since the emergence of optical activity in a reaction complex under the influence of a support/medium is complicated by a number of factors (steric, electronic and others).

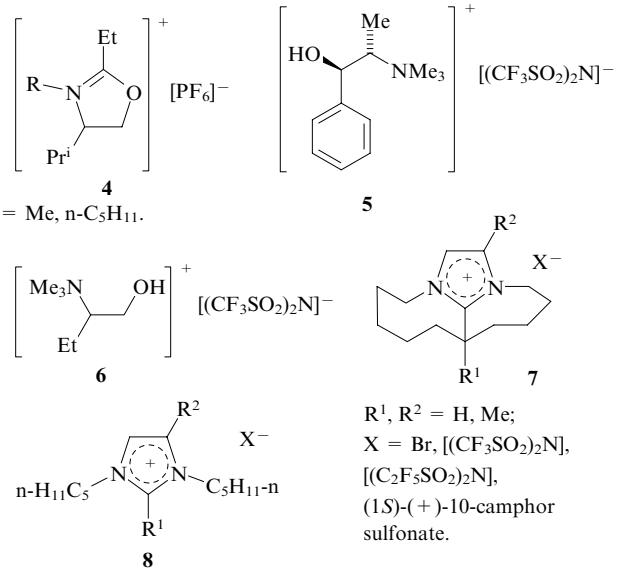
All the examples reported in the literature are mostly associated with the use of the first and third approaches, although the second approach seems quite promising. Note that the first study on enantioselective hydrogenation in ionic liquids appeared in 1997,[51] a serious interest in such

§ It should be noted that the use of supercritical media so far has not found wide application in industrial catalytic processes except for the hydrogenation of isophorone developed by Thomas Swan and Co.

¶ Ionization potential for substances in supercritical fluids is substantially decreased, therefore, one can expect an increase in the reactivity of many organic compounds in such media.

reactions arose only in the 21st century, thus one can expect new findings.

There are several original studies on the synthesis of chiral ionic liquids.[52,53] Thus synthesis of ionic liquids based on oxazoline (compound **4**), hydroxyalkylammonium salts (**5**, **6**), planar chiral cyclophane structures (**7**) and imidazole (**8**) was reported. All these ionic liquids were liquid at relatively low temperatures (m.ps. from −18 °C for compound **6** to 98 °C for compound **7**), and the ionic liquid **6** had an acceptable viscosity for being used in organic synthesis.



One can hope that such investigations will be continued, albeit so far the use of chiral ionic liquids is limited because of their high cost (in fact an ionic liquid is a medium rather than a catalyst taken at a very small concentration). Naturally, this limitation will be removed if chiral ionic liquids are completely recycled in asymmetric catalysis.

Enantioselective hydrogenation of 2-arylacrylic acids leads to the products that found practical application in pharmaceutical industry (ibuprofen and naproxen). The synthesis was carried out using the $[RuCl_2$–(*S*)-BINAP$]_2$–NEt_3 catalyst in $[BMIM]^+[BF_4]^-$ Ref. 51). Acceptable values of enantiomeric excess (*ee* 70%–90%) were achieved, and the ionic liquid could be re-used.

A heterogenized catalytic system composed of a polymer impregnated with an ionic liquid and a chiral rhodium or ruthenium catalyst was reported.[54] This system was employed for the hydrogenation of model susbtrates including cyclohex-2-en-1-one, cycloocta-1,3-diene and methyl acetoacetate. In the later case, the corresponding optically active alcohol was prepared with an enantiomeric excess of 97%. A repeated use of the catalyst was shown to be possible.

2. Hydrogenation in water, various biphase systems and without solvent

Water as a 'green' solvent for organic synthesis has been lately attracting researchers' close attention. However, not all organic compounds are water-soluble. This restricts the application area of this unique solvent, which, nevertheless, is quite broad.[55–62] The use of water in asymmetric synthesis reactions is reported (see, for example Ref. 63). The key aspect of metal complex catalysis in aqueous media is the selection of ligands with hydrophilic groups (for example, phosphines containing sulfonic acid fragments). It is also important that water and aqueous media are not miscible with many organic compounds and, hence, can be employed in reactions taking place in biphase systems.

Among reactions conducted in aqueous biphase systems, one should mention the hydrogenation of unsaturated aldehydes to unsaturated alcohols on Rh- and Ru-complexes, for example, on $RhCl(PPh_3)_3$, $[\{RhCl_2(m\text{-TPPMS})_2\}_2]$ and $[\{RuHCl(m\text{-TPPMS})_2\}_2]$, where *m*-TPPMS = $PPh_2(C_6H_4SO_3Na\text{-}3)$,[62] hydroformylation of alkenes on rhodium catalysts.[64] The later example underlies a Ruhrchemie/Rhone-Poulenc's industrial manufacturing of butanal from propene (~400 thousand tones per year). The reaction selectivity reaches 99%, the n-butanal : isobutanal ratio is 96 : 4. In this process, the catalyst is completely recovered.

Unsaturated aldehyde hydrogenation in aqueous media may exhibit unique selectivity; for example, when using the catalytic system Rh(III)–TPPTS [TPPTS is $P(C_6H_4SO_3Na)_3$], 3-methybut-2-enal results mainly in the saturated aldehyde, while the use of the Ru(III)–TPPTS catalytic system yields the unsaturated alcohol.[65,66] Analogous complexes can also participate in the hydrogenation of carbohydrate substrates.[67]

The 'green' solvents also include fluorous biphase systems (FBS),[68,69] in which one phase is a fluorinated organic solvent (perfluorinated alkanes, naphthenes, ethers or amines), and the other is a conventional organic or inorganic solvent immiscible with the fluorous solvent at low temperatures, which however forms a monophase system at elevated temperatures. This makes it possible to carry out the reactions at high temperatures and separate the phases at low temperatures. The advantages of such biphase systems over monophase ones were exemplified by hydrogenation of soluble substrates[70] as well as cross-coupling reactions including the Heck reaction.[71,72]

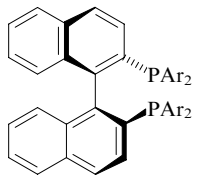
Finally, there is a sheer number of works describing solvent-free hydrogenation processes. Particularly topical are the processes performed under microwave activation, which selectively warms up polar molecules, activates hydrogen and, thus, facilitates the processes under exceptionally mild conditions.

The use of microwave activation and low-temperature plasma in catalysis, for example, in hydrogenation processes has also a huge potential. This is because of their effect on the catalyst and reaction medium (if it absorbs microwaves) during a catalytic reaction.[73–76] In particular, microwave heating was employed in catalytic alkene hydrogenation involving metal complexes.[74] The studies[73–76] demonstrated that microwave activation enables a decrease in the process temperature, an increase in catalyst activity, selectivity and lifetime, lowering power consumption and shortening the time required for the reaction completion.

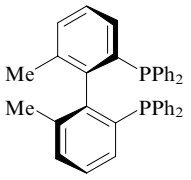
3. Enantioselective hydrogenation processes

In 2001, the Nobel Prize in Chemisty was awarded to R Noyori and W S Knowles 'for their work on chirally catalysed hydrogenation reactions' (and to K B Sharpless 'for his work on chirally catalysed oxidation reactions'). The key to successful accomplishment of such hydrogenation reactions was the choice of the catalytic system, namely, the selection of a chiral ligand. The most prominent

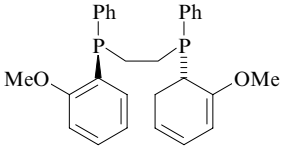
chiral ligands† used as part of ruthenium and rhodium complexes for hydrogenation of a variety of organic compounds are shown below.[77–79]



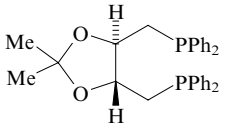
Ar = Ph [(*S*)-BINAP], C_6H_4Me-4 [(*S*)-TolBINAP], $C_6H_3Me_2$-3,5 [(*S*)-XylBINAP], $C_6H_3Bu^t_2$-3,5 [(*S*)-BuBINAP].



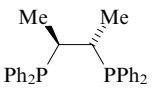
(*R*)-BIPHEMP



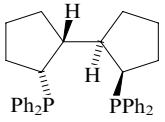
(*R*,*R*)-DIPAMP



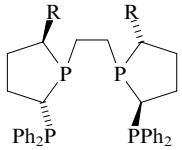
(*R*,*R*)-DIOP



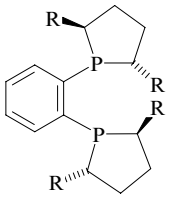
(*S*,*S*)-CHIRAPHOS



BICP

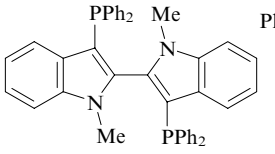


R-BPE

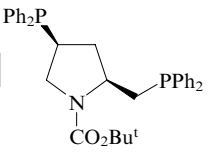


DuPhos

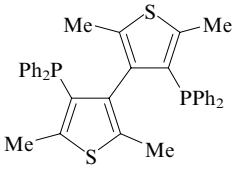
R = Me, Et, Pr^i.



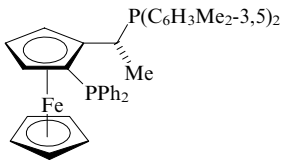
Me_2-BINP



(*R*,*S*)-BPPM



Me_4-BITIOP



Xyliphos

There are three major approaches to the heterogenization (immobilization) of metal complexes with chiral ligands:[80–87]

1. Covalent binding of a chiral ligand to the surface of a mineral or polymeric support. The immobilization of the functionalized ligand BINAP[82,83] resulting in an increase of the catalyst activity is an example. Using 'smart' polymers, which can dissolve under reaction conditions and precipitate upon a change in the temperature or pH of the reaction system, as the support, can provide additional advantages of such a heterogenized system compared with a homogeneous one.[84]

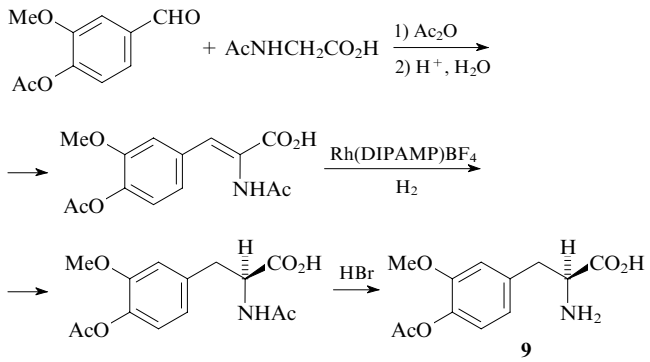
† Chiral heterogeneous catalysts for the hydrogenation of the bonds C=C or C=O, which are based on the Raney nickel, palladium or platinum nanoparticles with chiral modifiers (tartaric acid, cinchonine and other alkaloids), are beyond the scope of this review.

2. Catalyst immobilization by virtue of ionic interaction. In this case, the functionalization of the chiral ligand is not required.[85] Heteropoly acids can be used as supports, their anions serve as linkers for catalyst binding. Such an immobilization method was employed in the case of Rh- and Ru-complexes that are active in the asymmetric hydrogenation of methyl acetamidoacrylate (to *ee* 97%). Rhodium complexes were also successfully immobilized on the mesoporous support Al-MCM-41.[86]

3. Encapsulation of chiral catalytic complexes in a support matrix (most often a zeolite or a polymer). As a rule, the activity of catalytic system obtained in this way is still lower than that of homogeneous catalysts, and, in addition, in the case of swelling polymers the effect of catalyst leaching can be observed.[87]

Let us consider several examples of environmentally benign asymmetric hydrogenations. We confine ourselves only to the hydrogenation of double bonds and reduction of oxygen-containing functional groups, which are of industrial value. One of such processes is the hydrogenation of acetamides, particularly, the preparation (large-scale manufacturing) of L-DOPA derivative (**9**), a drug against Parkinson's disease (Scheme 3). This process was developed by the Nobel Prize winner W S Knowles, who introduced new chiral ligands, PAMP (Phenyl-*o*-Anisyl-Methyl-Phosphane) and DIPAMP into practice; the reaction enantioselectivity proved to be near 100%.[77]

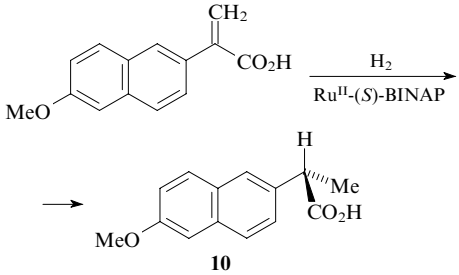
Scheme 3



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An undoubted success was the hydrogenation of α-arylenamides on the Rh-DuPhos complexes (see above) immobilized on mesoporous supports of the MCM-41 and SBA-15 types. In this process, the *ee* reached 99% at a conversion of 99% and chemoselectivity above 99%.[22]

Finally, one cannot help mentioning the example already turned classical of the enantioselective synthesis of (*S*)-naproxen (**10**), an antiinflammatory pharmaceutical, using ruthenium complexes with BINAP as the chiral ligand.[88]

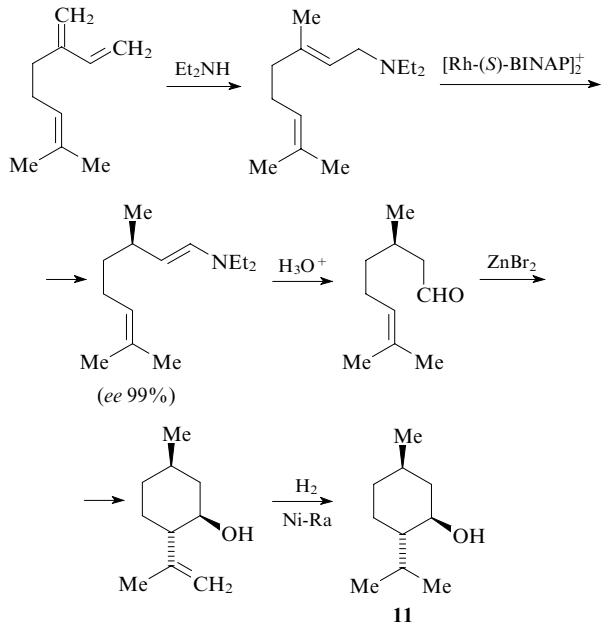


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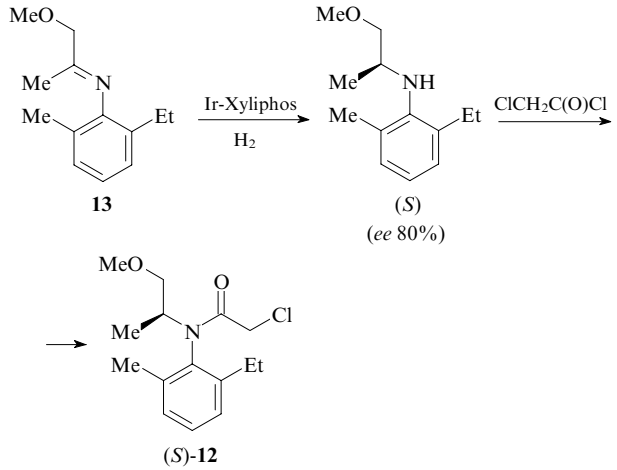
One of the asymmetric hydrogenation processes introduced into industry is the production of L-menthol (**11**)

(thousands of tonnes per year) with an enantiomeric excess of 99% with the use of the recyclable catalyst Rh-BINAP, for which the turnover number around 300 000 was reached (Scheme 4).[89]

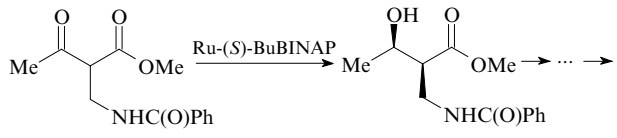
Scheme 4

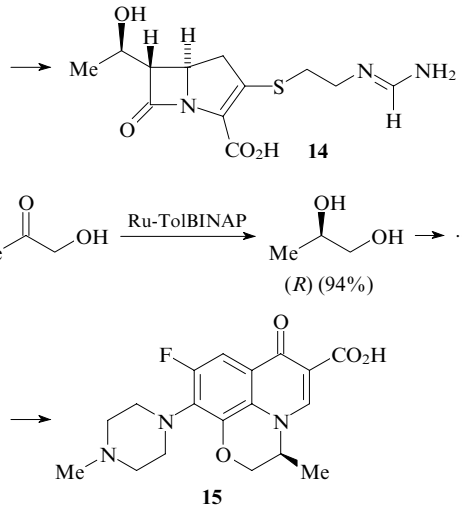


Yet another example of an industrial process is offered by the manufacturing of the herbicide (*S*)-metolachlor (**12**) by Novartis.[90] The pivotal stage is the asymmetric hydrogenation of prochiral imine **13** on the chiral complex Ir-Xyliphos (at a substrate : catalyst ratio equal to 750, the value of TOF > 1 800 000 h^{-1}, *ee* 80%).

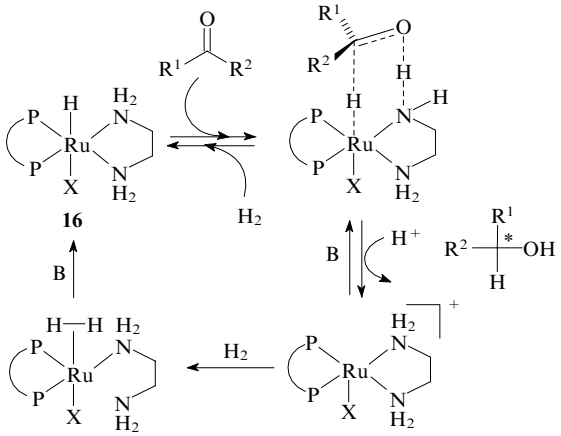


High enantioselectivity values, 95% – 97.5%, were also achieved in the hydrogenation of β-keto esters on the Ru-BINAP complexes, which was studied by R Noyori[91] and culminated in the synthesis of a number of drugs such as Imipenem (**14**) and Levofloxacin (**15**).



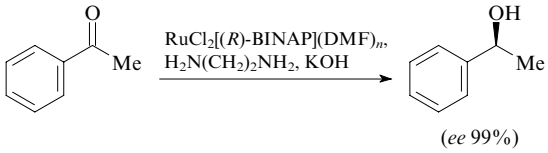


Noyori's success in the development of a catalyst of a new type, a ruthenium complex with BINAP and chiral diamines (**16**), allowed asymmetric hydrogenation of simple ketones to be accomplished.[92]

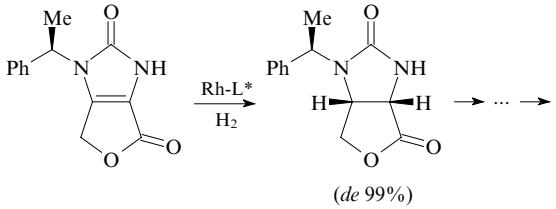


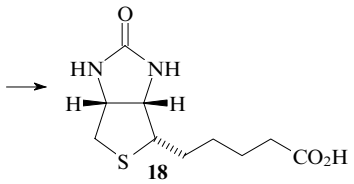
X = H, OR; B is a base.

The preparation of (*R*)-1-phenylethanol with an *ee* of 99% using such a catalyst was performed on an industrial scale [the substrate (S) : catalyst (C) ratio was 500 : 1].

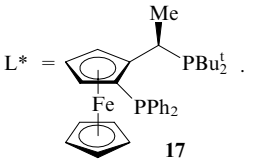


Ferrocene ligands of type **17** and catalyst based on them (for instance, Rh-catalysts) found application in the hydrogenation of the C=C bond in a manufacturing process of biotin (**18**) developed by Lonza.[93]



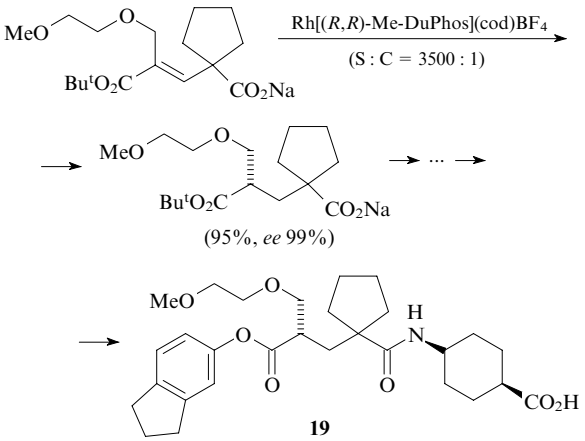


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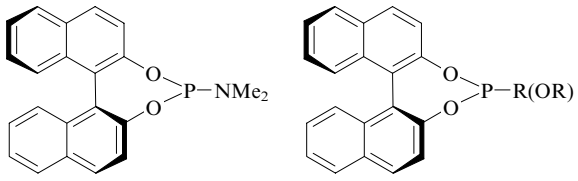
17

Substantial progress in asymmetric hydrogenation was achieved owing to the use of the novel chiral ligand DuPhos (see above). Rhodium complexes with (*R*,*R*)-Me-DuPhos (R = Me) were applied by Pfizer to the preparatiion of Candoxatril (**19**) for the treatment of cardiovascular diseases.[94]



19

The use of the indicated catalysts is limited due to the toxicity of phosphine ligands as well as due to to the complexity and high cost of their synthesis. Attempts to replace phosphine ligands with bisphosphonites or bisphosphites, as a rule, resulted in a decrease in activity and/or hydrogenation selectivity, and only monodentate phosphinates and phosphoramidate manifested themselves as promising ligands for the creation of hydrogenation catalysts.



In particular, rhodium complexes with such ligands contributed to a high efficiency in the asymmetric hydrogenation of prochiral alkenes.[4] Examples of successful enantioselective hydrogenation of prochiral carbonyl compounds, including those using heterogenized metal complexes are known.[95,96] Synthesis of SiO_2-supported chiral rhodium complexes with ligands based on *trans*-(1*R*,2*R*)-diaminocyclohexane, and their use in the enantioselective hydrogenation of phenylacetophenone have been reported.[97]

Examples of asymmetric hydrogenation of alkenes and their derivatives, for example, α-enamides, on metal complex catalysts in supercritical CO_2 are provided in the references.[98–100] A chiral Rh-complex immobilized on alumina with the use of a heteropoly acid anion as a linker was employed in a continuous hydrogenation process in a flow of supercritical CO_2.[100] A comparison was made[101] of the efficiency of new solvents — supercritical CO_2, ionic liquids and their combinations with each other and organic solvents — and conventional solvents in the asymmertic hydrogenation of prochiral unsaturated acids on ruthenium metal complexes. It was concluded that each particular substrate has its own optimal solvent or a combination of solvents, however, examples are given that demonstrate a substantial superiority of ionic liquids and supercritical CO_2 over conventional solvents. The rhodium complex provided considerably better results in the hydrophosphorylation of oct-1-ene when conventional solvents were replaced by supercritical CO_2.[102]

In overall, it should be noted that the research in the application of metal complex catalysis for enantioselective hydrogenation and partial oxidation (see below) is developing more rapidly than other catalysis branches, which is accounted for, in the first place, by the needs of medicine and increasing possibilities of combinatorial studies in catalysis, which allow several thousands of catalysts to be tested simultaneously.[103]

III. Partial oxidation

Partial oxidation of organic compounds is yet another application area of catalysis by metal complexes at present. When carrying out catalytic partial oxidation reactions, one usually faces the problem of higher reactivity of the final product than the starting substrate with respect to the oxidant. Unlike hydrogenation processes, the partial oxidation can be complicated also by a stronger interaction (complexation, adsorption) of the reaction product with the catalyst active site compared with the starting compound. However, in recent years quite a few novel 'green' oxidants appeared that proved efficient in the partial oxidation of a wide range of substrates. Among such oxidants especially attractive are H_2O_2, N_2O, NaOCl, organic peroxides and hydroperoxides, peroxy acids, methyltrioxorhenium, organic *N*-oxides, which either are converted to harmless products (H_2O, N_2, NaCl), or are easily recycled. Some of these systems can be employed in partial oxidation with oxygen transfer (Table 1).

Table 1. Oxidants used in partial oxydation of organic compounds.

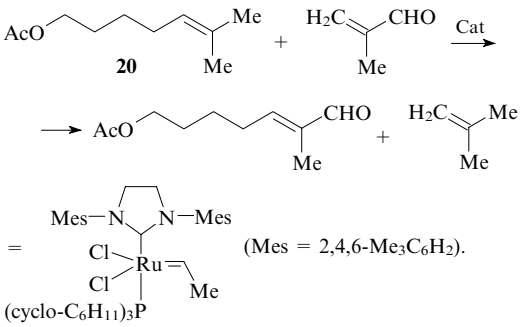
Oxygen donors	Active oxygen content (%)	Product derived from the oxidant
H_2O_2	47.0 (14.1 [a])	H_2O
N_2O	36.4	N_2
O_3	33.3	O_2
AcO_2H	21.1	AcOH
Bu^tO_2H	17.8	Bu^tOH
HNO_3	25.4	NO_x
NaOCl	21.6	NaCl
NaO_2Cl	35.6	NaCl
NaOBr	13.4	NaBr
n-$C_5H_{11}NO_2$	13.7	n-$C_5H_{11}NO$
$KHSO_5$	10.5	$KHSO_4$
$NaIO_4$	7.5	$NaIO_3$
PhIO	7.3	PhI

[a] For a 30% aqueous solution.

Carrying out parial oxidation reactions in supercritical media obviates some problems that complicate the conduction of these processes under conventional conditions, in particular, the problem of complete oxidation of the target product. Thus oxidation of alcohols to carbonyl compounds when treated with air on polymer [poly(ethylene glycol), PEG] supported palladium complexes was efficiently performed using supercritical CO_2.[104]

An example of the industrial use of catalytic metal complex systems in partial oxidation reactions is the manufacturing of citral (an intermediate for the subsequent preparation of perfumery articles and vitamins) developed by BASF.

Unique functionilization possibilities, particularly, of the introduction of oxygen-containing groups is offered by another approach that relies on cometathesis.‡ Alkene **20** is formally 'oxidized' (the process looks like an allylic oxidation) to the corresponding aldehyde by cometathesis with methacrolein.[105]

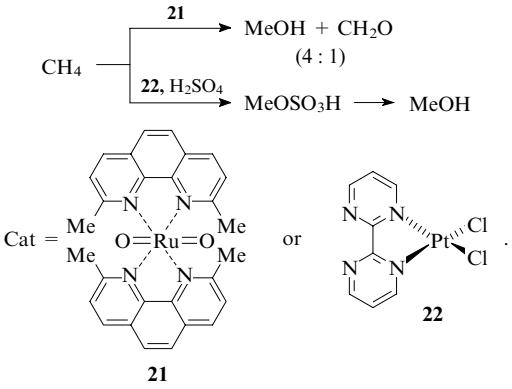


Let us consider some examples of the use of metal complex catalysts including polymer-supported ones or those dissolved in ionic liquids in partial oxidation of organic compounds.

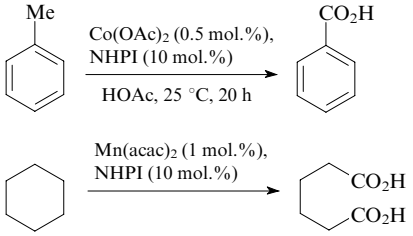
1. Alkane oxidation

The partial oxidation of alkanes offers the greatest challenge, since products of their oxidation — alkenes, alcohols, aldehydes — are oxidized significantly more readily than the starting alkanes. The employment of catalytic metal complex systems, which are normally more active than supported oxide or metal systems, gives rise to extra problems associated with possible oxidative destruction of a catalytic system and with an increasing contribution of radical processes that are difficult to control. For alkane oxidation by hydrogen peroxide, biomimetic systems based on iron or ruthenium in high oxidation states, Fe(V), Ru(VI), are applied.[106] The ruthenium complexes can also be exploited for oxidation by oxygen. *cis*-Dioxoruthenium complex **21** and platinum bispyrimidine complex **22** are most promising catalytic systems for the partial oxidation of alkanes, albeit the catalyst **22** is used in concentrated sulfuric acid, which is not very attractive from the green chemistry standpoint.[107] It is assumed that the mechanism of a reaction involving catalyst **21** includes insertion of the metal oxo complex at the C—H bond. Alkane activation *via* Olah's superacidic mechanism involving pentacoordinate carbonium ions is also possible.

‡ Cometathesis reactions are off the subject of the present review (a single example is given).

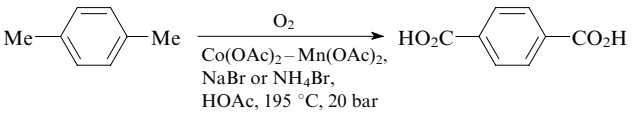


Recently, cobalt and manganese *N*-hydroxyphthalimide complexes have been used for the oxidation of C—H bonds in alkyl substituents of alkylaromatic compounds by atmospheric oxygen.[108] Toluene is oxidized on such catalysts to benzoic acid even at room temperature in high yield (84%) and with high selectivity (96%). In the case of cyclohexane, the oxidation results in adipinic acid with selectivity and conversion nearly 73%.



NHPI is *N*-hydroxyphthalimide, acac is acetylacetonate.

Yet another example of the oxidation of side alkyl chains in alkylaromatic compounds is the industrial oxidation of *p*-xylene by air to terephthalic acid in acetic acid medium, using the catalytic system Co^{II}/Mn^{II} at 200 °C, developed by the Amoco company.[109]



This process resulted in a *p*-xylene conversion above 95% and selectivity reaching 95%.

2. Alkene epoxidation

Methyltrioxorhenium is one of the most structurally simple catalysts with unique properties for alkene oxidation (as well as for the oxidation of alkanes, alkynes, sulfides, amines, silicon-containing compounds, alcohols) and many other reactions. The catalytic properties of this compound and application to more than 30 processes are examined in the review.[110] This catalyst was discovered in the 1990s. It was successfully applied to the epoxidation of alkenes by hydrogen peroxide. For instance, the epoxidation of cyclohexene in the presence of methyltrioxorhenium occurs in 90% yield even at a temperature < 10 °C. Higher temperatures favour (because of the epoxide ring opening) diol formation (at 82 °C, *trans*-diol was obtained in 97% yield). This catalyst exhibits strong acidic properties. In order to improve its activity and selectivity in the epoxidation of a large array of alkenes including those containing functional groups, Hermann [111] and Sharpless [112] proposed addition of

10% – 12% of a heterocyclic base (3-cyanopyridine, pyrazole, *etc.*) to the system. The use of 2,2,2-trifluoroethanol as a system component in the oxidation by aqueous solution of hydrogen peroxide allowed an increase (in some cases 10-fold) in the activity (TOF) of methyltrioxorhenium.[112] The reaction proceeds *via* a metal peroxo complex or metal diperoxo complex.[113] The major drawbacks of methyltrioxorhenium are a sophisticated and expensive synthesis of the catalyts and insufficient stability in basic aquesous media.

Unlike epoxidation reactions involving rhenium catalysts, which proceed *via* peroxo complexes, reactions involving ruthenium catalysts are connected with the formation of oxo complexes. Ruthenium systems catalyzing alkene oxidation by hydrogen peroxide were discovered in 2005 by Beller and co-workers.[114] Using ruthenium (terpyridine)(pyridine-2,6-dicarboxylate) complex (0.5% Ru), a variety of alkenes including allyllic structures were oxidized to epoxides on treatment with 30% hydrogen peroxide.

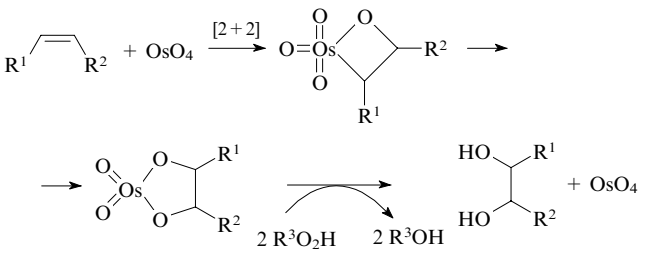
Mn(V) oxo complexes can also be employed as active forms for alkene epoxidation.[115] The Mn(III) porphyrin complex in the presence of hexylimidazole and the Mn(II) complex with trimethyl-1,4,7-triazacyclononane also demonstrated high activity in epoxide synthesis.[116] Jacobs and De Vos [117] modified the latter system with oxalate buffer in order to reduce the contribution of hydrogen peroxide decomposition. It is supposed that the reaction proceeds *via* Mn(IV) and Mn(V) oxo complexes. It should be noted that simpler systems, for example manganese sulfate with alkali additives, also proved active in alkene epoxidation.[118] Quite recently it was shown [119] that peracetic acid in the presence of the Mn(II) bipyridyl complex oxidizes alkenes to epoxides (TOF = 200 000 h^{-1}).

Iron complexes, which resemble manganese complexes in their properties, in particular tetradentate iron complexes with amines catalyze the epoxidation of substituted and terminal alkenes by H_2O_2.[120]

3. Alkene dihydroxylation

For vicinal dihydroxylation of alkenes involving oxygen donors (hydroperoxides or *N*-methylmorpholine-*N*-oxide), osmium systems are used.[121] Beller and Sharpless [122] applied OsO_4 to asymmetric dihydroxylation of alkenes. It is assumed that Os(VIII) oxo complexes interact with an alkene by a [2 + 2] cycloaddition mechanism with rearrangement to a diol complex (Scheme 5).

Scheme 5

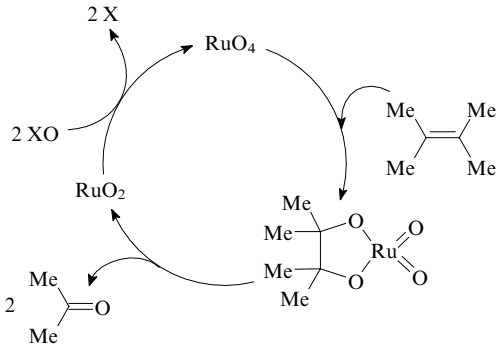


This method was extented to electron-deficient alkenes, for example, α,β-unsaturated amides. Beller and co-workers [123] demonstrated the possibility of using oxygen as an oxidant and potassium osmate as a catalyst in this process.

4. Oxidative cleavage of alkenes

Oxidative cleavage of alkenes across the double bond is achieved using ruthenium catalysts and oxidants ($NaIO_4$, NaClO).[124] Scheme 6 illustrates the catalytic cycle for the conversion of tetramethylethylene to acetone on treatment with an oxidant (XO).

Scheme 6



XO = NaOCl, $NaIO_4$, RCO_3H, *etc.*

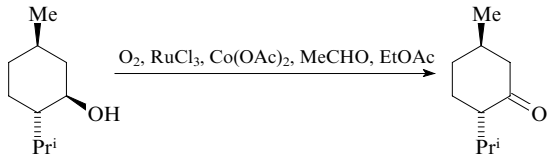
Unfortunately, attempts to employ hydrogen peroxide or oxygen as the oxidants were not crowned with success. However, the authors [125] managed to find a suitable catalytic system for the oxidative cleavage of the C=C bond in alkenes with H_2O_2. It proved to be the system $MoO_3 - RuCl_3$. Presumably, the reaction involves alkene epoxidation on molybdenum followed by cleavage of the diol. In the case of styrene, the yields reached ~ 80%.

5. Oxidation of functional derivatives on treatment with O_2 and H_2O_2

In alcohol oxidation processes, catalysts based on Ru, Pd, Pt, Au and Cu are commonly used. Particularly attractive is the exploitation of copper complexes instead of expensive noble metals. Hydrogen peroxide or organic hydroperoxides are employed as the oxidants.[126]

The alcohol oxidation mechanism proposed in the literature involves a change in the metal oxidation state. However, in the case of Pd(II), Ru(III) and Rh(III) complexes the reaction can proceed through alcohol dehydrogenation. The ruthenium systems were examined in most detail since in this case the reaction occurs under mild conditions.[127] When using ionic liquids as solvents, especially in the presence of trioctylmethylammonium chloride (Aliquat 336), the activity of a catalyst, for example $RuCl_2PPh_3$, increases.[128] The possibility of catalyst recycling was exemplified by the system $Me_4NCl - RuCl_2(PPh_3)_3$. An example of the use of low-valence ruthenium complexes in combination with benzoquinone in alcohol oxidation reactions involving hydrogen transfer has been reported.[129]

It was found [130] that the system $RuCl_2(PPh_3)_3 - O_2 - 1,4\text{-}(OH)_2C_6H_4$ is able to oxidize primary aliphatic, allylic and benzylic alcohols to aldehydes in nearly 100% yield. The use of the same ruthenium complex in combination with 2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO) brings about an increase in aldehyde yields since TEMPO suppresses the radical process of aldehyde oxidation to carboxylic acids. Ru(III) complexes are also employed for alcohol oxidation.



(95%)

Perruthenates including polymer-supported ones were applied to the oxidation of allylic alcohols by oxygen or *N*-methylmorpholine *N*-oxide.[131] Unfortunately, when re-used the polymer complex lost its activity.

The use of palladium complexes for alcohol oxidation by air is described in the review.[132] Peterson and Larock showed that the oxidation of various alcohols to aldehydes and ketones can be catalyzed even by $Pd(OAc)_2$ in the presence of bases.[133] The replacement of the organic solvent by an ionic liquid resulted in a threefold increase in the catalyst activity.[134] Additional introduction of zeolite 3A in the system $Pd(OAc)_2$–pyridine enhances the process parameters owing to the dehydrating ability of the zeolite.[135]

Aerobic oxidation of alcohols was accomplished using water-soluble palladium complexes in biphase water–alcohol systems,[136] whereas the (Neocuproine)$Pd(OAc)_2$ complex[137] turned out to be not only extremely active in the aerobic oxidation of alcohols, but also selective — the oxidation does not affect other bonds and groups present in the substrate, for example, C=C, C≡C, C–Hal bonds, β-carbonyl, ester and amino groups.

For the purpose of searching for more active and stable catalysts for alcohol oxidation palladium carbene complexes were explored,[138] however, until now no palladium catalysts were revealed that exhibit higher activity than that of phoshine catalysts.

Great expectations were associated with the use of copper complexes.[139] Particularly, the system CuCl–phenanthroline in the presence of bases was reported[140] to catalyze the oxidation of benzylic, allylic and even primary aliphatic alcohols by air. Replacement of CuCl by CuICl and introduction of 1-methylimidazole to the system brought about an increase in the activity of copper complexes.[141] Combining copper complexes with TEMPO also provides good results,[142] although such systems are mainly employed for the oxidation of activated alcohols. Successful application of copper complexes to oxidation processes is also evidenced by the data[143] according to which not only benzylic and allylic alcohols but also primary alcohols could be oxidized at room temperature in 60% to 100% yields in the system $CuBr_2$(bipy)–TEMPO–Bu^{t}OK (bipy is bipyridine).

The use of the system $Co(acac)_3$–*N*-hydroxyphthalimide for the oxidation of primary and secondary alcohols to carboxylic acids and ketones, respectively, was reported.[144]

Beller and co-workers[145] applied an osmium catalyst developed previously for alkene dihydroxylation to alcohol oxidation by oxygen in a biphase system; however, good selectivity was observed only for the oxidation of benzylic and secondary aliphatic alcohols.

The literature describes successful application of metal complex catalysts and environmentally friendly oxidants (hydrogen peroxide, air) for the oxidation of carbohydrates,[146] acyclic and cyclic ketones,[147] phenols,[148] ethers,[149] various nitrogen-containing compounds (amines, *N*,*N*-dimethylhydrazones, hydroxylamines, pyridines and amides).[150, 151]

6. Oxidation in ionic liquids, water and fluorous biphase systems

To date, the list of oxidation reactions carried out in ionic liquids is not large. Oxidation of aromatic aldehydes by oxygen to carboxylic acids in $[BMIM]^+[PF_6]^-$ in the presence of nickel complexes has been reported;[152] the yields of the acids were ~60%–70%. Epoxidation of alkenes and allylic alcohols was performed on treatment with methyltrioxorhenium and urea hydroperoxide in the ionic liquid $[EMIM]^+[BF_4]^-$ (the reaction conversion and selectivity reached 100%).[153] Also, oxidation of aliphatic and aromatic (including benzylic) alcohols by air to aldehydes and ketones on ruthenium catalysts (phosphine and chloride complexes) was conducted in a variety of ammonium ionic liquids (the product yields reached 99%).[154] It was demonstrated[154] that successful accomplishment of these reactions depends on the nature of the ionic liquid, in particular, of the anion. For example, the reaction does not take place in ionic liquids with the BF_4^- and PF_6^- anions, and the best outcomes were achieved when conducting the reactions in tetramethylammonium hydroxide and trioctylmethylammonium chloride.

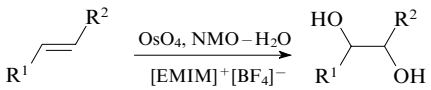
High yields and good selectivity were achieved when carrying out alkene oxidation (the Wacker process) in ionic liquids or mixed systems ionic liquid–supercritical CO_2 in the presence of $PdCl_2$–$CuCl_2$.[155]

Ionic liquids commonly used in the synthesis of organic compounds proved to be good media for the oxidation of a variety of substrates, involving palladium acetate as the catalyst precursor.[134] The major product of benzyl alcohol oxidation in an ionic liquid was benzaldehyde, that in water was benzoic acid. The same system was examined in the oxidation of ethybenzene to phenylethanol or acetophenone (the yield exceeded 50%). In the absence of an ionic liquid, acetophenone predominated.

For the oxidation of benzylic alcohols, the system CuCl–TEMPO was employed as the catalyst, and $[BMIM]^+[PF_6]^-$ was used as the solvent.[156]

Ruthenium catalysts (for instance, tetrapropylammonium perruthenate) were also studied in alcohol oxidation to ketones by oxygen or *N*-methylmorpholine *N*-oxide in diverse imidazolium ionic liquids.[157] Benzylic alcohols were naturally oxidized better (the conversion in $[BMIM]^+[PF_6]^-$ was 60%–70%) than aliphatic alcohols (the conversion was 24%–48%).

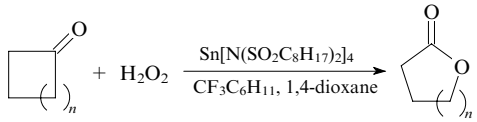
The activities of catalysts based on OsO_4 that were used for alkene dihydroxylation to diols was studied in ionic liquids. *N*-Methylmorpholine-*N*-oxide (NMO), hydrogen peroxide or *tert*-butyl hydroperoxide oxidized alkenes in the presence of $[EMIM]^+[BF_4]^-$ in up to 100% yields.[158]



An immobilized OsO_4-catalyst in the ionic liquid can be recovered and re-used for alkene hydroxylation.

Palladium complexes utilized in hydrogenation in aqueous phase can also be employed for the oxidation of primary and secondary alcohols to aldehydes (carboxylic acids) and ketones, respectively.[52, 53]

In the presence of fluorous biphase systems, primary and secondary alcohols were oxidized by oxygen (the catalytic system was CuBr – Me_2S-perfluoroalkylbipyridine – TEMPO) [159] and cyclic ketones were oxidized by hydrogen peroxide (the Baeyer – Villiger reaction), the catalyst was a perfluorinated tin complex, $Sn[N(SO_2C_8F_{17})_2]_4$.[160]



$n = 1-3$.

Examples of alcohol oxidation by using FBS and manganese complexes are provided in Ref. 161.

7. Asymmetric oxidation

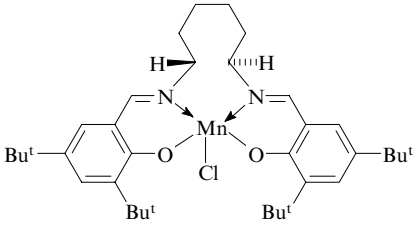
Alkene epoxidation is one of the most thoroughly studied reactions in which chiral metal complex catalysts are used. By analogy to the Sharpless [162] epoxidation, titanium diethyl tartrate complexes are employed in the process. The epoxidation of primary allylic alcohols leads to at least 90% optical yields. For the epoxidation of non-functionalized alkenes, chiral manganese or chromium salen complexes proved more efficient.[163, 164] Beller and co-workers [165, 166] employed Ti- and Ru-complexes to asymmetric epoxidation of alkenes involving hydrogen peroxide. Even for oct-1-ene, sufficiently high enantioselectivity was achieved (*ee* was 82%).

It was suggested [167] to use manganese complexes for asymmetric epoxidation and employ oxygen and an aldehyde as the oxidant.

Asymmetric dihydroxylation of alkenes occurs efficiently using osmium catalysts and *N*-methylmorpholine *N*-oxide as the oxidant. Beller [168] made a substantial contribution to the study of asymmetric oxidation reactions and achieved high values of enantiomeric excess (up to 96%). He also demonstrated the possibility of oxygen involvement in the process (potassium osmate played the role of a catalyst in the presence of organic bases).

Among other asymmertic oxidations with the use of chiral catalysts and 'green' oxidants, allylic oxidation of alkenes,[169] sulfoxidation,[170, 171] and the Baeyer – Villiger asymmertic oxidation should be mentioned.[172]

Let us demonstrate some examples of asymmertic oxidative catalysis in ionic liquids. Epoxidation of alkenes with NaOCl and chiral manganese salen complexes (**23**) in the ionic liquid $[BMIM]^+[PF_6]^-$ proved efficient, the enantiomeric excess reached 96%.[173] However, the system activity decreased from cycle to cycle.



(*R*,*R*)-**23**

Asymmertic alkene dihydroxylation in the ionic liquid $[BMIM]^+[PF_6]^-$ in the presence of an osmium catalyst with chiral ligands has been studied.[174] The yield and enantiomeric excess were sufficiently high, however, re-use of the catalyst resulted in loss of activity.

8. Heterogenized metal complex catalysts for partial oxidation

In recent years, many studies have emerged on the use of supported (heterogenized, immobilized) catalysts in partial oxidation reactions, in the first place, in alkene epoxidation,[175] oxidation of alcohols, aldehydes, amines and other functional derivatives. Let us note most interesting examples.

For alkene epoxidations, molybdenum and manganese systems immobilized on various supports are studied in most detail, whereas the immobilization of Co, Ni and Fe complexes and their application are reported in isolated studies. Manganese porphyrin and salen complexes and Mn complexes with Schiff bases immobilized on zeolite or mesoporous silicate matrices exhibited high efficiency and recycling in alkene epoxidation;[176 – 178] this also applies to cobalt salen complexes immobilzied on montmorillonite or the mesoporous support MCM-41;[179, 180] zeolite-supported nickel microcyclic tetraaza complexes,[181] mesoporous silicate-supported molybdenum peroxo complexes.[182, 183]

Active metal complex systems for alkene epoxidation encapsulated in polymeric matrices are discussed in the review.[184]

Theoretical studies on the role of the nearest environment of an active site by the example of manganese salen complexes immobilized on mesoporous materials were conducted by van Santen's research group.[185]

There are also numerous studies on enantioselective epoxidation of alkenes on supported chiral metal complexes. Thus titanium triazine tartrate systems immobilized on the mesoporous carrier MCM-41 for the epoxidation of cinnamic alcohol were developed,[20] manganese salen catalysts on MCM-41 for the epoxidation of non-functionalized alkenes [186] as well as Ru-systems were developed.[187]

The absence of studies on alkene dihydroxylation on heterogenized metal complex systems is quite explicable, since the produced diol is, apparently, adsorbed very strongly on the support, which results in a decrease in the yield of the target product in subsequent cycles.

For the selective oxidation of benzylic alcohols, chromium salen complex on MCM-41,[188] manganese porphyrin complexes on polystyrene [189] as well as polymer-supported palladium complexes with Schiff bases [32] were used.

IV. Formation of carbon – carbon and carbon – heteroatom bonds

1. Cross-coupling and related reactions

One of the most remarkable advances in the organic chemistry of the last century is the discovery of the cross-coupling reaction independently by two research groups in France and Japan in 1972. It was shown that organolithium and organomagnesium compounds with the $C(sp^2)-M$ bond react with aryl(vinyl) halides in the presence of nickel complexes to form coupling products. Two years later these reactions were accomplished on palladium complexes, which turned out to be most efficient and selective catalysts of such reactions.[190]

Note that the Ullman reaction of aryl iodides to produce biaryls required high temperatures and a great excess of the copper catalyst.

Over a short time, a variety of organometallic and organoelement compounds were involed in cross-coupling reactions; such reactions were named after the chemists who proposed the reactions.

$$R^1{-}X + R^2{-}M \xrightarrow{[Pd]} R^1{-}R^2$$

X = Hal, OTf; R^1 = Ar, Vin; R^2 = Ar, Vin, Alk; M = MgX (the Tamao–Kumada–Corriu reaction); ZnX (the Negishi reaction); $B(OH)_2$ (the Suzuki–Miyaura reaction); SnR_3 (the Stille reaction or the Migita–Kosugi—Stille reaction); SiR_3 (the Hayama reaction).

These reactions occupied a decent place in the arsenal of 'green' chemistry methods, because they enabled the preparation of a broad spectrum of novel organic compounds with exceptionally high selectivity, especially, when using heterogenized catalytic systems. A variety of biaryls, styrenes, dienes, stilbenes, enynes and recently also alkylaromatic compounds were obtained by these reactions. Cross-coupling reactions are widely used in the synthesis of natural compounds, polymers, materials for nonliner optics, *etc*. Examples of the synthesis of some natural compounds with the use of these reactions are listed in Table 2.[191] Note that high product yields when using transition metal complexes with suitable ligands could be obtained even in reactions with aryl triflates and aryl chlorides.

Aryl halide reactions occur likewise with cyanides and CH-acids (in the presence of bases). For example, α-arylation of enolizable ketones was carried out in this way. It is natural that depending on the reagent nature the rate-determining step can change; besides, the true mechanism of each step can be different in different processes.

The reactions described not only affected the development of organic synthesis, but also facilitated insights into the mechanism of catalysis by transition metal complexes and into the conversions of organic compounds. The generally accepted catalytic cycle for cross-coupling reactions

Table 2. Some examples of the synthesis of compounds with the use of cross-coupling reactions.

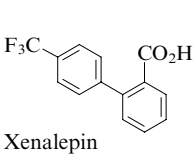
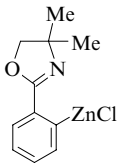
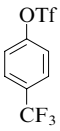
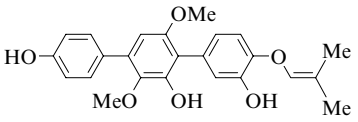
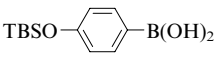
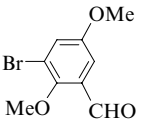
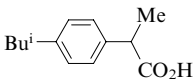
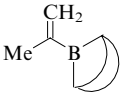
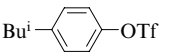
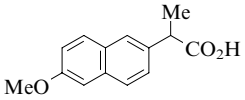
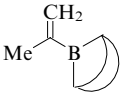
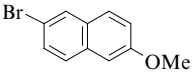
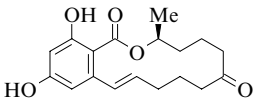
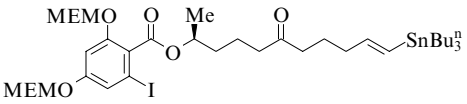
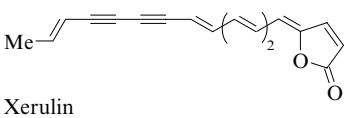
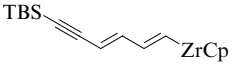
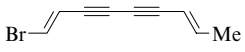
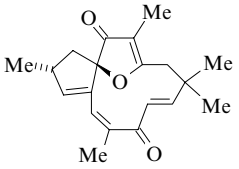
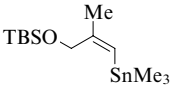
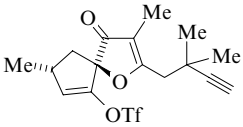
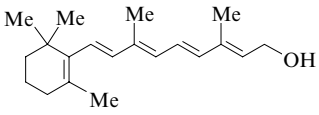
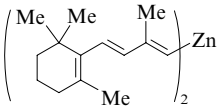
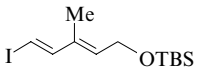
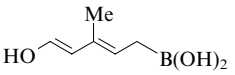
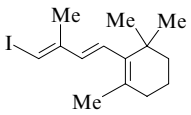
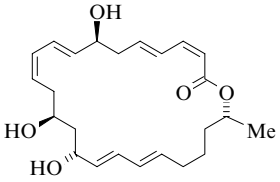
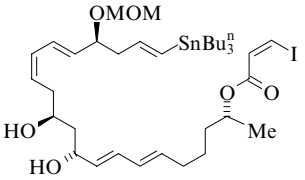
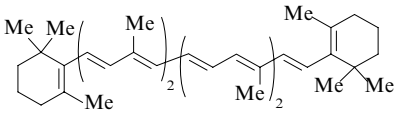
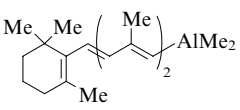
Natural compound	ArM	ArX	Catalyst	Additional reagent	Yield (%)
 Xenalepin			$Pd(PPh_3)_4$	–	78
 Terprenin			$Pd(PPh_3)_4$	Na_2CO_3	100
 Ibuprofen			$Pd(PPh_3)_4$	K_3PO_4	68
 Naproxen			$Pd(PPh_3)_4$	K_3PO_4	75
 (*S*)-Zearalenone			$Pd(PPh_3)_4$ (see [a])	–	54
 Xerulin			$PdCl_2(PPh_3)_2$	DIBAH, $ZnCl_2$	95
 (+)-Jatrophone			$Pd(PPh_3)_4$	–	100

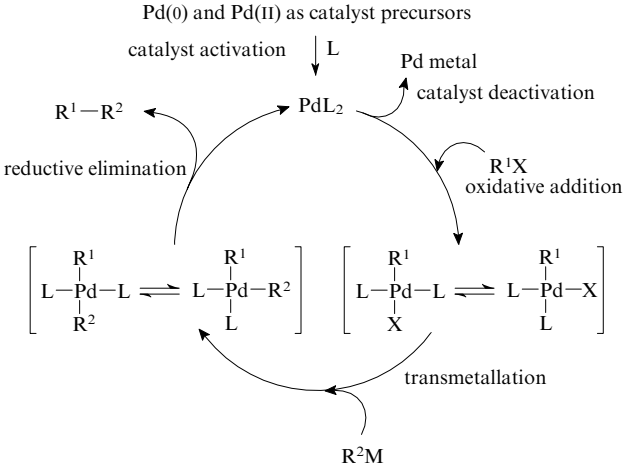
Table 2 (continued).

Natural compound	ArM	ArX	Catalyst	Additional reagent	Yield (%)
 Vitamin A			$Pd(PPh_3)_4$	–	87
			$Pd(PPh_3)_4$	TlOH	83
 Macrolactin A			Pd(0)	$AsPh_3$	58
 β-Carotene			$PdCl_2(PPh_3)_2$	DIBAH, $ZnBr_2$	68

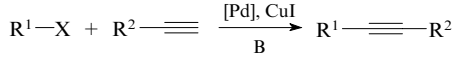
Note. DIBAH is diisobutylaluminium hydride; MEM is methoxyethylmethyl, TBS is *tert*-butyldimethylsilyl, MOM is methoxymethyl. [a] Polymer-supported.

involving palladium in two oxidation states — Pd(0) and Pd(II) — comprises the following steps: oxidative addition, transmetallation and reductive elimination resulting in a coupling product and the regenerated catalyst (Scheme 7).

Scheme 7



Aryl or vinyl halide (or triflate) reactions with terminal alkynes catalyzed by palladium complexes and CuI also belong to the cross-coupling reactions (the Sonogashira–Hagihara reaction).[192]

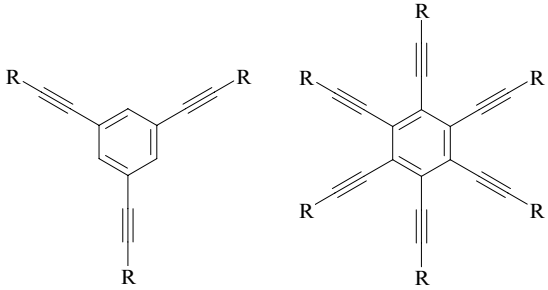


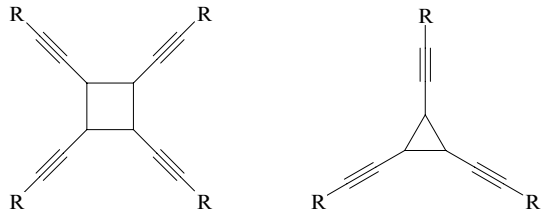
X = Hal, OTf; R^1 = Ar, Vin; R^2 = Ar, Alk.

Copper iodide is needed for alkyne activation resulting in copper acetylides. Noncatalytic reactions of aryl(vinyl) halides with copper acetylides were known earlier (the Stephens–Castro reaction),[193] however only after the discovery of the catalytic version, this process has gained popularity and began to be used for obtaining molecules of various architectures as well as for the synthesis of novel materials.

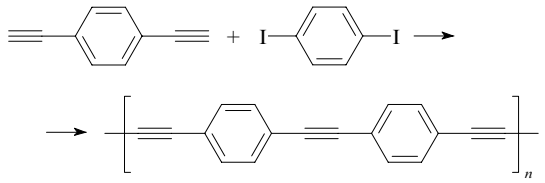
The catalytic cycle of the Sonogashira reaction differs from that of a cross-coupling reaction only in the presence of an additional step in which copper acetylide is derived from an alkyne and CuX in the presence of a base. The acetylide then participates in the main cycle with regeneration of CuX.

Using the Sonogashira reaction, polysubstituted molecules with different scaffolds can be designed for further use in the synthesis of dendrimeric structures.



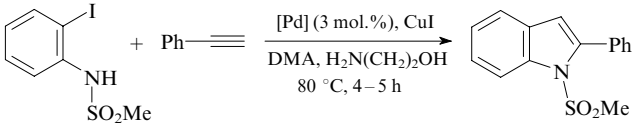


It is also possible to synthetize polymers (including nanosized structures) of the type:[190]



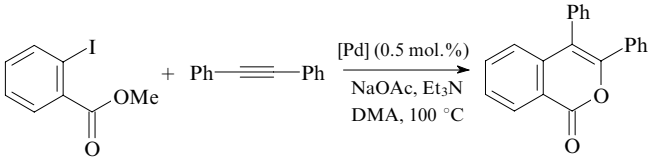
Using this reaction, a number of natural compounds were obtained: (+)-harveynone, gomobutenolide A, freelingine, (−)-calicheamicenone, *etc*.

Of great significance is the Sonogashira reaction for the synthesis of carbo- and heterocyclic systems (cyclization reactions). Below a synthesis of a substituted indole is presented that includes the Sonogashira reaction involving *N*-methylsulfonyl-2-iodoaniline, followed by cyclization with the use of 'ligand-free' nanosized palladium.[194]



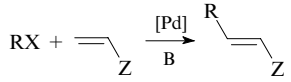
DMA is *N*,*N*-dimethylacetamide.

Likewise, substituted isocoumarin was synthesized from diphenylacetylene and methyl 2-iodobenzoate.[194]



Note that palladium nanoparticles located in a micelle produced by the block copolymer polystyrene–polyethylene oxide (PS–PEO) act as the catalyst in these reactions.

Another reaction leading to the formation of the $C(sp^2)-C(sp^2)$ bond is the catalytic arylation (or vinylation) of alkenes (the Mizoroki–Heck reaction).[195] It became exceptionally widespread owing to its easy accomplishment and high selectivity of the formation of the *trans*-product, replacing the methylene–carbonyl condensation in many cases.



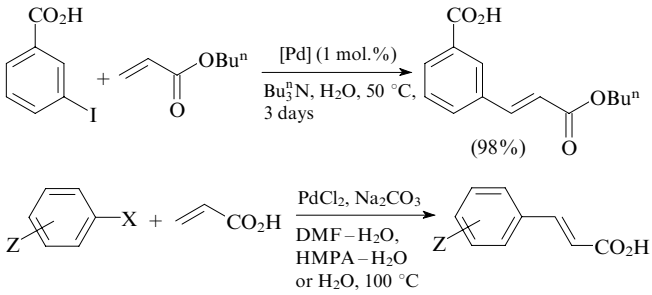
X = Hal, OTf; R = Ar, Vin; Z = Ar, CO_2H, CO_2R', CN; B is base.

The Heck reaction proceeds particularly easily with aryl iodides and monosubstituted alkenes bearing electron-withdrawing groups; in all other cases the use of more complex catalytic systems is required.[196] This reaction is widely applied to the preparation of carbo- and heterocyclic compounds.[197, 198]

In the catalytic cycle of the Heck reaction, the transmetallation step available in the catalytic cycle of cross-coupling is replaced by the step of insertion of an alkene molecule in the Pd–C bond. For this reaction to take place, preliminary coordination of the alkene to the palladium atom accompanied by a displacement of a ligand is required.

It is obvious that such distinctions between the catalytic cycles of cross-coupling and the Heck reaction require the use of different ligands. In general the impact of the ligand in the reactions outlined above is an exceptionally important factor. Phosphine ligands are most widely used. One can say that due to the development of the catalysis by transition metal complexes and, particularly, by palladium complexes, an extensive research area has emerged that changed the direction of studies in chemistry of organophosphorus compounds and set a new trend — the synthesis and use of phosphine ligands of various types (including chiral ones for asymmetric catalysis), which, in turn, gave rise to development of synthetic methods from the 'green' chemistry standpoint. It should be noted that lately along with phosphine ligands, phosphites, N-, S-, Se-containing ligands, hybrid ligands, carbenes as well as heterogenized palladium complexes have found wide application.

The Heck and cross-coupling reactions carried out with a 'ligand-free' palladium (*i.e*., without phosphine ligands) in aqueous solutions or pure water meet the demands of green chemistry to a greater extent. It is evident that catalysts in these reactions are nanosized palladium particles.[199] Thus the Suzuki reaction can be conducted in pure water under extremely mild conditions (20 °C) with simple palladium salts. Below are particular examples of the Heck reaction performed in aqueous solutions (or even in pure water) with the use of $PdCl_2$ ('ligand-free' palladium) as a catalyst precursor.



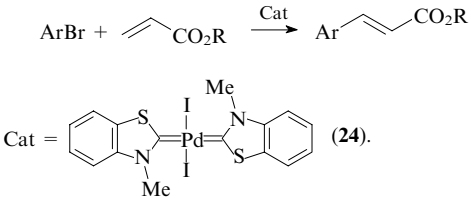
X = I, Br; Z = H, 4-Cl, 4-MeO, 4-Ac, 4-NO_2, 4-CHO, 4-OH, 3-CO_2H.

The Suzuki and Heck reactions are often employed for testing ligand efficiency and for examining various conditions and methodology (including the study of the influence of various media and physical impact). They are thoroughly explored in the reviews.[200, 201] Examples of successful application of catalyst microwave activation in these reactions are provided in the study.[202]

From the standpoint of green chemistry, particularly attractive is the use of ionic liquids in various cross-coupling reactions and the Heck reaction.[203–206] In many cases, the use of ionic liquids brings about some increase in

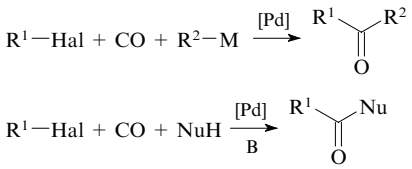
the activivty of both the catalyst (by 10% – 50%) and reactants, and a decrease in the reaction time. Ionic liquids permit catalyst recycling, which is their major advantage over conventional solvents.

Thus, for instance, it was shown that the Heck reaction involving a variety of electron-donating or electron-withdrawing aryl bromides, catalyzed by palladium complexes **24**, can be accomplished in ionic liquids with high product yields.[207, 208]



Carrying out the process in different ionic liquids with the use of palladium acetate and triphenylphosphine ligands results initially in palladium nanoparticles of the ~0.8 – 1.6 nm size stabilized by the ionic liquid and phosphine ligands.[41] Using palladacycles containing phosphorus atoms as catalyst precursors allows the reaction to be carried out at high temperatures, and, consequently, permits the use of low catalyst concentrations, which gives additional possibilities of increasing the activity of a catalytic system (high turnover number).[209, 210]

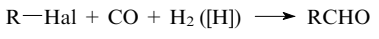
The trimolecular reaction of aryl halide carbonylation in the presence of various nucleophilic reagents is less studied and not so widely used, albeit very promising. Such a reaction, unlike hydroformylation occurs under very mild conditions (1 atm. CO, low temperatures) and allows the preparation of a wide range of oxygen-containing compounds: aromatic acids, amides, esters, thioesters, symmetric and unsymmetric ketones.[211] The reaction with organometallic (organoelement) compounds yields ketones, the reactions with alcohols and thiols give esters, that with water produces carboxylic acids, and the reactions with amines give acid amides.[212, 213]



R^1 = Ar, Vin; R^2 = Alk, Ar, *etc.*; NuH = H_2O, R^3OH, R^3NH_2, R^3_2NH, R^3SH.

The catalytic cycle of such a reaction includes insertion of the CO molecule in the C – Pd bond to produce the palladium acyl complex RC(O)PdX, which further reacts with a nucleophile giving the intermediate RC(O)PdNu. The following reductive elimination of the intermediate RC(O)PdNu yields a product and results in catalyst regeneration.

For the preparation of aldehydes, molecular hydrogen or hydride ion donors can be employed.



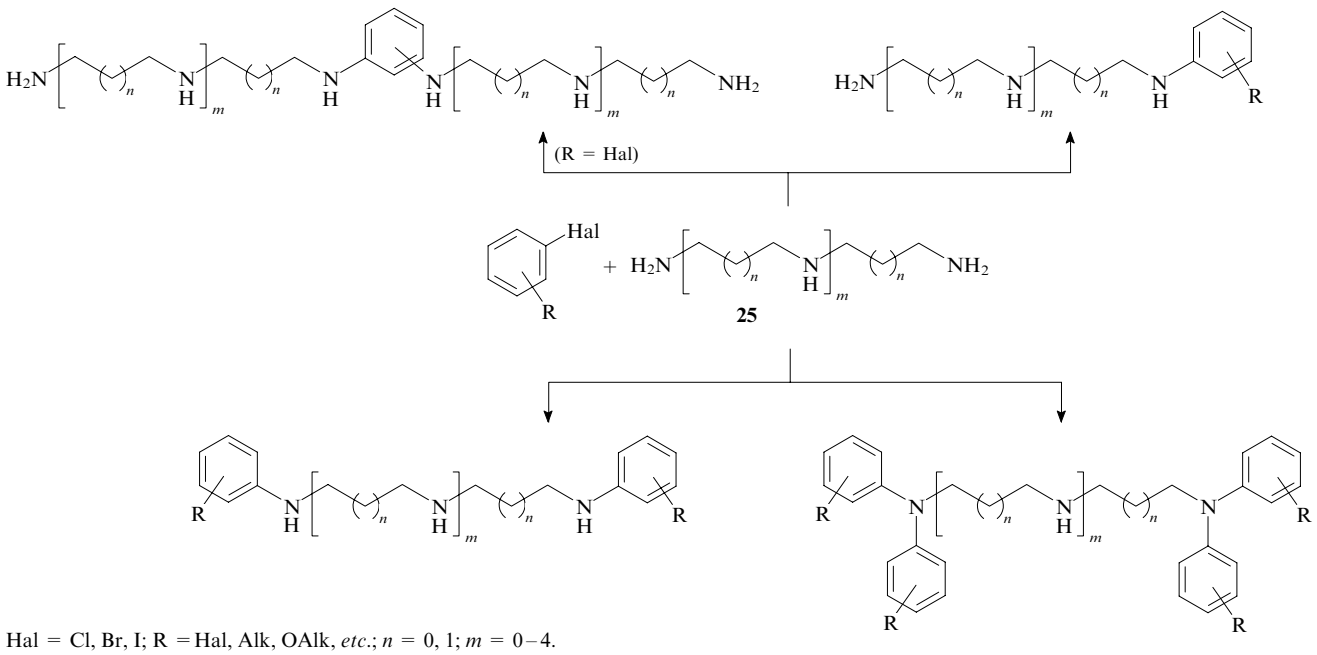
Aromatic acid synthesis was accomplished in water by using 'ligand-free' palladium[214] as well as nanosized palladium incroporated in the micelle PS – PEO.[215] In the latter case, the catalyst can be recycled 5 times without loss of the catalytic activity. In an analogous manner (also with catalyst recycling), the aminocarbonylation of water-insoluble aryl hadiles in methanol catalyzed by nanosized palladium immobilized on the copolymer poly(*N*-vinylimidazole) – poly(*N*-vinylcaprolactam) (PVI – PVC) was performed.

2. The carbon – heteroatom bond formation

The cross-coupling reaction can also be applied to the formation of a carbon – heteroatom bond: C – P(O)(OR)$_2$, C – P(O)R_2, C – PR_2, C – SR, C – SeR, C – OR, C – NR_2, C – NC(O)R, *etc.*

Of special interest, both for practical application and for mechanism determination, is the amination of aromatic compounds (the Buchwald – Hartwig amination).[216] This

Scheme 8



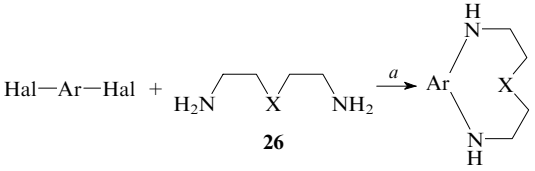
Hal = Cl, Br, I; R = Hal, Alk, OAlk, *etc.*; n = 0, 1; m = 0 – 4.

reaction was conducted for the first time by Japanese researchers Kosugi and Migita in 1983 with the use of tin and boron amides as the starting compounds, however, it had taken a lot of time before it was accomplished with free amines.

$$Ar{-}Hal + R_2NSnBu^n_3 \longrightarrow ArNR_2 + Bu^n_3SnHal.$$

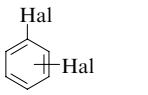
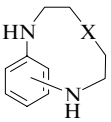
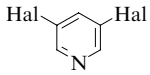
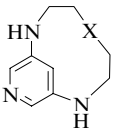
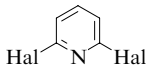
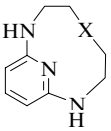
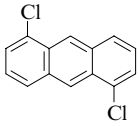
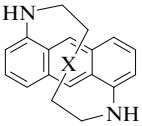
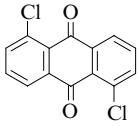
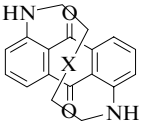
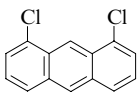
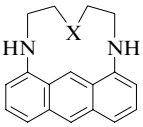
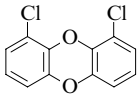
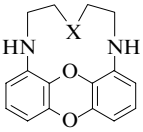
Currently, in the laboratory of organoelement compounds, Department of Chemistry, Moscow State University this reaction is successfully applied to the preparation of mono-, di- and tetraarylated products (Scheme 8) and polyaza(polyoxo)macrocycles (Scheme 9) by selective arylation of polyamines **25** and **26**.

Scheme 9



26

(*a*) $Pd(dba)_2$ – BINAP, Bu^tONa or Cs_2CO_3, 1,4-dioxane, 6 – 72 h.
Hal = Cl, Br; X = $NH(CH_2)_xNH$ (x = 2, 3), $CH_2NH(CH_2)_xNHCH_2$ (x = 2, 3), $NH[(CH_2)_2NH]_x$ (x = 2, 3), OCH_2O, $CH_2O[(CH_2)_2O]_2CH_2$, $CH_2O(CH_2)_4OCH_2$.

Starting arene	Product
 *ortho*, *meta*	
	
	
	
	
	
	

The polyazamacrocycles derived from dihaloarenes are capable of coordinating metal cations.[217,218] For these reactions to be carried out, the development of palladium complexes with sufficiently complex and expensive phosphine and later carbene ligands was required.

Although the use of the methods discussed above allows avoidance of multi-step syntheses with the formation of a large amount of waste, the objective of inreasing catalyst efficiency still remains vital. Numerous research groups continue investigations into the development of novel palladium-based catalytic systems. To this end, a variety of Pd(0) and Pd(II) complexes as catalyst precursors is applied as well as new ligands, a variety of environmentally friendly solvents inlcuding aqueous solutions and even pure water, biphase systems, fluorous solvents, ionic liquids, and supercritical CO_2 and water are employed.

An important trend of modern catalysis on palladium systems is the development of immobilized catalysts followed by their recycling. The Heck,[219–221] Suzuki[222–226] and Sonogashira[227] reactions are exploited as model reactions. In many cases, catalysts could be repeteadly used in successive cycles (from 3 to tens) without loss of catalytic activity. Note, however, that using a support having a phoshine or carbene as the coordinating centre, which strongly binds to palladium, one can expect that palladium will remain bound to the centre after reaction completion. Using a neutral or weakly coordinating support can result in palladium leaching when treated with an aryl halide followed by further aggregation of palladium particles up to the formation of inactive palladium black. It is such a scenario that seems most probable when using palladium nanoparticles immobilized on various polymeric and other analogous carriers containing no strong coordinating centres.[228]

Another important environmental problem that pertains to the use of the reactions under consideration on an industrial scale is the employment of cheap, but toxic aryl chlorides instead of aryl iodides and bromides. This problem was resolved in principle by using palladium complexes with sterically crowded ligands of the donor type as the catalysts,[229] for instance, Bu^t_3P and carbenes.

However in some cases more straighforward catalytic systems could be employed, for example, palladium complexes with the $(PhO)_3P$ ligand[230] or palladium nanoparticles stabilized by an ionic liquid.[231]

However, it should be borne in mind that the success of a reaction depends on all of the components, hence, the problem cannot be regarded completely solved. The scaling of the processes appears to be an equally important task. Usually these reactions are carried out at small reactant concentrations and with a small amount of a palladium catalyst, and only in rare instances the possiblity of reactions in gramm quantities is tested. This issue is addressed in the publication.[232]

The efforts to replace expensive palladium with cheaper metals such as nickel, copper and even iron have become an essential trend in metal complex catalysis.

Particularly remarkable progress was achieved in the use of various copper compounds [Cu(I), Cu(II), CuO; Cu(0) powder or nanoparticles] as the catalysts. Using such catalysts, many cross-coupling reactions could be accomplished. The greatest advances are associated with reactions yielding a carbon – heteroatom bond (C—N, C—S, C—O).[233] Even in this case, the problem of designing general procedures remains unsolved, since virtually in each new studied reaction a copper complex with a new ligand proves active, and there is no possibility of predicting

the activity of such complexes for other reactions. The issue is aggravated by difficulties in studying the mechanism of Cu-catalyzed reactions, which are less considerable for palladium-catalyzed reactions.

Quite recently it was established that iron complexes can also catalyze cross-coupling reactions,[234] albeit it is possible that for this reaction this effect is determined by the presence of traces of copper in these complexes. Probably, some reactions are catalyzed by iron complexes proper. The mechanism of such a catalytic action is far from being understood as yet; however, the potential of the use of iron complexes is clearly evident from both environmental and economical perpsectives.

V. Integrated processes and cascade catalytic reactions

In recent years, the line of research dealing with the realization of two successive processes in one reaction vessel appears fairly promising.[235–239] The advantages and economy of such an approach are obvious, although the use of metal complex systems is associated with a number of difficulties caused by the impact of the conditions of the second reaction on the properties of the active complex (Table 3).

Table 3. Merits and demerits of catalytic cascade processes.

Advantages	Limitations
Fewer operations	Incompatibility of catalysts
Equilibrium shift in the required direction	The rates of two processes can remarkably differ
Lesser consumption of solvents	It is difficult to find optimal conditions for two processes occuring simultaneously
Reduced reactor volume	Complication of catalyst recycling
Shortened process duration	Complicated isolation/purification of reaction mixture
Increased output of the process	
Decreased *E*-factor	
Reduced waste volume	

The cascade process with the use of a metal complex catalyst can be exemplified by the selective hydrogenation of benzene to cyclohexene on a ruthenium system followed by a hydration of the produced cyclohexene to cyclohexanol on a zeolite catalyst (Asahi Chemical).

Good examples are reported of combination of an enzymatic dynamic kinetic resolution process with a hydrogenation reaction on ruthenium complexes.[240–248] The role of the metal complex component is to catalyze dehydrogenation–hydrogenation cycles of substrates (alcohols, amines).

Bäckwell and co-workers[246, 247] demonstrated the efficiency of a similar approach in the synthesis of secondary alcohols followed by their acylation with the use of combined catalysis by a ruthenium complex combined with a lipase, while Sheldon and co-workers[248] applied a cascade reaction to the enantioselective synthesis of amino acids in water (immobilized ruthenium catalyst for asymmetric hydrogenation and aminoacylase).

* * *

New applications of metal complex systems, in addition to already established areas related to pharmaceutical, food and perfume industries, are the processing of renewable feedstock, in the first place, vegetable fats, carbohydrates (including cellulose), lignine and its derivatives, terpenes and other natural compounds. Particularly attractive is the combination of biocatalytic processes with hydrogenation or partial oxidation with compatible reaction conditions. Among target products one should indicate high-octane fuel additives, for example, furfural or tetrahydrofuran derivatives, lactic acid and lactates.

Routes to an enhanced efficiency of currently known metal complex systems lie, most likely, in developing novel improved ligands, the use of immobilized systems free from the shortcomings of heterogeneous catalysts, the use of new 'green' solvents in combination with a complex approach to the process organization (cascade processes, microwave technologies, supercritical media, extraction systems or reactive distillation methods).

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