Russian Chemical Reviews **74** (1) 97 – 111 (2005) © 2005 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2005v074n01ABEH000819

Design of supramolecular metal complex catalytic systems for organic and petrochemical synthesis

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Abstract. The state-of-the-art in investigations into the supramolecular catalysis by metal complexes using macrocyclic receptor molecules is surveyed. The emphasis is placed on issues related to the design of novel metal complex catalysts capable of molecular recognition and to their applications in organic synthesis, in particular, in such reactions as hydrogenation, hydroformylation, carbonylation, hydroxylation, Wacker oxidation, biomimetic oxidation, and some others. The factors affecting the activity, stability and selectivity of such catalytic systems are discussed. The bibliography includes 159 references.

I. Introduction

Nowadays, the vast majority of industrial processes are based on catalytic reactions. Catalysts are utilised in diverse fields ranging from large-scale processes, such as petroleum refining, hydrotreatment, production of ammonia, *etc*., to the synthesis of drugs and chemical reagents and sewage and exhaust gas purification. In this respect, catalysis is a key element of technological progress, since development and implementation of new highly efficient and selective catalysts will stimulate production and contribute to the solution of global problems, such as rational exploitation of natural resources and environmental protection.

Although numerous homogeneous and heterogeneous catalysts for oxidation, hydrogenation, hydroformylation, carbonylation, *etc*. are known, these catalysts do not always possess high selectivity for reactions involving substrates with several active sites. Furthermore, if the substrates contain heteroatoms, systems of conjugated bonds and functional groups, the reactions should be carried out under conditions as mild as possible in order to avoid side reactions, *e.g*., isomerisation or decomposition. Ordinary catalysts often exhibit low activities or selectivities under mild conditions. Metal complex catalysts represent an important alternative.

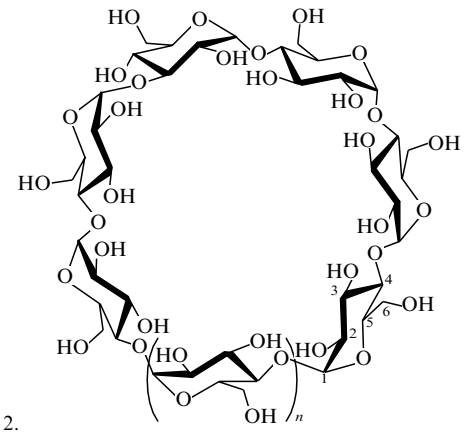
The application of principles of supramolecular chemistry, which deals with studies of ordered molecular ensembles secured by intermolecular forces,[1–5] to catalysis has an enormous potential in the design of novel highly selective catalysts. The design of compounds capable of molecular recognition of cations, anions or neutral molecules is the main area of progress in the chemistry of molecular ensembles and intermolecular bonding. When such compounds are used as catalysts, the conversion of reactants into reaction products is preceded by formation of a 'supramolecule' due to selective binding of a substrate molecule by the respective receptor molecule.[1,6,7] This approach enables development of catalysts whose activity and selectivity is governed by the intermolecular interactions of a substrate with the catalyst.

Among molecules capable of molecular recognition, macrocyclic receptors (*e.g*., cyclodextrins and calixarenes) are of primary interest. These can form host–guest complexes with substrates due to intermolecular interactions, such as van der Waals forces or H bonds.[1–7] These molecules possess hydrophobic cavities with diverse shapes enabling selective binding of the substrates that match the size and shape of the cavity, which implies molecular recognition.[1,8,9]

The present review is devoted to issues related to the design of novel metal complex catalytic systems containing macrocycles, primarily cyclodextrins and calixarenes.

It is of note that, despite intense development of investigations into supramolecular catalysis,[8] it is only recently that macrocyclic receptor molecules capable of molecular recognition have started to be exploited as components of metal complex catalytic systems, predominantly as models of enzymes.[7,10–13] The number of publications on this subject is relatively small as compared to, for instance, supramolecular catalysis with the use of dendrimers, which has been thoroughly surveyed.[14–20]

Cyclodextrins are cyclic oligomers built up of 1,4-linked D-glucopyranose residues.[21–27]



$n = 0–2$.

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Received 30 January 2003
Uspekhi Khimii **74** (1) 104 – 119 (2005); translated by Ya V Zubavichus

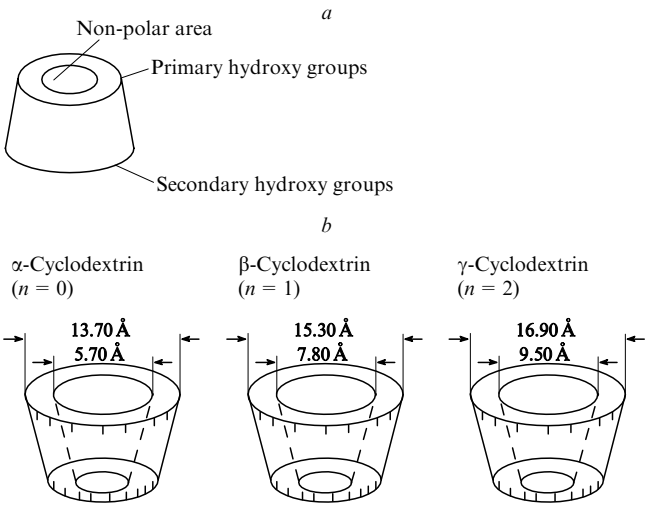
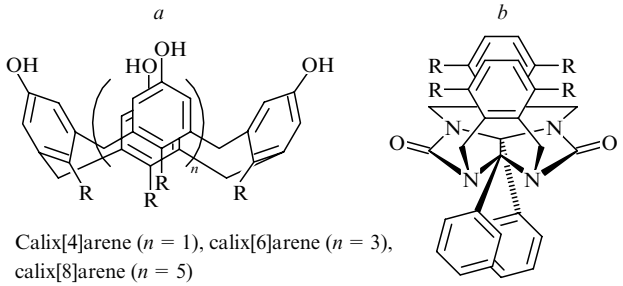


Figure 1. The arrangement of the hydroxy groups in cyclodextrins (*a*), the sizes of cyclodextrin molecules and of their internal cavities (*b*).

The most common representatives of this class are α-, β- and γ-cyclodextrins containing, respectively, 6, 7 and 8 glucose residues. The size of the cavity inside the macrocycle increases from 5.7 Å to 9.5 Å on going from α- to γ-cyclodextrin (Fig. 1). The hydrogen atoms H(3) and H(5) are always directed inward, toward the molecular cavity, whereas the hydroxy groups are directed outward. As a result, a hydrophobic cavity is formed, which is capable of accomodating fragments of molecules with suitable sizes and polarities to yield respective host – guest complexes. In the case of calixarenes, which represent cyclic oligomers of phenol and formaldehyde with different numbers of aromatic units, the non-polar cavity formed by several monomeric units has a bowl-like shape.[28–32] An increase in the number of these units from 4 in calix[4]arene to 8 in calix[8]arene substantially increases the sizes of the macrocycle and the cavity (Fig. 2 *a*). Both cyclodextrins and calixarenes can readily be functionalised with various complex-forming groups, which allows synthesis on their base of metal complex catalysts capable of molecular recognition.



Calix[4]arene ($n = 1$), calix[6]arene ($n = 3$), calix[8]arene ($n = 5$)

Figure 2. Calixarenes (*a*) and 'molecular clips' (*b*).

A few examples of metal complex catalysts based on other macrocycles, *e.g.*, modified 'molecular clips' [synthesised from diphenylglycoluril (Fig. 2 *b*)] and cyclophanes will also be given.

The review is subdivided into two sections. The first considers catalytic systems involving non-coordinated macrocyclic receptors. The second section is devoted to metal complex catalysts where the corresponding receptor molecules act as ligands.

II. Metal complex catalytic systems based on non-coordinated receptor molecules

Catalytic systems based on metal complexes can include compounds capable of forming host – guest complexes as their components. In the first step, the formation of an inclusion complex of the macrocyclic receptor with either the metal complex or the substrate occurs. Thus, the macrocyclic receptor can affect the mechanism of a catalytic process in two ways that are depicted in Figs 3 and 4.

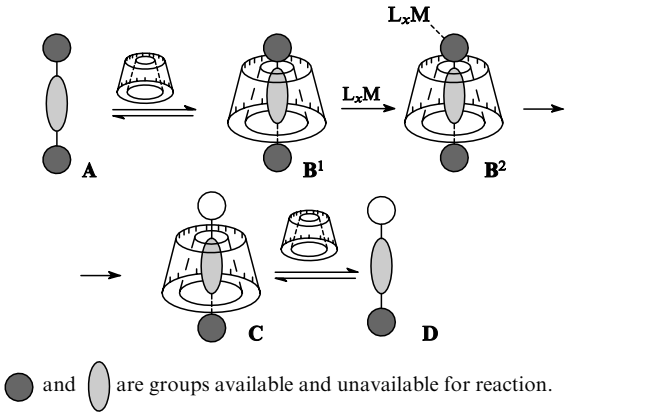


Figure 3. Formation of a host – guest complex with the substrate.
A is a substrate; $\mathbf{B}^1$ and $\mathbf{B}^2$ are inclusion complexes with the substrate; L_xM is a metal complex; **C** is an inclusion complex with the product; **D** is a reaction product.

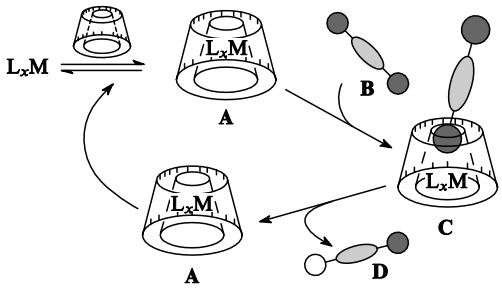


Figure 4. Formation of a host – guest complex with the metal complex L_xM.
A is an inclusion complex, **B** is a substrate, **C** is the inclusion compound metal complex – substrate, **D** is a reaction product.

In the first case, which is postulated in the majority of studies, the substrate inclusion complex rather than the substrate itself is involved in the catalytic cycle. The selectivity of the reaction with respect to the substrate is determined by the stability of the respective host – guest inclusion complex, which in turn depends on the size and structure of the host molecule (see Fig. 3).

The host molecule acts as a 'microreactor' and can stabilise the transition state of the reaction thus increasing its rate.[1, 6, 7] Furthermore, the formation of the inclusion complex can significantly affect the regio- and stereoselectivity of the process by favouring a specific orientation of the substrate (complexes $\mathbf{B}^1$ or $\mathbf{B}^2$). Some parts of the substrate molecule can be shielded and thus escape reaction. The reaction product can also form an inclusion complex with the receptor (**C**). This leads to a decrease in the concentration of the receptor molecules and to deceleration of the reaction [the so-called product inhibition effect (see Fig. 3)].

In the second of the two above cases, it is a ligand or the metal complex itself that acts as a guest in the formation of the inclusion complex (see Fig. 4). The role of the macroligand-host can consist of stabilisation of a catalytically active complex and the respective

activated complex or of the ligand environment of the metal atom. The regioselectivity and stereoselectivity of the reaction are governed by the orientation of the substrate in the metal complex.

The stability of the host – guest complex strongly depends on the nature of the solvent used for the reaction. In aqueous media, it is the hydrophobic interactions that make the dominant contribution to the energy of formation of the complex and thus substantially enhance its stability. In this respect, the use of calixarenes and cyclodextrins as components of biphasic catalytic systems based on water-soluble metal complexes is of particular interest.[13, 33–35] An advantage of this approach is that the water-soluble catalyst can easily be separated from insoluble products and recycled.

It should be stressed that the activities of traditional catalysts in the case of substrates poorly soluble in water are low. Owing to the formation of the host – guest inclusion complexes, the macrocyclic receptors can both affect the activity and the selectivity of the reaction and act as phase-transfer carriers of the substrate from an organic medium to the aqueous phase.

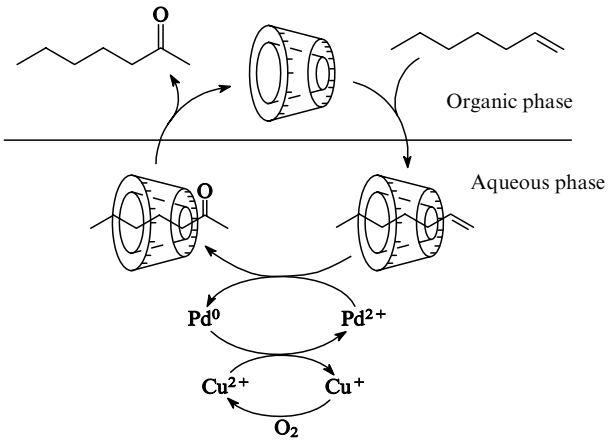


Figure 5. Cyclodextrin-assisted Wacker oxidation of alkenes.

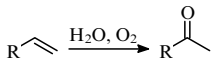
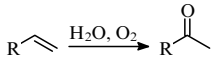
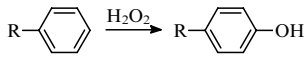
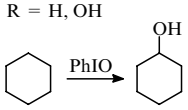
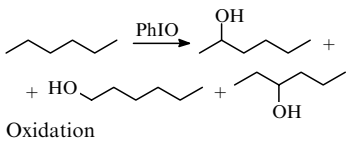
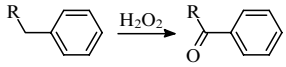
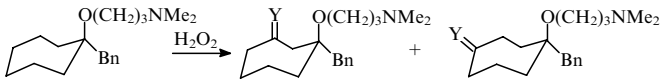
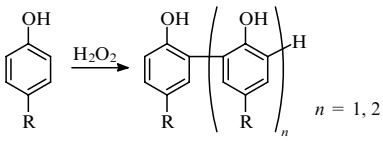
1. Oxidation

Catalytic systems involving cyclodextrins and calixarenes have been tested for Wacker oxidation, hydroxylation, oxidative coupling and oxidation of hydrocarbons (Table 1).

Biphasic Wacker oxidation of unsaturated compounds to ketones, catalysed by systems based on palladium and copper salts in combination with different cyclodextrins, has been studied.[36–42] In this case, a complex of cyclodextrin and alkene is formed and transferred to the aqueous phase, where the oxidation reaction occurs (Fig. 5).

The addition of β-cyclodextrin at the optimum concentration accelerates oxidation of dec-1-ene more than 20-fold.[36, 37] The activity of the catalytic system for the oxidation of linear alkenes and dienes depends on the nature of the cyclodextrin. Generally, systems containing β-cyclodextrin are somewhat more active than those containing α-cyclodextrin and substantially (by several times) more active than γ-cyclodextrin systems. In particular, the initial rate of the oxidation of dec-1-ene in the case of β-cyclodextrin is virtually the same as in the case of α-cyclodextrin and more than three times higher than in the case of γ-cyclodextrin.[36]

Table 1. Oxidation and hydroxylation reactions catalysed by systems containing receptor molecules.

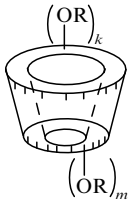
Catalytic system	Reaction	Ref.
	Wacker process	
Pd^{2+}/Cu^{2+} or $Pd^{2+}/Cu^{2+}/H_{3+n}[PV_nMo_{12-n}O_{40}]$, $n = 1-3$, non-modified and modified cyclodextrins		36–44
Pd^{2+}/Cu^{2+}, water-soluble calixarenes		34, 45–47
	Hydroxylation	
Fe^{3+}, oxyethylated β-cyclodextrin	 R = H, OH	34, 48–50
Iron(III) tetrakis(n-hexadecyloxyphenyl)-porphyrinate chloride, β-cyclodextrin and 2,6-dimethyl-β-cyclodextrin		51
Iron(III) tetrakis(n-hexadecyloxyphenyl)-porphyrinate chloride, β-cyclodextrin and 2,6-dimethyl-β-cyclodextrin		51
	Oxidation	
Fe^{3+}, β-cyclodextrin		52
Fe^{3+}, β-cyclodextrin	 Y = O; H, OH	52
	Oxidative coupling	
Fe^{3+}, α- or γ-cyclodextrin		53

Presumably, the difference in the activity is due to different stabilities of the respective host–guest inclusion complexes with the substrates. For α-cyclodextrin, complex formation is hampered by the relatively small volume of its cavity; for γ-cyclodextrin, the entrance to the cavity is too wide such that the resultant complex becomes unstable.[43]

It should be emphasised that the oxidation in the cases where terminal alkenes and isomeric alkenes with internal double bonds were present in the reaction mixture proceeded regioselectively: methyl ketones were the single carbonyl products. The rate of oxidation of non-terminal alkenes is too low due to the structure of the respective inclusion complexes: for such substrates, the double bond occurs inside the cyclodextrin cavity and thus is unavailable for reaction.[36,38–40] Isomeric ketones were detected as the oxidation products of dec-1-ene in the presence of α- or γ-cyclodextrins only where the reaction was conducted in a homogeneous solution (water–propan-2-ol), *i.e.*, when no formation of the inclusion complexes occurred.[36]

The substrate selectivity has been revealed for the oxidation of a number of linear alkenes in the presence of the catalytic systems listed in Table 1.[38,39] In the case of systems containing α-cyclodextrin, the maximum reactivity at atmospheric pressure of oxygen was found for non-1-ene whereas the system based on β-cyclodextrin is most active towards dec-1-ene.[40] Apparently, these two substrates provide the optimum matches to the sizes of the respective cyclodextrin molecules. This suggestion is further supported by data on the stability of complexes of β-cyclodextrin with linear alcohols: the complex with decan-1-ol is the most stable.[44] At elevated oxygen pressures, hept-1-ene manifested the highest rate of oxidation among alkenes studied.[42] With an increase in the cyclodextrin concentration, the reaction rate first abruptly increases and then remains virtually constant, which could be due to diffusion-limited formation of the complex.[35]

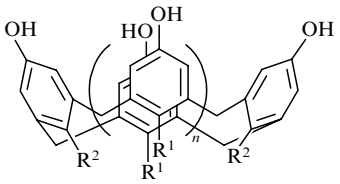
The rate of substrate interphase transfer can be substantially increased if modified β-cyclodextrins are used, in which methyl [2,6-dimethyl-β-cyclodextrin (**1**)] or hydroxypropyl (the compounds **3**, **4**) groups substitute some of the hydrogen atoms of the hydroxy groups.[35,39]



R = Me: $k + m = 14$ (**1**), $k + m = 21$ (**2**);
R = $CH_2CH(OH)Me$: $k + m = 4$ (**3**), 6 (**4**);
R = $SO_3^-Na^+$: $k + m = 6$ (**5**);
R = Ac: $k + m = 6$ (**6**), 14 (**7**), 21 (**8**);
R = $(CH_2CH_2O)_nH$: $k + m = 8$, $n = 2–5$ (**9**);
R = CH_2CH_2OH: $k + m = 5$ (**10**).

This gives rise to enhanced activity with retention of the substrate selectivity. The maximum activity with respect to oxidation of alkenes was observed for the system containing β-cyclodextrin **1**, which is well soluble in water and partly soluble in organic solvents thus providing fast phase transfer of the substrate. If respective sulfate **5** (which is insoluble in the organic phase) is used instead of β-cyclodextrin, the activity drops. Similar results were obtained for permethylated β-cyclodextrin **2** and partially or fully acylated β-cyclodextrins **6**–**8** that are virtually insoluble in water. A decrease in the binding constant of a methyl ketone, *i.e.*, the reaction product, to the respective cyclodextrins is yet another factor that enhances the activity of catalytic systems contaning substituted cyclodextrins. Indeed, no additional stabilisation of the complex of substituted cyclodextrins with the reaction product is possible, whereas for non-substituted cyclodextrins it is achieved through the H-bonding with the hydroxy groups.[35,41]

The catalytic activity of water-soluble sulfonated and glycidylated calixarenes **11**–**15** in the Wacker oxidation of alk-1-enes has also been studied [34,45,46]



$R^1 = R^2 = SO_3^-Na^+$: $n = 1$ (**11**), 3 (**12**), 5 (**13**);
$R^1 = R^2 = (CH_2CH_2(OH)CH_2O)_m$: $n = 1$, $m = 2–4$ (**14**),
$n = 3$, $m = 2–4$ (**15**); $R^1 = R^2 = CH_2NMe_2$: $n = 1$ (**16**);
$R^1 = CH_2NMe_2$, $R^2 = Bu^t$: $n = 3$ (**17**), 1 (**18**).

These systems are characterised both by high chemoselectivity (as regards formation of the respective methyl ketones) and substrate selectivity, which is governed by the correspondence between the sizes of the cavity within the host molecule and the substrate molecule, as for cyclodextrins considered above. In the oxidation of hex-1-ene, the reaction rate is a maximum in the case of water-soluble calix[4]arenes **11** and **14** and calix[8]arene **13**. Similarly, in the oxidation of oct-1-ene, calix[6]arenes **12** and **15** were the most active (Fig. 6).[47] The catalytic activity correlates with the stability constants of the respective host–guest complexes.[44]

Calixarene	Stability constant (k_s) /litre mol^{-1}	
	hex-1-ene	oct-1-ene
Tetrasodium calix[4]arene-tetrasulfonate (**11**)	280	50
Hexasodium calix[6]arene-hexasulfonate (**12**)	20	85

In the oxidation of different styrenes, the maximum yield of products was observed where the size of the substrate matched the size of the calixarene cavity: *p*-methylstyrene is the optimum substrate for calix[6]arene **12** whereas styrene is the optimum for calix[4]arene **11**.[47]

Modified β-cyclodextrins have been used as components of catalytic systems for the oxidation of aromatic hydrocarbons. Hydroxylation of benzene with hydrogen peroxide, catalysed by iron ions in a phase-transfer system containing β-cyclodextrin, gave rise to phenol in 29% yield. The yield increased to 69% with

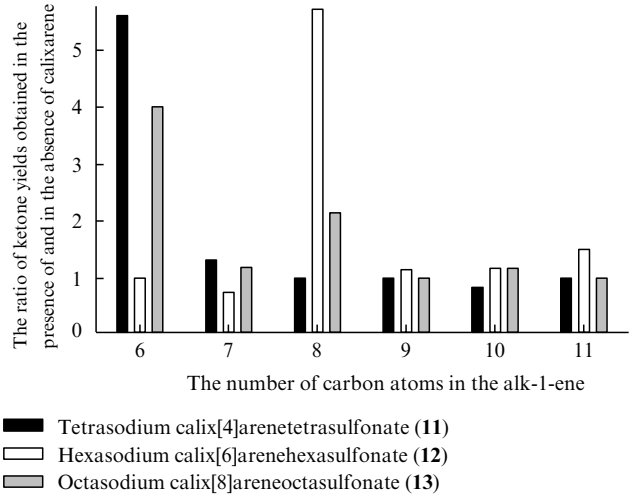


Figure 6. The substrate selectivity of the catalytic system $PdSO_4–CuCl_2$–water-soluble calixarene in the Wacker oxidation as a function of the nature of the calixarene and the number of carbon atoms in the alk-1-ene.[44]

oxyethylated β-cyclodextrin **9**, which is well soluble both in water and benzene.[34, 48–50]

Upon similar hydroxylation of phenol in the system dichloroethane–water, products with the hydroxy group in the *para*-position, *i.e.*, quinone and hydroquinone, are predominantly formed. The selectivity of hydroquinone formation was >95% with oxyethylated cyclodextrin. The reaction proceeds through the host–guest complexes,[50, 54–57] in which all the carbon atoms of the benzene ring except for that at the *para*-position are shielded, which results in the high selectivity (Fig. 7). Oxidation of alkyl-substituted aromatic hydrocarbons in the presence of oxyethylated cyclodextrins involves the alkyl groups yielding the corresponding ketones as the major products. In these cases, the whole aromatic moiety in the host–guest complexes is shielded against attack, and the reaction has been used in the synthesis of (hydroxyphenyl)acetic acids.[58]

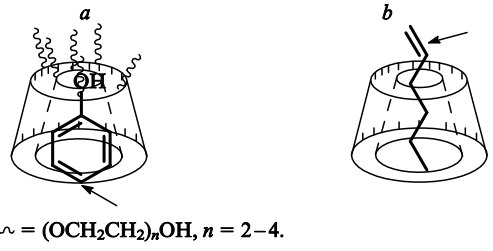


Figure 7. Orientation of the phenol molecule in the cavity of cyclodextrin **9** in the hydroxylation (*a*) and orientation of the hex-1-ene molecule in the cavity of β-cyclodextrin upon oxidation by PhIO (*b*).
The arrows indicate positions available to attack by the active species.

It has been shown that the formation of host–guest complexes with cyclodextrin can also affect the direction of the oxidative oligomerisation of alkylphenol derivatives.[51] In particular, in the oxidation of *p*-cresol by iron ions, the addition of α-cyclodextrin substantially increases the yield of a trimer whereas the addition of γ-cyclodextrin favours formation of a dimer. In the latter case, the complex of the dimer and γ-cyclodextrin is insoluble in the reaction medium, which prevents further oligomerisation.

In the oxidation of cyclohexane by a PhIO–iron(III)tetrakis(n-hexadecyloxyphenyl)porphyrin chloride catalytic system, the yield of cyclohexanol (relative to the oxidant consumed) increased from 0.8% to 9% and 14% upon addition of β-cyclodextrin and methylated cyclodextrin **1**, respectively.

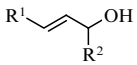
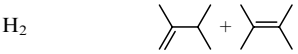
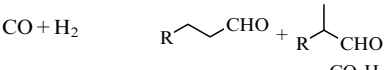
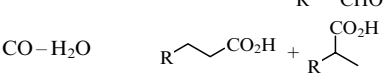
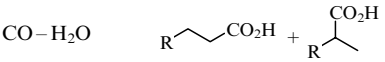
In the oxidation of n-hexane by the same catalytic system, an abrupt increase in the comparative reactivity of the methyl groups was observed. This was explained by partial shielding of the secondary C–H groups of the substrate in the host–guest complex that is formed in a biphasic system. The relative reactivity per terminal C–H bond in benzene as a solvent is 0.01 [the unity reactivity corresponds to that of the C(3)–H bond in hexane], whereas the use of catalytic systems containing β-cyclodextrin or 2,6-dimethyl-β-cyclodextrin increases this reactivity up to 0.59 and 0.77, respectively.[52]

The oxidation of bencyclane [1-benzyl-1-(3-dimethylaminopropoxy)cycloheptane fumarate] represents yet another example of the influence of β-cyclodextrin on the reaction selectivity.[53] Only C–H bonds of the cycloheptane ring in the molecule undergo oxidation in the presence of β-cyclodextrin whereas the aromatic moiety, being incorporated in a host–guest complex, is shielded and thus does not react. In a biphasic water–substrate system, the ratio of *cis*- and *trans*-isomers of γ-hydroxybencyclane is 7 : 1, while without the receptor, the respective ratio is ~1 : 1. Presumably, this increase in the stereoselectivity is due to specific orientation of the substrate in the inclusion complex.

2. Reactions with hydrogen and carbon monoxide

Receptor molecules were also employed as components of metal complex catalytic systems for such reactions as hydrogenation, hydroformylation and hydrocarboxylation (Table 2).

Table 2. Catalytic systems containing receptor molecules for reactions with hydrogen and carbon monoxide.

Catalytic system	Starting compound	Reagent	Reaction product	Ref.
	Hydrogenation			
$[(1,3\text{-HD})RhCl_2]_2$ – β-cyclodextrin		H_2	$ArCH_2R$	59–61
$RuCl_3$ – TPPTS – NaI	RC(O)H	H_2	RCH_2OH	60, 61
$RhCl_3$ – TPPTS – β-cyclodextrin		H_2		62
$CoCl_2$ – KCN – KCl – KOH – β-cyclodextrin		H_2		63
		H_2		64
		H_2		64
		H_2		65
$[Rh(COD)Cl]_2$ – chiral amine – β-cyclodextrin		H_2		66
	Hydroformylation			
$H(CO)Rh(TPPTS)_3$, modified β-cyclodextrins		$CO + H_2$		35, 67–70
$Rh_2(\mu\text{-}SBu^t)_2(CO)_2(TPPTS)_2$, β-cyclodextrin		$CO - H_2O$		35, 71–74
$H(CO)Rh(TPPMS)_3$, α-cyclodextrin		$CO - H_2O$		72–74
$PdCl_2$ – TPPTS, modified cyclodextrins		$CO - H_2O$		72–74

Note. 1,3-HD is cyclohexa-1,3-diene, COD is cycloocta-1,5-diene, TPPTS is trisodium tris(*m*-sulfophenyl)phosphine, TPPMS is monosodium (*p*-sulfophenyl)diphenylphosphine.

The use of supramolecular catalytic systems for selective hydrogenation and reduction of substrates containing functional groups (*e.g.*, alcohols, aromatic carbonyl compounds, linear aldehydes, dienes, *etc.*) enhanced the activity of metal complex catalytic systems and selectivity of the reactions.[59–72]

Hydrogenation of aromatic aldehydes and ketones by hydrogen in THF in the presence of rhodium(hexa-1,3-diene) chloride results in complete deoxygenation to yield alkylbenzenes. The addition of β-cyclodextrin accelerates the process more than fourfold and enhances the selectivity of hydrocarbon formation.[59] It was demonstrated[75] that alkyl aryl ketones form 1 : 1 inclusion complexes with β-cyclodextrins. In these complexes, the benzene ring is located inside the cavity and thus is protected from the attack by the reagent. This leads to enhanced selectivity of the reaction of the carbonyl group. If α-cyclodextrin is used instead, the reaction rate drops due to the low stability of the complexes formed by this receptor with aromatic ketones in THF.

Similar effects were observed in the hydrogenation of aromatic ketones catalysed by Ir/Al_2O_3 and Pt/C.[76,77] In these cases, the addition of β-cyclodextrin to the catalytic system abruptly decreased the yield of the hydrogenation product of the aromatic fragment. Hydrogenation of substituted pyridines catalysed by Pd/C is also decelerated in the presence of cyclodextrins.[78]

The rate of reduction of normal aldehydes by formate anions in the presence of ruthenium(II), rhodium(I) or iridium(I) complexes with sulfonylated triphenylphosphine ligands is abruptly decreased upon addition of β-cyclodextrin, which is explained by steric hindrance associated with formation of the inclusion complexes of the aldehyde with cyclodextrin.[60] However, in the case of hydrogenation of the same aldehydes by hydrogen in biphasic systems (water–aldehyde) catalysed by ruthenium complexes with trisodium tris(*m*-sulfophenyl)phosphine (TPPTS), the addition of cyclodextrin significantly increases the yield of the product, *i.e.*, normal alcohol, as in the case of the aforementioned Wacker oxidation. Substituted β-cyclodextrins, *viz.*, hydroxypropyl- (**3**, **4**), hydroxyethyl- (**10**) and 2,6-dimethylcyclodextrins (**1**) are even more active. The latter compound provides the maximum reaction rate, which was explained by the lowest stability of the complex with the reaction product and faster formation of the host–guest complexes.[61,62]

The $RhCl_3$–TPPTS system containing β-cyclodextrin is highly active in the hydrogenation of unsaturated acids in aqueous media. The use of β-cyclodextrin both accelerates the reaction and affects its selectivity due to structural features of the inclusion complexes formed. For instance, complete reduction of maleic and fumaric acids in the absence of β-cyclodextrin required 83 h and 104 h, respectively. Meanwhile, in the presence of cyclodextrin, 100% conversion of maleic acid was achieved in 17 h whereas the level of conversion of fumaric acid was still as low as 45% after 96 h. Hydrogenation of acrylic acid was slower than that of cinnamic acid in the absence of cyclodextrin. The opposite situation was observed after the receptor was added to the catalytic system. Presumably, this difference was due to formation of the inclusion complex, where the double bond of the substrate is located inside the cyclodextrin cavity and the active rhodium sites interact with the hydroxy groups of the host molecule. This suggestion also explains the fact that the difference in the hydrogenation rates for the two substrates is substantially decreased if methylated cyclodextrin **1** is used instead of β-cyclodextrin. Furthermore, the degree of hydrogenation of cinnamic acid using the catalytic system containing β-cyclodextrin was 2% after 50 h as compared to 80% after 24 h in the case of cyclodextrin **1**.[63]

Lee and Alper showed[64] that the use of cyclodextrins for the reduction of allylic alcohols to alkenes by hydrogen, catalysed by a system containing aqueous potassium hydroxide and the complex $HCo(CN)_5^{3-}$ generated *in situ*, allows one to significantly increase the activity of the catalyst and change the selectivity of the reaction. Without cyclodextrin, a mixture of *cis*- and *trans*-alkenes is obtained whereas *trans*-isomers are exclusively produced in its presence. However, in the case of those allylic alcohols that should yield terminal alkenes, virtually no reaction occurs. Presumably,[64] the *trans*-selectivity of the reaction is due to formation of a host–guest complex of cyclodextrin and the catalytically active anion $HCo(CN)_5^{3-}$, with subsequent reaction inside the cavity of cyclodextrin. Thus, it represents one of a few examples of a reaction proceeding according to the scheme depicted in Fig. 4. As in the previous cases, the activity of the system depends on the size of the cyclodextrin ring. The yields (%) of the reduction products of cinnamic alcohol in the presence and in the absence of cyclodextrins are listed below.

$$(E)\text{-PhCH}=\text{CHCH}_2\text{OH} \longrightarrow (E)\text{-PhCH}=\text{CHMe} + \text{Ph(CH}_2)_3\text{OH}$$

No cyclodextrin	62	12
α-Cyclodextrin	70	26
β-Cyclodextrin	80	11
γ-Cyclodextrin	3	15

Hydrogenation of dienes in a water–benzene system, like reduction of allylic alcohols, yields only *trans*-alkenes, the reaction occurs mainly as 1,2-addition due to shielding of one of the double bonds in the inclusion complex.[65] Hydrogenation of α,β-unsaturated carboxylic acids and of their deriatives gives rise to the products of the C=C bond reduction.[66] It is noteworthy that the use of catalytic systems containing β-cyclodextrin made it possible to achieve high yields of reduction products in the cases of acrylic acid (81%) and methacrylonitrile (80%). Furthermore, in these cases, no dimerisation occurred due to the formation of the inclusion complexes.

Asymmetric hydrogenation of α-keto esters to *R*-isomers of α-hydroxy esters is catalysed by a complex of *N*,*N*′-dimethyl-(1*R*,2*R*)-diphenylethylenediamine with rhodium cyclooctadiene chloride.[71] The addition of β-cyclodextrin to the catalytic system enhances both the reaction rate and the selectivity. It was suggested[71,79] that it is the complex of cyclodextrin and the substrate that reacts; this changes the polarity of the microenvironment and increases the yield of the *R*-product.

The addition of cyclodextrins to catalytic systems containing TPPTS and palladium dichloride substantially increases the rate of hydrocarboxylation of alkenes by carbon monoxide in aqueous media.[35,72] A comparison of different modified cyclodextrins as regards their activities in the hydrocarboxylation of dec-1-ene showed that hydroxypropyl- (**3**, **4**) and poly(oxyethyl)cyclodextrin (**9**) are nearly as active as β-cyclodextrin. Meanwhile, the activity and selectivity of methylated cyclodextrin **1**, as in other reactions studied, were significantly higher. In all cases, the effect of inhibition by the reaction product was observed due to the formation of H bonds between the carboxy group of the substrate and the oxygen atoms of cyclodextrin.[35]

In the example of the hydroformylation reaction catalysed by rhodium complexes in biphasic systems, it was shown that the influence of cyclodextrin on the reaction rate and selectivity can differ substantially depending on the structure of the host–guest complex involved. In the case of the hydroformylation of hex-1-ene by a rhodium complex with monosulfonylated triphenylphosphine [$(4\text{-}NaO_3SC_6H_4)Ph_2P$), *viz.*, $HRh(CO)(TPPMS)_3$], the addition of α-cyclodextrin gives rise to a decrease in the yield of aldehydes from 55% to 11%.[72] A similar effect was observed upon addition of α-cyclodextrin to the catalytic system based on the complex $HRh(CO)(PPh_3)_{3-n}(TPPMS)_n$. Presumably,[67] in this case, a complex of cyclodextrin with TPPMS is formed, which inhibits the reaction.

In contrast, in the hydroformylation catalysed by a rhodium complex with trisulfonylated phosphine (TPPTS), the addition of β-cyclodextrin, acylated cyclodextrin **7** or 2,6-dimethylcyclodextrin **1** increased the yield of aldehydes from 6% to 19%, 45% or even 80%, respectively.[35,68–70] The selectivity of aldehyde formation is also enhanced from 60% (without cyclodextrin) to 95% (in the presence of cyclodextrin **1**). This system also manifests the substrate selectivity related to different stabilities of the respective

inclusion complexes: the reaction rate in the case of dec-1-ene is significantly higher than that for undec-1-ene or dodec-1-ene. Vinylcyclohexane, styrene, propenyl- and butenylbenzenes react faster than n-alkenes. Finally, alkenes with an internal double bond are virtually inert in this reaction since such a bond is shielded in the inclusion complex.

The increase in the activity of the catalytic system Rh – TPPTS in hydroformylation upon addition of cyclodextrins is explained by the formation of not only host – guest complexes of the substrate with the receptor molecule, but of analogous complexes of β-cyclodextrin with TPPTS as well.[35,80] The existence of the latter complexes was confirmed by several methods.[73,81–84] The stability constant of the complex is 7110 M^{-1} at 298 K and decreases to 610 M^{-1} with an increase in temperature to 348 K. In the case of cyclodextrin **1**, the stability constant of the 1 : 1 complex with TPPTS is 2800 M^{-1} (see Refs. 82, 84). Structural studies of these complexes revealed that the phosphorus atom therein is arranged in a way that prevents its coordination to the metal ion. The addition of cyclodextrin changes the equilibrium between the rhodium complexes in the solution thus facilitating formation of the complex with an alkene, which leads to acceleration of the reaction. It is of note that this effect is weakened with an increase in the concentration of TPPTS. Meanwhile, the activity of the catalytic system significantly increases with an increase in the concentration of cyclodextrin up to a cyclodextrin : rhodium molar ratio of 30 : 1. It was shown that at elevated temperatures, the reaction rate is limited by diffusion of the inclusion complex into the aqueous phase. The activation energy of the reaction above 60 °C is slightly more than 5 kJ mol^{-1} (see Ref. 80).

In the hydroformylation of alkenes catalysed by $Rh_2(\mu\text{-}SBu^t)_2(CO)_2(TPPTS)_2$, the addition of β-cyclodextrin to the catalytic system significantly increases their conversion into aldehydes but decreases the fraction of linear isomers.[74] In particular, the selectivity with respect to n-nonanal is 98% in the absence of cyclodextrins and decreases to 76% in the presence of β-cyclodextrin. With cyclodextrin **1**, the selectivity with respect to n-nonanal under identical conditions is 92%.

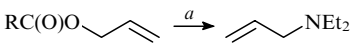
The decrease in the selectivity was rationalised assuming specific orientation of the substrate in the cavity of cyclodextrin, which favours an attack on the terminal CH_2 groups of the alkene by the rhodium hydride species.[74,85] If cyclodextrin **1** was used, the rates of the hydroformylation were equally high for alkenes $C_8 - C_{12}$.[84,85]

It should be noted that the rate of hydroformylation in the presence of β-cyclodextrin decreases with an increase in the number of carbon atoms in the alkene (the rate for dodec-1-ene was only 2% of the value observed for oct-1-ene).

In the case of cyclodextrin **1**, the activity of the catalytic system in an aqueous phase increases upon repetitive use. Dessoudeix *et al.*[85] explained this fact by the formation of supramolecular associates composed of two cyclodextrin molecules and the active rhodium complex in the solution.

3. Miscellaneous reactions

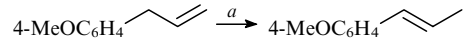
Decomposition of allyl carbonates catalysed by palladium complexes with sulfonylated triphenylphosphine in the presence of various modified cyclodextrins has been studied by Monflier and co-workers[86,87]



(*a*) $Pd(OAc)_2$ – TPPTS, modified cyclodextrins, NEt_3, Δ.

The activity of these catalytic systems is several times higher than that of systems containing unsubstituted β-cyclodextrin. The maximum activity was found for the system containing methylated cyclodextrin **1**, then the activity decreases in the following series: permethylated β-cyclodextrin **2**, hydroxypropyl- (**3**, **4**) and hydroxyethyl-β-cyclodextrin **10**. For this reaction, the dependence of the reaction rate on the substrate structure was elucidated in detail. It was found that, among alkyl allyl carbonates with linear substituents, the maximum activity is manifested by the derivative having 12 carbon atoms in the alkyl chain. For allyl decyl and allyl dodecyl carbonates it was shown that the introduction of additional methyl groups into the alkyl radical virtually did not affect the reaction rate whereas the introduction of bulkier substituents decelerated the reaction. The activity of allyl β-naphthylbenzyl carbonate was two times higher than that of allyl α-naphthylbenzyl carbonate; a similar situation was observed for allyl *p*-phenylbenzyl carbonate in comparison with allyl *o*-phenylbenzyl carbonate. These results can be rationalised in terms of correspondence between sizes of the cyclodextrin cavity and of the substrate molecule.[87]

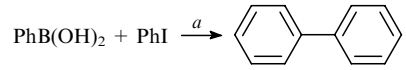
Isomerisation of *p*-allylanisole to anethole catalysed by iridium trichloride in a water – substrate system was studied by Barak *et al.*[88] The addition of either α- or β-cyclodextrin led to acceleration of isomerisation several-fold and to a decrease in the energy of activation of the process. Presumably, a complex of iridium trichloride with the substrate and cyclodextrin is formed in this case.



(*a*) $IrCl_3$ – β-cyclodextrin.

Hydrosilylation of alkenes on platinum- or palladium-containing catalysts represents yet another example of an increase in the product yield upon addition of β-cyclodextrin to a catalytic system. Thus, the rate of hydrosilylation of styrene by triethoxysilane or trimethylvinylsilane on Pt catalysts is increased in the presence of β-cyclodextrin by a factor of two and more than three, respectively. In the case of Pd-containing catalysts, the rate of the last mentioned reaction is negligibly low. The increase in the reaction rate can be explained by stabilisation of the transition state due to the formation of the host – guest complex. These reactions are nearly completely inhibited by decane, which itself forms stable complexes with β-cyclodextrin.[89]

Water-soluble calixarenes (**11**, **12**, **16** – **18**) and β-cyclodextrin have been tested as components of catalytic systems for the cross-coupling of iodobenzene with phenylboronic acid (the Suzuki reaction), catalysed by a palladium complex with sulfonylated triphenylphosphine.[90]



(*a*) $PdCl_2$ – TPPTS, β-cyclodextrin or modified calixarenes.

The addition of the receptors increased the yield of biphenyl more than twofold. Amino-containing calixarenes manifested the maximum activity. The stability constants for the respective inclusion complexes as well as the rates of their formation were substantially higher than those for non-substituted calixarenes (Table 3).

Table 3. The stability constants (k_s) of calixarene complexes with iodobenzene and yields of products in the Suzuki reaction.[90]

Calixarene	k_s of the 'guest – host' complex /M^{-1}	Relative yield
Tetrasodium calix[4]arene-tetrasulfonate (**11**)	60	2.4
Hexasodium calix[6]arene-hexasulfonate (**12**)	56	2.9
Tetrakis(*p*-dimethylamino-methyl)calix[4]arene (**16**)	402	5.8

Note. Relative to the yield obtained in the absence of the receptor molecule.

III. Catalysis by metal complexes with ligands based on receptor molecules

The catalysts that combine, within one molecule, properties of a metal complex and a phase-transfer reagent together with capabilities of molecular recognition, attract special attention from researchers.[12, 13, 23, 26] Such catalysts include a metal centre and a ligand containing one or several macrocyclic receptors (*e.g.*, cyclodextrin, calixarene, *etc.*) (Fig. 8).[91–93]

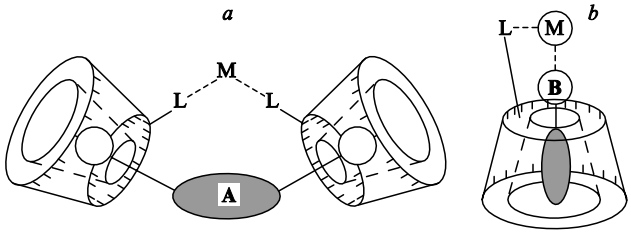


Figure 8. Different types of binding of a substrate by a metal complex containing fragments of receptor molecules.
L is a ligand bound to the receptor molecule; M is a metal ion; **A** is a group accessible for reaction; **B** is a group in the guest molecule.
(*a*) binding of two fragments of a guest molecule; (*b*) additional coordination of the group **B** in the guest molecule to the metal atom.

This combination of a host and a metal centre in one molecule not only retains all the features typical of catalytic systems discussed in the previous section but also confers new catalytically important properties. First of all, binding of a substrate by the cavity of the receptor ligand strictly defines its orientation with respect to the metal centre, which can strongly affect both the product distribution and the substrate selectivity of the reaction. The most interesting examples of this approach are enzyme models containing several host fragments in one ligand (Fig. 8 *a*).

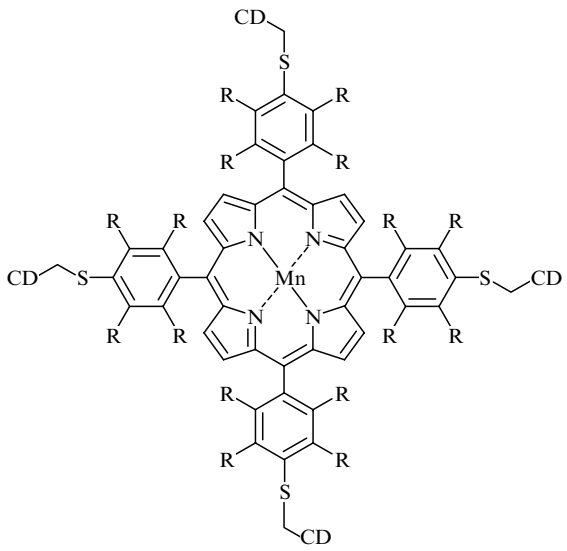
It has to be emphasised that if the substrate embedded into the host–guest complex is additionally coordinated to the metal centre in the course of reaction (Fig. 8 *b*), the stability of this inclusion complex, as well as of the transition state of the reaction, can be enhanced by several orders of magnitude. This effect is referred to as 'double recognition'.[92, 93] Due to concerted binding of the substrate, no additional step of the interaction of the substrate inclusion complex with the metal ion (which was typical of all catalytic systems considered in Section I) is necessary. As a consequence, such catalysts provide a substantial decrease in the energy of activation and the entropy of the reaction and thus increase its rate.[13, 94]

Complexes with receptor molecules were initially tested as models of hydrolytic enzymes.[12, 92, 93, 95–101] Up to now, issues related to the design and catalytic activities of such complexes have been elucidated in biomimetic oxidation, epoxidation, hydroxylation, Wacker oxidation, oxidation of sulfides and alcohols, hydroformylation, hydrogenation and other reactions.

1. Oxidation

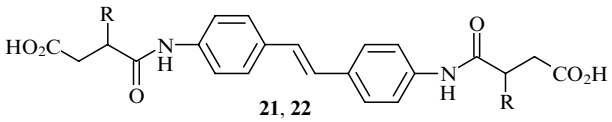
Breslow *et al.*[102–107] demonstrated the possibility of selective oxidation of different compounds on manganese porphyrinate complexes capable of selective substrate binding due to the presence of two or more cyclodextrin fragments.

The manganese complexes **19**, **20** enable epoxidation of unsaturated compounds by iodosylbenzene in aqueous media. The product yield is strongly dependent on the matching of the structures of the substrate and the metal complex.[102] In particular,



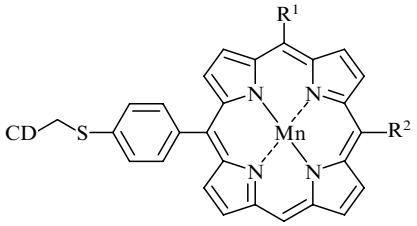
CD is cyclodextrin; R = H (**19**), F (**20**).

in the presence of compex **19**, the substrate **22** is epoxidised 50 times faster than the substrate **21** due to the presence of nitrophenyl groups, which are strongly bound by the cyclodextrin fragments. The activity of the complex **23**, in which the substrate is cooperatively bound by two cyclodextrin fragments simultaneously, is comparable to that of **19**. The activity of the catalyst **24** (where the arrangement of the receptor fragments does not correspond to the substrate shape and one of the cyclodextrin units does not take part in the substrate binding) is significantly lower.



21, **22**

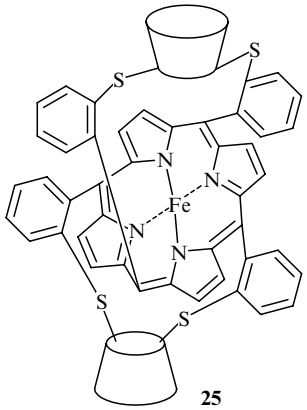
R = H (**21**), 4-$NO_2C_6H_4$ (**22**).



23, **24**

23: R^1 = H, R^2 = $C_6H_4SCH_2CD$; **24**: R^1 = $C_6H_4SCH_2CD$, R^2 = H.

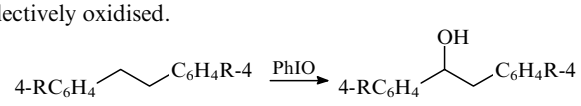
The iron porphyrinate complex **25**, containing two cyclodextrin fragments above and below the porphyrin plane, manifests



25

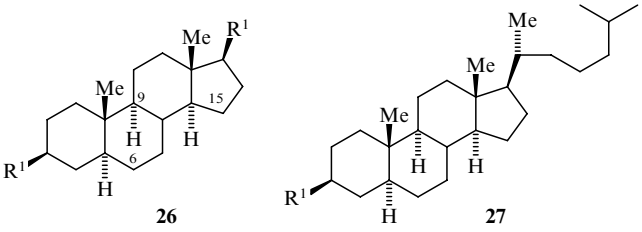
selectivity in the epoxidation of unsaturated compounds: in the case of cyclohexene, the reaction rate is several times higher than that of styrene. Furthermore, in the presence of a similar porphyrinate complex containing no cyclodextrin fragments, cyclohexene reacts significantly slower than in the presence of the complex **25**.[108]

The selectivity of the oxidation of C–H bonds with PhIO, catalysed by cyclodextrin-containing manganese porphyrinate **19**, also depends on the matching of the arrangement of binding centres within the ligand and the substrate structure.[103–107] In particular, in the oxidation of substituted 1,2-diphenylethanes, the aromatic moieties are not affected while the benzylic sites are selectively oxidised.

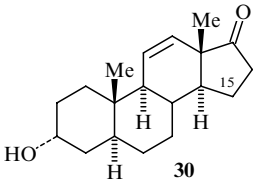


R = $OCH(CO_2H)C_6H_4Bu^t$-4.

Manganese porphyrinate complexes modified by cyclodextrins can catalyse selective oxidation of specific C–H bonds in steroids **26**–**30**. It was demonstrated that the selectivity is governed by the orientation of the substrate in the host–guest complexes due to specific binding of aromatic fragments of auxiliary groups in the steroid molecule.[102–104]



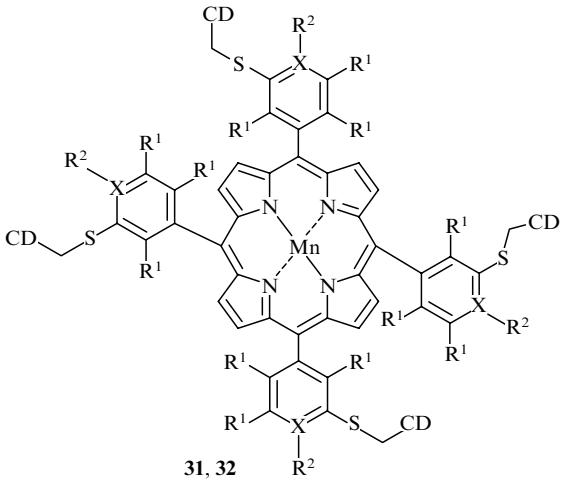
R^1 = 4-$Bu^tC_6H_4CHCH_2C(O)O$; R^2 = $CONHCH_2CH_2SO_3H$.



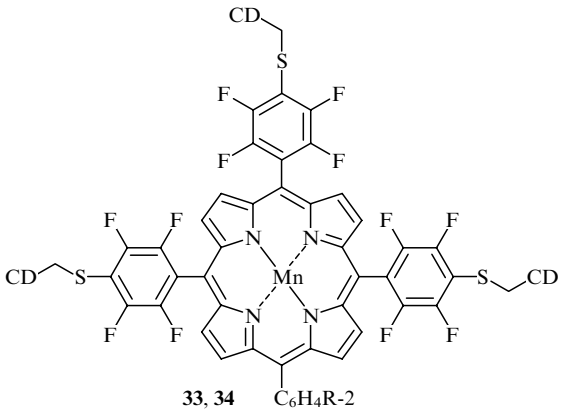
For instance, oxidation of steroid **26** catalysed by the complex **19** yields exclusively the 6-α-hydroxy derivative. Meanwhile, compound **27** devoid of one substituent R^1 yields a mixture of nine components.[102] The activity of manganese porphyrinates **20**, **31** and **32** containing tetrafluorophenyl groups is significantly higher.[105–107]

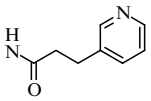
Selective oxidation of steroid **28**, catalysed by the complexes **20**, **33** and **34**, yields the 9-hydroxy derivative as the major product.[107] This could be due to involvement of all three cyclodextrin fragments in steroid binding. A minor hydroxylation product at C(15) is formed due to involvement of only two cyclodextrin fragments in binding. Therefore, oxidation of steroid **29** catalysed by porphyrinate **20** yields oxidation products at C(9) and C(15) in nearly equal proportions. The catalysts **31** and **32** enable strictly selective hydroxylation at C(9).

It is of note that substrate binding by only one cyclodextrin fragment allows selective introduction of a hydroxy group into a steroid molecule. In particular, oxidation of compound **30** catalysed by porphyrinate **20** yields mainly the hydroxylation product



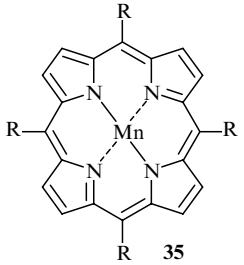
$R^1 = R^2$ = H, X = C (**31**); R^1 = F, X = N, R^2 is absent (**32**).

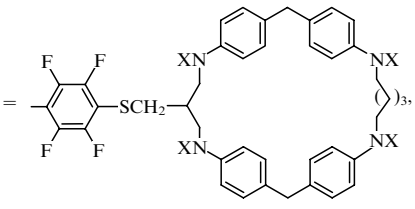


R = NO_2 (**33**),  (**34**).

at C(15) whereas neither the double bond nor the hydroxy group are affected.

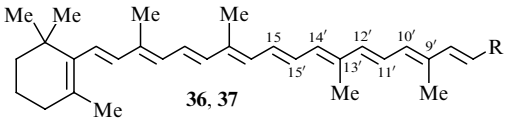
Manganese porphyrinate **35** containing cyclophane fragments[109] catalyses oxidation of compound **26** but the selectivity is significantly lower compared to that of the analogous complex containing cyclodextrin fragments [the ratio of the hydroxylation products at C(6) and C(15) is 3 : 1]. In the case of steroid **28**, the selectivity of hydroxylation at C(9) is only 60%. Apparently, the substrate, even bound by the cyclophane fragments, retains sufficient mobility resulting in non-oxidation.



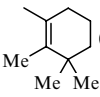
R = 

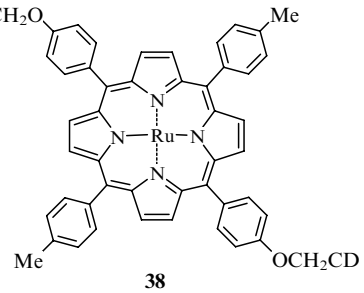
(X = $C(O)(CH_2)_2NHMe_2^+Cl^-$).

Similar effects of the 'rigidity' of substrate binding are observed for the oxidation of β,β-carotene **36** and its analogue **37** by *tert*-butyl hydroperoxide catalysed by ruthenium porphyrinate **38** containing two cyclodextrin fragments.[110–113]



36, **37**

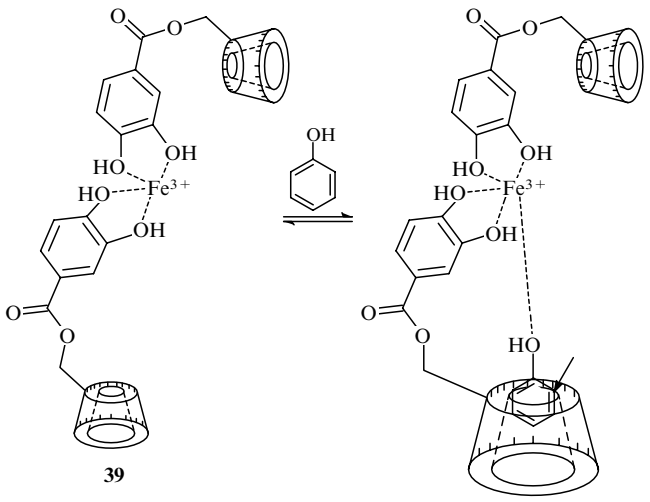
R =  (**36**),  (**37**).



38

In this case, the stability constant of the host–guest complex is very high (2.6×10^6 M^{-1}) due to cooperative binding of the carotene molecule by the cyclodextrin fragments. Nevertheless, oxidation of carotene proceeds non-selectively: the cleavage products of the C(15)–C(15′), C(11′)–C(12′) and C(9′)–C(10′) bonds are formed, although the two former products prevail. At the same time, if one of the cyclohexene fragments is replaced by an aromatic one (compound **37**), the cleavage product of the C(15)–C(15′) bond is selectively formed. Probably, in this case both the structural 'rigidity' of the inclusion complex and binding constant are increased, the latter is 5.6×10^6 M^{-1}.

The iron complex **39**, containing β-cyclodextrins modified by catechol groups, proved active with respect to phenol hydroxylation. Abnormally high regioselectivity was achieved in this system: the yield of catechol exceeded 90%. The use of the metal complexes results in a significant increase in the binding constant of phenol; its specific orientation in the host–guest complex owing to additional coordination provides selectivity for *ortho*-hydroxylation (Fig. 9).[34, 49, 50, 114] It was shown[115, 116] that the iron complexes formed at pH 2.5, which contain two ligands per iron ion, manifest the highest activity. The quantitative selectivity as regards catechol formation was achieved in the reaction with copper complexes containing ethylenediamine-modified cyclodextrins and, noteworthy, non-modified β-cyclodextrin. In the latter case, the catalytic activity is probably due to binuclear copper complexes with β-cyclodextrin, which, in turn, form stable complexes with phenol.[117–121]



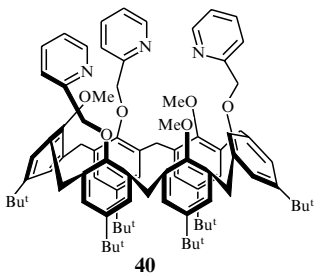
39

Figure 9. Formation of a complex of the catalyst with phenol in the hydroxylation of the latter by hydrogen peroxide.
The arrow marks the site available to hydroxylation.

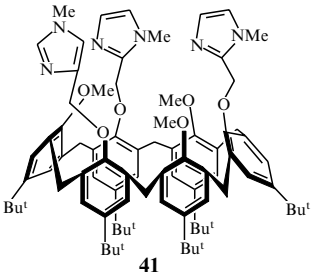
Catechol is also formed as the main product in hydroxylation of benzene by hydrogen peroxide, catalysed by the complex **39**. The yield of phenol, *i.e.*, the primary hydroxylation product, being about four times lower.[34, 50, 115] This is explained by the fact that phenol formed upon hydroxylation of benzene remains in the cyclodextrin cavity due to cooperative binding to the metal atom and thus undergoes further oxidation to catechol. With iron complexes containing β-cyclodextrin modified by catechol at the primary hydroxy group, hydroquinone is predominantly formed.[115, 116]

Copper complexes with cyclodextrins were used in the oxidation of isoborneol and borneol by peracetic acid and hydrogen peroxide in a acetic acid–pyridine mixture.[122, 123] The yield of camphor, the main product, and selectivity of the reaction were much higher than those in the process catalysed by copper sulfate. The catalytic effect is explained by specific orientation of the substrate molecule in the inclusion complex due to coordination of the alcohol group to the copper ion.

The copper complex of pyridine-modified calix[6]arene **40** [124–128] is active in the oxidation of benzene to quinone *via* phenol and hydroquinone. It is of note that no catechol is formed in this case. The same complex is active in the oxidation of ethylene to acetaldehyde and acetic acid.[129] A similar copper complex of calix[4]arene modified by the imidazole groups **41** catalyses oxidation of 3,5-di-*tert*-butylcatechol, benzene and ethanol by hydrogen peroxide to the corresponding quinone, benzoquinone and acetaldehyde, respectively.[129, 130]



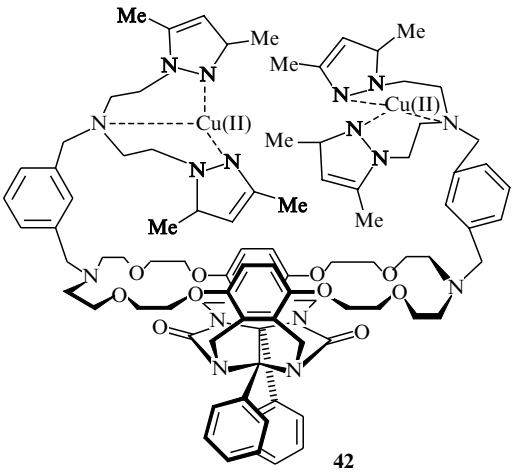
40



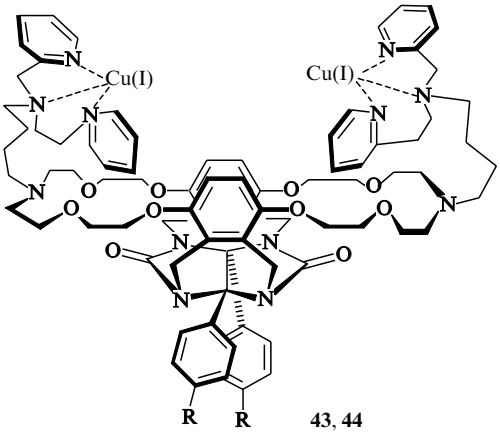
41

Interesting examples of supramolecular oxidation catalysts are given by compounds based on 'molecular clips'.[131–136] The copper complexes **42** and **43** of such molecules proved to be selective catalysts for biomimetic oxidation of alcohols to the respective aldehydes.[132–134] The analogous porphyrinates were efficient in the epoxidation of stilbene and pinene by hypochlorite.[135]

The rate of oxidation of 3-hydroxy- and 3,5-dihydroxybenzyl alcohols catalysed by the complex **42** was substantially higher than that of benzyl alcohol. Presumably, H bonds are formed between oxygen atoms of the oxy groups in the cavity and the hydroxy groups in the aromatic ring of the substrate, in addition to coordination of the benzyl group to the copper ions.[132] Oxidation of phenols by air in the presence of the copper complexes **43** and **45** with pyridine-containing ligands yields only polymeric products of oxidative coupling.[133] Martens *et al.* proposed[132] analogous catalysts **44** that are soluble in fluorous solvents.[134] Manganese porphyrinates **46** containing pyridine as an axial ligand are unstable. The use of 4-(*tert*-butyl)pyridine made it possible to stabilise the catalyst owing to another type of ligand coordination in the active complex: in contrast to pyridine, it cannot be accomodated in the cavity of the receptor and thus is coordinated from the outer side.[135, 136]

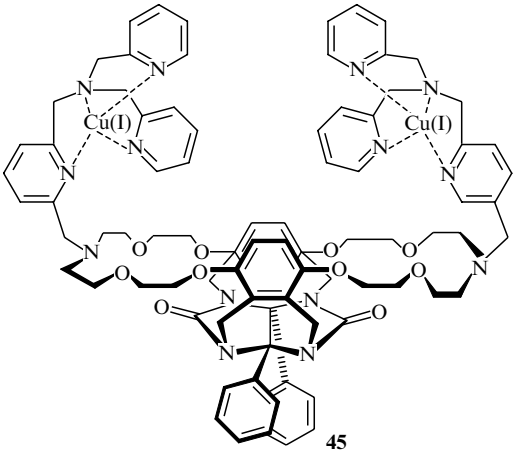


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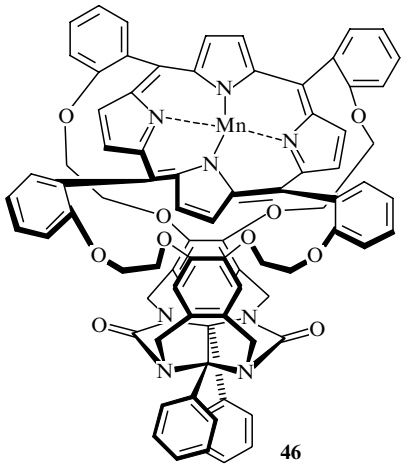


43, **44**

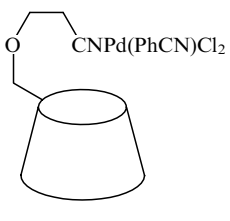
R = H (**43**), $SiMe_2R_F$ (**44**) (R_F is perfluorinated hydrocarbon fragment).



45



46



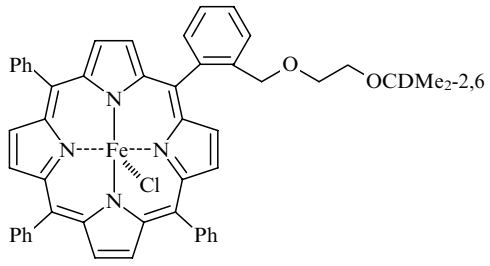
47

The palladium complex **47** with β-cyclodextrin modified by cyanoethyl group manifested significantly higher activity than the catalytic system $PdCl_2(PhCN)_2$ – β-cyclodextrin in the Wacker oxidation of higher alk-1-enes. Its activity is due to cooperative binding of the substrate and the increased stability constant of the catalyst – substrate complex. It was shown that the stability constants of the inclusion complexes significantly increase on going from non-modified cyclodextrin to the metal complexes of the type **47**. The energy of activation of the reaction decreases approximately twofold, which is explained [42] by additional coordination of an alkene to the palladium atom in the inclusion complex. The activity of the catalyst depends on the chain length of the alkene and is a maximum for hept-1-ene.[42]

The catalyst **47** demonstrates higher activity in reactions with aromatic substrates, *e.g.*, styrene, than with linear alkenes.[34, 42, 50, 137] Oxidation of styrene catalysed by a system containing the palladium complex and non-modified cyclodextrin, yields acetophenone as the major product. If the cyclodextrin in the catalytic system is modified by nitrile groups, phenylacetaldehyde is formed in about the same proportion as acetophenone. This means that the regiospecificity of the reaction is altered.

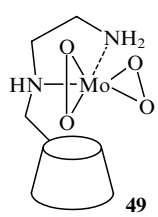
Palladium complexes with sulfocalixarenes modified by nitrile-containing groups manifest higher activities in the biphasic Wacker oxidation of alk-1-enes compared to systems composed of non-modified sulfocalixarenes. The catalytic activity strongly depends on the size of the calixarene cavity: calix[4]arene and calix[6]arene are most active towards hex-1-ene and oct-1-ene, respectively.[45]

Catalysts based on cyclodextrins are very promising for performing enantioselective catalytic reactions. Oxidation of a mixture of (*S*)- and (*R*)-pinenes by oxygen under irradiation with visible light, catalysed by the iron complex with porphyrin modified by 2,6-dimethyl-β-cyclodextrin (**48**), is an example of this approach.[138, 139] Under these conditions, the (*S*)-isomer was more reactive and the enantioselectivity was above 60%.

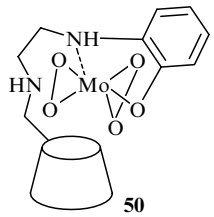


48

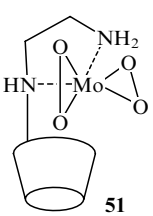
Only a few studies were aimed at the synthesis of macrocyclic receptors as catalysts of enantioselective reactions. Oxidation of aromatic sulfides to sulfoxides catalysed by the molybdenum complexes **49** – **51**, containing modified cyclodextrins as ligands, yields predominantly (*R*)-isomers. The yield of sulfoxide in the oxidation of thioanisole by hydrogen peroxide in biphasic systems, catalysed by the molybdenum complex **49** containing cyclodextrin with ethylenediamine as a substituent of one of the primary hydroxy groups, was 91% [*ee* 59% (*R*)]. In the case of the complexes **50**, containing β-cyclodextrin, and **51**, containing β-cyclodextrin with ethylenediamine as a substituent of a secondary hydroxy group, the enantioselectivities were substantially lower (from 17% to 24%).[140]



49



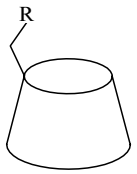
50



51

2. Hydrogenation and hydroformylation

A series of rhodium complexes **52**–**59** with cyclodextrins modified by various phosphine groups have been synthesised as potential catalysts for hydrogenation and hydroformylation reactions.



52–**56**

R = PPh_2 (**52**);

$S(CH_2)_nN(PPh_2)_2$, n = 2 (**53**), 3 (**54**), 4 (**55**);

$OPPh_2$ (**56**),



57–**59**

R^1 = N(PPh$_2$)$_2$, R^2 = OMe, n = 5, m = 14 (**57**);

$R^1 = R^2 = OC_6H_4(PPh_2)$-4, n = 4, m = 12 (**58**);

$R^1 = R^2 = PPh_2$, n = 5, m = 14 (**59**).

Reetz *et al.*[94, 141, 142] showed that these complexes possess substrate specificity in the hydrogenation of aromatic unsaturated compounds. Furthermore, rhodium complexes with cyclodextrin ligands are active in the hydroformylation of alkenes [13, 34, 142] and similar platinum, rhodium and iridium complexes are efficient catalysts for the hydrogenation of aromatic chloronitro compounds [143] (Table 4).

Table 4. Complexes with cyclodextrin-containing ligands catalysing hydroformylation and hydrogenation reactions.

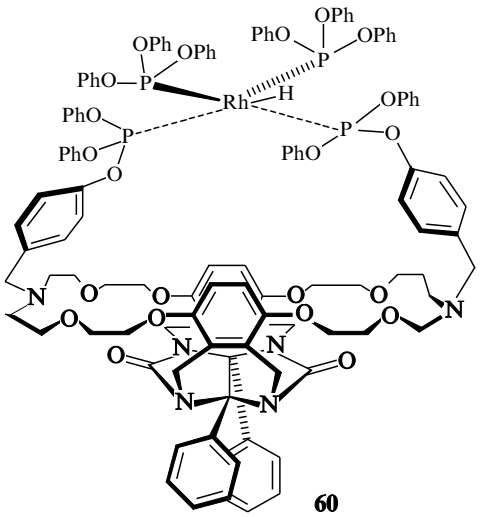
Ligand	Reaction	Conditions	Ref.
52	Hydrogenation of nitrobenzenes	toluene–water, 20 °C, H_2, 2 MPa	143
52–**55**, **57**	Hydrogenation, hydroformylation	25% DMFA in water, H_2, 0.1 MPa or synthesis-gas under 10 MPa, 25 °C and 60 °C	12, 13, 34, 94, 141, 142
56	Hydroformylation	DMFA, synthesis-gas, 2 MPa, 80 °C	144
59	Hydroformylation	methanol : water = 6 : 4, synthesis-gas, 4 MPa, 60 °C	145
60	Asymmetric hydrogenation	methanol, ethanol, THF, acetone, H_2, 0.1 MPa	146

The use of rhodium complexes with the ligands **52**–**55** as catalysts for hydroformylation increases the rates of the reactions compared to those for catalytic systems containing non-modified β-cyclodextrin and H(CO)Rh(TPPTS)$_3$. Furthermore, the selectivity of formation of linear aldehyde is also increased, which is explained by specific orientation of the substrate in the supramolecular complex with the cyclodextrin fragment. In contrast to the catalytic systems based on H(CO)Rh(TPPTS)$_3$, rhodium complexes with the ligands **52**–**55** enable conversion, in biphasic solvent systems, of alkenes even with an internal double bond [*e.g.*, (*E*)-oct-3-ene]. The catalyst remains in the aqueous phase and can be recycled. Hydrogenation of aromatic compounds on the rhodium complexes with the ligands **52**–**55** and **57** is characterised by much higher reaction rates than those of linear alkenes, which suggests molecular recognition of the aromatic substrates.

In the hydrogenation of chloronitrobenzene, a platinum complex with the ligand **52** provided the best selectivity. The yield of aminochlorobenzene was >95%. Virtually no hydrodechlorination products were observed due to shielding of the chlorine atom within the inclusion complex.[143] Rhodium complexes with methylated α-cyclodextrin (**58**) modified by phosphine groups and with β-cyclodextrin (**56**) modified by phosphite groups, have been tested as catalysts for homogeneous hydrogenation.[144, 145] In this case, substrate selectivity was also observed: hydrogenation of aromatic compounds proceeded much faster than that of alkenes due to the higher stability of the respective host–guest complexes.

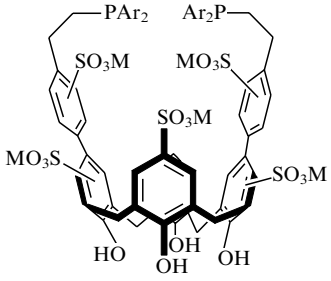
A rhodium complex with the permethylated β-cyclodextrin **59** modified by two triphenylphosphine groups at adjacent glucose fragments, was active in the enantioselective hydrogenation of various substituted α,β-unsaturated acids. The enantioselectivity ranged from 49% to 92% depending on the substrate and solvent. Apparently, in this case, cooperative binding of the substrate by the ligand cavity and the metal atom defines its specific orientation and favours formation of the *R*-isomer.[146]

Nolte and co-workers [147] synthesised the rhodium phosphite complex **60** with a non-polar cavity using molecular receptors based on diphenylglycoluril. Aromatic allylic compounds can be selectively hydrogenated in the presence of this complex with a rate much higher than that in the case of catalytic systems without host fragments, due to binding of the substrate in the cavity. The activity of the catalyst towards hydrogenation of *p*-allylcatechol could be increased by addition of resorcinol, probably owing to cooperative binding of both molcules, *viz.*, the substrate and resorcinol, in the cavity of the host.[147, 148]



60

A macromolecular rhodium complex containing modified calixarene **61** as a ligand, was tested as a catalyst for hydroformylation in biphasic systems.[149] Hydroformylation of oct-1-ene was conducted in an alkene–water system without other organic solvents; rhodium(I) acetylacetonatodicarbonyl served as a precursor of the catalyst.



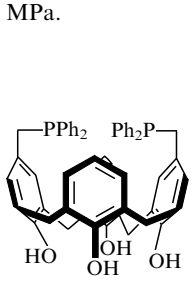
61 Ar = Ph, $C_6H_4SO_3H$-3.

At the pressure of synthesis-gas of 4.0 MPa and 100 °C, the substrate was converted into aldehydes with normal and *iso*-carbon skeletons in a ratio of 2 : 1. The degree of conversion was 70%–95% after 12 h. It is of note that the catalyst is active in the hydroformylation of not only alk-1-enes (*e.g.*, oct-1-ene) but of

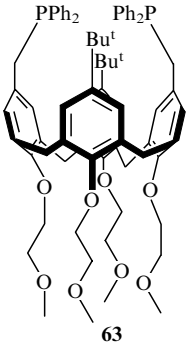
such relatively inert substrates as oct-2-ene and oct-4-ene as well. In the latter case, the reaction yielded a mixture of aldehydes.[150]

Complexes with calixarenes modified by phosphine and phosphite groups were also tested as catalysts for reactions with synthesis-gas under homogeneous conditions.[151–159] It should be noted that in this case the fragment of the receptor molecule served primarily as a template for the design of sterically hindered phosphine and phosphite ligands. Unfortunately, the process of formation of the inclusion complexes was not discussed by the authors.

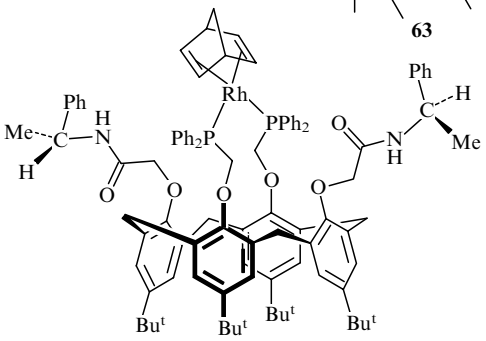
Hydroformylation of styrene and oct-1-ene using rhodium complexes of calixarenes **62**, **63** was described by Bagatin *et al.*[153] and by Fang *et al.*[154] Loeber *et al.*[155] have employed the complex **64** in the same reaction. Quantitative conversion of styrene into 2-phenylpropanal with a selectivity of 95% took 48 h at 40 °C and 4.0 MPa.



62

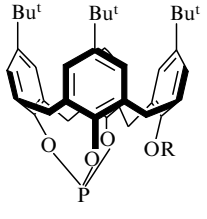


63



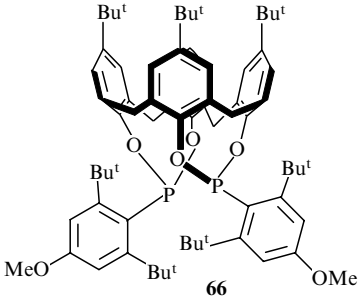
64

Calixarenephosphite **65** (R = H) with a non-protected hydroxy group was used as a ligand for the rhodium-catalysed hydroformylation of hex-1-ene.[156] Virtually complete conversion of the starting alkene was achieved in 3 h; the yield of aldehydes was 80%–85%. Unfortunately, the selectivity was rather low: the reaction mixture contained equal amounts of linear and branched aldehydes. A series of analogous phosphites have been tested [157] as components of catalytic systems for the hydroformylation of oct-1-ene. It was shown that the nature and steric volume of the substituent R insignificantly affects the major characteristics of the process. In particular, the degree of conversion was 80%–90% in all cases and the selectivity of nonanal formation about 60%.



65

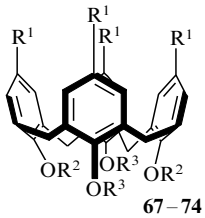
R = H, Me, Pr^i, Ar, Bz.



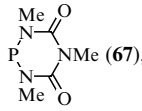
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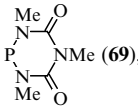
The use of chelate biphosphonite **66** gave rise to a significant increase in the regioselectivity of nonanal formation to 90%–92%.[151]

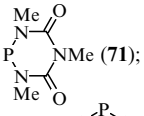
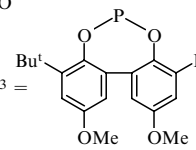
Hydroformylation of oct-1-ene in the presence of Rh complexes with phosphorus-containing calixarenes **67**–**74** was studied by Kunze *et al.*[158, 159] The maximum activity was observed for complexes with the ligand **73**, however, the presence of a calixarene fragment in the ligand did not enhance the catalytic activity. For instance, catalysts containing the ligands **67**, **69** and **71** provided the same activity as their analogue without calixarene whereas for complexes with the ligands **68** and **70**, the activity was even lower.

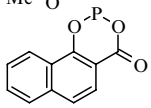
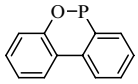


67–**74**

R^1 = H: R^2 = R^3 =  (**67**),  (**68**);

R^1 = Bu^t: R^2 = R^3 =  (**69**),  (**70**);

R^2 = Me, R^3 =  (**71**); R^2 = H, R^3 =  (**72**);

R^2 = Me, R^3 =  (**73**),  (**74**).

* * *

The data summarised in the present review demonstrate the rapidly growing interest of researchers in the design of supramolecular metal complex catalytic systems based on macrocyclic receptors. The number of publications in this area steadily increases.

Since it is high selectivity that becomes an increasingly important factor in chemical processes, there is no doubt that catalysts capable of molecular recognition will find broad applications in chemo-, regio- and stereoselective reactions.

References

1. J-M Lehn *Supramolecular Chemistry. Concepts and Perspectives* (Weinheim: VCH, 1995)
2. F Vogtle *Supramolecular Chemistry: an Introduction* (New York: Wiley, 1993)
3. H-J Schneider, A Yatsimirsky *Principles and Methods in Supramolecular Chemistry* (New York: Wiley, 1996)
4. I Haiduc, F T Edelmann *Supramolecular Organometallic Chemistry* (Chichester: Wiley, 1999)
5. J W Steed, J L Atwood *Supramolecular Chemistry* (New York: Wiley, 2000)
6. J-P Behr (Ed.) *The Lock-and-Key Principle. The State of the Art — 100 Years On* Vol. 1 (New York: Wiley, 1995)
7. M C Feiters, in *Comprehensive Supramolecular Chemistry* Vol. 10 (Ed. D N Rein-Houdt) (Oxford: Elsevier, 1996)
8. F Vogtle (Ed.) *Comprehensive Supramolecular Chemistry* Vol. 2 (Oxford: Elsevier, 1996)
9. J Szejtli, T Osa (Eds) *Comprehensive Supramolecular Chemistry* Vol. 3 (Oxford: Elsevier, 1996)
10. A J Kirby *Angew. Chem., Int. Ed. Engl.* **35** 707 (1996)
11. J K M Sanders *Chem.-Eur. J.* **4** 1378 (1998)
12. R Breslow, S D Dong *Chem. Rev.* **98** 1997 (1998)

13. M T Reetz *Top. Catal.* **4** 187 (1997)
14. S Hecht, J M J Frechet *Angew. Chem., Int. Ed.* **40** 9174 (2001)
15. H-F Chow, T K-K Mong, M F Nongrum, C-W Wan *Tetrahedron* **54** 8543 (1998)
16. L J Twyman, A S H King *J. Chem. Res.* **43** (2002)
17. I P Beletskaya, A V Chuchuryukin *Usp. Khim.* **69** 699 (2000) [*Russ. Chem. Rev.* **69** 639 (2000)]
18. D Astruc, F Chardac *Chem. Rev.* **101** 2991 (2001)
19. L J Twyman, A S H King, I K Martin *Chem. Soc. Rev.* **31** 69 (2002)
20. R Kreiter, A W Kleij, R J M K Gebbink, G van Koten *Top. Curr. Chem.* **217** 163 (2001)
21. G Wenz *Angew. Chem., Int. Ed. Engl.* **33** 803 (1994)
22. M L Bender, M Komiyama *Cyclodextrin Chemistry* (New York: Springer, 1978)
23. I Tabushi *Pure Appl. Chem.* **58** 1529 (1986)
24. C J Easton, S F Lincoln *Chem. Soc. Rev.* **25** 163 (1996)
25. Ch J Easton, S F Lincoln *Modified Cyclodextrins. Scaffolds and Templates for Supramolecular Chemistry* (London: Imperial College Press, 1999)
26. E Rizzarelli, G Vecchio *Coord. Chem. Rev.* **188** 343 (1999)
27. J Szejtli *Chem. Rev.* **98** 1743 (1998)
28. L Mandolini, R Ungaro (Eds) *Calixarenes in Action* (London: Imperial College Press, 2000)
29. C D Gutsche *Calixarenes* (Cambridge: Royal Society of Chemistry, 1989)
30. S Shinkai *Tetrahedron* **49** 8933 (1993)
31. S Shinkai, A Ikeda *Chem. Rev.* **97** 1713 (1997)
32. V Bohmer *Angew. Chem., Int. Ed. Engl.* **34** 713 (1995)
33. B Cornils, H Hermann (Eds) *Aqueous Phase Organometallic Catalysis — Concepts and Applications* (Weinheim: Wiley, 1998)
34. E A Karakhanov, A L Maximov, T Yu Filippova, Y S Kardasheva, T S Buchneva, M A Gayevskiy, A Yu Zhuchkova *Polym. Adv. Technol.* **12** 161 (2001)
35. S Tilloy, F Bertoux, A Mortreux, E Monflier *Catal. Today* **48** 245 (1999)
36. H A Zahalka, K Januszkiewcz, H Alper *J. Mol. Catal.* **35** 249 (1986)
37. H Alper *ACS Symp. Ser.* **326** 8 (1987)
38. A Harada, Y Hu, S Takahasi *Chem. Lett.* 2083 (1986)
39. E Monflier, E Blouet, Y Barbaux, A Mortreux *Angew. Chem., Int. Ed. Engl.* **33** 2100 (1994)
40. E Monflier, S Tilloy, G Fremy, Y Barbaux, A Mortreux *Tetrahedron Lett.* **36** 387 (1995)
41. E Monflier, S Tilloy, E Blouet, Y Barbaux, A Mortreux *J. Mol. Catal. A: Chem.* **109** 27 (1996)
42. A Ya Zhuchkova, A L Maksimov, T Yu Filippova, L M Karapetyan, E A Karakhanov *Neftekhimiya* **42** 206 (2002) [a]
43. M V Rekharsky, Y Inoue *Chem. Rev.* **98** 1875 (1998)
44. A Ueno, H Ikeda, K Imamura *Chem. Lett.* 516 (2002)
45. E Karakhanov, T Buchneva, A Maximov, M Zavertyaeva *J. Mol. Catal. A: Chem.* **184** 11 (2002)
46. E A Karakhanov, T S Buchneva, A L Maksimov, E A Runova *Neftekhimiya* **43** 42 (2003) [a]
47. K A Udachin, G D Enright, E B Brouwer, J A Ripmeester *J. Supramol. Chem.* **1** 97 (2001)
48. E A Karakhanov, A L Maximov, V V Predeina, T Yu Filippova, S A Martynova, I N Topchieva *Catal. Today* **44** 189 (1998)
49. E A Karakhanov, A L Maximov, P Poloznicova, K Suslov, in *Studies in Surface Science and Catalysis. Science and Technology in Catalysis* Vol. 121 (Eds H Hattory, K Otsuka) (Amsterdam: Elsevier, 1998) p. 127
50. E A Karakhanov, Yu S Kardasheva, A L Maksimov, E A Runova *Ros. Khim. Zh.* 53 (2002) [b]
51. K Ono, J Katsube *Chem. Pharm. Bull.* **31** 1267 (1983)
52. A B Sorokin, A M Khenkin, S A Marakushev, A E Shilov, A A Shteinman *Dokl. Akad. Nauk SSSR* **279** 939 (1984) [c]
53. K Asakura, T Watanabe, E Honda, Sh Osani *Chem. Lett.* 307 (1996)
54. S Divkar, M M Maheswaran *J. Inclusion Phenom. Mol. Recognit. Ability* **27** 113 (1997)
55. R Ravichandran *J. Mol. Catal. A: Chem.* **130** L205 (1998)
56. H Hirai *Polym. Adv. Technol.* **8** 666 (1998)
57. H Hirai, Yu Shiraishi, H Mihori, K Saito, T Kawamura *Polym. J.* **28** 91 (1996)
58. Ch Zhou, D-Q Yuan, R G Xie *Synth. Commun.* **24** 43 (1994)
59. H A Zahalka, H Alper *Organometallics* **5** 1909 (1986)
60. A Benyei, F Joo *J. Mol. Catal.* **58** 151 (1990)
61. T Lacroix, H Bricout, S Tilloy, E Monflier *Eur. J. Org. Chem.* 3127 (1999)
62. E Monflier, S Tilloy, Y Castanet, A Mortreux *Tetrahedron Lett.* **39** 2959 (1998)
63. H Arzoumanian, D Nue *C.R. Acad. Sci., Ser. IIc* **2** 289 (1999)
64. J T Lee, H Alper *Tetrahedron Lett.* **31** 4101 (1990)
65. J T Lee, H Alper *J. Org. Chem.* **55** 1854 (1990)
66. J T Lee, H Alper *Tetrahedron Lett.*, **31** 1941 (1990)
67. J R Anderson, E M Campi, W R Jackson *Catal. Lett.* **9** 55 (1991)
68. E Monflier, G Fremy, Y Castanet, A Mortreux *Angew. Chem., Int. Ed. Engl.* **34** 2269 (1995)
69. WO PCT 9 622 267; *Chem. Abstr.* **125** 220 843 (1996)
70. E Monflier, S Tilloy, G Fremy, Y Castanet, A Mortreux *Tetrahedron Lett.* **36** 9481 (1995)
71. K Hattori, K Takahashi, N Sakai *Bull. Chem. Soc. Jpn.* **65** 2690 (1992)
72. E Monflier, S Tilloy, F Bertoux, Y Castanet, A Mortreux *New J. Chem.* **21** 857 (1997)
73. M Canipelle, L Caron, C Christine, S Tilloy, E Monflier *Carbohydr. Res.* **337** 281 (2002)
74. Ph Kalck, M Dessoudeix, L Miquel *Catal. Today* **41** 431 (1998)
75. S Singh, G Usha, C H Tung, N J Turro *J. Org. Chem.* **51** 941 (1986)
76. E Rochini, R Spogliarich, M Graziani *J. Mol. Catal.* **91** 313 (1994)
77. R Fornasier, M Marcuzzi, D Zorzi *J. Mol. Catal.* **43** 21 (1987)
78. H Sfihia, A P Legranda, J Doussotb, A Guyb *Colloids Surf. A* **115** 115 (1996)
79. C Pinel, N Gendreau-Diaz, A Breheret, M Lemaire *J. Mol. Catal. A: Chem.* **112** 157 (1996)
80. Th Mathivet, C Meliet, Y Castanet, A Mortreux, L Caron, S Tilloy, E Monflier *J. Mol. Catal. A: Chem.* **176** 105 (2001)
81. E Monflier, S Tilloy, C Meliet, A Mortreux, S Fourmentin, D Landy, Gh Surpateanu *New J. Chem.* **23** 469 (1999)
82. L Caron, S Tilloy, E Monflier, J-M Wieruszeski, G Lippens, D Landy, S Fourmentin, Gh Surpateanu *J. Inclusion Phenom. Macr. Chem.* **38** 361 (2000)
83. A Da Costa, E Monflier, D Landy, S Fourmentin, Gh Surpateanu *Surf. Sci.* **470** 273 (2001)
84. L Caron, C Christine, S Tilloy, E Monflier, D Landy, S Fourmentin, G Surpateanu *Supramol. Chem.* **14** 11 (2002)
85. M Dessoudeix, M Urrutigoity, Ph Kalck *Eur. J. Inorg. Chem.* 1797 (2001)
86. J Cabou, H Bricout, F Hapiot, E Monflier *Catal. Commun.* **5** 265 (2004)
87. H Bricout, C Caron, D Bormann, E Monflier *Catal. Today* **66** 355 (2001)
88. G Barak, Y Sasson *Bull. Soc. Chim. Fr.* 584 (1988)
89. L N Lewis, C A Sumpter *J. Mol. Cat. A: Chem.* **104** 293 (1996)
90. M Baur, M Frank, J Schatz, F Schildbach *Tetrahedron* **57** 6985 (2001)
91. A Robertson, S Shinkai *Coord. Chem. Rev.* **205** 157 (2000)
92. I Tabusi *Acc. Chem. Res.* **15** 66 (1982)
93. I Tabushi, N Shimizu, T Sugimoto, M Shiozuka, K Yamamura *J. Am. Chem. Soc.* **119** 7100 (1997)
94. M T Reetz *Catal. Today* **42** 399 (1998)
95. R Breslow, L E Overman *J. Am. Chem. Soc.* **92** 1075 (1970)
96. B Zhang, R Breslow *J. Am. Chem. Soc.* **119** 1676 (1997)
97. S Liu, Z Luo, A D Hamilton *Angew. Chem., Int. Ed.* **36** 2678 (1997)
98. S Bhatacharya, K Snehalatha, S K Georg *J. Org. Chem.* **63** 27 (1998)
99. J Yan, R Breslow *Tetrahedron Lett.* **41** 2059 (2000)
100. J-M Yan, M Atsumi, D-Q Yuan, K Fujita *Tetrahedron Lett.* **41** 1825 (2000)
101. R Breslow, X Zhang, R Xu, M Maletic, R Merger *J. Am. Chem. Soc.* **118** 11 678 (1996)

102. R Breslow, X Zhang, Y Huang *J. Am. Chem. Soc.* **119** 4535 (1997)
103. R Breslow, B Gabriele, J Yang *Tetrahedron Lett.* **39** 2887 (1998)
104. J Yang, R Breslow *Angew Chem., Int. Ed.* **39** 2692 (2000)
105. R Breslow *Chem. Record.* **1** 3 (2001)
106. R Breslow, J Yang, J Yan *Tetrahedron* **58** 653 (2002)
107. R Breslow, J Yang, S Belvedere *Tetrahedron Lett.* **43** 363 (2002)
108. Y Kuroda, T Hiroshige, H Ogoshi *J. Chem. Soc., Chem. Commun.* 1594 (1990)
109. R Breslow, Zh Fang *Tetrahedron Lett.* **43** 5197 (2002)
110. R R French, J Wirz, W D Woggon *Helv. Chim. Acta* **81** 1521 (1998)
111. D Woggon *Chimia* **54** 564 (2000)
112. R R French, Ph Holzer, M Leuenberger, W D Woggon *Angew. Chem., Int. Ed.* **39** 1267 (2000)
113. R R French, Ph Holzer, M Leuenberger, M C Nold, W D Woggon *J. Inorg. Biochem.* **88** 295 (2002)
114. E A Karakhanov, Y S Kardasheva, A V Kirillov, A L Maximov, V V Predeina, E A Runova *Macromol. Symp.* **156** 137 (2000)
115. H Sakuraba, M Horii, T Takezutsumi *Nippon Kagaki Kaishi* 685 (2000)
116. H Sakuraba, S Iriuchijima, T Takezutsumi, M Horii *Nippon Kagaki Kaishi* 695 (2000)
117. Y Matsui, T Kurita, Y Date *Bull. Chem. Soc. Jpn.* **45** 3229 (1972)
118. Y Matsui, T Kurita, M Yagi, T Okayama, K Mochida, Y Date *Bull. Chem. Soc. Jpn.* **48** 2187 (1975)
119. R Fuchs, N Habermann, P Klufers *Angew. Chem., Int. Ed. Engl.* **32** 852 (1993)
120. Y Liu, C C You, B H Han, Y M Li, B Li, R T Chen *Chem. J. Chin. Univ.* **8** 1316 (1997)
121. K P Bose, P L Polavarapu *Carbohydr. Res.* **323** 63 (1999)
122. S Divakar, M M Maheswaran, R Ravichandran *Indian J. Chem., Sect. B* **33** 177 (1994)
123. R Ravichandran, S Divakar *Indian J. Chem., Sect. B* **35** 264 (1996)
124. S Blanchard, L Le Clainche, M-N Rager, B Chansou, J P Tuchagues, A Duprat, Y Le Mest, O Reinaud *Angew. Chem., Int. Ed.* **37** 2732 (1998)
125. L Le Clainche, M Giorgi, O Reinaud *Eur. J. Inorg. Chem.* 1931 (2000)
126. L Le Clainche, M Giorgi, O Reinaud *Inorg. Chem.* **39** 3436 (2000)
127. Y Rondelez, M-N Rager, A Duprat, O Reinaud *J. Am. Chem. Soc.* **124** 1334 (2002)
128. Y Rondelez, G Bertho, O Reinaud *Angew. Chem., Int. Ed.* **41** 1044 (2002)
129. L Le Clainche, Y Rondelez, O Seneque, S Blanchard, M Campion, M Giorgi, A F Duprat, Y Le Mest, O Reinaud *C.R. Acad. Sci., Ser. IIc* **3** 811 (2000)
130. O Seneque, M Campion, B Douziech, M Giorgi, E Riviere, Y Journaux, Y Le Mest, O Reinaud *Eur. J. Inorg. Chem.* 2007 (2002)
131. A E Rowan, J A A W Elemans, R J M Nolte *Acc. Chem. Res.* **32** 995 (1999)
132. C F Martens, G J M R Klein, M C Feiters, R J M Nolte *J. Am. Chem. Soc.* **116** 5667 (1994)
133. G J M R Klein, C F Martens, P J A Kenis, R J Jansen, H F Nolting, V A Sole, M C Feiters, K D Karlin, R J M Nolte *Inorg. Chem.* **38** 5755 (1999)
134. V S I Sparkel, M C Feiters, R J Nolte, in *Programme and Abstracts of 12th European Symposium on Organic Chemistry, Groningen, 2001* p. 1, 2-31
135. J A A W Elemans, E J A Bijsterveld, A E Rowan, R J M Nolte *Chem. Commun.* 2443 (2000)
136. E J Bijsterveld, A E Rowan, R J M Nolte, in *Programme and Abstracts of 12th European Symposium on Organic Chemistry, Groningen, 2001* P. 1, 2-07
137. E Karakhanov, A Maximov, A Kirillov *J. Mol. Catal. A: Chem.* **157** 25 (2000)
138. L Weber, I Imiolczyk, G Hauf, D Rehorek, H Henning *J. Chem. Soc., Chem. Commun.* 301 (1992)
139. L Weber, R Hommel, J Behling, G Haufe, H Henning *J. Am. Chem. Soc.* **116** 2400 (1994)
140. M Bonchio, T Carofiglio, F Di Furia, R Fornasier *J. Org. Chem.* **60** 5986 (1995)
141. M T Reetz, S R Waldwogel *Angew. Chem., Int. Ed. Engl.* **36** 865 (1997)
142. M T Reetz *J. Heterocycl. Chem.* **35** 1065 (1998)
143. M T Reetz, C Frombgen *Synthesis* 1555 (1999)
144. R M Dishpande, A Fukuoka, M Ichikawa *Chem. Lett.* 13 (1999)
145. D Armspach, D Matt *Chem. Commun.* 1073 (1999)
146. T Y Wong, Ch Yang, K-Ch Ying, G Jia *Organometallics* **21** 1782 (2002)
147. H K A Coolen, P W N M van Leeuwen, R J M Nolte *Angew. Chem., Int. Ed. Engl.* **31** 905 (1992)
148. H K A C Collen, J A M Meeuwis, P W N M van Leeuwen, R J M Nolte *J. Am. Chem. Soc.* **117** 11 906 (1995)
149. S Shimizu, Y Shirakawa, Y Sasaki, C Hira *Angew. Chem., Int. Ed.* **39** 1256 (2000)
150. Y Shirakawa, S Shimizu, Y Sasaki *New J. Chem.* **25** 777 (2001)
151. R Paciello, L Siggel, M Roper *Angew. Chem., Int. Ed.* **38** 1922 (1999)
152. Z Csok, G Szalontai, G Czira, L Kollar *J.Organomet. Chem.* **570** 23 (1998)
153. I A Bagatin, D Matt, H Thonnessen, P G Jones *Inorg. Chem.* **38** 1585 (1999)
154. X Fang, B L Scott, J G Watkin, C A G Carter, G J Kubas *Inorg. Chim. Acta* **317** 276 (2001)
155. C Loeber, C Wieser, D Matt, A de Cian, J Fischer, L Toupet *Bull. Soc. Chim. Fr.* **132** 166 (1995)
156. C J Cobley, D D Ellis, A G Orpen, P G Pringle *J. Chem. Soc., Dalton Trans.* 1109 (2000)
157. F J Parlevliet, C Kiener, J Fraanje, K Goubitz, A L Spek, P C J Kamer, P W N M van Leeuwen *J. Chem. Soc., Dalton Trans.* 1113 (2000)
158. C Kunze, D Selent, I Neda, R Schmutzer, A Spannenberg, A Borner *Heteroat. Chem.* **12** 577 (2001)
159. C Kunze, D Selent, I Neda, M Freytag, P G Jones, R Schmutzer, A Spannenberg, W Baumann A Borner *Z. Anorg. Allg. Chem.* **628** 779 (2002)

[a] — *Petrol. Chem. (Engl. Transl.)*
[b] — *Mendeleev Chem. J. (Engl. Transl.)*
[c] — *Dokl. Chem. (Engl. Transl.)*