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Molecules-Receptors: Different Approaches to Design Effective Catalysts

Edward A. Karakhanov, Lyusyen M. Karapetyan, Yulia S. Kardasheva, Anton L. Maksimov, Elena A. Runova, Maria V. Terenina, Tatyana Yu. Filippova*

Summary: The results of studying a number of reactions catalyzed by system based on macrocyclic receptors are presented. Rh complexes with modified calix[6]- and calix[4]arene were active in the hydroformylation of unsaturated compounds. Ru catalytic system based on cucurbit[6]uril was studied in hydrogen transfer hydrogenation of water insoluble aldehydes. Molecular imprinting method application for design of catalytic systems based on cyclodextrins for naphthols dimerization and oxidative coupling styrene and benzene were discussed.

Keywords: calixarene; cucurbituril; hydroformylation; molecular imprinting; oxidation

Introduction

Homogeneous catalysis plays an important role in nearly all areas of the chemical industry. Catalysts selectivity is becoming more and more the decisive factor in industrial processes. The design of active and selective metal-complex catalysts should combine concepts derived from various disciplines, such as organometallic and coordination chemistry, supramolecular chemistry, macromolecule science.

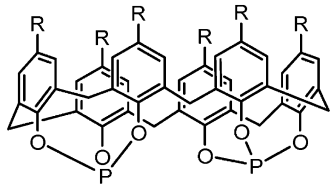
The use of macromolecular fragments in metal-complex catalysts enables one to subsantially change the microenvironment of the catalytic site and, thereby, the catalytic properties. The significant role in such a change is played by the supramolecular structures formed by macromolecular metal complexes. These structures can selectively bind the substrate, alter the geometry and energy of the transition state and cause mutual activation of the participants of catalytic reaction.

Promising approach in designing selective metal-complex catalytic system is the use of molecule-receptors for the construction of organized ligands. The application of cyclodextrins, calixarenes, resorcinarenes, cucurbiturils open up possibilities for development catalysts with molecular recognition abilities.[1–3] Such catalytic systems make it possible to regulate selectivity of reactions by means of supramolecular interactions with substrate due to host-guest inclusion complex formation.[4–6] In this paper, we present the new results of the study the of catalytic systems based on macrocyclic receptors. We used catalyst based on modified calixarens in homogeneous hydroformylation of olefins and catalist based on cucurbiturils in byphasic hydrogenation of aldehyde. Also the prospects of proposed approach are illustrated by given an examples of molecular imprinting method application for design of catalytic systems based on cyclodextrins.

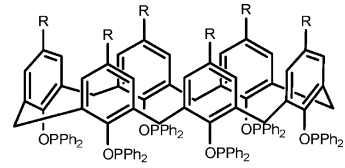
Hydroformylation Catalysts Based on Calixarenes

Calix[6]arenes **(I-IV)** modified with diphenylphosphine and phosphite substituents on the lower oxygen-containing ring were synthesized as ligands

Department of Chemistry, Moscow State University, Leninskie Gory, Moscow, 119992, Russia
E-mail: kar@petrol.chem.msu.ru



(I) R= ^{t}Bu
(II) R = H



(III)R= ^{t}Bu
(IV) R = H

Studies of complex formation between p-tert-butyl calix[6]arenediphosphite **(I)** and $Rh(acac)(CO)_2$ demonstrated that at the ratio $P/Rh \leq 4$ highly catalytic active complex Rh(acac)L becomes the dominating species in solution. Further increase in concentration of phosphite ligand leads to formation low active complex RhL_2.[7]

NMR-spectroscopy and mass-spectrometry were used to study the formation of complexes between calix[6]arenediphosphite **(II)** and $Rh(COD)_2BF_4$ at different ratios ligand-metal (COD – cyclooctadiene). Solutions of diphosphite **(II)** and $Rh(COD)_2BF_4$ in deuterochloroform were mixed in argone at molar ratio 0.25:1 (P/Rh = 0.5). In ^{31}P-NMR spectrum of the former mixture the doublet appears at δ 97.5 ppm ($^1J_{(Rh\text{-}P)}$ 256 Hz) in contrast to the signal of the initial calixarene **(II)** (Figure 1a). Meanwhile the only peak corresponding to $(M\text{-}BF_4)^+$, m/z = 903 is observed in the mass spectrum proving the formation of $[Rh(COD)L]BF_4$ complexes. Increasing concentration of macrocyclic compound four times (P/Rh = 2) results in another doublet at δ 106.7 ppm ($^1J_{P\text{-}Rh}$ = 220 MHz) and the signal M^+, m/z = 1488 in mass spectrum. That indicates the formation of RhL_2 complex. Increase of the signal intensity is observed with the further growth of the P/Rh ratio (Figure 1c). At P/Rh = 8 the doublet at 97.5 ppm vanishes and the singlet corresponding to free phosphite species is observed (Figure 1d)

In RhL_2 complex rhodium is shielded by two bulky macrocyclic substituents hindering coordination of olefin on the metal centre, thus inhibiting the catalytic reaction.

The series of synthesized macrocycles were tested as possible components of catalytic systems in hydroformylation of various 1-alkene and arylalkenes. Complexes of rhodium and calixarene ligands were obtained *in situ* from $Rh(acac)(CO)_2$ and the corresponding macrocycle. Hydroformylation of alkenes resulted in formation of normal and iso- aldehydes and isomeric alkenes. Hydroformylation of unsaturated compounds is usually conducted in the presence of some free phosphorous-containing ligand excess, which prevents formation of inactive rhodium-hydride complexes and leads to decrease aldehydes yields.[8] In our earlier studies we investigated the activity of catalytic systems with

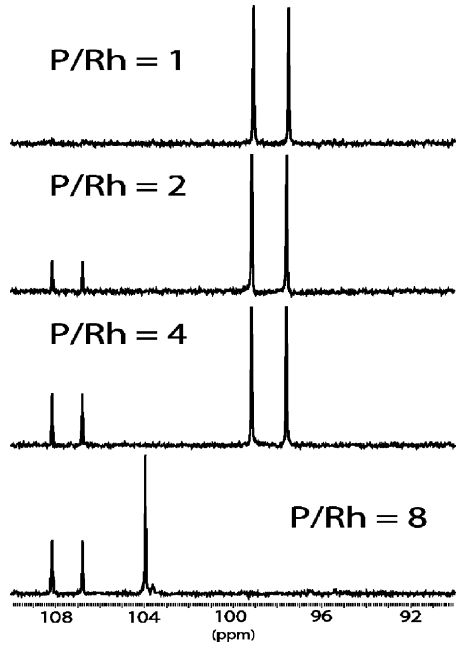


Figure 1.
^{31}P NMR spectra of solutions in $CDCl_3$ containing $Rh(COD)_2BF_4$ and **(II)** in the P/Rh ratio of.

different ratio (P/Rh) on the example of Rhodium complexes with p-tert-butylcalix[6]-arenephosphite**(I)**. Increase of phosphorous-containing calixarene concentration resulted in slight increase of the regioselectivity in 1-nonene hydroformylation but at ratio/ $Rh \geq 6$ a drastic decrease of conversion and aldehyde yield was observed (Figure 2a).[9]

Systems based on ditertbutylphosphite ligands exhibited the same tendency, the conversion decreased significantly at the ratio $P/Rh \geq 4$ (Figure 2c).

Due to the fact that calix[6]arenediphosphite is poor soluble in most of the organic solvents, all catalytic experiments with that compound were carried out at the ratio $P:Rh = 1$. Maximal yield of aldehydes with ligand **(III)** was achieved at the ratio of Phosphorus/Rhodium 3:1.

The conversion of the initial olefin and the yield of aldehydes depends considerably upon the temperature and reaches the maximum values at 50 °C (Table 1). Further increase of the temperature results in reduction of olefin conversion and aldehydes yield. It should be noted that the portion of isomerisation products is slightly more for the complex with diphosphite **(II)** than for the complex based on ligand **(I)**.

Changing the pressure of synthesis gas from 0.25 to 2.5 MPa accelerates the catalytic reaction dramatically, also decreasing the portion of by-products. The portion of isomerized alkenes decreases from 11% to 4% (Table 2).

Dependence of nonene-1 conversion from reaction time was obtained to investigate the kinetics of hydroformylation in the presence of ligand **(III)**. Data given in Figure 3 demonstrate that almost quantitative conversion of alkene occurs in two hours.

Rhodium complexes with phosphorous-containing calixarenes (**I-III**) provide high catalytic activity in hydroformylation of linear 1-alkenes (C_7-C_{12}), the yields slightly increase with the chain length of the substrate (Table 3). The ratio of linear and branched aldehydes remains almost constant.

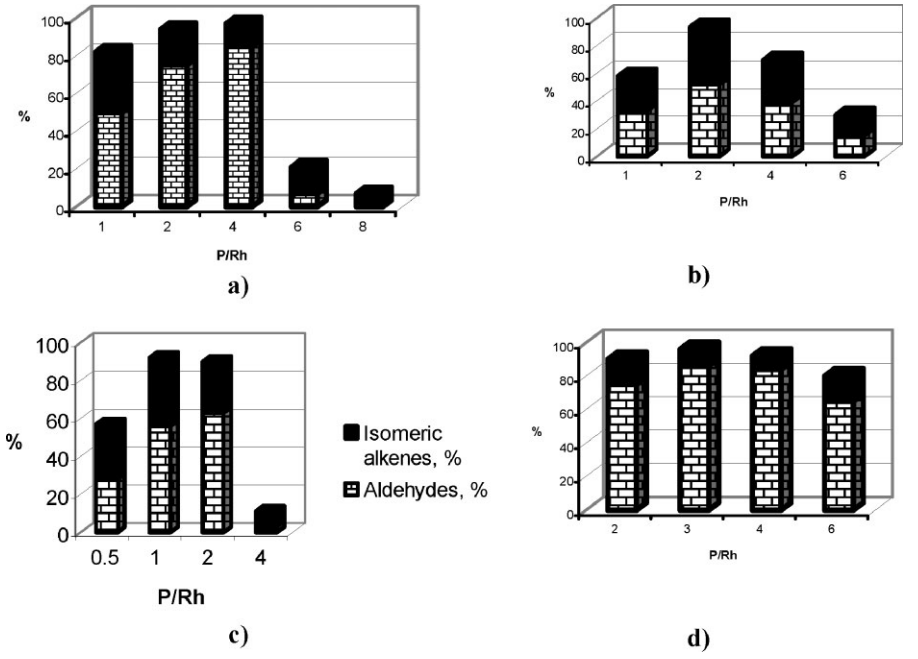
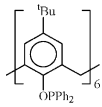
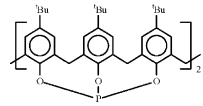
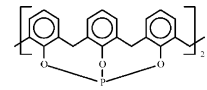


Figure 2.
Hydroformylation of 1-nonene at various P/Rh ratios. Reaction conditions: $Rh(acac)(CO)_2$, toluene 1.5 ml; 50 °C, reaction time 2 hour, 0.5 Mpa; a) Ligand I; S:C = 150; b) Ligand I; S:C = 500; c) Ligand II; S:C = 150; d) Ligan III; S:C = 150.

Table 1.
Hydroformylation of 1-nonene and 1-decene in presence of **(I-III)** as ligands at various temperatures. Reaction conditions: S:C = 150, toluene 1.5 ml; reaction time 2 hour, 0.5 MPa.

Ligand	 (III) [a)]	 (I) [b)]	 (II) [c)]					
Substrate	1-nonene		1-nonene		1-decene		1-nonene	
Temperature, °C	Conversion (%)	Aldehydes (%)	Conversion (%)	Aldehydes (%)	Conversion (%)	Aldehydes (%)	Conversion (%)	Aldehydes (%)
25	20	13	9	5	18	4	10	4
50	97	86	94	75	95	81	92	56
70	90	65	85	66	75	54	78	33
100	54	27	46	22	49	33	42	13

[a)] - P/Rh = 3;
[b)] - P/Rh = 2;
[c)] - P/Rh = 1.

Table 2.
Hydroformylation of 1-nonene in presence of **(III)** as ligand at various pressures. Reaction conditions: S:C = 150, toluene 1.5 ml; reaction time 2 hour, 50 °C, P/Rh = 3.

P, MPa	Conversion (%)	Aldehydes (%)	Regioselectivity (decanal/aldehydes) %
0.25	16	5	55
0.5	97	86	55
1.0	97	87	50
2.0	97	89	48
2.5	98	94	46

The presence of hydrophobic cavity of definite size and shape in the calixarene molecule allows the former to act in formation of inclusion host guest complexes, i.e. such macrocycles can be considered as molecular receptors capable of binding the substrate and changing it configuration, thus facilitating achievement

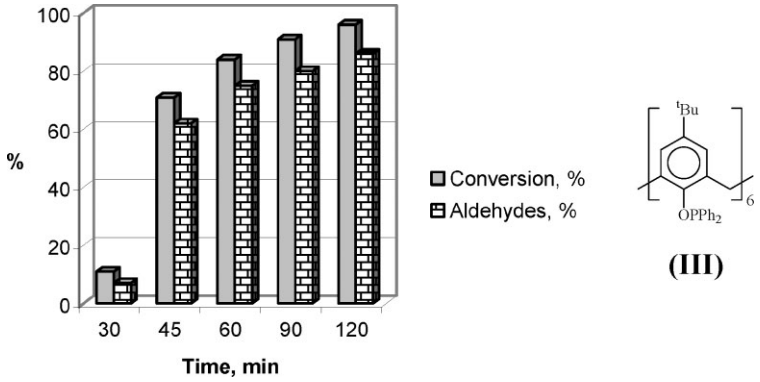
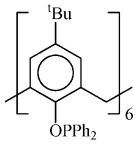


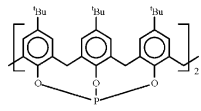
Figure 3.
Hydroformylation of 1-nonene in presence of **(III)**. Degree of conversion and aldehydes yield versus reaction time. Reaction conditions: $Rh(acac)(CO)_2$, S:C = 150, P/Rh = 3, 50 °C, 0.5 MPa.

Table 3.
Hydroformylation of alkenes. Reaction conditions: $Rh(acac)(CO)_2$, toluene 1.5 ml, reaction time 1 h, 50 °C, 0.5 MPa.

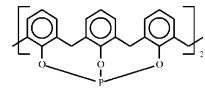
Ligand



(III)



(I)



(II)

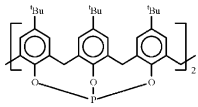
S: C	150[a]		150[b]		500[b]		150[c]	
Substrate	Conversion (%)	Aldehydes (%)	Conversion (%)	Aldehydes (%)	Conversion (%)	Aldehydes (%)	Conversion (%)	Aldehydes (%)
1-heptene	98	92	67	46	46	30	43	22
1-octene	95	85	70	54	53	33	54	38
1-nonene	96	86	80	60	60	37	84	39
1-decene	90	81	86	65	68	43	63	30
1-dodecene	91	74	90	67	72	55	75	30

[a] P/Rh = 3; 2 h,
[b] P/Rh = 2,
[c] P/Rh = 1.

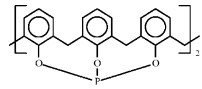
of the transition state. It has been reported earlier[10] that the inclusion complexes of calixarene with compounds containing aromatic fragment are significantly more stable than those with the linear olefins. That provides additional stability of acyl-rhodium intermediate. The formation of the former species is the key stage in

Table 4.
Hydroformylation arylalkenes. Reaction conditions: $Rh(acac)(CO)_2$; reaction time 1 h; toluene 1.5 ml, 50 °C, TOF, h^{-1} – turnover frequency, mol of product to mol of Rh for hour.

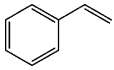
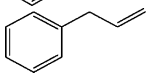
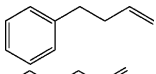
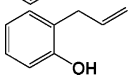
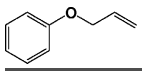
Ligand



(I)
(P/Rh =2)

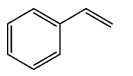
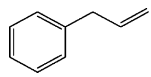
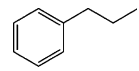
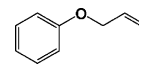
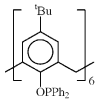
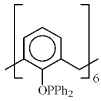


(II)
(P/Rh =1)

Conditions	S: C = 150 0.5 MPa		S: C = 500 0.5 MPa		S: C = 150 0.5 MPa		S: C = 150 2.5 MPa	
Substrate	TOF, h^{-1}	n/iso	TOF, h^{-1}	n/iso	TOF, h^{-1}	n/iso	TOF, h^{-1}	n/iso
	86	0.2	90	0.4	9	0.5	14	0.2
	96	1.6	90 470[a]	2	65	2.3	80	1.2
	114	1.9	100	0.9 2.3	66	2.6	93	1.2
	105	1.7	65	1.6	29	1.7	41 65[a]	1.0 0.8[a]
	114	0.6	45	0.6	68	0.7	99	0.4

[a] 5.0 MPa.

Table 5.
Hydroformylation arylalkenes. Reaction conditions: S:C = 150, 50°C, reaction time 1 h, 2,5 MPa, toluene 1.5 ml, P/Rh = 3.

								
	TOF h^{-1}	n/iso	TOF h^{-1}	n/iso	TOF h^{-1}	n/iso	TOF h^{-1}	n/iso
 **(III)**	36	i	117	1	130	0.9	138	0.3
 **(IV)**	48	i	147	1	143	1.1	143	0.3

hydroformylation. Therefore we studied catalytic activity of rhodium complexes with calixarene-based ligands in hydroformylation of various arylalkenes – styrene, allylbenzene, 4-phenylbutene-1, 2-allylphenol and allyl ester of phenol.

Catalytic systems based on diphospites **(I)** and **(II)** actively conduct hydroformylation of arylalkenes. Like in the case of linear alkenes the conversion l decreases significantly with the increase of substrate concentration (S:C = 500). It should be noted the increase of the synthesis gas pressure from 0.5 to 5.0 MPa drastically accelerates hydroformylation of allylbenzene and the aldehydes yield becomes almost quantitative, even at the ratio S:C = 500 (Table 4). The yields of the linear aldehydes are higher than the yield of isomeric aldehyde for allyl- and butenylbenzenes and also for o-allylphenol, while 2-phenyl- and 2-methyl-3-phenoxypropanale are the dominating products for styrene and allyl ester of phenol, respectively. Results given in Table 5 prove that catalytic systems based on phosphinites-calixarenes **(III-IV)** also demonstrate high activity in hydroformylation of arylalkenes, the yield increasing with the growth of the substrate chain length.

High solubility of p-tert-butylcalix[6]-arenephosphinite **(III)** in aromatic substrates permits to conduct reactions with synthesis gas without solvent (ratio S:C = 1000) which increases the efficiency of the metal complex significantly(Table 6).

A subtituent at the para-position of styrene's ring favors acceleration of the reaction's rate compared to unsubstituted styrene. In all cases we observed formation mainly of isomerized product(Table 7).

Hydroformylation of alkenes with the internal double bond was studied on the example of ligand **(III)** (Table 8). Internal

Table 6.
Hydroformylation of arylalkenes without addition of solvent in presence of **(III)** as a ligand. Reaction conditions: $Rh(acac)(CO)_2$, S:C = 1000, 50°C, reaction time 1 h, 2.5 MPa, P/Rh = 3.

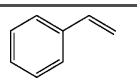
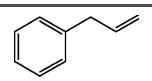
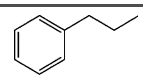
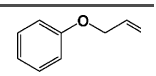
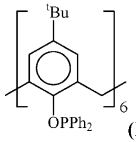
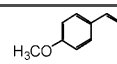
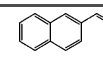
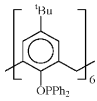
								
	TOF h^{-1}	n/iso	TOF h^{-1}	n/iso	TOF h^{-1}	n/iso	TOF h^{-1}	n/iso
 **(III)**	180	i	800	0.9	740	0.5	470	1.1

Table 7.
Hydroformylation of substituted styrenes and vinylnaphthalene in presence of **(I-III)** as ligands. Reaction conditions: $Rh(acac)(CO)_2$, S:C = 150, 50 °C, reaction time 1 h, 2.5 MPa, P/Rh = 3.

Substrate	TOF, h^{-1}					
						
	36	37	57	141	146	123
(III)						

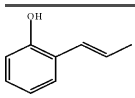
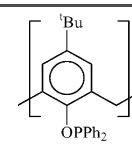
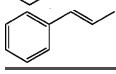
olefins have extremely low activity in hydroformylation reactions and usually harsh reaction conditions are needed to obtain aldehydes. It was demonstrated that after 1 hour at 2.5 MPa conversion of propenylphenol and propenylbenzene was about 10%, and after 6 hours conversion of propenylphenol achieved 74%.

Rhodium complex with p-tert-butylcalix[6]arenediphosphite **(I)** also allows interaction of synthesis gas with heptene-3. At the pressure 5.0 MPa heptene-3 conversion was 68% after 2 hours. The yield of aldehydes reached 50% after 6 hours even in mild conditions (pressure 0.5 MPa).

Catalytic System Based on Cucurbit[6]uryl

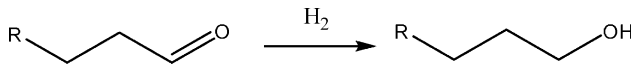
Cucurbit[6]uryl (CB[6]) is the cyclic hexamer formed from the condensation of glycouril and formaldehyde. Similar to cyclodextrins (CDs), the cavity can hold small organic molecules through hydrophobic interactions. Unlike CDs, however, the carbonyl groups at the portals allow CB[6] to bind ions and molecules through charge dipole as well as hydrogen-bonding interactions.[11] The cavity of CB[6] can be used as a reaction chamber to mediate chemical reactions.[12] We demonstrate that CB[6] can be used as a component of catalytic system in byphasic conditions. The hydrogen transfer hydroganation of water insoluble aldehydes to alkohol catalyzed by Ru(III) complex with TPPTS (TPPTS: trisulfonated triphenylphosphine sodium salt; $[P(m\text{-}C_6H_4SO_3Na)_3]$) was chosen as a model reaction. The reaction rate was increased for 1-hexanal and 1-octanal by adding CB[6] to an aqueous solution containing a ruthenium complex and HCOONa (Table 9).

Table 8.
Hydroformylation of aromatic substrates in presence of **(III)** as a ligand. Reaction conditions: S:C = 150, 50 °C, reaction time 1 h, 2.5 MPa, P/Rh = 3.

Substrate	Conversion (%)	Aldehydes (%)	n/iso	
	12	12	0.1	 **(III)**
	74[a)]	74[a)]	0.2	
	44	44	i	
	8	8	i	

[a)] 6 h.

Table 9.
Hydrogen transfer hydroganation of water insoluble aldehydes with CB[6] based catalytic system. [Ru(II)] = 0.005 mmol; [TPPTS]/[Ru(II)] = 4, [HCOONa] = 5M, CB[6] = 1 mmol, [substrate]/[Ru(II)] = 200.

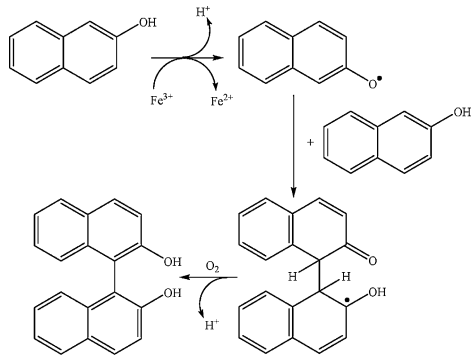


Substrate	Yield, %	
	Without CB[6]	With CB[6]
1-Hexanal	22	64
1-Octanal	18	32

Molecular Imprinting Technique for Design of Supramolecular Catalysts

Application of molecular imprinting techniques is one of the possible ways to development of effective catalysts employing receptor molecules.[13–14] Imprinting process with cyclodextrin molecules occurs according to the following scheme (Figure 4). On the first stage pre-organization of cyclodextrin and template molecule takes place, resulting in formation of the host guest inclusion complex. Subsequently the formed structure is fixed with binding agents, containing two or more functional groups which can react with cyclodextrins. On the last stage the template is removed via various techniques.

Synthesis of macroligands could allow macromolecular ligand to tune to the specific substrate[13–14] or the reaction transition state.[15–20] We have demonstrated that application of imprinting in the last case provides best results when a rigid molecule similar to the reaction transition state is used as a template.[15] 1,1′-Binaphtol is one of the most suitable molecules for such requirements, as it can be regarded as the transition state in dimeriztion of the corresponding naphtol.[21]



The efficiency of such approach for development catalysts was demonstrated on the series of macroligands (CD1-CD6), obtained with various modified binaphtols used as templates (Figure 5).

To the study of the influence of the template structure on the macroligand properties we used compounds with different substituents in the naphthalene ring. Synthesis of ligands was performed through reaction of cyclodextrin with epichlorhydrine, in the presence of 2 times excess of cyclodextrin against the template.

The synthesized ligands were characterized by NMR-spectroscopy and MALDI-TOF mass-spectrometry. The relative content of dimmers was determined as ratio of intensities of peaks corresponding to monomers and dimmers in mass-spectrum (Table 10). Increase in fraction of dimers was observed for all the rigid templates

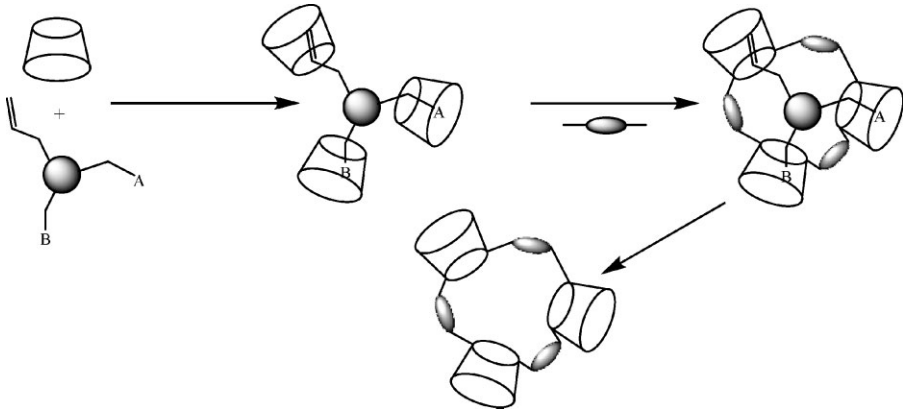


Figure 4.
Molecular imprinting with receptor molecules.

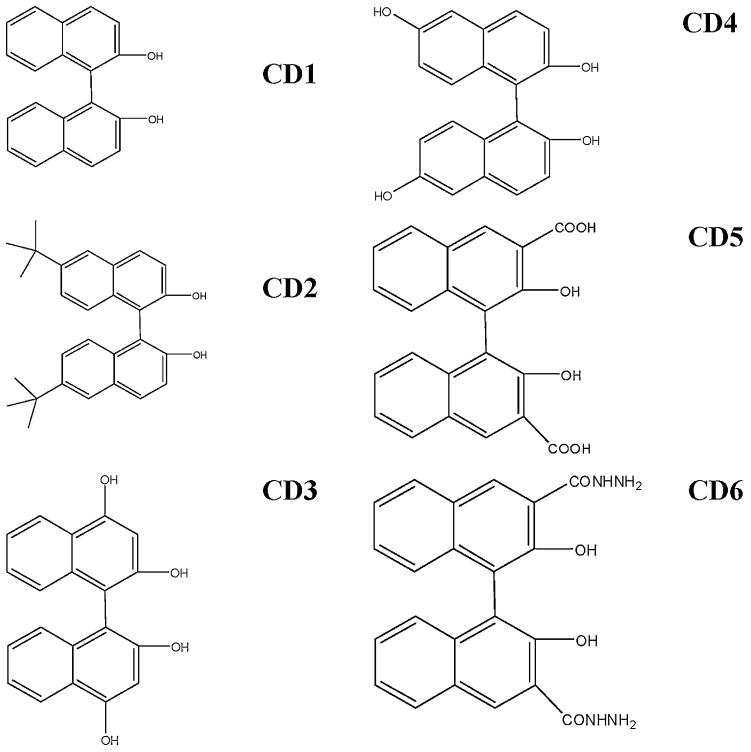


Figure 5.
Templates that used for macroligands CD1-CD6 synthesis.

compared to samples obtained without templates, excluding bis(1,3-dinaphtol). Fraction of dimers in reaction with the former did not exceed 2%.

The synthesized macroligands were tested in dimerization reaction of the corre-

Table 10.
Quantity of dimers based on MALDI-data

Ligand	CD1	CD2	CD3	CD4	CD5	CD6
Dimers %	8	6	<1	10	4	4.5

Table 11.
Dimerization of β-naphtol catalyazed y complexes of Fe(III) with macroligands [substrate] = 0.35 M, [substrate]/[Fe(III)]/[β-CD polymer] = 20/40/1. Solvent $CHCl_3/H_2O = 1$ by volume

Substrate	Ligand	Initial rate without imprinting ligand, mol/h	Initial rate with imprinting ligand, mol/h
2-naphthol	CD1	0.07	0.16
7-t-butyl-2-naphthol	CD2	0.04	0.1
2,4-naphtodiol	CD3	0.03	0.035
2,6-naphtodiol	CD4	0.06	0.16
2-naphthol-3-carbonic acid	CD5	0.06	0.14
2-naphthol-3-carbonic acid hydrazid	CD6	0.07	0.14

Table 12.
Dimerization of 1,1′-β-naphthol in $CHCl_3$ catalyzed by complexes of Fe(III) with macroligands [substrate] = 0.35 M, [substrate]/[Fe(III)]/[β-CD polymer] = 20/40/1. Solvent $CHCl_3$

Catalytic system	Time, min	Dimer yield, %
$FeCl_3$	30	26
	120	43
$FeCl_3$/β-CD polymer (without imprinting)	30	29
	120	66
$FeCl_3$/β-CD polymer (imprinting; CD1)	30	53
	120	85
$FeCl_3$/β-CD polymer (imprinting CD1), Second cycle	120	79

sponding naphtols in a two-phase system chloroform/water, macroligand and $FeCl_3$ used as catalyst. Initial rates of the reactions are given in Table 11.

Almost two times increase in the reaction rate was observed with ligands which had a considerable content of dimers. It corresponds to our assumption that the structure of macroligand obtained in the presence of 1,1′-bis-naphtols facilitates approaching of the reacting naphthaline fragments in the best way, thus increasing the rate of the reaction.

Also, a heterogeneous catalyst for dimerization reaction in chloroform was synthesized through reaction between $FeCl_3$ and macroligand, obtained via molecular imprinting technique. $FeCl_3$ and

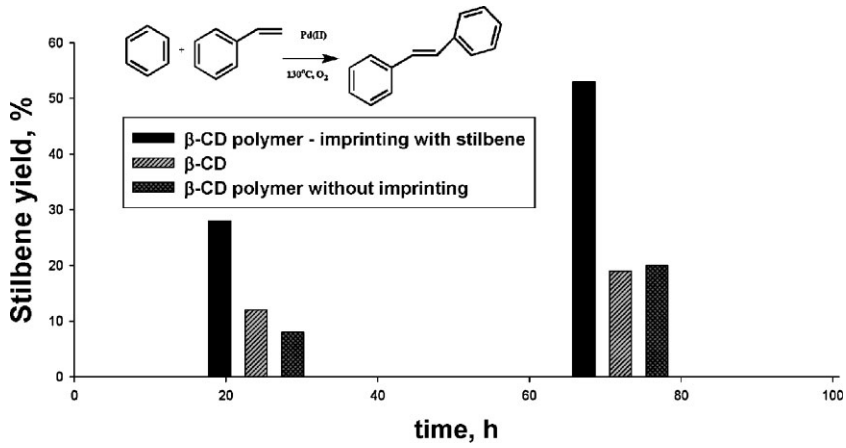


Figure 6.
Oxidative coupling of styrene and benzene. Pd(II) 3 mol%, 100 °C, 0.5 Mpa O_2.

catalyst based on template-free macroligand were used to compare the activity. It turned out that metallocomplex obtained via imprinting was considerably more active than systems with macroligands without imprinting (Table 12).The catalyst was easily isolated from the reaction products and could be used repeatedly without significant loss in activity.

This approach seems promising also for reactions of cross-combination, particularly for oxidative combination of styrene and benzene. Complex of Pd(II) with macroligand synthesized using stylbene as template was the most active catalyst, increasing the rate of reaction more than twice (Figure 6).

Conclusion

In summary, it has been demonstrated that the catalytic systems based on calixarenes, cucur[6]bituryl, cyclodextrins are efficient in biphasic and homogeneous conditions. The extension of the present approaches to may lead to development new highly active and selective supramolecular catalyst containing different types of receptor molecules, such as dendrimers, resorcinarens etc.

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