

Biphasic Wacker-oxidation of 1-octene catalyzed by palladium complexes with modified β -cyclodextrins

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Abstract

New water-soluble palladium complexes with molecular recognition abilities based on β -cyclodextrin (β -CD) modified by nitrile-containing groups have been designed. Complexes display high catalytic activity and selectivity in two-phase Wacker-oxidation of 1-octene under mild conditions. The correlation between binding constants for inclusion complexes of β -CD-based compounds with substrate and the reaction rates has been established. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the discovery of water-phase hydroformylation [1], creation of catalysts for reactions in water-organic two-phase system has been one of the rapidly developing branches of metal complex catalysis. A large number of catalytic systems for conducting reactions under these conditions has been proposed, which, as a rule, include a metal complex with the ligand (sulfonated phosphines, amines, polymer ligands) that renders the metal complex catalyst

water-soluble [2]. In some cases, in which the water solubility of the substrates is extremely low along with water-soluble metal complexes compounds functioning as phase transfer catalysts are used. Among such agents are cyclodextrins-cyclic oligosaccharides consisting of six or more D-glucopyranose units [3]. The possession of hydrophobic cavity makes cyclodextrins as component of catalytic systems extremely attractive subject for study. Cyclodextrins can accommodate a variety of organic compounds by forming host–guest inclusion complexes. The ability of β -cyclodextrin (β -CD) to promote reactions in two-phase systems is described in Refs. [4–7].

In our opinion, of particular interest is the study of metal complexes based on modified cyclodextrins as catalyst for various reactions.

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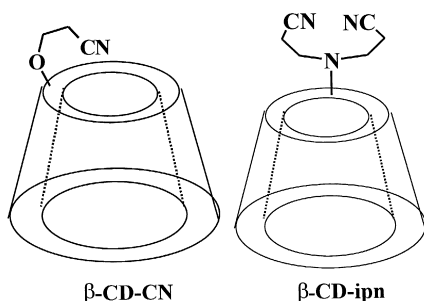


Fig. 1. Ligands based on β -CD.

The availability of many hydroxyls along cyclodextrin rims makes the attachment of functional groups in a number of ways possible. Metal complexes thus obtained from modified cyclodextrins not only retain the capability for producing host–guest compounds but also change the specificity of recognition because of the additional interaction between the functional group of the substrate and the metal center bound to host molecule. Such type of recognition was determined by Tabushi et al. [8,9] as a “double recognition”.

There are only a few publications in which the application of modified cyclodextrins as ligands in metal complex catalysis has been described [10–13]. Recently, Reetz and Waldvogel [12] have illustrated that rhodium complexes of phosphinated β -CD are active in two-phase hydrogenation and hydroformylation. We have previously described that iron complexes of catechol modified β -CD are highly selective catalysts in biomimetic hydroxylation of phenol [13].

The present study demonstrates that β -CD modified with nitrile-containing groups can be applied as ligands in two-phase Wacker-oxidation of higher olefines (Fig. 1).

2. Experimental

Palladium chloride, palladium sulfate and β -CD (Aldrich) were used without further purification. Bis(acetonitrile)palladium dichloride and bis(benzonitrile) palladium dichloride was obtained according to Ref. [14].

The β -CD-CN ligand was synthesized as follows. Acrylonitrile (0.053 g) was added at 55°C to a paste compounded of 1.13 g of β -CD and 0.5 ml of 10% NaOH. The mixture was stirred for 30 min and then poured out into 30 ml of methanol. A white precipitate formed was filtered off, dried in vacuum, and recrystallized twice from methanol. NMR ^1H data: 3.19–3.27 ppm — H4 and H2 β -CD; 3.51–3.9 ppm — H3, H5, H6 β -CD; 4.5–4.7 ppm — H1 β -CD; 3.47 ppm, 3.38 ppm — H $\text{CH}_2\text{CH}_2\text{CN}$, NMR, ^{13}C spectra — 118–119 ppm CN; 16, 56 ppm CH_2CH_2 ; 61 and 69.5 ppm — C6 β -CD; 72.6 ppm — C2 and C5 β -CD, 73.9 — C-3 β -CD, 81.9 — C4 β -CD, 102.6 C1 β -CD; FTIR: 2255- ν CN.

β -CD-ipn was prepared from corresponding tosylate as follows. To 15 g of β -CD tosylate, 1.2 ml of iminodipropionitrile in dry *N,N*-dimethylformamide was added. The mixture was boiled over anhydrous sodium carbonate for 12 h and then filtered off; the product was precipitated by acetone and recrystallized twice from water. NMR ^1H data: 3.19–3.27 ppm — H4 and H2 β -CD; 3.56–3.8 ppm — H3, H5, H6 β -CD; 4.5–4.7 ppm — H1 β -CD; 2.46, 2.8 ppm — H $\text{CH}_2\text{CH}_2\text{CN}$.

Palladium complexes were synthesized from corresponding ligand and a palladium chloride, palladium sulfate, bis(acetonitrile) palladium dichloride and bis(benzonitrile) palladium dichloride at ligand-to-palladium ratios of 1:1 and 2:1. Reaction was performed in water on heating to 80°C for 6 h. The solution was cooled and acetone was added. A precipitate formed was filtered off and dried in vacuum. Ratio of Pd^{2+} /ligand by data of atomic absorption spectroscopy for all complexes was 1.

Catalytic reactions were performed in a controlled-temperature autoclave with a magnetic stirrer at a pressure of oxygen of 0.2–0.5 MPa at a temperatures from 20–80°C. Copper dichloride, irone trichloride, heteropoly acid ($\text{H}_{3+n}\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}$, $n = 1,2,3$), benzoquinone, antron were used as cocatalysts. A reaction mixture contained 2 mmol of olefin, corre-

sponding amounts of metal complexes, cocatalyst and 2 ml of water. After completion, the organic layer was separated from the aqueous one and analyzed.

Ligands and metal complexes were characterized by ^1H , ^{13}C NMR and FTIR spectroscopies. NMR data were recorded on a Varian WXR-400 spectrometer. FTIR spectra were obtained with Perkin-Elmer 2000 spectrometer.

The reaction products were analyzed by GC (column with ‘‘Carbowax 20 M’’), HPLC (Lichosorb C18, 200×4 mm, eluent-methanol/water) and GC-MS using Finnigan-MAT 1125 GC-MS system

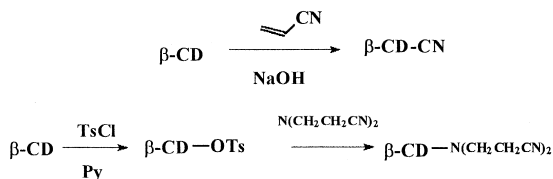
3. Results and discussion

The ligands were obtained via Scheme 1.

The ligands have been examined in the palladium-catalyzed Wacker-oxidation of 1-octene as representative of higher alkenes. Table 1 gives comparative data on 1-octene oxidation.

The main reaction product was 2-octanone. Under a pressure of 2 atm, the reaction rate was determined by reoxidation of palladium in a catalytic cycle. No difference was observed in activity between the examined catalysts based on unmodified and modified cyclodextrins. A four-fold decrease in the palladium concentration caused no change in the product yield. A higher pressure or a more efficient reoxidant, in particular, heteropoly acid, gave rise to a considerable difference in activity between the catalytic systems.

If the reaction was performed for a longer time, the yield of 2-octanone was found to be almost quantitative: 94% after 8 h at 60°C or



Scheme 1.

Table 1
Results on Wacker-oxidation of 1-octene with modified $\beta\text{-CD}^a$

Catalytic system	O_2 , MPa	2-Octanone yield, %
$\text{PdCl}_2/\text{CuCl}_2$	0.2	< 1
$\text{PdCl}_2/\text{CuCl}_2/\beta\text{-CD}$	0.2	20
$\text{PdCl}_2/\text{CuCl}_2/\beta\text{-CD-CN}$	0.2	19
$\text{PdCl}_2/\text{CuCl}_2/\beta\text{-CD-ipn}$	0.2	17
$\text{PdCl}_2/\text{CuCl}_2/\text{HPA}^b$	0.2	20
$\text{PdCl}_2/\text{CuCl}_2/\text{HPA}/\beta\text{-CD}$	0.2	50
$\text{PdCl}_2/\text{CuCl}_2/\text{HPA}/\beta\text{-CD-CN}$	0.2	73
$\text{PdCl}_2/\text{CuCl}_2^c$	0.5	< 1
$\text{PdCl}_2/\text{CuCl}_2/\beta\text{-CD}^c$	0.5	30
$\text{PdCl}_2/\text{CuCl}_2/\beta\text{-CD-CN}^c$	0.5	56
$\text{PdCl}_2/\text{CuCl}_2/\beta\text{-CD-ipn}^c$	0.5	40

^aConditions: $T = 60^\circ\text{C}$, $\text{Pd}^{2+}/1\text{-octene} = 1/100$; $\text{Pd}^{2+}/\text{Cu}^{2+} = 1/10$ reaction time 2 h.

^bHPA — heteropoly acid ($\text{H}_{3+n}[\text{PV}_n\text{Mo}_{12-n}\text{O}_{40}]$, $n = 1,2,3$).

^c $T = 80^\circ\text{C}$.

after 6 h at 80°C . The isomerization product amount was insignificant (Fig. 1).

A substantial enhancement of the activity of the catalytic systems was also attained by using palladium sulfate or benzo- and acetonitrile complexes of palladium as palladium sources for in situ complex formation (Figs. 2–3). In this case, the reaction product yields exceeded 70% in 2 h. The activities of the $\beta\text{-CD}$ -based catalysts changed in the order:

$\beta\text{-CD-CN} > \beta\text{-CD-ipn} > \beta\text{-CD}$.

In this case, both modified and unmodified $\beta\text{-CD}$ s selectively combine with the substrate and transfer it to the aqueous phase, where it can be oxidized. The fact that the activity of the catalysts based on modified $\beta\text{-CD}$ s is higher than that of a palladium–salt– $\beta\text{-CD}$ mixture can be explained as follows. The combination of $\beta\text{-CD}$ and a metal complex into a single molecule substantially raises the stability constant of the host–guest complex owing to the coordination of the double bond of the substrate with the metal ion, which increases the substrate concentration in the aqueous phase. Reaction proceeds via the conventional mechanism.

To prove this regularity, the formation of inclusion complexes of $\beta\text{-CD}$ and $\beta\text{-CD-}$

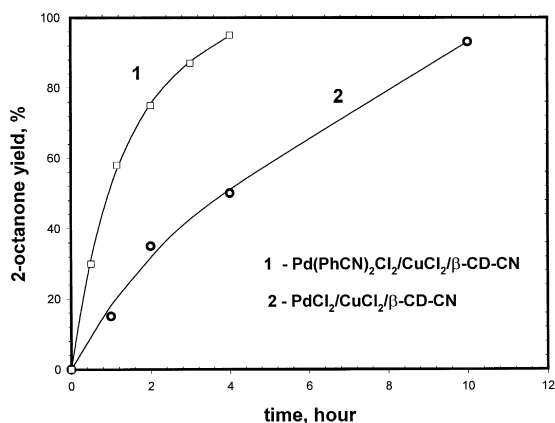


Fig. 2. The yield of 2-octanone vs. reaction time; $T = 60^\circ\text{C}$, $P = 0.5\text{ MPa}$ $[\text{1-octene}] = 0.67\text{ M}$, $\text{Pd}^{2+}/\text{Cu}^{2+}/\beta\text{-CD}/\text{1-octene} = 1:10:1:100$.

CN/Pd^{2+} with 1-octene in an equimolar water–acetonitrile mixture was studied by HPLC. The binding constants (K_b) were estimated from

the inverse of the capacity factor (k) of 1-octene and $\beta\text{-CD}$ concentration by the formula proposed in Refs. [15,16]:

$$\frac{1}{k} = \frac{1}{k_0} + K_b \frac{[\text{CD}]}{k_0},$$

where $[\text{CD}]$ is the $\beta\text{-CD}$ concentration, and k_0 is the capacity factor of 1-octene in the absence of $\beta\text{-CD}$. The fact that K_b of $\beta\text{-CD-CN}/\text{Pd}$ is almost twice as large as that of unmodified $\beta\text{-CD}$ explains much higher activity of the complex (Table 2).

In addition, unlike the catalytic system based on unmodified $\beta\text{-CD}$, the formation of such a complex renders unnecessary an additional reaction step, namely, reaction of the host–guest complex with free palladium. This results in a considerable increase in the reaction rate, particularly, in using palladium compounds that

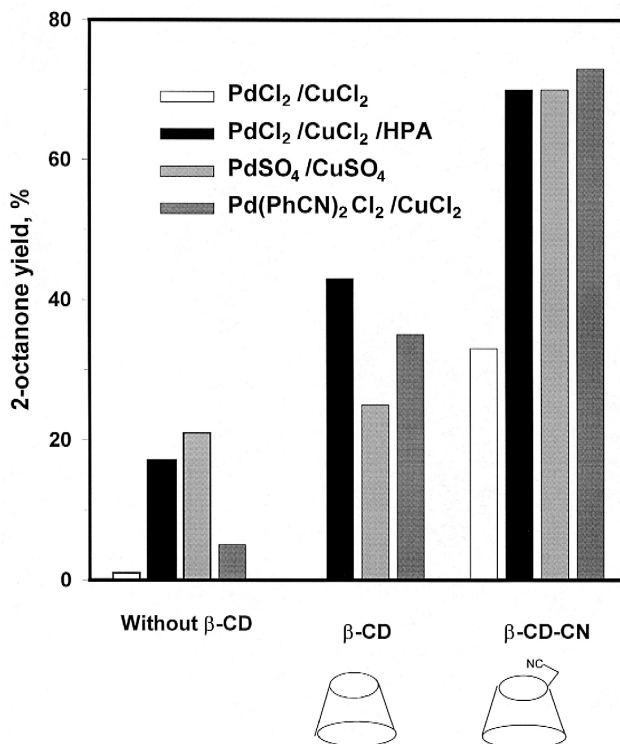
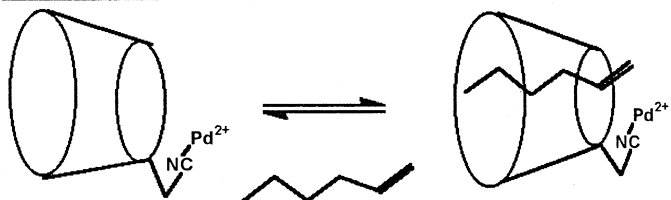
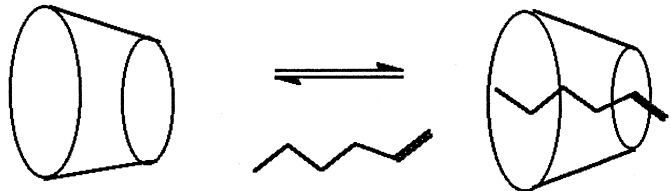


Fig. 3. Results of 1-octene oxidation with various palladium catalysts. $T = 60^\circ\text{C}$, $P = 0.5\text{ MPa}$ $[\text{1-octene}] = 0.67\text{ M}$, $\text{Pd}^{2+}/\text{Cu}^{2+}/\beta\text{-CD}/\text{1-octene} = 1:10:1:100$, reaction time — 2 h.

Table 2
Binding constants (K_b) for inclusion complexes

	K_b , M^{-1}	Initial rate, $mmol \cdot min^{-1}$	Selectivity, %	Yield, %
	210	9	98	95
	90	2.4	91	46

rapidly form complexes with modified β -CD on retaining comparatively labile ligands (sulfate and benzonitrile) in the coordination sphere.

To corroborate this assumption, complexes of nitrile-containing β -CD with palladium dichloride, palladium sulfate, and palladium complex with benzonitrile were separated. The signal of the nitrile group of the ligand in the IR spectra

of the complexes was shifted toward higher frequencies as a wide band ($2280\text{--}2370\text{ cm}^{-1}$). The free ligand signal was retained only if the ligand-to-Pd compound ratios exceeded 1:1, which indicates that only one ligand molecule is coordinated with the palladium ion. The spec-

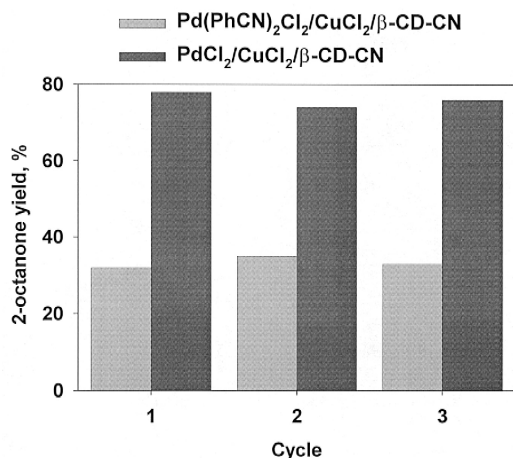
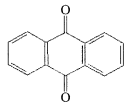
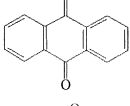
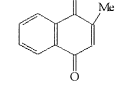


Fig. 4. Catalyst recycling; Pd^{2+}/β -CD-CN/ Cu^{2+} /1-octene = 1:1:10:100, $T = 60^\circ C$, $P = 0.5$ MPa, reaction time — 2 h.

Table 3
1-Octene oxidation with various cocatalysts. $T = 60^\circ C$, $P = 0.5$ MPa

Cocatalyst	Ratio PdCl ₂ /Cocatalyst/Substrate	Time, h	2-Octanone yield, %
CuCl ₂	1:10:100	2	33
CuCl ₂ +HPA	1:10:100	2	72
FeCl ₃	1:10:100	2	36
	1:10:100	6	10
	1:100:100	6	43
	1:100:100	6	29

trum of the complex obtained by reaction of palladium sulfate with benzonitrile exhibited signals of the sulfo-group bound to the palladium (939 cm^{-1}). The spectra of the complex produced by interaction of bis(benzonitrile)palladium dichloride with β -CD displayed also signals of free and bound benzonitrile (2280 and 2230 cm^{-1}). Furthermore, a band of free hydroxyl groups emerged, which apparently indicates a decomposition of a part of hydrogen bonds owing to the occurrence of benzonitrile in the palladium coordination sphere.

It must be emphasized that the activities of the complexes separated were virtually the same as those produced in situ in the reaction mixture.

The catalysts remained active in reuse of the aqueous phase containing the catalyst and the cocatalyst (Fig. 4).

Notice that the reaction rate is also affected strongly by using various cocatalysts, both organic, and inorganic. As Table 3 demonstrates, the activity is maximal for the catalytic system with a mixture of heteropoly acid and copper salt as a cocatalyst. Different quinones are active as cocatalysts only at the substrate-to-reoxidant ratio 1:1.

4. Conclusion

It is clear that the most obvious advantage of metal complexes based on chemically modified β -CDs is their ability to accelerate reaction rates and enhance selectivities. This should be at-

tributed to the efficiency of formation of host-guest complexes. These catalysts can be multiply reused without loss of catalytic activity.

There is good reason to believe that in the future, the application of new host molecules (calixarenes, dendrimers) in metal complex catalysis will attract particular attention [17,18].

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