Novel Phosphinite Capped Cyclodextrin-Rhodium Catalysts in Substrate Selective Hydroformylation

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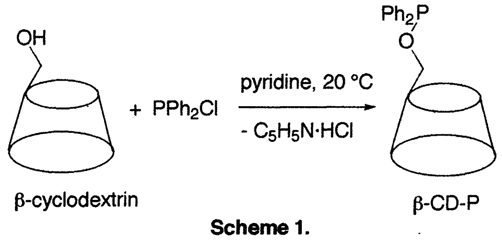
A Rh-cyclodextrin phosphinite catalyst exhibits substrate selectivities in hydroformylation of C_8 and C_{10} olefins due to the inclusion of substrates in the cyclodextrin cavity.

Metalloenzymes, the highly active and selective catalysts in nature, are examples to mimic in the development of new intelligent catalysts. In this effort new ligands are being synthesized which have the potential of interacting with the substrates to achieve high substrate selectivity.[1-5] The availability of proper binding sites in ligands would be a great benefit in the design of such ligands. Cyclodextrins (CDs) with internal hydrophobic cavities are ideal host compounds on which to build such substrate sensitive catalysts.[6,7] Owing to the molecular-sized internal cavities, CDs are useful in designing systems according to their inclusion properties.[3,5] We report herein the synthesis of phosphinite CD ligands and their substrate selective behavior in Rh-catalyzed hydroformylation reactions.

A novel phosphinite ligand, diphenyl β-CD monophosphinite (β-CD-P), was synthesized according to the procedure for phosphinites of carbohydrates[8] using β-CD (8.8 mmol) and equimolar PPh_2Cl in pyridine at 20 °C (Scheme 1). White microcrystals of β-CD-P were obtained from degassed water in 60-70% yields. $^{31}P\{^1H\}$ NMR of β-CD-P in dmso-d_6 gave only a singlet at δ 19.3 in the typical phosphinite region. ^1H NMR gave signals of CD and a multiplet at δ 7.28-7.76 due to Ph. The ratio of Ph:C_1 of β-CD (δ 4.8) protons was 10:7, indicating monophosphination, which probably took place at the most reactive OH on C_6 as in the monotosylation.[9] Microanalysis of β-CD-P was in good agreement with that of hexahydrates (C 45.53%, H 6.35%, calcd C 45.44%, H 6.38%); the presence of water being confirmed by ^1H NMR. No IR frequency was detected at 1100-1200 cm^{-1}, showing that the compound was not an oxide.[10] α-CD monophosphinite (α-CD-P) was similarly prepared.



Scheme 1.

β-CD-P was tested in the Rh-catalyzed hydroformylation of olefins. The catalyst was prepared in situ by interaction of $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene) with β-CD-P in DMF. DMF was an excellent solvent for dissolving the catalyst, the ligand, the olefins, and aldehyde products. Benzene, toluene, and other hydrocarbons are not ideal since they form inclusion compounds with CDs, therefore they are not applicable to catalytic test reactions.[11] β-CD-P was, in addition, practically insoluble in these solvents.

Linear olefins, 1-octene and 1-decene, as well as aryl substituted styrene and 4-phenyl-1-butene (Phb) were employed as C_8 and C_{10} olefins for hydroformylation reactions by $[Rh(cod)Cl]_2$/β-CD-P at 80 °C (Table 1). The activities for 1-decene and Phb were quite similar, i.e., TOF 31.4 and 31.0 h^{-1} (Run 1 and 2), whereas for styrene it is rather poor.[12] A control reaction with $[Rh(cod)Cl]_2$/β-CD gave a low conversion (2-3%) in 2 h. One can thus conclude that Rh(β-CD-P) complex is indeed formed in situ, and that the intrinsic activity of unmodified Rh carbonyls such as $HRh(CO)_4$ is extremely low under the reaction conditions.[13] In Table 1, the n/iso ratios of the aldehydes for the linear olefins were higher than those for the phenyl substituted olefins. The high selectivity to the branched aldehyde for styrene is as reported in earlier studies.[14]

Table 1. Hydroformylation of olefins using $[Rh(cod)Cl]_2$/β-CD-P catalyst[a]

Run	Olefin	TOF, h^{-1} [b]	n/iso
1	1-decene	31.4	2.38
2	4-phenyl-1-butene	31.0	1.80
3	1-octene	26.4	2.88
4	styrene	19.1	0.34

[a]Conditions: olefin 5 vol% in DMF, reaction volume 10 ml, 80 °C, CO/H_2 (1:1) 20 kg cm^{-2}, Rh 6.0 x 10^{-5} mol, Rh:b-CD-P = 1:1. [b]TOF calculated as (mol aldehyde product formed / mol catalyst / h).

In order to study the substrate selectivity, competitive reactions were done using a mixture of Phb and 1-decene under the same conditions. As shown in Figure 1, the substrate selectivity of Phb:1-decene (defined as the molar ratio of hydroformylation products) at 80 °C was 61:39 at ca. 60% conversions.[15] A control experiment by Rh/PPh_3 gave a selectivity of 55:45, which is similar to the molar concentration of the two olefins charged (TOF > 100 h^{-1}). The enhanced selectivity difference (from 10 to 22%) for Phb over 1-decene by use of β-CD-P may be due to the preferential inclusion of Phb in the β-CD-P cavity (Scheme 2). The n/iso ratios for 1-decene and Phb by Rh/β-CD-P were 2.37 and 1.76, respectively, while those by Rh/PPh_3 were 2.72 and 2.00. The slight lowering of the n/iso ratios in Rh/β-CD-P system could also be attributed to the inclusion of Phb in CD, which leads to a preferable configuration to form a branched alkylrhodium species than a liner one.

The effect of the cavity size of α- and β-CD (4.5 and 7.0 Å) was studied. Their inclusion properties are quite different,[6] and these often give rise to interesting substrate selectivities. Indeed, the selectivities (Phb:1-decene) for Rh/α-CD-P and Rh/β-CD-P at 50 °C were 56:44 and 63:37, respectively (Figure 1). Rh/α-CD-

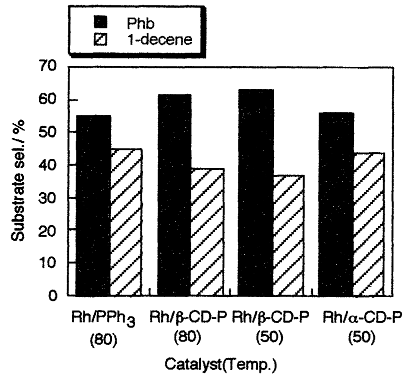
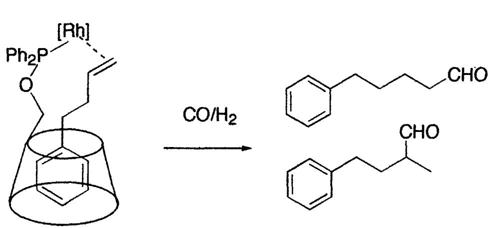


Figure 1. Substrate selectivity in hydroformylation of a Phb/1-decene mixture using $[Rh(cod)Cl]_2$/β-CD-P or PPh_3 catalysts. Conditions: 5 vol% of each olefin and Rh:P = 1:1 under the same conditions as in Table 1.



Scheme 2.

P showed no substrate selectivity, and this may arise from the cavity size of α-CD, which is too small to cause any proper inclusion and access for the catalyst site. The results are in agreement with the reported trends in inclusion compounds of CDs.[7]

The hydroformylation of a mixture of C_8 styrene and 1-octene by Rh/β-CD-P was done similarly. As shown in Figure 2, the substrate selectivity in this case was reversed, and 1-octene was preferentially hydroformylated over styrene (70:30), which is greatly different from the estimated value (approximately 50:50) for the non-substrate selective case from the activity difference (Table 1) and the molar ratio of the two olefins. The stability of inclusion compounds of linear C_8 to C_{10} alkanes is very high, and among the aryl substituted alkanes, 2-methylethylbenzene forms the most stable inclusion compounds.[16,17] The stability of inclusion compounds of linear olefins such as 1-octene and 1-decene is expected to be similar to that of octane and decane. As noted above, Phb with a side chain longer than 2-methylethylbenzene was preferred over 1-decene. On the other hand, styrene with a shorter side chain may form less stable inclusion compounds than 1-octene, thus resulting in the reverse trend observed in the competitive hydroformylations of C_8 and C_{10} olefins.

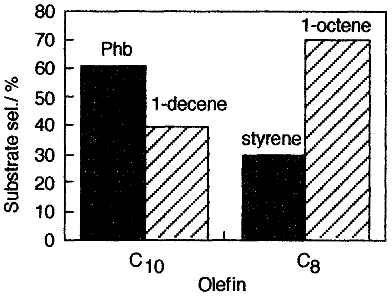


Figure 2. Substrate selectivity in hydroformylations of C_{10} or C_8 olefins using $[Rh(cod)Cl]_2$/β-CD-P catalysts. Conditions: see Figure 1.

The above results show that the internal cavity of the CD phosphinite recognizes the shape and size of the selected substrates adapting the catalytic sites due to the formation of its inclusion complex. The substituents and functional groups play a dominant role in controlling the substrate selectivity.

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10 The TOF-MS of β-CD-P in water gave no M or M+1 peak. However, a strong peak was observed at 1157 which could be due to the loss of a glucose ($C_6H_{10}O_5$) unit from the M ion (m/z 1319.14). A smaller peak at 1173 arises from the loss of the $C_6H_{10}O_4$ unit from the M peak. The observation of these two peaks indicates that the compound is a monophosphinite of β-CD, since the formation of these fragments is impossible otherwise. The TOF-MS in DMF shows a similar m/z pattern as in water but a peak is observed at m/z of 1333.4. This could arise from interactions of β-CD-P with DMF. The appearance of a peak at such a high mass is possible only if the monophosphinite is formed.

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12 Although no hydrogenation of olefin took place, isomerization was observed in case of 1-decene and Phb; ca. 30% at conversions over 80%.

13 Although the reaction of $[Rh(cod)Cl]_2$ with β-CD in DMF gave no change, the reaction of $[Rh(cod)Cl]_2$ with β-CD-P showed a definite color change of the solution, suggesting the coordination of P to Rh. Under hydroformylation conditions, the Rh(β-CD-P) complex may convert to (β-CD-P)RhH$(CO)_2$ as a possible catalytic intermediate. Characterization of the Rh complexes is in progress.

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