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Supramolecular transition metal catalysts in two-phase systems

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Abstract

The concept of covalently connecting a catalytically active transition metal center with a water-soluble receptor (host molecule) makes a new type of supramolecular catalysis possible in which the features of molecular recognition, phase transfer catalysis and transition metal catalysis are combined in a single system. The first examples of this principle make use of the commercially available β-cyclodextrin (β-CD) as the receptor and rhodium complexes of diphosphanes as the catalytically active center, these being covalently connected to one another via a spacer. In competitive hydrogenation of certain olefins unusual degrees of substrate selectivity based on the molecular recognition are observed, not possible by conventional transition metal catalysts. The two-phase (H_2O/organic) hydrogenation of nitro-aromatics also is a smooth process with these supramolecular catalysts. They also constitute an unusually active catalyst system for the selective hydroformylation of higher olefins such as 1-octene in a two-phase system. © 1998 Elsevier Science B.V. All rights reserved.

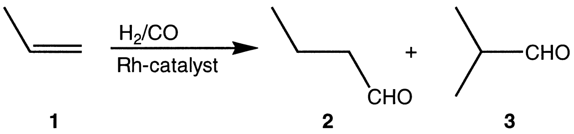
Keywords: Transition metal catalysis; Phase transfer catalysis; Molecular recognition; β-Cyclodextrins; Hydrogenation; Hydroformylation

1. Introduction

1.1. General background

The development of efficient methods for the separation and re-use of transition metal catalysts currently constitutes an active area of academic and industrial research [1]. Scheme 1 summarizes some of the most important approaches which have been described so far.

As far as the industrial viability is concerned, none of the concepts have reached reasonable degrees of generality, although single cases of successful industrial applications are in fact known. Perhaps the most spectacular example is the Ruhrchemie/Rhone-Poulenc/Hoechst-hydroformylation of propene **1**, pioneered by Cornils and coworkers [2]. Accordingly, Rh-complexes of the water-soluble phosphane $P(C_6H_4SO_3Na)_3$(TPPTS) perform as catalysts in the aqueous phase, separation of the product *n*-butanal **2** being particularly efficient. About 400 000 tons are being produced each year. Regioselectivity in favor of the *n*-isomer **2** is >99%.



Unfortunately, the process cannot be generalized in its original form to include the hydroformylation of

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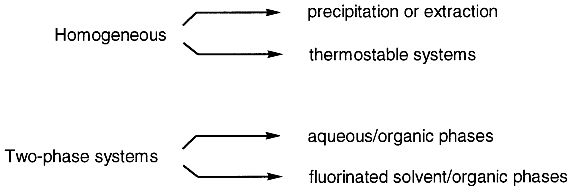
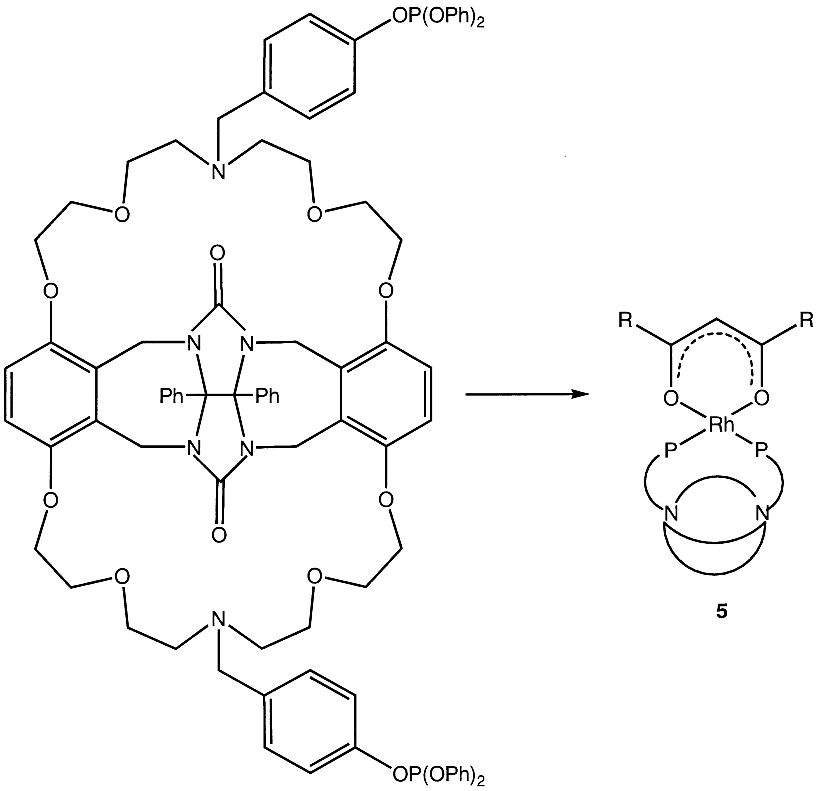


Scheme 1. Current approaches to catalyst recovery.

higher olefins such as 1-octene [2]. This has to do with the fact that such olefins have an extremely low solubility in water, in contrast to propene which apparently enters the aqueous phase to a sufficiently high degree necessary for high turnover. Therefore, several ideas were developed in order to solve this problem, but at this point industrial viability has yet to be demonstrated. These include the use of PPh_3 as a promote-ligand in the organic phase [3], additional immobilization of aqueous catalysts as in SAP-catalysis [4], and the utilization of additives functioning as phase transfer catalysts [5]. In what has been described as a breakthrough in the two-phase catalytic hydroformylation of higher olefins such as 1-octene or 1-decene, the Ruhrchemie process based on Rh-complexes of TPPTS was modified to include an O-methylated derivative of β-cyclodextrin (β-CD) as the phase-transfer catalyst [5]. In the hydroformylation of terminal olefins a Rh : TPPTS : β-CD ratio of 1 : 5 : 14 was used at 80°C, resulting in rate enhancements by a factor of 2–10 relative to the use of the same system in the absence of the β-CD-derivative. Selectivity amounted to 85–95% and regioselectivity, i.e., the *n*/iso ratio turned out to be about 60 : 40. Unfortunately, the catalytic activity of this system is somewhat limited in that only terminal olefins such as 1-octene react at a reasonable rate. Indeed, it was reported that less reactive substrates such as internal olefins (e.g., 3-hexene) do not react at all [5]. Also, detailed information regarding the amount of undesired rhodium in the organic product after completion of the reaction is lacking. Thus, more efforts are required in two-phase hydroformylation, and indeed in the general area of transition metal catalysis based on water-soluble catalysts. An interesting and novel alternative was recently described by Leitner, who showed that certain phosphanes bearing per-fluoro alkyl chains are excellent ligands in the Rh-catalyzed hydroformylation in supercritical CO_2 as a cheap and environmentally benign solvent [6]. Previously, the basic problem of using supercritical CO_2 in certain transition metal catalyzed reactions was the low degree of solubility of conventional transition metal catalysts in this medium [7].

Our own interest in metal catalysis involving the two-phase systems was originally purely academic. We sought to combine supramolecular catalysis with transition metal catalysis. The term 'supramolecular catalysis' is well known in the area of host/guest chemistry and refers to the synthetic receptor molecules (hosts) which bind substrate molecules (guests) selectively in such a way that some kind of molecular transformation is triggered [8]. The vast majority of the reactions studied so far refer to the hydrolysis of esters or phosphates, as pioneered by Bender et al. [8]. Frequently, β-CD in combination with zinc or copper salts was used, resulting in dramatically enhanced rates of hydrolysis. Redox reactions have also been studied in supramolecular systems. In contrast, very little is known concerning the catalysis of C–C bond forming reactions in which host/guest interactions play the pivotal role. A rare example was described by Diederich, who prepared a synthetic macrocycle containing a thiazolium moiety which catalyzes the benzoin condensation [9].

The extensive area of traditional transition metal catalysis [10], encompassing such metals as Pd, Ni, Pt, Rh or Ru as catalysts and such important organic transformations as hydrogenation, hydroformylation, carbonylation, hydrocyanation, hydrovinylation, carboxylation or arylation, has hardly been studied within the context of supramolecular catalysis. A rare example pertains to the Rh-containing receptor **5** as described by Nolte [11]. The polar urea-function inside the basket-like molecule was shown to be instrumental in binding guest molecules via hydrogen-bonding. In particular, the catechol derivative **6** capable of forming hydrogen bonds was shown to bind somewhat more strongly than other potential guests such as **7** or **8**. These molecular recognition phenomena were then shown to operate in the catalytic hydrogenation of the olefinic substrates. Although the effects in catalysis turned out to be small, the system does constitute an interesting case of supramolecular catalysis.



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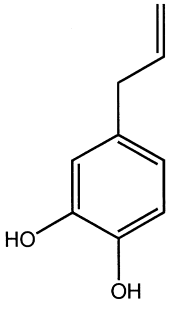

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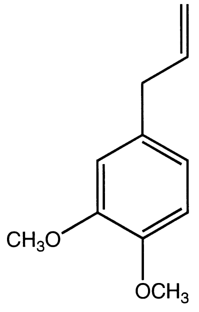

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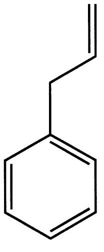

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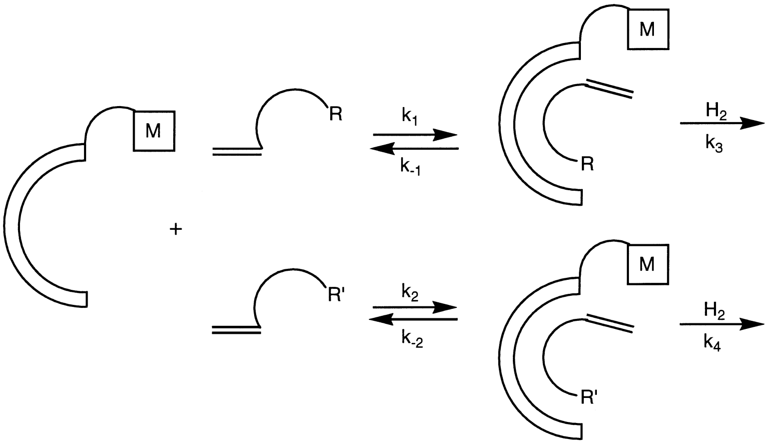
1.2. New concepts

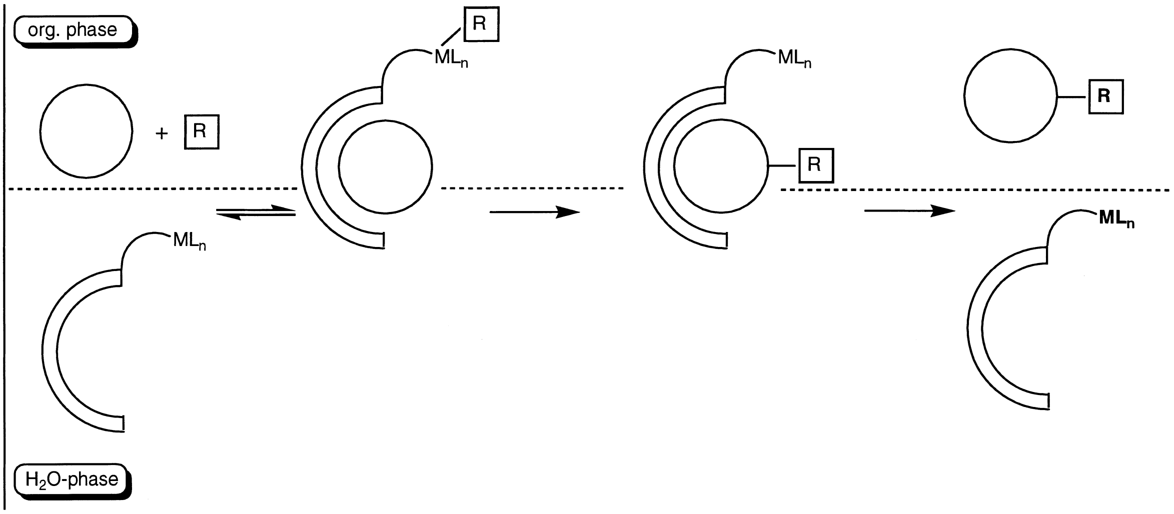
In our own research relating to supramolecular chemistry we first designed and prepared host molecules which bear covalently bonded boron or aluminum centers, e. g., boronic acid ester containing crown ethers [12]. Although they were shown to display novel host/guest chemistry, e.g., the first synthetic receptors which bind selectively two different classes of organic compounds simultaneously with the formation of termolecular supramolecules, catalytic functions could not be observed. We therefore turned our attention to the supramolecular catalysis using transition metal centers attached to the proper host molecules, hoping to study in a general way such typical transition metal catalyzed reactions as hydrogenation, hydroformylation, carboxylation and other C–C bond forming processes. In the case of hydrogenation, substrate selectivity involving two different olefins CH_2=CHR and CH_2=CHR′ had already been



Scheme 2. Hydrogenation using a supramolecular transition metal catalyst.

documented using classical homogeneous transition metal catalysts such as Wilkinson's catalyst [10]. However, if the R- and R′-groups are far removed from the olefinic moiety, conventional catalysts are incapable of distinguishing between the two molecules. In this case the supramolecular catalyst, designed to embrace major parts of the substrate via van der Waals' interactions, hydrogen bonding, π–π stacking or even metal-substrate bonding, could lead to novel types of substrate selectivity as illustrated in Scheme 2. Although this is reminiscent of enzyme catalysis, we prefer not to use the term enzyme mimetics at this time. Of course, this scheme is not restricted to hydrogenation, other types of transition metal catalyzed reactions are also possible.

We then surmised an additional element of complexity by considering the case of water-soluble transition metal containing supramolecular catalysts, as illustrated in Scheme 3. In this case two-phase catalysis is envisioned, the catalyst being in the aqueous phase. If it has an amphiphilic character, it could easily reach the phase boundary or go beyond, thereby



Scheme 3. Two-phase reaction using a water-soluble supramolecular catalyst. (M=transition metal; L=ligand; R=small molecules such as CO, H_2, etc.; circle=organic substrate).

making selective binding of a substrate in the organic phase possible. Activation of small molecules R as reagents (e.g., H_2, CO, etc.) before or after the complexation would set up an entropically favorable situation, triggering the desired reaction. Ideally, the receptor must be designed so as to prevent the substrate inhibition. Of course, it is conceivable that part of the reaction could also proceed without the intervention of a host/guest intermediate (reaction occurring outside the cavity). In any case, considering the vast number of different transition metals and the different classes of reactions and types of water-soluble receptors, there seem to be many opportunities in two-phase catalysis based on these concepts.

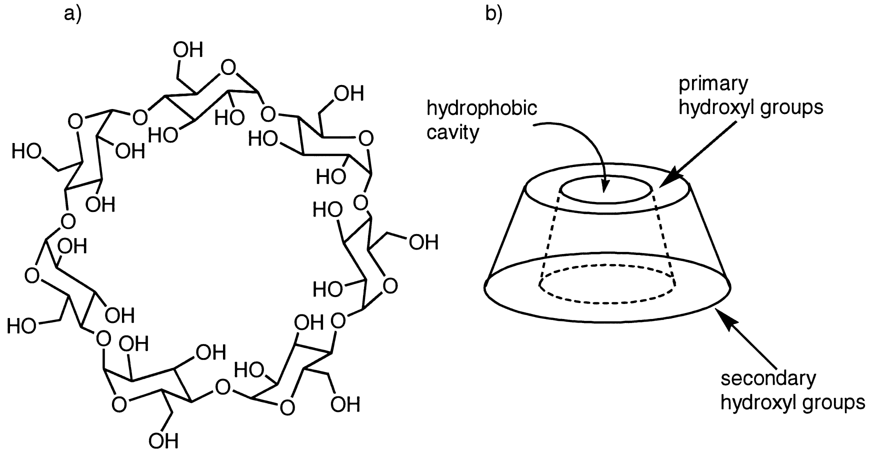
We first turned to the general class of cyclodextrins as possible host molecules [13]. Three well-known representatives, namely α-, β- and γ-CD, are commercially available. They consist of 6, 7 and 8 glucose rings, respectively, arranged in a cyclic array. Importantly, the barrel-shaped molecules contain hydrophobic cavities. The cheapest of the three carbohydrates is β-CD (Scheme 4), the cost of bulk quantities being almost like that of a typical organic solvent. A great deal of host/guest chemistry is known involving β-CD. For example, aromatics are known to bind selectively, although alkanes also easily enter the hydrophobic cavity [13]. The upper brim of β-CD is a little smaller than the lower one, although this difference should not be overemphasized (see Scheme 4(b)). The solubility of β-CD in water amounts to 19g/l. The corresponding value of γ-CD is about 5–6 times higher.

In preparing supramolecular transition metal catalysts based on α- or β-CD, the basic problem is selective mono-functionalization. Once formed, the mono-functionalized cyclodextrin needs to be transformed into a phosphane, setting up the possibility of complexation with transition metal salts.

2. Water-soluble β-cyclodextrin-based diphosphanes as ligands for supramolecular Rh-catalysts

2.1. Synthesis

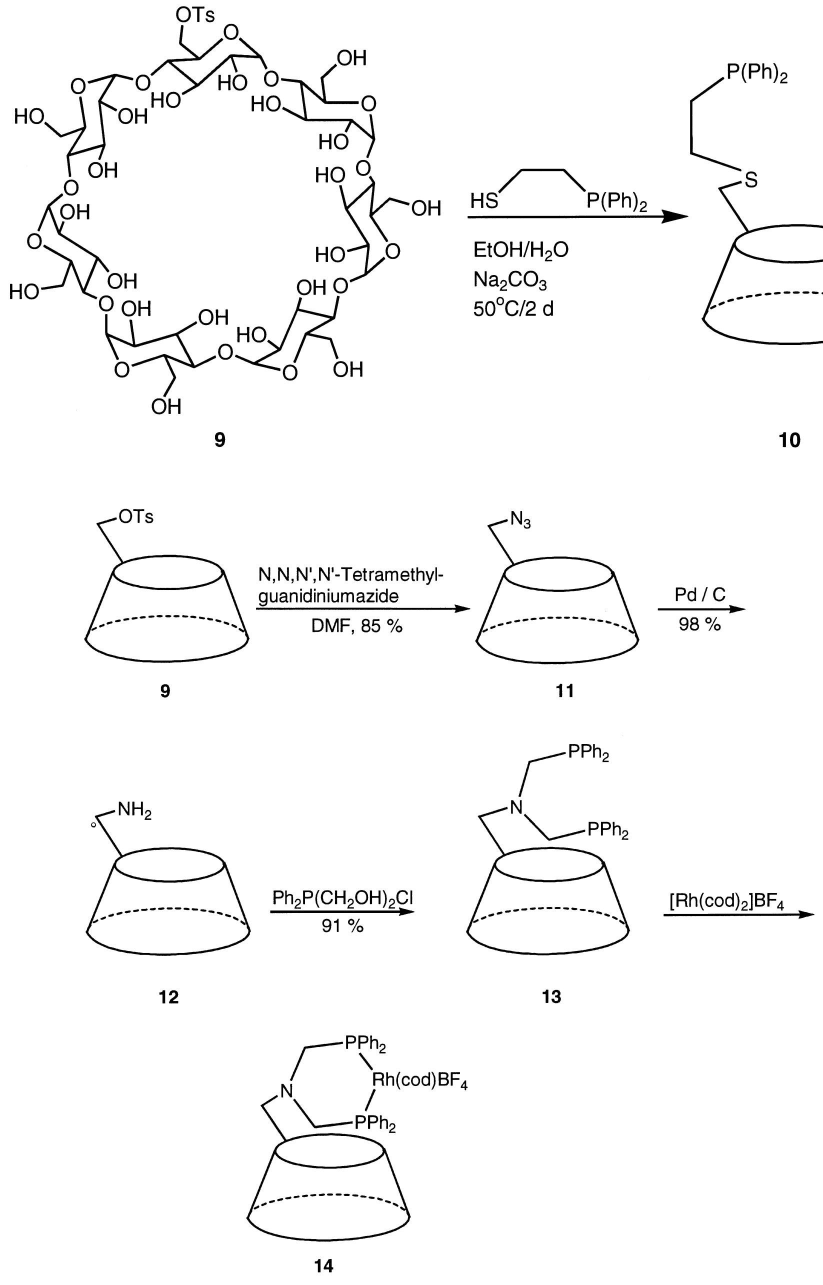
We first prepared the β-CD-modified monophosphane **10**, hoping to obtain a ligand in two simple steps [14]. The improved procedure for preparing the mono-tosylate **9** by tosylation of β-CD in water proceeds with yields of only 4–7%, but affords pure product in 50 g amounts. Isolation is best performed by cooling the reaction mixture, which results in the precipitation of the product. Nucleophilic reaction with the known thiol $HSCH_2CH_2PPh_2$ did, indeed, afford the desired ligand **10**, which was reacted with Rh-salts to form the corresponding cationic Rh-chelates in which sulfur and phosphorus function as donor ligands. Rh-chelates of the parent compound $CH_3SCH_2CH_2PPh_2$ previously were reported to be hydrogenation catalysts [15]. However, the Rh-complexes of **10** turned out to be extremely poor hydrogenation catalysts. In control experiments we



Scheme 4. β-Cyclodextrin (a) molecular structure, (b) short-hand representation.

demonstrated that this also pertains to the aforementioned parent compound, in contrast to the literature report. Hydrogenation occurs only under forced condition, leading to the formation of colloidal rhodium which then acts as a (poor) catalyst.

Although compound **10** was later shown to display the novel host/guest chemistry [16], it was obvious that this simple ligand is not suited for supramolecular hydrogenation. We also concluded that the Rh-complex is not ideal for other reactions such as hydro-

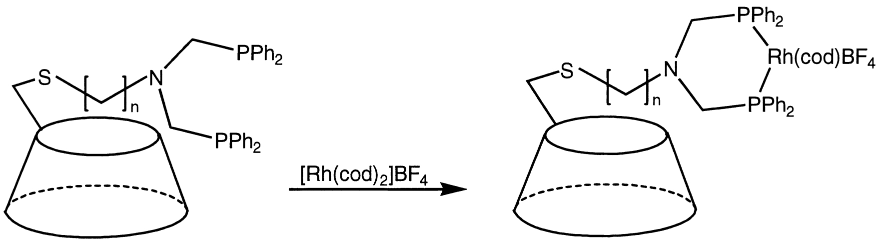


Scheme 5. Synthesis of β-CD-modified diphosphane **13** and catalyst **14**.

formylation, although this specifically needs to be demonstrated experimentally. Attention was then turned to converting the monotosylate **9** into some kind of a disphosphane.

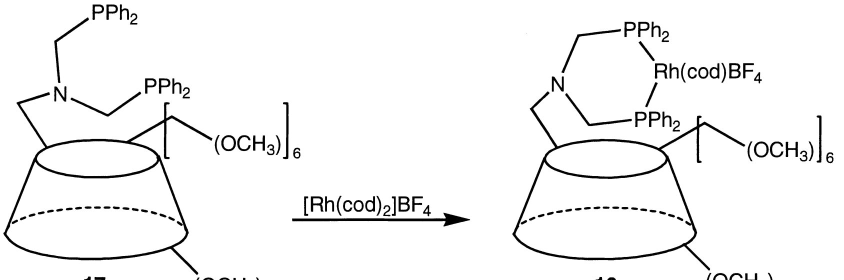
Although this is synthetically not a trivial task, we finally devised a rather simple and efficient method (Scheme 5) [16,17]. The basic idea is to convert the tosylate **9** into the corresponding primary amine **12** using conventional reactions, followed by phosphanomethylation with formation of the desired diphosphane **13**. This route appeared particularly attractive because phosphanomethylation of simple primary amines RNH_2 using $Ph_2P(CH_2OH)_2Cl$ with formation of the corresponding disphosphane $RN(CH_2PPh_2)_2$ had been reported by others to be a highly efficient process [18]. Indeed, in our particular case the reaction occurred very smoothly, conversion to the diphosphane **13** being almost quantitative. It was isolated in pure form with a yield of 91%. Although every single C-atom in the ^{13}C-NMR spectrum of the β-CD part of the molecule is anisotropic, multidimensional NMR studies carried out by R. Mynott allowed for complete assignment of all peaks [19]. Upon reaction of **13** with $[Rh(cod)_2]BF_4$, smooth formation of complex **14** occurred, which was characterized by elemental analysis and NMR spectroscopy.

In order to study related systems in which the length of the spacer between receptor and catalytically active center varies systematically, ligands **15a**-**c** were prepared and converted into the corresponding Rh-complexes **16a**-**c** [16,17]. The per-methylated analog of **14** was also synthesized (cf. **18**). In all the cases the cationic Rh-complexes were prepared by reaction with $[Rh(cod)_2]BF_4$ in DMF. The catalysts were characterized by NMR spectroscopy and showed a high degree of purity. For example, the ^{31}P-NMR spectrum of **16a** displays only one absorption at δ=+7.14 as a doublet [J (P,Rh)=143 Hz].



15a n = 2
b n = 3
c n = 4

16a n = 2
b n = 3
c n = 4



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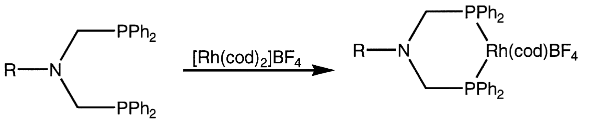
The parent complexes **20a**-**b** were also prepared in high yield by conventional means. In the case of **20a** it was possible to perform an X-ray structural analysis (Fig. 1) [20]. The metallacycle adopts an approximate chair conformation with a Rh···N distance of 3.797(5) Å, which is too long for a direct interaction (complexation). The P–Rh–P bite angle amounts to 91.8(1)°.



19a R = C_6H_5
b R = n-C_3H_7

20a R = C_6H_5
b R = n-C_3H_7

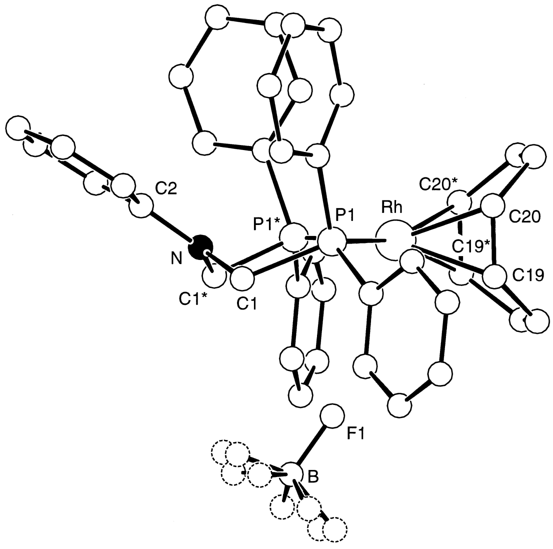
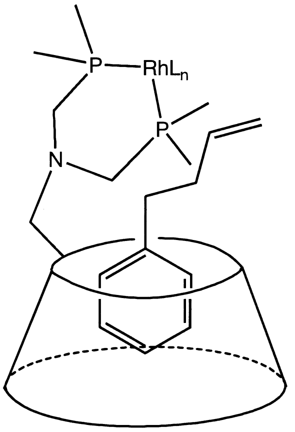


Fig. 1. Crystal structure of **20a**.

2.2. *Selective hydrogenation*

In order to establish whether the β-CD modified rhodium catalysts function as supramolecular catalysts, the alkenes **21** and **22**, which possess similar substitution patterns at the double bonds, were subjected to competition experiments [17]. In these experiments, 1 : 1 mixtures of the two olefins were hydrogenated up to 10% conversion in a solvent at room temperature in the presence of a catalyst. The ratio of the products **23** and **24** as determined by gas chromatography was used as a measure of substrate selectivity.

As expected, no substrate selectivity was achieved in the control experiment with the β-CD-free catalyst **20a** in a one-phase system (DMF) (product ratio **23** : **24**=50 : 50). In contrast, the use of the β-CD-modified rhodium catalysts in the one-phase system led to a substantial substrate selectivity: the phenyl-substituted alkene **21** was preferentially converted to the alkane **23**. The length of the spacer between the β-CD and the diphosphane group plays a crucial role in these reactions (Table 1). If it is too long, as in **16c**, only a 66 : 34 product ratio is observed. We postulate that a recognition step precedes the hydrogenation in which the phenyl group of **21** preferentially enters the hydrophobic cavity of the β-CD framework (cf. **25**). In the case of competitive hydrogenation in a two-phase system (H_2O/org.), selectivity is consistently higher. In the case of **18**, it reaches almost 90%. Significantly, catalytical activity is also higher in all of the two-phase reactions by a factor of 3 to 6, inspite of the problem of mass transport.



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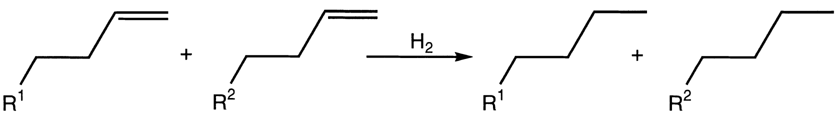
The above observations support the postulated interplay of molecular recognition, phase transfer catalysis, and rhodium catalysis. Indeed, substrate selectivity decreases drastically when working in the presence of *p*-xylene, which competes for the



21 **22** **23** **24**

R^1=Ph R^2=n-C_6H_{13}

Table 1
Substrate selectivity in the hydrogenation (1 atm H_2) of 23/24 in DMF at 22°C

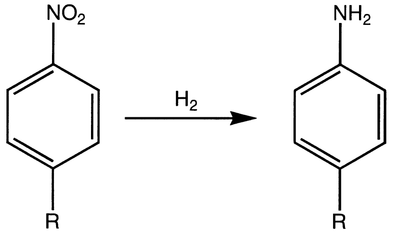
Catalyst [a]	**23**	:	**24**
20a	50	:	50
14	68	:	32
16a	74	:	26
16b	71	:	29
16c	66	:	34
14 [b]	82	:	18
18 [b]	87	:	13
16a [b]	81	:	19

[a] 0.5 mol% catalyst.

[b] Two-phase system; aqueous phase contains 30% DMF.

space in the β-CD cavity; for instance, in the case of the catalyst **16a** selectivity is reduced from 81 : 19 to 57 : 43 upon adding *p*-xylene.

Although other olefin pairs still need to be investigated kinetically, we have started to study other types of hydrogenation reactions, specifically the conversion of nitro-aomatics **26** into the corresponding amines **27** [21].



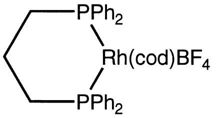
26a R=H
b R=Cl

27a R=H
b R=Cl

In control experiments using the parent compound **20a** as the catalyst in a one-phase reaction (DMF), excellent yields of the desired amines **27a**-**b** were obtained. Exploratory experiments employing the water-soluble supramolecular catalyst **16a** in a two-phase system also turned out to be successful. For example, in the two-phase system $H_2O/HCCl_3$, only 0.1 mol% of this catalyst leads to 96% conversion of substrate **26b**, selectivity in favor of product **27b** being 98%. Only about 0.5% of the corresponding de-halogenated product (aniline) is formed [21].

2.3. Selective hydroformylation

Before the water-soluble β-CD-modified diphosphanes were tested as ligands for Rh-catalyzed hydroformation, the parent compounds were first studied in a one-phase system consisting of toluene and an olefin (e.g., 1-octene) [17]. Under otherwise identical conditions the well known propano-bridged analog **28** was also tested.



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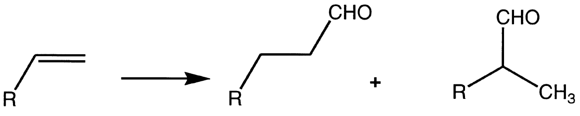
The kinetics of the hydroformylation of 1-octene **29** at 60°C using syngas (CO/H_2=1 : 1) at 100 bar revealed that catalyst **20a** is about four times as active as the propano-bridged analog **28** (TOF 240 versus 57), regioselectivity in favor of the *n*-isomer **30** being about 62 : 38 in both cases [20]. Regioselectivity in the case of the *N*-propyl-analog **20b** was measured to be 60 : 40.

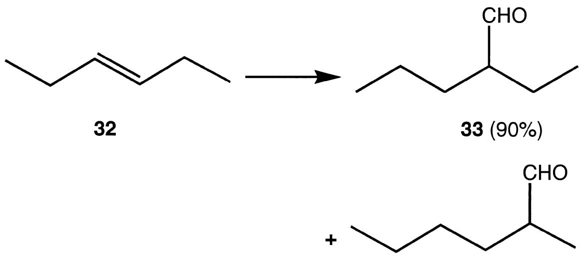


29 R=n-C_6H_{13} **30** **31**

We then turned to the two-phase hydroformylation of 1-octene **29** and of other olefins using the water-soluble supramolecular catalysts **14** and **16a**-**c** [17]. Three significant results were obtained. First, unexpectedly high catalyst activities pertain in all cases. For example, in the reaction of 1-octene **29** in the two-phase system H_2O (30% DMF)/olefin with 0.03 mol% of the catalyst **16a** at 80°C and 100 bar (H_2 : CO=1 : 1), quantitative conversion was achieved in less than 18 h (TON=3172). Second, regioselectivity is significantly higher in going from the parent catalysts **20a**-**b** to the supramolecular catalysts. For example, in the case of catalyst **16a** the *n* : iso ratio is 76 : 24, compared to 60 : 40 obtained by using **20b**. Third, all two-phase reactions show complete (>99%) chemoselectivity with respect to aldehyde formation, i.e., there is no undesired olefin hydrogenation. Similar results with respect to activity, regio- and chemoselectivity were observed in additional experiments involving the two-phase system H_2O/olefin in the absence of any DMF. In fact, in the initial studies DMF was used because it is the solvent of choice in the preparation of the ionic catalyst.

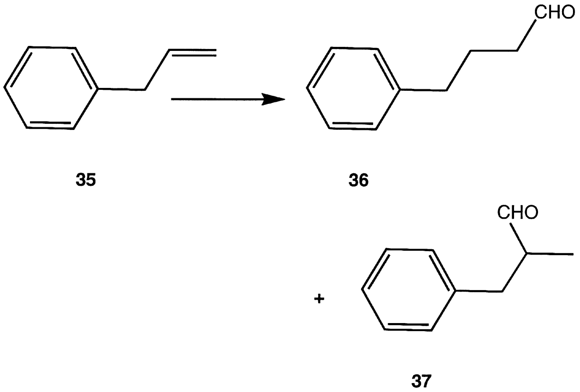
In a control experiment with the likewise water-soluble rhodium catalyst based on $P(C_6H_4SO_3Na)_3$ which is used industrially in the hydroformylation of propene [2], less than 1% conversion to **30/31** was obtained under the same reaction conditions. Higher temperatures (120°C) were required to produce about 4% of 30 and 31 after 18 h. Based on these results, our catalytic system is >150 times more active at 80°C than the traditional system at 120°C. At comparable temperatures the factor must be much higher. In fact, the reaction with **16a** can also be performed cleanly at 60°C (95% conversion after 18 h, *n*/iso=76 : 24, <1% isomerization products). Even at lower pressures (10 bar at 60°C), the results are still acceptable (69% conversion after 18 h, *n*/iso=74 : 24, 9.5% isomerization products).

It is clear that these systems are much more active than the aqueous catalyst system based on Rh-complexes of $P(C_6H_4SO_3Na)_3$ in the presence of such phase transfer catalysts as per-methylated β-CD [5]. Indeed, even relatively unreactive olefins such as (*E*)-3-hexene **32** react cleanly in the two-phase system (0.03 mol% **16a**, 60°C, 100 bar H_2/CO 1/1, 70 h, TON 3008). In the commonly used two-phase system Rh/$P(C_6H_4SO_3Na)_3$, olefins of this type cannot be converted even in the presence of O-methylated β-CD-derivatives acting as phase transfer catalysts (Section 1) [5]. Other substrates which we have hydroformylated successfully in the two-phase system include cyclic olefins such as cyclopentene, 1-methylcyclopentene, cyclooctene and cyclododecene as well as conjugated olefins such as styrene and 4-methyl-1,3-pentadiene [16,17].



32 **33** (90%) **34** (4%)

It is also interesting to note that substrate **35**, which is known to easily isomerize to the corresponding conjugated olefin, is smoothly hydroformylated in the two-phase system solely at the two original olefinic sites with formation of **36** and **37** in a product ratio of 72 : 28 [16].



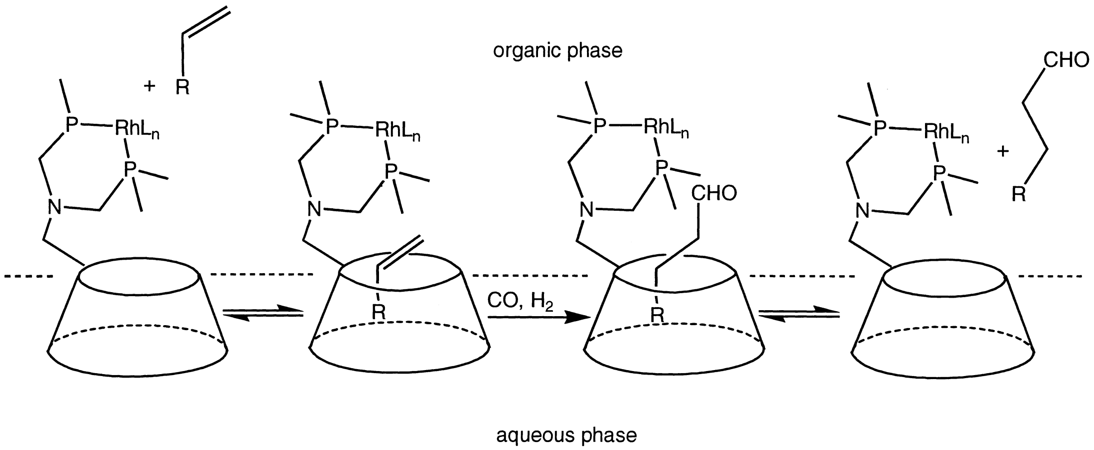
35 **36** **37**

A likely explanation for all of these observations, including enhanced regioselectivity, is the participation of a host/guest complex, which plays an important role in the phase-transfer catalysis (Scheme 6) [17,22]. If the water-soluble catalyst moves into the region of the phase boundary or beyond, the olefin molecules can easily enter the hydrophobic cavity of the β-cyclodextrin. Since the catalytically active metal center is geometrically fixed nearby, a rapid entropy-favored reaction is possible. In the presence of excess toluene, which also enters the β-CD cavity, regioselectivity is reduced to 65 : 35. These and other results clearly show that the participation of phosphane-free $Rh(CO)_n$ species can be excluded.

Our hypothesis is supported by the molecular modeling studies of the host/guest complex involving the supramolecular Rh-catalyst **16a** and 1-octene **29** [23]. Fig. 2 shows that the catalytically active Rh-center bearing CO and two H-atoms is in close vicinity to the olefinic double bond of 1-octene, poised to initiate the reaction.

If Scheme 6 does in fact represent the approximate state of affairs, then the catalyst is expected to have an amphiphilic character. Indeed, β-CD-modified diphosphanes as well as their Rh-complexes are surface active species, as shown by the surface tension measurements: Distilled water: 73.6 $N\,m^{-1}$; H_2O/DMF 3/1: 55.6 $N\,m^{-1}$; 1.2×10^{-3} M **15a** in H_2O/DMF 3/1: 53.3 $N\,m^{-1}$; 1.2×10^{-3} **16a** in H_2O/DMF 3/1: 43.6 $N\,m^{-1}$ [17].

Although only very small amounts of the rhodium catalyst were used in the hydroformylation



Scheme 6. Mode of action of host/guest complexes in phase transfer and Rh-catalysis in two-phase hydroformylation.

(0.03 mol% and less), it appeared appropriate to perform experiments oriented toward studying the stability and recovery of the catalyst. Thus, the phases were separated after completion of the reaction and the organic phase was washed once with water. In a standard reaction with approximately 10 ml of the olefin and 0.03 mol% of the rhodium catalyst, as little as 6 ppm rhodium were detected by atomic absorption spectroscopy in the organic phase, depending upon the olefin and the catalyst ligand [17]. This amounts to about 3% of the total rhodium being in the organic phase. In other cases it is more [16,17]. Additional washings lead to further reduction in the rhodium concentration. Upon re-using the aqueous phase in the hydroformylation, a remaining catalytic activity of approximately 50% was observed. These data do not meet the rigid specifications of an industrial process. However, they are promising. Thus, efforts at refining, optimizing and extending the general concepts outlined in this section are likely to be rewarding. One of the approaches that we are currently considering is the use of the present β-CD-modified diphosphanes in which the phenyl groups at the phosphorus centers are replaced by substituents bearing water-soluble moieties [21]. The use of α-CD, which is considerably more water-soluble than β-CD, is also being explored. The problem of increasing the regioselectivity may solve itself as a consequence of these important modifications. Enantioselectivity is another aspect which needs to be addressed in relevant systems.

3. Conclusions

The first generation of water-soluble transition metal containing supramolecular catalysts has turned out to be surprisingly effective, although industrial viability has yet to be achieved. It is also clear that of the many different kinds of reactions known in traditional transition metal catalysis, only a few select cases have been examined so far within the context of supramolecular catalysis.

The types of receptors (host molecules) and catalytic centers (transition metals) tested so far have also not been varied greatly. Thus, cyclodextrins are not the only candidates for this type of chemistry, the large family of calixarenes [8,24] constituting another possibility. The principles are likely to be similar. Indeed, on the basis of our initial work it has become clear that the combination of molecular recognition, phase transfer catalysis and transition metal catalysis can lead to the novel types of substrate selectivities, in addition to influencing regioselectivity. Perhaps even more important is the expectation that such supramolecular catalysts, if water-soluble and amphiphilic in nature, are likely to be highly active and selective, the possibility of catalyst recovery and re-use in two-phase systems being particularly attractive [17,22].

Fig. 2. Molecular model (calculation [23]) of the host/guest supramolecular complex involving **16a** as the β-CD derivative and 1-octene **29** as the guest. The top view shows the olefinic function pointing out of cavity, in close vicinity to the catalytically active Rh-center (to the left). Purple: phosphorus; gray: rhodium; green: carbon; red: oxygen; white: hydrogen.

References

[1] M. Barton, J.D. Atwood, J. Coord. Chem. 24 (1991) 43; B. Cornils, Angew. Chem. 107 (1995) 1709; Angew. Chem. Int. Ed. Engl. 34 (1995) 1575; T. Bartik, B.B. Bunn, B. Bartik, B.E. Hanson, Inorg. Chem. 33 (1994) 164; J.W. Ellis, K.N. Harrison, P.A.T. Hoye, A.G. Orpen, P.G. Pringle, M.B. Smith, Inorg. Chem. 31 (1992) 3026; W.A. Herrmann, C.W. Kohlpaintner, Angew. Chem. 105 (1993) 1588; Angew. Chem., Int. Ed. Engl. 32 (1993) 17; I.T. Horváth, J. Rabai, Science 266 (1994) 72; F. Joó, Á. Kathó, J. Mol. Catal. A: Chem. 116 (1997) 3; J. Chen, H. Alper, J. Am. Chem. Soc. 119 (1997) 893.

[2] B. Cornils, E.G. Kuntz, J. Organomet. Chem. 502 (1995) 177; G. Papadogianakis, R.A. Sheldon, New J. Chem. 20 (1996) 175.

[3] R.V. Chaudhari, B.M. Bhanage, R.M. Deshpande, H. Delmas, Nature (London) 373 (1995) 501.

[4] J.P. Arhancet, M.E. Davis, J.S. Merola, B.E. Hanson, Nature (London) 339 (1989) 454.

[5] E. Monflier, G. Fremy, Y. Castanet, A. Mortreux, Angew. Chem. 107 (1995) 2450; Angew. Chem. Int. Ed. Engl. 34 (1995) 2269; E. Monflier, S. Tilloy, G. Fremy, Y. Castanet, A. Mortreux, Tetrahedron Lett. 36 (1995) 9481.

[6] S. Kainz, D. Koch, W. Baumann, W. Leitner, Angew. Chem. 109 (1997) 1699; Angew. Chem. Int. Ed. Engl. 36 (1997) 1628.

[7] M.T. Reetz, W. Könen, T. Strack, Chimia 47 (1993) 493; P.G. Jessop, T. Ikariya, R. Noyori, Nature (London) 368 (1994) 231.

[8] J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, Germany, 1995; F. Vögtle, Supramolecular Chemistry: An Introduction, Wiley, Chichester, UK, 1991; M.C. Feiters, in: D.N. Reinhoudt (Ed.), Compr. Supramol. Chem. vol. 10, Elsevier, Oxford, UK, 1996, p. 267.

[9] D.R. Benson, R. Valentekovich, F. Diederich, Angew. Chem. 102 (1990) 213; Angew. Chem. Int. Ed. Engl. 29 (1990) 191.

[10] G.W. Parshall, S.D. Ittel, Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes, Wiley, New York, 1992.

[11] H.K.A.C. Coolen, P.W.N.M. van Leeuwen, R.J.M. Nolte, Angew. Chem. 104 (1992) 906; Angew. Chem. Int. Ed. Engl. 31 (1992) 905; H.K.A.C. Coolen, J.A.M. Meeuwis, P.W.N.M. van Leeuwen, R.J.M. Nolte, J. Am. Chem. Soc. 117 (1995) 11906.

[12] M.T. Reetz, C.M. Niemeyer, K. Harms, Angew. Chem. 103 (1991) 1517; Angew. Chem. Int. Ed. Engl. 30 (1991) 1474; M.T. Reetz, B.M. Johnson, K. Harms, Tetrahedron Lett. 35 (1994) 2525.

[13] G. Wenz, Angew. Chem. 106 (1994) 851; Angew. Chem. Int. Ed. Engl. 33 (1994) 803; (b) M.L. Bender, M. Komiyama, Cyclodextrin Chemistry, Springer, Berlin, Germany, 1978; I. Tabushi, Pure Appl. Chem. 58 (1986) 1529; R. Breslow, Science, 218 (1982) 532; C.J. Easton, S.F. Lincoln, Chem. Soc. Rev. 25 (1996) 163.

[14] M.T. Reetz, J. Rudolph, Tetrahedron: Asymmetry 4 (1993) 2405; J. Rudolph, Dissertation, Universität Bochum, Germany, 1995.

[15] M. Bressan, C. Bonuzzi, F. Morandini, A. Morvillo, Inorg. Chim. Acta 182 (1991) 153.

[16] S.R. Waldvogel, Dissertation, Universität Bochum, Bochum, Germany, 1996.

[17] M.T. Reetz, S.R. Waldvogel, Angew. Chem. 109 (1997) 870; Angew. Chem. Int. Ed. Engl. 36 (1997) 865.

[18] K. Issleib, M. Lischewski, A. Zschunke, Z. Chem. 14 (1974) 243; K. Kellner, W. Hanke, A. Tzschach, Z. Nagy-Magos, L. Markó, J. Organomet. Chem. 268 (1984) 175; J. Fawcett, P.A.T. Hoye, R.D.W. Kemmit, D.J. Law, D.R. Russell, J. Chem. Soc. Dalton Trans. (1993) 2563; A.L. Balch, M.M. Olmstead, S.P. Rowley, Inorg. Chim. Acta 168 (1990) 255.

[19] R. Mynott, unpublished results, 1996.

[20] M.T. Reetz, S.R. Waldvogel, R. Goddard, Tetrahedron Lett. 38 (1997) 5967.

[21] M.T. Reetz, C. Frömbgen, unpublished results.

[22] M.T. Reetz, Top. Catal., 4 (1997) 187.

[23] K. Angermund, unpublished results, 1996.

[24] C.D. Gutsche, Calixarenes, Royal Society of Chemistry, Cambridge, UK, 1989; V. Böhmer, Angew. Chem. 107 (1995) 785; Angew. Chem., Int. Ed. Engl. 34 (1995) 713.