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The covalent connection of a catalytically active transition metal center with a water-soluble receptor (host molecule) generates a new type of supramolecular catalyst 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 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 molecular recognition are observed, not possible by conventional transition metal catalysts. The two-phase (water/organic) hydrogenation of nitro-aromatics also is a smooth process catalyzed by these supramolecular complexes. They also constitute an unusually active catalyst system for the selective hydroformylation of higher olefins such as 1-octene in a two-phase system. Dendrimers having diphosphane moieties on the surface provide ligands for transition metals, the corresponding metal complexes (*e.g.*, Pd) functioning as efficient catalysts which can be recycled due to their nanoscopic properties.

J. Heterocyclic Chem., **35**, 1065 (1998).

1. Introduction.

Heterocycles such as crown ethers or cryptands have played a decisive role in the development of supramolecular chemistry [1]. In the initial phase of research, molecular recognition within the context of host/guest chemistry was the main point of interest. Thus, research was directed towards the design and synthesis of receptors (hosts) which bind substrates (guests) selectively, noncovalent interactions such as hydrogen bonding, van-der-Waals forces, π-π stacking and metal-ligand bonding being the primary factors. Thereafter functional properties associated with supramolecular interactions became another important focus of interest. Among these, catalytic aspects received the most attention. Accordingly, the concept of supramolecular catalysis as "catalysis involving supermolecules and/or supramolecular aggregates" is now well accepted [2]. Several comprehensive reviews on "Supramolecular Catalysis" have appeared, covering more than 500 publications [2-4]. In most cases the studies concern the hydrolysis of carboxylic acid esters or phosphates, catalyzed by supramolecular catalysts, the latter consisting of a host molecule bearing a catalytically active center [2,3]. A wide range of synthetic receptors have been devised. A different strategy is to utilize a receptor available in nature or readily accessible from a natural product. One such popular host is β-cyclodextrin, available by enzymatic degradation of starch [2-4]. It consists of 7 glucose units bonded in a cyclic array so as to produce a molecular barrel in which the bottom and the top are open (Figure 1a). This molecule is conventionally represented in short-hand form (Figure 1b), which illustrates the fact that the opening on the top is slightly smaller than the one on the bottom. β-Cyclodextrin is known to have a hydrophobic inner cavity, about 6.2 Å in diameter, which functions as a receptor for a variety of lipophilic organic guest compounds such as alkanes or aromatics. Since β-cyclodextrin is water-soluble (18.5 g/l), the driving force for host/guest interactions in aqueous medium is mainly the so-called hydrophobic effect [4].

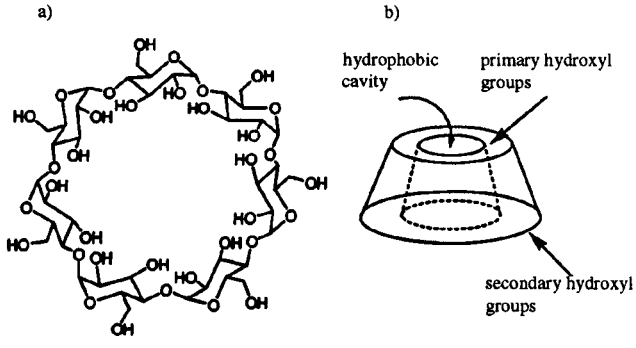


Figure 1. a) Structure of β-cyclodextrin; b) Short-hand symbol of β-cyclodextrin.

Many research groups have attached catalytically active centers to β-cyclodextrin and used such functionalized species as catalysts [2-4]. For example, β-cyclodextrins modified by Cu(II)-bearing dipyridines catalyze the hydrolysis of certain carboxylic acid esters, selectivity being due to specific host/guest interactions prior to the actual hydrolysis [5]. Another recent example concerns ethylene triamine functionalized β-cyclodextrins of the type shown in Figure 2, which have been designated as nuclease mimics [6]. The terms "biomimetic chemistry" and "artificial enyzmes" were created to describe phenomena of this type [7].

The types of reactions studied within the framework of supramolecular chemistry are limited. In addition to hydrolysis, some redox reactions have been studied [2-4], but very few C-C bond forming processes [8]. The extensive area of transition metal catalysis [9] based on metals

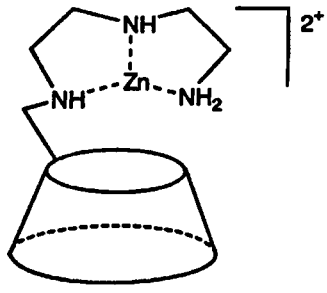
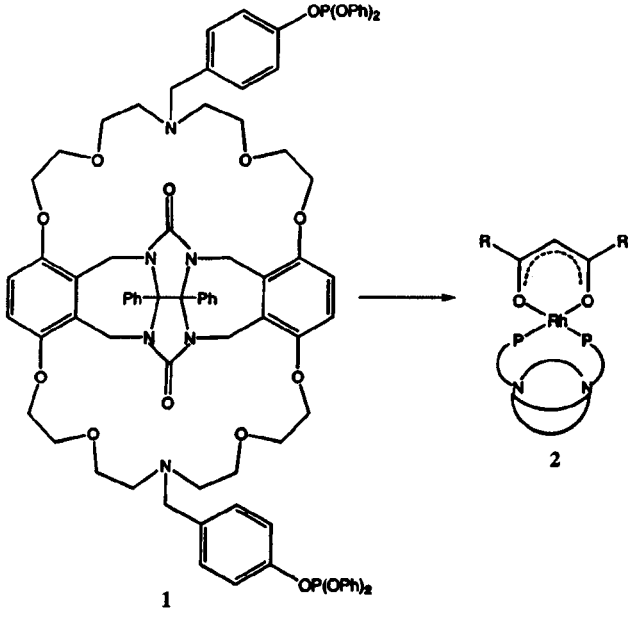


Figure 2. A nuclease mimic based on β-cyclodextrin [6].

such as Pd, Ni, Pt, Rh, Ru or Ir and such synthetically important reactions as hydrogenation, hydroformylation, carbonylation, hydrovinylation, hydrocyanation, arylation or carboxylation has hardly been studied from the perspective of supramolecular chemistry. A rare example pertains to the Rh-containing host molecule **2** derived from the bisphosphite **1** [10]. The molecule has a basket-like geometry with polar urea functions inside the cavity capable of forming hydrogen bonds with the proper guest molecules. Indeed, certain olefins bearing hydroxy moieties are selectively captured by the receptor **2** *via* H-bonding, a recognition event which sets up the process of substrate-selective Rh-mediated hydrogenation. Although the actual effects are small, the principles are clear.



Formulae 1

In our own work we are taking a more general approach to supramolecular transition metal catalysis [11]. It is based on the combination of molecular recognition, transition metal catalysis and phase transfer catalysis. Concerning the first two aspects, we sought to attach chelating diphosphanes to commercially available receptors, hoping that the corresponding transition metal complexes will induce unusual substrate selectivity based on molecular recognition. For example, the scheme shown in Figure 3 indicates that alkenes which are structurally identical at the olefinic function and differ only at remote positions may be hydrogenated substrate-selectively. In contrast, classical hydrogenation catalysts would be expected to deliver 1:1 mixtures of products in competition experiments.

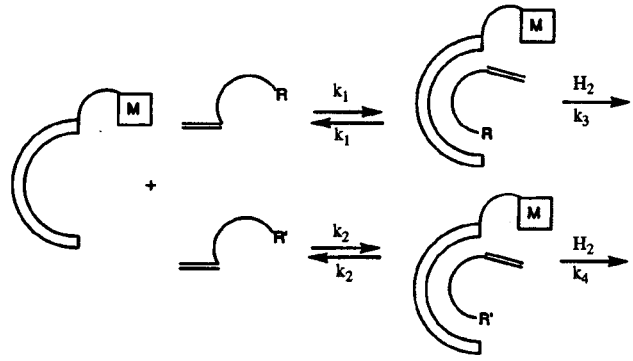


Figure 3. Scheme for substrate-selective hydrogenation based on supramolecular catalysis.

An additional element of complexity was then introduced by considering the case of water-soluble transition metal containing supramolecular catalysts, as illustrated in Figure 4 [11]. In this case biphasic catalysis [12] is anticipated, the catalyst being in the aqueous phase. If it has amphiphilic character, it could easily reach the phase boundary or go beyond, thereby 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 complexation would set up an entropically favorable situation, triggering the desired reaction. Ideally, the receptor must be chosen so as to prevent 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 of 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.

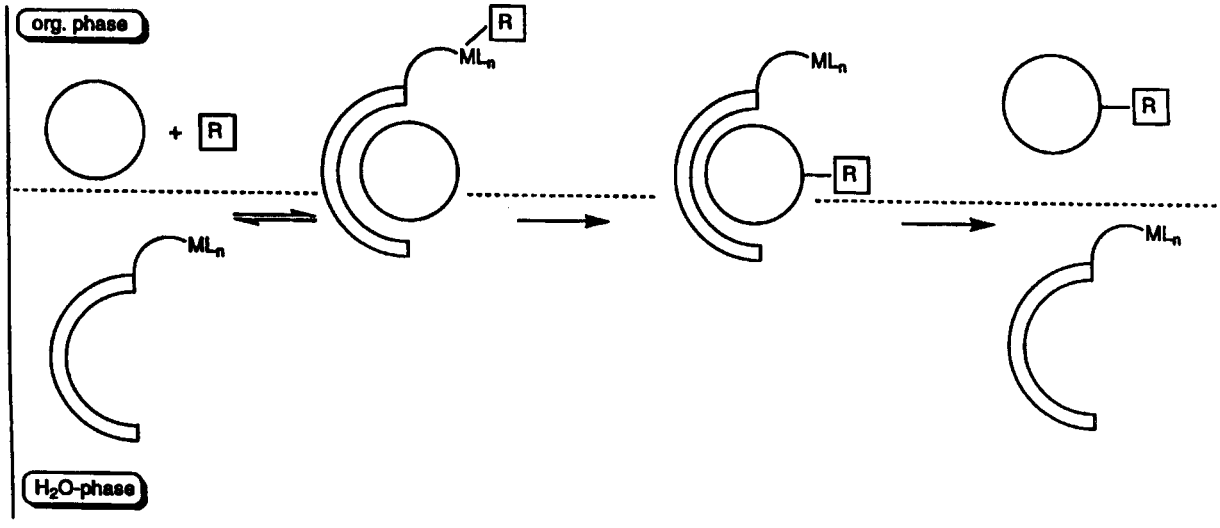


Figure 4. Scheme for two-phase supramolecular catalysis.

2. Water-soluble β-Cyclodextrin-based Diphosphanes as Ligands for Supramolecular Rh-Catalysts.

2.1. Synthesis.

Heterocycles are ideal candidates for the receptors shown in Figures 3 and 4. Indeed, there are many different possibilities, one of them being cyclodextrins. In preparing supramolecular transition metal catalysts based on α- or β-cyclodextrin, the basic problem is selective mono-functionalization. Once formed, the mono-functionalized cyclodextrin needs to be transformed into a diphosphane, setting up the possibility of complexation with transition metal salts as outlined in Figures 3 and 4. Although this is synthetically not a trivial task, we finally devised a rather simple and efficient method (Figure 5). The basic idea is to convert the tosylate **3**, which can be prepared by tosylation of β-cyclodextrin in water, into the corresponding primary amine **5** using conventional reactions, followed by phosphanomethylation with formation of the desired diphosphane **6** [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 [14]. Indeed, in our particular case the reaction occurred very smoothly, conversion to the diphosphane **6** being almost quantitative [13]. It was isolated in pure form with a yield of 91%. Upon reaction of **6** with $[Rh(cod)_2]BF_4$, smooth formation of complex **7** occurred, which was characterized by elemental analysis and nmr spectroscopy.

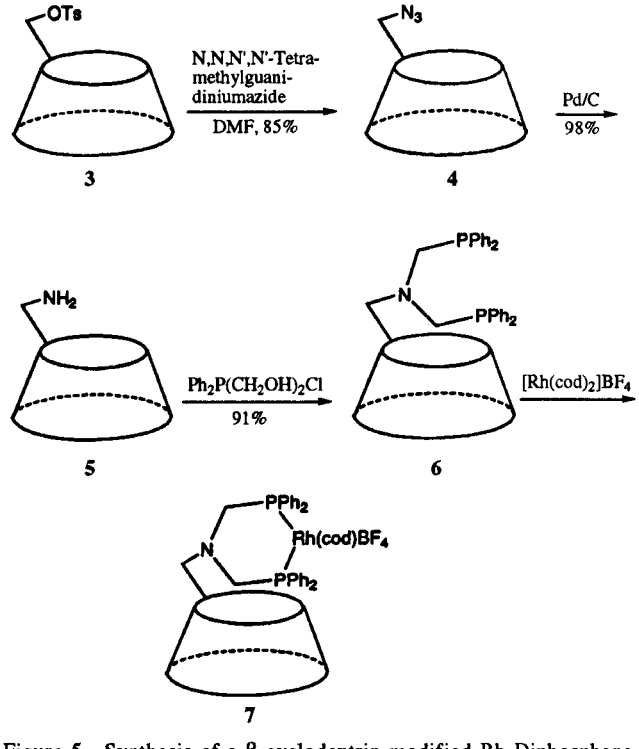


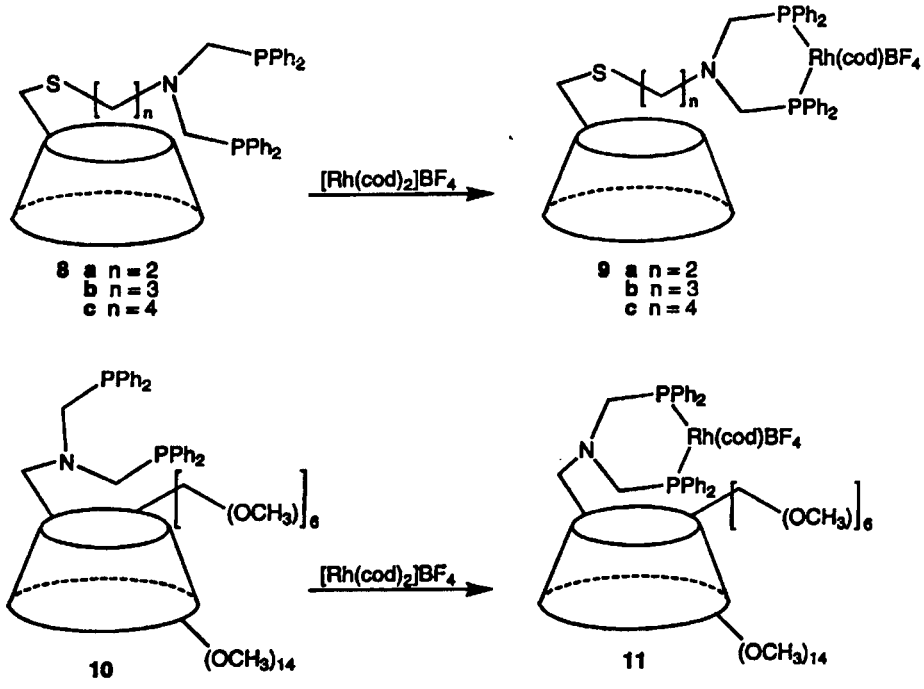
Figure 5. Synthesis of a β-cyclodextrin-modified Rh-Diphosphane Complex **7**.

We were particularly interested in related systems in which the length of the spacer between receptor and catalytically active center varies systematically. Thus, ligands **8a-c** were prepared and converted into the corresponding Rh-complexes **9a-c** [13]. The per-methylated analog of **7** was also synthesized (*cf.* **10**). In all cases the

cationic Rh-complexes were prepared by reaction with $[Rh(cod)_2]BF_4$ in dimethylformamide. The catalysts were characterized by nmr spectroscopy and showed a high degree of purity.

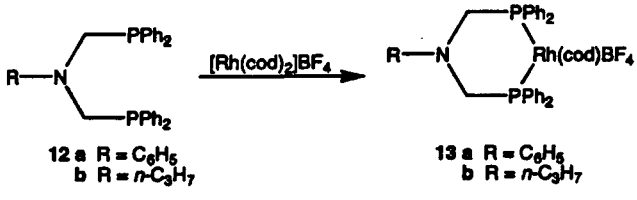
2.2. Selective Hydrogenation.

It was of special interest to determine whether the β-cyclodextrin modified rhodium catalysts function as supramo-



Formulae 2

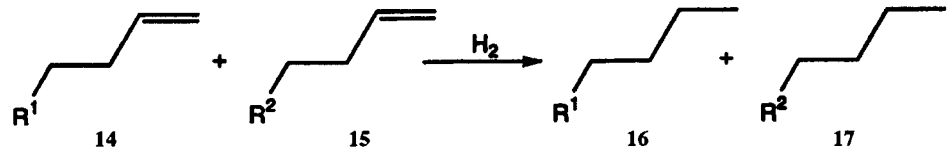
The parent complexes **13a-b** were also prepared in high yield by conventional means [13,15]. In the case of **13a** it was possible to perform an X-ray structural analysis. The metallacycle adopts an approximate chair conformation with a Rh···N distance of 3.797(5) Å, which is too long for a direct interaction (complexation). The P-Rh-P bite angle amounts to 91.8(1)°.



Formulae 3

lecular catalysts. Therefore, the alkenes **14** and **15**, which possess identical substitution patterns at the double bonds, were subjected to competition experiments. In these studies, 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 **16** and **17** as determined by gas chromatography was used as a measure of substrate selectivity.

We did not expect any selectivity in the hydrogenation of **14/15** using conventional catalysts. Indeed, no substrate selectivity was achieved in the control experiment with the β-cyclodextrin-free catalyst **13a** in a one-phase system (dimethylformamide) (product ratio **16**:**17** = 50:50). In contrast, the use of the β-cyclodextrin-modified rhodium catalysts in the one-phase system led to a substantial substrate selectivity: the phenyl-substituted alkene **14** was preferentially converted to the alkane **16** [13]. Importantly, the length of the spacer between the β-cyclodextrin and the diphosphane group plays a crucial role in these reactions (Table 1). If it is too long, as in **9c**, only a 66:34 product ratio is observed. We postulate that a recog-

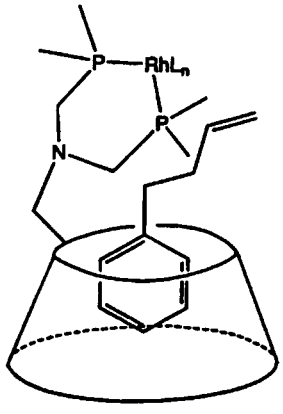


14 15 16 17

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

Formulae 4

nition step precedes the hydrogenation in which the phenyl group of **14** preferentially enters the hydrophobic cavity of the β-cyclodextrin framework (*cf.* **18**). In the case of competitive hydrogenation in a two-phase system (H_2O/organic), selectivity is consistently higher. For example, using catalyst **11**, 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 [11,13].



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Formulae 5

Table 1. Substrate selectivity in the hydrogenation (1 atmosphere of H_2) of **16/17** in dimethylformamide at 22°. a) 0.5 mol% catalyst. b) Two-phase system; aqueous phase contains 30% dimethylformamide.

Table 1

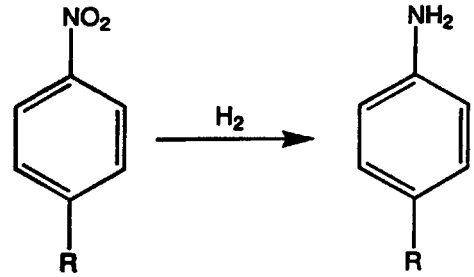
Substrate Selectivity in the Competitive Hydrogenation of Olefins **14/15** (1 atmosphere of H_2)

Catalyst [a]	16	:	17
13a	50		50
7	68		32
9a	74		26
9b	71		29
9c	66		34
7 [b]	82		18
10 [b]	87		13
9a [b]	81		19

[a] 0.5 mole% catalyst; [b] two-phase system (H_2O/olefin).

All of these observations support the postulated interplay of molecular recognition, phase transfer catalysis, and rhodium catalysis. Indeed, substrate selectivity decreases drastically when working the presence of *p*-xylene, which competes for the space in the β-cyclodextrin cavity; for instance, in the case of the catalyst **9a** selectivity is reduced from 81:19 to 57:43 upon adding *p*-xylene [13,16].

Other olefin pairs need to be investigated kinetically along similar lines. Nevertheless, we have started to study other types of hydrogenation reactions, specifically the conversion of nitro-aromatics **19** into the corresponding amines **20** [17].



19a R = H **20a** R = H
b R = Cl **b** R = Cl

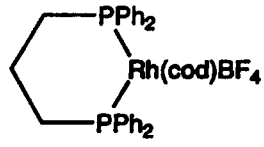
Formulae 6

In control experiments using the parent catalyst **13a** as the catalyst in a one-phase reaction (dimethylformamide), excellent yields of the desired amines **20a-b** were obtained. Exploratory experiments employing the water-soluble supramolecular catalyst **9a** in a two-phase system also turned out to be successful [17]. For example, in the two-phase system $H_2O/HCCl_3$, only 0.1 mol% of this catalyst leads to 96% conversion of substrate **19b**, selectivity in favor of product **20b** being 98%. Only about 0.5% of the corresponding de-halogenated product (aniline) is formed.

2.3. Selective Hydroformylation.

It was of interest to see if the above concepts also apply to C-C bond forming reactions such as hydroformylation [11,13,16]. The parent catalysts devoid of β-cyclodextrin

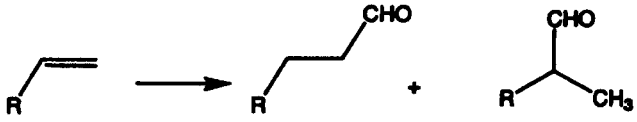
receptors were first studied in a one-phase system consisting of toluene and an olefin (*e.g.*, 1-octene). Under otherwise identical conditions the well known propano-bridged analog **21** was also tested [15].



21

Formulae 7

The kinetics of the hydroformylation of 1-octene **22** at 60° using syngas (CO/H_2 = 1:1) at 100 bar revealed that catalyst **13a** is about 4 times as active as the propano-bridged analog **21** (TOF 240 versus 57), regioselectivity in favor of the *n*-isomer **23** being about 62:38 in both cases [15]. Regioselectivity in the case of the *N*-propyl-analog **13b** was measured to be 60:40. These exploratory results set the stage for the really interesting experiments described below.



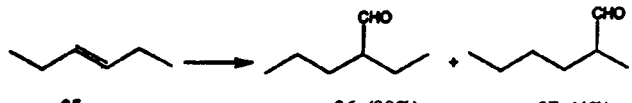
22 R = *n*-C_6H_{13} **23** **24**

Formulae 8

Since biphasic hydroformylation is of considerable current interest [18], attention was then turned to the two-phase hydroformylation of 1-octene **22** and of other olefins using the water-soluble supramolecular catalysts **7** and **9a-c**. Three significant results were obtained. First, unexpectedly high catalyst activities pertain in all cases. For example, in the reaction of 1-octene **22** in the two-phase system H_2O (30% dimethylformamide)/olefin with 0.03 mol% of the catalyst **9a** at 80° and 100 bar (H_2:CO = 1:1), quantitative conversion was achieved in less than 18 hours (TON = 3172). Second, regioselectivity is significantly higher in going from the parent catalysts **13a-b** to the supramolecular catalysts. For example, in the case of catalyst **9a** the *n:iso* ratio is 76:24, compared to 60:40 obtained by using **13b**. 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 dimethylformamide. In fact, in the initial studies dimethylformamide was used because it is the solvent of choice in the preparation of the ionic catalyst [11,13,16].

The results obtained here had to be compared to other known two-phase systems [18-22]. 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 [18,21], less than 1% conversion to **23/24** was obtained under the same reaction conditions. Higher temperatures (120°) were required to produce about 4% of **23** and **24** after 18 hours. Based on these results, our catalytic system is >150 times more active at 80° than the traditional system at 120°. At comparable temperatures the factor must be much higher. In fact, the reaction with **9a** can also be performed cleanly at 60° (95% conversion after 18 hours, *n/iso* = 76:24, <1% isomerization products). Even at lower pressures (10 bar at 60°), the results are still acceptable (69% conversion after 18 hours, *n/iso* = 74:24, 9.5% isomerization products) [11,13,16].

It also became 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 additives which function as phase transfer catalysts, *e.g.*, permethylated β-cyclodextrin [22]. Indeed, even relatively unreactive olefins such as (*E*)-3-hexene **25** react cleanly in the two-phase system (0.03 mol% **9a**, 60°, 100 bar H_2/CO 1/1, 70 hours, 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-cyclodextrin-derivatives acting as phase transfer catalysts [22]. 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 [11,13,16].



25 **26** (90%) **27** (4%)

Formulae 9

We believe that the 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 (Figure 6) [11,13,16]. 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-cyclodextrin 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.

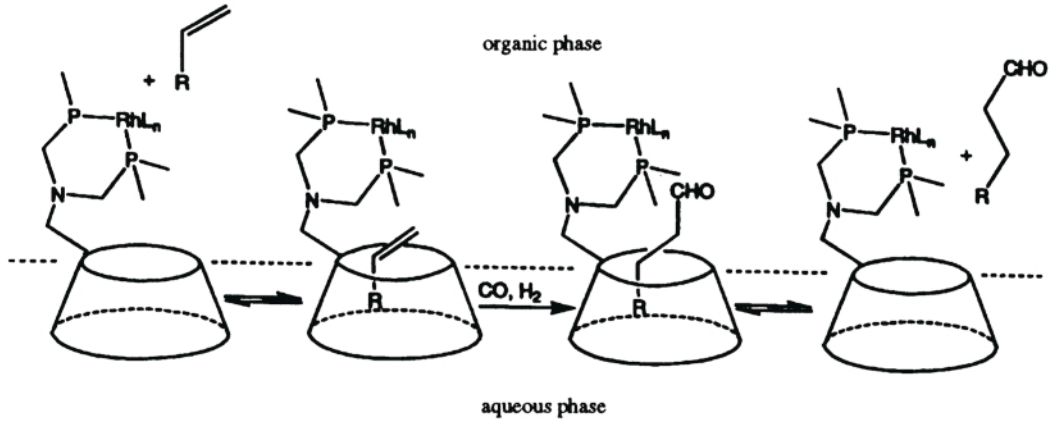


Figure 6. Scheme for two-phase supramolecular hydroformylation.

These conjectures are supported by molecular modeling studies of the host/guest complex involving the supramolecular Rh-catalyst **9a** and 1-octene **22** [23]. Figure 7 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 Figures 6 and 7 do in fact represent the approximate state of affairs, then the catalyst is expected to have an amphiphilic character. Indeed, β-cyclodextrin-modified diphosphanes as well as their Rh-complexes are surface active species, as shown by surface tension measurements [11,13,16]: Distilled water: 73.6 $N\ m^{-1}$; H_2O/dimethylformamide 3/1: 55.6 $N\ m^{-1}$; 1.2 x 10^{-3} M **8a** in H_2O/dimethylformamide 3/1: 53.3 N m^{-1}; 1.2 x 10^{-3} **9a** in H_2O/dimethylformamide 3/1: 43.6 $N\ m^{-1}$.

Extremely small amounts of the rhodium catalyst were used in the hydroformylation (0.03 mol% and less). Nevertheless, 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. This amounts to about 3% of the total rhodium being in the organic phase. In other cases it is more. 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 review are likely to be rewarding. One of the approaches that we are currently considering is the use of the present β-cyclodex-

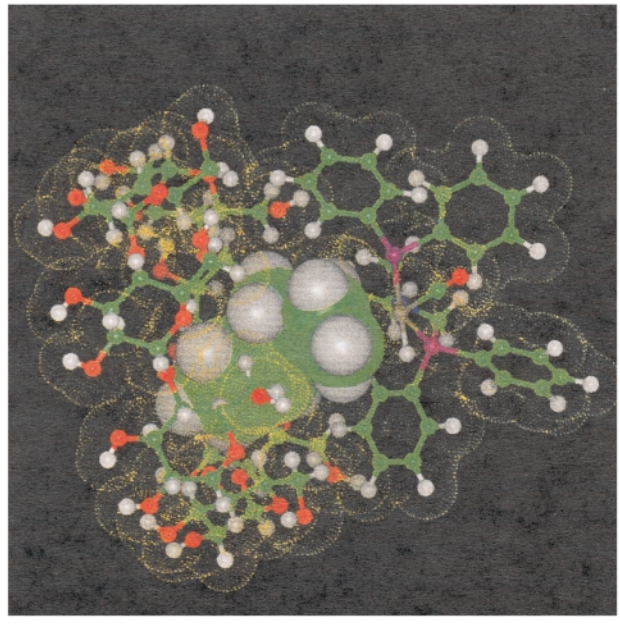


Figure 7.

trin-modified diphosphanes in which the phenyl groups at the phosphorus centers are replaced by substituents bearing water-soluble moieties. The use of α-cyclodextrin, which is considerably more water-soluble than β-cyclodextrin, is also being explored. The problem of increasing regioselectivity may solve itself as a consequence of these important modifications. Enantioselectivity is another aspect which needs to be addressed in relevant systems.

3. Dendritic Transition Metal Complexes as Supramolecular Catalysts?

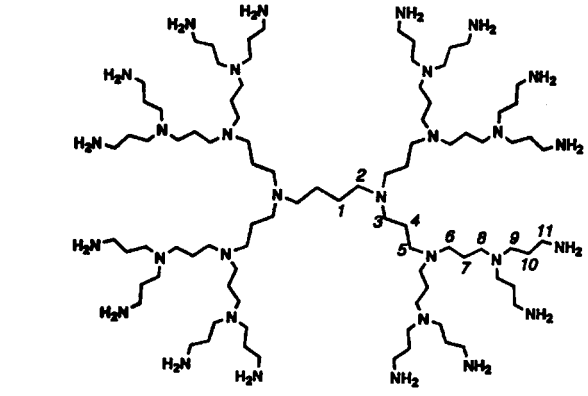
Many metal containing dendrimers have been prepared, but only a few have been tested in catalysis [24,25]. As first delineated by van Koten such catalysts can be considered to be at the interface between homogeneous and heterogeneous catalysis, combining the positive aspects of both types of processes [26]. However, it took some time to actually demonstrate the advantages, namely the existence of a specified number of structurally defined catalytically active centers as well as the possibility of simple separation based on the nanoscopic properties of the dendrimer. We were able to illustrate this principle for the first time by performing Heck reactions of the Pd-complexes of dendrimer **29** prepared in quantitative yield from the commercially available amino-dendrimer **28** [27]. Higher rates of reactions were observed, a phenomenon which had not been observed previously when comparing dendritic catalysts with the "monomeric" parent compound. Separation of the dendritic catalyst based on its nanoscopic properties was also readily accomplished [27], similar to polymeric catalysts [28].

The results are very encouraging. Nevertheless, the principle of molecular recognition needs to be implemented for genuine supramolecular catalysis. Since certain dendrimers function as host molecules [29], this should be possible, especially if the catalytically active centers are in the core of the dendrimer [30].

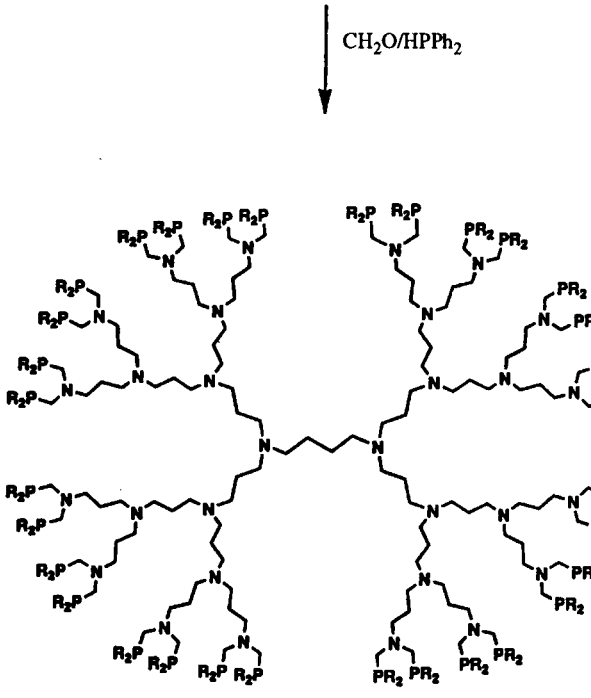
4. Conclusions.

This review is a summary of the present status of supramolecular transition metal catalysis in hydrogenation and C-C bond forming reactions. 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 thus far within the context of supramolecular catalysis.

The types of receptors (host molecules) and catalytic centers (transition metals) tested so far all involve heterocycles. However, they have not been varied greatly. Thus, cyclodextrins are not the only candidates for this type of chemistry, the large family of calixarenes constituting



28



29 (R = C_6H_5)

Formulae 10

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 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.

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