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The Immobilization of Rhodium-4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine (Rh-PPM) Complexes: A Systematic Study

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Abstract: A modular toolbox for the immobilization of homogeneous catalysts to various supports is described. It consists of functionalized chiral diphosphines and three different linkers based on isocyanate chemistry and it is used to attach the 4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine (PPM) ligand to a large variety of soluble, swellable and non-swellable solid organic polymers and to silica gels. As model reaction the hydrogenation of acetamidocinnamic acid derivatives, catalyzed with high enantioselectivity was chosen. Besides information on the usefulness of a particular type of support for synthetic applications, the experiments were also designed to address the question how parameters such as solubility, swellability, cage or pore size and solvent affect the rate and enantioselectivity of an immobilized catalyst. Rhodium complexes of ligands attached to soluble polymers and inorganic supports achieved *ee*s up to 95% and turnover frequencies between 700 and 1400 h^{-1}, very close to the values of the homogeneous Rh catalyst (*ee* 95%, TOF 1320 h^{-1}). Insoluble or strongly cross-linked organic polymers led to catalysts with lower enantioselectivity and activity. PPM ligands attached to water soluble dendrimer fragments allowed hydrogenation in water solution with *ee*s up to 94%, albeit with much lower activity compared to reactions in methanol with the homogeneous catalyst.

Keywords: α-acetamidocinnamic acid derivatives; 4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine (PPM); hydrogenation; immobilization; rhodium; supported catalysts

Introduction

First efforts to heterogenize enantioselective homogeneous catalysts *via* attachment to insoluble carriers started very shortly after the discovery of effective rhodium complexes for hydrogenation reactions. The basic idea was to combine the best features of homogeneous and heterogeneous catalysis, i.e., the enantioselectivity of the homogeneous catalysts with the good handling and separation properties of heterogeneous catalysts. Early pioneers were Kagan, who covalently attached his diop ligand to a Merrifield resin[1a] and later to graphite,[1b] Stille,[2a] the first to study the effect of additional chiral groups in the polymer backbone,[2b] Achiwa, who immobilized the 4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine (PPM) ligand by copolymerization[3] and Hetfleijs, the first to use silica gel as support.[4] Later, various different immobilization strategies were developed and today, there are hundreds of publications on immobilized catalysts[5–7] and a large number of research groups both in academia and in industry is still developing new immobilization methods or adapting known ones for specific reactions.

Despite many successful examples, it became clear very early that immobilization is no panacea for enantioselective catalysis. The heterogenized catalysts are not only much more complex (and much more expensive) than the homogeneous analogues, but in many cases their catalytic performance with respect to enantioselectivity and/or activity was far below that of their homogeneous counterparts. Many attempts were reported in the literature to identify and understand the positive as well as negative effect of various immobilization methods on the catalytic performance and a number of possible reasons can be postulated:

Interactions between immobilized complexes due to high local concentration on the carrier. This can result in both positive effects due to cooperation[8] and negative effects due to catalyst deactivation *via*

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dimerization.[9] On the positive side, fixing a complex on a rigid support with high dilution can lead to an enforced isolation of the active sites.

Interactions between the active center and the support material, e.g., silanol groups of silica gel or aromatic rings of an organic polymer may affect the performance of the immobilized catalyst.

Restriction of conformational freedom due to steric interaction with the support, especially inside small pores or the network of strongly cross-linked polymers, i.e., the effect of small cages. Also here, positive (e.g., when the ligand is too flexible) as well as negative effects (e.g., for an optimized catalyst) on enantioselectivity and rate can be expected.

Mass transport effects due to diffusion limitations of one or several reactants. Here the dominant effect is the rate of the reaction, but due to mechanistic reasons, enantioselectivity can be affected as well.

Since it is not (yet) possible to predict which ligand and support will be suitable for a given substrate and process, the ligand selection occurs *via* a screening approach. To do this successfully, a large variety of chiral ligands and metal precursors has to be immediately at hand since time constraints for process development can be rather severe.[10] In view of the fact that almost no immobilized ligands are commercially available the screening has to be carried out with homogeneous catalysts. The best ligand should then be immobilized as fast and reliably as possible and without any loss in performance.

Inspired by the seminal paper of Nagel[11] describing a very active and selective Rh-pyrphos catalyst covalently attached to silica gel we have developed the modular toolbox schematically depicted in Figure 1. The main elements of our system are functionalized chiral diphosphines, three different linkers based on isocyanate chemistry and various carriers.[12–14] This approach allows a systematic and quick access to a variety of immobilized chiral catalysts with the possibility to adapt their material and catalytic properties to the specific needs.

In order to make such a toolbox useful for industrial applications, the following criteria have to be fulfilled:

(1) General and efficient preparation: The linkers depicted in Figure 3 as well as a variety of inorganic and organic support materials are commercially available and the isocyanate chemistry is well developed.

(2) Access to a variety of properly functionalized chiral diphosphines: This is a major drawback of the covalent attachment strategy since most commercially available diphosphines have to be modified, requiring an often sizeable synthetic effort.

(3) Reasonable "molecular weight" of the immobilized catalyst: For practical reasons, this should not exceed 10 kD per mole of immobilized metal complex.

Here we report on a systematic study where different carriers were attached to the same ligand using a common linker strategy. The goal was to study the effect on rate and enantioselectivity of a reaction with a high intrinsic enantioselectivity. As model we chose the hydrogenation of acetamidocinnamic acid derivatives, catalyzed by Rh-PPM complexes [15] covalently attached to various supports (see Figure 2). Besides information on the usefulness of a particular support for synthetic application, the experiments were also designed to study the effect of various parameters

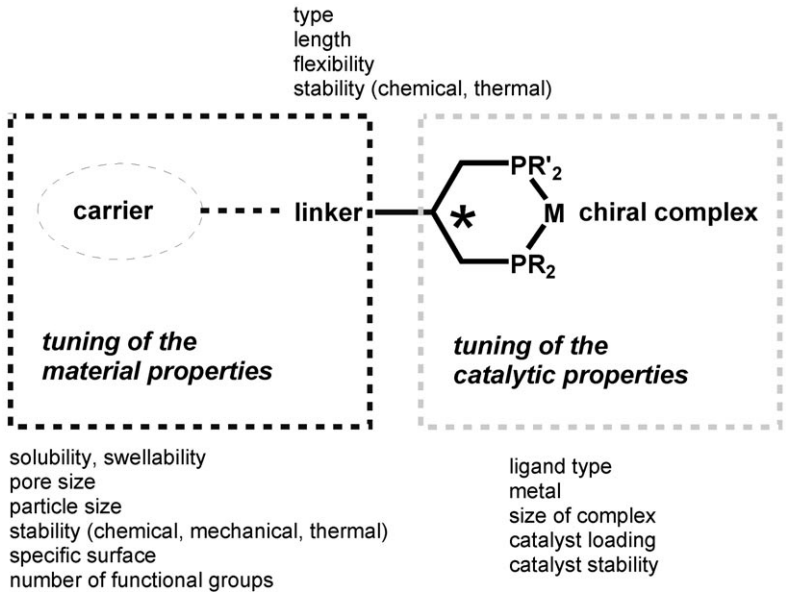

Figure 1. Elements and parameters of the modular toolbox

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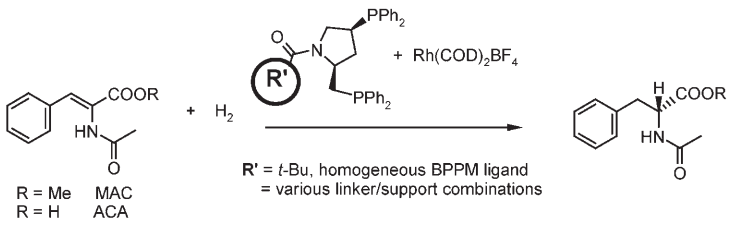

Figure 2. Test reaction using various rhodium-4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine (Rh-PPM) catalysts.

(e.g., solubility, swellability, cage or pore size, solvent) on rate and enantioselectivity of the heterogenized catalyst.

Results and Discussion

Preparation and Characteristics of Immobilized Catalysts

All immobilized ligands were assembled from PPM, an appropriate isocyanate linker and the desired support as schematically depicted in Figure 3 (polymer-supported ligands) and Figure 5 (water-soluble ligands). A schematic overview on important properties of different supports types is given in Table 1. The specific polymeric and inorganic supports used in this investigations are listed in Table 2, where also information on some structural characteristics can be found.

For the immobilization of a ligand on a polymeric support, two routes are possible: Either the linker is first reacted with the N- or O-function of the ligand and then with the support (reactive ligand route) or the linker is first attached to the support and then reacted with the ligand (reactive support route). For inorganic supports, only the reactive ligand route is used[14] whereas for organic polymers with TDI (toluene-2,4-diisocyanate) as linker precursor, both routes are feasible but due to the different reactivity of the two isocyanate groups the position of the methyl group is different for the two routes (see Figure 4). However, we did not find any systematic differences in the catalytic behavior between catalysts prepared *via* the two methods (results not described here). The reactive support route is more flexible than the reactive ligand route. First, not all OH or NH_2 groups of the support have to be reacted with TDI and, secondly, the loading of the PPM ligand can also be controlled. In case of incomplete loading with PPM, the second isocyanate group is either reacted with an alcohol, allowing modification of the polarity of the polymeric ligand (usually EtOH) or it can be used for cross-linking (see below). While we have not fully characterized the immobilized ligands, we have estimated the apparent molecular weight *via* phosphorus elemental analysis (see Tables 3 and 4).

The structure of the water soluble carriers are depicted in Figure 5. Their synthesis is rather straightforward, first reacting carbonyl diimidazole with the carrier followed by reaction with the PPM fragment. While the polyacrylic acid has already been used by Andersson[16] to immobilize selected ligands, the applications of the two dendrimer fragments is new. For the synthesis of AcidD, the condensation reaction has to be carried out with the corresponding triester followed by base catalyzed hydrolysis after attachment of the ligand.

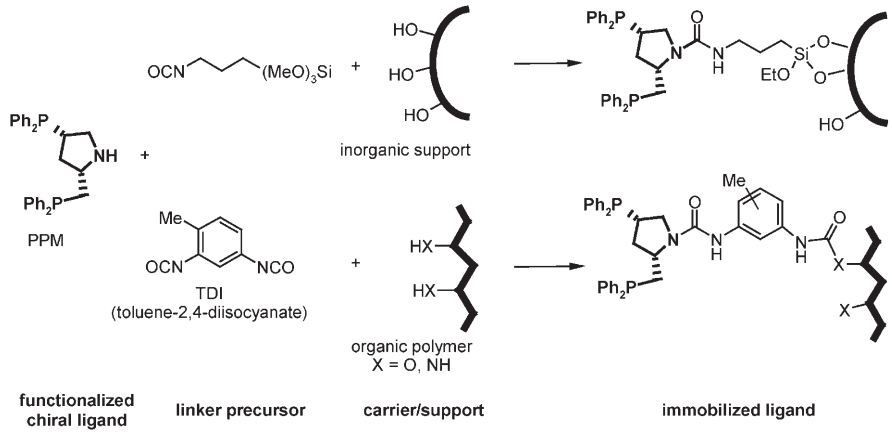

Figure 3. Structure of ligand, linker precursor and immobilized ligand assembly for the various carriers/supports.

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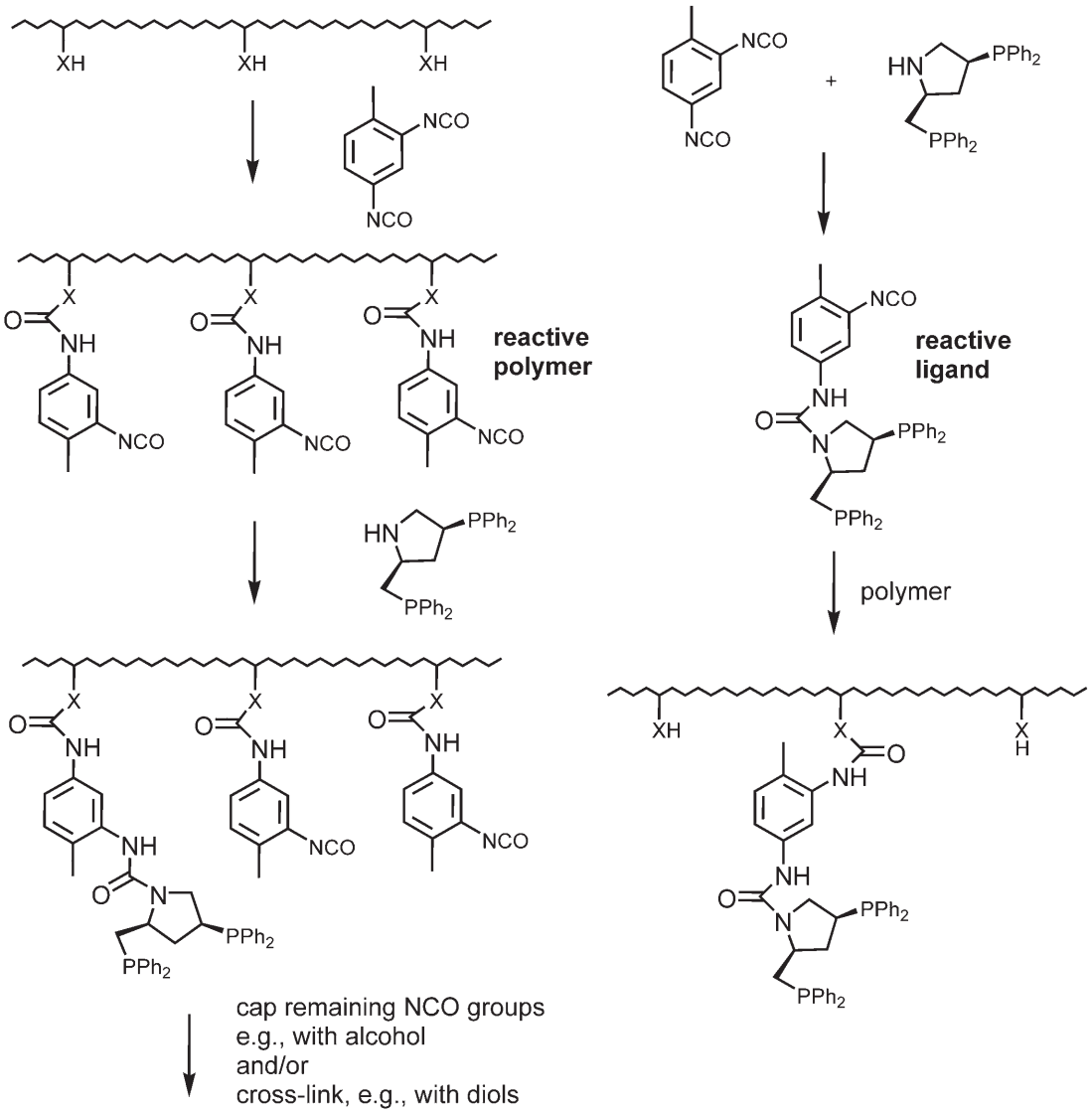


Figure 4. Preparation of 4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine (PPM) ligands immobilized on organic polymers (X=O, NH).

Table 1. Organic polymers and inorganic solids used for the immobilization of metal complex catalysts.

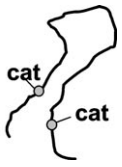
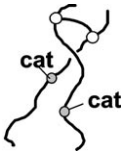
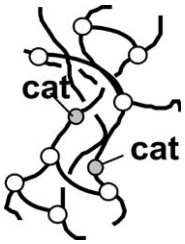
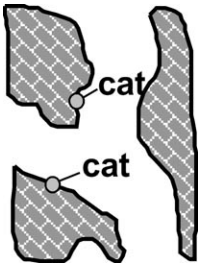
Linear polymer	Slightly cross-linked polymer	Highly cross-linked polymer	Amorphous inorganic support
			
E.g., non-cross-linked polymers such as HEMA, PKHH	E.g., polystyrene with 0.5-3% divinylbenzene	E.g., polystyrene with >5% divinylbenzene	E.g., silica gel, alumina
Soluble, solvent dependent performance	Swellable, solvent dependent performance	Insoluble, slightly solvent dependent performance	Insoluble, solvent independent performance

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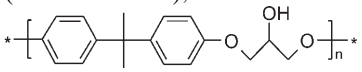
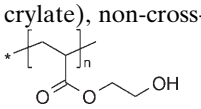
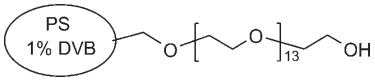
Table 2. Abbreviations and selected characteristics of the polymer and inorganic supports used in this study.

Support	MW,[a] D,[b] P[c]	Soluble in	Insoluble in	mmol OH [g]
PKKH, commercially available polyphenoxy resin (Union Carbide), non-cross-linked 	MW 50,000 D	CH_2Cl_2, THF, MeOH/THF	hexane, alcohols	3.5
HEMA (Aldrich 192066), poly(2-hydroxyethylmethacrylate), non-cross-linked 	MW 300,000 D	MeOH/THF, alcohols, DMF	hexane, CH_2Cl_2, swells in THF	7.7
PS-PEG 1% (Fluka 81185). Polyethylene glycol bound to PS cross-linked with 1% DVB 	slightly cross-linked	swells in THF, slightly in alcohol	all solvents	0.35
PS 25% (Rohm & Haas, XAD-2). Polystyrene, cross-linked with 25% divinylbenzene, hydroxymethylated 	highly cross-linked, macroporous	-	all solvents	1.49
Silica gels[d]				
Grace 332	D 35–70 μm, P 19 nm		all solvents	9-10 μmol/ m^2
Merck 100	D 200–500 μm, P 14 nm			
Merck 60	D 60–200 μm, P 10 nm			
Merck 40	D 60–200 μm, P 4.4 nm			

[a] Average molecular weight.
[b] Particle size (μm)
[c] Mean pore diameter (nm).
[d] For more detailed information, see ref.[14]

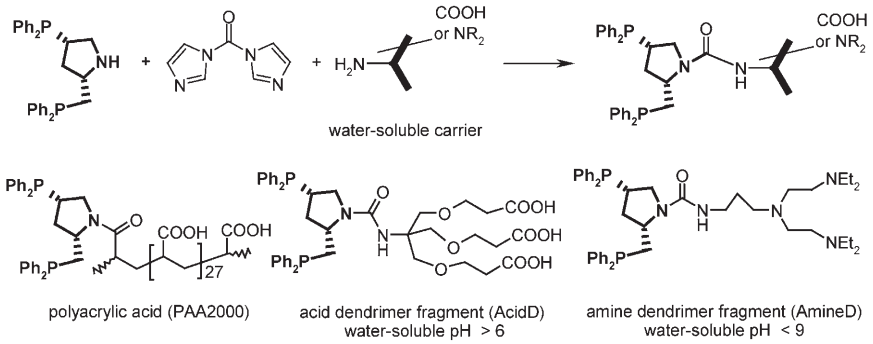


Figure 5. 4-(Diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine (PPM) tethered to various water soluble carriers.

Hydrogenation Experiments

The supported ligands described in the preceding paragraph were applied for the Rh-catalyzed hydrogenation of methyl α-acetamidocinnamate (MAC) and α-acetamidocinnamic acid (ACA) (Figure 1), i.e., the most important standard test reaction for enantioselective hydrogenation. The PPM ligand was chosen for two reasons: First, it was well documented that homogeneous Rh-PPM catalysts have a very good performance for this reaction[15] and, secondly, the nitrogen atom of the pyrrolidine ring is ideally suited to be attached to a variety of linkers using our isocyanate technology. The hydrogenation experiments with MAC (see Tables 3 and 4) were carried out in methanol, the preferred solvents for this reaction and MeOH/THF mixtures in order to dissolve or swell some of the immobilized catalysts. For the hydrogenation of ACA with the water-soluble catalysts, water and MeOH were used as solvents (see Table 5). The catalysts were prepared *in situ* from the appropriate ligand and $Rh(COD)_2BF_4$ (COD = 1,4-cycloocta-

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diene) and the reactions were usually run to high conversions.

As can be seen from the results listed in Table 3, the performance of the homogeneous Rh-BPPM catalyst is very little solvent dependent: The *ee*s vary between 95 and 96%, TOFs between 1300 and 1380 h^{-1} (entry 3.1). Similar catalyst performances are observed for anchored catalysts on dissolved polymers (entries 3.2 and 3.3). With few exceptions, ligands attached to polymers achieve significantly lower TOFs and somewhat lower *ee*s as soon as the polymer is no longer soluble. When a linear polymer is precipitated the TOF drops to 12 h^{-1} (entry 3.2). We also observed that catalysis comes to a complete standstill when a catalyst attached to a swellable support was used in solvents where it does not swell (unpublished results). Interestingly, while the TOF and *ee* of the highly cross-linked Rh-PPM-PS 25% catalyst are low (TOF ~80, *ee* ~87%, entry 3.5) its performance is almost unaffected by the solvent, indicating that the high degree of cross-linking results in a rigid support that has no more swelling properties. The performance decline may be attributed to the attachment of the catalyst within too small pores, which affects mass transport and restricts the conformational freedom of the catalytic species. The solvent effects are also much less pronounced when inorganic supports are used (entry 3.7). Whereas the silica gel with the larges pores achieves a TOF up to 1400 h^{-1} (entry 3.6), smaller pores lead to a decrease in activity which is pronounced only for the catalyst with very small pores and high ligand loading (entry 3.11). Enantioselectivities vary less systematically but in general the same trend is observed: Restrictions of any kind lead to a drop of *ee* between a few percent to 25% (entry 3.2). From this series of experiments we tentatively conclude that making the Rh-PPM centers less and less accessible leads first to a reduction in rate and only later to a decrease in enantioselectivity. This interpretation was tested with a series of PKKH supports cross-linked to various degrees with two different agents and the results are summarized in Table 4. It has to be stressed that the degree of cross-linking was not determined quantitatively and therefore we

Table 3. Enantioselectivity (*ee*, %) and activity (TOF at ~50% conversion, h^{-1}) for the hydrogenation of methyl α-acetamidocinnamate (MAC) with various supported Rh-PPM catalysts.[a]

Entry	Catalyst	MW[b]	MeOH		MeOH/THF[c]		Comments
			ee [%]	TOF [h^{-1}]	*ee* [%]	TOF [h^{-1}]	
3.1	Rh-BPPM	554	95	1380	96	1320	homogeneous catalyst
3.2	Rh-PPM-PKKH	2650	70	12	95	1200[d])	A[e], insoluble in MeOH
3.3	Rh-PPM-HEMA	1905	91	480	95	1320	B[e], soluble polymer
3.4	Rh-PPM-PS-PEG 1%	15500	87	240	90	420	B, not swellable in MeOH
3.5	Rh-PPM-PS 25%	4700	86	70	87	90	
3.6	Rh-PPM-Grace 332[e]	12900	92	~1400			B
3.7	Rh-PPM-Merck 100[f]	17500	93	~1200	92	~800	B, low PPM loading
3.8	Rh-PPM-Merck 100[f]	8200	92	~800			B, high PPM loading
3.9	Rh-PPM-Merck 60[f]	9500	93	~920			B
3.10	Rh-PPM-Merck 40[f]	11300	90	~800			B, low PPM loading
3.11	Rh-PPM-Merck 40[f]	4700	89	~270			B, high PPM loading

[a] *Reaction conditions:* Ligand/Rh $(COD)_2BF_4 = 1.2$, S/C 200, 1 bar, 25 °C.
[b] Estimated molecular weight of immobilized ligand.
[c] MeOH/THF 3.5/1 (vol/vol).
[d] At > 99% conversion.
[e] A: reactive polymer method, B: reactive ligand method.
[f] Data based on ref.[14]

Table 4. Effect of cross-linking for Rh-PPM supported on PKKH prepared *via* the reactive polymer route A. Enantioselectivity (*ee*, %) and activity (TOF at ~50% conversion, h^{-1}) for the hydrogenation of MAC in MeOH/THF 3.5/1.[a]

Entry	Catalyst/Cross-linking agent	MW[b]	*ee* [%]	TOR [h^{-1}]	Comments
4.1	Rh-BPPM	554	96	1320	homogeneous catalyst
4.2	Rh-PPM-PKKH	2650	95	1200	not cross-linked
4.3	Rh-PPM-PKKH/PEG200-1	3670	93	560	partially cross-linked
4.4	Rh-PPM-PKKH/PEG200-2	3450	88	520	strongly cross-linked
4.5	Rh-PPM-PKKH/decanediol-1	3760	87	160	partially cross-linked
4.6	Rh-PPM-PKKH/decanediol-2	3260	74	< 5	strongly cross-linked

[a] *Reaction conditions:* Ligand/$Rh(COD)_2BF_4 = 1.2$, S/C 200, 1 bar, 25 °C.
[b] Estimated molecular weight of immobilized ligand.

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Table 5. Enantioselectivity (*ee*) and activity (TOF at high conversion) for the hydrogenation of α-acetamidocinnamic acid (ACA) with water soluble Rh-PPM catalysts.[a]

Entry	Catalyst	MeOH		H_2O		Comments
5.1	Rh-BPPM	96	2600	89	1	homogeneous catalyst
5.2	Rh-PPM-PAA2000	-	-	92	12	
5.3	Rh-PPM-AcidD	95	2400	94	240	H_2O at 15 bar: *ee* 96%, TOF 2000 h^{-1}
5.4	Rh-PPM-AmineD	97	500	92	100	

[a] *Reaction conditions:* Ligand/Rh $(COD)_2BF_4 = 1.2$, S/C 200, 1 bar, 25 °C.

are not able to directly compare results of the different types of polymers but only those with the same cross-linker. Nevertheless, the results agree very well with our tentative conclusion: While any type of cross-linking leads to lower activity, *ee*s drop only when the cross-linking is higher and/or when the linking agent leads to more restriction (compare PEG200 *vs.* 1,10-decanediol). Under extreme conditions activity drops to almost zero (entry 4.6).

As discussed in the Introduction, various effects can be responsible for the observed decrease in catalyst performance. Even though we cannot rigorously exclude this, we think that it is rather unlikely that the results summarized in Tables 3 and 4 are due to chemical differences of the linkers and/or support materials. The reason for this conclusion is that the same trends are observed for the different systems when the ligands are more and more constricted either by increased cross-linking or by smaller pores. If we accept this interpretation, there are still several interpretations possible. The first and at the moment the most plausible is that enclosing the catalyst in a relatively rigid polymer matrix or in a very small pore no longer allows the Rh-PPM catalyst to adopt the optimal geometry during the catalytic cycle. This can lead to a decrease in *ee* if the product determining intermediates are affected and/or to a decrease in rate if, e.g., access of the substrate is hindered. On the other hand, the restriction could lead to closer interactions of the Rh centers either with each other (dimer formation due to high local concentration) or with the support and/or linker. To test the effect of high local Rh concentration we prepared a PPM dimer, linked *via* a short chain diamine depicted in Figure 6 and tested the Rh complex for the hydrogenation of MAC under our standard conditions. Both in MeOH and MeOH/THF the *ee* and TOF were the same as for the Rh-BPPM catalyst, demonstrating that Rh-Rh interactions are not a probable cause for the observed decrease in *ee* and TOF. On the other hand, we cannot exclude forced interactions with either linker and support.

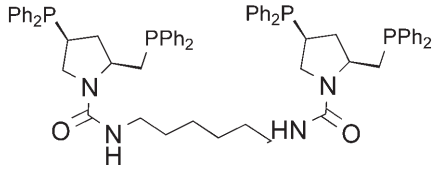

Figure 6. Dimeric PPM ligand.

There are two motivations to render a catalyst water-soluble. One is the possibility to work in a two phase system where the substrate is soluble in the organic phase while the catalyst is "immobilized" in an aqueous phase. This strategy allows catalyst recovery *via* phase separation but in many cases transport restriction occurs between the two phases.[7] In this series of experiments we were interested in the second opportunity, namely the possibility to hydrogenate water-soluble substrates in water as the only solvent.[17] The results summarized in Table 5 clearly demonstrate that the isocyanate linker technology is basically suitable for this purpose.

While the BPPM-Rh complex is insoluble in water and as a consequence shows extremely low activity in water (entry 5.1), the catalysts bound to a water-soluble dendrimer fragment achieve moderate to good TOFs (entries 5.3 and 5.4). Nevertheless, when we compare the results in water with those in methanol there are obvious limitations. Somewhat surprising was the very low TOF for the catalyst based on polyacrylic acid (entry 5.2). But also the ligands attached to the two dendrimer fragments achieved much lower TOFs and somewhat lower *ee*s in water than in MeOH. One reason could be the much lower solubility of hydrogen in water, leading to a lower hydrogen concentration. Indeed, when we increased the pressure to 15 bar, both TOF and *ee* improved significantly for the Rh-PPM-AcidD catalyst (entry 5.4). Furthermore, at 15 bar it was also possible to use this particular catalyst with S/C ratios up to 10,000 (*ee* 94%, TOF 5000 h^{-1}). This last results indicates that some of our experiments might actually be at least partially mass transport controlled and that with a more effective gas-liquid mixing system even higher TOF could be reached.

Finally we briefly discuss the potential of our modular toolbox for synthetic and technical applications. Our results clearly show that it is possible to prepare immobilized catalysts with a synthetically useful performance, in several cases close to that of the homogeneous analogue. Indeed, we have recently applied this technology to the Ir-catalyzed hydrogenation of a herbicide intermediate with a diphosphine immobi-

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lized on silica where turnover numbers > 100,000 have been achieved[18] as well as to the Rh-catalyzed hydrogenation of folic acid to L-tetrahydrofolic acid in water with a diphosphine attached to acid with moderate selectivity but very good turnover numbers.[19] While we have not systematically investigated the filtration and leaching behavior of our immobilized catalysts, we have indications that we can recover > 95 % of our Rh complexes *via* filtration and that in most cases Rh and P content is < 5 ppm.

However, there are obvious limitations to our immobilization strategy especially for technical applications:

(1) In all cases, the ligand which has been identified to have a sufficient catalyst performance has to be functionalized with an appropriate O or N function for tethering. While this is possible (we have synthesized about ten relevant ligands), it makes the catalyst much more expensive.

(2) Many of the polymer-based catalysts are either not as active as the homogeneous catalyst or are very sensitive to solvent effects. Furthermore, the separation of soluble polymeric catalyst which have the best catalyst performance needs either ultrafiltration equipment (which is expensive) or a change in solvent to precipitate the catalyst (which is inconvenient).

(3) Highly cross-linked polymers have high OH group density but unfortunately the pore structure of the PS 25 % polymer seems not be optimal. To get a useful polymer, optimization of the pore structure would be required without affecting the functional group density which might be difficult to achieve.

The more active silica gel-based catalysts have a larger apparent molecular weight due to limited surface area of the large pore material but are in principle suitable for technical application, especially on a small scale. An alternative to the amorphous silica gels are mesoporous crystalline materials such as MCM-41[6a] which we have not applied in this study.

Conclusions

We have shown that the covalent attachment of diphosphine ligands to various organic and inorganic supports as well as water-soluble carriers is a feasible strategy to heterogenize homogeneous catalysts. While ligands attached to soluble polymers and inorganic supports have similar catalyst performance as the homogeneous analogue, insoluble or strongly cross-linked polymers lead to catalysts with lower enantioselectivity and activity. There are indications that this negative effect is mainly due to a confinement of the catalytically active species inside the polymer matrix or very narrow pores, although interactions with the linker and/or support cannot be excluded. PPM ligands attached to water-soluble dendrimer fragments allow hydrogenation in water solution with *ee*s up to 94 %. However, catalyst activity is much lower compared to reactions in methanol, maybe due to mass transfer restrictions. Many of the immobilized catalysts described in principle fulfill the criteria for a technical application, but there are also obvious limitations.

Experimental Section

Reagents and solvents used in this study purchased from Aldrich or Fluka and used as received unless otherwise stated. All manipulations were carried out under an Argon atmosphere.

Synthesis of Immobilized Ligands

The preparation of ligands immobilized on silica gels is described in ref.[14] that of the water-soluble ligands and their use in catalytic hydrogenations are described in ref.[19]

Polymers: PKHH, phenoxy resin, Union Carbide. HEMA, poly(2-hydroxyethyl methacrylate), non-cross-linked, Aldrich 192066. PS-PEG600 1 %, polyethylene glycol bound to polystyrene cross-linked with 1 % divinylbenzene, Fluka 81185. PS(25 % DVB)-OH, polystyrene, cross-linked with 25 % divinylbenzene. This support was prepared starting from macroporous polystyrene (XAD-2, Rohm & Haas) which was first chloromethylated and then hydrolyzed as described in the literature.[20,21]

Representative Example for the Preparation of Polymer-Supported 4-(Diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine Ligand by the 'Reactive Polymer Method' A

PPM-PKHH: Toluene-2,4-diisocyanate (2.84 mL, 19.8 mmol) was added dropwise to a solution of 350 mg (1.23 mmol OH groups) of PKHH phenoxy resin in 10 mL of dichloromethane. After addition of 0.020 mL of triethylamine (catalyst) the solution was stirred at 50 °C for 200 min. After cooling to room temperature, the excess of toluene-2,4-diisocyanate was removed by repeating the following procedure 4 times: Precipitation of the polymer by addition of 50 mL of hexane, decantation of the supernatant solution, re-dissolve polymer in 10 mL of dichloromethane.

After the last decantation, the polymer was dissolved in 10 mL of dichloromethane, 140 mg (0.31 mmol) of 4-(diphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine were added and the reaction mixture was stirred at 25 °C for 20 h. Then 5 mL of ethanol and 0.020 mL of triethylamine were added and the mixture stirred at 50 °C for 4 h. Finally the product was washed by repeating the following procedure 4 times: precipitation with 50 mL of hexane/diethyl ether 3:2, decantation of the supernatant solution, re-dissolve or swell product with 10 mL of dichloromethane. After the last decantation the product was dried under reduced pressure at room temperature. The product was obtained as a white powder that is practically soluble in dichloromethane. The P-content was determined by microanalysis.

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For details on the preparation of all polymer supported ligands by the 'reactive polymer' method see Supporting Information.

Preparation of Polymer-Supported 4-(Diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine Ligands by the 'Reactive Ligand Method' B

Preparation of the 'reactive ligand' (TDI-PPM): A solution of 180 mg (0.4 mmol) of 4-(diphenylphosphino)-2-(diphenylphosphinomethyl)-pyrrolidine in 3 mL of dichloromethane was added to a solution of 0.58 mol of toluene-2,4-diisocyanate in 4 mL of dichloromethane at −50 °C. The cooling bath was removed after stirring for 1 h and the solvent was evaporated under reduced pressure at room temperature. Addition of 25 mL of hexane under vigorous stirring caused the product separate as an oil which sticks to the glass wall. The hexane was decanted and the oil is washed 5 times with 30 mL hexane. Finally the TDI-PPM (reactive ligand) was dried under high vacuum.

PPM-HEMA: A solution of 100 mg of HEMA polymer in 3 mL of dimethylformamide was added to a solution of 170 mg of TDI-PPM in 2 mL of dimethylformamide. After addition of 0.01 mL of triethylamine (catalyst) the reaction mixture was stirred at 55 °C for 16 h. After cooling to room temperature, the product was washed in several steps: (1) addition of hexane and vigorous stirring led to the formation of two phases. The upper phase was separated. (2) addition of diethyl ether. Stirring caused the product to oil out/solidify and the supernatant solution was removed (3–6) the oil/solid was stirred in 5 mL of methanol, then 50 mL of hexane were added. The supernatant solution was decanted from the precipitate. After the last washing the product was dried under reduced pressure at room temperature.

PPM-PS-PEG 1 %: A solution of approx. 130 mg of TDI-PPM in 3 mL of dichloromethane was added to a suspension of 2 g of the PS-PEG polymer in 12 mL of dichloromethane. After addition of 0.01 mL of triethylamine (catalyst) the reaction mixture was stirred at reflux temperature for 20 h. After cooling to room temperature, the product was washed several times with dichloromethane and finally dried under reduced pressure.

Hydrogenation Experiments

The ligand (0.015 mmol) was stirred for 15 min in either tetrahydrofuran or a mixture of tetrahydrofuran and methanol to allow the polymer supports either to dissolve or to swell. Then a solution of 0.0125 mmol of $[Rh(COD)_2]BF_4$ in 1 mL of methanol was added. The mixture was stirred for further 15 min. During this time, the insoluble beads became intensely orange yellow while the solution discolored. Then, a solution of 2.5 mmol of methyl acetamidocinnamate in 16 mL of the solvent(s) indicated in the Tables was added. The argon atmosphere was exchanged against hydrogen (ambient pressure) and the hydrogenation started by vigorous stirring. The course of the hydrogenation was followed by monitoring the hydrogen consumption. Conversion and *ee* were determined by GC (Chirasil-L-val, 50 m capillary column, carrier gas: helium).

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