Immobilization of ruthenium catalysts for allylations with allyl alcohol

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ABSTRACT

$[RuCp(PP)]^+$ complexes active for allylation of alcohols with allyl alcohol as the allylating agent were immobilized on solid supports. Two different immobilization methods have been applied: (1) via electrostatic interactions of the cationic complex on ion-exchange resins, where the anion is present on the support and (2) via a coordination bond with a ligand covalently-bound on the support. Both methods give high yields of immobilized complex through relatively simple procedures. The catalysts immobilized via ionic interactions prove to be able to allylate both 1-octanol and 4-*tert*-butylphenol with very low leaching of the catalyst, thus forming allyl octyl ether and C-allylated phenol, respectively. The accumulation of water in the highly hydrophilic resin precludes the O-allylation of phenol and also retards the C-allylation reaction. The catalysts immobilized via a coordination bond are not hydrophilic; with these catalysts selective O-allylation of phenols is achieved, with recycling of the catalysts over multiple runs. Leaching of the catalyst from the support is somewhat higher than for the electrostatically-bound catalyst and quarternisation (allylation) of the excess of phosphine groups present on the support plays an important role in the activity of the immobilized catalysts for the allylation reaction.

1. Introduction

Nowadays allylations on industrial scale still depend on stoichiometric salt chemistry and employ allyl halides as allyl donors. Allyl alcohol as the allylating agent is an environmentally benign alternative for the production of allyl ether, since only water is co-produced as a byproduct when no other stoichiometric additives are needed for the reaction to proceed.

Several homogeneous catalysts are known to catalyze the reaction between an aliphatic or aromatic alcohol and allyl alcohol, all being precious metal-ion complexes [1–6]. The successful ruthenium-based systems previously described by us only need catalyst amounts of 0.1 mol% on substrate or less and do not rely on the use of stoichiometric amounts of additives to control activity and selectivity; however, the catalytic system is present in the same phase as the substrates and products, from which it is difficult to recover after the reaction [1–3]. It would be desirable to find a means of recycling of the catalyst, which may be achieved by immobilization of the active complex onto a non-soluble support. A simple filtration after the reaction could then be performed or the catalyst could thus be used in a continuous process by flushing the substrates through a fixed-bed.

Immobilization of homogeneous catalysts on solid supports is a well-studied field of research. Several methods can be used to attach a metal complex onto an insoluble support. One often applied method is to covalently link one of the ligands of the reactive complex onto the support. Typical supports are polystyrenes [7] and inorganic materials [8]. A complex with a free coordination site can be added to a resin with coordinating groups (Scheme 1a) [9], but a more common approach is the substitution of a ligand from the complex with a ligand present on the support (Scheme 1b) [10,11]. The advantage of covalently-bound ligands is that the linkage between ligand and support is very stable, but a disadvantage is that a change of synthesis is required of at least one of the catalyst ligands and thus the complex, which can be cumbersome and expensive. It may also affect the catalyst's structure, which is undesirable as it may change the reactivity of the catalyst. These disadvantages can be overcome by immobilizing the catalyst using non-covalent interactions for which several methods are known, ranging from strongly ionic to weak Van der Waals interactions to confine the catalyst to a support [12]. Amongst the non-covalent interactions, the ionic interaction is the most stable [13–15]. By adding a cationic catalyst to an anionic ion-exchange resin, an electrostatically-immobilized catalyst is obtained (Scheme 1c). Advantages of this method are that the immobilization process is often fairly easy and the active catalyst does not need to be modified. Furthermore, reloading of the support with fresh catalyst is readily achieved using this method. A disadvantage of this method is that it can only be applied for ionic catalysts, which have to keep

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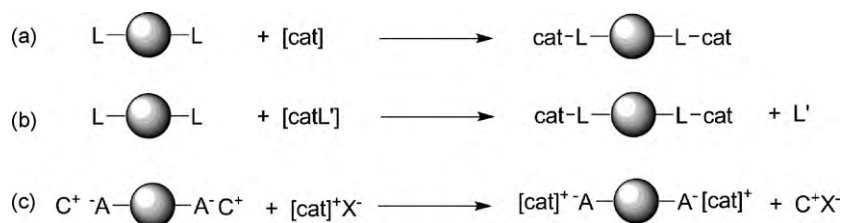
Scheme 1. Immobilization strategies: (a) coordination of an unsaturated complex onto a support with a coordinating residue, (b) coordination of a saturated complex onto a support via ligand substitution with a coordinating residue and (c) absorption of a cationic complex onto an anionic ion-exchange support.

their charge throughout the whole catalytic cycle in order to remain immobilized.

In this paper, the immobilization of a number of the complexes described previously [1–3] is demonstrated, and their application as catalysts in allylation reactions is explored. The ionic as well as the covalent immobilization approach was used and the resulting heterogenized catalysts were tested in allylation reactions of aliphatic alcohols and phenols with allyl alcohol as the allyl donor.

2. Experimental

2.1. General

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. Solvents were dried and distilled by standard procedures and stored under argon. DOWEX 50 WX 4 (1.1 mequiv. H$^+$/ml), Amberlyst (4.7 mequiv. H$^+$/g) and Nafion (0.8 mequiv. H$^+$/g) ion-exchange resins were purchased from Sigma–Aldrich. Resin-bound triphenylphosphine (resinPhPPh$_2$) (3 mequiv. phosphine residue/g; 2% DVB/polystyrene) and [RuCp(ACN)$_3$]PF$_6$ (ACN = acetonitrile) were commercially available and used as received.

[RuCpCl(PPh$_3$)$_2$] [16], [RuCpCl(dppe)] [17], [RuCpCl(dppdep)] [2] and [RuCpCl(dppb)] [18], were prepared according to the literature procedures. The products of the allylation reactions were described previously in Refs. [1,19]. Loading and leaching of the ruthenium complexes was quantified by determination of the Ru-content of the filtrates with a Varian-MPX CCD simultaneous ICP-AES. Pictures of resin were taken with a Zeiss Axiovert 125M microscope equipped with a colorview camera. Solid state CP MAS ^{31}P-NMR spectra were recorded on a Bruker MSL 400 spectrometer operating at 161.99 MHz with a rotational spin speed of 11 kHz.

2.2. General procedure for the immobilization of complexes on ion-exchange resins

0.025 mmol of [RuCp(PP)Cl] and 0.05 mmol of AgOAc were charged into a reaction vessel which was flushed with argon. Degassed methanol was added (5 ml) and the mixture was refluxed for 1 h. After cooling to room temperature, Celite (200 mg) was added and the suspension was filtered under argon. The residue was washed with methanol (3 ml × 2 ml) and to the combined filtrate, the resin (0.25 mmol H$^+$ residues) was added. This mixture was stirred (100 rpm) for 15 h at room temperature. Finally the yellow beads were collected by filtration and washed with methanol (3 ml × 2 ml). The efficiency of the loadings was estimated by means of measuring the Ru-content in the combined filtrates with ICP-AES.

2.3. Immobilization of [RuCp(PPh$_3$)$_2$](OTs) onto resin-bound triphenylphosphine (catalyst A)

[RuCpCl(PPh$_3$)$_2$] (72 mg; 0.1 mmol) was reacted with AgOTs (50 mg; 0.2 mmol) by refluxing in dichloromethane (5 ml) for 10 min. The reaction mixture was then filtered under argon

over Celite and to the filtrate was added the resin-bound triphenylphosphine (135 mg; 0.4 mmol phosphine residues) and stirred (100 rpm) at room temperature for 48 h. The resin was collected and washed with dichloromethane (3 ml× 4 ml). The efficiency of the loading was measured in duplicate by means of measuring the Ru-content in the combined filtrates with ICP-AES to find that 91% of the initial Ru-complex was present on the support.

2.4. Immobilization of [RuCp(PPh$_3$)$_2$](OTs) onto resin-bound triphenylphosphine (catalyst B)

[RuCpCl(PPh$_3$)$_2$] (72 mg; 0.1 mmol) was reacted with AgOTs (25 mg; 0.1 mmol) by refluxing in dichloromethane (5 ml) for 10 min. The reaction mixture was then filtered under argon over Celite and to the filtrate was added the resin-bound triphenylphosphine (135 mg; 0.4 mmol phosphine residues) and stirred (100 rpm) at room temperature for 48 h. The resin was collected and washed with dichloromethane (3 ml × 4 ml). The efficiency of the loading was measured in duplicate by means of measuring the Ru-content in the combined filtrates with ICP-AES to find that 97% of the Ru-complex was present on the support.

2.5. Immobilization of [RuCp(ACN)$_3$](PF$_6$) onto resin-bound triphenylphosphine (catalyst C)

[RuCp(ACN)$_3$](PF$_6$) (44 mg, 0.1 mmol) was dissolved in dichloromethane (5 ml) and resin-bound triphenylphosphine was added 133 mg, 0.4 mmol phosphine residues). The resulting suspension was stirred (100 rpm) for 1 h, after which the solid was collected by filtration, washed with dichloromethane (3 ml × 2 ml) and dried *in vacuo*. The efficiency of the loading was measured in duplicate by means of measuring the Ru-content in the combined filtrates with ICP-AES to find that 99% of the initial Ru-complex was present on the support.

2.6. General procedure for catalytic reactions using catalyst immobilized on ion-exchange resins

To the immobilized complex (0.025 mmol) under argon atmosphere, 2.5 mmol of 1-octanol or 4-*tert*-butylphenol was added. Degassed and dried toluene was added (4 ml) and the mixture was stirred for 5 min. Allyl alcohol was then added (5 mmol) and the reaction was stirred (100 rpm) for 20 h at 80 °C. Samples were taken at certain time intervals with an airtight syringe and analyzed by gas chromatography. After the reaction, the solid was collected by filtration, washed with methanol (3 ml × 2 ml) and dried *in vacuo*. Leaching amounts were measured in duplicate by means of measuring the Ru-content in the combined filtrates with ICP-AES.

2.7. General procedure for catalytic reactions using catalyst immobilized on resin-bound triphenylphosphine

To the immobilized complex (0.025 mmol) under argon atmosphere, 2.5 mmol of 1-octanol or 4-*tert*-butylphenol and 0.05 mmol
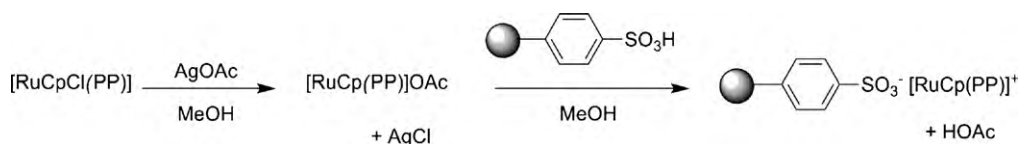
Scheme 2. Synthesis of cationic [RuCp(PP)]+ complexes and immobilization on anionic-exchange resin.

of *p*-toluenesulfonic acid were added. Degassed and dried toluene was added (4 ml) and the mixture was stirred for 5 min. Allyl alcohol was added (5 mmol) and the reaction was stirred (100 rpm) for 3 h at 80 °C or 20 h at 60 °C. Samples were taken at certain time intervals with an airtight syringe and analyzed by gas chromatography. After the reaction, the solid was collected by filtration, washed with dichloromethane (3 ml × 2 ml) and dried *in vacuo*. Leaching amounts were measured in duplicate by means of measuring the Ru-content in the combined filtrates with ICP-AES.

2.8. GLC method

Quantitative gas liquid chromatography analyzes were carried out on a Varian CP-3800 apparatus equipped with a VF-1 ms (25 m × 0.25 mm) column with decane as internal standard. The temperature gradient used was: isothermal for 5 min at 40 °C, heating 10 °C/min to 250 °C and finally isothermal for 5 min at 250 °C.

3. Results and discussion

3.1. Ionic immobilization of [RuCp(PP)]+

3.1.1. Catalyst synthesis

The RuCp-complexes with bidentate phosphine ligands previously used in allylation reactions required a non-coordinating anion in order to be catalytically active. The presence of a tosylate (*p*-toluenesulfonate) anion gives very active catalysts, but also other anions like triflate (trifluoromethanesulfonate) or PF_6^- can be used. Many commercially available ion-exchange resins carry tosylic and triflic acid-type residues, such as DOWEX 50 WX (tosylate), Amberlyst 15 (tosylate) and Nafion NR 50 (triflate). The polystyrene scaffold is expected to be very stable and unreactive under the reaction conditions described previously in Refs. [1,2]. Therefore these resins were chosen for immobilization. Other supports like silicates or aluminates contain hydroxyl residues and may therefore interfere in the desired allylation reactions.

The [RuCp(PP)Cl] complexes were synthesized following the procedure reported previously [1,2]. The chloride ion was then exchanged for an acetate anion, by reaction of the complex with silver(I) acetate in methanol (Scheme 2). Methanol was used as a solvent, as it enhances swelling of the resin, making its reactive sites more accessible. The acidic ion-exchange resin was then added to the solution of the acetate complex.

The lower pK_a of the acidic residues (<1) on the resins compared to the pK_a of acetic acid (~3.5) favors formation of the immobilized complex and acetic acid. A ratio acidic residues over Ru-complex of 10 was used, to ensure that enough accessible sites for the complex to bind were available; the presence of an excess of acidic residues was shown previously to improve activity for allylation reactions [1–3]. Different catalysts that are used to allylate both aliphatic alcohols and phenol were thus immobilized. An overview of the various immobilized catalysts thus prepared and the efficiency of loading of the various combinations is summarized in Table 1.

The precursor complex [RuCp(dppe)]+ of the most active catalysts was immobilized on the commercially available DOWEX 50 WX resins. These are gel-type resins and different cross-linking percentages were employed (entries 1–3). Loading efficiencies were calculated by analysis of the Ru-content of the filtrate using ICP-

Table 1
Efficiencies of loading of RuCp-complexes on ion-exchange resins.

Entry	[RuCp(PP)]+ PP=	Resin	Loading efficiency[a] (%)
1	dppe	DOWEX 50 WX 2	72
2	dppe	DOWEX 50 WX 4	85
3	dppe	DOWEX 50 WX 8	62
4	dppe	Amberlyst 15	79
5	dppe	Nafion NR 50	78
6	dppdep	DOWEX 50 WX 4	94
7	dppb	Nafion NR 50	98
8	(PPh3)2	Nafion NR 50	96

Amount of Ru-complex initially present in solution transferred onto the resin.

[a] 0.025 mmol of [RuCp(PP)](OAc) was added to 0.25 mmol H+ on resin.

AES (inductively coupled plasma atomic-emission spectroscopy) and were in the range of 70–85%. The Amberlyst 15 resin, also containing tosylic acid residues, but with a macroreticular structure, was used for comparison (entry 4). Loading was in the same range as for the DOWEX resins. Finally for [RuCp(dppe)]+, the Nafion NR 50 resin, with triflic acid residues, was used as a support (entry 5). Again, immobilization proved to be successful and a high loading efficiency was achieved. For the other complexes, either DOWEX 50 WX 4 or Nafion NR 50 was used as the support, because with these resins the highest immobilization efficiencies were obtained (entries 6–8). Upon introduction of the resins to the ruthenium solutions the color of the solutions rapidly faded with the concurrent coloration of the resin. For the Nafion NR 50 resin, the beads were homogeneously colored and when cut in half, the yellow color was also clearly present inside the bead, indicating penetration of the complex throughout the whole resin.

Interesting is the observation that when a second batch of resin was added to the loaded resin in solution and the mixture was stirred for several hours at room temperature, the complex did not migrate into the fresh resin. Also at reaction temperature (80 °C), migration was not observed. Despite the use of an excess of 10 equiv. of acidic sites with respect to the Ru-complex quantitative loadings were not achieved after 15 h of reaction time, indicating that not all acidic sites present on the resin are accessible for the ruthenium complex to bind. An equilibrium reaction is not playing a role since increasing the amount of ruthenium complex in solution does not significantly increase the final loading.

3.1.2. Catalysis

The aliphatic alcohol 1-octanol was investigated for its reactivity in the allylation with allyl alcohol (Scheme 3). The catalyst of choice was immobilized [RuCp(dppe)]+, as this proved to be a good catalyst in the homogeneous system [1]. For [RuCp(dppe)]+ on DOWEX 50 WX2 and DOWEX 50 WX4 (Table 1; entries 1–2), catalytic activity was observed; however, over multiple runs irreproducible results were obtained, possibly due to the loss of small amounts of the relatively small, powdery resin beads during the multiple Schlenk filtrations. The complex on DOWEX 50 WX8 resin (Table 1; entry 3) did not show any activity in the allylation reaction. This is most likely caused by limited substrate accessibility due to high cross-linking percentage of the polystyrene chains in this resin.

For the Nafion NR 50 support, no detectable loss of resin occurred, since this resin has large beads (10–35 mesh), unlike the DOWEX 50 WX resins. The results of the multiple catalytic
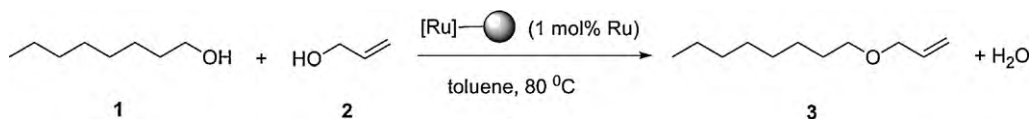
Scheme 3. Allylation of 1-octanol with allyl alcohol as allylating agent, in the presence of immobilized Ru-catalyst.
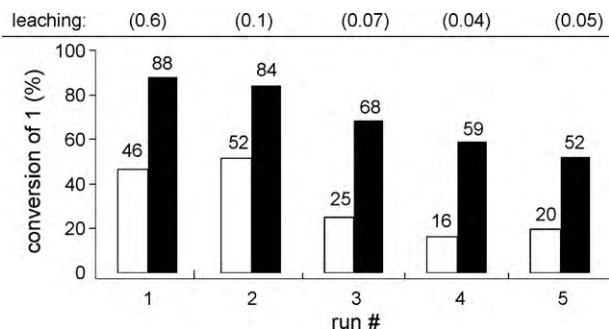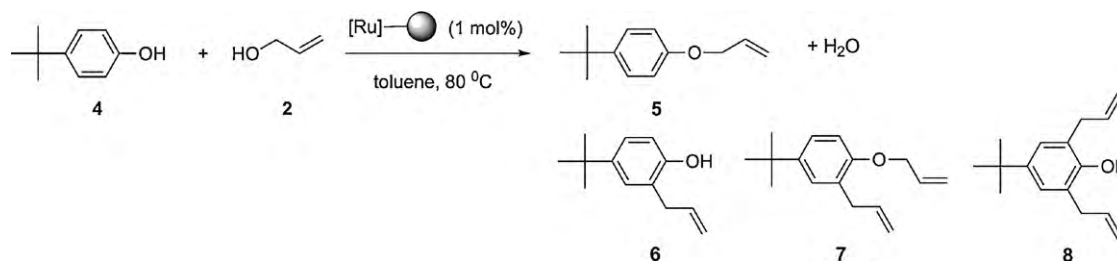

Fig. 1. Allylation of 1-octanol with allyl alcohol using immobilized [RuCp(dppe)]⁺ on Nafion NR 50 over multiple runs. Reaction conditions: ratio 1-octanol/allyl alcohol/Ru-complex = 100/200/1, toluene, 80 °C. 2.5 mmol of 1-octanol was used in each run. White bars represent conversion after 6 h, black bars after 20 h. Exact conversion numbers are indicated on top of the bars. Values in parentheses give percentage of Ru-complex leached from the resin relative to total Ru-complex present after 20 h.
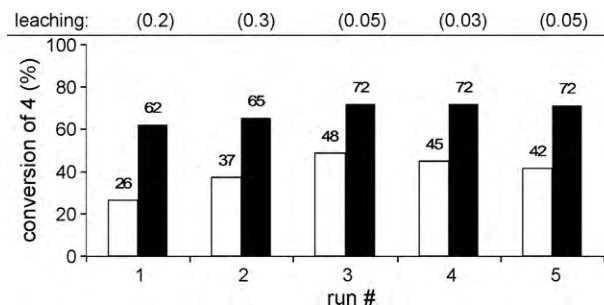

Fig. 2. Allylation of 4-*tert*-butylphenol with allyl alcohol using immobilized [RuCp(dppe)]⁺ on Nafion NR 50 over multiple runs. Reaction conditions: ratio 4-*tert*-butylphenol/allyl alcohol/Ru-complex = 100/200/1, toluene, 80 °C. White bars represent conversion after 6 h, black bars after 20 h. Only C-allylated products (**6 + 8**) are formed. Exact conversion numbers are indicated on top of the bars. Values in parentheses give percentage of Ru-complex leached from the resin relative to total Ru-complex after 20 h.

reaction runs using [RuCp(dppe)]⁺ on Nafion NR 50 are shown in Fig. 1.

It was shown previously that the use of an apolar solvent like toluene is essential to obtain a reasonable conversion in the allylation reaction. However, the use of such an apolar solvent is not beneficial for the swelling of the hydrophilic resins. Nonetheless, the allylation of 1-octanol with [RuCp(dppe)]⁺ on Nafion NR 50 proceeded nicely with high yields and a very low level of leaching of the catalyst from the support. The ruthenium complex is necessary for allylation activity; the unloaded acidic resin does not show activity for allylation under the reaction conditions used. Over five consecutive runs, the conversions decreased significantly; however, this seems not to be caused by leaching of the catalyst, which is orders of magnitude lower than the decrease in conversion. The liquid reaction mixture which was separated by filtration from the immobilized catalyst did not show any activity in allylation reactions, indicating that the complex leached from the support is not causing activity during a reaction run. The decrease in activity could be caused by the retention of water in the resin due to the strongly hydrophilic sulfonate groups; during the multiple runs water thus accumulates in the resin, as a result shifting the reaction equilibrium towards the starting materials. When the beads are thoroughly warmed under vacuum (at 60 °C for 2 h), loss of water is observed. A second explanation could be that chemical degradation of the catalyst occurs on the support without loss of its cationic nature, therefore staying immobilized.

Also 4-*tert*-butylphenol was used as a substrate in the heterogeneously-catalyzed allylation reaction. Phenols can be O-allylated as well as C-allylated, thus forming several products (Scheme 4) and it was previously found that the structure of the catalyst plays a crucial role in determining the selectivity of this reaction. The results of the multiple reaction runs using [RuCp(dppe)]⁺ immobilized on Nafion NR 50 as the catalyst are shown in Fig. 2.

The reaction of 4-*tert*-butylphenol with allyl alcohol using the catalyst [RuCp(dppe)]⁺ on Nafion resin proceeded again with relatively high conversion and low leaching. This catalytic system is completely selective for C-allylation; O-allylated product was not observed, not even at very short reaction times. Unlike in the allylation of 1-octanol, no significant deactivation was observed over multiple runs. C-allylation of phenols is thermodynamically favored over O-allylation and is an irreversible process [1]. In contrast to O-allylation, the presence of water in the hydrophilic resin does not thermodynamically hinder the C-allylation reaction. However, the water environment inside the resin will change the local reaction medium and thus will certainly have its effect on the catalysis, for example by limiting conversion to about 72% after 20 h. This water is also formed in the reaction of two molecules of allyl alcohol into diallyl ether, which also is an allylating agent, as was described previously in Ref. [1]. The hydrophobic diallyl ether will not be easily taken up in the hydrophilic resin, which limits its use as allyl donor.

In order to further investigate the possibilities for O-allylation, catalysts that were found to be highly selective for O-allylation

Scheme 4. Allylation of 4-*tert*-butylphenol with allyl alcohol as allylating agent, in the presence of immobilized Ru-catalyst.

Table 2
Allylation of 4-*tert*-butylphenol with allyl alcohol using immobilized [RuCp(PP)]$^{+a}$.

Entry	[RuCp(PP)]$^+$ PP=	Resin	Conversion of **4** (%)		Selectivity (%)^b	
			6 h	20 h	**5**	**6–8**
1	dppdep	DOWEX 50 WX 4	4	11	37	63
2	dppb	Nafion NR 50	13	30	12	88
3	(PPh$_3$)$_2$	Nafion NR 50	1	2	100	0

^{a} Reaction conditions: ratio 4-*tert*-butylphenol/allyl alcohol/Ru-complex = 100/200/1, toluene, 80 °C.
^{b} After 6 h.

were also immobilized onto the resin in a similar fashion (Table 1; entries 6–8) and tested for their activity in the allylation of 4-*tert*-butylphenol (Table 2). Unfortunately, the immobilized catalyst [RuCp(dppdep)]$^+$ is far less selective for O-allylation than the homogeneous counterpart, for which selectivities of 80% and higher were obtained at conversions below 50% [2]. The complexes [RuCp(dppb)]$^+$ (entry 2) and [RuCp(PPh$_3$)$_2$]$^+$ (entry 3), which have been shown to be very selective in the homogeneous allylation reaction [1,3], show a very different catalytic behavior when immobilized onto an ion-exchange resin. The immobilized catalyst [RuCp(dppb)]$^+$ showed relatively high conversion of 4, but selectivity for O-allylation was low. The immobilized catalyst [RuCp(PPh$_3$)$_2$]$^+$ showed very low activity, although the trace amount of product formed was the desired allyl phenyl ether. The fact that no propanal was formed indicates that the acidic residues on the support are available for catalysis and in this case clearly block the undesired allyl alcohol isomerization reaction. The different behavior of these catalysts when immobilized on ion-exchange resins is ascribed to the accumulation of water in the hydrophilic pores of the resin. Although seemingly the catalyst in Table 2, entry 3 is not active in the allylation of phenol, diallyl ether and thus water is formed in all cases. The O-allylation equilibrium therefore is shifted toward the starting material side, while the irreversible formation of C-allyl phenol is not hindered by the local high concentrations of water.

3.2. Coordinative immobilization of [RuCp(PP)]$^+$

3.2.1. Catalyst synthesis

In order to avoid the hydrophilic character of the anionic-exchange resins, another type of linkage between the catalyst and the support was investigated; a coordinative interaction between a covalently-bound phosphine at the support and a Ru-complex is used. Such an immobilization should not change the structure of the catalyst too much, as large changes in the coordination sphere of the metal-ion may have a dramatic effect on the catalytic behavior of the ruthenium complex [1–3]. Therefore a covalently immobilized triphenylphosphine analogue (resinPhPPh$_2$) on a polystyrene backbone (Merrifield-type) was chosen as the solid support [20]. The use of monodentate phosphine ligands on ruthenium, together with an acidic promoter, has been shown to create a very active catalyst with high selectivity for the desired O-allylated phenol [3].

The resin used has 3 mequiv. phosphine groups per gram of resin, supported on a polystyrene resin with 2% divinyl-benzenepolystyrene cross-linking. In solid state ^{31}P-NMR, a single resonance is clearly observed (Fig. 3a). An excess of 4 equiv. of resinPhPPh$_2$ was used with respect to the Ru-complex. [RuCp(PPh$_3$)$_2$](OTs), synthesized from [RuCpCl(PPh$_3$)$_2$] and 2 equiv. of AgOTs, was reacted with resinPhPPh$_2$ in the non-coordinating solvent dichloromethane. After stirring for 48 h, the solution was almost completely colorless and the resin had obtained a yellow color. The efficiency of the loading was determined again with ICP-AES of the filtrate and it was found that 91% of the complex was transferred from solution onto the resin. The catalyst on resin, however, may consist of various species,
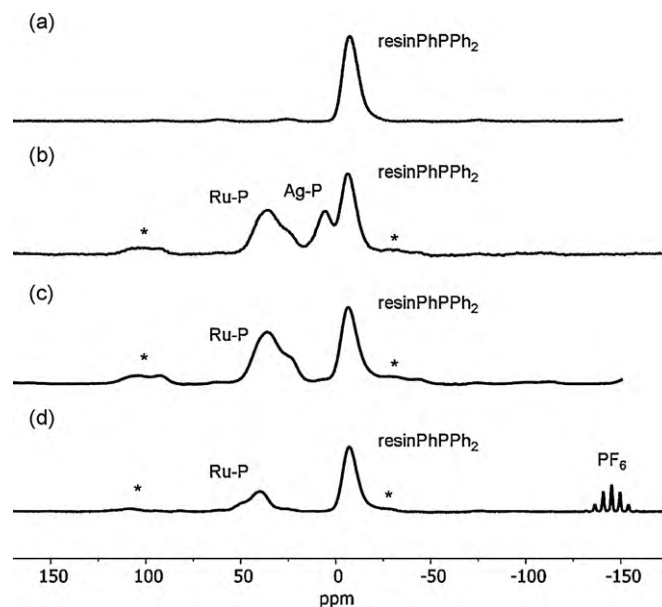

Fig. 3. CP MAS ^{31}P-NMR spectra of (a) resinPhPPh$_2$, (b) AgPPh$_3$/RuCp(PPh$_3$)$_2$(resinPhPPh$_2$)](OTs) (catalyst A), (c) RuCp(PPh$_3$)$_2$(resinPhPPh$_2$)](OTs) (catalyst B) and (d) [RuCp(ACN)(resinPhPPh$_2$)](PF$_6$) (catalyst C). Signals originating from the excess of free resin-bound phosphine are marked resinPhPPh$_2$, whereas those originating from Ru-coordinated phosphines are marked Ru–P and Ag-coordinated phosphines Ag–P. Signals originating from spinning side-bands are denoted *.

depending on the extent of substitution of the triphenylphosphine ligands. After stirring for 48 h at room temperature, ^{31}P-NMR of the filtrate did not show a signal corresponding to free triphenylphosphine, not even when the immobilized resin was washed thoroughly with dichloromethane by means of Soxhlet extraction. Solid state ^{31}P-NMR of the loaded resin (Fig. 3b) indicates the presence of multiple phosphine-containing species: the free phosphine on resin (resinPhPPh$_2$) at −6.3 ppm (also present in Fig. 3a), Ru-coordinated phosphine at +36.6 ppm, and a P species with a resonance at +5.2 ppm (Fig. 3b). The latter resonance is assigned to a silver–phosphine species, that is present due to the excess of AgOTs used in the dehalogenation step (Scheme 5a). It was confirmed that triphenylphosphine coordinated to Ag(I)(OTs) in solution indeed shows a resonance around +5 ppm. The fact that no free triphenylphosphine liberated from the Ru-complex was found in the filtrate is thus most likely caused by the coordination of the released phosphine ligand onto the Ag$^+$ ion. Indeed, when [RuCpCl(PPh$_3$)$_2$] is reacted with 1 equiv. of AgOTs and the resulting mixture is added to the resin after filtration, the peak at +5.2 ppm is not present (Fig. 3c; Scheme 5b) and the filtrate was shown to contain free triphenylphosphine.

The complex [RuCp(ACN)$_3$](PF$_6$) (ACN = acetonitrile) was also immobilized onto the resin-bound phosphine (Scheme 5c). This precursor compound is a starting material often employed for the synthesis of various Ru(II)Cp-complexes and its coordination behavior has been widely studied [21]. Since it is known that
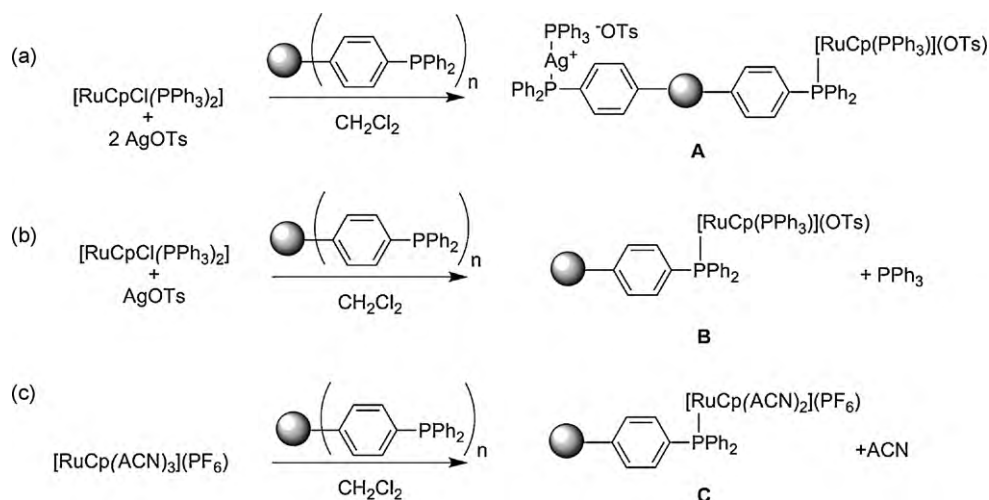
Scheme 5. Synthesis of (a) immobilized [RuCpCl(PPh$_3$)$_2$] + 2 AgOTs on resin-bound phoshine (catalyst A), (b) immobilized [RuCpCl(PPh$_3$)$_2$] + 1 AgOTs on resin-bound phosphine (catalyst B) and (c) immobilized [RuCp(ACN)$_3$](PF$_6$) on resin-bound phosphine (catalyst C). ACN = acetontrile.

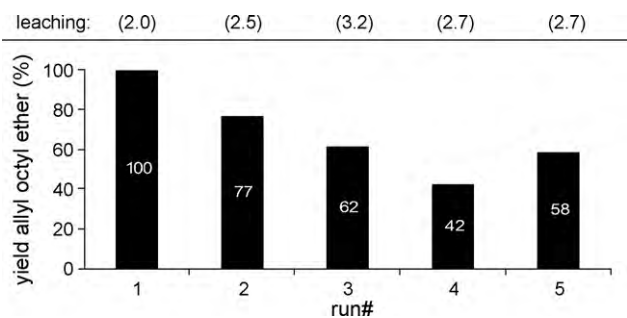**Fig. 4.** Allylation of 1-octanol with allyl alcohol using immobilized [RuCp(PPh$_3$)$_2$](OTs) (catalyst A) on resin-bound triphenylphosphine over multiple runs. Reaction conditions: ratio 1-octanol/allyl alcohol/[Ru]/HOTs = 100/200/1/2; toluene; 80 °C, 60 min; exact conversion number indicated on top of bar. Values in parentheses give percentage of [Ru] leached from the resin after 60 min.

Fig. 5. Allylation of 4-tert-butylphenol with allyl alcohol using immobilized [RuCp(PPh$_3$)$_2$]$^+$ (catalyst A) over multiple runs. Reaction conditions: ratio 4-tert-butylphenol/allyl alcohol/[Ru]/HOTs = 100/200/1/2; toluene; 80 °C, 3 h; yield of O-allylated product (**5**) represented by black bar, with exact number in white; yield of C-allylated products (**6–8**) represented by the white bar, with exact number in black. Values in parentheses give percentage of [Ru] leached from the resin after 3 h.

Fig. 6. Allylation of 4-tert-butylphenol with allyl alcohol using immobilized [RuCp(PPh$_3$)$_2$]$^+$ (catalyst A) over multiple runs. Reaction conditions: ratio 4-tert-butylphenol/allyl alcohol/[Ru]/HOTs = 100/200/1/2; toluene; 60 °C, 20 h; yield of O-allylated product (**5**) represented by black bar, with exact number in white; yield of C-allylated product (**6–8**) represented by the white bar, with exact number in black. Values in parentheses give percentage of [Ru] leached from the resin after 20 h.

phosphines easily displace an acetonitrile ligand from this ruthenium complex [22], this compound was added to resinPhPPh$_2$ in dichloromethane. Indeed immediate coordination to the resin took place and a complex with the proposed formulation [RuCp(ACN) (resinPhPPh$_2$)$_2$] (PF$_6$) was obtained. From the initial amount of Ru-complex present in solution, 99% was loaded onto the resin. This newly obtained immobilized catalyst was analyzed by solid state ^{31}P-NMR (Fig. 3d) and it was clearly observed that the resinPhPPh$_2$ was coordinated to ruthenium. Also the presence of the PF$_6$ anion is clearly indicated by the NMR spectrum. Most likely two resinPhPPh$_2$ moieties are coordinated to the ruthenium center, since it has been reported that displacement of two acetonitrile ligands with two phosphine ligands readily occurs at room temperature [22].

The complexes thus immobilized are air stable when properly dried and can be used after several weeks without a significant decrease in activity.

3.2.2. Catalysis

The catalytic activity of catalyst A was investigated in the allylation of 1-octanol with allyl alcohol (Fig. 4).

The homogeneous catalyst [RuCp(PPh$_3$)$_2$]$^+$ was previously demonstrated to be only active for allylation in the presence of strong acid [3]. For the catalysts immobilized on ion-exchange resins described in Section 2.1, the acid required for catalytic activity was present on the support, but in this case external acid HOTs is needed to be added and was therefore present in solution. Cata-
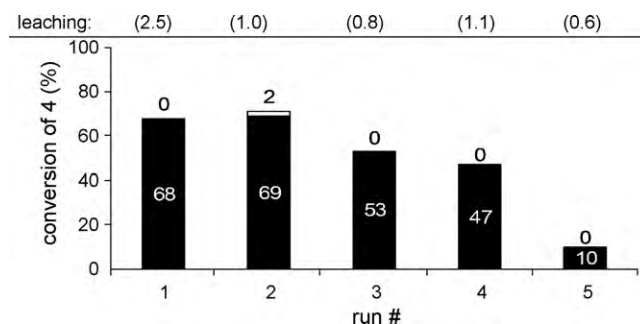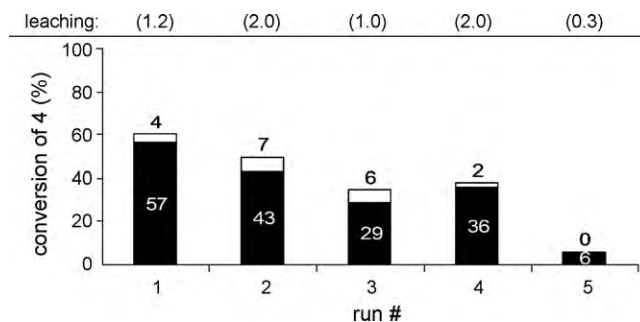
lyst A showed a very high activity in the first run of the allylation of 1-octanol. The substrate was fully converted within 60 min into allyl octyl ether. In the following runs the conversion after 60 min was significantly lower, while the amount of complex leached from the support was constant. It must be noted that these conversions after 60 min were obtained with a catalyst loading much higher than that used in the homogeneous system (1.0 mol% vs. 0.1 mol%
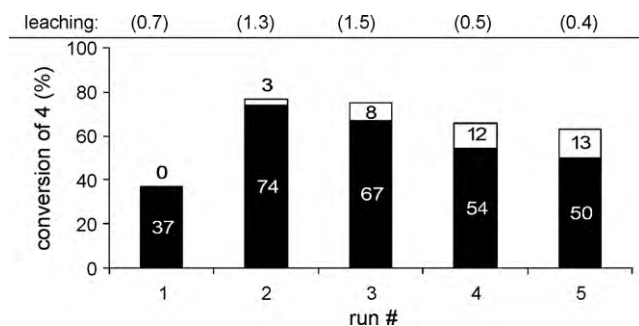
Fig. 7. Allylation of 4-tert-butylphenol with allyl alcohol using immobilized [RuCp(PPh$_3$)$_2$]$^+$ (catalyst B) over multiple runs. Reaction conditions: ratio 4-tert-butylphenol/allyl alcohol/[Ru]/HOTs = 100/200/1/2; toluene; 80 °C, 3 h; yield of O-allylated product (**5**) represented by black bar, with exact number in white; yield of C-allylated products (**6–8**) represented by the white bar, with exact number in black. Values in parentheses give percentage of [Ru] leached from the resin after 3 h.
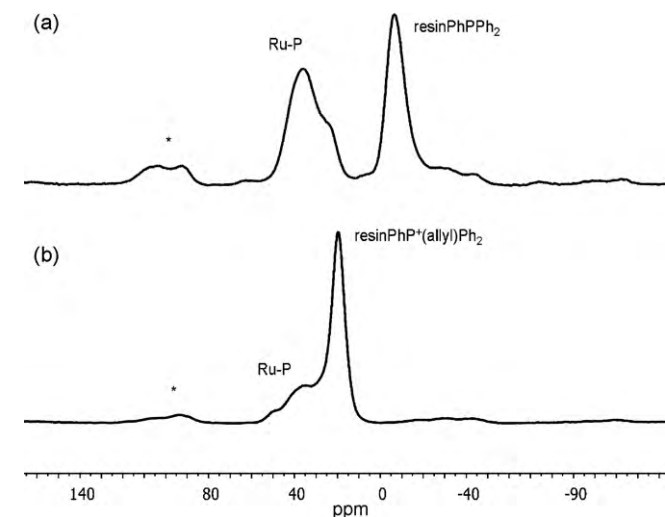

Fig. 9. Allylation of 4-tert-butylphenol with allyl alcohol using immobilized [RuCp(ACN)$_3$](PF$_6$) (catalyst C) on resin-bound triphenylphosphine over multiple runs. Reaction conditions: ratio 4-tert-butylphenol/allyl alcohol/[Ru]/HOTs = 100/200/1/2; toluene; 80 °C, 3 h; yield of O-allylated product (**5**) represented by black bar, with exact number in white; yield of C-allylated product (**6–8**) represented by the white bar, with exact number in black. Values in parentheses give percentage of Ru-complex leached from the resin after 3 h.

Fig. 8. CP MAS ^{31}P-NMR spectra of (a) RuCp(PPh$_3$)$_2$(resinPhPPh$_2$)](OTs) (catalyst B) and (b) catalyst B after first run in allylation of 4-tert-butylphenol with allyl alcohol. Signals originating from the excess of free resin-bound phosphine are marked resinPhPPh$_2$, whereas those originating from Ru-coordinated phosphines are marked Ru–P and those originating from allyl phosphonium salts resinPhP$^+$(allyl)Ph$_2$. Signals originating from spinning side-bands are denoted *.

Scheme 6. Substitution of an ACN ligand from [RuCp(resinPhPPh$_2$)$_2$(ACN)](PF$_6$) (catalyst C) with allyl alcohol.

on octanol for the homogenous catalysts) [3]. Leaching of ruthenium was considerably higher than for the catalysts immobilized using electrostatic interactions. This is indicative for a lower stability of a coordination bond compared to the electrostatic interaction. The liquid phase reaction mixture containing the complex leached from the support was separately tested for catalytic activity, but showed no conversion of added 1-octanol and this proved that the allylation activity is really due to the heterogeneous catalyst.

The challenge is of course, to perform selective O-allylation of phenol and therefore the allylation of 4-tert-butylphenol was performed using catalyst A; the results are shown in Fig. 5.

While the catalysts immobilized on ion-exchange resin formed predominantly C-allylated product, this coordinatively-bound catalyst selectively forms O-allylated product; only traces of C-allylated products were observed. After 3 h, conversions approaching 70% were reached. It must again be noted that similar conversions were obtained after 3 h with the homogeneous system [3] with the difference that a much higher catalyst loading was used here and a higher temperature is used (80 °C vs. 60 °C for the homogeneous system). Thus the heterogeneous system is significantly less active, which is most likely caused by diffusion limitations of the substrates into the solid support.
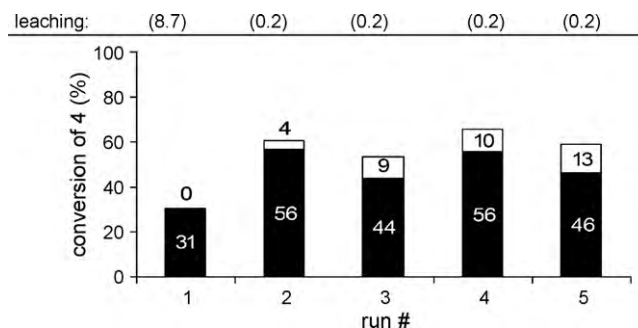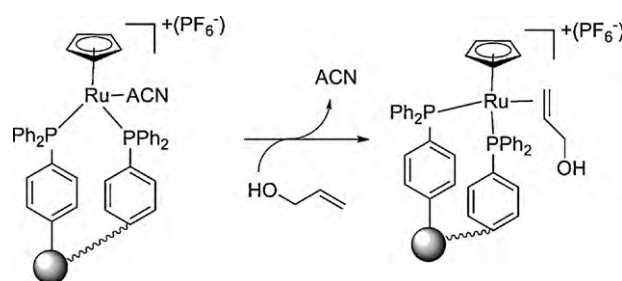
The conversion gradually decreased over the first consecutive four runs; in the fifth run only 10% of phenol was converted. The amount of leached complex does not account for this rapid decrease and therefore a change or chemical deactivation of the complex present on the support must occur. The reaction was also performed at 60 °C in order to investigate whether this rapid decrease of activity could be prevented by lowering the reaction temperature (Fig. 6).

The activity of catalyst A at 60 °C of course is lower than at 80 °C and therefore the reaction was run for 20 h; again, a high selectivity for O-allylation was observed. Intriguingly, the fifth consecutive run shows again a large decrease in conversion; apparently deactivation of the catalyst is also taking place at this reaction temperature.

Catalyst B was also tested as catalyst for the allylation of phenol and the results over five subsequent runs are shown in Fig. 7. The large difference between the first and second run can be explained by the consumption of the acid added to the reaction. Phosphines (here immobilized) react with allyl alcohol and strong acid into
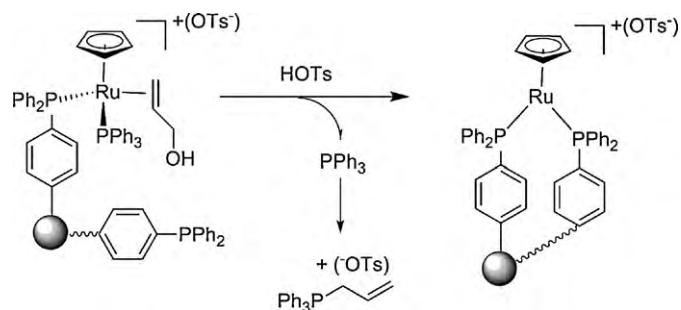
Scheme 7. Proposed substitution of triphenylphosphine with resin-bound triphenylphosphine.
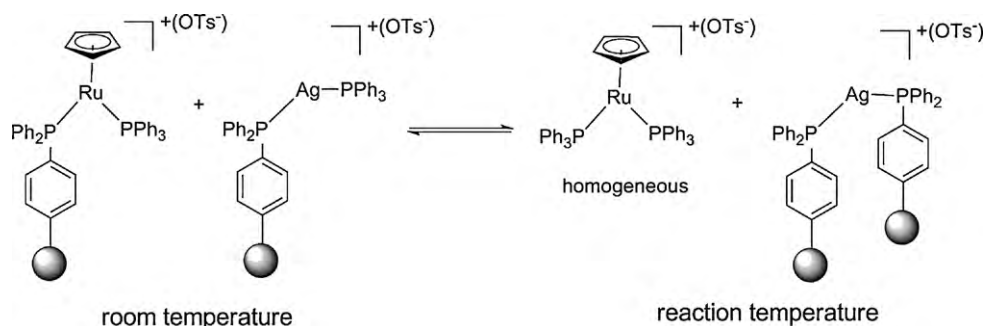
Scheme 8. Proposed mechanism for conversion of heterogeneous Ru-complex to homogeneous Ru-complex.

allyl phosphonium salts and water, but only in the presence of an allylation catalyst [3]. Due to consumption of the acid propanal is also formed by isomerization of allyl alcohol [3]. The immobilized allylphosphonium groups are observed in solid state ^{31}P-NMR (Fig. 8), where the resonance at −6.3 ppm from the resinPhPPh$_2$ (Fig. 8a) has disappeared with the appearance of a resonance at 19.7 ppm assigned to the allyl phosphonium species (Fig. 8b).

In the second run with catalyst B, when the free resinPhPPh$_2$ moieties have been totally converted into phosphonium species, the acid co-catalyst (HOTs) is not consumed, thus making the catalyst active for O-allylation. In the following runs, conversions and selectivities towards O-allylation slowly decreased, but the catalyst B appeared to be more stable than catalyst A. The fact that catalyst A shows a much higher conversion in the first run is most likely caused by the coordination of the silver(I)tosylate to the resinPhPPh$_2$ moiety, making them inaccessible for quarterisation and preventing acid consumption. This hypothesis is supported by the observation that propanal is not formed in the first run when catalyst A is used.

When catalyst C was used as a catalyst in the reaction between 4-*tert*-butylphenol and allyl alcohol in the presence of acid (Fig. 9), in the first run only 35% of allyl phenyl ether was obtained and propanal was formed, again indicative of the consumption of acid and quarternisation of the remaining free phosphines. The remaining molecule of acetonitrile is not playing a role during the catalysis, since it is most likely replaced by the large excess of substrate allyl alcohol present during the reaction (Scheme 6), creating an almost identical complex as described earlier with two coordinated triphenylphosphine ligands and a non-coordinating anion. The amount of ruthenium leached from the support is high in the first run, but rather low in the following runs. Conversions of phenol after 3 h are relatively stable over multiple runs and the selectivity is similar to that in the reactions with catalyst B.

3.2.3. Chemical deactivation of the catalysts

Analysis with ^{31}P-NMR of the filtrate after the first run in the series with catalysts A–C shows the presence of phosphonium salts, indicating that free triphenylphosphine was present during the reactions, which is rapidly converted by the catalyst into allyl phosphonium salts (Scheme 7) as described previously in Ref. [3]. When a triphenylphosphine ligand is released, its place will be taken by an immobilized phosphine group (Scheme 7). However, the immobilized phosphines also form immobilized phosphonium salts as indicated by the NMR spectra in Fig. 8. Coordinated phosphines are not prone to allylation; however, when the concentration of the substrate decreases, it is expected that some quarternization of coordinated phosphines occurs, thus causing deactivation of the catalyst [3].

3.2.4. Physical deactivation of the catalysts

After each run the reaction mixture was cooled to room temperature, filtered and the residual resin was washed with dichloromethane. Leaching of ruthenium was determined by quantifying the amount of Ru present in the combined filtrates after each reaction run. For catalyst A, it appeared that the leaching is considerably higher when the reaction mixture was filtered while still hot (8.4% vs. 2.5% in a single run). This indicates that when the immobilized catalyst is heated to reaction temperature, it dissociates from the support and can be active as if it were a homogenous catalyst. The equilibrium reaction shown in Scheme 8 determines the amount of homogeneous complex present in solution. Most likely, the triphenylphosphine ligand still present on the silver ions plays a crucial role to facilitate this process, because for the catalysts B and C such a difference in the amount of leached Ru is not observed and leaching of ruthenium at reaction temperature is similar to that at room temperature. Also, after the first run a difference between cold and warm filtration is not present anymore for catalyst A, probably because the excess of phosphine is converted to allyl phosphonium salt. The extra equivalent of PPh$_3$ induces this difference in leaching, because at higher temperatures, the weakly coordinated PPh$_3$ on silver(I) dissociates, migrates to a Ru-species, and displaces a resinPhPPh$_2$ group, thus resulting in a homogeneous complex. At room temperature, the Ag–PPh$_3$ complex is more stable and the PPh$_3$ ligand present on Ru can migrate back to the silver ion present on the resin.

Such a "boomerang" effect, where the catalyst dissociates from the support during the reaction and returns after the reaction is finished (in our case when the reaction is cooled down) has been reported earlier for other catalytic systems [23,24]. The advantage of such a system is that the catalyst is homogeneous during the reaction and thus shows a high activity and selectivity. After the reaction, the catalyst becomes heterogeneous again and is easily separated from the reaction mixture. A disadvantage is that the amount of complex leached is significantly higher than for a fully heterogeneous system.

4. Conclusions

The use of ion-exchange resins as support has been shown to yield stable immobilized cationic Ru-complexes with which catalytic allylation reactions were successfully performed. Due to the hydrophilicity of these resins, however, water is retained in the resin, which is detrimental for the selective O-allylation of phenol. The retention of water in the resin causes the formation of only C-allylated products in the catalytic allylation of phenol. The immobilization of the ruthenium catalysts by covalently-bound phosphine onto supports without hydrophilic residues makes O-allylation possible. Although leaching from the resin is considerably

higher than for the catalyst immobilized on ion-exchange resins, the activity over multiple runs is relatively stable. The activity of all heterogeneous systems described in this paper is significantly lower than that of the homogenous catalysts [1–3].

Acknowledgements

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