Article

An Electrostatically-Anchored Rhodium(I) Catalyst for the Hydroformylation and Tandem Hydroformylation/Acetalization of Biorenewable Allyl Benzenes

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Um catalisador de ródio ancorado em uma resina de troca iônica comercial (IRA900/TPPMS/Rh) foi preparado de maneira direta, através de um protocolo simples, a partir de precursores prontamente disponíveis. O material foi usado como um catalisador heterogêneo para a hidroformilação e a sequência tandem hidroformilação/acetalização do eugenol e do estragol em condições brandas. A regiosseletividade para os produtos lineares foi cerca de 62%, mas para os alil benzenos os produtos ramificados são também valiosos. O desempenho do catalisador ancorado na hidroformilação foi comparável aos catalisadores homogêneos de ródio convencionais, entretanto, sua eficiência na etapa de acetalização foi significativamente mais elevada. O material pode ser separado da solução reacional por decantação e pode ser reutilizado sem perda significativa de atividade ou seletividade. Este método catalítico simples representa uma rota alternativa economicamente atrativa para compostos de valor comercial como fragrâncias partindo de substratos prontamente disponíveis de fontes bio-renováveis.

A rhodium catalyst anchored in a commercial anion exchange resin (IRA900/TPPMS/Rh) was prepared straightforwardly through a simple protocol from readily available precursors. The material was used as a heterogeneous catalyst for the hydroformylation and tandem sequence hydroformylation/acetalization of eugenol and estragole under mild conditions. The regioselectivity for linear products was ca. 62%, but for the allyl benzenes the branched isomer are also valuable. The performance of the anchored catalyst in hydroformylation was comparable to that of the conventional homogeneous rhodium system; however, its efficiency in the acetalization step was significantly higher. The material can be separated from the reaction solutions by decantation and re-used without a significant loss in activity and selectivity. This simple catalytic method represents an economically attractive route to commercially valuable fragrance compounds starting from the substrates easily available from natural bio-renewable sources.

**Keywords:** anchored rhodium catalyst, tandem, hydroformylation, acetalization

Introduction

Hydroformylation (oxo synthesis) is an industrially relevant reaction catalyzed by rhodium or cobalt complexes in solutions. The word production of oxo derivatives is in the order of 6 millions ton *per* year. Rhodium-catalyzed hydroformylation is also employed for fine chemicals syntheses,[1] as showed in a recent review.[2] In the last years our group has been interested in the hydroformylation of naturally occurring olefins, such as monoterpenes[2-10] and allyl benzenes.[11] The hydroformylation of allyl benzenes (**1a**-**c**) and propenyl benzenes (**2a**-**c**) (Scheme 1) represents a potential route to fragrance ingredients. In particular, aldehydes **5b** and **5c** are commercialized as valuable fragrance components under the trade names of Chantoxal® (**5b**) and Helional® or Tropional® (**5c**).[12,13]

For industrial processes involving rhodium complexes, the recycling of the catalyst has to be guaranteed due to the high price of this metal. Distillation is inconvenient or even not viable for heavy products as it leads to the thermal deactivation of the catalyst. Many strategies have been investigated to recover the catalyst before the distillation
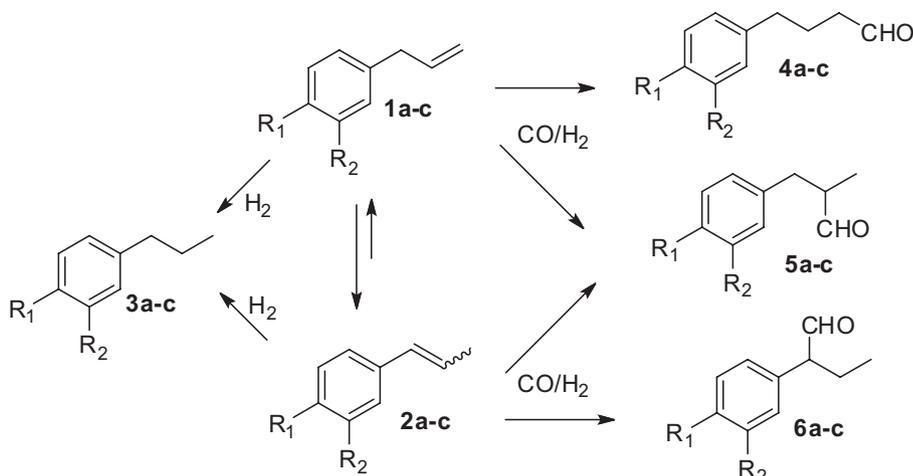
a: R$_1$ = -OH, R$_2$ = -OCH$_3$ **b**: R$_1$ = -OCH$_3$,R$_2$ = -H **c**: R$_1$-R$_2$ = -OCH$_2$-

Scheme 1. The hydroformylation products of allyl and propenyl benzenes.

step, such as the employment of biphasic systems[14] or anchoring the catalyst on a solid support.[15] The latter approach is more attractive from process viewpoint as it allows catalyst separation by simple filtration or the operation in fixed-bed continuous tubular reactors. Among the drawbacks associated with this approach is the difficulty to prepare suitable supports, which must have a functional group capable to bind the catalyst through a chemical bond. The preparation of these supports involves either the synthesis of monomers containing functional groups followed by polymerization or the chemical modification of preformed polymers such as macroporous poly(styrene/divinylbenzene) or silica gel.[15]

An alternative approach is to anchor the catalyst through electrostatic interactions on a solid polyelectrolyte, such as ion-exchange resins.[16] Some grades of ion-exchange resins are considerably cheap and are used in large scale, e.g., for water purification or in agricultural formulations. To be effective, the catalyst has to bear an electric charge throughout the catalytic cycle and a way to fulfill this requirement is to employ ligands with an ionic fragment which binds the metal center of the catalysts.[17-21] A great variety of phosphines containing ionic moieties have their synthetic routes well established.[22] The most readily synthesized one is 3-sulfonatophenyldiphenylphosphine, monosodium salt (TPPMS), which has been anchored on anion-exchange resins and used for the immobilization of ruthenium[18,23] and rhodium[24] catalysts for the hydrogenation of olefins.

In the present work we propose a straightforward protocol to prepare an effective and recyclable anchored rhodium catalyst for the hydroformylation as well as for the tandem sequence hydroformylation/acetalization of allyl benzenes.

Experimental

General procedures

The strongly basic anion-exchange resin IRA900 purchased from Fluka was alternately washed with solutions of HCl (1 mol L^{-1}), NaOH (1 mol L^{-1}), HCl (1 mol L^{-1}), and finally, with deionized water. Eugenol and estragole purchased from Aldrich were passed through a short column of neutral alumina to remove peroxides. Hydrogen (99.999%) and carbon monoxide (99%) were purchased from Praxair. Bis[(μ-methoxy)(1,5-cyclooctadiene)rhodium(I)] ([Rh(cod)(OMe)]$_2$)[25] and 3-sulfonatophenyldiphenyl-prosphine monosodium salt (TPPMS)[26] were prepared according to published procedures. Manipulations under argon were performed employing Schlenk techniques. Toluene was refluxed with sodium/benzophenone for 8 h. Methanol and anhydrous ethanol were refluxed with the corresponding magnesium alkoxyde prepared *in situ* for 6 h. Deionized water was refluxed under argon for 6 h. After the treatment, all solvents were distilled and stored under argon.

Catalyst preparation and characterization

Under argon, TPPMS (0.364 g, 1.0 mmol) dissolved in water (10.0 mL) was kept in contact with wet IRA900 (1.0 g) for 24 h with occasional stirring. The remaining solution was filtered off and the resin was washed twice with water (5 mL) and dried under vacuum (5 × 10^{-4} atm) at room temperature for 5 h. The resulting solid was kept in contact with a solution of [Rh(cod)(OMe)]$_2$ (0.0488 g, 0.100 mmol) in toluene (10.0 mL) at room temperature for 24 h with occasional stirring. The remaining solution was filtered off and the solid was washed twice with toluene (5 mL) and dried

under vacuum (5×10^{-4} atm) at room temperature for 5 h. The catalyst was analyzed by infrared (IR) spectrometry in KBr pellets (4000-400 cm^{-1}) in a Perking-Elmer GX apparatus. The rhodium content of the catalyst was measured by X-ray Kevex and inductively coupled plasma mass spectrometry (ICP-MS), and showed the value of 0.90 wt.%. The phosphorus content was determined by molecular absorption spectrometry resulting in 1.1 wt.%.

Catalytic runs

A mechanically stirred stainless steel Parr 4560 bomb coupled with a 4282 control module with a PID temperature controller and tachometer was employed as the reaction vessel. The bomb was loaded with the solid catalyst and three cycles of vacuum/argon were made. The solvent (15 mL) and the substrate (5 mmol) were introduced with a syringe through a valved port under argon. The vessel was pressurized with carbon monoxide followed by hydrogen up to the reported pressure. Stirring and heating were then started, and the desired temperature was attained in about 5 min. At appropriate time intervals, stirring was stopped and liquid samples were taken through a valved dip tube after quick catalyst settling. Recycling experiments were performed maintaining the catalyst in the vessel and washing it with the same solvent employed in the reaction before a new cycle to remove product residues.

Product analysis

The products were quantitatively analyzed by gas chromatography (GC) using a Shimadzu 17B instrument equipped with a split/splitless injection port and flame ionization detector, fitted with a Restek Rtx-wax capillary column (30m × 0.25 mm × 0.25 µm). Conversion and product distribution were determined by GC. Qualitative analysis was made by GC coupled with mass spectrometry in a Shimadzu GC2010/QP2010-plus instrument fitted with a Restek Rtx-5 MS capillary column (30 m × 0.25 mm × 0.25 µm), operating at 70 eV.

Aldehydes **4a**, **4b**, **5a** and **5b**. These compounds were described in our previous work.[11]

Acetal **4'a** (R' = CH_3). MS (*m/z* rel.int.): 240/3 (M$^+$); 208/6 (M$^+$-CH_3OH); 177/18; 151/11; 150/100; 135/14; 75/21; 44/10.

Acetal **5'a** (R' = CH_3). MS (*m/z* rel. int.): 240/8 (M$^+$); 208/41 (M$^+$-CH_3OH); 177/14; 161/13; 137/80; 75/100; 44/55.

Acetal **4'a** (R' = CH_2CH_3). EM (*m/z* rel. int.): 268/0.55 (M$^+$); 223/1.4 (M$^+$-CH_3CH_2OH); 177/23; 150/100 (M$^+$-$CH_2CH(OCH_2CH_3)_2$).

Acetal **5'a** (R' = CH_2CH_3). EM (*m/z* rel. int.): 268/4.3 (M$^+$); 222/46.3 (M$^+$-CH_3CH_2OH); 177/12; 137/100 (M$^+$-$CH_3CH_2CH(OCH_2CH_3)_2$).

Acetal **4'b** (R' = CH_3). MS (*m/z* rel. int.): 224/1 (M$^+$); 192/11 (M$^+$-CH_3OH); 161/24; 135/12; 134/100; 75/23.

Acetal **5'b** (R' = CH_3). MS (*m/z* rel. int.): 224/2 (M$^+$); 192/44 (M$^+$-CH_3OH); 161/26; 145/11; 121/91; 91/12; 77/11; 75/100; 47/13.

Results and Discussion

Catalyst preparation and characterization

The aim of the present work was to provide a simple and inexpensive protocol to prepare an anchored rhodium(I)/arylphosphine catalyst and test the material in the hydroformylation and hydroformylation/acetalization of allyl benzenes. Thus, we have chosen [Rh(cod)(µ-OMe)]$_2$ as the catalyst precursor, which is prepared straightforwardly in two steps from rhodium trichloride in a high yield. This complex contains labile ligands that can be readily exchanged by a phosphorus(III) ligand. TPPMS is also readily prepared from triphenylphosphine by sulfonation with fuming sulfuric acid (20% SO_3). The macroporous anion exchange resin IRA-900 is a commercial and inexpensive material.

The IRA900/TPPMS/Rh catalyst was prepared according to Scheme 2. The commercial, strongly basic anion exchange resin IRA900 in its chloride form was let in contact with an aqueous solution of TPPMS. The resin containing TPPMS anchored by electrostatic interaction (IRA900/TPPMS) was let in contact with a toluene solution of [Rh(cod)(µ-OMe)]$_2$ ([RhL$_n$]$_2$). The rhodium complex was absorbed by the resin, as it could be noticed by discoloring the pale-yellow solution.

The anchoring process was followed by infrared spectrometry. Although the support and the catalyst have been dried under vacuum (5×10^{-4} atm) at room temperature for 5 h, a significant amount of water remained, as shown by a strong and broad band with a maximum at 3450 cm^{-1}. This fact stresses the strongly hygroscopic character of this support. The introduction of TPPMS in the IRA900 material causes the appearance of a strong absorption at 1196 cm^{-1}, which is characteristic of the sulfonate group. No significant change in the IR spectrum was observed with the introduction of the rhodium complex.

The results of the elemental analysis allowed us to calculate a molar ratio between the components in the final IRA900/TPPMS/Rh material. The phosphorus analysis gave the value of 1.1 wt.% for the phosphorus content. Comparing this value with the nominal ion-exchange
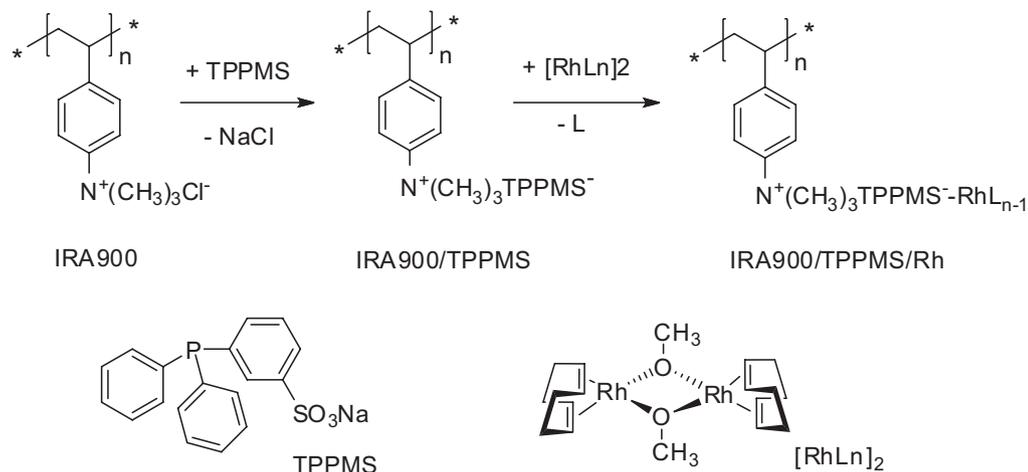
Scheme 2. Catalyst synthesis.

capacity of the IRA900 resin (1.5 meq g^{-1}), it is possible to estimate that only one chloride out of four has been exchanged with TPPMS. Therefore, the TPPMS/chloride molar ratio in the catalyst is about 1:3. The rhodium content of 0.90 wt.% indicates a rhodium/TPPMS molar ratio of 1:3. Thus, the molar ratio of Rh:TPPMS$^-$:Cl$^-$ in the catalyst is 1:3:9.

Catalytic runs

In the present work, we propose the use of eugenol as a convenient model substrate for hydroformylation, as it is a cheap, non-toxic, naturally occurring olefin and is readily available from commercial sources in high purity. In addition, the hydroformylation of eugenol, as well as related allyl benzenes, is a potential route to produce the components of synthetic fragrances (Scheme 1).[12] In many previously reported studies, 1-hexene was used as a model substrate for the catalytic hydroformylation of olefins.[21] However, four double-bond isomers and three aldehydes can be formed from 1-hexene and these products are difficult to be separated by GC. Moreover, their GC peaks may overlap with those of commonly used solvents, such as toluene. On the other hand, the isomerization of eugenol produces only two isomers (**2a**, Scheme 1), which are difficult to be hydroformylated under mild conditions. The hydrogenated product, double-bond isomers and aldehydes derived from eugenol are easily separated under regular GC conditions and their GC peaks do not overlap with those of usual solvents. Therefore, the catalyst parameters such as conversion, reaction rate, chemoselectivity and regioselectivity can be easily and unequivocally determined by GC.

We first tested the performance of the anchored IRA900/TPPMS/Rh catalyst at different temperatures using a substrate to rhodium molar ratio of ca. 550 (Table 1, runs 1 and 2). At 50 °C and 60 atm of equimolar mixture of CO/H$_2$, the reaction occurred slowly reaching 60% of conversion in 24 h and showed a combined selectivity for aldehydes of only 60% because of the extensive isomerization and hydrogenation of the substrate. Expectedly, at the same pressure, the reaction was significantly accelerated by the increase in temperature and was completed in 15 h at 70 °C. The reaction rates were calculated as turnover frequencies (TOF) from the kinetic curves (conversion *versus* time) as shown in Figure 1. The TOF were 14 h^{-1} at 50 °C and 63 h^{-1} at 70 °C. These data expressed by means of the Arrhenius equation yielded for the activation energy a reasonable value of ca. 70 kJ mol^{-1}.

The comparison of the product distribution in the reactions performed at different temperatures revealed a remarkable trend. At higher temperature, the reaction is much more selective for the aldehydes, as they correspond to 89% of the mass balance at 70 °C but only 60% at 50 °C. These results would suggest to test the catalyst at a higher temperature, but the stability of the support is limited to 77 °C. Thus, we decided to keep 70 °C as the standard temperature for the following experiments.

In Table 1, runs 2-6, the effect of the total and partial pressures of CO and H$_2$ is shown. The TOF is rather independent of the total pressure in the range of 40-80 atm (CO/H$_2$ = 1, runs 2, 3 and 4) indicating that the reaction is not limited by the diffusion of the gases to the catalytic site and is either independent of both the CO and H$_2$ concentration or a positive dependence is compensated by a negative one. For triarylphosphine-promoted rhodium catalysts in solution, the rate of hydroformylation is usually independent of the H$_2$ concentration and presents a slightly negative order in CO pressure under "standard" conditions. However, it is important to stress out that the kinetics of

Table 1. The hydroformylation of eugenol (**1a**) in toluene solutions catalyzed by the IRA900/TPPMS/Rh catalyst[a]

Run	Pressure CO:H$_2$ / atm	time[b] / h	TOF[c] / h^{-1}	Selectivity[d] / % for the products of	
				hydroformylation (**4a** and **5a**)	isomerization (**2a**)
1[e]	30:30	24[f]	14	60	22
2	30:30	15	63	94	5
3	20:20	15	68	82	12
4	40:40	15	68	95	5
5	40:20	24	42	89	10
6	20:40	7	174	90	9
7[g]	30:30	17	50	92	7
8[g]	30:30	15	55	91	8

[a]Conditions: solvent: toluene (15 mL), catalyst (0.10 g: TPPMS = 3.6 × 10^{-2} mmol, Rh = 9.0 × 10^{-3} mmol), substrate (5.0 mmol), 70 °C. Conversion and selectivity are based on the substrate reacted; [b]reaction time required for nearly complete conversion; [c]reaction rate (TOF - turnover frequency taken from the linear part of conversion *vs.* time plots); [d]the rest of the mass balance was due to the hydrogenation product **2a**. The regioselectivity for the linear product (**4a**) was ca. 62% in all runs; [e]50 °C; [f]60% conversion; [g]runs 7 and 8 were the second and the third use of the catalyst separated after run 2.

the hydroformylation reactions is extremely sensitive to the experimental conditions.[27]
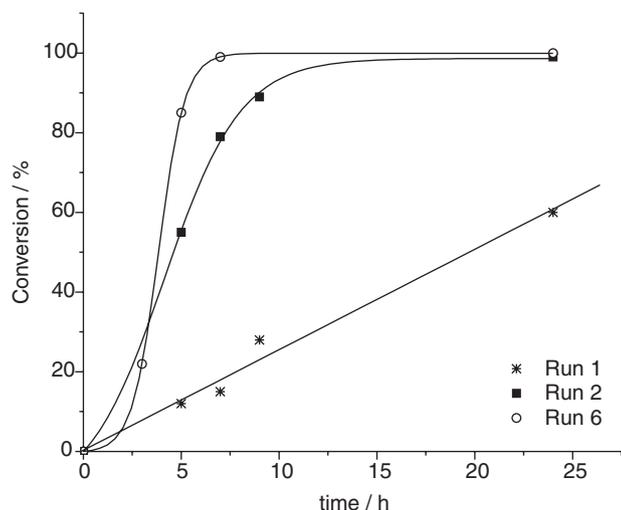
Figure 1. Kinetic curves for selected runs in the hydroformylation of **1a**. For conditions see Table 1.

The results obtained for the reactions performed with different proportions between CO and H$_2$ are shown in runs 5 and 6. The total pressure of the equimolar gas mixture had no significant effect on the hydroformylation of eugenol, which could reflect a net result of the opposite kinetic effects of the gas reagents. Really, a positive order in hydrogen (run 6 *vs.* run 3) and negative order in carbon monoxide (run 5 *vs.* run 3) were found for this reaction. It should be mentioned that the variation of either the total pressure or the partial pressures of CO or H$_2$ does not affect significantly the product distribution at high conversions indicating that essentially the same catalytically active species operate under those conditions. The regioselectivity for the linear aldehyde (**4a**) is quite low (62%), but for allyl

benzenes the branched isomers are even more valuable than the linear ones.

Runs 7 and 8 are the second and third uses of the catalyst first used in run 2. All three reactions were essentially completed in 15-17 h, without a significant decrease in the reaction rates on the stationary periods (TOF = 63 h^{-1}, 50 h^{-1} and 55 h^{-1} in the first, second and third uses, respectively). Thus, the anchored IRA900/TPPMS/Rh catalyst can be separated from the reaction solutions and re-used without a significant loss in activity and selectivity at least for three times.

Tandem hydroformylation/acetalization

For some applications, it is desirable to transform aldehydes in acetals both for protection purposes and because some acetals, instead of the corresponding aldehydes, can be the desired products.[28] Chaudhari *et al.*[21] demonstrated that a rhodium catalyst containing the tris(3-sulfonatophenyl)phosphine trisodium salt (TPPTS) supported on the ion-exchange resin IRA93 transformed the aldehydes primarily formed in the hydroformylation of 1-hexene into acetals when methanol or ethanol were used as solvents. IRA 93 is a neutral polymer containing amine groups that has to be treated with a strong acid such as HCl in order to be converted into an anion-exchanger and thus this catalyst has ammonium ions with an acidic proton, which account for the acid-catalyzed acetalization of the aldehydes. In the IRA900 resin, the exchanging groups are trimethylarylammonium groups without acidic hydrogens and, although the acetalyzation was not expected to be efficient, we tested the catalyst for the tandem sequence hydroformylation/acetalization of eugenol using alcohols as solvents (Scheme 3). The results are presented in Table 2.
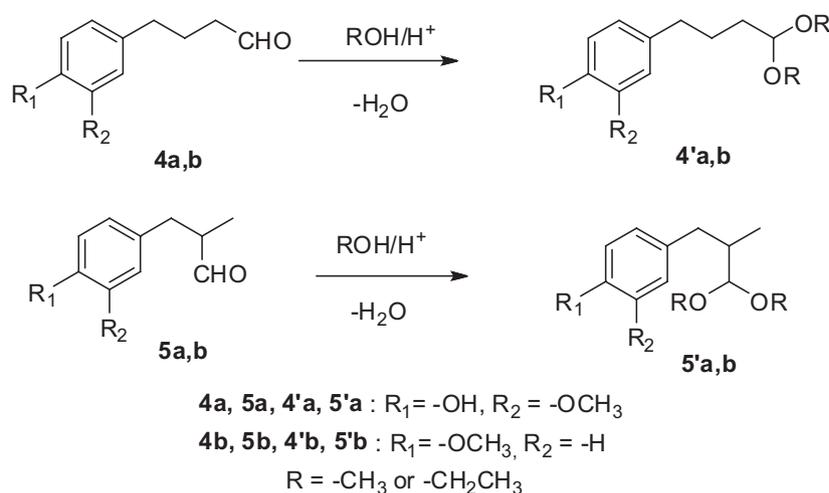
Scheme 3. The step of the aldehyde acetalization.

The rate of eugenol conversion at the stationary period was nearly the same (ca. 60 h^{-1}) in all solvents used, i.e., toluene, methanol, and ethanol, with the reactions being nearly completed in 24 h (Table 2, runs 2, 9 and 10). However, the reactions in alcohols gave corresponding acetals as main products, whereas in toluene the main products were the aldehydes. The total selectivity for the hydroformylation products (aldehydes and acetals) was nearly 95% in all solvents. The regioselectivity of the hydroformylation was also similar in all solvents, with the regioselectivity for the linear aldehydes and acetals (**4 + 4'**) being nearly 62% in all runs. The relative amount of the acetals increased with the reaction time indicating that the acetalization of the aldehydes occurred at a lower rate than their formation. At the end of the 24-hour reaction, the acetals accounted for 77 and 91% of the mass balance in ethanol and methanol, respectively.

To compare the performance of the anchored rhodium catalyst with the conventional homogeneous system, we tested the [Rh(cod)(μ-OMe)]$_2$ complex dissolved in methanol in the presence of TPPMS as the catalyst precursor (Table 2, entry 11). The activity of the homogeneous catalyst was expectedly higher and the reaction was completed in 5 h. A possible explanation could be a faster formation of catalytically active species under the homogeneous conditions, although the diffusional restrictions during the substrate transfer in the polymer domain cannot be ruled out. The product distribution, including regioselectivity, was quite similar considering the aldehydes and corresponding acetals together. This indicates that active organometallic species in the catalytic cycle seems to be similar in both systems. However, in the homogeneous system, the rate of the acetalization step was remarkably lower, with corresponding acetals accounting

Table 2. The hydroformylation and hydroformylation/acetalization of eugenol (**1a**) and estragole (**1b**) in various solvents catalyzed by the IRA900/TPPMS/Rh catalyst[a]

Run	Substrate	Solvent	Conversion / %	Selectivity for hydroformylation[b] / %		
				Total	Aldehydes (**4** and **5**)	Acetals (**4'** and **5'**)
2	**1a**	toluene	99	94	94	0
9	**1a**	ethanol	96	94	17	77
10	**1a**	methanol	98	96	5	91
11[c]	**1a**	methanol	100	95	85	10
12[d]	**1a**	methanol	96	97	9	88
13[d]	**1a**	methanol	94	97	9	88
14	**1b**	methanol	94	99	21	71
15	**2a**	methanol	9	41	18	23

[a]Conditions: solvent (15 mL), catalyst (0.10 g: TPPMS = 3.6×10^{-2} mmol, Rh = 9.0×10^{-3} mmol), substrate (5.0 mmol), 60 atm (CO/H$_2$ = 1/1), 70 °C, 24 h. Conversion and selectivity are based on the substrate reacted; [b]the rest of the mass balance was due to the hydrogenation and isomerization products, **2** and **3**, respectively. The regioselectivity for the linear products (**4 + 4'**) was ca. 62% in all runs; [c]catalyst: [Rh(cod)(μ-OMe)]$_2$ (5.0×10^{-3} mmol) and TPPMS (5.0×10^{-2} mmol) instead of IRA900/TPPMS/Rh. The reaction was nearly completed in 5 h; [d]runs 12 and 13 were the first and the second re-using of the catalyst separated after run 10.

only for 10% of the mass balance at the end of the 24-hour reaction. A possible explanation for this observation is that, differently from the chloride-free homogeneous system, in the anchored system HCl can be released during the formation of catalytically active species from the rhodium precursor and this acid will favor the acetalization step.

After run 10 the catalyst was recovered and used two more times (Table 2, runs 12 and 13). In both recycles, eugenol was completely transformed into the hydroformylation products in 24 h (ca. 90% acetals) at nearly the same rate and with similar selectivity as in the original reaction.

The catalyst is also useful to other naturally occurring allyl benzene, i.e., estragole **1b** (Table 2, run 14). The reaction was also nearly completed in 24 h giving hydrofomylation products in 99% selectivity, albeit with slightly lower relative amounts of the corresponding acetals (71%).

Isoeugenol (**2a**) was also tested under the hydroformylation conditions in methanol solutions (Table 2, run 15). The rate of the conversion of this internal olefin was very low: only 9% of the substrate was converted in 24 h. Moreover, most of the converted substrate was transformed into the terminal isomer, eugenol **1a**. The latter yielded aldehydes **4a** and **5a** and corresponding acetals **4'a** and **5'a**. Aldehyde **6a** (Scheme 1), one of the expected product of the direct hydroformylation of **2a**, was not observed at all. This result shows that the catalyst can be used for the selective hydroformylation of allyl benzenes, even in the presence of a large quantity of propenyl benzenes.

Conclusions

A solid catalyst for the hydroformylation of allyl benzenes was prepared in a simple manner by anchoring rhodium(I) complexes to a cheap, commercially available anion-exchange resin through a readily prepared anionic phosphine, i.e., TPPMS. The catalyst can be easily recovered from the reaction mixture and re-used without a significant loss of the activity. The catalyst is also useful for the tandem sequence hydroformylation/acetalization of allyl benzenes in methanol or ethanol solutions, in which the primarily formed aldehydes could be essentially converted to the corresponding acetals in the absence of auxiliary acid co-catalysts.

Acknowledgements

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