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Hydroformylation of styrene catalyzed by a rhodium thiolate binuclear catalyst supported on a cationic exchange resin

J. Balué, J.C. Bayón *

Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Spain

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Abstract

The binuclear complex $[Rh_2(\mu\text{-}S(CH_2)_2NMe_2)_2(cod)_2]$ **1** (cod = 1,5-cyclooctadiene) was anchored to a sulfonic exchange resin through the residual amine groups. The reaction of the immobilized complex with CO and PPh_3 yielded the catalytically active complex $[Rh_2(\mu\text{-}S(CH_2)_2NHMe_2)_2(CO)_2(PPh_3)_2]^{2+}$ supported in the polymer matrix. When methanol was used as solvent, the metal complex loaded cationic resin behaved as a multifunctional catalyst, since it was active in the hydroformylation of styrene and the subsequent formation of the acetals, directly rendering 1,1-dimethoxy-2-phenylpropane in 85% selectivity. Furthermore, the immobilized catalyst can be separated from the reaction mixture and recycled. A homogeneous model of the supported catalyst was generated by reacting complex **1** with HTsO, PPh_3, and CO. Thus, the methanol soluble complex $[Rh_2(\mu\text{-}S(CH_2)_2NHMe_2)_2(CO)_2(PPh_3)_2](TsO)_2$ was also found to be active in the hydroformylation of styrene yielding identical selectivity in the branched isomer to that of the immobilized catalyst, although the latter is much slower (20-fold) than the homogeneous catalyst. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The hydroformylation of olefins is one of the most important industrial processes using a transition metal homogeneous catalyst. Rhodium complexes are the most efficient catalysts for this reaction in terms of both activity and selectivity [1–3]. When continuous distillation of the aldehydes from the reaction is not feasible, different strategies have been attempted to overcome the problem of the recovery of the metal from the reaction products. Water-soluble catalysts have been applied successfully in the hydroformylation of propene at industrial scale, but this approach is less efficient for higher molecular weight alkenes [4]. Molecular catalysts immobilized on different types of support have also been widely explored, since they can combine the advantages of heterogeneous and homogeneous catalysts [5]. Functionalized organic polymers have, perhaps, been the most extensively studied [6]. Cation or anion exchange resins are a special case of this type of support, for which a limited number of reports are found in the literature, concerning the hydroformylation of alkenes. Although non-mod-

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* Corresponding author.

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ified anionic catalysts have been supported on an exchange resin [7], the common approach for binding the catalyst to the ionic group of the resin is generally the use of an ancillary P-donor ligand with the appropriate functionality. Thus, phosphine ligands containing ammonium [8–11] and sulfonate [12] groups have been used to immobilize rhodium hydroformylation catalysts on cationic or anionic exchange resins. There is also an example of a phosphonium–phosphine rhodium complex anchored on a macroreticular cation-exchange resin, but it was only assayed as a hydrogenation catalyst [13].

Rhodium thiolato catalysts of general formula $[Rh_2(\mu\text{-}SR)_2(CO)_2(PR'_3)_2]$ are active in the hydroformylation of 1-alkenes [14]. From the point of view of their chemical modification, these catalysts are attractive, since they have two ligands, namely the thiolato and the P-donor, into which ionic groups can be introduced for the immobilization of the catalysts. Kalck et al. [15] has reported the anchoring of these catalysts to phosphinated polystyrene, and to polystyrene containing thiolate groups [16–18], and has described the performance of these supported catalysts in the hydroformylation of 1-alkenes. Here we report the immobilization of a catalyst containing an ammoniumthiolato ligand supported on a cationic exchange resin group, and its catalytic properties in the hydroformylation of styrene. Furthermore, the results obtained using the immobilized catalyst are compared with those of the homogeneous catalyst with the same molecular structure.

2. Experimental

2.1. General

The rhodium complexes were synthesized using standard Schlenk techniques under nitrogen atmosphere. The loaded exchange resin was manipulated in a vacuum/atmospheres glove box. Solvents were dried, distilled, and deoxygenated before use. $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ and $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ were prepared as previously described in Refs. [19,20]. C, H and N were analyzed using a Carlo-Erba EA-1108 microanalyser. IR spectra were recorded on a Perkin Elmer FT-2000 instrument. ^1H and ^{13}C NMR spectra were obtained on Bruker AC250 and AM400 spectrometers, and chemical shifts were quoted in ppm downfield from internal TMS. ^{31}P NMR were obtained on the same instruments using external 85% H_3PO_4 as reference. UV–visible spectra were performed on a KONTRON UVIKON 860 spectrometer. Hydroformylation reactions were carried out on a magnetically stirred, home-made 80 ml stainless steel autoclave. During the reaction, the syn-gas pressure in the autoclave was kept constant through a regulator feed from a reservoir. The drop in the pressure of the reservoir was used to register the evolution of the reaction. Gas chromatographic analyses were run on a Konik 3000-HRGC apparatus equipped with a Chromosorb-W-HP (5% of OV-17) column (4 m × 2 mm ∅). Data were treated with Millennium software from Waters Chromatography.

2.2. Synthesis of $[Rh_2(\mu\text{-}S(CH_2)_2NMe_2)_2(cod)_2]$: **1**

A solution of K^tBuO (726 mg, 6.5 mmol) and $[HS(CH_2)_2NHMe_2]Cl$ (458 mg, 3.2 mmol) in MeOH (5 ml) was stirred at room temperature for 10 min. This solution was then added to a stirred solution of $[Rh_2(\mu\text{-}Cl)_2(cod)_2]$ (797 mg, 1.62 mmol) in CH_2Cl_2 (5 ml). After 30 min the suspension was evaporated to dryness. The solid was extracted with CH_2Cl_2 (3 × 10 ml) and filtered over kieselguhr. The resulting orange solution was concentrated to 1 ml, and then CH_3CN (20 ml) was added. The solution was cooled to −20°C and a crystalline material (840 mg) was obtained, which was filtered, rinsed with cool CH_3CN (2 × 3 ml) and vacuum dried (yield 82%). Elemental analysis (%), found: C, 45.6; H, 7.2; N, 4.4. Calculated for $C_{24}H_{44}N_2S_2Rh_2$: C, 45.7; H, 7.0; N, 4.4. IR (in KBr, cm^{-1}): 3007 (w), 2990 (w), 2960 (w), 2926 (m), 2871 (m), 2816 (m), 2767 (m). ^{1}H-NMR (CD_2Cl_2, δ): 4.16 (s br, 2H, $=\mathrm{C}H$, cod); 2.41 (m, 2H, $\mathrm{C}H_2$, exo cod); 2.35 (m, 1H, $\mathrm{NC}H_2$); 2.16 (s, 3H, $\mathrm{NC}H_3$); 2.11 (m, 1H, $\mathrm{SC}H_2$); 2.02 (pseudo d, $J = 8$ Hz, 2H, $\mathrm{C}H_2$ endo cod). ^{13}C-NMR (CD_2Cl_2, δ): 79.7 (d, $J_{\mathrm{Rh-C}} = 10$ Hz, $=C\mathrm{H}$, cod); 62.2 ($\mathrm{N}C\mathrm{H}_2$); 45.7 ($\mathrm{N}C\mathrm{H}_3$); 31.9 ($C\mathrm{H}_2$ cod); 23.1 ($\mathrm{S}C\mathrm{H}_2$).

2.3. Synthesis of $[Rh_2(\mu\text{-}S(CH_2)_2NHMe_2)_2(cod)_2](TsO)$: 2

A MeOH (5 ml) solution of $TsOH \cdot H_2O$ (48.3 mg, 0.254 mmol) was added to a stirred solution of **1** (80.0 mg, 0.127 mmol) in MeOH (5 ml). The resulting solution was concentrated to 1 ml, and then EtOEt (10 ml) was added. A yellow oil formed, from which the remaining solution was decanted. The oil was treated twice with toluene (5 ml), and evaporated to dryness. Finally, the oil was dissolved in CH_3CN and precipitated with EtOEt, yielding a very hygroscopic yellow solid, which was rinsed with EtOEt and characterized spectroscopically. IR (in KBr, cm^{-1}): 3013 (m), 2921 (m), 2873 (m), 2827 (m), 2713 (w), 1220 (sh), 1193 (s), 1123 (m), 1034 (m). ^{1}H-NMR (CD_3OD, δ): 7.71, 7.25 (d, $J = 8$ Hz, 4H, aromatic); 4.27 (s br, 4H, $=\mathrm{C}H$ cod); 3.19 (pseudo t, $J = 8$ Hz, 2H, $\mathrm{NC}H_2$); 2.85 (s, 6H, $\mathrm{NC}H_3$); 2.45 (m, 4H, $\mathrm{C}H_2$ exo cod); 2.39 (t, $J = 8$ Hz, 2H, $\mathrm{SC}H_2$); 2.37 (s, 3H, $\mathrm{PhC}H_3$); 2.08 (pseudo d, $J = 8$ Hz, 4H, $\mathrm{C}H_2$ endo cod). ^{13}C-NMR (CD_3OD, δ): 143.5, 141.8, 129.9, 127.0 (aromatic), 81.8 (br, $=C\mathrm{H}$ cod), 60.1 ($\mathrm{N}C\mathrm{H}_2$); 43.6 ($\mathrm{N}C\mathrm{H}_3$), 32.4 ($C\mathrm{H}_2$ cod), 21.4 ($\mathrm{Ph}C\mathrm{H}_3$), 20.0 ($\mathrm{S}C\mathrm{H}_2$).

2.4. Synthesis of $[Rh_2(\mu\text{-}S(CH_2)_2NHMe_2)_2(CO)_4](TsO)_2$: 3

The complex was generated in solution for spectroscopic analysis. Thus, complex **1** (115 mg, 0.182 mmol) and $HTsO \cdot H_2O$ (69.7 mg, 0.364 mmol) were dissolved in CH_2Cl_2. The solution was saturated with carbon monoxide and stirred for 1 h, and its IR spectrum was then recorded. For the NMR spectra, d_4-methanol was used instead of CH_2Cl_2. IR (in CH_2Cl_2, cm^{-1}): 2085 (m), 2065 (s), and 2018 (s). ^{1}H-NMR (CD_3OD, δ): 7.72, 7.26 (d, $J = 8$ Hz, 4H, aromatic), 3.45 (m, 2H, $\mathrm{NC}H_2$), 3.45 (m, 2H, $\mathrm{SC}H_2$), 2.94 (s, 6H, $\mathrm{NC}H_3$), 2.38 (s, 3H, $\mathrm{PhC}H_3$). ^{13}C-NMR (CD_3OD, δ): 184.9 (d, $J_{\mathrm{Rh-C}} = 70$ Hz, CO), 143.3, 141.8, 130.0, 127.0 (aromatic), 59.9 ($\mathrm{N}C\mathrm{H}_2$), 43.9 ($\mathrm{N}C\mathrm{H}_3$), 29.5 ($\mathrm{S}C\mathrm{H}_2$), 21.4 ($\mathrm{Ph}C\mathrm{H}_3$).

2.5. Synthesis of $[Rh_2(\mu\text{-}S(CH_2)_2NHMe_2)_2(CO)_2(PPh_3)_2](TsO)_2$: 4

The complex was generated in solution for spectroscopic analysis. Complex **1** (152 mg, 0.241 mmol), $HTsO \cdot H_2O$ (92.1 mg, 0.484 mmol) and PPh_3 (126.5 mg, 0.482 mmol) were dissolved in CH_2Cl_2 (10 ml). The solution was saturated with carbon monoxide, and its IR spectrum was recorded. An identical spectrum was obtained when syn-gas was used instead of CO. In a separate experiment, the same solids were dissolved in d_4-methanol and again the solution was saturated with CO or syn-gas, and the NMR spectra were then recorded. IR (in CH_2Cl_2, cm^{-1}) 2022 (w), 1949 cm^{-1} (s). ^{1}H-NMR (CD_3OD, δ): 7.75, 7.21 (d, $J = 8$ Hz, 4H, aromatic TsO), 7.89, 7.47 (m br, 15H, aromatic PPh_3), 2.92 (s br, 2H, $\mathrm{NC}H_2$), 2.54 (s br, 6H, $\mathrm{NC}H_3$), 2.31 (s, 3H, $\mathrm{PhC}H_3$), 2.22 (s br, 2H, $\mathrm{SC}H_2$). ^{13}C-NMR (CD_3OD, δ): 189.7 (s br, CO); 143.4, 141.6, 129.8, 126.9 (aromatic TsO), 135.1, 132.9, 129.6, 129.5 (aromatic PPh_3), 60.3 ($\mathrm{N}C\mathrm{H}_2$), 43.3 ($\mathrm{N}C\mathrm{H}_3$), 27.4 ($\mathrm{S}C\mathrm{H}_2$), 21.4 ($\mathrm{Ph}C\mathrm{H}_3$). ^{31}P-NMR (CD_3OD, δ): 38.7 (d, $J_{\mathrm{Rh-P}} = 157$ Hz); 37.9 (d, $J_{\mathrm{Rh-P}} = 148$ Hz); the intensity of the last doublet was about 25% of the first.

2.6. Anchoring of $[Rh_2(\mu\text{-}S(CH_2)_2NMe_2)_2(cod)_2]$ to the cationic exchange resin: 2P

Amberlite IR-118H (Sigma-Aldrich) is a polystyrene polymer, cross-linked with 4.5% of *p*-divinylbenzene, and containing 5.0 mmol of sulfonic groups per g of dry material. The commercial resin in acid form was pretreated as follows. A sample of the wet resin (20 ml) was rinsed in MeOH (3 × 30 ml). The remaining soluble material of the resin was then extracted in a Soxhlet for 24 h, with further MeOH (60 ml). The exchange resin was dried at 60°C under vacuum and stored in a glove box. To anchor the complex, a 100 ml Schlenk flask was loaded in a glove box with complex **1** (200 mg, 0.317 mmol) and cationic resin (1.522 g, 7.61 mmol SO_3H). The flask was then removed from the glove box, and dry MeOH was added (50 ml). The suspension was stirred for 2 h with a flow of N_2 saturated with MeOH. After this time, the nearly colorless solution was removed with a cannula. The loaded exchange resin was rinsed in MeOH (3 × 10 ml), extracted for 24 h with a Soxhlet in an inert atmosphere with MeOH (50 ml), and finally dried under vacuum at 40°C. The dried material was handled and stored in a glove box, since it becomes dark in a few seconds on exposure to air.

2.7. Anchoring of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$ to the cationic exchange resin

The same procedure used for **2P** was used, replacing complex **1** by 155 mg (0.32 mmol) of $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$.

2.8. Reaction of **2P** with CO: **3P**

An autoclave was charged with 100 mg of **2P** (equivalent to 0.0182 mmol of the binuclear complex) and 16 ml of MeOH. It was then pressurized at 4 bar with CO for 16 h, while the temperature was kept at 80°C. The suspension was removed from the autoclave, filtered, and the resin was dried under vacuum. A sample of the reacted resin was dispersed in paraffin mull, and its IR spectrum was recorded. The same spectrum was obtained when syn-gas (7 bar) was used instead of carbon monoxide. IR (paraffin mull, cm^{-1}): 2084 (w), 2063 (s), 2012 (s).

2.9. Reaction of **2P** with CO and PPh_3: **4P**

The same conditions as in the previous experiment were used, but PPh_3 (121 mg, 0.460 mmol) was added to the reaction mixture. IR (paraffin mull, cm^{-1}): 2011 (w), 1977 (s, br).

2.10. Analysis of the Rh in the resin and in the hydroformylation solution

A method adapted from that described by Beamish [21] was used. A sample of the resin containing about 1 mg of rhodium was treated with 5 ml of concentrated HNO_3, 10 ml of concentrated HCl, and 5 ml of water. The mixture was heated at reflux temperature for 2 h, or until the nitrous vapor disappeared. When the suspension had cooled, the solid was filtered off and washed in 10 ml of water. The filtrate (containing the metal in a soluble form) was evaporated to dryness, treated with 10 ml of concentrated HCl, and again evaporated to dryness. The residue was dissolved in 5 ml of water and then mixed with 10 ml of an aqueous solution of $SnCl_2$ (59.5 g of $SnCl_2 \cdot 2H_2O$ and 80 ml of concentrated HCl in 500 ml). The resulting solution was heated in a water bath for 1 h, and 2 M HCl was added to a total volume of 25 ml. Finally, the absorbance of the solution at 475 nm was measured.

To analyze the rhodium leached in a catalytic experiment, the solution was separated from the resin by filtration with a PTFE membrane, and the methanolic solution was evaporated under vacuum. One milliliter of concentrated HCl was then added to the residue. The resulting mixture was evaporated to dryness and treated as in the analysis of rhodium in the resin.

The standard curve was prepared with samples of complex **1**, and it shows a linear range between 0.01 and 3 mg of rhodium in the sample. Furthermore, it was checked that the resin did not interfere with the method.

2.11. Hydroformylation experiments

2.11.1. Heterogeneous

In a typical experiment, the autoclave and its glass container were dried and placed in a glove box. The autoclave was then loaded with the resin and the magnetic bar, closed, and removed from the glove box. The autoclave was connected to the gas system and evacuated. In a Schlenk flask, a solution was prepared with the PPh_3 and the styrene (filtered on neutral activated aluminum oxide) dissolved in MeOH. The solution was injected into the autoclave, and then pressurized with syn-gas to 6 bar. The pre-heated water jacket circuit was then opened, and after 5 min the pressure was adjusted to 8 bar, while the magnetic stirring was connected. After the desired reaction time, the autoclave was cooled and the syn gas was replaced by N_2 at 1 bar. The water jacket was dried and the autoclave was returned to the glove box, and then opened. The resin was filtered from the mixture, washed in MeOH, and then re-loaded into the autoclave for the next experiment.

2.11.2. Homogeneous

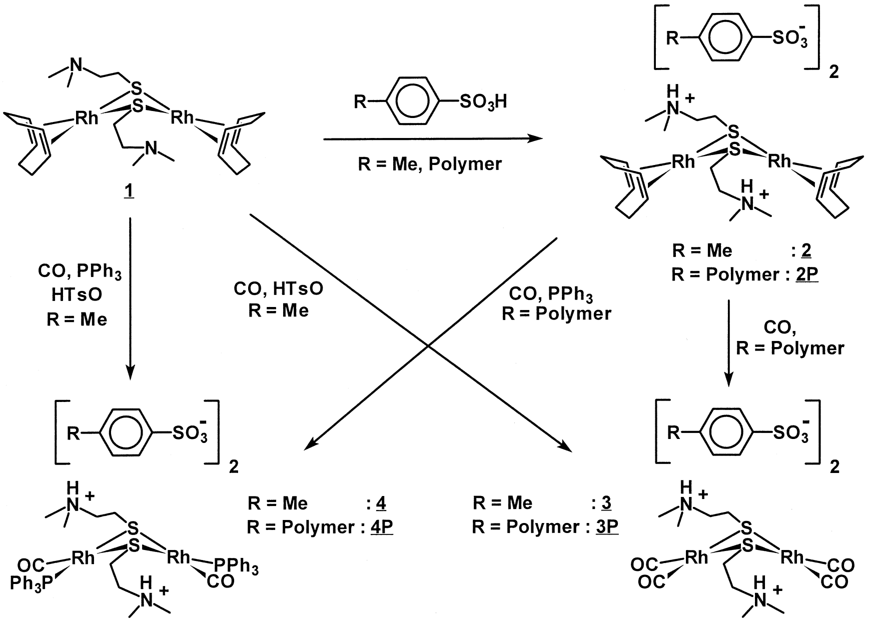
A similar procedure was used, except that the soluble catalyst was added to the solution containing the substrate and PPh_3.

2.11.3. Product analysis

The reaction mixture was analyzed by ^1H-NMR, ^{13}C-NMR and GC, and the retention time of the products (ethylbenzene, 2-phenylpropanal and 3-phenylpropanal) was compared with that of commercial samples. The corresponding methyl acetals were synthesized as follows and fully characterized by ^1H-NMR and ^{13}C-NMR.

2.12. Dimethylacetals of 2- and 3-phenylpropanal: **7**, **8**

The cationic exchange resin (500 mg) Amberlite IR-118H was added to a MeOH solution (25 ml) of the corresponding aldehyde (1 g). The mixture was heated in the autoclave at 80°C, which reproduces the conditions in which the acetals form during the hydroformylation.



Scheme 1.

After 16 h, the resin was filtered, and the crude was evaporated under vacuum with 10 ml of benzene. The residue was purified by chromatography on silica (EtOEt/petroleum ether: 1/5). Yield was 75%.

3. Results and discussion

3.1. Synthesis and characterization of the catalysts

The complex $[Rh_2(\mu\text{-}S(CH_2)_2NMe_2)_2(cod)_2]$ **1** (cod = 1,5-cyclooctadiene) was obtained using the procedure reported for a closely related complex [22]. Spectroscopic characterization of **1** revealed its binuclear structure, and that the nitrogen atoms are not involved in the coordination sphere of the metal.

A sulfonic exchange resin Amberlite IR-118H was used to anchor complex **1**. This resin efficiently swells in methanol, both in the acid form, and also when the metal complex is bound. Thus, methanol was used for the anchoring process and for the catalytic experiments.

A sketch of the reactions carried out is shown in Scheme 1.

When complex **1** was added to a suspension of the cationic exchange resin in MeOH, stirred with a N_2 flow, the solvent initially became bright yellow, but this color soon fades. The polymer darkened and after 2 h it was filtered, exhaustively washed, and dried in anaerobic conditions. The supported complex **2P** is air sensitive, especially when dry, and it was handled in a glove box. Complex **1** was also reacted with *p*-toluenesulfonic acid (HTsO) to yield the cationic complex $[Rh_2(\mu\text{-}S(CH_2)_2NHMe_2)_2(cod)_2](TsO)_2$ **2**, which is the homo-

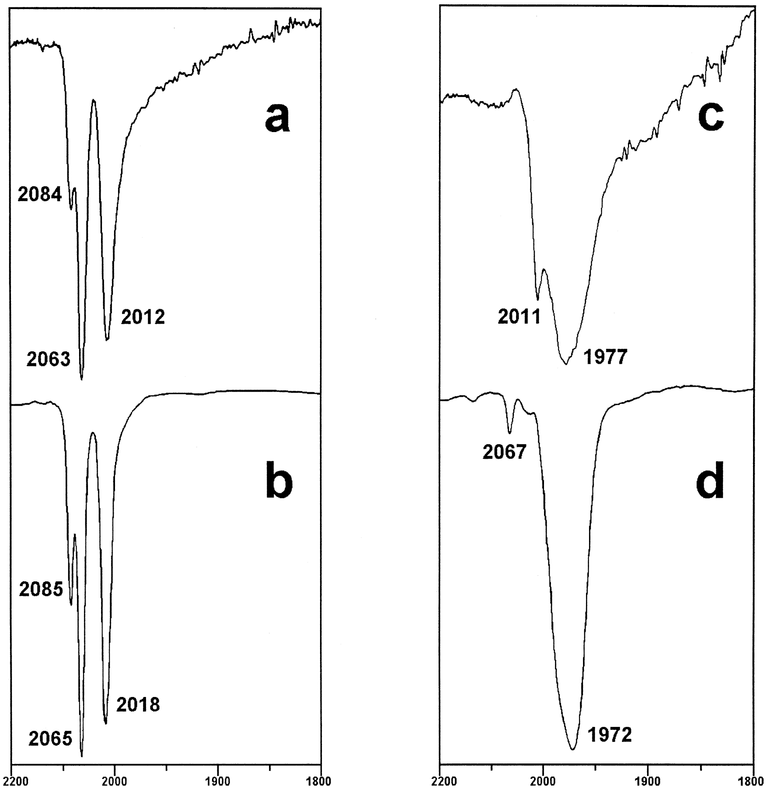


Fig. 1. Carbonyl region of the IR spectra for: (a) supported complex **3P**; (b) soluble complex **3**; (c) supported complex **4P**; (d) soluble complex **4**.

Table 1
Hydroformylation of styrene with a recycled sample of the supported catalyst, using the stoichiometric amount of PPh_3 with respect to metal complex

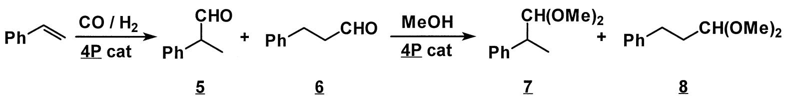
Run	Conversion (%)[a]	Chemoselectivity (%)[b]	Selectivity (%)[c]
1	8	98	83
2	7	98	85

[a] Measured as % of styrene reacted.
[b] % Acetals formed with respect of the styrene reacted. The only side product is ethylbenzene.
[c] Selectivity in branched acetal **7**.
Reaction conditions: 10 mmol of styrene; 0.025 mmol of anchored binuclear catalyst as **2P**; PPh_3: 0.1 mmol in run 1 and 0.05 mmol in run 2; 16 ml of MeOH; $P = 8$ bar; $[CO]/[H_2] = 1$; time = 16 h; $T = 80°C$.

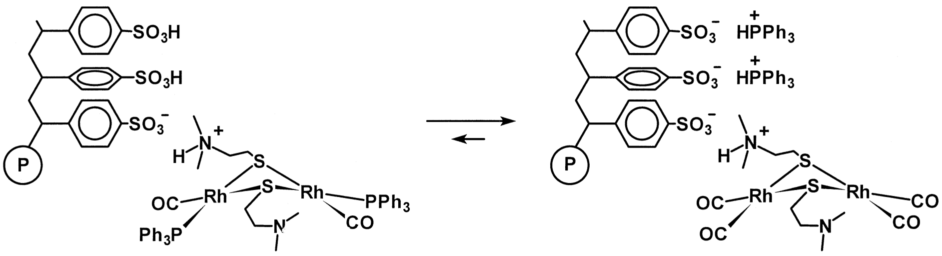
geneous version of the anchored species **2P**. Complex **2** was characterized spectroscopically, showing that the binuclear structure was retained in the reaction with HTsO, while the amine group was protonated.

To demonstrate that the binuclear structure is preserved in **2P**, samples of the supported complex were reacted with CO, and with CO and PPh_3. The carbonyl regions of the infrared spectra of the resulting supported species were used as a probe to investigate the structure of the polymer supported species. To this end, the infrared spectra of the carbonylic supported species were compared with those of the homologous soluble species, the structure of which was unequivocally established through NMR spectroscopy. Thus, a suspension of **2P** was reacted with CO, and the solid-state infrared spectrum of the carbonylated sample **3P** was recorded as a paraffin mull. The carbonyl region of the spectrum is shown in Fig. 1a. The reaction of the soluble complex **1** with CO, in the presence of the stoichiometric amount of HTsO, yields the cationic binuclear complex $[Rh_2(\mu\text{-}S(CH_2)_2NHMe_2)_2(CO)_4](TsO)_2$ **3**, which was characterized spectroscopically. Fig. 1b shows the carbonyl region of the infrared spectrum of **3**, which reveals the classical pattern for binuclear folded tetracarbonyl species [23,24]. Since the relative intensity and the position of the three bands are identical to those observed for the supported carbonylic complex **3P**, the same binuclear structure has to be inferred for both species. In a similar experiment, a sample of **2P** was treated with a large excess of PPh_3 in MeOH, under CO pressure. The solid-state infrared spectrum of the resulting anchored complex **4P** is shown in Fig. 1c. Fig. 1d corresponds to the complex $[Rh_2(\mu\text{-}S(CH_2)_2NHMe_2)_2(CO)_2(PPh_3)_2](TsO)_2$ **4**, which is a mixture of the *trans*- and *cis*-isomers, although the first is the major specie. Complex **4** was generated by bubbling CO through a mixture of **1**, and the stoichiometric amount of HTsO and PPh_3. Again, the infrared spectra of the two related complexes evidenced the same binuclear structure for the soluble and supported species.

The rhodium content of several samples of **2P** was analyzed. The average value obtained was 0.18 ± 0.02 mmol of binuclear complex per g of loaded resin. Since the resin also contains 5 mmol of sulfonic groups per g, only a small fraction of the acid groups were used as binding groups. Obviously, not all the cavities in the matrix polymer containing sulfonic groups are accessible to the large dinuclear complex. Furthermore, during the anchoring process, additional cross-linking may be produced in the polymeric structure when both amino groups of the complex are protonated. For this reason, the content of the metal in the polymer varies within a narrow range, far below the theoretical saturation ratio.



Scheme 2.



Scheme 3.

3.2. Catalytic results

Table 1 shows the results of the hydroformylation of styrene in MeOH catalyzed by a sample of the supported catalytic precursor **2P**. The active species **4P** was generated in situ, under the syn-gas of the autoclave, by the addition of a small excess of PPh_3. After run 1, the solid catalyst was filtered and reused following the addition of fresh styrene and PPh_3. Interestingly, the products of the reaction are the methyl acetals **7** and **8** of the corresponding aldehydes **5** and **6**, respectively. Thus, in the reaction conditions, the free sulfonic acid groups of the resin catalyzed the acetalization of the aldehydes, as is shown in Scheme 2.

The direct synthesis of acetals in hydroformylation reactions is well established. Both Lewis [25] and protic acid [26,27] catalysts have been used, but in both cases $HC(OEt)_3$ was the source of the alkoxy groups. In our study, a multifunctional system [28–31] catalyses the consecutive hydroformylation and acetalization reactions owing to the presence of two different functionalities: the anchored rhodium thiolato complex and the acidic HTsO or triphenylphosphonium derivative.

The solution was analyzed for the rhodium leached. Less than 1% of the total metal was detected in solution, after 16 h of reaction. However, the catalyst was barely active, since only 0.05 mmol of styrene were converted per hour. This corresponds to 2 catalytic turns per binuclear catalyst per hour, assuming that all the metal present in the polymer is active. Furthermore, as shown below, in these experiments the leached metal accounts for a large part of the styrene converted. As expected for a rhodium catalysts, the system was highly chemoselective ($> 98\%$) and the regioselectivity in the branched acetal was around 85% in both runs.

The infrared spectrum of the catalyst after use revealed that the most of the binuclear complex is in the form of the tetracarbonyl species **3P**, although a slight excess over the stoichiometric amount of PPh_3 was used in the catalytic reactions. The most plausible explanation for this result is that the sulfonic groups compete with the metal complex for the PPh_3, as shown in Scheme 3. [1] Since the tetracarbonyl complexes are known to be inactive [17,18], the conversions obtained are consistently low.

Therefore, a new set of catalytic experiments was designed, in which the catalytic precursor **2P** was first reacted under syn-gas with sufficient PPh_3 to guarantee that all the sulfonic groups were blocked, and that there was a surplus of free phosphine to form the active catalyst **4P**. The same sample was recycled in a number of experiments to check the stability of the catalytic system. At the end of each experiment, the supported catalyst was filtered from catalytic solution, and reused following addition of a solution containing fresh olefin, together with a small amount of PPh_3 ($[PPh_3]/\mathbf{4P}_{eq} = 2$) in order to shift the equilibrium to the active carbonyl phosphine complex **4P**. The results are shown in Table 2. The acetals were also pro-

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[1] The values of pK_a for TsOH and $[HPPh_3]^+$ are 0.7 and 2.9, respectively, which indicates that the K for the acid–base reaction is $\approx 10^2$.

duced in the reaction, showing either that the phosphonium sulfonate groups of the resin were acidic enough to catalyze the acetalization reaction, or that some catalytically active free sulfonic acid groups remained in the polymer matrix, which may not be accessible to the relatively bulky phosphine. In all the experiments, the regioselectivity was nearly constant, reaching values of about 89% in the branched acetal **7**. Furthermore, the rhodium leaching was determined in most of the experiments, being in all cases around 1% of the total metal initially anchored. Working at constant reaction time (16 h), the conversions increased in each run. Since the polymer was mechanically degraded by the stirring system of the autoclave, the improvement in the activity of the system is may be due to the higher area surface of the reused supported catalysts exposed to the solution. This result indicates that the overall reaction rate is controlled by the diffusion of the reagents to the active sites of the cationic resin.

Table 2
Hydroformylation of styrene with a recycled sample of the supported catalyst, using a large excess of PPh_3 (see text)

Run	Conversion (%)[a]	Selectivity (%)[b]	Leaching (%)[c]
3	55	89	1.5
4	70	88	n.d.[d]
5	60	88	1.5
6	68	89	n.d.
7	82	89	n.d.
8	87	89	0.82
9	92	89	0.41
10	99	88	0.68

[a] Acetals formed as % of the initial styrene; ethylbenzene formed was always less than 2%.

[b] Selectivity in the branched acetal **7** as % of the total acetals formed.

[c] Expressed as % of initial metal supported in the resin.

[d] Not determinated.

Reaction conditions: 10 mmol of styrene; 0.025 mmol of anchored binuclear catalyst as **4P**; 0.05 mmol of PPh_3; 16 ml of MeOH; $P = 8$ bar; $[CO]/[H_2] = 1$; time = 16 h; $T = 80°C$.

For comparative purposes, the related homogeneous catalyst **4** was assayed in the same conditions as the supported catalyst. In this case, the catalyst was also generated in situ from complex **1**, PPh_3 and HTsO, under syn-gas. The results are collected in Table 3.

Runs 11 and 12 show that the homogeneous catalyst produced similar selectivities to the anchored form, although it is about 20 times faster than the supported one. In these cases, aldehydes are the reaction products since the system is not acidic enough to catalyze the acetal formation. Run 13 shows that the tetracarbonylic complex **3** formed in these conditions is practically inactive. Runs 14 to 18 tried to simulate the ratio of sulfonic groups vs. metal present in the resin. In homogeneous conditions, and in the presence of large excesses of $(HPPh_3)(TsO)$, the system was not active. These results indicate

Table 3
Hydroformylation of styrene with soluble catalytic precursor **2**

Run	$[PPh_3]/[\mathbf{2}]$	$[HTsO]/[\mathbf{2}]$	Conversion (%)[a]	Products	*t* (h)	Selectivity (%)[b]
11	2	2	99	aldehydes	0.7	84%
12	4	2	96	aldehydes	0.8	91%
13	0	2	0.7	aldehydes	4	64%
14	2	25.2	0	–	4	–
15	12.6	25.2	0	–	4	–
16	19.7	25.2	0	–	4	–
17	25.2	25.2	0	–	4	–
18	27.2	25.2	0	–	4	–
19[c]	2	2	9	aldehydes	16	81%

[a] Products formed as % of the initial styrene; ethylbenzene formed was always less than 0.2%.

[b] Selectivity in the branched aldehyde **5** or acetal **7** as % of the total acetals formed.

[c] An amount of 0.0004 mmol of catalytic precursor **2** were used to simulate the amount of metal leached in heterogeneous experiments (see text).

Reaction conditions: 10 mmol of styrene; 0.025 mmol of catalytic precursor **2**; 16 ml of MeOH; $P = 8$ bar; $[CO]/[H_2] = 1$; $T = 80°C$.

that the acid protonates the phosphine, thus shifting the equilibrium to the inactive tetracarbonyl complex **3** or **3P**. Although there was a certain amount of non-protonated PPh_3 in runs 17 and 18, these catalytic systems were not active. The results suggest an interaction between the *p*-toluenesulfonate anions and the metal, similar to the effect of bromide anion previously observed in these catalysts [32]. In contrast, a matrix isolation effect [6] in the supported system prevents any contact between the rhodium and the sulfonate groups of the resin. Finally, run 19 simulates the hydroformylation of the rhodium leached during the reaction. Therefore, the amount of catalyst used was reduced to 1.5% of that previously used for either homogeneous or heterogeneous experiments, while the other reaction conditions were the same. Thus, the olefin catalyst/molar ratio was about 30,000. After 16 h, the conversion was only 9%. This value may be taken as the maximum contribution of the leached complex to the conversion observed in the supported catalyst. However, this limit is conservative, since all the leached metal complex may not have been present at the beginning of the reaction, as was the case in this homogeneous catalytic experiment.

Finally, to corroborate the crucial role of the aminothiolato ligand in this catalytic system, a comparative experiment was carried out in which complex **1** was replaced by $[Rh_2(\mu\text{-}OMe)_2(cod)_2]$. This complex was anchored to the cationic exchange resin, and tested as a catalyst in the conditions described in Table 1. In the first run most of the rhodium was leached from the resin, and the selectivity in the branched acetal **7** was 58%. Both results clearly reveal the distinct nature of this catalytic system and that containing the aminothiolato ligand.

4. Conclusions

The supported catalyst **4P** behaves as an immobilized form of the homogeneous catalyst **4** for hydroformylation of styrene. Furthermore, the loaded cationic resin acts as a multifunctional catalyst, since it also converts the hydroformylation products to the corresponding acetals. The supported catalyst can be recycled with very low leaching of metal without loss of selectivity or activity. The major drawback for this new system is that it is much slower than the homogeneous catalyst with the same molecular structure.

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