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Phosphino-functionalised acetals of polyvinyl alcohol as the matrix for the immobilisation of Rh-based pre-catalysts for interfacial catalysis☆

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Abstract

Use of polyvinyl alcohol (PVA) to support the immobilisation of phosphines shall be presented. Phosphino functionalisation is introduced in the polymer by a one-step transacetalation reaction and high acetalation degrees are reached. By complexation of the phosphino groups to a [(COD)RhCl] complex fragment, [Rh]-modified polymers are obtained with Rh contents of higher than 15% and the transition metal in a defined molecular environment. The phosphino or [Rh]-modified PVAs are characterised unambiguously by comparing their spectroscopic data with those of model compounds, the syntheses of which are reported as well. Use of the [Rh]-modified polymers as pre-catalysts will be presented with the hydroformylation of 1-octene being taken as an example. It leads to a selectivity in the product distribution that is identical to that of the model complexes. Recycling experiments were performed and the catalyst rest state on the polymer was identified after 10 consecutive runs. Adsorption of the [Rh]-modified PVA on an inorganic support leads to the formation of stable polymer layers on its surface, which cannot be mobilised by extraction with organic solvents. The stability of these layers, together with their tuneable polarity, allow for their application in interfacial catalysis comparable to SAPC or SILC.

Keywords: Polyvinyl alcohol; Acetalation; Phosphine; Immobilisation; Interfacial catalysis

1. Introduction

Modern development of catalysis involves the aspects of green chemistry [1] and sustainability [2] or responsible care [3]. This includes the development of new processes that were originally based on homogeneous systems as well as catalysts recycling. The best-known examples of catalyst recycling based on a simple phase separation technology with the utilisation of a polar phase and the dissolution of the catalyst are the SHOP process [4] and the Ruhrchemie–Rhône–Poulenc process for the hydroformylation of propene [5]. For the hydroformylation of longer-chain olefins the Ruhrchemie–Rhône–Poulenc process is not applicable because of the high polarity of the aqueous catalyst phase, which leads to a reduced olefin solubility and, hence, to a small substrate/catalyst contact. This eventually decreases the reaction rates.

This problem could be solved by the application of phases, where the catalyst is immobilised in a stationary phase with a tuneable polarity. It was therefore proposed to use polyvinyl alcohol (PVA) as the matrix for the immobilisation of catalysts (Fig. 1). PVA results from the polymerisation of vinyl acetate with subsequent hydrolysis of the ester groups yielding a polymer with 98% of head-to-tail-linked vinyl alcohol units.

PVA itself is a polymer, it is the free hydroxyl groups of which contain a lot of reactive centres which might be funtionalised with donor groups. The most obvious and common approach to functionalising PVA is the transformation of two hydroxyl groups localised in the 3-position into cyclic acetals (Fig. 1) [6]. In their 2-position, these acetals might carry a functionalisation in the form of a spacer to which a donor group can be connected that is eventually binding a catalytically active transition metal fragment. Via the degree of transformation of the hydroxyl groups into 1,3-dioxanes (ratio *n*/*m*, Fig. 1), which can be controlled by the stoichiometry of the reaction, the polarity of the functionalised PVA can be tuned. In this way, even unpolar substrates, such as longer-chain olefins, may enter the polymer material and be catalytically transformed. Adsorption

☆ In memory of Prof. Dr. Birgit Drießen-Hölscher.

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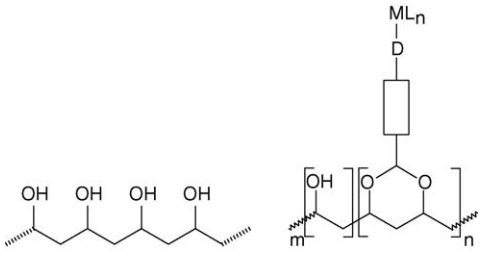


Fig. 1. Schematic view of a representative part of polyvinyl alcohol (left) and of polyvinyl alcohol functionalised by transacetalation (spacer, D: donor function, MLn: transition metal fragment).

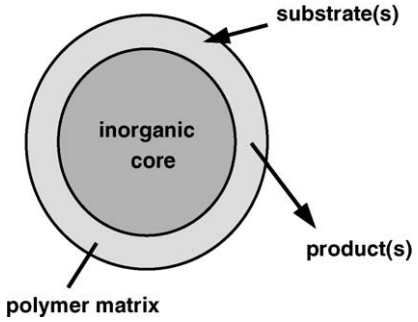


Fig. 2. Schematic view of a PVA layer on the surface of an inorganic support with its possible application as a support in a catalytic reaction, the catalyst being immobilised in the polymer matrix.

of the modified PVA on an inorganic support would lead to an additional heterogenisation of the system with layers of the modified PVA being formed on the surface of the inorganic support. Pre-catalysts prepared in this way could be applied in interfacial catalysis comparable to SAPC [7], SILP [8] or other supported systems (Fig. 2) [9].

Here, it shall be reported about the introduction of phosphino functionalisations in PVA via transacetalation reactions with acetals under the formation of 1,3-dioxanes on the polymer backbone. The coordination of the polymer-bound phosphines to a [(COD)RhCl] complex fragment shall be presented. The polymers will be characterised by comparing their spectroscopic and catalytic behaviour with that of suitable model complexes.

2. Experimental

All reactions were performed in an inert gas atmosphere using standard Schlenk techniques. Chlorodiisopropylphosphine purchased from Aldrich and chlorodiphenylphosphine from Fluka were degassed and stored under an inert atmosphere before use. For the syntheses reported, a PVA with a molecular weight of 22,000 was used. The molecular sieve (5 Å, particle size 2.4–4.8 mm for reasons of better handling) used for coating was purchased from Carl Roth Chemicals. The following chemicals have already been described and were prepared according to literature: $[(COD)RhCl]_2$ [10], $[Rh(CO)_2Cl]_2$ [11], 2-(*para*-bromophenyl)-1,3-dioxane [12], diphenylphosphine [13], *ortho*-(dimethoxymethylphenyl)diphenylphosphine (**1c**) [14], *ortho*-(dimethoxymethylphenyl)diisopropylphosphine (**1d**) [14], 2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxane (**1g**) [15], 2-(*ortho*-diisopropylphosphino-phenyl)-1,3-dioxane (**1h**) [15] and {chloro(COD)[2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxane]rhodium(I)} (**2g**) [15], {chloro(COD)[2-(*ortho*-diisopropylphosphinophenyl)-1,3-dioxane]rhodium(I)} (**2h**) [15]. Solvents were dried and purified by standard methods. NMR spectra were recorded using a 250 MHz Bruker AVANCE or a Varian Unity INOVA 400 MHz spectrometer at 25 °C and referenced to the residual proton signal of the solvent $CDCl_3$ ($\delta = 7.27$ ppm, ^{1}H NMR spectra) or its carbon frequency ($\delta = 77.5$ ppm, $^{13}C\{^1H\}$ NMR spectra) or to H_3PO_4 as external standard ($^{31}P\{^1H\}$ NMR spectra). All non-proton NMR spectra were registered under proton decoupling. The mass spectra were obtained using a Hewlett-Packard LC MSD Serie 1100, ionisation method API-ES from methanol solutions of the compounds containing NH_4OAc. Infrared spectra and FIR spectra were recorded by a Perkin-Elmer 2000 spectrometer. The elemental analyses of solid products were performed using a Vario EL CHN analyser.

For the crystallographic details of the single-crystal X-ray diffraction measurements, see Table 3. The X-ray analyses were performed using a Siemens SMART CCD 1000 diffractometer with an irradiation time of 10–20 s/frame, thus collecting a full sphere of data using an ω-scan technique with $\Delta\omega$ ranging from 0.3 to 0.45°. For searches relating to single-crystal X-ray diffraction data, the Cambridge Structural Database was used [16]. Crystallographic data of the structures have been deposited at the Cambridge Crystallographic Database Centre, supplementary publications nos. CCDC 256144 (**1b**), 256145 (**2b**), 256146 (**2e**), 256147 (**2f**), and 286209 (**3f**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

2.1. Description of the general procedure for the syntheses of the ligands *1*

A bromobenzaldehyde acetal solution in THF reacted at −78 °C with an equimolar amount of BuLi. After stirring for 1 h at −78 °C, an equimolar amount of the corresponding chlorodiphenyl- or chlorodiisopropylphosphine was added to this solution and the reaction mixture was allowed to warm up to room temperature. After hydrolysis, phase separation, and re-extraction of the aqueous phase with 20 ml dichloromethane, the organic solvents were removed in vacuum. Solid phosphines were purified by recrystallisation, liquids were distilled in vacuum.

2.1.1. Amounts, yields, and spectroscopic data of the ligands *1*

*(p-Dimethoxymethylphenyl)(diphenyl)phosphine, **1a***:
12.27 g (53 mmol) 4-bromobenzaldehydedimethylacetal in 200 ml THF. Yield: 8.250 g (25 mmol, 46%) **1a** in the form of a colourless liquid with a bp of 190 °C at 1×10^{-5} mbar.

IR (KBr, cm^{-1}): 3070 (m), 3052 (m), 2951 (s), 2932 (s), 2828 (s), 1585 (m), 1479 (s), 1464 (m), 1434 (ss), 1395 (m), 1350 (s),

1103 (ss), 1089 (ss), 1055 (ss), 1027 (m), 998 (m), 811 (s), 744 (ss), 696 (ss), 505 (s).

^{1}H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 3.35 (s, 6H, CH_3), 5.39 (s, 1H, CHO_2), 7.32–7.45 (m, 14H, Ar).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = −5.3 (s).

^{13}C NMR (63 MHz, $CDCl_3$, 300 K): δ (ppm) = 52.9 (s, 2C, OCH_3), 103.1 (s, 1C, CHO_2), 126.8–138.6 (m, 18C, Ar).

MS (*m*/*z*, %): 336 ($C_{21}H_{21}O_2P^+$, 97%), 305 ($C_{20}H_{18}OP^+$, 76%), 290 ($C_{19}H_{15}OP^+$, 31%), 183 ($C_{12}H_8P^+$, 100%), 108 ($C_6H_5P^+$, 25%).

(p-Dimethoxymethylphenyl)(diisopropyl)phosphine, ***1b***: 12.27 g (53 mmol) 4-bromobenzaldehydedimethylacetal in 200 ml THF. Yield: 11.72 g (44 mmol, 83%) **1b** in the form of a colourless liquid with a bp of 130 °C at 1 mbar.

IR (KBr, cm^{-1}): 3076 (w), 2986 (m), 2950 (s), 2928 (s), 2866 (s), 2828 (s), 1563 (w), 1464 (s), 1445 (s), 1396 (s), 1382 (s), 1362 (s), 1350 (s), 1103 (ss), 1057 (s), 811 (s), 661 (s), 609 (s), 547 (m), 534 (m), 501 (m).

^{1}H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.71 (dd, ^3J (H,H) = 6.9 Hz, ^3J (H,P) = 11.3 Hz, 6H, CH_3), 0.88 (dd, ^3J (H,H) = 6.9 Hz, ^3J (H,P) = 15.2 Hz, 6H, CH_3), 1.91 (sept, ^3J (H,H) = 6.9 Hz, 2H, PCH), 3.14 (s, 6H, OCH_3), 5.19 (s, 1H, CHO_2), 7.21–7.31 (m, 4H, Ar).

^{31}P NMR (162 MHz, $CDCl_3$, 300 K): δ (ppm) = 11.2 (s).

^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 18.6 (d, ^2J (C,P) = 8.6 Hz, 2C, CH_3), 19.8 (d, ^2J (C,P) = 18.4 Hz, 2C, CH_3), 22.7 (d, ^1J (C,P) = 11.5 Hz, 2C, PCH), 52.8 (s, 2C, OCH_3), 103.1 (s, 1C, CHO_2), 126.0–138.6 (m, 6C, Ar).

MS (*m*/*z*, %,): 268 ($C_{15}H_{25}O_2P^+$, 53%), 237 ($C_{14}H_{22}OP^+$, 33%), 195 ($C_{11}H_{16}OP^+$, 100%), 183 ($C_9H_{12}O_2P^+$, 38%), 152 ($C_8H_9OP^+$, 62%).

2-(para-Diphenylphosphinophenyl)-1,3-dioxane, ***1e***: 6.79 g (27.9 mmol) 4-(1,3-dioxane-2-yl)bromobenzene in 50 ml THF. Yield: 5.74 g (16.5 mmol, 59%) of colourless **1e**, with mp of 81 °C.

IR (KBr, cm^{-1}): 3068 (m), 3046 (m), 2972 (s), 2951 (m), 2922 (m), 2856 (s), 1605 (m), 1584 (m), 1572 (w), 1477 (s), 1466 (m), 1437 (s), 1434 (s), 1376 (s), 1148 (s), 1101 (s), 1087 (s), 1025 (m), 1020 (m), 821 (s), 745 (s), 696 (s), 553 (s) 508 (s), 491 (s).

FIR (PE, cm^{-1}): 490 (s), 470 (m), 449 (s), 415 (m), 399 (w), 394 (w), 364 (m), 377 (m), 320 (m), 281 (m), 270 (m), 256 (m).

^{1}H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.38 (dpsept, ^2J (H,H) = 13.0 Hz, ^3J (H_{eq},H_{ax}) = 2.0 Hz, ^3J (H_{eq},H_{eq}) = 1.0 Hz, 1H, $(OCH_2)_2CH\mathit{H}_{eq}$), 2.15 (pqt, ^2J (H,H) = 13.0 Hz, ^3J (H_{ax},H_{ax}) = 12.5 Hz, ^3J (H_{ax},H_{eq}) = 5.0 Hz, 1H, $(OCH_2)_2CH\mathit{H}_{ax}$), 3.92 (ptd, ^2J (H,H) = 12.0 Hz, ^3J (H_{ax},H_{ax}) = 12.5 Hz, ^3J (H_{ax},H_{eq}) = 2.0 Hz, 2H, $OCH\mathit{H}_{ax}$), 4.20 (ddd, ^2J (H,H) = 12.0 Hz, ^3J (H_{eq},H_{ax}) = 5.0 Hz, ^3J (H_{eq},H_{eq}) = 1.0 Hz, 2H, $OCH\mathit{H}_{eq}$), 5.43 (s, 1H, CHO_2), 7.19–7.40 (m, 14H, Ar).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = −4.4 (s).

^{13}C NMR (100 MHz, $CDCl_3$, 300 K): δ (ppm) = 26.1 (s, 1C, $(OCH_2)_2\mathit{C}H_2$), 67.8 (s, 2C, OCH_2), 101.8 (s, 1C, CHO_2), 126.4–139.6 (m, 18C, Ar).

MS (*m*/*z*, %): 348 ($C_{22}H_{21}O_2P^+$, 100%), 290 ($C_{19}H_{15}OP^+$, 16%), 262 ($C_{18}H_{15}P^+$, 25%), 183 ($C_{12}H_8P^+$, 48%), 108 ($C_6H_5P^+$, 14%), 87 ($C_4H_7O_2^+$, 6%).

$C_{22}H_{21}O_2P$ (%)—calc.: C 75.85, H 6.08, found: C 75.83, H 6.23.

2-(para-Diisopropylphosphinophenyl)-1,3-dioxane, ***1f***: 4.52 g (18.6 mmol) 4-(1,3-dioxane-2-yl)bromobenzene in 50 ml THF. Yield: 2.18 g (7.8 mmol, 42%) **1f** as colourless liquid with bp of 135 °C at 1 mbar.

IR (CsI, cm^{-1}): 3078 (w), 2962 (ss), 2951 (ss), 2925 (s), 2892 (m), 2865 (ss), 1605 (w), 1563 (w), 1467 (ss), 1428 (m), 1378 (ss), 1362 (m), 1237 (s), 1150 (ss), 1110 (ss), 1089 (m), 1019 (ss), 814 (ss), 661 (m), 610 (m).

FIR (CsI, cm^{-1}): 483 (m), 433 (w), 385 (m), 353 (w).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.87 (dd, ^3J (H,H) = 6.9 Hz, ^3J (H,P) = 11.3 Hz, 6H, CH_3), 1.04 (dd, ^3J (H,H) = 7.0 Hz, ^3J (H,P) = 15.2 Hz, 6H, CH_3), 1.43 (dpsept, ^2J (H,H) = 13.4 Hz, ^3J (H_{eq},H_{ax}) = 2.6 Hz, ^3J (H_{eq},H_{eq}) = 1.3 Hz, 1H, $(OCH_2)_2CH\mathit{H}_{eq}$), 2.08 (dsept, ^3J (H,H) = 7.0 Hz, ^2J (H,P) = 1.7 Hz, 2H, PCH), 2.22 (pqt, ^2J (H,H) = 13.4 Hz, ^3J (H_{ax},H_{ax}) = 12.4 Hz, ^3J (H_{ax},H_{eq}) = 5.0 Hz, 1H, $(OCH_2)_2CH\mathit{H}_{ax}$), 3.97 (ptdd, ^2J (H,H) = 10.5 Hz, ^3J (H_{ax},H_{ax}) = 12.4 Hz, ^3J (H_{ax},H_{eq}) = 2.6 Hz, ^4J (H_{ax},H_{eq}) = 1.7 Hz, 2H, $OCH\mathit{H}_{ax}$), 4.26 (ddpt, ^2J (H,H) = 10.5 Hz, ^3J (H_{eq},H_{ax}) = 5.0 Hz, ^3J (H_{eq},H_{eq}) = 1.3 Hz, ^4J (H_{eq},H_{ax}) = 1.7 Hz, 2H, $OCH\mathit{H}_{eq}$), 5.49 (s, 1H, CHO_2), 7.45–7.46 (m, 4H, Ar).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 12.1 (s).

^{13}C NMR (63 MHz, $CDCl_3$, 300 K): δ (ppm) = 19.0 (d, ^2J (C,P) = 8.0 Hz, 2C, CH_3), 20.1 (d, ^2J (C,P) = 18.4 Hz, 2C, CH_3), 23.1 (d, ^1J (C,P) = 11.5 Hz, 2C, PCH), 26.1 (s, 1C, $(OCH_2)_2\mathit{C}H_2$), 67.8 (s, 2C, OCH_2), 101.8 (s, 1C, CHO_2), 125.8–139.6 (m, 6C, Ar).

MS (*m*/*z*, %): 280 ($C_{16}H_{25}O_2P^+$, 55%), 238 ($C_{13}H_{19}O_2P^+$, 22%), 195 ($C_{10}H_{12}O_2P^+$, 47%), 163 ($C_{10}H_{11}O_2^+$, 15%), 137 ($C_7H_6OP^+$, 25%), 109 ($C_6H_6P^+$, 70%), 87 ($C_4H_7O_2^+$, 53%), 43 ($C_3H_7^+$, 100%).

2.2. Description of the general procedure for the syntheses of the complexes *2*

Half of the stoichiometric amount of $[Rh(COD)Cl]_2$ was added to a solution of the ligands **1** in an appropriate amount of dichloromethane. After stirring for 30 min to 1 h at RT, the solvent was removed in vacuum. The crude products were purified by extraction with diethylether or pentane.

2.2.1. Amounts, yields, and spectroscopic data of the complexes *2*

{Chloro(COD)[(diisopropyl)(para-dimethoxymethylphenyl) phosphin]rhodium(I)}, ***2b***: 1.46 g (5.3 mmol) **1b** in 5 ml dichloromethane. Extraction with pentane for 24 h yields 2.50 g (91%) **2b** in the form of yellow crystals.

IR (KBr, cm^{-1}): 3052 (w), 2981 (m), 2952 (m), 2870 (m), 2831 (m), 1600 (w), 1494 (w), 1473 (m), 1462 (m), 1425 (m),

1380 (m), 1101 (ss), 1052 (ss), 818 (m), 651 (m), 623 (m), 545 (m), 520 (m).

FIR (PE, cm^{-1}): 281 (s), ν (Rh-Cl).

^{1}H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.18 (dd, ^3J (H,H) = 6.9 Hz, ^3J (H,P) = 13.6 Hz, 6H, CH_3), 1.46 (dd, ^3J (H,H) = 7.0 Hz, ^3J (H,P) = 15.5 Hz, 6H, CH_3), 1.86 (m, 2H, CH_2 (COD)), 1.97 (m, 2H, CH_2 (COD)), 2.34 (m, 4H, CH_2 (COD), 2.70 (poct, ^2J (H,P) = ^3J (H,H) = 7.5 Hz, 2H, PCH), 3.22 (s (br), 2H, CH $(COD)_{trans\ to\ Cl}$), 3.35 (s, 6H, OCH_3), 5.36 (s (br), 2H, CH $(COD)_{trans\ to\ P}$), 5.39 (s, 1H, CHO_2), 7.47–7.49 (m, 4H, Ar).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 39.4 (d, ^1J (P,Rh) = 147.0 Hz).

^{13}C NMR (63 MHz, $CDCl_3$, 300 K): δ (ppm) = 18.9 (s, 2C, CH_3), 20.0 (d, ^2J (C,P) = 4.6 Hz, 2C, CH_3), 23.6 (d, ^1J (C,P) = 22.4 Hz, 2C, PCH), 28.6 (s, 2C, CH_2 (COD)), 32.9 (s, 2C, CH_2 (COD)), 53.0 (s, 2C, OCH_3), 70.2 (d, ^1J (C,Rh) = 13.8 Hz, 2C, CH $(COD)_{trans\ to\ Cl}$), 102.7 (s, 1C, CHO_2), 103.1 (dd, ^1J (C,Rh) = 7.5 Hz, ^2J (C,P) = 11.5 Hz, 2C, CH $(COD)_{trans\ to\ P}$), 126.2–139.7 (m, 6C, Ar).

ESI-MS (*m/z*, %): 479 ($C_{23}H_{37}O_2PRh^+$, 100%), 269 ($C_{15}H_{26}O_2P^+$, 9%).

$C_{23}H_{37}ClO_2PRh$ (%)—calc.: C 53.65, H 7.24, found: C 53.70, H 7.24.

{*Chloro(COD)[2-(para-diphenylphosphinophenyl)-1,3-dioxane]rhodium(I)*}, ***2e***: 361 mg (1.0 mmol) **1e** in 5 ml dichloromethane. Extraction for 2 days with diethylether yields 535 mg (0.9 mmol, 86%) **2e** as yellow crystals.

IR (KBr, cm^{-1}): 3050 (w), 2958 (m), 2936 (m), 2917 (m), 2868 (m), 2829 (m), 1481 (m), 1468 (w), 1435 (m), 1377 (m), 1149 (m), 1103 (ss), 1092 (ss), 1018 (m), 814 (m), 748 (m), 698 (ss), 527 (s).

FIR (PE, cm^{-1}): 284 (s), ν (Rh-Cl).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.43 (dpsept, ^2J (H,H) = 13.6 Hz, ^3J (H_{eq},H_{ax}) = 2.5 Hz, ^3J (H_{eq},H_{eq}) = 1.3 Hz, 1H, $(OCH_2)_2HH_{ax}$), 1.88 (m, 2H, CH_2 (COD)), 2.04 (m, 2H, CH_2 (COD)), 2.19 (pqt, ^2J (H,H) = 13.6 Hz, ^3J (H_{ax},H_{ax}) = 12.4 Hz, ^3J (H_{ax},H_{eq}) = 4.9 Hz, 1H, $(OCH_2)_2CHH_{ax}$), 2.37 (m, 4H, CH_2 (COD)), 3.11 (s (br), 2H, CH $(COD)_{trans\ to\ Cl}$), 3.96 (ptdd, ^2J (H,H) = 10.8 Hz, ^3J (H_{ax},H_{ax}) = 12.4 Hz, ^3J (H_{ax},H_{eq}) = 2.5 Hz, ^4J (H_{ax},H_{eq}) = 1.1 Hz, 2H, $OCHH_{ax}$), 4.24 (dd, ^2J (H,H) = 12.5 Hz, ^3J (H_{eq},H_{ax}) = 5.0 Hz, 2H, $OCHH_{eq}$), 5.49 (s, 1H, CHO_2), 5.55 (s (br), 2H, CH $(COD)_{trans\ to\ P}$), 7.35–7.78 (m, 14H, Ar).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 31.5 (d, ^1J (P,Rh) = 149.8 Hz).

^{13}C NMR (63 MHz, $CDCl_3$, 300 K): δ (ppm) = 26.15 (s, 1C, $(OCH_2)_2CH_2$), 29.3 (s, 2C, CH_2 (COD)), 33.5 (s, 2C, CH_2 (COD)), 67.8 (s, 2C, OCH_2), 71.1 (d, ^1J (C,Rh) = 13.8 Hz, 2C, CH $(COD)_{trans\ to\ Cl}$), 101.3 (s, 1C, CHO_2), 105.5 (d, ^1J (C,Rh) = 5.2 Hz, 2C, CH $(COD)_{trans\ to\ P}$), 126.0–140.9 (m, 18C, Ar).

ESI-MS (*m/z*, %): 559 ($C_{30}H_{33}O_2PRh^+$, 100%), 349 ($C_{22}H_{22}O_2P^+$, 11%).

$C_{30}H_{33}ClO_2PRh$ (%)—calc.: C 60.57, H 5.59, found: C 59.41, H 5.89.

{*Chloro(COD)[2-(para-diisopropylphosphinophenyl)-1,3-dioxane]rhodium(I)*}, ***2f***: 447 mg (1.6 mmol) **1f** in 5 ml dichloromethane. Extraction with pentane for 24 h yields 643 mg (1.2 mmol, 76%) **2f** in the form of yellow crystals.

IR (KBr, cm^{-1}): 3056 (w), 2970 (m), 2960 (m), 2952 (m), 2930 (m), 2913 (m), 2867 (m), 2836 (m), 1523 (w), 1475 (m), 1463 (m), 1434 (m), 1424 (m), 1382 (m), 1377 (m), 1366 (m), 1235 (s), 1152 (s), 1104 (ss), 1017 (ss), 821 (m), 653 (m), 629 (m), 537 (s).

FIR (PE, cm^{-1}): 283 (ss), ν (Rh-Cl).

^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.14 (dd, ^3J (H,P) = 13.6 Hz, ^3J (H,H) = 7.0 Hz, 6H, CH_3), 1.44 (dd, ^3J (H,P) = 15.7 Hz, ^3J (H,H) = 7.2 Hz, 7H, CH_3, $(OCH_2)_2CHH_{eq}$), 1.80 (m, 2H, CH_2 (COD)), 1.93 (m, 2H, CH_2 (COD)), 2.24 (pqt, ^2J (H,H) = 13.6 Hz, ^3J (H_{ax},H_{ax}) = 12.4 Hz, ^3J (H_{ax},H_{eq}) = 4.9 Hz, 1H, $(OCH_2)_2CHH_{ax}$), 2.28 (m, 4H, CH_2 (COD)), 2.68 (septd, ^3J (H,H) = 7.1 Hz, ^2J (H,P) = 1.1 Hz, 2H, PCH), 3.16 (s (br), 2H, CH $(COD)_{trans\ to\ Cl}$), 3.98 (ptdd, ^2J (H,H) = 10.8 Hz, ^3J (H_{ax},H_{ax}) = 12.4 Hz, ^3J (H_{ax},H_{eq}) = 2.5 Hz, ^4J (H_{ax},H_{eq}) = 1.1 Hz, 2H, $OCHH_{ax}$), 4.26 (ddpt, ^2J (H,H) = 10.8 Hz, ^3J (H_{eq},H_{ax}) = 4.9 Hz, ^3J (H_{eq},H_{eq}) = 1.1 Hz, ^4J (H_{eq},H_{ax}) = 1.2 Hz, 2H, $OCHH_{eq}$), 5.31 (s (br), 2H, CH $(COD)_{trans\ to\ P}$), 5.49 (s, 1H, CHO_2), 7.40–7.52 (m, 4H, Ar).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 40.4 (d, ^1J (P,Rh) = 146.6 Hz).

^{13}C NMR (63 MHz, $CDCl_3$, 300 K): δ (ppm) = 19.2 (s, 2C, CH_3), 20.4 (d, ^2J (C,P) = 4.0 Hz, 2C, CH_3), 24.1 (d, ^1J (C,P) = 22.3 Hz, 2C, PCH), 26.1 (s, 1C, $(OCH_2)_2CH_2$), 28.9 (d, ^2J (C,Rh) = 1.7 Hz, 2C, CH_2 (COD)), 33.1 (d, ^2J (C,Rh) = 2.3 Hz, 2C, CH_2 (COD)), 67.8 (s, 2C, OCH_2), 70.7 (d, ^1J (C,Rh) = 13.8 Hz, 2C, CH $(COD)_{trans\ to\ Cl}$), 101.3 (s, 1C, CHO_2), 103.3 (dd, ^1J (C,Rh) = 7.5 Hz, ^2J (C,P) = 12.1 Hz, 2C, CH $(COD)_{trans\ to\ P}$), 125.9–140.4 (m, 6C, Ar).

ESI-MS (*m/z*, %): 491 ($C_{24}H_{37}O_2PRh^+$, 100%), 281 ($C_{16}H_{26}O_2P^+$, 16%).

$C_{24}H_{37}ClO_2PRh$ (%)—calc.: C 54.71, H 7.08, found: C 54.35, H 7.32.

*2.3. Description of the general procedure for the syntheses of the modified PVA derivatives **P1***

An overstoichiometric amount of the phosphino-functionalised benzaldehydedimethylacetals (**1a**–**1d**), together with a stoichiometric amount of PVA, were dissolved in an appropriate amount of NMP. Gaseous HCl was added and the reaction mixture was warmed up to about 115 °C for a minimum of 12 h. The biggest part of the solvent was removed in vacuum, and the polymers (**P1e**–**P1h**) were precipitated either by the addition of pentane after isolation by the addition of basic water or by the direct addition of basic water-containing KOH. For removal of salts, the polymers were purified by extraction with water for several days. Subsequent extraction with diethylether over CaH_2 for several days eliminates the remaining traces of water and yields the polymers as colourless or slightly coloured powders after treatment in vacuum.

*2.3.1. Amounts, yields, and spectroscopic data of the phosphino-functionalised polymers **P1e–P1h***

*Synthesis of **P1e***: 528 mg (1.6 mmol) **1a** and 109 mg PVA (22.000) in 40 ml NMP. Extraction with water for 5 days, followed by extraction with a 1:1 mixture of pentane and diethylether for 3 days, and with diethylether over CaH_2 for 3 days. After drying for 12 h in vacuum, 329 mg (88%) slightly beige coloured **P1e** were isolated.

IR (KBr, cm^{-1}): 3069 (w), 3051 (w), 2943 (m), 2911 (m), 2860 (m), 1584 (w), 1479 (m), 1433 (s), 1116 (s), 1063 (s), 1018 (ss), 812 (s), 742 (ss), 694 (ss), 496 (s).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = −5.2 (s).

^1H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.7 (s (br, sh), CH_n), 2.1 (s (br), $CH H_{ax}$), 4.2 (s (br, sh), $CHOR_2$, ROH), 5.5 (s (br), CHO_2), 5.8 (s (br), CHO_2), 7.3 (s (br, sh), Ar-H).

Analysis (%)—found: C 74.32, H 6.05.

Acetalation degree: 79% (^1H NMR), 77% (analysis).

Molar mass of the monomer unit: 384 g/mol.

*Synthesis of **P1f***: 1.34 g (5.0 mmol) **1b** and 437 mg PVA in 20 ml NMP. **P1f** was extracted with water for 2 days and with diethylether (over CaH_2 as drying agent) for 1 day. After drying for 24 h at 1 mbar and 80 °C, 865 mg (2.7 mmol, 71%) beige coloured **P1f** were obtained.

IR (KBr, cm^{-1}): 3078 (w), 3027 (w), 2949 (s), 2922 (s), 2866 (s), 1462 (m), 1380 (m), 1117 (ss), 1058 (s), 1018 (ss), 813 (s), 660 (w), 609 (w).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 11.3 (s).

^1H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.9 (s (br), CH_3), 1.1 (s (br), CH_3), 1.6 (s (br), CH_n), 2.1 (s (br, sh), PCH), 4.2 (s (br, sh), OCHR, ROH), 5.6 (s (br), CHO_2), 5.8 (s (br), CHO_2), 7.5 (s (br), Ar-H).

Analysis (%)—found: C 65.54, H 7.43.

Acetalation degree: 77% (^1H NMR), 55% (analysis).

Molar mass of the monomer unit: 319 g/mol (^1H NMR).

*Synthesis of **P1g***: 748 mg (2.2 mmol) of **1c** and 192 mg PVA in 30 ml of NMP. Extraction with boiling water for 3 days, followed by extraction with methanol for 12 h and with Et_2O over CaH_2 for 2 days. The resulting polymer was dried for 18 h at 70 °C and 1 mbar, yielding 484 mg (81%) of beige coloured **P1g**.

IR (KBr, cm^{-1}): 3067 (m), 3053 (m), 2941 (m), 2913 (m), 2861 (m), 1955 (w), 1884 (w), 1816 (w), 1585 (m), 1570 (w), 1479 (m), 1433 (s), 1111 (s), 1048 (s), 1000 (s), 758 (s), 741 (ss), 693 (ss), 500 (m), 492 (s).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = −16.3 (s).

^1H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.4 (s (br, sh), CH_n), 2.0 (s (br), CH_n), 3.8 (s (br, sh), $CHOR_2$, ROH), 4.0 (s (br), $CHOR_2$), 6.0 (s (br), CHO_2), 6.4 (s (br), CHO_2), 6.9–7.8 (m, Ar-H).

Analysis (%)—found: C 74.02, H 6.20.

Acetalation degree: 68% (^1H NMR), 67% (analysis).

Molar mass of monomer unit: 404 g/mol.

*Synthesis of **P1h***: 828 mg (3.1 mmol) **1d** and 204 mg PVA in 30 ml NMP. Purification by extraction with water (16 h), methanol (6 h), Et_2O (containing CaH_2 as drying agent, 16 h), and pentane (16 h). After drying for 12 h at 90 °C in vacuum, 457 mg (75%) **P1h** were obtained as a colourless solid.

IR (KBr, cm^{-1}): 3060 (w), 2949 (w), 2917 (w), 2864 (w), 1116 (ss), 758 (m), 638 (m), 618 (m).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = −7.2 (s).

^1H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 0.9 (s (br), CH_3), 1.1 (s (br), CH_3), 1.6 (s (br), CH_2), 2.1 (s (br, sh), PCH), 4.1 (s (sh), OCHR, ROH), 6.3 (s (br, sh), CHO_2), 6.6 (s (br, sh), CHO_2), 7.4–7.9 (m, Ar-H).

Analysis (%)—found: C 66.62%, H 6.49%.

Acetalation degree: 85% (^1H NMR), 63% (analysis).

Molar mass of monomer unit: 308 g/mol (^1H NMR).

*2.4. Description of the general procedure for the syntheses of the Rh-modified PVA derivatives **P2e–P2h***

A slightly overstoichiometric amount of $[Rh(COD)Cl]_2$ was added to a THF solution of the polymers **P1e–P1h**. After stirring for at least 12 h at room temperature, the solvent was reduced to a volume of 5 ml and the polymers **P2e–P2h** were precipitated by the addition of pentane. After washing with pentane, the Rh-modified polymers were extracted with refluxing pentane for several days. Drying in vacuum releases **P2e–P2h**.

*2.4.1. Amounts, yields, and spectroscopic data of the Rh-modified polymers **P2e–P2h***

*Synthesis of **P2e***: 182 mg (0.47 mmol) **P1e** and 168 mg (0.3 mmol) $[Rh(COD)Cl]_2$ in 50 ml THF. Yield: 233 mg (0.37 mmol, 78%) yellow coloured **P2e**.

IR (KBr, cm^{-1}): 3053 (w), 2940 (m), 2913 (m), 2869 (m), 2828 (m), 1594 (w), 1573 (w), 1482 (w), 1436 (m), 1116 (ss), 1094 (ss), 1068 (s), 1011 (ss), 810 (m), 748 (m), 695 (ss), 528 (s), 510 (s).

FIR (PE, cm^{-1}): 285 (s), ν (Rh-Cl).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 30.9 (d, ^1J (P,Rh) = 151 Hz).

^1H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.7–2.0 (m (br), CH_n), 2.4 (s (br), CH_2 (COD)), 3.1 (s (br), CH (COD)), 4.3 (s (br, sh), $CHOR_2$, ROH), 5.6 (s (br, sh), CH (COD), CHO_2), 5.8 (s (br), CHO_2), 7.4–7.7 (m, Ar-H).

Molar mass of monomer unit: 631 g/mol.

*Synthesis of **P2f***: 428 mg (1.34 mmol) **P1f** and 561 mg (1.1 mmol) $[Rh(COD)Cl]_2$ in 50 ml THF. Yield: 569 mg (1.01 mmol, 75%) of yellow coloured **P2f**.

IR (KBr, cm^{-1}): 3030 (w), 2954 (ss), 2943 (ss), 2916 (ss), 2870 (ss), 2830 (s), 1461 (s), 1386 (s), 1364 (s), 1120 (ss), 1034 (s), 1017 (ss), 814 (s), 655 (m), 629 (m).

FIR (PE, cm^{-1}): 284 (s), ν (Rh-Cl).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 39.3 (d, ^1J (P,Rh) = 144 Hz).

^1H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.3 (s (br, sh), CH_3), 1.7 (s (br, sh), CH_2 (COD), CH_n), 2.5 (s (br, sh), PCH), 3.2 (s (br), CH (COD)), 4.2 (s (br, sh), OCHR, ROH), 5.4 (s (br), CH (COD)), 5.6 (s (br, sh), CHO_2), 7.5 (s (br), Ar-H).

Molar mass of monomer unit: 566 g/mol.

*Synthesis of **P2g***: 212 mg (0.52 mmol) **P1g** and 244 mg (0.5 mmol) $[Rh(COD)Cl]_2$ in 50 ml THF. Yield: 299 mg **P2g** (0.46 mmol, 88%) as a yellow solid.

IR (KBr, cm^{-1}): 3051 (m), 2935 (s), 2912 (s), 2870 (s), 2830 (s), 1964 (w), 1896 (w), 1820 (w), 1479 (m), 1433 (s), 1186 (w), 1114 (s), 1091 (s), 1049 (s), 998 (s), 757 (s), 745 (ss), 695 (ss), 532 (m), 512 (m).

FIR (PE, cm^{-1}): 286 (s), ν (Rh-Cl).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 24.2 (s (br)).

^{1}H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.3–1.9 (m, CH_n), 2.4 (s (br), CH_2 (COD)), 3.3 (s (br), CH (COD), $CHOR_2$), 4.1 (s (br), $CHOR_2$, ROH), 5.5 (s (br, sh), CH (COD), CHO_2), 7.4–7.8 (m, Ar-H).

Molar mass of monomer unit: 651 g/mol.

*Synthesis of **P2h***: 476 mg (1.55 mmol) **P1h** and 806 mg (1.6 mmol) $[Rh(COD)Cl]_2$ in 60 ml THF. Yield: 730 mg (1.32 mmol, 85%) yellow coloured **P2h**.

IR (KBr, cm^{-1}): 3059 (w), 2936 (ss), 2913 (ss), 2871 (ss), 2830 (s), 1466 (m), 1388 (m), 1369 (m), 1129 (s), 1108 (s), 1056 (m), 1030 (m), 759 (s), 647 (w), 618 (w).

FIR (PE, cm^{-1}): 280 (s), ν (Rh-Cl).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 23.4 (s (br)).

^{1}H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.3 (s (br, sh), CH_n), 1.9 (s (br), CH_2 (COD)), 2.4 (s (br), PCH), 3.5 (s (br), CH (COD)), 4.4 (s (br, sh), OCHR, ROH), 5.3 (s (br), CH (COD)), 7.3–7.8 (m, Ar-H, CHO_2).

Molar mass of monomer unit: 554 g/mol.

{*Carbonyl-chloro-trans-bis-[2-(para-diisopropylphosphinophenyl)-1,3-dioxane]rhodium(I)*}, ***3f***: At RT, 1.085 g (3.87 mmol) **1d** was added to a solution of 376 mg (0.97 mmol) $[Rh(CO)_2Cl]_2$ in 15 ml dichloromethane. After stirring for 30 min, the solvent was removed in vacuum. The residue was washed two times with portions of 15 ml of pentane. Purification proceeded via heat extraction with pentane, yielding 1.272 g (1.75 mmol, 90%) yellow coloured **3f**. Crystallisation was performed by layering a solution of **3f** in chloroform with pentane.

IR (KBr, cm^{-1}): 3042 (w), 2964 (m), 2929 (m), 2965 (m), 1968 (ss), 1461 (w), 1382 (m), 1151 (m), 1100 (s), 1018 (m), 808 (m), 573 (m), 530 (m).

FIR (PE, cm^{-1}): 295 (s), ν (Rh-Cl).

^{1}H NMR (250 MHz, $CDCl_3$, 300 K): δ (ppm) = 1.06 (pt, ^{3}J (H,H) = ^{3}J (H,P) = 7.0 Hz, 6H, CH_3), 1.09 (pt, ^{3}J (H,H) = ^{3}J (H,P) = 6.9 Hz, 6H, CH_3), 1.23 (pt, ^{3}J (H,H) = ^{3}J (H,P) = 7.5 Hz, 6H, CH_3), 1.27 (pt, ^{3}J (H,H) = ^{3}J (H,P) = 7.5 Hz, 6H, CH_3), 1.46 (dpsept, ^{2}J (H,H) = 13.5 Hz, ^{3}J (H_{eq},H_{ax}) = 2.8 Hz, ^{3}J (H_{eq},H_{eq}) = 1.4 Hz, 2H, $(OCH_2)_2CH\mathit{H}_{eq}$), 2.24 (pqt, ^{2}J (H,H) = 13.5 Hz, ^{3}J (H_{ax},H_{ax}) = 12.5 Hz, ^{3}J (H_{ax},H_{eq}) = 5.0 Hz, 2H, $(OCH)_2CH\mathit{H}_{ax}$), 2.92 (s (br), 4H, PCH), 4.00 (ddpt, ^{2}J (H,H) = 10.7 Hz, ^{3}J (H_{ax},H_{ax}) = 12.5 Hz, ^{3}J (H_{ax},H_{eq}) = 2.8 Hz, ^{4}J (H_{ax},H_{eq}) = 1.5 Hz, 4H, $OCH\mathit{H}_{ax}$), 4.29 (ddpt, ^{2}J (H,H) = 10.7 Hz, ^{3}J (H_{eq},H_{ax}) = 5.0 Hz, ^{3}J (H_{eq},H_{eq}) = 1.4 Hz, ^{4}J (H_{eq},H_{ax}) = 1.5 Hz, 4H, $OCH\mathit{H}_{eq}$), 5.54 (s, 2H, CHO_2), 7.54–7.81 (m, 8H, Ar).

^{31}P NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 45.7 (d, ^{1}J (P,Rh) = 124.4 Hz).

^{13}C NMR (63 MHz, $CDCl_3$, 300 K): δ (ppm) = 18.2 (s, 4C, CH_3), 19.3 (s, 4C, CH_3), 22.2 (pt, ^{1}J (C,P) = ^{2}J (C,Rh) = 12.1 Hz, 4C, PCH), 26.1 (s, 2C, $(OCH_2)_2\mathit{C}H_2$), 67.8 (s, 4C, OCH_2), 101.5 (s, 2C, CHO_2), 125.6–140.7 (m, 12C, Ar).

ESI-MS (*m/z*, %): 708 ($[C_{33}H_{50}O_5P_2Rh{\cdot}NH_3]^+$, 100%), 691 ($C_{33}H_{50}O_5P_2Rh^+$, 39%, $M^+ - Cl$).

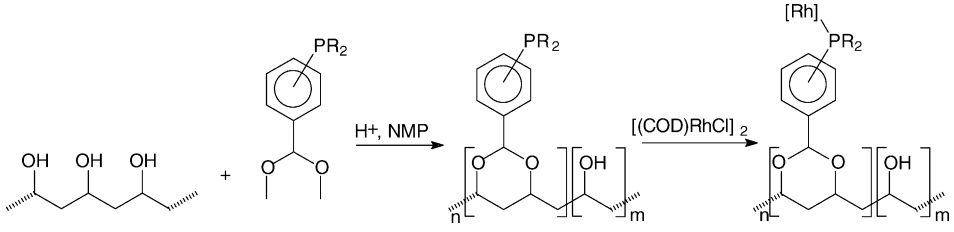
$C_{33}H_{50}ClO_5P_2Rh$ (%)—calc.: C 54.52, H 6.93, found: C 52.59, H 6.60.

3. Results and discussion

The transformation of the free hydroxyl groups of commercially available PVA into cyclic 1,3-dioxanes substituted at the 2-, 4-, and 6-positions can be performed via the transacetalation reaction in NMP under acidic catalysis (Scheme 1).

For this phosphino functionalisation of PVA, phosphino-functionalised dimethylacetals are needed. The corresponding *para*- or *ortho*-substituted benzaldehyde derivatives **1** were synthesised by subsequent lithiation of the *para*- or *ortho*-bromobenzaldehydedimethylacetal, followed by a reaction with the corresponding chlorophosphine (Scheme 2).

The methanol released during the transacetalation reaction is distilled off under reaction conditions. The resulting polymers **P1e**–**P1h** can be characterised by spectroscopic methods. Characterisation of polymers just by their spectroscopic properties, however, is somewhat uncertain when their spectra cannot be compared to those of suitable model compounds. For this reason, phosphino-functionalised benzaldehyde derivatives were synthesised with the aldehyde functionality transformed into a



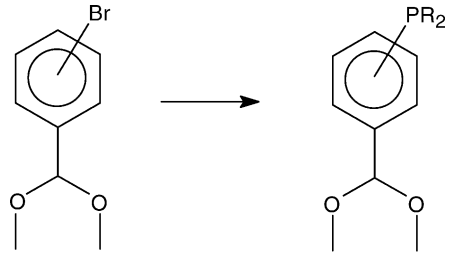
PVA

1a, *p*-PPh_2
1b, *p*-P^iPr_2
1c, *o*-PPh_2
1d, *o*-P^iPr_2

P1e, *p*-PPh_2
P1f, *p*-P^iPr_2
P1g, *o*-PPh_2
P1h, *o*-P^iPr_2

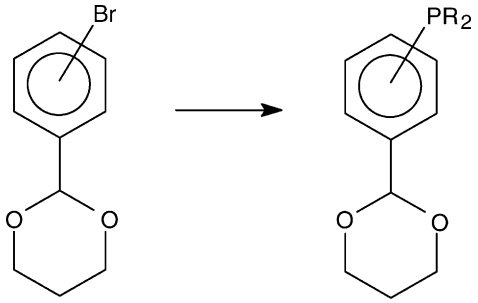
P2e, *p*-PPh_2
P2f, *p*-P^iPr_2
P2g, *o*-PPh_2
P2h, *o*-P^iPr_2

Scheme 1. Transacetalation of PVA, formation of the phosphino-functionalised polymers **P1e**–**P1h** and of the corresponding [Rh]-modified PVAs **P2e**–**P2h** ([Rh]: [(COD)RhCl]) by complexation.



1a, *p*-PPh_2
1b, *p*-P^iPr_2
1c, *o*-PPh_2
1d, *o*-P^iPr_2

Scheme 2. Formation of the ligands **1a**–**1d**.



1e, *p*-PPh_2
1f, *p*-P^iPr_2
1g, *o*-PPh_2
1h, *o*-P^iPr_2

Scheme 3. Formation of the ligands **1e**–**1h**.

cyclic 1,3-dioxane as the simplest and smallest representative part of the PVA backbone. In analogy to the acyclic derivatives, the syntheses were performed by lithiation of the bromophenyl-1,3-dioxanes functionalised in the 2-position. After this, they reacted with the corresponding chlorophosphine (Scheme 3) to the ligands **1e**–**1h**.

As three of the ligands (**1e**, **1g** [15], **1h** [15]) crystallise, their molecular structures could be determined (Table 3; Fig. 3; Section 2). On this basis, the corresponding polymers **P1e**–**P1h** were identified by comparing the spectroscopic data of the model ligands **1e**–**1h** that correlate with the absolutely defined

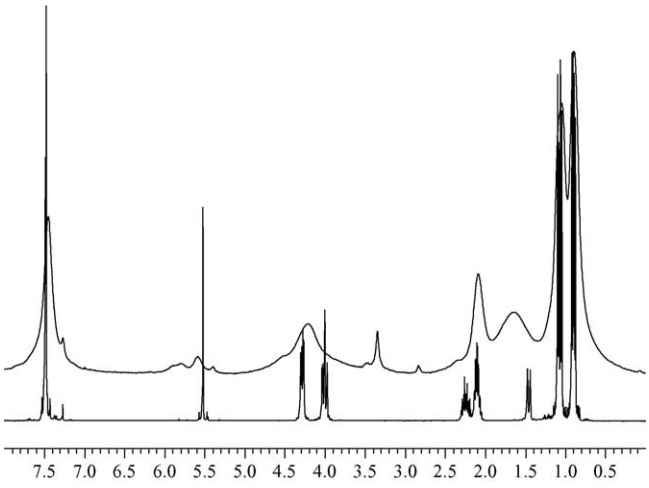


Fig. 4. ^{1}H NMR spectrum of the polymer **P1f** (top) and its corresponding model ligand **1f** (bottom).

structure motifs. For the ligand **1e**, for instance, the molecular crystal structure shows the substitution pattern at the phenyl ring of the benzaldehyde unit as well as the successful embedding of the aldehyde functionalisation in the 1,3-dioxane ring system (Fig. 3).

The spectroscopic data of the model ligands **1e**–**1h** and their corresponding modified PVAs **P1e**–**P1h** reveal a generally very high agreement and confirm that the structure motifs of the ligands **1e**–**1h** also occur on the PVA derivatives. This is obvious from a comparison of the ^{1}H NMR spectra of **1f** with **P1f**, where the functionalisation of the PVA is reflected by resonances for the methyl groups of the isopropyl residues at frequencies lower than 1 ppm (Fig. 4). Furthermore, proton resonances of the polymer **P1f** belonging to the aromatic protons (at 7.5 ppm) as well to the acetal H atom (5.5 ppm) confirm the successful modification of the PVA. Slight differences in the NMR spectra of **P1f** and its model compound **1f** can be explained by the fact that the model is simple, as it does not reflect the different substitution patterns at the polymer backbone in the 4,6-positions of the 1,3-dioxane rings on the polymer **P1f**. However, resonances of the polymer backbone are observed at 4.2 ppm and at 1.7 ppm as broad signals. Additional resonances at 3.3 ppm for the hydroxyl groups

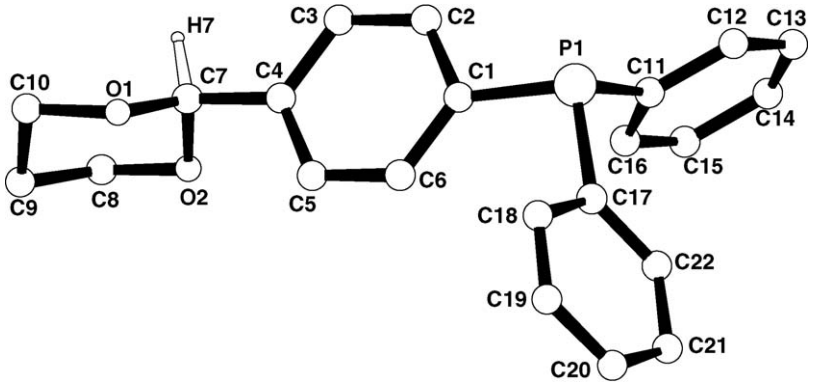


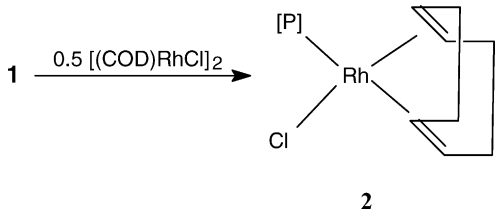
Fig. 3. Molecular structure of **1e** in the crystal. Selected bond distances [pm] and angles [°]: P1–C11 182.7(1), P1–C17 183.0(1), P1–C1 183.2(1), O1–C7 138.4(2), O1–C10 144.6(2), O2–C7 139.4(2), O2–C8 143.8(2), H7–C7–C6–C5 178.6.

of **P1f** are observed, whereas they are missing for the model compound.

From the ^{1}H NMR spectrum of **P1f** (Fig. 4), it can be seen easily that the functionalisation of the PVA with diisopropylphosphinophenyl moieties reaches high degrees, as very intense resonances caused by these moieties can be observed in addition to the signals of the PVA backbone. Indeed, ^{1}H NMR spectroscopy is one suitable tool for the determination of the acetalation degree of the polymers **P1e**–**P1h**. For **P1f**, for instance, it can be calculated by integrating its aromatic proton resonances and all other proton resonances. According to the formula of **P1f** (Scheme 1), the integral of the aromatic protons is set equal to 4 ($n = 1$ in Scheme 1) and the integral of all other proton resonances has been determined to be 23.4, which has to be equal to $21 + 4m$ (occupancy m for the vinyl alcohol unit in Scheme 1). This leads to a final value of $m = 0.6$ that corresponds to an acetalation degree of 77% for **P1f**. This corresponds to a formula for **P1f** of $C_{17}H_{25}O_2P{\cdot}0.6C_2H_4O$ with a molecular weight of this fictitious unit of 319 g/mol. With this high degree of functionalisation, **P1f** possesses phosphorous contents of 9.7%. If complexation of these phosphine units on the polymer proceeded quantitatively with [(COD)RhCl] fragments, this would lead to a polymer **P2f** with an Rh content of 18% in a well-defined molecular environment, but bound to a polymeric support.

Loading with Rh complex fragments of the PVA that were phosphino-functionalised by acetalation proceeds in analogy to the ligands **1** by reaction with $[(COD)RhCl]_2$ in CH_2Cl_2 solution under the formation of pre-catalysts of the type [chloro(COD)(phosphine)rhodium(I)] (Schemes 1 and 4) [17].

As the ligands **1a**–**1d** at their metal-binding phosphine part are very similar to the ligands **1e**–**1h**, their Rh complexes **2a**–**2d** might act as suitable models for the description of the Rh environment of the Rh-modified PVAs as well. Accordingly, the spectroscopic data related to the metal part (e.g. $^{31}P\{^1H\}$ NMR data) of the complexes **2b** and **2f** exhibit values that are very similar to those of the corresponding polymer **P2f**. All ^{31}P resonances are observed at about 40 ppm within 1 ppm (Fig. 5) and



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Scheme 4. Formation of the complexes **2b**, **2e**, **2f**, **2g**, **2h** (with [P]: **1b**, **1e**, **1f**, **1g**, **1h**).

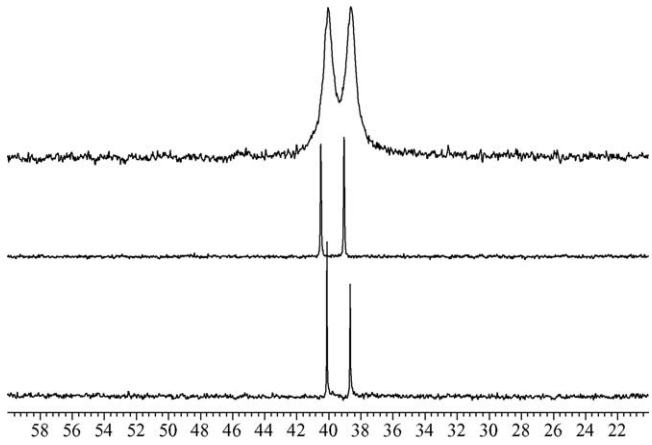

Fig. 5. $^{31}P\{^1H\}$ NMR spectra of the complex **2b** (bottom), **2f** (middle), and its corresponding analogue **P2f** immobilised on PVA (top).

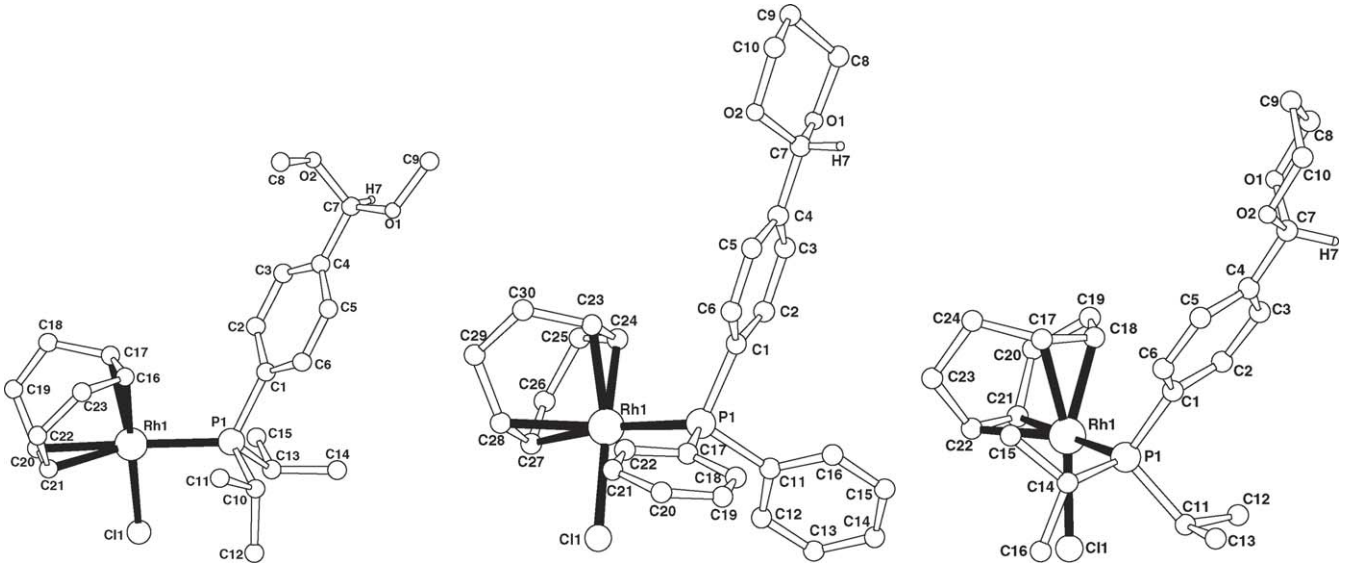

Fig. 6. Molecular structures of **2b** (left), **2e** (centre), and **2f** (right) in the crystal. Selected bond lengths [pm] and angles [°]—**2b**: Rh1–C17 212.3(4), Rh1–C16 213.1(3), Rh1–C21 219.5(3), Rh1–C20 222.0(4), Rh1–P1 232.88(9), Rh1–Cl1 237.04(9), O1–C7 140.1(4), O2–C7 140.9(4), H7–C7–C6–C5 124.1; **2e**: Rh1–C24 213.9(5), Rh1–C23 214.0(5), Rh1–C27 222.2(5), Rh1–C28 222.9(5), Rh1–P1 232.69(14), Rh1–Cl1 236.95(13), O1–C7 137.9(6), O2–C7 137.5(7), H7–C7–C4–C5 73.3; **2f**: Rh1–C18 211.9(2), Rh1–C17 213.9(2), Rh1–C22 219.3(2), Rh1–C21 223.7(2), Rh1–P1 232.97(6), Rh1–Cl1 236.63(6), O1–C7 141.5(3), O2–C7 139.8(3), H7–C7–C4–C5 121.8.

Table 1
E and product distribution [%] after the hydroformylation of 1-octene, catalysed by the complexes **2**, **3f** or the Rh-modified polymer **P2**

Catalyst	Nonanal	2-Methyl-octanal	2-Ethyl-heptanal	2-Propyl-hexanal	Olefins/octane	Alcohols
2b	48.7	36.6	9.6	4.3	0.8	0
2e	50.8	38.1	7.7	2.4	1.0	0
2f	55.5	36.1	6.3	1.9	0.3	0
2g	49.0	38.7	8.9	2.9	0.5	0
2h	52.8	37.0	7.5	2.4	0.3	0
P2e	48.8	36.3	10.1	4.3	0.6	0
P2f	49.1	38.4	8.1	4.1	0.4	0
P2g	50.8	34.1	9.8	4.7	0.6	0
P2h	46.1	36.9	10.8	5.6	0.6	0
3f	26.1	18.2	0	0	55.7[a]	0

Experiments performed with 0.02 mmol catalyst/5 mmol octene in 50 ml dichloromethane at ~65 °C and ~50 bar syngas pressure for 15 h. The catalyses were performed almost to complete conversion. Selectivity is based on GC/MS data.
[a] Major part (>95%): 1-octene.

the ^1J (P,Rh) coupling constants which could even be resolved for the polymer **P2f** were determined to be ~146 Hz.

Consequently, the complexes **2** and their spectroscopic properties allow for an unambiguous characterisation of the corresponding Rh-modified polymers **P2e**–**P2h**. The X-ray analyses performed on single crystals of the complexes **2b**, **2e**, **2f** (Fig. 6; Table 3), and **2g**, **2h** [15] additionally confirm the molecular structures of the complexes and, hence, of the polymer-bound complexes and do not show any irregularity [15,18].

According to our idea of developing a new approach to immobilising catalysts suitable for hydrophobic substrates, the complexes **2** as well as for their polymer-bound analogues, **P2e**–**P2h** were tested for their catalytic selectivity in hydroformylation.

As substrate, the highly unpolar 1-octene was chosen, because a solution still has to be found for the biphasic hydroformylation of long-chain olefins, because it was to be found whether the highly functionalised PVA-based pre-catalysts **P2e**–**P2h** really are unpolar enough to transform even unpolar substrates, and because there are a lot of reference data available in literature [19]. Other substrates or even mixtures of substrates have not yet been analysed for discrimination as a function of the polarity of the polymer, but such investigations certainly will be useful.

In the hydroformylation of octene, selectivities for the complexes **2** or the [Rh]-modified PVAs **P2** are very similar to each other (Table 1). The overall aldehyde selectivity is high and the complexes do not show any high activity in the hydrogenation of octene or the aldehydes produced. All of the pre-catalysts exhibit isomerisation activity, transforming 1-octene into 2-octene, 3-octene, and 4-octene, which then may also be hydroformylated by the catalysts. As the hydroformylation activity of the terminal olefin is much higher than that of the inner olefins, the most important products representing 90% of the selectivity are *n*-nonanal and 2-methyloctanal, their formation ratio being 1.25:1. This low *n*/*iso* ratio is typical of hydroformylation reactions in the absence of a large phosphine excess [19].

The polymeric pre-catalysts may be adsorbed on an inorganic support. Especially when the functionalisation of PVA has reached a high degree, the resulting polymers can be dissolved easily in organic solvents, such as dichloromethane. Adsorption on the inorganic supports proceeds by a simple removal of the solvent in the presence of the support. By the stoichiometric ratio of the polymer to the support, the thickness of the resulting polymer layers on the support can be controlled. For the SEM analysis shown in Fig. 7, an inorganic support has been surrounded by a relatively thick [Rh]-modified PVA layer of about 10 μm for better resolution. Generally, a more homogeneous thickness of the layers can be achieved by the formation of layers of about 1 μm. The porosity of the inorganic support is reflected well by the backscattered electrons, where the polymeric layer on the particle shows a homogeneous structure. BET measurements for the pure inorganic support revealed a BET surface of 430 m^2/g, whereas a value of 22–25 m^2/g was determined for the particles surrounded by the polymer. This decrease can be explained by the fact that the polymer layer on the inorganic support shields its total surface. Consequently, the polymer does not enter the inner core of the inorganic support, which is also reflected by the EFM analyses. According to elemental EFM analyses, Rh, P, and Cl are distributed homogeneously in the polymeric layer on the surface of the support, whereas the elements only present in the inorganic core, such as Si or Al, are placed inside the particle. Once formed, the layers are stable and cannot be removed from the surface by extraction of **P2d**

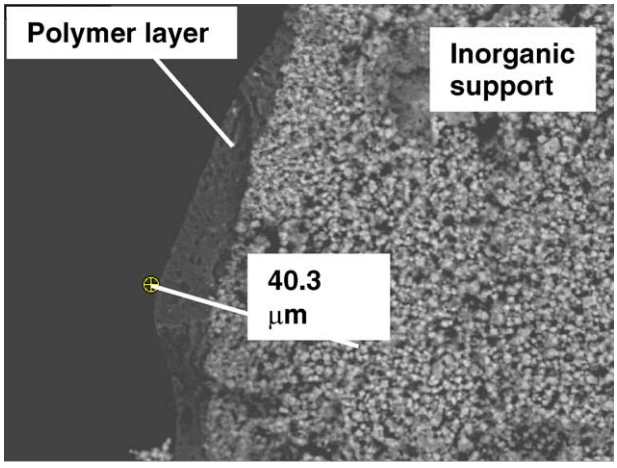

Fig. 7. Surface of an inorganic support (molecular sieve, 5 Å, particle size 2.4–4.8 mm) surrounded by a layer of a Rh-loaded phosphino-functionalised PVA.

Table 2
E and product distribution [%] in the hydroformylation of 1-octene, during 10 consecutive runs, catalysed by the Rh-modfied PVA **P2f**

Run	Nonanal	2-Methyl-octanal	2-Ethyl-heptanal	2-Propyl-hexanal	Olefins/octane	Alcohols
1	50.4	36.0	9.7	3.3	0.6	0
2	50.3	35.5	9.9	3.7	0.6	0
3	49.7	34.8	8.2	3.1	0.8	3.4
4	48.8	33.6	9.8	4.0	1.0	2.8
5	49.2	35.2	10.1	4.4	1.1	0
6	48.4	34.0	8.5	3.5	5.2	0.4
7	49.8	35.3	8.5	3.8	2.5	0
8	48.3	32.2	7.6	3.3	5.1	3.4
9	48.5	31.7	5.0	0.9	13.9	0
10	49.2	31.7	6.3	3.2	9.6	0

Experiments performed with 0.02 mmol Rh-catalyst/5.2 mmol octene in 50 ml pentane at ~65 °C and ~60 bar syngas pressure for 15 h. Constitution of the mixtures based on GC/MS data.

with THF or methanol for 3 days. It may therefore be expected that the layers will also be stable under catalytic conditions and suitable for an application in interfacial catalysis.

In order to demonstrate that the Rh-modified PVA can act as a recyclable catalyst, the polymer **P2f** was selected as a pre-catalyst in consecutive experiments. This choice was based on the well-resolved NMR spectra obtained from this polymer (Fig. 5). As the spectroscopic characterisation of the polymer itself, once it has been adsorbed on an inorganic surface, is more complicated than for an unsupported polymer, these experiments were performed with **P2f** embedded in a Soxhlet-extraction container. In order to reduce the solubility of the polymer in the system, pentane instead of dichloromethane was used as a co-solvent in these experiments. Ten consecutive runs for the hydroformylation of 1-octene were performed. This corresponded to an overall time of more than 150 h of use in catalysis, with a certain decrease in activity, however (Table 2). This is obvious from run no. 10, where nearly 10% of the 1-octene was still found to be present as unreacted substrate. This decrease in activity may be caused by several factors: (i) uncontrolled leaching of the Rh into the organic phase without any break of the acetals on the polymer, (ii) an uncontrolled cleavage of the acetals of the polymer, (iii) a certain oxidation of the ligand, then leading to metal leaching, or (iv) the formation of less active complexes on the polymer with possible partial leaching of the metal. All these cases will have an influence on the spectroscopic data of the polymer. Therefore, the polymeric catalyst **P2f** was analysed by IR spectroscopy after 10 consecutive uses in the hydroformylation of 1-octene (Fig. 8). In the region of coordinated CO stretching vibrations, the IR spectrum shows three absorptions at 2087, 2004, and 1972 cm^{-1}, respectively (Fig. 8, middle). From a catalytic run with the model complex **2f**, a complex of the type [carbonyl-chloro-*trans*-(disphosphine)rhodium(I)] (**3f**) was isolated, with the phosphine being 2-(*para*-diisopropylphosphinophenyl)-1,3-dioxane, **1f**. However, **3f** can also be synthesised by the reaction of **1f** with $[Rh(CO)_2Cl]_2$. The IR spectrum of **3f** shows one CO absorption band at 1968 cm^{-1} (Fig. 8, top) that corresponds well to that of the polymeric **P2f** after catalysis at 1972 cm^{-1}.

In the IR spectrum of **P2f** after catalysis, an absorption at 1724 cm^{-1} was observed. It was caused by traces of aldehydes, which were present in the polymer matrix after its use in catalysis. Alternatively, the phosphino-functionalised polymer **P1f** (not containing any Rh) was subjected to a reaction with $[(CO)_2RhCl]_2$ and the IR spectrum of the resulting Rh-modified polymer was measured (Fig. 8, bottom). The high congruence of this IR spectrum with the one of **P2f** after catalysis shows that these two polymers have an identical composition. The existence of the two other CO stretching vibrations at 2087 and 2004 cm^{-1} can only be explained by the presence of complexes on the polymer **P2f** of the type [*cis*-(dicarbonyl)(chloro)(phosphine)Rh(I)] with two CO ligands coordinated to the Rh centre, one in trans position to the phosphine and the other to the chloro ligand. This coordination behaviour leads to two CO stretching vibrations that are significantly separated in the IR spectrum and in high agreement with literature values [20]. These findings plus the result of a single-crystal X-ray analysis of crystals of **3f** (Fig. 9; Table 3) confirm that the catalyst rest state on the polymer **P2f** after 10 uses in catalysis is {*cis*-(dicarbonyl)(chloro)[2-(*para*-diisopropylphosphinophenyl)-1,3-dioxane]Rh(I)}.

Concerning the quantification of the amount of catalytically active species, $^{31}P\{^1H\}$ NMR spectroscopic investigations were carried out on the polymer obtained by the reaction of $[(CO)_2RhCl]_2$ with **P1f**. Two ^{31}P resonances were observed, one at 45.7 ppm and the other at 46.6 ppm with a $^1J_{PRh}$ coupling constant of 126 Hz, respectively. By comparison

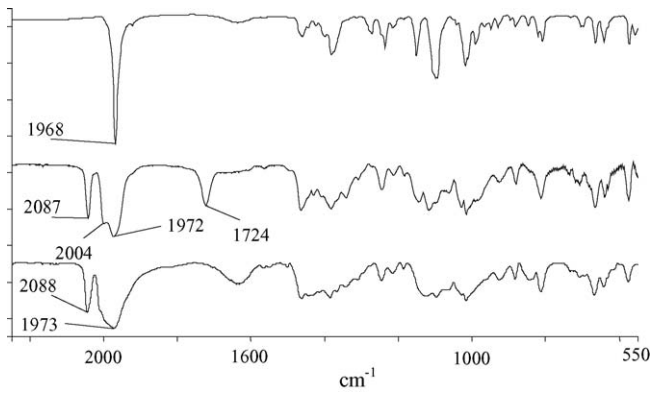

Fig. 8. IR spectra of {carbonyl-chloro-*trans*-bis-[2-(*para*-diisopropylphosphinophenyl)-1,3-dioxane]rhodium(I)} (top), **P2f** after 10 runs in the hydroformylation of 1-octene (middle), and an alternatively synthesised Rh-loaded polymer obtained from the reaction of **P1f** with $[Rh(CO)_2Cl]_2$ (bottom).

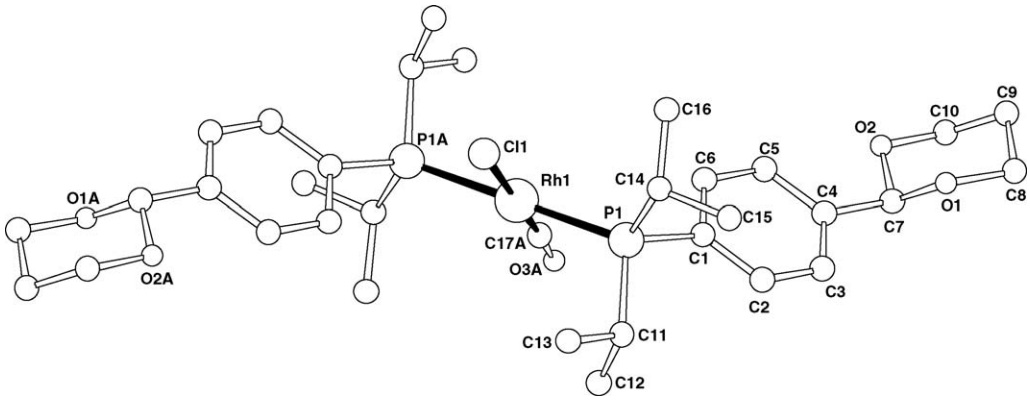

Fig. 9. Molecular structure of **3f** in the crystal. **3f** crystallises in the centrosymmetric triclinic space group *P*-1 with the Rh atom located at the inversion centre. Selected bond lengths [pm] and angles [°]: Rh1–C17A 173.2(7), Rh1–P1 232.76(5), Rh1–Cl1 241.9(3), C17A–O3A 116.2(7) P1–Rh1–P1A 180.0 (0), Cl1–Rh1–C17A 179.2(2), Cl1–Rh1–P1 90.12(7), P1–Rh1–C17A 89.8(2).

Table 3
Crystallographic data

Compound	**1e**	**2b**	**2e**	**2f**	**3f**
Empirical formula	$C_{22}H_{21}O_2P$	$C_{23}H_{37}ClO_2PRh$	$C_{30}H_{33}ClO_2PRh$	$C_{24}H_{37}ClO_2PRh$	$C_{33}H_{50}ClO_5P_2Rh$
Formula weight	348.36	514.86	594.89	526.87	727.06
Crystal size	0.35 mm × 0.35 mm × 0.4 mm	0.40 mm × 0.40 mm × 0.20 mm	0.3 mm × 0.2 mm × 0.15 mm	0.4 mm × 0.35 mm × 0.2 mm	0.4 mm × 0.35 mm × 0.2 mm
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	Pn (no. 7)	P-1 (no. 2)	$P2_1/c$ (no. 14)	P-1 (no. 2)
Unit cell dimensions	a = 1044.3(1) b = 1912.8(2) c = 935.4(1) pm α = 90.0° β = 97.076(2)° γ = 90.0°	a = 860.12(3) b = 807.35(3) c = 1738.80(6) pm α = 90.0° β = 102.041(1)° γ = 90.0°	a = 808.64(14) b = 1243.8(2) c = 1347.2(2) pm α = 88.447(3)° β = 79.137(3)° γ = 85.682(3)°	a = 823.2(1) b = 1402.1(2) c = 2100.0(3) pm α = 90.0° β = 92.334(2)° γ = 90.0°	a = 857.33(7) b = 937.70(8) c = 11.4291(9) pm α = 107.327(1)° β = 93.938(1)° γ = 95.974(1)°
Volume	1854.5(4) × 10^6 pm^3	1180.89(7) × 10^6 pm^3	1326.8(4) × 10^6 pm^3	2421.9(5) × 10^6 pm^3	867.5(1) × 10^6 pm^3
Z	4	2	2	4	1
Density (calculated)	1.248 g/cm^3	1.448 g/cm^3	1.489 g/cm^3	1.445 g/cm^3	1.392 g/cm^3
Temperature	200 K	200 K	200 K	200 K	200 K
θ range	$1.52 \le \theta \le 28.28°$	$1.68 \le \theta \le 28.27°$	$1.54 \le \theta \le 28.26°$	$1.75 \le \theta \le 28.27°$	$1.88 \le \theta \le 28.31°$
Scan	ω-Scan, $\Delta\omega$ = 0.3°	ω-Scan, $\Delta\omega$ = 0.3°	ω-Scan, $\Delta\omega$ = .45°	ω-Scan, $\Delta\omega$ = .45°	ω-Scan, $\Delta\omega$ = 0.3°
Index ranges	$-13 \le h \le 13$, $-25 \le k \le 25$, $-12 \le l \le 12$	$-11 \le h \le 11$, $-10 \le k \le 10$, $-23 \le l \le 22$	$-10 \le h \le 10$, $-16 \le k \le 16$, $-17 \le l \le 17$	$-10 \le h \le 10$, $-18 \le k \le 18$, $-27 \le l \le 27$	$-11 \le h \le 11$, $-12 \le k \le 12$, $-14 \le l \le 14$
Number of					
Reflections measured	18798	12151	14456	25369	9207
Unique reflections	4506	5419	6332	5904	4134
Reflections observed	3784 ($I > 2\sigma$)	4894 ($I > 2\sigma$)	3538 ($I > 2\sigma$)	4771 ($I > 2\sigma$)	3574 ($I > 2\sigma$)
Parameters refined	231	271	320	313	
Residual electron density	0.574 × 10^{-6} e/pm^3	0.412 × 10^{-6} e/pm^3	2.139 × 10^{-6} e/pm^3	0.513 × 10^{-6} e/pm^3	0.541 × 10^{-6} e/pm^3
Corrections	Lorentz and polarisation, exp. absorption correction [21]				
Structure solution	Direct methods				
Structure refinement	Full matrix least square on F^2				
Programs used	SHELX-97 [22], xpma [23], winray [24]				
R indices	R_1 = 0.0422 ($I > 2\sigma$) R_w = 0.1244 (all data on F^2)	R_1 = 0.0319 ($I > 2\sigma$) R_w = 0.0646 (all data on F^2)	R_1 = 0.0567 ($I > 2\sigma$) R_w = 0.1362 (all data on F^2)	R_1 = 0.0315 ($I > 2\sigma$) R_w = 0.0710 (all data on F^2)	R_1 = 0.0324 ($I > 2\sigma$) R_w = 0.0769 (all data on F^2)

with the ^{31}P NMR spectrum of **3f** having its resonance at 45.7 ppm and a coupling constant of 124.4 Hz, the second resonance can be assigned to the polymer bound analogous to **3f** that exhibits hardly any catalytic activity. The resonance at 45.7 ppm with its $^1J_{PRh}$ coupling constant of 143 Hz is therefore caused by the catalytically active species of the type [*cis*-(dicarbonyl)(chloro)(phosphine)Rh(I)]. Integration of these two signals yields a 2:1 ratio for the *cis*-(dicarbonyl) complex as

compared to the minor complex on the polymer of the type [(carbonyl)(chloro)-*trans*-(disphosphine)rhodium(I)]. As in this complex, two phosphine ligands are bound to one Rh atom, the Rh distribution between the complexes resulting in 4:1, leaving 80% of the polymer-bound Rh in the catalytically active species [*cis*-(dicarbonyl)(chloro)(phosphine)Rh(I)]. This corresponds to 66% of the initial Rh content on the polymer and explains the reduced activity of the system. However, it is implied that at least 17% of the initial Rh contents have to be removed from the polymer by mobilisation. Indeed, crystals of $[(COD)RhCl]_2$ were isolated from the yellow coloured solutions of the first two catalytic runs. In the later runs, however, no coloured solutions were obtained. ICP analyses of the solutions of all runs were not performed. For a future improvement of the system, they will have to be included. Nevertheless, our results show clearly that after 10 consecutive uses (or more than 150 h) in the hydroformylation, the polymeric pre-catalyst **P2f** has changed by the formation of well-defined complexes on the polymer. No uncontrolled leaching or degradation of the polymer-bound complexes was observed. A certain loss of Rh was noticed at the beginning, but once the stable complexes were formed on the polymer, it could not be detected visually any longer. Due to these results, it may well be expected that the modified PVA systems might be an alternative to existing technologies for catalyst immobilisation in the future even for a longer use.

4. Conclusion

It was demonstrated that a phosphino functionalisation of polyvinyl alcohol (PVA) can be achieved. The phosphino substituents were introduced in the polymer by a one-step transacetalation reaction. High acetalation degrees were reached. Polymers with Rh contents higher than 15% and the transition metal in a defined molecular environment were obtained. The phosphino-modified PVAs or the Rh-modified PVAs resulting from the complexation of the phosphino groups towards a [(COD)RhCl] complex were characterised unambiguously by comparison of their spectroscopic data with those of model compounds, the syntheses of which were reported as well. Finally, the Rh-modified PVAs were tested in the catalytic hydroformylation of 1-octene. Their selectivity in the product distribution was found to be identical to that of the model complexes. The Rh-modified PVA was adsorbed on an inorganic support under the formation of stable polymer layers on its surface, which cannot be mobilised by extraction with organic solvents. The stability of these layers, together with their tuneable polarity, allow for an application in interfacial catalysis. Analyses performed on a polymer that had not been adsorbed on an inorganic support and had been used 10 times as the catalyst in the hydroformylation of 1-octene revealed that the polymeric pre-catalyst **P2f** had changed by the formation of well-defined complexes on the polymer. Sixty-six percent of the initial Rh contents were transformed in the catalytically active polymer-bound species [*cis*-(dicarbonyl)(chloro)(phosphine)Rh(I)], 17% were found to rest in a catalytically inactive form of polymer-bound [carbonyl-chloro-*trans*-(diphosphine)Rh(I)], and 17% were lost in the first runs in the form of soluble and, hence, mobile $[(COD)RhCl]_2$. These first attempts of using phosphino-functionalised PVA for the immobilisation of transition metal catalysts have shown that this system has its potential and might represent an alternative for catalyst immobilisation.

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