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# Syntheses and coordination behaviour of 2-(*ortho*-phosphinophenyl)-functionalised 1,3-dioxolanes and 1,3-dioxanes towards a [(COD)Rh]-complex fragment – models for immobilised complexes

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Dedicated to Prof. Dr. Eckhard Dinjus to the occasion of his 60th birthday

**Abstract**

The syntheses are reported of the ether–phosphine ligands: 2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxolane (**1a**), 2-(*ortho*-diisopropylphosphinophenyl)-1,3-dioxolane (**1b**), 2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxane (**1c**), 2-(*ortho*-diisopropylphosphinophenyl)-1,3-dioxane (**1d**). Their reaction with $[(COD)RhCl]_2$ (COD: 1,5-cyclooctadiene) results in the formation of the mononuclear complexes: {chloro(COD)[2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxolane]rhodium(I)} (**2a**), {chloro(COD)[2-(*ortho*-diisopropylphosphinophenyl)-1,3-dioxolane]rhodium(I)} (**2b**), {chloro(COD)[2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxane]rhodium(I)} (**2c**), and {chloro(COD)[2-(*ortho*-diisopropylphosphinophenyl)-1,3-dioxane]rhodium(I)} (**2d**). The chloride ligands of compounds **2a** and **2b** were abstracted with $TlPF_6$, with accompanied insertion of an acetal oxygen atom of the ligands **1a** and **1b** into the coordination sphere of the metal centre, producing {(COD)[$\eta^2$-*P*,*O*-2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxolane]rhodium(I)}$PF_6$ (**3a***$PF_6$) and {(COD)[$\eta^2$-*P*,*O*-2-(*ortho*-diisopropylphosphinophenyl)-1,3-dioxolane]rhodium(I)}$PF_6$ (**3b***$PF_6$). In contrast the dioxane analogues of **3**, **3c***$BF_4$ and **3d***$BF_4$, were formed by reacting the ligands **1c**, **1d** with $[Rh(COD)_2]BF_4$. The ligands **1** and the complexes **2** serve as model compounds for their via acetalation to a polyvinylalcohol resin bound analogues. The complexes synthesised were employed as pre-catalysts in the hydroformylation reaction of 1-octene.


*Keywords:* Ether–phosphines; Hemilabile ligands; Rh-complexes; Catalysis; Immobilisation; Polyvinylalcohol

## 1. Introduction

Ligands containing functional groups with varying donor strengths show potential for application in catalysis. During a catalytic reaction, functional groups with a tendency for weaker coordination may enter the metal coordination sphere and stabilise intermediates in a similar manner to solvent molecules without inhibiting the reaction by formation of too stable complexes. If such a development is successful the use of a solvent in such a reaction would no longer be required. Accordingly the use of cyano-phosphines in the Pd-catalysed co-oligomerisation of butadiene and $CO_2$ had lead to the possibility of working under solvent free conditions [1]. Of the potential ligand systems with donor groups of differing coordinative potentials, transition metal complexes of ether–phosphine ligands have attracted most attention due to their interesting catalytic properties [2].

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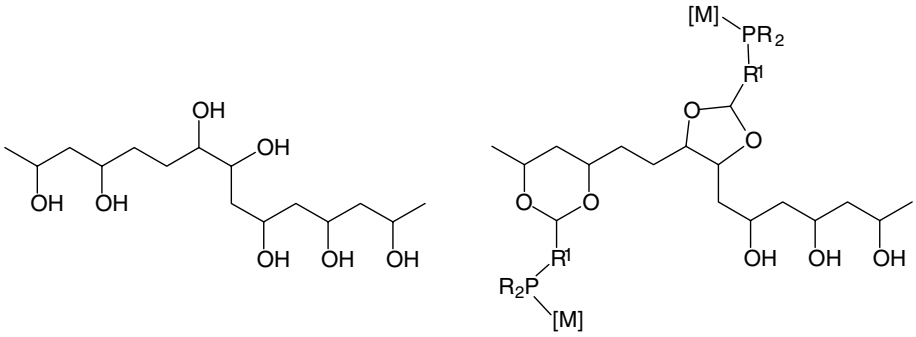



Fig. 1. Schematic view of polyvinylalcohol (left) and, via acetalation, phosphino-functionalised polyvinylalcohol (right, $R^1$: spacer, [M]: transition metal fragment).

Our interest, however, in these compounds did not lie in the possible use of ether–phosphines as chelating ligands, but the complexes described here serve as model compounds for transition metal complexes which are bound to polyvinylalcohol via transformation of its free hydroxyl groups into 1,3-dioxanes or 1,3-dioxolanes (Fig. 1). The 1,3-dioxolane ligands functionalised at the 2-position and their complexes act correspondingly as models for "head to head" linked vinylalcohol units; the 1,3-dioxanes functionalised at the 2-position are the corresponding models for the "head to tail" linkage.

The results on the syntheses and modifications performed on the polymeric material are the subject of a patent [3] and the details will be published elsewhere [4].

The ligands **1**, and their complexes **2** and **3** described here contribute to the description of phosphino-functionalised polyvinylalcohol (PVA). The spectroscopic data of the ligands **1** and their complexes **2** will allow the characterisation of their PVA analogues. The use of the complexes as pre-catalysts will form the starting point for the development of the on PVA immobilised systems towards a catalytic application.

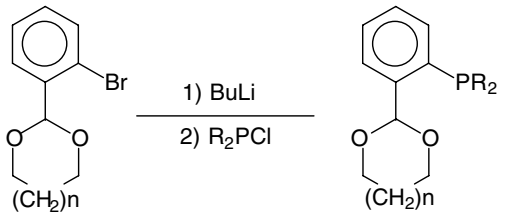
## 2. Results and discussion

Although the 2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxolane (**1a**) has been reported in the literature [5], there are very few reported coordination compounds of 2-(*ortho*-phosphino)-functionalised benzaldehyde acetals [6]. We synthesised the ligands by first lithiation of 2-(*ortho*-bromophenyl)-1,3-dioxolane, or its 1,3-dioxane derivative, with butyllithium at low temperature and then by reacting the lithiated dioxolane or dioxane with a disubstituted chlorophosphine. After purification by condensation or crystallisation the ligands were obtained in yields of 70–80% (Scheme 1).

The spectroscopic data of the ligands **1a**–**1d** are in accordance with their structures. So e.g., the characteristic signal of the acetal H-atom of the ligands is observed in the $^1$H NMR spectra as a doublet (due to $^4J_{PH}$ couplings) at 6.14–6.67 ppm. Besides the spectroscopic data, the constitution of the ligands **1b**–**1d** was determined by X-ray crystallography (Fig. 2, Table 1 and Section 5). Crystals of the ligands were obtained by direct recrystallisation of the crude product or by allowing the oils to crystallise slowly at low temperature.

As from the results of the single-crystal X-ray analyses it is evident that the ligands do not show any unusual bond lengths and angles we refrain from a detailed discussion and reporting of bond lengths and angles. Of structural importance in this context is only the rotational position of the planar phenyl ring in comparison to the non-planar dioxolane or dioxane ring. A quantitative analysis can be performed on the basis of the torsion angle comprised of the proton on the acetal C-atom, the acetal C-atom itself, the carbon atom of the phenyl ring bound to the acetal C-atom and one of its neighbouring C-atoms in the phenyl ring. For **1b** the angle [H(7)–C(7)–C(6)–C(5)] has been determined to be equal to 1.1° (Fig. 2) demonstrating that the acetal proton lies essentially within the plane containing the phenyl ring, with the two ring systems perpendicular to one another. For **1c** and **1d** the corresponding torsion angles are 25° or 47° showing that in the ligands **1** the different ring systems may adopt a range of rotational positions.

The reaction of 2-(*ortho*-phosphinophenyl)-functionalised 1,3-dioxolanes or dioxanes (**1**) with $[(COD)RhCl]_2$




**1a**, R: Ph, n: 0
**1b**, R: $^i$Pr, n: 0
**1c**, R: Ph, n: 1
**1d**, R: $^i$Pr, n: 1

Scheme 1. Formation of the ligands **1**.

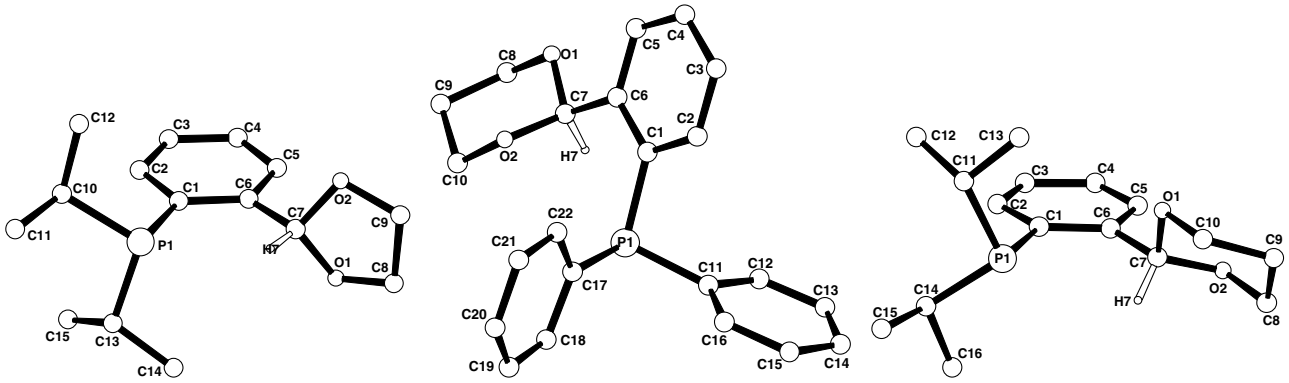



Fig. 2. View of the molecular structures of **1b** (left), **1c** (centre, view of one of the molecules in the independent unit) and **1d** (right). Torsion angles (°) discussed **1b**: H7–C7–C6–C5 1.1°, **1c**: H7–C7–C6–C1 −48.6° (corresponding angle for the second molecule in the independent unit: 25.1°), **1d**: H7–C7–C6–C1 45.1°.

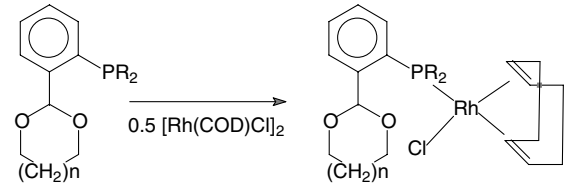
Table 1
Crystallographic data of the ligands **1**

| Compound | **1b** | **1c** | **1d** |
|---|---|---|---|
| Empirical formula | $C_{15}H_{23}O_2P$ | $C_{22}H_{21}O_2P$ | $C_{16}H_{25}O_2P$ |
| Formula weight | 266.30 | 348.36 | 280.33 |
| Crystal size ($mm^3$) | $0.45 \times 0.45 \times 0.1$ | $0.4 \times 0.3 \times 0.25$ | $0.3 \times 0.3 \times 0.2$ |
| Crystal system | Monoclinic | Triclinic | Tetragonal |
| Space group | $P2_1$ (No. 4) | $P\bar{1}$ (No. 2) | $P4_3$ (No. 78) |
| Unit cell dimensions | | | |
| $a$ (pm) | 840.68(6) | 1036.2(2) | 856.78(3) |
| $b$ (pm) | 1008.98(7) | 1370.0(2) | 856.78(3) |
| $c$ (pm) | 899.76(7) | 1504.6(2) | 2136.5(1) |
| $\alpha$ (°) | 90.0 | 66.242(2) | 90.0 |
| $\beta$ (°) | 94.270(1) | 85.205(2) | 90.0 |
| $\gamma$ (°) | 90.0 | 68.979(2) | 90.0 |
| Volume ($pm^3$) | $761.1(1) \times 10^6$ | $1820.1(4) \times 10^6$ | $1568.3(1) \times 10^6$ |
| $Z$ | 2 | 4 | 4 |
| $D_{calc}$ ($g/cm^3$) | 1.162 | 1.271 | 1.187 |
| Temperature (K) | 200 | 200 | 200 |
| $\theta$-Range (°) | $2.27\ \theta \leqslant 28.30$ | $1.48 \leqslant \theta \leqslant 28.33$ | $2.38 \leqslant \theta \leqslant 28.29$ |
| Scan (°) | $\omega$-Scan, $\Delta\omega = 0.3$ | $\omega$-Scan, $\Delta\omega = 0.45$ | $\omega$-Scan, $\Delta\omega = 0.45$ |
| Index ranges | $-11 \leqslant h \leqslant 10$, $-13 \leqslant k \leqslant 13$, $-10 \leqslant l \leqslant 11$ | $-13 \leqslant h \leqslant 13$, $-18 \leqslant k \leqslant 18$, $-18 \leqslant l \leqslant 19$ | $-11 \leqslant h \leqslant 11$, $-11 \leqslant k \leqslant 11$, $-27 \leqslant l \leqslant 28$ |
| Number of | Flack $x$: −0.04(6) | | Flack $x$: 0.04(8) |
| Reflections measured | 8001 | 19,351 | 16,647 |
| Unique reflections | 3610 | 8671 | 3849 |
| Reflections observed | 3368 ($I > 2\sigma$) | 6513 ($I > 2\sigma$) | 3140 ($I > 2\sigma$) |
| Parameters refined | 174 | 461 | 183 |
| Residual electron density ($e/pm^3$) | $0.23 \times 10^{-6}$ | $0.509 \times 10^{-6}$ | $0.21 \times 10^{-6}$ |
| Corrections | Lorentz and polarisation, experimental absorption correction [20] | Lorentz and polarisation, experimental absorption correction [20] | Lorentz and polarisation, experimental absorption correction [20] |
| Structure solution | Direct methods | Direct methods | Direct methods |
| Structure refinement | Full-matrix least-square on $F^2$ | Full-matrix least-square on $F^2$ | Full-matrix least-square on $F^2$ |
| Programs used | SHELX-97 [21], XPMA [22], WINRAY [23] | SHELX-97 [21], XPMA [22], WINRAY [23] | SHELX-97 [21], XPMA [22], WINRAY [23] |
| $R$ indices | $R_1 = 0.0277$ ($I > 2\sigma$) $R_w = 0.0731$ (all data on $F^2$) | $R_1 = 0.0611$ ($I > 2\sigma$) $R_w = 0.1332$ (all data on $F^2$) | $R_1 = 0.0342$ ($I > 2\sigma$) $R_w = 0.0789$ (all data on $F^2$) |

Standard deviations are given in parentheses.

results in the formation of the corresponding [(COD)RhCl(Phosphine)] complexes (**2**) (Scheme 2) according to a well known literature reaction [7].

Purification of complexes **2** was readily achieved by extraction of the crude product with refluxing pentane. During the extraction procedure yellow single crystals




**1a**, R: Ph, n: 0 **2a**, R: Ph, n: 0
**1b**, R: $^{i}$Pr, n: 0 **2b**, R: $^{i}$Pr, n: 0
**1c**, R: Ph, n: 1 **2c**, R: Ph, n: 1
**1d**, R: $^{i}$Pr, n: 1 **2d**, R: $^{i}$Pr, n: 1

Scheme 2. Formation of the complexes **2**.

of the complexes **2b**–**2d** were obtained which were suitable for X-ray diffraction analyses. Only complex **2a** crystallised in the form of thin needles which diffracted poorly. The coordination geometry at the Rh-centre in **2** can be described as distorted square planar (Fig. 3).

Accordingly the bond angles at the Rh-centre between two ligands in a *cis*-position to each other were found to be in the range of 86.2° and 96.7° (taking the centre of the double bonds of the COD as the reference point for a coordination site). The bond angles for the *trans*-positioned groups were determined to be larger than 170°. The Rh–C distances vary depending on the ligand which is in the *trans*-position to the corresponding π-bond of the COD unit; the Rh–C bond distances for the C-atoms in *trans*-positions to the chloride ligand were determined to be 5–10 pm shorter than the Rh–C distances for the double bond *trans* to the P-atom. This is a consequence of the higher π-acceptor character of the phosphine ligand compared to the chloride ligand, and is in agreement with results obtained from similar coordination complexes [8].

The acetal O-atoms in the complexes **2** are not bound to the Rh-centre and, as was observed in the crystal structure for **1b**, a twisting of the phenyl ring with respect to the dioxolane or dioxane ring was observed. For all of the complexes **2** the torsion angle, comprised of the acetal proton, the acetal C-atom itself, the carbon atom of the phenyl ring bound to the acetal C-atom, and one of its neighbouring C-atoms in the phenyl ring, was found to be less than 10°. This is close to the perpendicular orientation of the two ring systems observed for **1b** and furthermore an indication that the overall steric hindrance in the complexes **2** has increased due to the coordination of the ligands **1** to a transition metal fragment.

The coordination of the COD ligands in the complexes **2** is reflected in their $^{1}$H and $^{13}$C NMR spectra. In comparison to $[Rh(COD)Cl]_2$, where the two coordinated olefin units of the COD ligand show only one resonance signal due to their chemical identity, for the complexes **2** a splitting of the corresponding resonances is observed. This indicates that a rotational exchange between the two different positions does not occur rapidly at room temperature. Correspondingly, in the $^{1}$H NMR spectra of the complexes **2** the proton resonances of the olefin unit coordinated *trans* to the chlorine ligand are observed between 3.24 and 3.50 ppm, whereas the protons of the coordinated olefinic unit in the *trans*-position to the phosphine ligands are found between 5.38 and 5.59 ppm. A similar behaviour is observed in the $^{13}$C NMR spectra of the complexes **2**, proving the unsymmetrical coordination of the COD-ligand in **2**.

The existence of a Rh–Cl bond is evident from the FIR spectra where the absorptions of the Rh–Cl-stretching vibrations are located around 283 cm$^{-1}$. Finally, the $^{31}$P NMR spectra of the coordinated phosphine ligands in the complexes **2** show resonances which are well

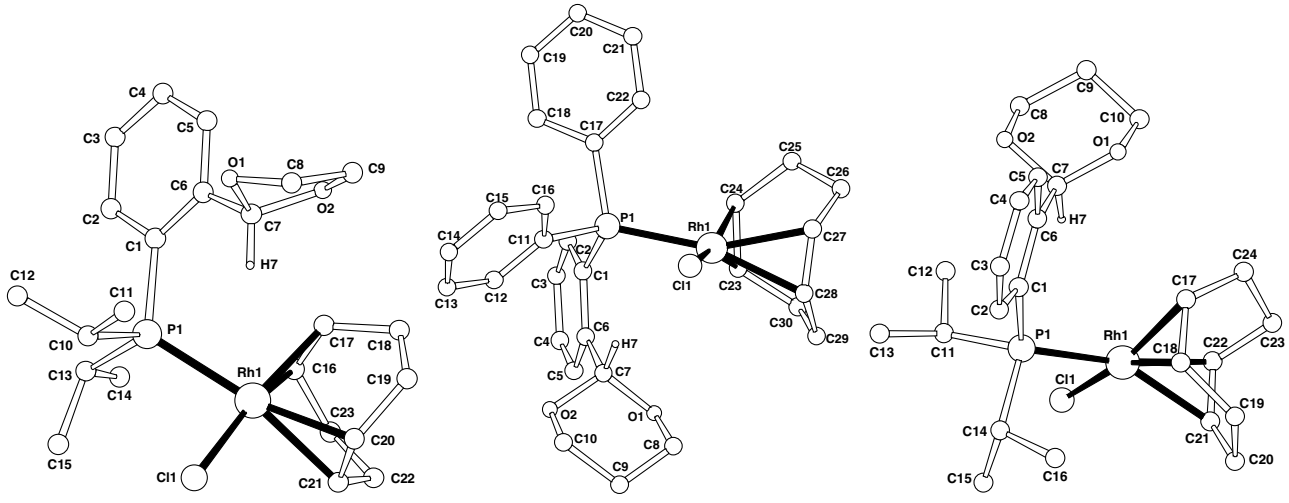



Fig. 3. View of the molecular structures of **2b** (left), **2c** (centre), **2d** (right) determined by single crystal X-ray diffraction. Discussed bond distances (pm) and torsion angles (°), **2b**: O1–C7 141.6(3) pm, O(2)–C(7) 142.7(3) pm, H7–C7–C6–C5 7.2°; **2c**: C7–O1 141.5(7) pm, C7–O2 142.6(6) pm, H7–C7–C6–C1 −4.8°; **2d**: C7–O1 141.0(3) pm, C7–O2 142.2(3) pm, H7–C7–C6–C1 −9.2°.

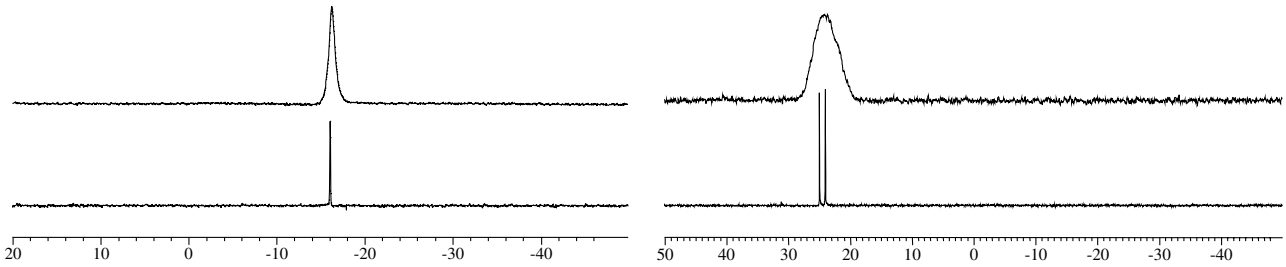



Fig. 4. $^{31}P\{^{1}H\}$ NMR spectra of the ligand **1a** (left, bottom) and its via acetalation PVA immobilised derivative (left, top) and of the complex **2a** (right, bottom) and its on PVA immobilised corresponding complex (right, top).

shifted compared to the free ligands **1**; the resonances in **2** appear as doublets with $^{1}J_{Rh-P}$ coupling constants in the range of 145 Hz.

If the ligands **1** or complexes **2** are reasonable model compounds their spectroscopic data must be very similar to the corresponding on the PVA matrix immobilised ligands or complexes. A comparison of the spectroscopic data of the ligands **1** and the complexes **2** with their corresponding derivatives on a PVA matrix show high analogy. The main difference lies in the lower resolution of the solution NMR spectra of the polymer bound derivatives, according to their polymeric structure [3,4]. This can be seen e.g., from the $^{31}P\{^{1}H\}$ NMR spectra of **1a** compared with its PVA derivative (Fig. 4). The corresponding spectrum of complex **2a** compared with its PVA derivative shows that the complexation on the

Table 2
Crystallographic data of the complexes **2**

| Compound | **2b** | **2c** | **2d** |
|---|---|---|---|
| Empirical formula | $C_{23}H_{35}ClO_2PRh$ | $C_{30}H_{33}ClO_2PRh$ | $C_{24}H_{37}ClO_2PRh$ |
| Formula weight | 512.84 | 594.89 | 526.87 |
| Crystal size ($mm^3$) | $0.35 \times 0.20 \times 0.20$ | $0.2 \times 0.1 \times 0.05$ | $0.30 \times 0.40 \times 0.15$ |
| Crystal system | Triclinic | Monoclinic | Orthorhombic |
| Space group | $P\bar{1}$ (No. 2) | $P2_1/c$ (No. 14) | $Pna2_1$ (No. 33) |
| Unit cell dimensions | | | |
| $a$ (pm) | 846.98(4) | 1461.1(1) | 2494.1(3) |
| $b$ (pm) | 969.33(4) | 878.03(8) | 808.87(8) |
| $c$ (pm) | 1581.79(7) | 2023.1(2) | 1167.2(1) |
| $\alpha$ (°) | 94.287(1) | 90.0 | 90.0 |
| $\beta$ (°) | 104.748(1) | 91.591(2) | 90.0 |
| $\gamma$ (°) | 112.6648(1) | 90.0 | 90.0 |
| Volume ($pm^3$) | $1136.9(9) \times 10^6$ | $2594.5(4) \times 10^6$ | $2354.8(4) \times 10^6$ |
| $Z$ | 2 | 4 | 4 |
| $D_{calc}$ ($g/cm^3$) | 1.498 | 1.523 | 1.486 |
| Temperature (K) | 200 | 200 | 200 |
| $\theta$-Range (°) | $1.36 \theta \leqslant 28.29$ | $1.39 \leqslant \theta \leqslant 28.30$ | $1.63 \leqslant \theta \leqslant 28.25$ |
| Scan (°) | $\omega$-Scan, $\Delta\omega = 0.3$ | $\omega$-Scan, $\Delta\omega = 0.3$ | $\omega$-Scan, $\omega = 0.45$ |
| Index ranges | $-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-21 \leqslant l \leqslant 21$ | $-19 \leqslant h \leqslant 19$, $-11 \leqslant k \leqslant 11$, $-26 \leqslant l \leqslant 26$ | $-33 \leqslant h \leqslant 33$, $-10 \leqslant k \leqslant 10$, $-15 \leqslant l \leqslant 15$ |
| Number of | | | Flack $x$: 0.12(3) |
| Reflections measured | 11,971 | 27,229 | 23,186 |
| Unique reflections | 5402 | 6348 | 5602 |
| Reflections observed | 4774 ($I > 2\sigma$) | 2827 ($I > 2\sigma$) | 5549 ($I > 2\sigma$) |
| Parameters refined | 268 | 389 | 322 |
| Residual electron density ($e/pm^3$) | $0.573 \times 10^{-6}$ | $0.591 \times 10^{-6}$ | $0.314 \times 10^{-6}$ |
| Corrections | Lorentz and polarisation, experimental absorption correction [20] | Lorentz and polarisation, experimental absorption correction [20] | Lorentz and polarisation, experimental absorption correction [20] |
| Structure solution | Direct methods | Direct methods | Direct methods |
| Structure refinement | Full-matrix least-square on $F^2$ | Full-matrix least-square on $F^2$ | Full-matrix least-square on $F^2$ |
| Programs used | SHELX-97 [21], XPMA [22], WINRAY [23] | SHELX-97 [21], XPMA [22], WINRAY [23] | SHELX-97 [21], XPMA [22], WINRAY [23] |
| $R$ indices | $R_1 = 0.0305$ ($I > 2\sigma$) $R_w = 0.852$ (all data on $F^2$) | $R_1 = 0.0457$ ($I > 2\sigma$) $R_w = 0.1278$ (all data on $F^2$) | $R_1 = 0.0288$ ($I > 2\sigma$) $R_w = 0.0736$ (all data on $F^2$) |

Standard deviations are given in parentheses.

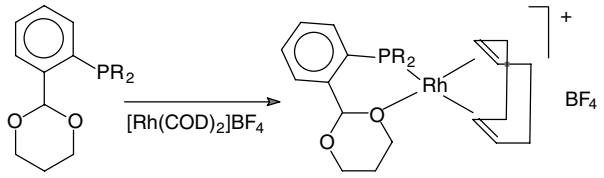
polymer proceeds quantitatively as no resonance for the free ligand on the polymer at −16.3 ppm is observed any more. The high congruence between the chemical shifts of **1a** and **2a**, respectively, to those of their immobilised analogues indicate that the ligands **1** as well as their complexes **2** are suitable model compounds for via acetalation on a PVA matrix immobilised systems.

The spectroscopic data of the complexes **2** as well as the results from the single crystal X-ray analyses show that the acetal groups do not form any interaction with the Rh-centres (Fig. 3 and Table 2). To investigate the effectiveness of the acetal O-atoms in the complexes **2** for coordination, a free coordination site at the metal centre has to be created. Chloride abstraction from the complexes **2** would liberate such a position which could subsequently be occupied by coordination of one O-acetal atom from the dioxolane or dioxane unit of the ligands [9]. This is of direct relevance for e.g., hydroformylation reactions, as it has been hypothesised that, during the course of catalysis, the chloride ligands of the pre-catalysts leave the metal coordination sphere [10].

By reacting the complexes **2a**, **b** in dichloromethane with $TlPF_6$ (as the dehalogenating agent) an insoluble salt is formed and after filtration and removal of the solvent the cationic complexes **3a**, **b**$*PF_6$ could be isolated in good yields (Scheme 3).

Chloride abstraction however is not suitable for creating the corresponding dioxane derivatives **3c**, **d**, where at least in one case a $TlPF_6$ adduct was isolated and characterised as the main product [11]. However, the complexes **3c**, **d**$*BF_4$ could be prepared in good yields by direct reaction of the ligands **1c**, **d** with $[Rh(COD)_2]BF_4$ (Scheme 4).

The signal patterns in the NMR spectra of the neutral complexes **2** and the complex cations **3** are very similar. The coordination of one acetal O-atom in **3** does not cause a splitting of the resonances of the coordinated dioxolane or dioxane rings, indicating that in solution there is a fast exchange between the two possible coordinated O-atoms. For the corresponding complexes of the type fac-{bromotricarbonyl[$\eta^2$-*P*,*O*-(**1**)]rhenium(I)} this exchange is slow such that all the




**1c**: R = Ph
**1d**: R = $^i$Pr

**3c**: R = Ph
**3d**: R = $^i$Pr

Scheme 4. Reaction of the dioxane derivatives **1c**, **d** with $[Rh(COD)_2]BF_4$.

ring protons can be assigned to different resonances in the NMR spectra [12].

The coordination of the acetal O-atoms in complexes **3** is evident in the FIR and IR spectra of the complexes **3**, moreover, the observed strong absorptions for the $\nu_{Rh-Cl}$ stretching vibrations at 283 $cm^{-1}$ in complexes **2** are no longer present in the complex cations **3**.

Furthermore, significant changes in the energies of the C–O stretching vibrations were observed in comparing the IR spectra of the ligands **1** and the complexes **2** to those of the cationic complexes **3** (Fig. 5), indicating that the dioxolane or dioxane ring systems are in different environments, as for e.g., an acetal O-atom coordinated to the Rh-centre. C–O stretching vibrations are observed at 1130 and 1080 $cm^{-1}$ for ligand **1b** and its

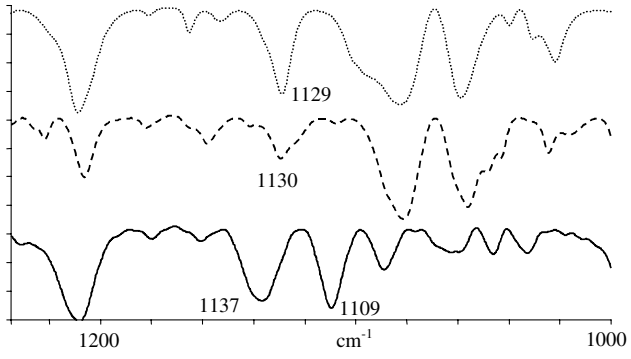
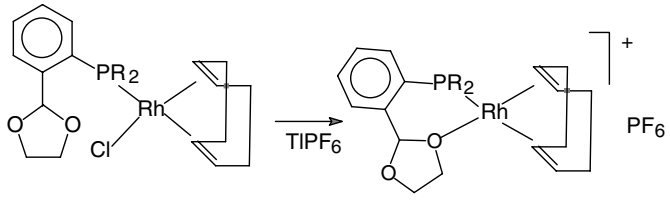



Fig. 5. IR spectra of the ligand **1b** (top) and its complexes **2b** (middle) and **3b** (bottom) (from 1000 to 1240 $cm^{-1}$).




**2a**, R: Ph
**2b**, R: $^i$Pr

**3a**, R: Ph
**3b**, R: $^i$Pr

Scheme 3. Dehalogenation of the neutral complexes **2**, formation of the complex cations **3**.

complex **2b**; the cationic complex **3b** shows two strong absorptions at 1137 and 1109 $cm^{-1}$. These IR spectroscopic observations are in agreement with the results obtained from X-ray analyses proving the coordination of the acetal O-atom to the Rh-centre in the complex cations **3a**–**3d** (Fig. 6 and Table 3).

Single crystals of the complexes **3a**, **b***$PF_6$ or **3c**, **d***$BF_4$ were obtained either by extraction with diethyl ether or by diffusion of pentane into a dichloromethane solution containing the complexes. The details of the X-ray analyses are given in Table 3 and show that only **3a***$PF_6$ crystallises with half a molecule of dichloromethane per unit located on the inversion centre of the unit cell.

The complex cations (**3a**–**3d**) show, like the neutral complexes **2**, a distorted square planar coordination at the Rh-centre. The coordination sphere of the Rh-centres in **3** is formed by the COD ligand occupying two neighbouring positions and the phosphine ligands of **1** acting as bidentate ligands via *P*,*O*-coordination (Fig. 6). The Rh–C-bond lengths for the C-atoms in *trans*-positions to the O-atoms are determined to be 10 pm shorter than the Rh–C-distances to the π-bound C-atoms *trans* to the P-atom. As for the complexes **2** this observation is in good agreement with other complexes of this type and is a consequence of the higher π-acceptor character of phosphorus compared to oxygen [13]. All the phenyl substituents on the dioxolane or dioxane rings for all the structures reported here are in axial positions except for **3c** where the phenyl substituent is placed in the more favoured equatorial position on the dioxane ring. This causes some larger ring torsions which effects the resulting Rh–O distance. Correspondingly the Rh–O distances in **3** are determined to be 212–215 pm, except for **3c** (220.9 pm) where it is found to be significantly longer.

For the complexes **3c**, **d***$BF_4$ the confirmed solid state structures were found also to exist in solution.

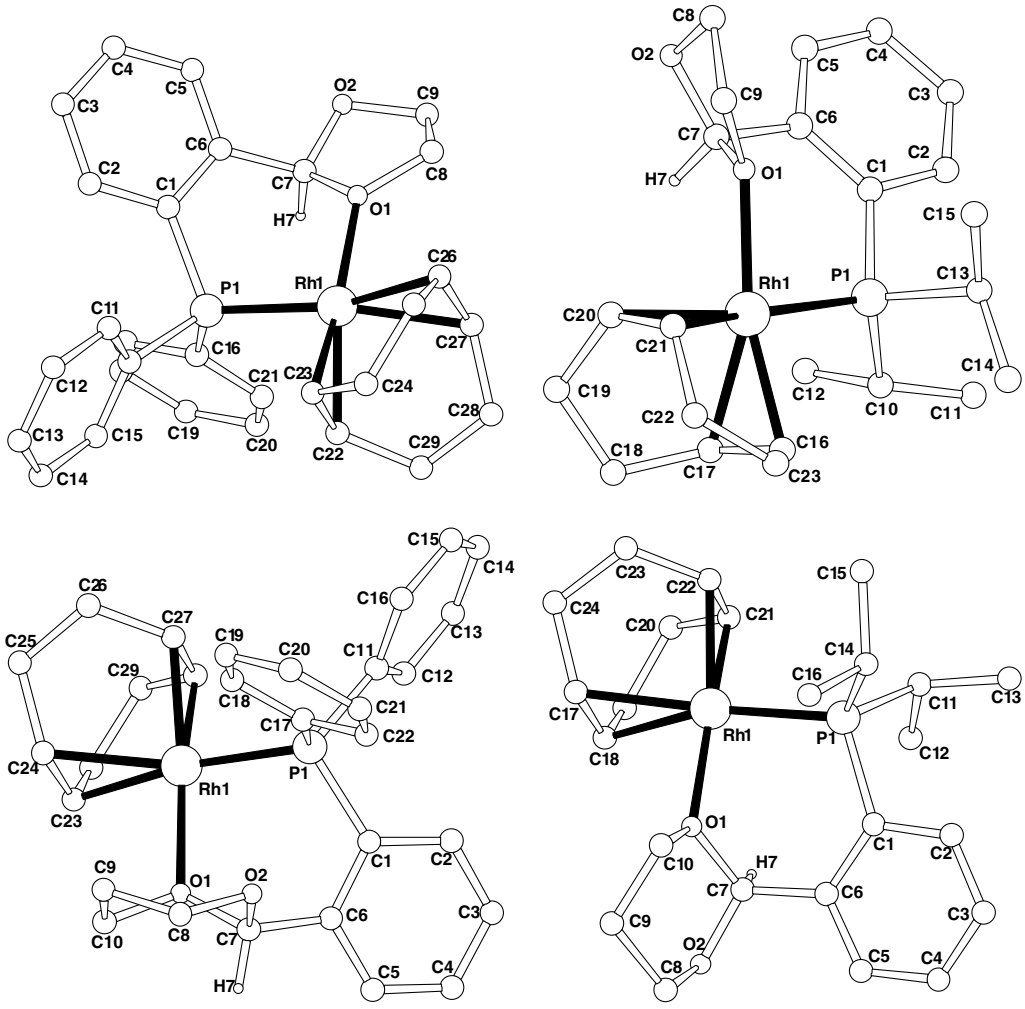



Fig. 6. View of the molecular structures of the complex cations **3a** (top left), **3b** (top right), **3c** (bottom left), **3d** (bottom right) determined by X-ray diffraction. Selected bond distances (pm) and torsion angles (°) for **3a**: O1–C7 147.4(3) pm, O2–C7 139.1(3) pm, H7–C7–C6–C5 59.0°; **3b**: O1–C7 145.6(3) pm, O2–C7 139.5(3) pm, H7–C7–C6–C5 77.0°; **3c**: O1–C7 146.1(4) pm, O2–C7 139.9(5) pm, H7–C7–C6–C1 −172.4°; **3d**: C7–O1 144.1(4) pm, C7–O2 140.0(4) pm, H7–C7–C6–C5 72.7°.

Table 3
Crystallographic data of the cationic complexes **3**

| Compound | 3a*$PF_6$*0.5$CH_2Cl_2$ | 3b*$PF_6$ | 3c*$BF_4$ | 3d*$BF_4$ |
|---|---|---|---|---|
| Empirical formula | $C_{29.5}H_{32}ClF_6O_2P_2Rh$ | $C_{23}H_{35}F_6O_2P_2Rh$ | $C_{30}H_{33}BF_4O_2PRh$ | $C_{24}H_{37}BF_4O_2PRh$ |
| Formula weight | 732.85 | 622.36 | 646.25 | 578.23 |
| Crystal size ($mm^3$) | $0.30 \times 0.30 \times 0.35$ | $0.30 \times 0.40 \times 0.15$ | $0.2 \times 0.1 \times 0.2$ | $0.2 \times 0.15 \times 0.1$ |
| Crystal system | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space group | $P2_1/c$ (No. 14) | $P\bar{1}$ (No. 2) | $P2_1/c$ (No. 14) | $P\bar{1}$ (No. 2) |
| Unit cell dimensions | | | | |
| $a$ (pm) | 1391.37(7) | 1054.90(4) | 1097.28(6) | 1030.34(4) |
| $b$ (pm) | 1089.86(6) | 1074.45(4) | 1315.97(7) | 1092.32(5) |
| $c$ (pm) | 2023.1(1) | 1417.33(5) | 1931.3(1) | 1359.30(6) |
| $\alpha$ (°) | 90.0 | 83.4202(6) | 90.0 | 76.970(1) |
| $\beta$ (°) | 105.764(1) | 68.2027(6) | 96.659(1) | 68.781(1) |
| $\gamma$ (°) | 90.0 | 61.9296(5) | 90.0 | 62.777(1) |
| Volume ($pm^3$) | $2952.5(3) \times 10^6$ | $1312.59(8) \times 10^6$ | $2770.0(3) \times 10^6$ | $1264.94(9) \times 10^6$ |
| $Z$ | 4 | 2 | 4 | 2 |
| $D_{calc}$ ($g/cm^3$) | 1.646 | 1.575 | 1.550 | 1.518 |
| Temperature (K) | 200 | 200 | 200 | 200 |
| $\theta$-Range (°) | $1.52 \leqslant \theta \leqslant 28.28$ | $1.55 \leqslant \theta \leqslant 28.30$ | $1.87 \leqslant \theta \leqslant 28.28$ | $1.61 \leqslant \theta \leqslant 28.30$ |
| Scan (°) | $\omega$-Scan, $\Delta\omega = 0.3$ | $\omega$-Scan, $\Delta\omega = 0.3$ | $\omega$-Scan, $\Delta\omega = 0.45$ | $\omega$-Scan, $\Delta\omega = 0.3$ |
| Index ranges | $-17 \leqslant h \leqslant 17$, $-14 \leqslant k \leqslant 14$, $-26 \leqslant l \leqslant 26$ | $-13 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 14$, $-18 \leqslant l \leqslant 18$ | $-14 \leqslant h \leqslant 14$, $-17 \leqslant k \leqslant 17$, $-25 \leqslant l \leqslant 25$ | $-13 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 14$, $-18 \leqslant l \leqslant 18$ |
| Number of | | | | |
| Reflections measured | 29,805 | 14,081 | 29,506 | 13,701 |
| Unique reflections | 7188 | 6295 | 6798 | 6102 |
| Reflections observed | 6081 ($I > 2\sigma$) | 5342 ($I > 2\sigma$) | 3922 ($I > 2\sigma$) | 4450 ($I > 2\sigma$) |
| Parameters refined | 389 | 322 | 361 | 313 |
| Residual electron density ($e/pm^3$) | $1.387 \times 10^{-6}$ | $0.594 \times 10^{-6}$ | $0.669 \times 10^{-6}$ | $0.733 \times 10^{-6}$ |
| Corrections | Lorentz and polarisation, experimental absorption correction [20] | Lorentz and polarisation, experimental absorption correction [20] | Lorentz and polarisation, experimental absorption correction [20] | Lorentz and polarisation, experimental absorption correction [20] |
| Structure solution | Direct methods | Direct methods | Direct methods | Direct methods |
| Structure refinement | Full-matrix least-square on $F^2$ | Full-matrix least-square on $F^2$ | Full-matrix least-square on $F^2$ | Full-matrix least-square on $F^2$ |
| Programs used | SHELX-97 [21], XPMA [22], WINRAY [23] | SHELX-97 [21], XPMA [22], WINRAY [23] | SHELX-97 [21], XPMA [22], WINRAY [23] | SHELX-97 [21], XPMA [22], WINRAY [23] |
| $R$ indices | $R_1 = 0.0382$ ($I > 2\sigma$) $R_w = 0.1086$ (all data on $F^2$) | $R_1 = 0.0288$ ($I > 2\sigma$) $R_w = 0.0736$ (all data on $F^2$) | $R_1 = 0.0457$ ($I > 2\sigma$) $R_w = 0.1100$ (all data on $F^2$) | $R_1 = 0.0498$ ($I > 2\sigma$) $R_w = 0.1044$ (all data on $F^2$) |

Standard deviations are given in parentheses.

On the basis of two-dimensional NOESY experiments relevant intramolecular NOEs between the different ligands at the Rh-centres were identified and confirm that in solution no conformational changes of the complexes occur.

Furthermore temperature dependent $^1$H NMR experiments showed that the phenyl substituents at the 2-position of the dioxane ring in **3c**, **3d** keep their positions showing no ring inversion of the dioxane rings.

In agreement with the IR spectroscopic data, the results from the X-ray analyses of the complexes **3**∗anions show significant changes in the bond lengths between the acetal C-atoms and the two acetal O-atoms. Generally the bond distances between the acetal C-atom and the coordinated O-atom (144–147 pm) were determined to be at least 3 pm longer than their corresponding distances to the non coordinated O-atom which were determined to be 139–140 pm. Comparing these values with the corresponding values observed in the complexes **2** or the free ligands **1**, it appears that the acetal C–O-distance of the coordinated O-atom is elongated where the one of the non-coordinated O-atom is shortened. This is an effect of coordination to the metal centre which is also observed in other complexes with coordinated 1,3-dioxolanes [14] or 1,3-dioxanes [12,15], even if in some cases this tendency seems to be only marginal [16].

A comparison of the rotational positions of the dioxolane or dioxane rings in the **3**∗anion to the complexes **2** can be performed on the basis of the torsion angle comprised of the acetal proton, the acetal C-atom itself, the carbon atom of the phenyl ring bound to the acetal C-atom, and one of its neighbouring C-atoms in the phenyl ring. The values of the complexes **2** were found to be less than 10° (Fig. 3) demonstrating the nearby perpendicular position of the different ring systems involved. For the complex cations **3a**, **b**, **d** these torsion angles were determined to be 59.0° for (**3a**) and 77.0° for (**3b**) which are much higher than those determined for complexes **2**, showing that coordination of the acetal O-atoms results in a rotation of about 60° around the axis described by the acetal C-atom and the C-atom of the phenyl ring it is bound to. Complex cation **3c** is an exception; the corresponding torsion angle (7.6°) is small and has a similar value to the values found in complexes **2**. This observation is an effect of the substitution pattern on the dioxane ring in **3c** where the phenyl substituent is found in a more favoured axial position. This allows the phenyl ring and the dioxane ring of **3c** to occupy perpendicular positions to one another, which is preferred on the grounds of sterics but results in the elongation of the Rh–O bond length.

The coordination behaviour of the ligands **1** in the complex cations **3** show coordination properties flexible enough for the stabilisation of free coordination sites at a metal centre possibly formed as intermediates in a catalytic cycle.

The complexes described here act as model compounds for complexes bound to a polyvinylalcohol resin with the polymer linkage to be used for an effective catalyst recycling. Therefore, the Rh-complexes **2** and the salts of the complex cations **3** were tested towards their catalytic selectivity in the hydroformylation of octene (Table 4).

The general selectivities in the hydroformylation of octene of the complexes **2** and the salts of the complex cations **3** are very similar to each other and comparable to other systems with no large phosphine excess involved [17]. The overall selectivity to the aldehydes is high and the complexes do not show high activity in the hydrogenation of octene or the aldehydes produced. All the pre-catalysts show isomerisation activity, transforming 1-octene into 2-octene, 3-octene and 4-octene which then are also hydroformylated by the catalysts. As the hydroformylation activity of 1-octene is higher than of its isomers, the most important products, representing 90% of the selectivity, are *n*-nonanal and 2-methyloctanal, which are formed in a 1.25:1 ratio. This *n*/*iso* ratio is typical for hydroformylation reactions carried out in the absence of large amounts of phosphine [17]. The very similar selectivity in the catalytic experiments of the neutral pre-catalysts **2** compared to their cationic analogues **3**∗anion might indicate that during the catalysis the chloro ligands in **2** leave the coordination sphere

Table 4
Selectivity (%) of the complexes **2** and **3**∗anion in the hydroformylation of octene

| Catalyst | Nonanal | 2-Methyl-octanal | 2-Ethyl-heptanal | 2-Propyl-hexanal | Olefins/octane | Alcohols |
|---|---|---|---|---|---|---|
| **2a** | 50.9 | 38.4 | 7.9 | 2.5 | 0.2 | 0 |
| **2b** | 51.6 | 37.9 | 7.5 | 2.4 | 0.5 | 0 |
| **2c** | 49.0 | 38.7 | 8.9 | 2.9 | 0.5 | 0 |
| **2d** | 52.8 | 37.0 | 7.5 | 2.4 | 0.3 | 0 |
| **3a**∗$PF_6$ | 52.1 | 39.7 | 5.9 | 1.5 | 0.6 | 0.2 |
| **3b**∗$PF_6$ | 52.4 | 40.1 | 5.8 | 1.4 | 0.2 | 0 |
| **3c**∗$BF_4$ | 47.7 | 41.3 | 5.5 | 1.6 | 0.3 | 3.6 |
| **3d**∗$BF_4$ | 52.8 | 38.4 | 6.5 | 2.1 | 0.2 | 0 |

Experiments performed with 0.02 mmol catalyst per 5 mmol octene in 50 ml dichloromethane at 65 °C and about 50 bar syngas pressure during 15 h. Selectivity is based on conversion reported on the base of GC/MS data.

of the metal so that independently from the neutral or ionic nature of the starting complex similar intermediates can be formed finally causing the observed comparable selectivity in the catalysis [10]. Whether during the catalysis $\eta^2$-*P*,*O*-coordination of the ligands **1** occurs can not be determined on the basis of the present data as in situ spectroscopic investigations actually have not been performed.

The data obtained from these catalytic experiments will form the basis for the evaluation of the results on catalytic transformations performed with the Rh loaded modified polyvinylalcohol.

## 3. Conclusions and outlook

The syntheses of the ligands **1** as well as their corresponding complexes **2** presented here is straightforward and proceed in good yields. With their 1,3-dioxanyl or 1,3-dioxolanyl residues representing a small part of the polymer backbone they act as model compounds for via *trans* acetalation on a polyvinylalcohol matrix immobilised systems in terms of characterisation and evaluation of the catalytic behaviour.

The complexes **2** and the cationic complexes **3** are catalysts for the hydroformylation of 1-octene and on the basis of an analysis of the product distribution it seems to be very probable that in the catalysis both complexes form similar intermediates as generally the product distribution is equal. If during the catalysis $\eta^2$-*P*,*O*-coordination of the ligands to the metal centre proceeds cannot be determined.

Investigations are ongoing on the pre-catalysts bound to PVA concerning their transformations during the catalysis via the identification of the complexes on the polymer after the catalysis. The long term behaviour of the PVA bound pre-catalysts in terms of Rh-leaching and the stability of the acetales is of essential interest and objective of present research as well the development of complexes which will show a higher selectivity in the hydroformylation of 1-octene. However, the complexes described here act as the first simple models for the characterisation of pre-catalysts which are via acetalation bound to a PVA resin and therefore contribute to the development of this system.

## 4. Experimental

All reactions were performed under 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. $TlPF_6$ was purchased from Fluorochem. $[(COD)RhCl]_2$ [18],and 2-(*ortho*-bromophenyl)-1,3-dioxolane or -dioxane [5] were synthesised from the literature procedures. Solvents were dried and purified by standard methods. NMR-spectra were recorded on a 250 MHz Bruker AVANCE or on a Varian Unity INOVA 400 MHz spectrometer at 25 °C and referenced to the residual proton signal of the solvent ($^1$H NMR spectra) or its carbon frequency ($^{13}$C NMR spectra) or to $H_3PO_4$ as external standard ($^{31}$P NMR spectra). The heteronuclear spectra were recorded with proton decoupling. The variable temperature NMR measurements were performed in $d^8$ toluene instead of $CDCl_3$ due to its higher boiling point. The two-dimensional NMR spectra were recorded in $CDCl_3$ due to the higher solubility of the complexes in it. The NOESY spectra were recorded at mixing times of 450 ms using 1 K of data points in f2 dimension and performing 512 experiments in f1 with 48 transients per experiment. The mass spectra were obtained on 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 on a BIORAD FT spectrometer. The elemental analyses were performed on a Vario EL CHN-analyser. For the details of the single crystal X-ray diffraction measurements see Tables 1–3 and Section 5. The X-ray analyses were performed with an irradiation time of 10 s per frame collecting a full sphere of data. For searches on single crystal X-ray diffraction data the Cambridge Structural Database has been used [19].

### 4.1. 2-(Ortho-diisopropylphosphinophenyl)-1,3-dioxolane, *1b*

7.8 ml of a 2.7 N *n*-BuLi solution in heptane (21.06 mmol) was added dropwise to a solution of 4.80 g (21.0 mmol) 2-(*ortho*-bromophenyl)-1,3-dioxolane in 50 ml THF at −78 °C. After stirring for another hour at −78 °C, 3.12 g (21.0 mmol) chlorodiisopropylphosphine was added and the reaction mixture was allowed to warm up to room temperature. After hydrolysis, phase separation and drying of the organic phase the solvent was removed in vacuo. The low melting-point residue was recondensed at 1 mbar and 120–150 °C (oil bath temperature) yielding 4.12 g (15.5 mmol, 74%) **1b** with a melting point of 50–51 °C.

IR (KBr)/cm$^{-1}$: 3063 (w), 2979, 2958, 2949, 2916 (s), 1473, 1437 (m), 1389, 1383, 1364, 1361, 1129 (s), 1082, 1058 (ss), 762, (ss).

MS (*m*/*z*): 265, $(M - H)^+$, 2%, 237, $C_{13}H_{18}PO_2^+$, 66%, 152, $C_7H_5PO_2^+$, 100%, 110, $C_6H_7P^+$, 84%.

$^1$H NMR ($CDCl_3$): $\delta = 0.92$ (dd, $^3J_{HH} = 6.8$ Hz, $^3J_{HP} = 12.4$ Hz, 6H, $CH_3$), 1.16 (dd, $^3J_{HH} = 7.0$ Hz, $^3J_{HP} = 15.3$ Hz, 6H, $CH_3$), 2.15 (m (br), 2H, PCH), 4.07 (m, 2H, OC*H*H), 4.17 (m, 2H, OCH*H*), 6.67 (d, $^4J_{HP} = 6.8$ Hz, 1H, $CHO_2$), 7.34–7.71 (m, 4H, Ar–H).

$^{31}$P NMR ($CDCl_3$): $\delta = -8.67$ (s).

$^{13}$C NMR ($CDCl_3$): $\delta$ = 18.75 (d, $^2J_{CP}$ = 8.9 Hz, 2C, $CH_3$), 19.38 (d, $^2J_{CP}$ = 18.6 Hz, 2C, $CH_3$), 23.37 (d, $^1J_{CP}$ = 10.5 Hz, 2C, PCH), 64.69 (s, 2C, $OCH_2$), 100.46 (d, $^3J_{CP}$ = 30.8 Hz, 1C, $O_2C$), 125. 64 (s, 1C, Ar–C), 127.65 (s, 1C, Ar–C), 128.27 (s, 1C, Ar–C), 131.27 (s, 1C, Ar–C), 142.89 (d, $^1J_{CP}$ = 19.4 Hz, 1C, Ar–C)

**1b** ($C_{15}H_{23}O_2P$): C, 67.01 (67.65 calc.); H, 9.15 (8.70 calc.).

### 4.2. 2-(Ortho-diphenylphosphinophenyl)-1,3-dioxane, *1c*

5.7 ml of a 2.7 normal *n*-BuLi solution in heptane (15.39 mmol) was added added dropwise to a solution of 3.77 g (15.5 mmol) 2-(*ortho*-bromophenyl)-1,3-dioxane in 50 ml THF at −78 °C. After stirring for another hour at −78 °C 3.42 g (15.5 mmol) chlorodiphenylphosphine was added and the reaction mixture was allowed to warm up to room temperature. After hydrolysis, phase separation and drying of the organic phase the solvent was removed in vacuo. The residue was resolved in dichloromethane and the solvent removed in vacuo and the resulting oily residue was recrystallised from pentane yielding 4.52 g (13.0 mmol, 84%) **1c** with a melting point of 96 °C.

IR (KBr)/cm$^{-1}$: 3065 (m), 3054 (m), 2972 (s), 2953 (s), 2853 (m), 1591 (w), 1583 (m), 1568 (w), 1477 (s), 1466 (s), 1460 (m), 1437 (s), 1432 (s), 1392 (m), 1376 (m), 1129 (m), 1098 (ss), 1027 (m), 1002 (ss), 759 (ss), 748 (ss), 698 (ss), 546 (s), 520 (s), 507 (s), 488 (s).

FIR (PE): 467 (m), 423 (m), 414 (m), 397 (m), 386 (m).

MS (*m*/*z*): 349,(M + H)$^+$, 100%.

$^1$H NMR ($CDCl_3$): $\delta$ = 1.36 (d (br), $^2J_{H,H}$ = 13.4 Hz, 1H, $(OCH_2)_2CHH_{eq}$), 2.16 (pqt, $^2J_{H,H}$ = 13.4 Hz, $^3J_{Hax,Hax}$ = 12.8 Hz, $^3J_{Hax,Heq}$ = 5.1 Hz, 1H, $(OCH_2)_2CHH_{ax}$), 3.87 (dpt, $^2J_{H,H}$ = 11.1 Hz, $^3J_{Hax,Hax}$ = 12.8 Hz, $^3J_{Hax,Heq}$ = 2.3 Hz, 2H, $OCHH_{ax}$), 4.07 (dd, $^2J_{H,H}$ = 11.1 Hz,$^3J_{Heq,Hax}$ = 5.1 Hz, 2H, $OCHH_{eq}$), 6.13 (d, $^4J_{H,P}$ = 5.8 Hz, 1H, $CHO_2$), 6.94–7.75 (m, 14H, Ar).

$^{31}$P NMR ($CDCl_3$): $\delta$ = −16.1 (s).

$^{13}$C NMR ($CDCl_3$): $\delta$ = 25.0 (s, 1C, $(OCH_2)_2CH_2$), 66.6 (s, 2C, $OCH_2$), 99.5 (d, $^3J_{C,P}$ = 26.3 Hz, 1C, $CHO_2$), 125. 3–142.3 (m, 18C, Ar).

**1c** ($C_{22}H_{21}O_2P$): C, 74.99 (75.85 calc.); H, 6.08 (6.04 calc.).

### 4.3. 2-(Ortho-diisopropylphosphinophenyl)-1,3-dioxane, *1d*

3.396 g (14.0 mmol) 2-(*ortho*-bromophenyl)-1,3-dioxane was dissolved in 50 ml THF at −78 °C. After dropwise addition of 5.2 ml of a 2.7 N *n*-BuLi solution in heptane and stirring for 1 h at this temperature 2.132 g (14.0 mmol), chlorodiisopropylphosphine was added and the reaction mixture was allowed to warm up to room temperature. After hydrolysis, phase separation and drying of the organic phase, the solvent was removed in vacuo. The oily residue was recondensed at 140–170 °C and 1 mbar yielding 3.13 g (11.2 mmol, 80%) of **1d** as colourless crystals with a melting point of 82 °C.

IR (KBr)/cm$^{-1}$: 3090 (w), 3072 (w), 3057 (m), 2986 (s), 2965 (ss), 2950 (ss), 2895 (s), 2865 (ss), 2847 (ss), 1589 (w), 1568 (w), 1519 (w), 1467 (ss), 1459 (ss), 1448 (m), 1437 (m), 1387 (ss), 1371 (ss), 1364 (ss), 1362 (ss), 1248 (m), 1233 (s), 1149 (ss), 1125 (m), 1101 (ss), 1007 (ss), 992 (ss), 963 (ss), 759 (ss), 657 (m), 606 (m), 532 (m), 506 (s).

FIR (PE): 471 (s), 460 (s), 417 (s), 390 (m), 377 (m), 359 (s), 292 (m).

$^1$H NMR ($CDCl_3$): $\delta$ = 0.91 (dd, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 12.4 Hz, 6H, $CH_3$), 1.14 (dd, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 14.9 Hz, 6H, $CH_3$), 1.44 (dpsept, $^2J_{H,H}$ = 13.4 Hz, $^3J_{Heq,Hax}$ = 2.0 Hz, $^3J_{Heq,Heq}$ = 1.0 Hz, 1H, $(OCH_2)_2CHH_{eq}$), 2.13 (m, 2H, PCH), 2.25 (pqt, $^2J_{H,H}$ = 13.4 Hz, $^3J_{Hax,Hax}$ = 12.4 Hz, $^3J_{Heq,Heq}$ = 5.0 Hz, 1H, $(OCH_2)_2CHH_{ax}$), 4.05 (ptd, $^2J_{H,H}$ = 11.7 Hz, $^3J_{Hax,Hax}$ = 12.4 Hz, $^3J_{Hax,Heq}$ = 2.0 Hz, 2H, $OCHH_{ax}$), 4.22 (ddd, $^2J_{H,H}$ = 11.7 Hz, $^3J_{Heq,Hax}$ = 5.0 Hz, $^3J_{Heq,Heq}$ = 1.0 Hz, 2H, $OCHH_{eq}$), 6.42 (d, $^4J_{H,P}$ = 7.2 Hz, 1H, $CHO_2$), 7.30–7.78 (m, 4H, Ar).

$^{31}$P NMR ($CDCl_3$): $\delta$ = −7.5 (s).

$^{13}$C NMR ($CDCl_3$): $\delta$ = 18.6 (s, 2 C, $CH_3$), 19.0 (d, $^2J_{C,P}$ = 16.9 Hz, 2 C, $CH_3$), 23.0 (d, $^1J_{C,P}$ = 11.3 Hz, 2C, PCH), 24.8 (s, 1C, $(OCH_2)_2CH_2$), 66.2 (s, 2C, $OCH_2$), 98.4 (d, $^3J_{C,P}$ = 31.9 Hz, 1C, $CHO_2$), 125.2–130.8 (m, 6C, Ar).

MS (*m*/*z*): 281, (M + H)$^+$, 100%.

**1d** ($C_{16}H_{25}O_2P$): C, 68.43 (68.55 calc.); H, 8.93 (8.99 calc.).

### 4.4. {Chloro(COD)[2-(ortho-diphenylphosphinophenyl)-1,3-dioxolane]rhodium(I)}, *2a*

0.174 g (0.35 mmol) $[(COD)RhCl]_2$ was dissolved in 10 ml dichloromethane and after addition of 0.236 mg (0.7 mmol) 2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxolane (**1a**) the solution was stirred for 60 min at room temperature. The solvent was removed in vacuo and the residue was extracted with refluxing pentane for 50 h yielding 0.33 g (0.6 mmol, 81%) **2a**.

IR (KBr)/cm$^{-1}$: 3059, 3043 (w) 2951, 2937, 2884, 2871, 1480, 1437, 1433 (m) 1123 (m), 1092 (ss), 761, 746, 740 (m), 694 (s).

FIR (PE): 283 (s, $\nu$(Rh–Cl)).

$^1$H NMR ($CDCl_3$): $\delta$ = 1.96 (s, br, 2H, $CH_2$ (COD)), 2.05(s, br, 2H, $CH_2$ (COD)), 2.41 (s, br, 4H, $CH_2$ (COD)), 3.34 (s, br, 2H, CH (COD)), 3.95 (m, 2H, $OCHH$), 4.20 (m, 2H, $OCHH$), 5.59 (s, br, 2H, CH (COD)), 7.26–7.81 (m, 14H, Ar–H), 7.49 (m, 1H, $CHO_2$).

$^{31}$P NMR ($CDCl_3$): $\delta$ = 23.40 (d, $^1J_{PRh}$ = 146.5 Hz).

$^{13}$C NMR ($CDCl_3$): $\delta$ = 27.94 (s, 2C, $CH_2$ (COD)), 31.95 (s, 2C, $CH_2$ (COD)), 64.63 (s, 2C, $OCH_2$), 70.19 (s, br, 2C, CH (COD)), 101.01 (d, $^3J_{CP}$ = 15.0 Hz, 1C, $HCO_2$), 102.67 (s, 2C, CH (COD)), 127.10–134.27 (m, 18C, Ar).

MS/ESI (*m*/*z*): 545, $(M - Cl)^+$, 100%.

**2a** ($C_{29}H_{31}ClO_2PRh$): C, 60.14 (59.96 calc.); H, 5.88 (5.38 calc.).

### 4.5. {Chloro(COD)[2-(ortho-diisopropylphosphinophenyl)-1,3-dioxolane]rhodium(I)}, 2b

190.8 mg (0.39 mmol) $[(COD)RhCl]_2$ was dissolved in 10 ml dichloromethane and after addition of 207 mg (0.78 mmol) 2-(*ortho*-diisopropylphosphinophenyl)-1,3-dioxolane (**1b**) it was stirred for 30 min at room temperature. The solvent was removed in vacuo and the residue was extracted with refluxing pentane for 12 h yielding 0.336 g (0.65 mmol, 84%) **2b** as a crystalline solid.

IR (KBr)/cm$^{-1}$: 3097, 3061, 3040 (w), 2963 (s), 2883 (s), 1471, 1439, 1431 (m), 1129 (m), 755 (s).

FIR (PE): 285 (m, *v*(Rh–Cl)).

MS/ESI (*m*/*z*): 477, $(M - Cl)^+$, 100%.

$^1$H NMR ($CDCl_3$): $\delta$ = 1.32 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 15.0 Hz, 6H, $CH_3$), 1.32 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{HP}$ = 13.4 Hz, 6H, $CH_3$) 1.97 (m, 4 H, $CH_2$ (COD)), 2.38 (m, 4H, $CH_2$ (COD)), 2.56 (s, br, 2H, PCH), 3.50 (s, br, 2H, CH (COD)), 4.19 (m, 2H, OCHH), 4.30 (m, 2H, OCHH), 5.38 (s, br, 2H, CH (COD)), 7.65 (d, $^4J_{HP}$ = 3.8 Hz, 1H, $CHO_2$), 7.35–7.82 (m, 4H, Ar–H).

$^{31}$P NMR ($CDCl_3$): $\delta$ = 25.91 (d, $^1J_{PRh}$ = 144.7 Hz).

$^{13}$C NMR ($CDCl_3$): $\delta$ = 18.51 (s, 2C, $CH_3$), 19.24 (s, 2C, $CH_3$), 23.12 (d, $^1J_{CP}$ = 18.8 Hz, 2C, PCH), 27.60 (s, 2C, $CH_2$ (COD)), 31.95 (s, 2C, $CH_2$ (COD)), 64.69 (s, 2C, $(OCH_2)_2$), 69.78 (d, $^1J_{CRh}$ = 11.3 Hz, 2C, CH (COD)), 100.67 (d, $^1J_{CRh}$ = 15.0 Hz, 2C, CH (COD)), 101.10 (s, 1C, $HCO_2$), 127.45 (s, 1C, Ar–C), 128.16 (s, 1C, Ar–C), 129.04 (s, 1C, Ar–C), 129.58 (s, 1C, Ar–C), 140. 97 (s, 1C, Ar–C).

**2b** ($C_{23}H_{35}ClO_2PRh$): C, 53.57 (53.86 calc.); H, 7.29 (6.88 calc.).

### 4.6. {Chloro(COD)[2-(ortho-diphenylphosphinophenyl)-1,3-dioxane]rhodium(I)}, 2c

To a solution of 150.3 mg (0.3 mmol) $[Rh(COD)Cl]_2$ in 5 ml dichloromethane, 213.4 mg (0.6 mmol) 2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxane (**1c**) was added. After stirring for 45 min the solvent was removed in vacuo and the resulting powder extracted with pentane for 3 days. 297.1 mg (0.5 mmol, 83%) of **2c** as yellow crystals was isolated.

IR (KBr)/cm$^{-1}$: 3053 (w), 2960 (m), 2938 (m), 2916 (m), 2872 (m), 2829 (m), 1586 (w), 1571 (w), 1480 (m), 1467 (m), 1435 (m), 1123 (m), 1099 (ss), 998 (s), 759 (m), 749 (m), 695 (s), 546 (w), 529 (s), 516 (s), 510 (s).

FIR (PE): 493 (s), 467 (w), 419 (s), 385 (s), 341 (w), 284 (s).

$^1$H NMR ($CDCl_3$): $\delta$ = 1.26 (dd (br), $^2J_{H,H}$ = 13.2 Hz, $^3J_{Heq,Hax}$ = 1.4 Hz, 1H, $(OCH_2)_2CHH_{eq}$), 1.95 (m, 2H, $CH_2$ (COD)), 2.10 (m, 1H, $CH_2$ (COD), 2.15 (pqt, $^2J_{H,H}$ = 13.2 Hz, $^3J_{Hax,Hax}$ = 12.1 Hz, $^3J_{Hax,Heq}$ = 4.9 Hz, 2H, $(OCH_2)_2CHH_{ax}$), 2.44 (m, 4H, $CH_2$ (COD)), 3.24 (s (br), 2H, CH $(COD)_{trans\,to\,Cl}$), 3.45 (dpt, $^2J_{H,H}$ = 11.3 Hz, $^3J_{Hax,Hax}$ = 12.1 Hz, $^3J_{Hax,Heq}$ = 1.4 Hz, 2H, $OCHH_{ax}$), 3.96 (dd, $^2J_{H,H}$ = 11.3 Hz, $^3J_{Heq,Hax}$ = 4.9 Hz, 2H, $OCHH_{eq}$), 5.57 (s (br), 2H, CH $(COD)_{trans\,to\,P}$), 5.92 (d, $^4J_{H,P}$ = 2.1 Hz, 1H, $CHO_2$), 7.28–7.97 (m, 14H, Ar–H).

$^{31}$P NMR ($CDCl_3$): $\delta$ = 24.4 (d, $^1J_{P,Rh}$ = 150.2 Hz).

$^{13}$C NMR ($CDCl_3$): $\delta$ = 24.5 (s, 1C, $(OCH_2)_2CH_2$), 27.9 (s, 2C, $CH_2$ (COD)), 32.0 (s, 2C, $CH_2$ (COD)), 66.4 (s, 2C, $OCH_2$), 70.6 (d, $^1J_{C,Rh}$ = 13.1 Hz, 2C, CH $(COD)_{trans\,to\,Cl}$), 98.9 (d, $^1J_{C,Rh}$ = 9.4 Hz, 2C, CH $(COD)_{trans\,to\,P}$), 103.2 (s, 1C, $CHO_2$), 127.2–140.8 (m, 18C, Ar).

MS/ESI (*m*/*z*): 559 $(M - Cl)^+$, 100%, 349 ($C_{22}H_{22}O_2P^+$, 19%).

**2c** ($C_{30}H_{33}ClO_2PRh$): C, 60.55 (60.57 calc.); H, 5.74 (5.59 calc.).

### 4.7. {Chloro(COD)[2-(ortho-diisopropylphosphinophenyl)-1,3-dioxane]rhodium(I)}, 2d

To a solution of 120.3 mg (0.24 mmol) $[Rh(COD)Cl]_2$ in 5 ml dichloromethane, 137.4 mg (0.49 mmol) 2-(*ortho*-diisopropylphosphinophenyl)-1,3-dioxane (**1d**) was added. After stirring for 45 min the solvent was removed in vacuo, the residue extracted with pentane for 15 h yielding 200.6 mg (0.38 mmol, 78%) of **2d** as yellow crystals.

IR (KBr)/cm$^{-1}$: 3060 (w), 2989 (m), 2973 (s), 2956 (m), 2939 (m), 2869 (s), 2833 (m), 1567 (w), 1520 (w), 1467 (sh) (m), 1430 (m), 1391 (m), 1385 (s), 1369 (m), 1364 (m), 1250 (m), 1233 (m), 1145 (s), 1123 (m), 1095 (ss), 994 (ss), 982 (ss), 948 (s), 759 (ss), 650 (m), 615 (m), 525 (s).

FIR (PE): 472 (s), 432 (m), 409 (m), 389 (m), 378 (s), 334 (w), 282 (s).

$^1$H NMR ($CDCl_3$): $\delta$ (ppm = 1.24 (dd, $^3J_{H,H}$ = 7.0 Hz, $^3J_{H,P}$ = 13.4 Hz, 6H, $CH_3$), 1.50 (dd, $^3J_{H,H}$ = 7.3 Hz, $^3J_{H,P}$ = 15.1 Hz, 6H, $CH_3$), 1.52 (dd, $^2J_{H,H}$ = 15.5 Hz, $^3J_{Heq,Hax}$ = 1.3 Hz, 1H, $(OCH_2)_2CHH_{eq}$), 1.93 (m, 4H, $CH_2$(COD)), 2.36 (pqt, $^2J_{H,H}$ = 15.1 Hz, $^3J_{Hax,Hax}$ = 12.0 Hz, $^3J_{Hax,Heq}$ = 4.7 Hz, $(OCH_2)_2CHH_{ax}$), 2.38 (m, 4H, $CH_2$ (COD), 2.59 (s (br), 2H, PCH), 3.31 (s (br), 2H, CH $(COD)_{trans\,to\,Cl}$), 4.26 (dd, $^2J_{H,H}$ = 11.2 Hz, $^3J_{Heq,Hax}$ = 4.7 Hz, 2H, $OCHH_{eq}$), 4.40 (ptd, $^2J_{H,H}$ = 11.2 Hz, $^3J_{Hax,Hax}$ = 12.0 Hz, $^3J_{Hax,Heq}$ = 1.3 Hz, 2H, $OCHH_{ax}$), 5.42 (s (br), 2H, CH $(COD)_{trans\,to\,P}$), 7.29–7.92 (m, 4H, Ar), 7.36 (d, $^4J_{H,P}$ = 3.6 Hz, 1H, $CHO_2$).

$^{31}$P NMR ($CDCl_3$): $\delta$ = 25.5 (d, $^1J_{P,Rh}$ = 143.8 Hz).

$^{13}$C NMR ($CDCl_3$): $\delta$ (ppm = 19.1 (s, 4C, $CH_3)_2$), 23.8 (d, $^1J_{C,P}$ = 16.9 Hz, 2C, PCH), 25.1 (s, 1C, $(OCH_2)_2CH_2$), 27.5 (s, 2C, $CH_2$ (COD)), 31.9 (s, 2C, $CH_2$ (COD)), 66.4 (s, 2C, $OCH_2$), 70.4 (s, 2C, CH $(COD)_{trans\,to\,Cl}$), 98.9 (d, $^3J_{C,P}$ = 15.0 Hz, 1C, $CHO_2$), 100.6 (s, 2C, CH $(COD)_{trans\,to\,P}$), 127.1–141.8 (m, 6C, Ar).

MS/ESI (*m*/*z*): 491, $((M - Cl)^+$, 100%), 281 $(C_{16}H_{26}O_2P)^+$, 36%.

**2d** ($C_{24}H_{37}ClO_2PRh$): C, 55.14 (54.71 calc.); H, 7.00 (7.08 calc.).

### 4.8. {(COD)[$\eta^2$-P,O-2-(ortho-diphenylphosphinophenyl)-1,3-dioxolane]rhodium(I)} hexafluoro-phosphate, ***3a**PF$_6$***

0.228 g (0.46 mmol) $[(COD)RhCl]_2$ and 0.301 g (0.93 mmol) 2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxolane were dissolved in 5 ml dichloromethane and stirred at room temperature for 30 min. 0.324 mg (0.93 mmol) $TlPF_6$ was added and it was stirred for 1 h. The resulting precipitate was filtered off from the reaction mixture and discarded. The remaining solution was layered with THF and pentane and after two days at room temperature, 0.567 g (0.77 mmol, 83%) orange crystals of **3a***$PF_6$*0.5 dichloromethane were isolated.

IR (KBr)/cm$^{-1}$: 3049 (m), 2968, 2946, 2920, 2885 (m), 1437, 1435 (ss), 1114 (s), 1094 (ss), 841, 742, 700, 695 (ss), 558 (ss).

MS/ESI (*m*/*z*): 545 $(M - PF_6)^+$, 100%, 335 $(C_{21}H_{20}O_2P)^+$, 13%.

$^1$H NMR ($CD_2Cl_2$): $\delta$ = 1.99 (m, 2H, $CH_2$ (COD)), 2.15 (m, 2H, $CH_2$ (COD)), 2.53 (m, 4H, $CH_2$ (COD), 3.26 (s, br, 2H, =CH (COD)), 4.13 (m, 2H, OC*H*H), 4.20 (m, 2H, OCH*H*), 5.50 (s, br, 2H, =CH (COD)), 5.57 (s, 1H, $CHO_2$), 7.34–7.77 (m, 14H, Ar–H).

$^{31}$P NMR ($CD_2Cl_2$): $\delta$ = 21.96 (d, $^1J_{PRh}$ = 146.7 Hz), −143.69 (sept., $^1J_{PF}$ = 711.4 Hz).

$^{13}$C NMR ($CD_2Cl_2$): $\delta$ = 28.67 (s, 2C, $CH_2$ (COD)), 32.86 (s, 2C, $CH_2$ (COD)), 68.14 (s, 2C, $OCH_2$), 72.40 (d, $^1J_{CRh}$ = 12.2 Hz, 2C, CH (COD)), 104.46 (d, $^3J_{CP}$ = 12.2 Hz, 1C, $CHO_2$), 108.36 (s, 2C, CH (COD)), 125.69–138.97 (m, 18C, Ar–C).

**3a***$PF_6$*0.5 dichloromethane ($C_{29.5}H_{32}ClF_6O_2P_2Rh$): C, 48.65 (48.35 calc.); H, 4.56 (4.40 calc.).

### 4.9. {(COD)[$\eta^2$-P,O-2-(ortho-diisopropylphosphinophenyl)-1,3-dioxolane]rhodium(I)} hexa-fluorophosphate, ***3b**PF$_6$***

0.203 g (0.58 mmol) $TlPF_6$ was dissolved in 5 ml dichloromethane. To the resulting suspension 0.117 g (0.23 mmol) **2** was added and the mixture was stirred for 2 h at room temperature. After filtration and removal of the solvent, 0.113 g (0.18 mmol, 79%) **3b***$PF_6$ was isolated as a yellow powder. Single crystals of **3b***$PF_6$ were obtained by extraction of the product with refluxing diethyl ether for 1 day.

IR (KBr)/cm$^{-1}$: 3062 (w), 2963, 2924, 2879, 1471, 1439, 1435, 1462, 1387, 1364, 1137, 1109, 1090, 1060 (m), 839 (ss), 766 (m ), 558 (ss).

MS/ESI (*m*/*z*): 477, $(M - PF_6)^+$, 100%.

$^1$H NMR ($CD_2Cl_2$): $\delta$ = 1.26 (dd, $^3J_{HH}$ = 6.9 Hz, $^3J_{HP}$ = 14.6 Hz, 12H, $CH_3$), 2.14 (s (br), 2H, $CH_2$ (COD)), 2.16 (s (br), 2H, $CH_2$ (COD)), 2.29 (s (br), 2H, PCH), 2.57 (m, 4H, $CH_2$ (COD)), 3.93 (m, 2H, OC*H*H), 4.04 (s (br), 2H, CH (COD)), 4.09 (s (br), 2H, OCH*H*), 5.28 (s (br), 2H, CH (COD)), 7.29 (s, 1H, $CHO_2$), 7.53–7.70 (m, 4H, Ar–H).

$^{31}$P NMR ($CD_2Cl_2$): $\delta$ = 22.18 (d, $^1J_{PRh}$ = 141.7 Hz), −144.24 (sept., $^1J_{PF}$ = 711.4 Hz).

$^{13}$C NMR ($CD_2Cl_2$): $\delta$ = 18.22 (s, 2C, $CH_3$), 19.26 (s, 2C, $CH_3$), 25.80 (s (br), 2C, PCH), 27.64 (s, 2C, $CH_2$ (COD)), 32.61 (s, 2C, $CH_2$ (COD)), 66.20 (s, 2C, $(OCH_2)_2$), 72.01 (s (br), 2 C, CH (COD)), 104.39 (s (br), 2 C, CH (COD)), 104.81 (d, $^4J_{CP}$ = 5.6 Hz, 1C, $CHO_2$), 123.77 (d, $J_{CP}$ = 30.0 Hz, 1C, Ar), 125.54 (d, $J_{CP}$ = 7.5 Hz, 1C, Ar), 129.92 (d, $J_{CP}$ = 3.8 Hz, 1C, Ar), 131.64 (s, 1C, Ar), 141.14 (d, $J_{CP}$ = 9.4 Hz, 1C, Ar).

**3b***$PF_6$ ($C_{23}H_{35}F_6O_2P_2Rh$): C, 43.82 (44.39 calc.); H, 5.84 (5.67 calc.).

### 4.10. {(COD)[$\eta^2$-P,O-2-(ortho-diphenylphosphinophenyl)-1,3-dioxane]rhodium(I)} tetrafluoro-borate, ***3c**BF$_4$***

To a solution of 67.0 mg (0.16 mmol) $[(COD)_2Rh]BF_4$ in 10 ml THF, 57.5 mg (0.16 mmol) 2-(*ortho*-diphenylphosphinophenyl)-1,3-dioxane (**1c**) was added. After stirring for 2 h at 67 °C the solvent was removed in vacuo and the residue was washed twice with 20 ml pentane. The orange solid was dissolved in dichloromethane and layered successively with THF and pentane. After 24 h, 79.2 mg (0.12 mmol, 77%) of **3c***$BF_4$ was isolated as orange crystals.

IR (KBr)/cm$^{-1}$: 3055 (w), *v*(Ar–H), 2977 (w), 2955 (w), 2933 (w), 2875 (w), 2834 (w), *v*(C–H), 1584 (w), 1571 (w), 1480 (m), 1464 (w), 1452 (w), 1437 (m), 1368 (w), *v*(C=C) and *δ*(C–H), 1167 (m), 1152 (m), 1133 (m), 1101 (ss), 1067 (ss), 1037 (ss), *v*(C–O) and *v*(B–F), 755 (sh) (ss), 702 (s), $\rho_{wag}$(Ar–H), 525 (s), 512 (s).

$^1$H NMR ($CDCl_3$): $\delta$ = 1.83 (d (br), $^2J_{H,H}$ = 14.3 Hz, 1H, $(OCH_2)_2CH_{eq}$), 2.04 (m, 2H, $CH_2$ (COD)), 2.11 (m, 2H, $CH_2$ (COD)), 2.24 (m, 1H, $(OCH_2)_2CH_{ax}$), 2.56 (s (br), 4H, $CH_2$ (COD)), 3.25 (s (br), 2H, CH $(COD)_{trans\,to\,O}$), 3.93 (dd (br), $^2J_{H,H}$ = 12.0 Hz, $^3J_{Heq,Hax}$ = 3.5 Hz, 2H, $OCH_{eq}$), 4.15 (pt (br), $^2J_{H,H}$ = $^3J_{Hax,Hax}$ = 12.0 Hz, 2H, $OCH_{ax}$), 5.53 (s (br), 2H, CH $(COD)_{trans\,to\,P}$), 5.74 (s, 1H, $CHO_2$), 7.35–7.70 (m, 14H, Ar–H).

$^{31}$P NMR ($CDCl_3$): $\delta$ = 28.2 (d, $^1J_{P,Rh}$ = 147.0 Hz).

$^{13}$C NMR ($CDCl_3$): $\delta$ = 27.4 (s, 1C, $(OCH_2)_2CH_2$), 27.6 (s, 2C, $CH_2$ (COD)), 32.6 (s, 2C, $CH_2$ (COD)), 70.6 (d, $^1J_{C,Rh}$ = 15.5 Hz, 2C, CH $(COD)_{trans\,to\,O}$), 71.6 (s, 2C, $OCH_2$), 106.5 (d, $^3J_{C,P}$ = 5.2 Hz, 1C, $CHO_2$), 108.5 (dd, $^1J_{C,Rh}$ = 6.9 Hz, $^2J_{C,P}$ = 9.2 Hz, 2C, CH $(COD)_{trans\,to\,P}$), 124.2–140.8 (m, 18C, Ar).

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

**3c***$BF_4$ ($C_{30}H_{33}BF_4O_2PRh$): C, 55.47 (55.72 calc.); H, 5.44 (5.15 calc.).

### *4.11. {(COD)[η²-P,O-2-(ortho-diisopropylphosphinophenyl)-1,3-dioxane]rhodium(I)} tetrafluoro-borate, **3d***$BF_4$*

To a solution of 189.0 mg (0.47 mmol) $[(COD)_2Rh]BF_4$ in 20 ml THF, 131.5 mg (0.47 mmol) 2-(*ortho*-diisopropylphosphinophenyl)-1,3-dioxane (**1d**) was added. After refluxing for 2 h the volume of solvent was reduced in vacuo to 3 ml. **3d***$BF_4$ was precipitated by addition of 40 ml pentane. After filtration, the solid was washed three times with 10 ml of pentane. The residue was dissolved in dichloromethane and layered successively with THF and pentane. After 48 h, 189.2 mg (0.33 mmol, 70%) of **3d***$BF_4$ as orange crystals were isolated.

IR (KBr)/$cm^{-1}$: 3021 (w), 2963 (m), 2936 (m), 2925 (m), 2976 (m), 2832 (m),, 1591 (w), 1530 (w), 1480 (w), 1470 (m), 1461 (m), 1451 (m), 1437 (m), 1430 (m), 1386 (m), 1135 (m), 1097 (ss), 1055 (ss), 1032 (ss), 762 (m), 711 (m), 652 (m), 528 (m).

$^1$H NMR ($CDCl_3$): $\delta$ = 1.10 (d, $^3J_{H,H}$ = 6.7 Hz, 6H, $CH_3$), 1.16 (d, $^3J_{H,H}$ = 6.4 Hz, 6H, $CH_3$), 1.82 (d (br), $^2J_{H,H}$ = 13.9 Hz, 1H, $(OCH_2)_2CH\mathit{H}_{eq}$), 2.06 (s (sh), 5H, $CH_2$(COD), $(OCH_2)_2CH\mathit{H}_{ax}$), 2.22 (s (br), 2H, PCH), 2.53 (s (br), 4H, $CH_2$ (COD)), 4.00 (s (br), 2H, CH $(COD)_{trans\,to\,O}$), 4.26 (s (br), 4H, $OCH_2$), 5.31 (s (br), 2H, CH $(COD)_{trans\,to\,P}$), 7.26 (s, 1H, $CHO_2$), 7.38–7.82 (m, 4H, Ar).

$^{31}$P NMR ($CDCl_3$): $\delta$ = 23.7 (d, $^1J_{P,Rh}$ = 143.3 Hz).

$^{13}$C NMR ($CDCl_3$): $\delta$ = 18.4 (s, 4C, $CH_3$), 19.2 (d, $^1J_{C,P}$ = 3.4 Hz, 2C, PCH), 26.2 (s, 1C, $(OCH_2)_2CH_2$), 27.6 (s, 2C, $CH_2$ (COD)), 32.9 (s, 2C, $CH_2$ (COD)), 65.3 (s, 2C, $OCH_2$), 72.0 (s (br), 2C, CH $(COD)_{trans\,to\,O}$), 99.9 (d, $^3J_{C,P}$ = 8.6 Hz, 1C, $CHO_2$), 106.2 (s (br), 2C, CH $(COD)_{trans\,to\,P}$), 129.4–140.2 (m, 6C, Ar).

MS/ESI (*m*/*z*): 491, $M^+$, 100%, 281 $(C_{16}H_{16}O_2P)^+$, 31%.

**3d***$BF_4$ ($C_{24}H_{37}BF_4O_2PRh$): C, 49.04 (49.85 calc.); H, 6.45 (6.45 calc.).

## 5. Supplementary material

Crystallographic data of the structures have been deposited at the Cambridge Crystallographic Database Centre, supplementary publication Nos. CCDC 161581 (**1b**), 222146 (**1c**), 222145 (**1d**), 161582 (**2b**), 222148 (**2c**), 222147 (**2d**), 161583 (**3a**), 161584 (**3b**), 222149 (**3c**), 222150 (**3d**). 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:www.ccdc.cam.ac.uk).

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