Synthesis of sulfated mono- and ditertiary phosphines, complex chemistry and catalysis

H. Gulyás, A. Dobó, and J. Bakos

Abstract: Cyclic and bicyclic sulfates have been prepared from commonly available alcohols. Nucleophilic cleavage of the cyclic sulfates affords a new type of water-soluble mono- and ditertiary phophines bearing -OSO_3Li groups in distinguished positions in the molecular framework. Both phosphines have amphiphilic character. Reactions of the chiral **2** and the dppp analogue **5** with $[Rh(COD)Cl]_2$ and $Pt(PhCN)_2Cl_2$ provide novel zwitterionic complexes. Rhodium complexes of **2** and **5** have been successfully applied in liquid biphasic hydroformylation of styrene and octene-1. When the rhodium complex of **5** was used as catalyst in hydroformylation of styrene, less then 4 ppm rhodium could be detected in the organic phase.

Key words: cyclic sulfates, water soluble phosphines, amphiphilic character, Rh complexes, Pt complexes, hydroformylation.

Résumé : On a préparé des sulfates cycliques et bicycliques à partir d'alcools disponibles facilement. Le clivage nucléophilique des sulfates cycliques conduit à la formation d'un nouveau type de phosphines mono- et ditertiaires, solubles dans l'eau, portant des groupes -OSO_3Li dans des positions définies du squelette moléculaire. Les deux types de phosphines présentent un caractère amphiphilique. Les réactions du $[Rh(COD)Cl]_2$ et du $Ph(PhCN)_2Cl_2$ avec composé chiral **2** et de son analogue à la dppp, **5**, conduisent à la formation de nouveaux complexes zwitterioniques. On a pu appliquer avec succès les complexes **2** et **5** du rhodium à l'hydroformylation biphasique liquide du styrène et de l'oct-1-ène. Quand on a utilisé le complexe de rhodium **5** comme catalyseur dans l'hydroformylation du styrène, on n'a détecté que quatre ppm de rhodium dans la phase organique.

Mots clés : sulfates cycliques, phosphines solubles dans l'eau, caractère amphiphilique, complexes du rhodium, complexes du platine, hydroformylation.

[Traduit par la Rédaction]

Introduction

Much effort has been directed toward the synthesis of new catalytic species with recent focus on water-soluble catalysts (for recent reviews see ref. 1). Transition-metal complexes can easily be rendered water soluble by incorporating polar substituents (2) e.g., -SO_3Na, -CO_2Na, -OH, -PMe_3^+, -NMe_3^+, -$PO(ONa)_2$, and polyethers.

Recently we introduced a novel route to a new class of water-soluble phosphines (3). We have reasoned that this methodology will be of particular interest since: (*i*) a wide range of starting compounds (e.g., diol, triol, tetrol) is available; (*ii*) the synthesis is simple; and (*iii*) provides an easy access to a series of amphiphilic or water-soluble phosphines. Water solubility of these phosphines is provided by the -OSO_3Li group.

Salts of sulfuric acid hemiesters are known to be excellent detergents. For example sodium dodecylsulfate is used in many aqueous organometallic catalytic systems to improve the catalytic activity and (or) selectivity of the reaction (4). In our case the sulfate group is attached to the ligand itself, rendering it not only water-soluble, but also amphiphilic. To our knowledge, only a very few ligands with amphiphilic properties have been reported (5). These ligands are expected to increase the activity of organic–aqueous biphasic catalytic systems by improvement of the miscibility of the two liquid phases (6). Also quite few ligands are known, where the coordinating functional group is not affected by the group providing the water solubility (7). In these molecules the -PPh_2 unit is remote enough from the -OSO_3Li function so that the electronic nature of the -PPh_2 group will be unaffected.

Hemilabile ligands have recently come into focus. Weak coordination of a functional group can stabilize certain conformations of the catalytically active complex and improve the selectivity of a reaction (8). Another advantage of a

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Dedicated to Professor Brian James on the occasion of his 65th birthday.

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weakly coordinating functional group is that it can be easily replaced by the substrate resulting in an increase in the activity of the catalyst. A hard sulfate group is not expected to have strong coordination ability toward soft metal centers, but its labile coordination should not be overlooked.

We report here detailed synthetic route for the preparation of mono- and ditertiary phosphines. Complex formation and catalytic application of the model compounds are presented.

Experimental

General information

Synthesis of the phosphines and their complexes were carried out under a purified argon atmosphere using standard Schlenk-type techniques. Tetrahydrofuran (THF), diethyl ether (Et_2O), toluene, and benzene were distilled from sodium benzophenone ketyl under argon. Methylene chloride (CH_2Cl_2) and pyridine were distilled from CaH_2 and methanol (MeOH) was distilled from $Mg(OMe)_2$ under argon. Water (H_2O) was distilled twice under argon. Deuterated methanol and water (CD_3OD and D_2O) were deoxygenated by bubbling with argon for 10 min. Deuterated chloroform ($CDCl_3$) was deoxygenated by distillation under argon. Pentaerythritol was purchased from Aldrich and used as received. (2*R*,4*R*)-2,4-Pentanediol was prepared by the slightly modified literature method (9). GC analyses were performed using a Hewlett–Packard 5830A gas chromatograph (SPB-1 30 m column, film thickness (0.1 μm), N_2 carrier gas (2 mL min^{-1})). Optical rotations were obtained using a Schmidt Haensch 21245 polarimeter. Nuclear magnetic resonance spectra were recorded on a Varian Unity 300 and Bruker DRX-500 spectrometer using $CDCl_3$, CD_3COCD_3, D_2O, and CD_3OD as solvents. The ^1H and ^{13}C NMR chemical shifts are referenced to internal or external standard $SiMe_4$, and to residual portio-solvent peaks (i.e., $CHCl_3$). The ^{31}P NMR spectra were recorded with 85% H_3PO_4 as an external standard. The ^{195}PtNMR (64 MHz) chemical shift is given in ppm relative to Na_2PtCl_6 as an external standard. Positive chemical shifts are downfield from the standard. Adjustments of pH were performed using an OP-211/1 Laboratory Digital pH Meter. Rhodium content of the organic phase was determined by atom absorption using a PerkinElmer 5100 PC atom absorption spectrometer, electrothermal atomization HGA 600, AS 70 autosampler, and GEM software. Fast atom bombardment (FAB) mass spectrometric measurements were performed using a VG-ZAB-2SEQ reverse geometry instrument operating at an accelerating voltage of 8 kV. A cesium ion gun producing 30 keV ions was utilized for ion bombardment. Glycerol was used as the FAB matrix.

Catalysis

Two-phase hydroformylation reactions of styrene and 1-octene with rhodium complexes of **2** and **5** were carried out in a 20 mL stainless steel autoclave. The catalysts were made in situ. Mixing the water, toluene, alkene, phosphine, and $[Rh(COD)Cl]_2$ resulted in an orange emulsion which was transferred into the autoclave under argon atmosphere. The autoclave was pressurized with CO–H_2 and then placed in a heating mantle preheated to the desired reaction temperature. The autoclave was shaken at a frequency of 180 min^{-1}, 75 deg from the upright position, with a horizontal amplitude of 3 cm. The reaction was monitored by the change in pressure.

Leaching of rhodium was determined as follows: The toluene phase was separated. 0.5 mL of cH_2SO_4 and 1 mL of cH_2O_2 were added. Further 5x1mL of cH_2O_2 was added during one week. All volatiles were evaporated from the homogenous solution. 10 mL of deionised water and 0.1 g of Na_2SO_4 were added. Analysis was undertaken on a Perkin Elmer 5100 PC atom absorption spectrometer in conjunction with a series of rhodium standards.

Cyclic sulfates

Cyclic sulfate **1** was prepared using the general literature method described by Gao and Sharpless (10).

Synthesis of (4*R*,6*R*)-4,6-dimethyl-2,2-dioxide-1,3,2-dioxathiane (1)

Thionyl chloride (4.6 mL, 0.064 mol) was added, via a dropping funnel, to (2*R*,4*R*)-2,4-pentanediol (5.5 g, 0.053 mol) in 50 mL CCl_4. The resulting light brown solution was refluxed for 1 h to complete the sulfite formation. HCl was removed under reduced pressure (the water aspirator was adjusted to a quite gentle flow). CH_3CN (50 mL), $NaIO_4$ (16 g, 0.075 mol), and $RuCl_3$ hydrate (0.008 g, 0.032 mmol, 40% ruthenium) were added to the solution. The resulting brown mixture was cooled to 0°C and 75 mL of water was added slowly. The mixture turned orange within 5 min. The reaction was allowed to stir at ambient temperature for 1 h. The mixture was then diluted with Et_2O (400 mL). The organic phase was separated, washed with water (20 mL), saturated $NaHCO_3$ solution (2 × 20 mL), and brine (20 mL). After being dried over $MgSO_4$ the solution was filtered through a pad of SiO_2 to remove the ruthenium. The solvent was removed in vacuum. Recrystallization of the product from Et_2O–hexane yielded a white crystalline solid (8.85 g, 82%), mp 34 to 35°C. $[\alpha]_D^{24}$ = 37.5° (c 5.02, $CHCl_3$). ^1H NMR (300.15 MHz, $CDCl_3$) δ: 1.64 (d, J_{HCCH} = 6.6 Hz, 6H, CH_3), 2.03 (t, J_{HCCH} = 5.6 Hz, 2H, CH_2), 5.03 ppm (pseudo-sext due to signal overlap, 2H, CH). ^{13}C NMR (75.42 MHz, $CDCl_3$) δ (ppm): 20.0 (s, CH_3), 35.5 (s, CH_2), 80.3 (s, CH).

Synthesis of 2,4,8,10-tetraoxa-3,9-dithiaspiro[5.5]undecane 3,9-dioxide (3)

A solution of $SOCl_2$ (17.5 mL, 0.24 mol) in pyridine (20 mL) was added dropwise to a solution of pentaerythritol (13.6 g, 0.1 mol) in pyridine (250 mL). The reaction mixture was stirred for 3 h. The solvent, remaining $SOCl_2$, and most of the pyridine–hydrochloride were removed under reduced pressure. The brownish-white solid residue was washed with water, $NaHCO_3$ solution, water again, and with diethyl ether. After drying, the product was obtained as a white, microcrystalline solid (19.3 g, 85%), mp 152°C. ^1H NMR (500.13 MHz, CD_3COCD_3) δ: 3.929 (d, J_{HCH} = 12.0 Hz, 1H, CH_2), 3.934 (d, J_{HCH} = 12.0 Hz, 1H, CH_2), 4.406 (d, J_{HCH} = 12.1 Hz, 1H, CH_2), 4.411 (d, J_{HCH} = 12.1 Hz, 1H, CH_2, 4.61 (d, J_{HCH} = 12.1 Hz, 2H, CH_2), 4.94 ppm (d, J_{HCH} = 12.3 Hz, 2H, CH_2). ^{13}C NMR (75.42 MHz, CD_3COCD_3) δ (ppm): 35.68 (s, C), 59.95 (s, CH_2), 59.99 (s, CH_2).

Synthesis of 2,4,8,10-tetraoxa-3,9-dithiaspiro[5.5]undecane 3,3,9,9-tetraoxide (4)

$NaIO_4$ (54.3 g, 0.25 mol) and $RuCl_3$ hydrate (27.2 mg, 0.107 mmol, 40% ruthenium) were added to the bicyclic sulfite **3** (19.3 g, 0.085 mol) in 400 mL of CH_3CN. Water (240 mL) was added slowly to the brown suspension. The mixture turned orange and a considerable amount of white solid precipitated. The reaction was stirred further for 1.5 h. The white solid was filtered and washed exhaustively with water. The white residue was dried at ambient temperature and extracted with hot acetone. Removal of the solvent under reduced pressure yielded a white, microcrystalline solid (17.6 g, 68% calculated for pentaerythritol), mp 280–282°C. ^{1}H NMR (300.15 MHz, CD_3COCD_3) δ (ppm): 5.01 (s, 8H, CH_2). ^{13}C NMR (75.42 MHz, CD_3COCD_3) δ (ppm): 34.30 (s, C), 74.4 (s, CH_2).

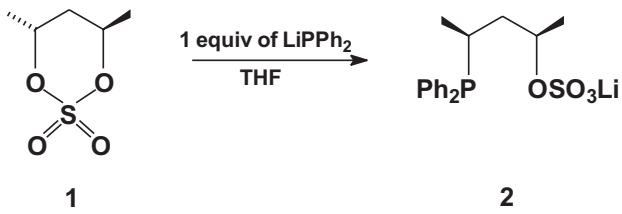
Synthesis of (2*R*,4*S*)-4-(diphenylphosphino)-pent-2-yl sulfate lithium salt (2)-butyl sulfate lithium salt

(4*R*,6*R*)-4,6-Dimethyl-2,2-dioxide-1,3,2-dioxathiane (**1**) (2.0 g, 0.012 mol) in THF (15 mL) was added to $LiPPh_2$·dioxane adduct (4.4 g, 0.016 mol) in THF (50 mL) at 0°C, meanwhile the bright red color turned light brown. The mixture was stirred at ambient temperature for 1 h. The THF was removed under reduced pressure, then deoxygenated water (40 mL) and Et_2O (20 mL) were added. The aqueous phase was separated and washed with Et_2O (20 mL) again. The pH of the solution was adjusted to 7.0 using diluted H_2SO_4 solution. The water was removed under reduced pressure, then CH_2Cl_2 (20 mL) was added. Li_2SO_4 was removed by filtration. Evaporation of the solvent under vacuum yielded a white, solid foam (3.1 g, 72%). FAB-MS$^-$: 351 (M – Li$^+$). ^{1}H NMR (300.15 MHz, $CDCl_3$) δ (ppm): 0.84 (dd, J_{PCCH} = 15.1 Hz, J_{HCCH} = 6.6 Hz, 3H, CH_3), 1.01 (d, J_{HCCH} = 6.0 Hz, 3H, CH_3), 1.02 (overlapped by the signal of CH_3, 1H, diastereotopic CH_2), 1.57 (br m, 1H, diastereotopic CH_2), 2.55 (br s, 1H, C*H*-PPh_2), 4.49 (br m, 1H, C*H*-OSO_3Li), 6.91 (br m, 6H, Ar), 7.23 (br m, 4H, Ar). ^{31}P NMR (121.42 MHz, $CDCl_3$) δ (ppm): 1.13. ^{13}C NMR (125.77 MHz, D_2O) δ: 17.99 (d, J_{PCC} = 14.7 Hz, *C*H_3-CH-PPh_2), 23.40 (s, *C*H_3-CH-OSO_3Li), 27.37 (d, J_{PC} = 6.9 Hz, CH_3-*C*H-PPh_2), 42.63 (d, J_{PCC} = 15.8 Hz, *C*H_3-CH-OSO_3Li), 77.71 (d, J_{PCCC} = 12.3 Hz, CH_3-*C*H-OSO_3Li), 131.03 (s, Ar), 131.50 (d, J_{PCC} = 6.3 Hz, Ar), 135.99 (d, J_{PCC} = 17.6 Hz, Ar), 138.41 (d, J_{PCC} = 32.7 Hz, Ar).

Preparation of 1,3-bis(diphenylphosphino)-2,2-bis(lithiumsulfatemethyl)-propane (5)

2,4,8,10-Tetraoxa-3,9-dithiaspiro[5.5]undecane 3,3,9,9-tetraoxide (**4**) (3.0 g, 0.012 mol) in THF (20 mL) was added to $LiPPh_2$·dioxane adduct (8.4 g, 0.035 mol) in THF (60 mL) at 0°C, meanwhile the red color of the reaction mixture faded. The mixture was stirred at ambient temperature for 1 h. The THF was removed under reduced pressure, then deoxygenated water (40 mL) and Et_2O (20 mL) were added. After separation of the phases, the aqueous phase was washed with Et_2O (20 mL) again. The pH of the solution was adjusted to 7.0 using a diluted H_2SO_4 solution. The water was removed under reduced pressure, then CH_2Cl_2 (20 mL) and CH_3OH (6 mL) were added. Li_2SO_4 was removed by filtration. The solvent was evaporated in vacuum

Scheme 1.



to give a white solid foam (5.42 g, 73%). FAB-MS$^-$: 637 (M – Li$^+$). ^{1}H NMR (500.13 MHz, D_2O) δ (ppm): 2.28 (s, 4H, CH_2), 3.89 (s, 4H, CH_2), 6.89 (m, 8H, Ar), 6.95 (t, J_{HCCH} = 7.1 Hz, 4H, Ar), 7.09 (m, 8H, Ar). ^{31}P NMR (202.45 MHz, D_2O) δ (ppm): –28.9. ^{13}C NMR (125.77 MHz, D_2O) δ (ppm): 33.05 (m, CH_2), 42.20 (t, J_{PCC} = 12.1 Hz, C), 71.62 (m, CH_2), 128.98 (d, J_{PCCC} = 3.8 Hz, Ar), 129.29 (s, Ar), 133.15 (d, J_{PCC} = 21.4 Hz, Ar), 138.35 (d, J_{PC} = 7.5 Hz, Ar).

Results and discussion

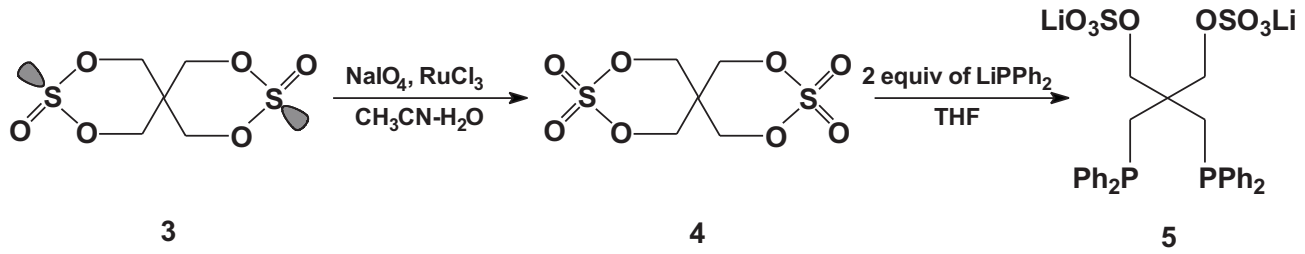
Preparation of cyclic sulfates

Cyclic sulfate of (2*R*,4*R*)-2,4-pentanediol (**1**) (Scheme 1) was obtained by a simple one pot reaction following the procedure developed for 1,2-cyclic sulfates by Gao and Sharpless (10). The synthesis involves the treatment of diols with thionyl chloride followed by ruthenium-catalyzed oxidation. Sulfate **1** could be obtained in this way with high yield (82%).

The bicyclic sulfate of pentaerythritol (**4**) could not be prepared by the general literature method. Pentaerythritol and $SOCl_2$ react with negligible reaction rate in CCl_4, which is the recommended solvent for the sulfite formation. Obviously, this fact is due to the poor solubility of the tetrol in CCl_4. Although, upon addition of dioxane to the CCl_4, the bicyclic sulfate could be isolated after the oxidation step, the yield was still very poor (17%).

To gain the product in a satisfying yield, a different procedure has been developed for the synthesis of **4** (Scheme 2). (*i*) The formation of sulfite and the oxidation were carried out in consecutive manner by the isolation of the intermediate sulfite **3**. Reaction of pentaerythritol and $SOCl_2$ in pyridine provided the corresponding bicyclic sulfite **3** with good yield (85%). Even though this spiro-compound is a known molecule of great practical importance (11), its stereochemistry has not been discussed in the literature in details. In a double chair conformation this molecule should have a C_2 axis as the only symmetry element, but its ^{1}H NMR spectrum exhibits a more complex picture. Details of the stereochemical investigation of the bicyclic sulfite will be presented in a subsequent publication. (*ii*) Racemic bicyclic sulfite was dissolved in CH_3CN. $NaIO_4$ and a catalytic amount of $RuCl_3 \cdot 3H_2O$ were added. Slow addition of water to this mixture initiated the oxidation. The crude product was precipitated from the reaction mixture spontaneously. The modified procedure afforded the bicyclic sulfate ester **4** in a 68% overall yield after purification.

Scheme 2.



3 4 5

Preparation, stability, and characterization of the novel phosphines

The monotertiary phosphine **2** has been prepared by the nucleophile cleavage of the cyclic sulfate of (2*R*,4*R*)-2,4-pentanediol **1** with $LiPPh_2$ in THF (Scheme 1). Nucleophilic attack occurred with complete inversion at the stereogenic center.

The bicyclic sulfate ester **4** reacts smoothly with 2 equivalents of $LiPPh_2$ to give the new water-soluble "sulfated" phosphine **5**, which has two hydrophilic tails attached to the bridgehead carbon atom (Scheme 2). It is interesting to note that the ditertiary phosphine **5** is a structural analogue of the well-known ligands dppp (1,3-(diphenylphosphino)propane) and dpppts (tetrasulfonated dppp). Both dppp and dpppts have important catalytic applications (12).

Although it is known that an ionic sulfate group can act as a leaving group (13), it was clear that its anionic nature renders it kinetically much less reactive than a $ROSO_2OR'$. The negative charge decreases the polarity of C—O bond, and the electrostatic repulsion between the "leaving group" and an anionic attacking group also increases the activation energy of the substitution. Accordingly, no replacement of the $-OSO_3Li$ was experienced in THF at ambient temperature, even when an excess of $LiPPh_2$ was used. The sulfated phosphines proved to be stable in hot, neutral, or slightly basic aqueous solution also. For example, when the aqueous solution of **5** was heated at 80°C for 1 h, or the aqueous solution of **2** was heated at 90°C, pH = 10 for several hours no appreciable amount of decomposition or hydrolysis could be detected.

NMR and FAB-MS data are in agreement with the formula in the case of both phosphines. Both phosphines feature amphiphilic character. For example, at ambient temperature solubility of **2** is 490 g L^{-1} in H_2O and 290 g L^{-1} in CH_2Cl_2. For a comparison, the water solubility of TPPMS (monosulfonated triphenylphosphine) having about the same size and one sulfonate group is 12 g L^{-1} (14). Ditertiary phosphine **5** with two sulfated tails attached to the bridgehead carbon atom has a great water solubility and is also soluble in a number of organic solvents (alcohols, THF).

Characterization of Rh(I) and Pt(II) complexes

Rh(I) and Pt(II) complexes are often applied catalysts in homogenous catalysis (15). To study the coordination features of the new phosphines, reactions of **2** and **5** with $[Rh(COD)Cl]_2$ (COD = 1,5-cyclooctadiene) and $Pt(PhCN)_2Cl_2$ were carried out. Reactions were monitored by ^{31}PNMR spectroscopy since the coordination shifts and metal–phosphorus coupling constants are diagnostic features for the identification of the products.

Coordination chemistry of the ligands with rhodium

The monotertiary phosphine **2** was reacted with $[Rh(COD)Cl]_2$ at a 2:1 phosphorus:Rh ratio in CD_3OD and D_2O (Scheme 3). In both solvents two complexes were formed and some of the ligand remained uncoordinated. The ^{31}P NMR spectrum (CD_3OD) exhibited resonances at 36.8 ppm (d, $J_{Rh\text{-}P}$ = 147 Hz) and 30.4 ppm (d, $J_{Rh\text{-}P}$ = 147 Hz). The coordination shifts ($\Delta\delta = \delta_{complex} - \delta_{free\ ligand}$) are 29.5 and 35.9 ppm, respectively. Relative intensity of the two doublets (signal at 30.4 ppm compared to the signal at 36.8 ppm) was 0.3. The broad signals were indicative of a dynamic equilibrium between the complexes and the free ligand, which was more significant in D_2O than in CD_3OD. For example doublet character of the signal at 30.4 ppm was not perceptible in D_2O.

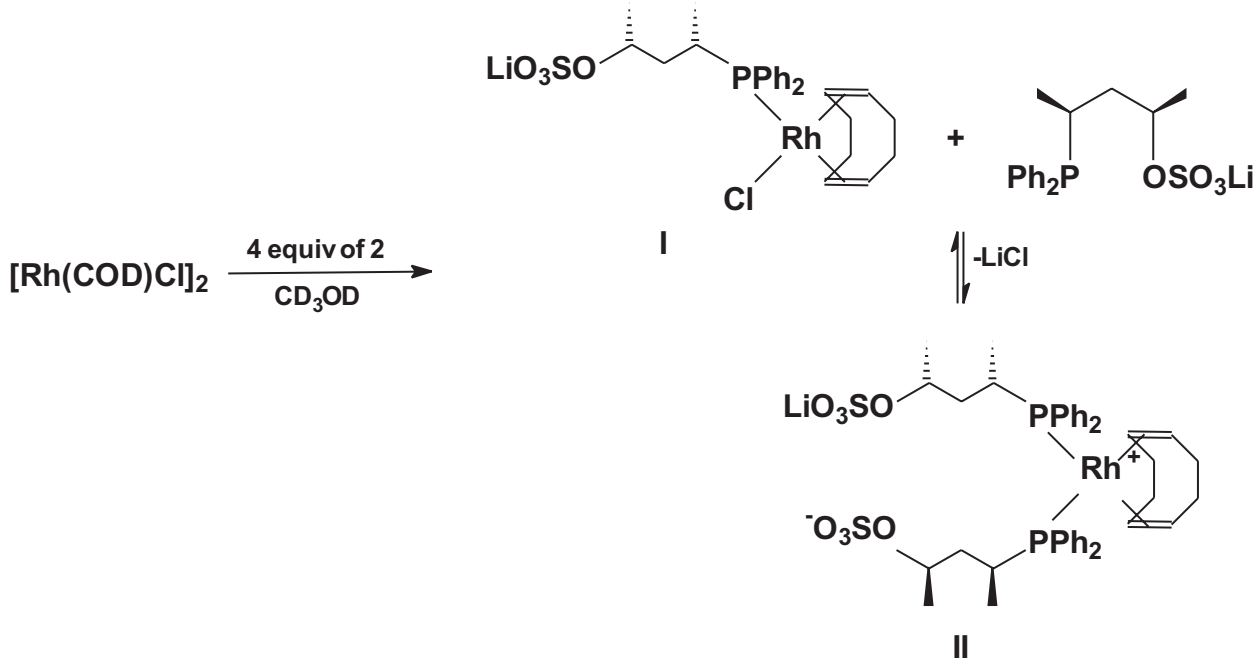
We presumed that $[Rh(COD)Cl]_2$ was cleaved by 2 equiv of the phosphine to give complex **I**, but the substitution of chloride leading to complex **II** did not take place completely. To prove our hypothesis, the experiment was repeated in CD_3OD saturated with KCl. Under these conditions, chloride substitution didn't take place at all, which resulted in the disappearance of the doublet at 30.4 ppm and an increase in the intensity of the signal of the free ligand.

When ligand **2** was reacted with $[Rh(COD)Cl]_2$ at a 1:1 or lower phosphorus:Rh ratio in CD_3OD the doublet at 30.4 ppm was absent from the spectrum again. When phosphorus:Rh ratio was increased to 4, the relative intensity of the two signals (30.4 vs. 36.8 ppm) was found to increase to 0.66, and a new species appeared at about 50 ppm. All signals were broad probably as a result of an exchange between the free and coordinated phosphine. Doublet character of the signal at 36.8 ppm and multiplicity of the new resonance were not observable. Finally, $[Rh(COD)Cl]_2$ was treated with $AgNO_3$ in CD_3OD to obtain $[Rh(COD)(CD_3OD)_2]NO_3$. This complex, with two weakly coordinating ligands, was reacted with 2 equiv of the phosphine. Now the spectrum displayed only a doublet at 30.4 ppm.

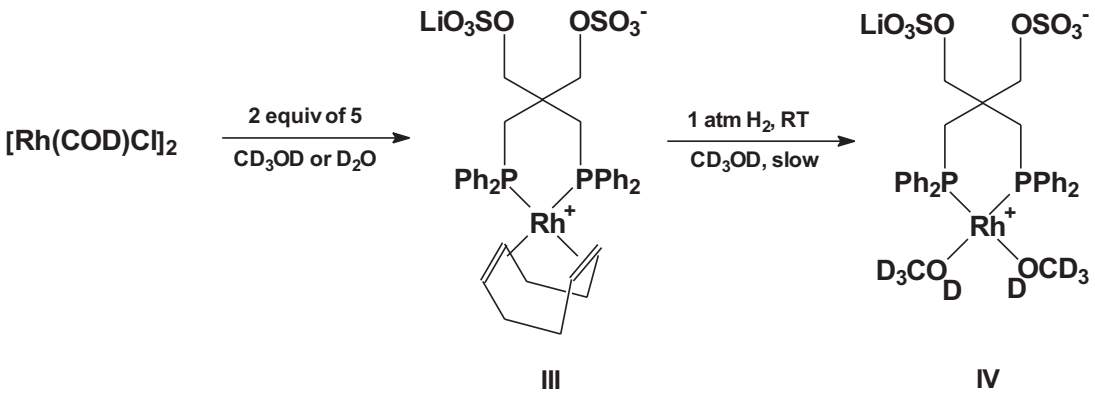
These results clearly indicate that the doublet at 36.8 ppm belongs to the complex **I**, and the other doublet at 30.4 ppm can be assigned to the complex **II**. Chemical shifts are consistent with the proposed structures. Since chloride is expected to be a weaker σ-donor and a stronger π-acceptor ligand than phosphine **2**, electron density of the central atom should be larger in **II** than in **I** resulting a more downfield resonance for complex **I**.

When chelating phosphine **5** was reacted in a 2:1 ratio with $[Rh(COD)Cl]_2$ in CD_3OD or D_2O–EtOAc, complex **III** formed as the only species (Scheme 4). ^{31}P NMR data of **III** (δ 13.9 ppm (d, J_{RhP} = 141 Hz), in CD_3OD or D_2O) do not significantly differ from that of the analogue complex of

Scheme 3.



Scheme 4.



dppp (16). MS-FAB$^+$ and MS-FAB$^-$ spectra of the complex showed parent ions [M + Li^+] (*m*/*z* = 855) and [M – Li^+] (*m*/*z* = 848). A zwitterionic structure for the complex is suggested in which one of the -OSO_3^- groups of the ligand acts as a counterion for the rhodium.

When H_2 was bubbled into the solution of **III**, a minor amount (13% based on ^{31}P NMR) of complex **IV** arose (δ 37.5 ppm (d, J_{RhP} = 187 Hz) in CD_3OD). The relative resistance of **III** against oxidative addition of H_2 is not surprising. Analogous complexes behave in a similar way as described in the literature (16). Complexes containing NBD (NBD = 2,5-bicyclo[2.2.1]heptadiene) instead of COD tends to react with hydrogen without difficulty, since NBD is easily saturated under a hydrogen atmosphere (17).

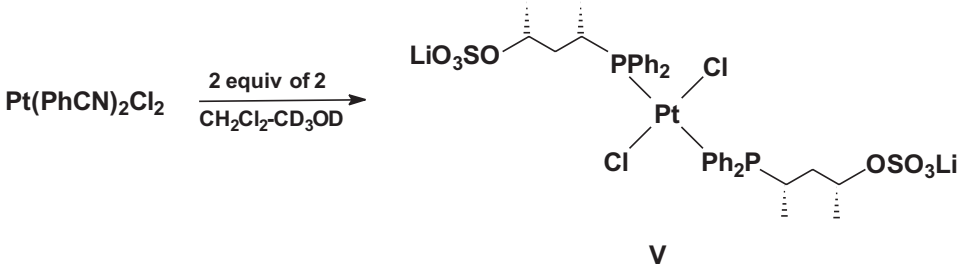
Coordination chemistry of the ligands with Pt(II)

When amphiphilic phosphine **2** was reacted in a 2:1 ratio with $Pt(PhCN)_2Cl_2$ in CH_2Cl_2 or in a mixture of CH_2Cl_2 and MeOH, complex **V** formed exclusively. ^{31}P NMR spectrum of the complex is characteristic of a square-planar, *dsp*^{2} hybrid PtP_2X_2 species (δ 27.7 (s, $J_{Pt\text{-}P}$ = 2544 Hz) in CD_3OD). The value of $J_{Pt\text{-}P}$ clearly indicates the presence of two phosphine ligands *trans* to each other (Scheme 5).

Compound **5** forms three complexes when reacted in a 1:1 ratio with $Pt(PhCN)_2Cl_2$ in a mixture of CH_2Cl_2–D_2O. Complex **VI** (δ –1.8 ppm (s, $J_{Pt\text{-}P}$ = 3467 Hz), in D_2O), **VII** (δ –3.0 ppm (s, $J_{Pt\text{-}P}$ = 2215 Hz), in D_2O), and **VIII** (δ –6.8 ppm (s, $J_{Pt\text{-}P}$ = 3438 Hz), in D_2O) are generated in a 1:0.81:0.73 ratio (Scheme 6). ^{31}P NMR data clearly indicated that both of the phosphorus on the chelating ligand are coordinated and that they are equivalent (i.e., the other two coordination sites should be occupied by the same species in each complex). The coupling values of $J_{Pt\text{-}P}$ of **VI** and **VIII** suggested chloride or solvent coordination *trans* to the phosphorus, whereas $J_{Pt\text{-}P}$ of **VII** is characteristic of Pt(II) phosphine complexes with phosphorus atoms *trans* to each other.

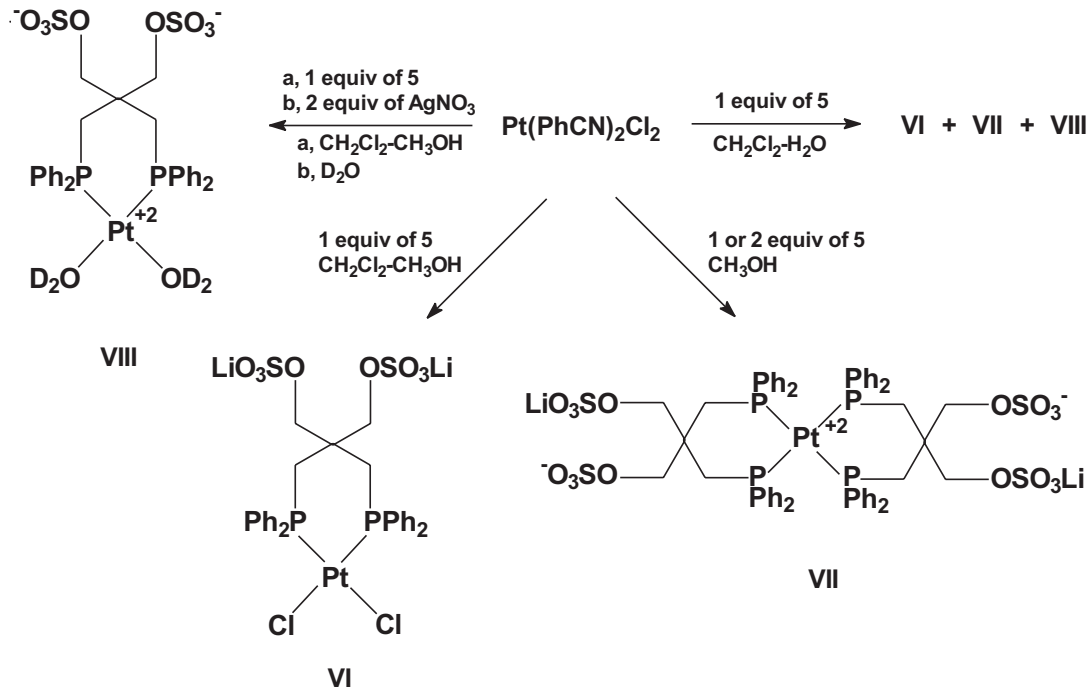
Complex **VII** could be obtained as the only product from the reaction mixture when the experiment was carried out in

Scheme 5.



V

Scheme 6.



VIII VI VII

CD_3OD at a 1:1 or 1:2 ligand:metal ratio. Some of the starting complex remained unreacted when a 1:1 ligand to platinum ratio was used. Based on the ^{31}P NMR data and the experimental evidence, either a dimeric or a monomeric square-planar PtP_4 structure could be imagined for complex **VII**. The $^{195}Pt\{^1H\}$-NMR spectrum clearly showed the presence of four equivalent phosphorus atoms coordinating to the platinum (δ –5011 ppm (q, $J_{Pt\text{-}P}$ = 2215 Hz), in D_2O) (Fig. 1). This fact confirms the square-planar, zwitterionic PtP_4 structure, in which two OSO_3^- groups act as counter ions for the central atom. Further evidence of the structure was obtained by FAB-MS spectroscopy. The parent ion [M – Li^+] was detected and the measured isotopic distribution showed nice agreement with the simulated one (Fig. 2). Note that the formation of **VII** as a single product even at a 1:1 ligand-to-metal ratio under the conditions above is probably due to the poor solubility of the precursor in MeOH and as a consequence an excess of the ligand was present in the solution.

To inhibit the substitution of chlorides either by a second phosphine ligand or solvent, the ligand was dissolved in MeOH and was added to a CH_2Cl_2 solution of the precursor [$Pt(PhCN)_2Cl_2$] in a 1:1 ratio (Scheme 6). In this case only one complex was formed which was assumed to be complex **VI** based on ^{31}P NMR data (CD_3OD, δ –1.5 ppm (s, $J_{Pt\text{-}P}$ = 3445 Hz), in CD_3OD). The slight difference in the spectroscopic data is probably due to the different nature of the solvent.

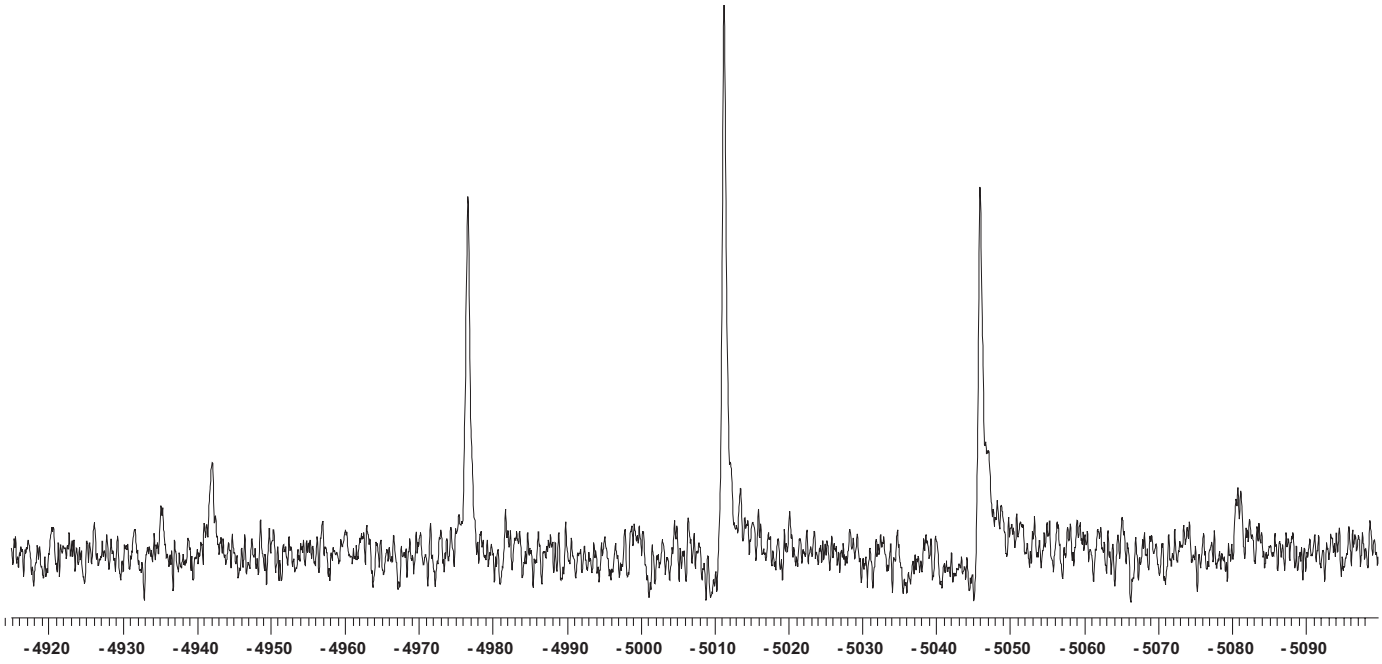
Dichloro-complex **VI** could be transformed into the aqua complex **VIII** by treatment with $AgNO_3$ in H_2O (D_2O) or with CF_3SO_3Ag in a THF–H_2O (D_2O) solvent mixture. A negligible amount of **VII** was also formed in both cases. Since the NMR data of the complex **VIII** are independent of the applied silver salt, strong coordination of NO_3^- or $CF_3SO_3^-$ can be excluded. The broad resonances of complex **VIII** were indicative of an exchange of H_2O molecules in the coordination sphere.

Hydroformylation of styrene and octene-1

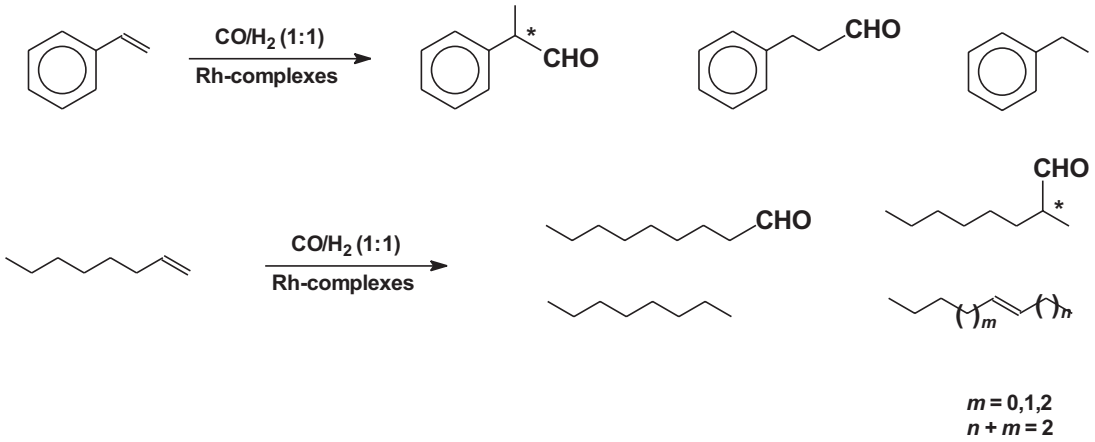
Rhodium complexes of **2** and **5** were used for hydroformylation of styrene and octene-1 (Scheme 7). Both systems proved to be suitable catalysts for hydroformylation (Table 1).

Ligands **2** and **5** gave complete chemoselectivity toward hydroformylation of styrene: no hydrogenation of the substrate was observed.

Fig. 1. ^{195}Pt NMR spectrum of the complex **VII**.



Scheme 7.



Up to 90% regioselectivity towards the more valuable branched aldehyde was observed when **2** was used as the ligand. At the same time, though, no optical induction was detected. It is not surprising, since optically active monodentate ligands usually provide very poor enantioselectivity even in relatively apolar medium. Additionally, the enantiomeric excess of the chiral products obtained in aqueous media is generally much lower than in organic solvents (17). An explanation for the lower enantiomeric excess could be the partial racemization via an enol intermediate, which is known to proceed swiftly in protic media (18). The evaluation of the suitability of the chiral ligand **2** for other asymmetric catalysis is in progress.

The rhodium complex of **5** gives a lower regioselectivity (81%) in a toluene–H_2O two-phase system. An important finding was that after separation of the phases, less than 4 ppm of the rhodium with respect to the amount of the rhodium catalyst employed was detected in the colorless organic phase. The aqueous phase could be recycled. The decrease in activity is probably due to the partial oxidation of the phosphine and a small loss of the catalyst during phase separation. In the absence of organic solvent, the regioselectivity toward the branched aldehyde increased to 86%.

No hydrogenation side product was observed in the hydroformylation of octene-1 either, although both ligands allow a moderate isomerization of the substrate (Table 2). Both ligands provide rather low selectivity under the applied conditions toward the more valuable normal aldehyde. Increasing the ligand **2**:rhodium ratio from 2 to 4 led to a slight increase in selectivity to *n*-aldehyde, but the activity

Table 1. Hydroformylation of styrene.

Ligand	Subst./Rh	Solvent	*T* (°C)	*t* (h)	Conv. (%)	Selectivity b/n (%)
2[a]	250	PhMe–H_2O	60	3	100	90/10
5[b, c]	300	PhMe–H_2O	80	4	100	81/19
5[d]	300	PhMe–H_2O	80	12	95	81/19
5[e]	300	PhMe–H_2O	80	12	84	79/21
5[f]	300	H_2O	80	10	87	86/14

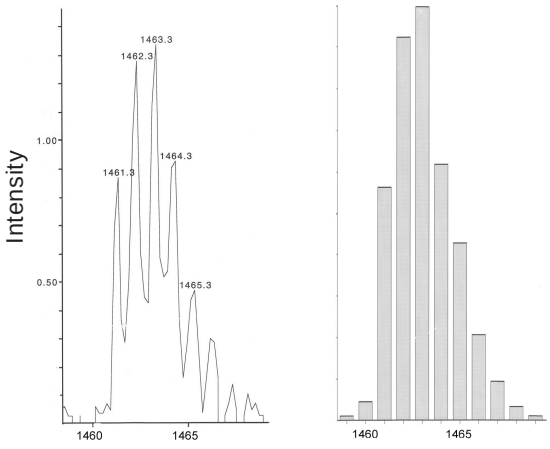
Note: Conditions: catalyst: $[Rh(COD)Cl]_2$ + ligand; initial pressure: 70 bar ($CO:H_2$ = 1:1); P/Rh = 2.2; water (3mL); toluene (3 mL) (if used).
[a][Rh] = 1.0×10^{-2} M.
[b][Rh] = 2.2×10^{-2} M.
[c]Less than 4 ppm rhodium could be detected in the organic phase.
[d]First recycling of the aqueous phase.
[e]Second recycling of the aqueous phase.
[f][Rh] = 2.9×10^{-2} M.

Table 2. Hydroformylation of octene-1.

							Select. (%)			
Ligand	Subst./Rh	P/Rh	Solvent	*T* (°C)	*t* (h)	Conv. (%)	isom[a]	n-ald	b-ald[b]	n/b
2[c]	250	2.05	H_2O	60	6	100	2.6	53.7	43.7 (4.7)	1.23
2[c]	250	2.20	PhMe–H_2O	60	6	100	2.8	53.4	43.8 (5.3)	1.21
2[c]	250	4.00	PhMe–H_2O	60	8	79	7.1	59.1	33.8 (-)	1.75
5[d]	300	2.40	PhMe–H_2O	80	5	99	5.8	46.7	47.5 (11.5)	0.98
5[d]	300	2.40	H_2O	80	17	85	16.0	53.5	30.5(0.3)	1.75

Note: Conditions: catalyst: $[Rh(COD)Cl]_2$ + ligand; initial pressure: 70 bar ($CO:H_2$ = 1:1), 3.5 mL of water, 3.5 mL of toluene (when used).
[a]Percentage of 2-, 3-, 4-octenes formed.
[b]Percentage of 2-ethylheptanal and 2-propylhexanal formed.
[c][Rh] = 1.5×10^{-2} M.
[d][Rh] = 2.9×10^{-2} M.

Fig. 2. Measured and simulated isotopic distribution of the parent ion of the complex **VII** (FAB-MS^-:M – Li^+).



decreased. The complex modified with **5** provided the highest normal:branched ratio in a substrate–water two-phase system, but a considerable amount of isomerized octenes was formed.

Conclusions

We have discovered a versatile route for the synthesis of water-soluble mono- and ditertiary phosphines. The starting materials are readily available, and the transformations highly selective. The synthetic route is sufficiently flexibile to allow fine tuning of the structure of water-soluble ligands. Reaction of **2** with $[Rh(COD)Cl]_2$ resulted in an equilibrium of Rh(COD)Cl(**2**) and zwitterionic $Rh(COD)(\mathbf{2})_2$ complexes, meanwhile **5** gave the zwitterionic Rh(COD)(**5**) complex as the only product. Treatment of **2** with $Pt(PhCN)_2Cl_2$ gave the square-planar *trans*-$PtCl_2(\mathbf{2})_2$ complex. Reaction of **5** with $Pt(PhCN)_2Cl_2$ in a D_2O–CH_2Cl_2 two-phase system provided three complexes, which could be identified as $PtCl_2(\mathbf{5})$, and zwitterionic complexes $Pt(\mathbf{5})_2$ and $Pt(D_2O)_2(\mathbf{5})$.

Rhodium complexes of **2** and **5** could be successfully applied as catalysts for hydroformylation of styrene and octene-1. The use of **2** in the hydroformylation of styrene resulted in high regioselectivity toward the branched aldehyde (up to 90%), however, no optical induction was observed. When the rhodium complex of **5** was applied as a catalyst in the biphasic hydroformylation of styrene, only 4 ppm of rhodium could be detected in the organic phase.

The application of these sulfated phosphines in other biphasic and aqueous transition-metal catalyzed reactions is being studied.

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