

Immobilization of Optically Active Rhodium-Diphosphine Complexes on Porous Silica via Hydrogen Bonding

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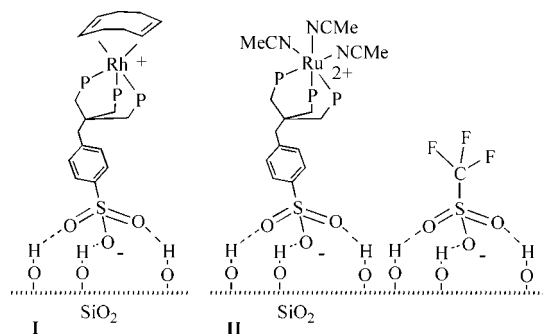
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Catalyst recovery is of paramount importance in fine chemical production when sophisticated ligands are used, whose cost often exceeds that of the noble metal employed. This is certainly the case for the hydrogenation of prochiral olefins with rhodium catalysts containing chiral diphosphine ligands. The heterogenization of rhodium-diphosphine complexes is therefore a research topic of much current interest. Common immobilization procedures of chiral Rh-phosphine complexes involve either their covalent grafting to both organic and inorganic supports or the dissolution of the precursor in a hydrophilic solvent which is then adsorbed as a thin layer onto a porous support material with a hydrophilic surface.^[1,2,3] The use of heteropoly acids as anchoring agents for chiral rhodium complexes has also been reported.^[4]

We have recently introduced an alternative, facile and clean method for preparing silica-tethered polyphosphine metal catalysts, denoted supported hydrogen-bonded (SHB) catalysts, for use in both solid-gas and solid-liquid reactions in hydrocarbon solvents.^[5,6]

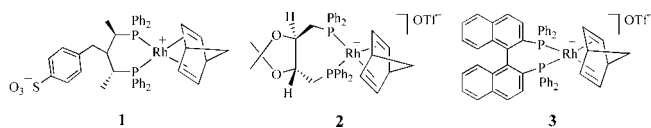
The procedure involves a hydrogen bonding interaction between the silanol groups of silica and sulphonate groups from the phosphine ligands and, possibly, also from triflate counter-anions [OTf = O₃SCF₃]. Some of these SHB catalysts, namely (sulphos)Rh(cod)/SiO₂ (I) and [(sulphos)Ru(NCMe)₃]/OTf/SiO₂ (II) (Scheme 1), were successfully employed in the heterogeneous hydrogenation of alkenes, nitriles and α,β -unsaturated ketones [sulphos = ⁻O₃S(C₆H₄)CH₂C(CH₂PPh₂)₃, cod = cycloocta-1,5-diene].^{[5], [6]} In all the cases investigated there was no evidence whatsoever for the formation of con-

tiguous Rh–Rh sites, indicating that the catalytic active sites were isolated rhodium complexes, as in the homogeneous phase.



Scheme 1.

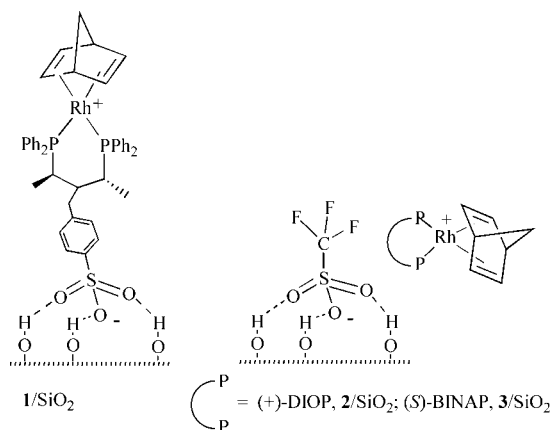
In this paper we describe, for the first time, the SHB immobilization of various optically pure Rh(I)-diphosphine complexes, including [((*R*)-(*R*)-BDPBzPSO₃)Rh(nbd)] (1), which contains the new chiral anionic ligand (*R*)-(*R*)-3-(4-sulphonate)benzyl-2,4-bis(diphenylphosphino)pentane, [(*(+)*-DIOP)-Rh(nbd)]OTf (2), and [(*(S)*-BINAP)Rh(nbd)]OTf (3) (nbd = norbornadiene). A preliminary study of the potential of the resulting SHB catalysts in the enantioselective hydrogenation of prochiral olefins is also reported.



Scheme 2.

The ligand $[(R)-(R)\text{-BDPBzPSO}_3]^-$ has been prepared by treatment of $(R)-(R)\text{-3-benzyl-2,4-bis(diphenylphosphino)pentane}$ ^[7] with H_2SO_4 (96%) at 100°C and was isolated as its sodium salt. This reaction represents a new protocol^[8] for the regioselective sulphonation of a phosphine ligand in a remote benzyl group. Previous examples involve, in fact, the sulphonation of the ligand framework prior to introduction of the phosphino groups.^[9,10,11] The simple reaction of $[(R)-(R)\text{-BDPBzPSO}_3]\text{Na}$ with $[\text{Rh}(\text{nbd})\text{Cl}]_2$ yields **1**. Compounds **2** and **3** have similarly been prepared by reaction of the corresponding diphosphine ligand with $[\text{Rh}(\text{nbd})\text{Cl}]_2$, followed by addition of silver triflate as chloride scavenger. This immobilization procedure of a chiral metal catalyst is the simplest ever reported since it does not imply any modification of the ligand structure.

The heterogenization of the Rh complexes (Scheme 3) was carried out by the solvent impregnation method using anhydrous dichloromethane as solvent and activated Davison 62 silica as support.^[5,6] The grafting procedure was complete and reproducible up to ca. 1 wt % metal loading (determined by ICP-AES). Once grafted to silica, the Rh complexes were not extracted back into CH_2Cl_2 solutions even after repeated washings. In contrast, stirring the grafted complexes in MeOH or EtOH at room temperature resulted in their complete delivery into solution (^{31}P NMR experiments in CD_3OD). No immobilization whatsoever was observed when the triflate counter-anion in either **2** or **3** was replaced by counter-anions such as BPh_4^- that are not capable of hydrogen-bonding interactions with silica.



Scheme 3.

All the SHB complexes have properly been characterized by DRIFT and CP MAS ^{31}P NMR spectroscopy.^[5,6] The CP MAS ^{31}P NMR spectrum of **1/SiO₂** is shown in Figure 1 a and consists of a broad signal centered at 39.9 ppm. The spectrum is substantially similar to

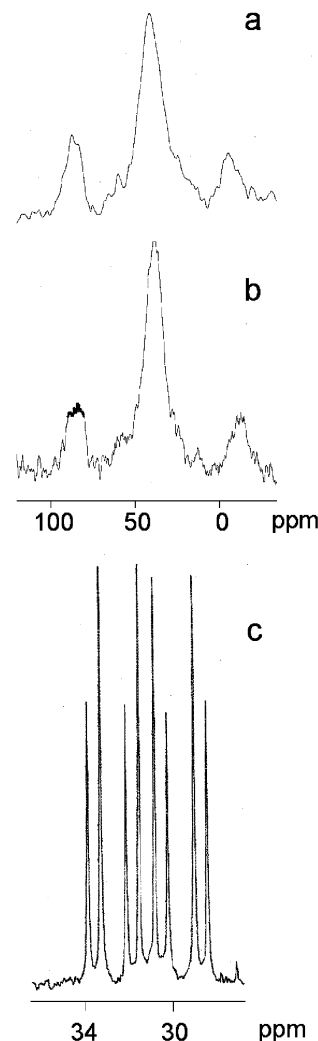


Figure 1. CP MAS ^{31}P NMR (109.4 MHz) spectra of **1/SiO₂** (a) and **1** (b); $^{31}\text{P}\{^1\text{H}\}$ NMR (81.01 MHz, CD_2Cl_2) spectrum of **1** (c).

that of unsupported **1** (Fig. 1 b), which is consistent with the immobilization of the complex on the silica through a functional group away from the metal coordination sphere.^[5,6] For comparative purposes, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in CD_2Cl_2 is reported in Figure 1 c.

In addition to CP MAS ^{31}P NMR spectroscopy, **2/SiO₂** and **3/SiO₂** have been characterized by ^{31}P and ^{19}F NMR experiments on slurries in CD_2Cl_2 . The ^{31}P NMR spectra of **2/SiO₂** (a) and **2** (b) are shown in Figure 2. The ^{31}P signal of **2/SiO₂** is apparently much broader than that of the free complex due to the restricted mobility of the complex cation on the silica surface. Indeed, the electrostatic interaction with the H-bonded triflate ion forces $[(+)\text{-DIOP}]\text{Rh}(\text{nbd})^+$ to remain close to the counter-anion even in the presence of a solvent. Consistent with this picture are the following observations: i) The addition of $(\text{NBu}_4)\text{BPh}_4$ to a CD_2Cl_2 slurry of **2/SiO₂** reduces the line-width of

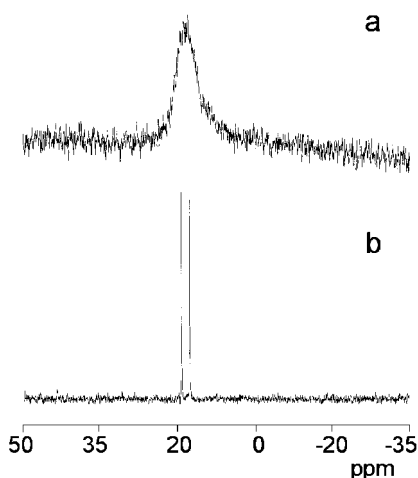


Figure 2. ^{31}P NMR (81.01 MHz, CD_2Cl_2) spectra: **2**/ SiO_2 (a), **2** (b).

the ^{31}P signal to the value observed for free **2** as a consequence of the delivery of the complex cation into solution; ii) The ^{19}F NMR spectrum of **2** consists of a sharp singlet at -79.6 ppm, while **2**/ SiO_2 gives rise to a very large resonance centered at ca. -79 ppm, which does not sharpen upon addition of $(\text{NBu}_4)\text{BPh}_4$ to the slurry (thus indicating that the triflate ion remains tethered to silica). A similar NMR behaviour is observed for **3**/ SiO_2 .

Three olefins [dimethyl itaconate, ethyl *trans*- β -(methyl)cinnamate, and methyl α -(acetamido)acrylate] have been chosen at random from the prochiral pool to compare the catalytic performance of the immobilized and free rhodium precursors, especially in terms of activity, enantioselectivity and ease of recycling. Standard hydrogenation conditions have been

Table 1. Asymmetric catalytic hydrogenations of olefins using free and anchored Rh(I)-chiral diphosphine complexes.

Precursor	T [$^{\circ}\text{C}$]	t [h]	Substrate	Yield [%] ^[a] , ee [%] ^[a]	
				homogeneous ^[b]	heterogeneous ^[c]
1	60	4		73, 4 (S)	100, 3 (S)
1	r. t.	24		100, 57 (S)	100, 53 (S)
1	r. t.	3		100, 16 (S)	100, 14 (S)
2	60	4		24, 16 (R)	56, 11 (R)
2	60	4		100, 41 (R)	100, 24 (R)
2	r. t.	3		100, 55 (R)	62, 20 (R)
3	60	4		9, 22 (S)	41, 20 (S)
3	60	4		100, 33 (S)	99, 32 (S)
3	r. t.	3		100, 25 (S)	100, 30 (S)

^[a] Reaction mixture, GC. Product absolute configuration in brackets.

^[b] Reaction conditions: Rh = 0.0052 mmol, H_2 pressure = 20 bar, solvent (MeOH) volume = 20 mL, 350 rpm, substrate/Rh = 100.

^[c] Reaction conditions: Rh = 0.0078 mmol, H_2 pressure = 20 bar, solvent (*n*-heptane) volume = 30 mL, 1500 rpm, substrate/Rh = 100.

employed for both homogeneous and heterogeneous reactions which have been carried out in methanol and *n*-heptane, respectively (Table 1). Although the use of solvents with different polarity rules out a reliable comparison between the tethered and homogeneous catalysts, one may draw out some general conclusions: i) The hydrogen-bonding immobilization of the [(*R*)-(*R*)-BDPBzPSO₃][−] and BINAP complexes on silica does not reduce the enantioselectivity (this latter is intrinsically low for the catalyst/substrate systems employed in this work).^[12,13,14] ii) The supported DIOP complex is less enantioselective than the homogeneous derivative, which may tentatively be related to the presence of ether oxygen atoms in the ligand backbone and hence to possible H-bonding interactions with the support leading to less efficient enantio-discrimination. However, a different hydrogenation mechanism in the two-phase systems cannot be ruled out. iii) The reduction of ethyl *trans*- β -(methyl)cinnamate is generally faster in the heterogeneous phase than in the homogeneous phase, which may again be due to the reasons given above. iv) In all cases, no rhodium leaching (<1 ppm) was observed within three consecutive heterogeneous runs, while an effective catalyst recycling, with no loss of activity or enantioselectivity, was accomplished by using a dip pipe with a sintered metal piece at its dipping end to remove the fluid reaction mixture and leave the catalyst in the reactor. Dichloromethane cannot be used to carry out heterogeneous reactions due to appreciable rhodium leaching under catalytic conditions.

The results reported in this work define neutral and cationic metal complexes containing groups with hydrogen bond acceptor properties as viable precursors for preparing efficient and easily recyclable enantioselective catalysts supported over materials with a hydrophilic surface.

Experimental Section

The compounds [Rh(nbd)Cl]₂^[15] and (*R*)-(*R*)-3-benzyl-2,4-bis(diphenylphosphino)pentane^[7] were synthesized as previously reported. The chiral ligands (+)-DIOP and (S)-BINAP were obtained from Aldrich. High resolution ³¹P solid state NMR spectra were performed on a Jeol GSE 270 (6.34 T) spectrometer operating at 109.4 MHz under conditions of ¹H → ³¹P cross-polarization, high power proton decoupling and magic angle spinning. The spectra were recorded at a spinning rate of 5 kHz. The 90° pulse was 6.0 μ s and the contact pulse was 5 ms. The spectra of the unsupported complexes were collected after 400 scans using a recycle delay of 10 s, while the spectra of the supported complexes were acquired with 6000 transients and a relaxation delay of 10 s. The line broadening was set to be 100 Hz for pure complexes and 150 Hz for the silica-grafted derivatives. 85% H₃PO₄ was used as a reference (δ = 0). Cylindrical 6 mm o.d. zirconia

rotors with sample volume of 120 μ L were employed with spinning speed in the range from 4.5 to 5.5 kHz. For all samples the magic angle was carefully adjusted from the ⁷⁹Br MAS spectrum of KBr by minimizing the line-width of the spinning side band satellite transitions. Optical rotations were measured with a Perkin-Elmer 341 polarimeter using 10 cm cells. GC analyses were performed either on a Shimadzu GC-14A gas-chromatograph equipped with a flame ionization detector and a 30 m (0.25 mm i.d., 0.25 μ m FT) SPB-1 Supelco fused silica capillary column and coupled with a Shimadzu C-R6A Chromatopac operating in the corrected area method or with a Shimadzu GC-17A gas chromatograph equipped with a flame ionization detector and a 40 m (0.25 mm i.d.) ChiralDEX G-TA capillary column and coupled with a Shimadzu C-R7A Chromatopac.

Synthesis of [(*R*)-(*R*)-BDPBzPSO₃]Na

A solution of (*R*)-(*R*)-3-benzyl-2,4-bis(diphenylphosphino)pentane (2.65 g, 5 mmol) in conc. H₂SO₄ (96%, 10 mL) was heated with stirring for 20 h at 100 °C. After cooling to 0 °C, water (50 mL) was added dropwise. The solution was neutralized by addition of 10% aqueous NaOH, leading to the precipitation of a white solid. The solid compound was filtered and washed with cold water (20 mL). The solid obtained was dissolved in CH₂Cl₂ (50 mL), dried over MgSO₄ and the solvent was evaporated in vacuo. Elemental analysis calcd for C₃₆H₃₅NaO₃P₂S: C 68.34, H 5.58; found: C 67.97, H 5.55. ³¹P{¹H} NMR (81.01 MHz, CDCl₃): δ = −1.1 (s, −10.8 (s)); ¹H NMR (200.13 MHz, CDCl₃): δ = 7.7–6.5 (m, 24H; Ph), 5.32 (m, 1H; CH₂CH), 3.08 (dd, *J* = 15.1, 4.2 Hz, 1H; CHH), 2.71 (t, *J* = 15.1 Hz, 1H; CHH), 2.33 (m, 1H; CH₂CH), 1.89 (m, 1H; CH), 1.08 (dd, *J* = 15.4, 7.1 Hz, 3H; CH₂CH), 0.88 (dd, *J* = 14.2, 6.9 Hz, 3H; CH₂CH); [α]_D²⁵ = +58.5 (*c* = 3.7 in CHCl₃).

Synthesis of [(*R*)-(*R*)-BDPBzPSO₃]Rh(nbd) (1)

Solid [Rh(nbd)Cl]₂ (0.09 g, 0.19 mmol) was added to a solution of [(*R*)-(*R*)-BDPBzPSO₃]Na (0.24 g, 0.38 mmol) in CH₂Cl₂ (15 mL). After stirring for 30 min at room temperature, the red-orange solution was washed with water (30 mL). The addition of diethyl ether (50 mL) to the organic phase caused the precipitation of an orange oil which solidified on standing. The solid compound was washed with diethyl ether (50 mL) and dried in vacuo. Yield 82%. Elemental analysis calcd for C₄₃H₄₃NaO₃P₂RhS: C 62.40, H 5.24; found: C 62.47, H 5.35; ³¹P{¹H} NMR (81.01 MHz, CD₃OD): δ = 32.6 (dd, ²*J*(P,P) = 49.5 Hz, ¹*J*(P,Rh) = 145.9 Hz), 29.8 (dd, ¹*J*(P,Rh) = 151.4 Hz); ¹H NMR (200.13 MHz, CD₃OD): 7.7–6.7 (m, 24H), 4.82 (bs, 2H), 4.62 (bs, 1H), 4.08 (bs, 1H), 3.83 (bd, 2H), 2.9–2.6 (m, 3H), 2.49 (t, 1H), 2.03 (m, 1H), 1.52 (bs, 1H), 1.40 (dd, 3H), 1.22 (m, 1H), 1.11 (dd, 3H); CP MAS ³¹P NMR (109.4 MHz): **1**, δ = 39.8 (s, *w*_{1/2} = 1.4 kHz); 1/SiO₂, δ = 39.9 (s, *w*_{1/2} = 1.9 kHz).

Synthesis of [(+)-DIOP]Rh(nbd)OTf (2)

Solid [Rh(nbd)Cl]₂ (0.07 g, 0.15 mmol) was added to a solution of (+)-DIOP (0.15 g, 0.30 mmol) in CH₂Cl₂ (10 mL). Silver trifluoromethanesulphonate (0.08 g, 0.30 mmol) was then added and the resulting suspension was stirred for 15 min. After AgCl was filtered off, the addition of *n*-pentane (30 mL) to the organic phase caused the precipitation of an orange oil which solidified on standing. The solid compound was washed with *n*-pentane and dried in vacuo. The com-

pound obtained was recrystallized from $\text{CH}_2\text{Cl}_2/n$ -pentane. Yield 77%. Elemental analysis calcd for $\text{C}_{59}\text{H}_{40}\text{F}_5\text{O}_5\text{P}_2\text{RhS}$: C 55.59, H 4.78; found: C 55.63, H 4.69; $^{31}\text{P}\{^1\text{H}\}$ NMR (81.01 MHz, CD_2Cl_2): $\delta = 18.5$ (d, $^1J(\text{P,Rh}) = 155.5$ Hz); ^1H NMR (200.13 MHz, CD_2Cl_2): $\delta = 7.9$ – 7.3 (m, 20H), 4.51 (m, 4H), 4.02 (m, 2H), 3.80 (m, 2H), 3.77 (m, 4H), 1.55 (s, 2H), 1.24 (s, 6H); CP MAS ^{31}P NMR (109.4 MHz): 2, $\delta = 15.4$ (s, $w_{1/2} = 1.2$ kHz); 2/SiO₂, $\delta = 37.1$ (s, $w_{1/2} = 5.1$ kHz).

Synthesis of [(S)-BINAP]Rh(nbd)OTf (3)

Solid $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (0.04 g, 0.08 mmol) was added to a solution of (S)-BINAP (0.10 g, 0.16 mmol) in CH_2Cl_2 (10 mL). Silver trifluoromethanesulphonate (0.04 g, 0.16 mmol) was then added and the resulting suspension was stirred for 15 min. After AgCl was filtered off, diethyl ether (30 mL) was added causing the precipitation of orange microcrystals. The product obtained was recrystallized from CH_2Cl_2 /diethyl ether. Yield 82%. Elemental analysis calcd for $\text{C}_{52}\text{H}_{40}\text{F}_5\text{O}_5\text{P}_2\text{RhS}$: C 64.60, H 4.17; found: C 64.52, H 4.22; $^{31}\text{P}\{^1\text{H}\}$ NMR (81.01 MHz, CD_2Cl_2): $\delta = 28.6$ (d, $^1J(\text{P,Rh}) = 156.8$ Hz); ^1H NMR (200.13 MHz, CD_2Cl_2): $\delta = 7.7$ – 6.4 (m, 32H), 4.20 (m, 4H), 4.16 (m, 2H), 1.61 (m, 2H); CP MAS ^{31}P NMR (109.4 MHz): 3, $\delta = 22.5$ (s, $w_{1/2} = 0.4$ kHz); 3/SiO₂, $\delta = 32.2$ (s, $w_{1/2} = 2.7$ kHz).

Heterogeneous Hydrogenation Reactions

In a typical hydrogenation reaction, the silica-supported catalyst precursor (0.008 mmol of rhodium) was placed under argon into a Parr 4565 autoclave equipped with a dip pipe with a sintered (2 μm) metal piece at its dipping end. A solution of the prochiral substrate (0.8 mmol) in the appropriate solvent (30 mL) was then transferred *via* a Teflon capillary into the autoclave under argon. Argon was then replaced by hydrogen with three cycles at 5 bar/normal pressure. The autoclave was finally charged with the desired pressure of H₂ and then heated with stirring at 1500 rpm. After the desired time, the reactor was cooled to room temperature, the reaction mixture was filtered through the sintered metal pipe. The filtrate was analyzed by GC, GC/MS. After the solvent was removed in vacuo, the residue was analyzed by ICP-AES (inductively coupled plasma atomic emission) as well as NMR spectroscopy. The solid catalyst left in the reactor was re-used for a second run.

The procedures for carrying out the homogeneous reactions have been described previously.^[5,6,7]

Acknowledgments

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