

**Immobilization of rhodium complexes in aqueous HBF_4 .
The enantioselective hydrogenation of prochiral olefins
with $\{[\text{CH}_3\text{CHP}(\text{p-C}_6\text{H}_4\text{NMe}_2\text{H})_2\text{CH}_2\text{CHP-}$
 $(\text{p-C}_6\text{H}_4\text{NMe}_2\text{H})_2\text{CH}_3]\text{RhNBD}\}^{5+}$**

Imre Tóth ^a, Brian E. Hanson ^{a*} and Mark E. Davis ^b

^a Department of Chemistry and ^b Department of Chemical Engineering Virginia Polytechnic Institute and State University Blacksburg, VA 24061 (U.S.A.)

(Received February 13th, 1990; in revised form April 1st, 1990)

Abstract

The complex $\{[\text{CH}_3\text{CHP}(\text{p-C}_6\text{H}_4\text{NMe}_2\text{H})_2\text{CH}_2\text{CHP}(\text{p-C}_6\text{H}_4\text{NMe}_2\text{H})_2\text{CH}_3]\text{RhNBD}\}^{5+}$ is active for the enantioselective hydrogenation of cinnamic acid derivatives at low pH in aqueous solutions of the noncoordinating acid HBF_4 . Analytical data are consistent with protonation occurring exclusively at the dimethylamino groups and not at the metal. Enantiomeric excesses of 67 to 97% are obtained for the hydrogenation of *Z*-(4-OMe, 3-OAcC₆H₃CH=C(NHC(O)Me)-COOH in aqueous HBF_4 at 14 bar H_2 . The use of aqueous acidic solutions allows for the convenient workup of the product and recycling of the catalyst.

Introduction

Catalytic reactions are typically classified by the phase that contains the catalytically active species. Heterogeneous catalysts comprise those systems in which the catalytically active species and the substrate are in different phases while homogeneous catalysts are contained within the same phase as the substrate. Less easy to classify are hybrid systems in which the distinction between phases is not as obvious. For example phase transfer catalysts [1] consist of two reactants which are dissolved in separate immiscible phases and a phase transfer agent serves to transport the reacting species across the interface of the two liquids. Immobilized homogeneous catalysts are homogeneous catalysts [2] which are bound, chemically or physically, to a stationary phase.

Immobilization techniques attempt to capitalize on the relative merits of homogeneous and heterogeneous catalysts. For homogeneous catalysts the merits are generally listed as mild reaction conditions and good selectivity [3], while for

heterogeneous catalysts the main advantage is in product separation. (Other specific advantages for the two classes of catalysts depend on the nature of the reaction to be catalyzed.) However, for many major homogeneous catalytic processes that are currently in operation, separation of the products from the homogeneous catalyst is not a problem. Two of these are the hydroformylation of propene by the Union Carbide [4] and the Rhone-Poulenc [5] processes. The butyraldehyde products, which are formed either in the gas phase or as a separate liquid phase depending on the reaction conditions, are easily removed from the catalytic liquid phase. The catalytic reactions are clearly homogeneous; however, since the catalyst and products end up in different phases, these systems are best classified as immobilized homogeneous catalysts.

Product separation is, of course, a problem for some other homogeneous catalytic reactions. Examples include the removal of cobalt carbonyl from liquid phase hydroformylation reactions [6], and the removal of rhodium complexes from homogeneous hydrogenation reactions [7]. Efficient methods for the immobilization of the active catalysts in these systems are not currently available. Current practice for the enantioselective hydrogenation of amino acid precursors is to not recycle the catalyst; this is possible due to the high value of the products and the high activity of the catalysts [3b,7].

One strategy for the immobilization of homogeneous catalysts is to simplify the catalyst separation step by placing a functional group on the catalyst that can serve as a "handle" to aid in the recycling of the active catalyst. Recently a great deal of work has appeared in which sulfonate groups have been added to phenyl-substituted phosphines to enhance their water solubility [5,8–10]. The presence of sulfonate groups allows the products to be extracted into a nonaqueous phase or for the catalytic reactions to be performed in a heterogeneous fashion between two immiscible liquids. Alternatively, the aqueous phase containing the catalyst may be adsorbed onto hydrophilic metal oxides as a supported aqueous phase [11]. Phosphines which contain methyl quaternized amines have also been shown to be effective in generating water soluble and ion exchange resin bound catalysts for hydrogenation and hydroformylation [12]. Here we describe catalytic systems in which the "handles" for catalyst immobilization are *N,N*-dimethylaniline groups. These are incorporated into chiral phosphines and are readily protonated in aqueous HBF_4 to give water soluble rhodium complexes. Importantly, the protonation is quantitative, completely reversible and occurs at the amine functionality rather than at the metal. Catalysts derived from both the neutral and protonated forms of the ligand are active for enantioselective hydrogenations in either methanol or water solution.

Results and discussion

The incorporation of *N,N*-dimethylaniline groups into the Skewphos ligand [13] is readily achieved by the reaction of $[\text{P}(p\text{-C}_6\text{H}_4\text{-N,N-CH}_3)_2]^-$ [14] with (*R,R*)-2,4-pentanedioditosylate to yield the ligand (*S,S*)- $\text{CH}_3\text{CHP}(p\text{-C}_6\text{H}_4\text{NMe}_2)_2\text{CH}_2\text{CHP}(p\text{-C}_6\text{H}_4\text{NMe}_2)_2\text{CH}_3$, **1** [15]. Reaction of **1** with $(\text{Rh}(\text{L}_2)\text{Cl})_2$, $\text{L}_2 = \text{COD}$ or NBD , yields cationic complexes of the type $[(\text{1})\text{RhL}_2]^+$, **2**. The ligand can be quaternized at the dimethylamino groups with $(\text{CH}_3)_3\text{OBF}_4$ by a literature procedure [16] when the phosphorus atoms are protected through complexation to rhodium [15]. The resulting rhodium complexes of the methyl quaternized ligand

have unlimited water solubility and are efficient catalysts for the hydrogenation of DOPA and phenylalanine precursors in water alone as a solvent [15].

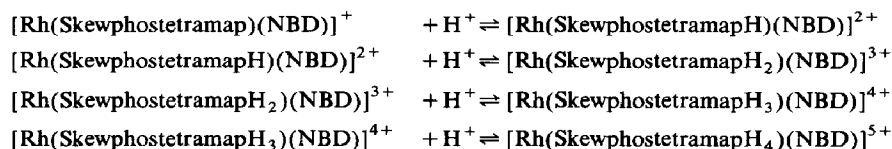
Quaternization of the dimethylamino groups by protonation would be very desirable for the design of recyclable catalytic systems. However, protonation at the metal must be considered to be a real possibility. For example HCl is known to oxidatively add to the bis-chelating complexes, $[\text{Rh}(\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)_2]^+$ [17,18], where $n = 1, 2$, or 3 . Also protonation at rhodium with the noncoordinating acids HBF_4 , HPF_6 and HClO_4 has been shown to occur for $[\text{Rh}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)(\text{S})_2]^+$, $\text{S} = \text{solvent}$, in coordinating solvents such as methanol or acetonitrile [19].

Protonation of **2**

In contrast to the examples above protonation of **2** occurs cleanly at the amine nitrogen upon addition of HBF_4 to methanol or acetone solutions of **2**. The protonated product can be isolated as a crystalline solid that analyzes for $\{[(\text{S}, \text{S})-(\text{CH}_3\text{CHP}(\text{p-C}_6\text{H}_4\text{NMe}_2\text{H})_2\text{CH}_2\text{CHP}(\text{p-C}_6\text{H}_4\text{NMe}_2\text{H})_2\text{CH}_3)]\text{RhL}_2\} \cdot \{\text{BF}_4\}_5 \cdot (\text{CH}_3)_2\text{CO}$, **3a**.

A comparison of the ^{31}P NMR spectrum of **2** and **3a** is presented in Fig. 1. Protonation at the dimethylamino groups causes a downfield shift of 5 ppm in the position of the phosphorus signal while the rhodium–phosphorus coupling constant remains essentially unchanged. The ^{31}P chemical shift of **3a** and the ^{31}P – ^{103}Rh coupling constant are virtually identical to the values obtained for **2** when methyl quaternized. These facts are consistent with protonation at the dimethylamino groups and retention of a square planar configuration at the metal. The ^{13}C and ^1H NMR signals for the dimethylamino groups are shifted 7 and 0.5 ppm downfield, respectively, for **3a** compared to **2**. The protonation is also completely reversible. Thus the addition of NEt_3 to solutions of **3a** quantitatively generates **2** and the addition of HBF_4 to solutions of **2** quantitatively generates **3a** as determined by ^{31}P NMR (Fig. 1c).

The quantity of HBF_4 required to completely protonate **2** was determined by monitoring the NMR spectrum as a function of added HBF_4 . In these experiments there was a continuous downfield shift in the signals due to the dimethylamino groups as well as the phosphorus atoms as HBF_4 was added. After the addition of a ten-fold excess of HBF_4 no further shifts were observed. It is concluded then that a ten-fold excess of a HBF_4 is sufficient to completely protonate all four dimethylamino groups; the pH of the resulting solutions was typically < 1 . A ratio of 4:1 of HBF_4 to **2** is not sufficient to take **2** completely into aqueous solution.



The reaction of **2** with aqueous HCl does not lead to **3a** but follows more closely the reactivity expected from the literature [17–19]. Immediately upon the addition of $\text{HCl}(\text{aq})$ to methanol solutions of **2** a color change from orange to pale yellow occurs. The room temperature ^{31}P NMR spectrum of the resulting solution shows a disappearance of the doublet at 26 ppm and the appearance of a broad signal at ca

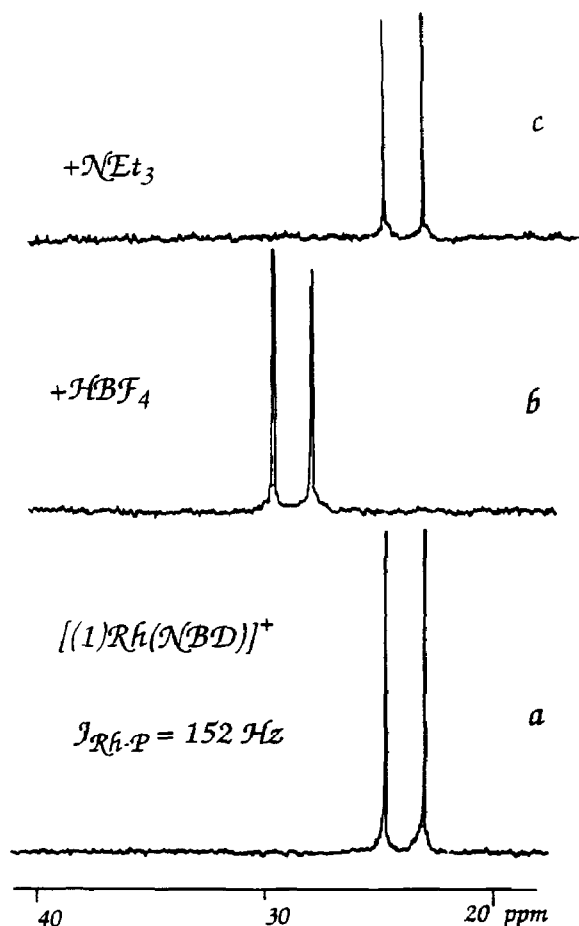
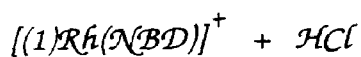


Fig. 1. The ^{31}P NMR spectrum of $[(S,S)\text{-CH}_3\text{CHP}(p\text{-C}_6\text{H}_4\text{NMe}_2)_2\text{CH}_2\text{CHP}(p\text{-C}_6\text{H}_4\text{NMe}_2)_2\text{CH}_3]\text{Rh}(\text{NBD})^+$, **2**, in methanol is shown in 1a. After the addition of ten equivalents of HBF_4 to the NMR tube the NMR spectrum characteristic of **3a** was obtained as shown in 1b. Addition of excess triethylamine quantitatively regenerates **2** as demonstrated in spectrum 1c.

38 ppm. This signal sharpens as the sample is cooled. At 220 K two separate sets of doublets of doublets (35.7 and 39.6 ppm and $J(^{31}\text{P}\text{--}^{103}\text{Rh})$ coupling constants of 106.4 and 119.8 Hz, respectively; $J(^{31}\text{P}\text{--}^{31}\text{P}) = 40.1$ Hz) are observed. The low temperature spectrum is reproduced in Fig. 2. The small value for the rhodium–phosphorus coupling constants is consistent with octahedral coordination at rhodium. During the reaction with HCl the complete liberation of coordinated diene can be monitored by ^{13}C and ^1H NMR. The solid isolated from the reaction with HCl has a Rh–H stretch at 2168 cm^{-1} in the infrared spectrum. Unfortunately the expected hydride signal in the NMR spectrum could not be detected even at 190 K. It is likely that the hydride rapidly exchanges with the excess protons including those on the dimethyl amine groups. The product from the reaction with HCl is best described as the result of oxidative addition of HCl to the rhodium with concomitant displacement of the diene. Since the two phosphorus atoms are inequivalent the most likely product is the octahedral rhodium(III) complex, **4**, shown schemati-



$$J_{\text{Rh-P}} = 119.8, 106.4 \text{ Hz}$$

$$J_{\text{P-P}} = 40.1 \text{ Hz}$$

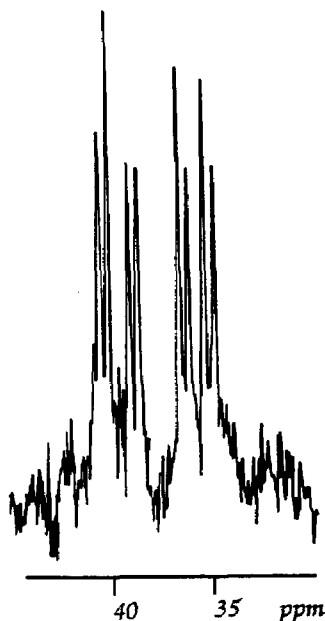
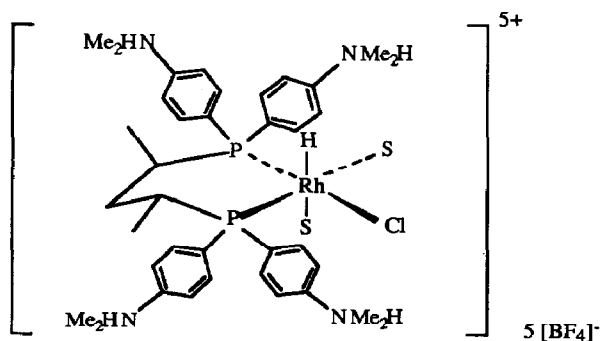


Fig. 2. The low temperature ^{31}P NMR spectrum of the product of **4** in methanol.

cally below. Two solvent molecules are included to complete the octahedral geometry.

The reactions described above demonstrate that protonation of **2** with HBF_4 does not take place at the metal atom. However, the possibility exists that protonation at the metal may occur after the diene is hydrogenated to yield the presumed intermediate in catalytic hydrogenations, $[(1)\text{Rh}(\text{S})_2]^+$, where S is coordinated



solvent. These are the conditions observed by Halpern et al. for protonation of $[\text{Rh}(\text{Ph}_2\text{P}(\text{CH}_2)_2\text{PPh}_2)(\text{S})_2]^+$ [19]. In the present case this appears not to occur as judged by the comparative catalytic behavior of **2**, its proton quaternized derivative **3a**, its methyl quaternized derivative, **3b**, and the HCl adduct, **4** (vide infra).

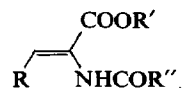
Hydrogenation activity

A comparison of the catalytic activities of the complexes described above is presented in Table 1. The substrates are numbered as described in the accompanying scheme. The catalytic activity of **4**, the HCl adduct, is not shown in Table 1. Aqueous solutions of **4** show only moderate activity for the hydrogenation of **5**. Incomplete conversion and low selectivities (< 5% ee) are observed after 36 hours at 14 bar H_2 pressure.

For the set of substrates studied there is little difference in the selectivities observed for catalysts **2** and **3a** in methanol solution. Thus protonation at the dimethylamine groups has no effect on the catalytic chemistry of the complexes. For the free acid substrates, **5** and **6**, there is a loss in enantioselectivity upon increasing the pressure and changing the solvent from methanol to water when **3a** and **3b** are used as the catalysts. The overall optical yield drops from 95–97% in methanol to 76–79% in water. The optical yield of the isolated product, however, can be as high as 97% when the product is isolated directly from the reaction solutions by filtration. Improvement in optical purity by crystallization is a well known phenomenon [20]. Substrates **5** and **6** have limited solubility in both water and ethylacetate/benzene; thus reactions with these substrates were run as slurries in water alone as

Table 1

Hydrogenation of prochiral dehydroamino acid derivatives ^a



	R	R'	R''
5	3-OMe,4-OAc-C ₆ H ₄	H	CH ₃
6	C ₆ H ₅	H	CH ₃
7	C ₆ H ₅	CH ₃	CH ₃
8	C ₆ H ₅	CH ₃	C ₆ H ₅

Substrate	ee (reaction time) with catalyst			
	2 in Methanol ^b	3a in Methanol ^b	3a in H ₂ O ^c	3b in H ₂ O ^{c,d}
5	95% (20 min)	97% (20 min)	97% (3 h) ^{e,f} 79% ^{e,g}	86% (6 h) ^{e,f} 76% ^{e,g}
6	92% (5.1 min)	87% (5.3 min)	95% (4 h) ^{e,f} 71% ^{e,g}	93% (6 h) ^{e,f} 67% ^{e,g}
7	76% (3.3 min)	72% (3.3 min)	50% (3 h) ^h	45% (1 h) ^h
8	56% (3.8 min)	57% (5.4 min)	67% (9 h) ^h	54% (9 h) ^h

^a Catalyst concentration 0.025 mmol in 10 ml solvent, substrate/Rh = 100. All reactions were run to 100% conversion. ^b 1 bar H_2 , 20 °C. ^c 14 bar H_2 , 20 °C, 10-fold excess HBF_4 added as 48% $\text{HBF}_4(\text{aq})$.

^d Ref. 15. ^e Hydrogenation performed as a slurry in 10 ml water. ^f Work up by filtration; the chemical yields were 66, 81, 64, and 62% for substrate **5** with **3a** and **3b** and substrate **6** with **3a** and **3b**, respectively. ^g Work up by extraction. ^h Two phase hydrogenation; solvent 5 ml water–5 ml ethyl acetate/benzene, 1/1.

the solvent. For substrate **7** there is also a drop in enantioselectivity as the solvent and pressure are changed.

The catalytic results with **3a** in water are reported in the presence of excess HBF_4 . The similarity of the results here compared with the results for **2** and the methyl quaternized derivative, **3b**, are consistent with protonation occurring only at the dimethylamino groups. The ease of protonation over methyl quaternization makes **3a** a more desirable catalyst than **3b** for the substrates shown here.

The enantioselectivities achieved here are the same as previously reported for substrates **5** and **6** with water as the solvent [8a]. For example with either sulfonated Skewphos or sulfonated Chiraphos as the ligand, **6** is hydrogenated to give phenylalanine with 65 or 87% ee, respectively [8a]. The position of the functional group on the phenyl rings in the ligand apparently has no effect on the enantioselectivity. There is a solvent effect on the catalytic behavior as the solvent changes from methanol to water.

Catalyst recycling

Recycling of the catalysts is easy to accomplish since **2** is reversibly protonated. Workup from methanol solutions involves acidification with HBF_4 (aq) followed by extraction of product. From aqueous solutions of **3a** filtration or extraction of the product with a nonaqueous solvent is sufficient to effect the separation of catalyst and substrate. In either case one obtains an aqueous solution of **3a** which is an active form of the catalyst. The results for the recycling of the catalyst by protonation are presented in Table 2. The different values for the enantioselectivity with **5** and **6** as the substrate than those reported in Table 1 are due to the fact that the recycling experiments were performed with a different batch of the catalyst. Also shown in Table 2 are the results for recycling a two-phase catalytic system with the ester, **7**, as the substrate. No loss in enantioselectivity is observed after four catalytic runs. Of course the retention of good enantioselectivity requires that oxygen be rigorously excluded from the catalyst.

Metal loss is always a potential problem in recycling immobilized catalysts. In the cases above the rhodium content in the isolated product after separation of the

Table 2

Recycling of catalysts **2** and **3a**

Substrate	ee (%) with catalyst		Rhodium loss ^b ppm
	2 ^a	3a	
5	93 ^c	97 ^{c,d}	3.7, 1.1
6	84	79 ^c	2.5, 1.2
7 (1) ^e		49.5	0.72
(2)		51.4	0.60
(3)		46.3	0.91
(4)		48.1	0.48

^a 1 bar H_2 , substrate/Rh = 100; in methanol. ^b Rhodium contamination in the product. ^c The optical purity was measured on the material isolated by filtration. The isolated yields were 68 and 71%, respectively, with **2** and **3a** as the catalysts. ^d 14 bar H_2 , substrate/Rh = 100; as a slurry in water. The catalyst **3a** was generated in situ from the workup of the reaction represented in the column for **2**. ^e Recycling of the in situ prepared **3a** solution. 14 bar H_2 , substrate/Rh = 100; as a two-phase reaction in water/ethyl acetate–benzene.

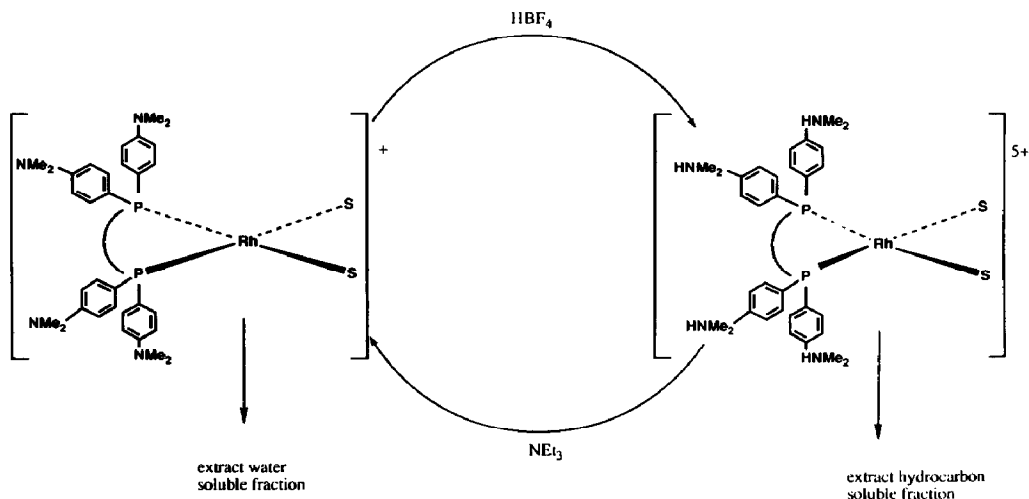


Fig. 3. Proposed scheme for the recycling of amine functionalized catalysts by interconverting the water soluble and hydrocarbon soluble forms of the complexes.

catalyst was in the range 0.5 to 3.5 ppm. This was true for both the experiments going from catalyst **2** to **3a** and the recycling of **3a** directly in the two-phase reactions. Rhodium loss could be further reduced by repetitive washing of the products.

The ability to tune the catalyst solubility with pH leads to a versatile reagent which can be readily separated from a wide variety of substrates. Immobilization through cycling the catalyst between aqueous and nonaqueous phases is represented schematically in Fig. 3. The catalyst is appropriate at low pH for water soluble substrates and in the nonprotonated form for water insoluble substrates.

Conclusions

The most remarkable feature of these complexes is their stability under acidic conditions. A ten-fold excess of HBF_4 is required to completely protonate all four dimethylamino groups in **2**. Even with this large excess of acid no evidence for protonation at rhodium is seen. The catalytic activity and selectivity are excellent in strongly acidic aqueous solutions at moderately high pressure (14 bar H_2). These reaction conditions are novel for the hydrogenation of α -acetamidocinnamic acid derivatives and quite unexpected based on the reactivity reported in the literature for the protonation of rhodium complexes of chelating phosphines [17–19].

Experimental section

Microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Proton, ^{13}C , and ^{31}P -NMR spectra were run at 25°C on a Bruker WP-200 instrument. ^{31}P -NMR chemical shifts are references to external 85% H_3PO_4 . Optical rotations were determined on a Perkin-Elmer 241 polarimeter. All preparations and operations before hydrogenation were carried out under an atmosphere of dry deoxygenated argon. Solvents were degassed before use. The substrates were pre-

pared by the literature methods [21–23]. (*S,S*)-CH₃CHP(*p*-C₆H₄NMe₂)₂-CH₂CHP(*p*-C₆H₄NMe₂)₂CH₃, **1**, was synthesized by analogy with the reported preparation of Skewphos [24] from (2*R*,4*R*)-pentanediolditosylate and potassium bis(diphenylphosphino)phosphide [14].

[Rh(COD)(**1**)]BF₄, [Rh(NBD)(**1**)]BF₄, **2**, were prepared in the manner reported in ref. 24. [Rh(COD)(**1**)]BF₄: Anal. calc. for C₄₅H₆₂BF₄N₄P₂Rh: C, 59.3; H, 6.81; N, 6.15; P, 6.81; Rh, 11.30. Found: C, 57.3; H, 6.80; N, 5.96; P, 6.39; Rh, 10.90. P{¹H}NMR (81.01 MHz, *d*₆-acetone): 23.73 ppm (d, *J*(Rh–P) = 142.4 Hz). [Rh(NBD)(**1**)]BF₄·CH₂Cl₂: Anal. calc. for C₄₅H₆₀BCl₂N₄P₂Rh: C, 55.1; H, 6.13; N, 5.72; P, 6.33; Rh, 10.51. Found: C, 53.5; H, 6.34; N, 5.64; P, 6.25; Rh, 10.48. ³¹P{¹H}NMR (81.01 MHz, CD₃OD): 24.41 ppm (d, *J*(Rh–P) = 152 Hz).

Preparation of **3**

Aqueous HBF₄ (708 μl of 48% solution) was added to a dark red solution containing 740 mg (0.82 mmol) of **2** in 10 ml acetone. There was no change in color of the reaction solution after the addition of the acid. Compound **3** was precipitated from the solution by the addition of 40 ml diethyl ether. The separated orange-red solid was washed with ether and dried under vacuum. Yield: 780 mg (76%), **3**·(CH₃)₂CO. Anal. calc. for C₄₇H₆₈(BF₄)₅ON₄P₂Rh: C, 43.20; H, 5.21; N, 4.29. found: C, 42.40; H, 5.19; N, 4.04. ¹H NMR (200.1 MHz, *d*₆-acetone): 1.26 (m), 1.57 (s), 2.06 (m), 3.12 (m), 3.51; 359 (s; s), 4.05 (m), 4.69 (m), 5.12 (m), 7.93 (m), 8.05 (m). ¹³C{¹H} NMR (50.32 MHz): 17.86 (br. s), 26.98 (m), 37.10 (m), 46.87; 46.99 (s; s), 55.42 (s), 71.2 (m), 88.73 (m), 92.29 (m), 122.38; 122.80 (d, d; d, d) 131.3; 132.6 (m; m), 135.42; 138.70 (d, d; d, d), 145.54; 146.57 (s; s). ³¹P{¹H} NMR (81.01 MHz): 29.07 ppm (*J*(Ph–P) = 151.5 Hz).

[Rh(COD)(**1**)]BF₄ was protonated in situ before it was used as a hydrogenation catalyst. NMR data are for the protonated complex generated in situ. ¹H NMR (200.1 MHz, CD₃OD): 1.02 (m), 1.80 (m), 2.05 (m), 2.55 (m), 2.87 (m), 3.40; 3.45 (s; s), 4.12 (m), 4.75 (m); 7.70 (m), 7.84; 7.93 (d; d), 8.45 (m). ¹³C{¹H} NMR (50.32 MHz): 18.74 (br.s), 28.20 (m), 33.28 (s), 37.84 (m), 46.54; 46.87 (s; s), 100.71 (m), 106.75 (m), 122.54 (m), 132.10; 134.2 (m; m); 133.16; 139.94 (d, d; d, d), 145.46; 147.74 (s; s). ³¹P{¹H}NMR (81.01 MHz): 28.75 ppm (*J*(Ph–P) = 142.6 Hz).

Preparation of **4**

Compound **4** was prepared from either [Rh(NBD)(**1**)]BF₄ or [Rh(COD)(**1**)]BF₄. Concentrated HCl solution 150 μl (~ 1.7 mmol) was added to a solution of 0.175 mmol of Rh-diene complex in 5 ml MeOH. An immediate color change from orange-red to green-yellow was observed. A few hours later pale yellow crystals separated, which were collected, washed with cold methanol and dried. Yield: 100 mg (57%). Anal. calc. for C₃₇H₅₉Cl₆O₂N₄P₂Rh, C, 45.80; H, 6.08; N: 5.78. Found: C, 45.44; H, 5.50; N, 5.63. ³¹P{¹H} NMR (81.01 MHz; CD₃OD) at 220 K: 35.68; 39.63 (d, d, *J*(Rh–P) = 106.4 Hz, *J*(P–P) = 39.6 Hz; d, d, *J*(Rh–P) = 119.8 Hz, *J*(P–P) = 39.6 Hz), IR: ν(Rh–H) = 2168 cm^{–1}.

Hydrogenation experiments

Hydrogenations were performed either in a glass reactor connected to a gas burette at atmospheric pressure or in a 30 ml stainless steel autoclave at 14 bar under the reaction conditions given in Table 1. When water was used as a solvent

both in two phase and slurry hydrogenations 100 μ l 48% HBF_4 was added to keep the catalyst in the water phase.

Amino acid products were worked up by the following methods: With the nonquaternized complex **2** as the catalyst the solvent was removed under vacuum and replaced with 10 ml 5% HCl solution. When the catalyst was to be recycled aqueous HBF_4 was used in place of HCl. The products were then extracted with Et_2O with the exception of the product from the hydrogenation of **5** which was collected by filtration.

When in situ or previously quaternized complexes were used as the catalyst, e.g. catalyst **3a**, the products were extracted directly from the water phase. Again the product from the hydrogenation of **5** was collected by filtration. After isolation, the reaction products were analyzed by ^1H NMR and the optical yields were determined by polarimetry by comparison with the literature values for the optically pure compounds [25–27].

Rhodium contamination of the products was determined by atomic absorption spectroscopy, by comparison of the product solutions digested in 5% HCl with standard rhodium solutions.

Acknowledgements

Support for this work was provided by the NSF (CBT-8719560). A loan of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ from Johnson Matthey is gratefully acknowledged.

References

- (a) L. Cassar and M. Foa, *J. Organomet. Chem.*, 134 (1977) C15; (b) H. Alper and H. Des Abbayes, *J. Organomet. Chem.*, 134 (1977) c11.
- (a) C.U. Pittman, Jr., G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, London, 1982, Chap. 55; (b) F.R. Hartley, *Supported Metal Complexes*, D. Reidel Publishing Co., Dordrecht, 1985.
- (a) G.W. Parshall, *Homogeneous Catalysis*, Wiley Interscience, New York, 1980; (b) G.W. Parshall and W.A. Nugent, *Chemtech*, 18 (1988) 184; 314; 376.
- R. Fowler, H. Conner and R.A. Baehl, *Chemtech*, 6 (1976) 772.
- E. Kuntz, U.S. Patent 4,258,802, 1981.
- L.H. Slaugh, R.D. Mullineaux, *J. Organomet. Chem.*, 13 (1968) 468.
- W.S. Knowles, M.J. Sabacky and B.D. Vineyard, in: D. Forster and J. Roth (Eds.), *Homogeneous Catalysis*, American Chemical Society, Washington, 1974, p. 271.
- (a) Y. Amrani, L. Lecomte, D. Sinou, J. Bakos, I. Tóth and B. Heil, *Organometallics*, 8 (1989) 542; (b) F. Alario, Y. Amrani, Y. Colleuille, T.P. Dang, D. Morel and D. Sinou, *J. Chem. Soc., Chem. Commun.*, (1986) 202.
- T.P. Dang, J. Jenck and D. Morel, U.S. Patent 4,654,176, 1987.
- (a) F. Joo and Z. Tóth, *J. Mol. Catal.*, 8 (1980) 369; (b) L. Vigh, F. Joo, P.R. Van Hasselt and P.J. Kuiper, *J. Mol. Catal.*, 22 (1983) 15.
- (a) J.P. Arhancet, M.E. Davis, J.S. Merola and B.E. Hanson, *Nature*, 334 (1989) 454; (b) J.P. Arhancet, M.E. Davis, J.S. Merola and B.E. Hanson, *J. Catal.*; in press.
- R.T. Smith, R.K. Ungar, L.J. Sanderson and M.C. Baird, *Organometallics*, 2 (1983) 1138.
- P.A. MacNeil, N.K. Roberts and B. Bosnich, *J. Am. Chem. Soc.*, 103 (1981) 2273.
- I. Tóth, B.E. Hanson and M.E. Davis, *Organometallics*, 9 (1990) 675.
- I. Tóth, B.E. Hanson and M.E. Davis, *Catal. Lett.*, in press.
- U. Nagel and E. Kinzel, *Chem. Ber.*, 119 (1986) 1731.
- B.R. James and D. Mahajan, *Can. J. Chem.*, 58 (1979) 996.
- D.A. Slack, I. Greveling and M.C. Baird, *Inorg. Chem.*, 18 (1979) 3125.

- 19 J. Halpern, D.P. Riley, A.S.C. Chan and J.J. Pluth, *J. Am. Chem. Soc.*, 99 (1977) 8055.
- 20 W.S. Knowles, M.J. Sabacky and B.D. Vineyard, U.S. Patent, 4,008,281, 1977.
- 21 R.M. Herbst and D. Shemin, *Org. Synth.*, col vol. 2, (1943) 1.
- 22 H.B. Gillespie and H.R. Snyder, *Org. Synth.*, col. vol. 1, (1941) 489.
- 23 H.E. Carter and W.C. Risser, *J. Biol. Chem.*, 159 (1981) 255.
- 24 J. Bakos, I. Tóth, B. Heil and L. Marko, *J. Organomet. Chem.*, 279 (1985) 23.
- 25 T.P. Dang, J.C. Poulin and H.B. Kagan, *J. Organomet. Chem.*, 9 (1975) 105.
- 26 M.D. Fryzuk and B. Bosnich, *J. Am. Chem. Soc.*, 99 (1977) 6262.
- 27 R. Glaser and S. Geresh, *Tetrahedron*, 35 (1979) 2381.