SYNTHESIS OF A CHIRAL RHODIUM CATALYST ANCHORED TO AN INORGANIC SUPPORT AND ITS APPLICATION TO ASYMMETRIC SYNTHESIS*

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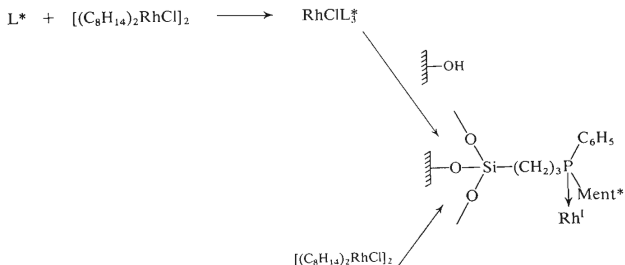
Chiral rhodium(I) complexes coordinately bound to inorganic supports have been prepared using optically active $(C_2H_5O)_3Si(CH_2)_3P(C_6H_5)$menthyl as ligand. These complexes catalysed enantioselective hydrosilylation of ketones. Their asymmetric efficiency was affected to a certain extent by the way of preparing the anchored catalyst. The more important factor has been solubilization of the anchored complex as a result of dynamic ligand exchange. The solubilization proceeds *via* the cleavage of the P/Rh coordination bond, the bond between the ligand and the support remaining essentially intact.

In recent years growing interest has been shown in both so called heterogenization of homogeneous catalysts which combines the high selectivity of homogeneous catalysts with the easy handling of heterogeneous catalysts[1,2], and in the synthesis of optically active substances catalysed by transition metal complexes containing chiral ligands[3,4]. Some effort has been expended upon combining these approaches, by preparing heterogenized optically active catalysts[5-7]. The catalysts of this type have so far been both less active and less stereoselective compared to their soluble analogues. As this fact could be caused by a number of factors[2], in the present work we have compared several homogeneous and heterogenized catalysts under identical experimental conditions, preserving the same environs of the reaction center with the aim to examine the importance of some of the above factors. Very suitable for such a comparison are transition metal complexes bound to inorganic supports *via* phosphines substituted by alkoxysilyl groups[8,9]. For the purpose of the present study we have utilized chiral (3-triethoxysilylpropyl)menthylphenylphosphine prepared recently by us[10]. The use of the chiral catalyst rendered it possible to investigate the effects of anchoring and supports on the course of enantioselective synthesis which in general is much more sensitive to changes in the environs of the reaction center.
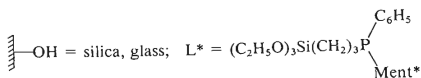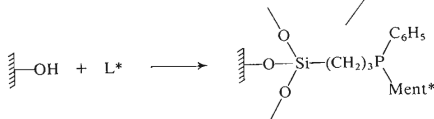
Using the above mentioned chiral coupling agent, anchored complexes were prepared by two different ways which are schematically depicted in Scheme 1. *a*) Tetra-(cyclooctene)-μ,μ'-dichlorodirhodium was allowed to react *in situ* with the chiral silylsubstituted phosphine and the homogeneous complex so obtained (which was also used as homogeneous catalyst for comparative purposes) was treated with silica or glass. *b*) Supports were treated first with the phosphine to give a phosphinated support which was then reacted with the rhodium–cyclooctene complex.

a)

$$L^* \ + \ [(C_8H_{14})_2RhCl]_2 \ \longrightarrow \ RhClL_3^*$$

b)

$\equiv$—OH = silica, glass; $L^* = (C_2H_5O)_3Si(CH_2)_3\overset{\displaystyle C_6H_5}{\underset{\displaystyle Ment^*}{P}}$
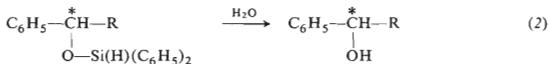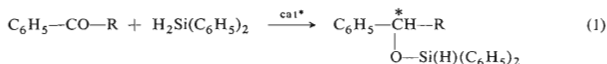
Ment* = menthyl.

Scheme 1

Prepared complexes, which are one of the still few examples of chiral transition compounds coordinately bound to inorganic supports, and the homogeneous analogue were tested as catalysts for the enantioselective hydrosilylation of acetophenone and phenyl ethyl ketone by diphenylsilane[1]. The silyl ethers formed (Eq. (1)

$R = CH_3, C_2H_5$; cat* $= ((C_6H_{14})_2RhCl)_2$ + homogeneous or heterogenized $(C_2H_5 . O)_3Si(CH_2)_3P(C_6H_5)$menthyl) were hydrolysed (Eq. (2)) and the optical purity of the resulting carbinols was measured.

$$C_6H_5-CO-R + H_2Si(C_6H_5)_2 \xrightarrow{\text{cat*}} C_6H_5-\overset{*}{C}H-R \quad (1)$$
$$\underset{O-Si(H)(C_6H_5)_2}{}$$

$$C_6H_5-\overset{*}{C}H-R \xrightarrow{H_2O} C_6H_5-\overset{*}{C}H-R \quad (2)$$
$$\underset{O-Si(H)(C_6H_5)_2}{} \qquad \underset{OH}{}$$

RESULTS AND DISCUSSION

The results presented in Table I demonstrate how the stereoselectivity of the reactions catalysed by the soluble rhodium silylalkylenephosphine complex depends upon temperature and the Rh : P molar ratio. Under suitable conditions, particularly on using the chiral ligand in sufficient excess, the corresponding alcohols have been obtained in optical yields higher than 20%. These are comparable with the yields reported for Rh-DIOP catalyst[5]. Compared to the previous case, in the presence

TABLE I

The Effect of Temperature and Ph : P mol. Ratio on the Optical Yields of the Alcohols Obtained by Hydrosilylation of Ketones

t, °C	Rh : P mol. ratio[a]	Ligand	PhCH(OH)Me[b]		PhCH(OH)Et[b]	
			e.e., % (confg.)		e.e., % (confg.)	
25	1 : 5	L* — homogeneous	3·8	S	5	S
0	1 : 2	L* — homogeneous	1.	S	racemic	
0	1 : 5	L* — homogeneous	23	S	20·5	S
25	1 : 5	SiO_2—O—L* — heterogeneous	4·2	R	4	R
0	1 : 2	SiO_2—O—L* — heterogeneous	—	—	1·4	R
0	1 : 5	SiO_2—O—L* — heterogeneous	4·1	R	3·8	S
0	1 : 5	reused SiO_2—O—L*	3·3	S	3·1	S

[a] Toluene, 4 ml; ketone, 10 mmol; diphenylsilane, 12 mmol; $((C_8H_{14})_2RhCl)_2$, 0·02 mmol or anchored Rh(I) complex, 0·04 mmol; the phosphine, 0·2 mmol, L* = $(EtO)_3Si(CH_2)_3PPh$(menthyl); reaction time 24 h. [b] The hydrosilylation produced a mixture of the corresponding silyl ether and silylenol ether in 5 : 1 molar ratio[12].

of silica-supported catalysts the hydrosilylation of ketones proceeded at a slower rate, was not so strongly dependent upon temperature and Rh : P ratio, and also its stereoselectivity was lower.

In many cases, on using the anchored catalyst the alcohols produced had the opposite configuration with respect to the homogeneous case. However, the same configuration as with the homogeneous analogue has been observed when the anchored catalyst was reused.

To study this phenomenon, the effect of different supports and ways of anchoring has been investigated. As follows from the results summarized in Table II the asymmetric efficiency of heterogenized catalysts is in general very low. It could be somewhat affected by e.g. the loading of the support, the way of anchoring or by the morphology of the support (i.e. porosity, external surface etc.). In spite of this, it was poorly comparable with the efficiency of the homogeneous analogue. On the other hand, a marked increase in the stereoselectivity of the reaction has been achieved by addition of the free ligand to the anchored rhodium catalyst. The hydrosilylation of both ketones proceeded analogously as with homogeneous catalyst, producing the alcohols of the same configuration with comparable optical purity. This situation bears

TABLE II

The Effect of Supports and Anchoring on the Optical Yields of the Alcohols Obtained by Hydrosilylation of Ketones

Ligand[a]		Proce-dure	PhCH(OH)Me[b]		PhCH(OH)Et[b]	
			e.e., % (confg.)		e.e, % (confg.)	
Glass—O—L*	porous	a	0·5	R	1·7	R
Glass—O—L*	nonporous with low spec. surface[c]	a	inactive			
SiO₂—O—L*	high surface concentration of P	a	0·4	S	racemic	
SiO₂—O—L*	low surface concentration of P	b	1·6	R	3·1	R
SiO₂—O—L*	low surface concentration of P	a	4·1	R	3·8	S
SiO₂—O—L*	low surface concentration of P, 0·2 mmol of homogenues L* added		18·7	S	19·7	S

[a] Toluene, 4 ml; ketone, 10 mmol; diphenylsilane, 12 mmol; anchored Rh(I) complex, 0·04 mmol (Rh : P ratio = 1 : 5), reaction temp. 0°C, time 24 h. [b] See footnote [b] in Table I. [c] Toluene 12 ml, reaction time 72 h.

upon the fact that with the homogeneous catalyst (Table I) high optical yields have been obtained only when the effective excess of the chiral ligand was present in the solution, which shifts the equilibrium to the left side (3).

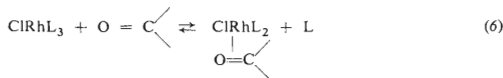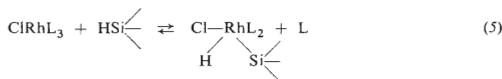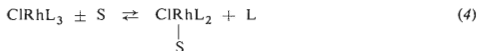$$RhL_n \; \rightleftarrows \; RhL_{n-1}Cl \; + \; L \tag{3}$$

The presence of chiral ligand(s) in the coordination sphere of rhodium is a prerequisite for asymmetric induction.

Although the same excess of the ligand is in fact present even in the anchored catalyst (as shown by the Rh : P molar ratio), because of the relatively rigid attachment of these ligands to inorganic polymer surface they cannot participate efficiently in the above equilibrium.

The lower catalytic activity of the reused anchored catalyst can be accounted for by the loss of the transition metal by the solubilization of a part of immobilized complex during the previous application. The rhodium complex is attached to the surface of the support mainly in two ways
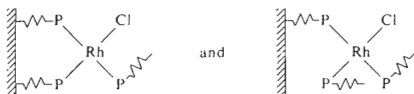
However, the phosphine ligands are not coordinated to the central atom strongly enough to resist an exchange with solvent, silane and ketone (Eqs (3)–(5)). If the ligand displaced is the anchored phosphine, the complex is solubilized and acts as homogeneous catalyst.

$$ClRhL_3 \pm S \; \rightleftarrows \; \underset{\underset{S}{|}}{ClRhL_2} \; + \; L \tag{4}$$

$$ClRhL_3 + HSi\!\!\diagup \; \rightleftarrows \; \underset{\underset{H \quad Si\diagdown}{}}{Cl\!-\!RhL_2} \; + \; L \tag{5}$$

$$ClRhL_3 + O = C\!\!\diagdown \; \rightleftarrows \; \underset{\underset{O=C\diagup}{|}}{ClRhL_2} \; + \; L \tag{6}$$

The low optical yields obtained with the anchored catalyst indicates that this solubilization proceeds *via* the cleavage of the Rh—P bond rather than by the cleavage

of the bond between the ligand and the surface. By the latter process a sufficient excess of the chiral ligand would be present in solution and the optical yields obtained with the anchored complex should be comparable with those obtained with homogeneous catalyst, which was not the case.

EXPERIMENTAL

General

3-(Triethoxysilylpropyl)phenylmenthylphosphine[10], tetra(cyclooctene)-μ,μ'-dichlorodirhodium[13], and diphenylsilane[14] were prepared by reported procedures as indicated. The supports were commercial products: Kieselguhr 60 (230—400 mesh, Merck FRG), porous glass (Jena Glass, GDR), and a glass fabric (Vertex Litomyšl, Czechoslovakia). Commercial solvents and ketones were distilled prior to using. All syntheses and experiments were carried out under dry argon[15].

Hydrosilylation of ketones, hydrolysis of the silyl ethers formed and the determination of optical yields were made according to ref.[11]. Reaction conditions are given in Tables I and II. When the anchored catalyst was reused, it was separated from the reaction mixture by filtration and washed with two 5 ml portions of toluene.

Anchored Complexes

Most of these complexes were prepared by procedure *a*), using Rh : P molar ratio = 1·5, unless stated otherwise. The rhodium content in the catalysts was determined indirectly, from the difference in the amount of rhodium in the starting solution and in eluents.

SiO_2—O—L* (low loading). A solution of (3-triethoxysilylpropyl)menthylphenylphosphine (905 mg, 2 mmol) and $((C_8H_{14})_2RhCl)_2$ (144 mg, 0·2 mmol) in toluene (20 ml) was added to a suspension of silica (16 g) in toluene (50 ml). The discolouration of the solution was complete after 5 min. The solution was then refluxed for 1 h, toluene was partially removed by distillation (25 ml) and the anchored complex was filtered off, washed twice with 50 ml of toluene and dried 2 h at a pressure of 0·1 mm Hg (Rh content = 0·25%).

SiO_2—O—L* (low loading, Rh : P ratio = 1 : 2) was prepared similarly as the preceding complex, using 362 mg of the phosphine. The catalyst contained 0·25% Rh.

SiO_2—O—L* (high loading). To a suspension of silica (3·6 g) in toluene (20 ml), a solution of the silylsubstituted phosphine (905 mg, 2 mmol) and the rhodium–cyclooctene complex (114 mg 0·2 mmol) was added with stirring. The mixture was stirred for 0·5 h, then refluxed for 0·5 h, the solvent was partially removed by distillation (20 ml), the anchored complex was filtered off, washed with 8 × 25 ml of toluene (unless the eluent was colourless) and dried *in vacuo* (Rh content = 0·9%).

SiO_2—O—L* (low loading, procedure *b*). To a suspension of silica (10 g) in toluene (30 ml), 0·1M toluene solution of the silylsubstituted phosphine (10 ml) was added and most of the solvent was distilled off. The phosphinated silica was then washed thrice with 25 ml of benzene and a solution of the rhodium–cyclooctene complex (72 mg, 0·1 mmol) in toluene (50 ml was added with stirring. The mixture was allowed to stir for another 1 h, the anchored complex was filtered off, washed twice with 50 ml of toluene (the eluent was colourless) and dried *in vacuo* (Rh content = = 0·2%).

Glass—O—L* (porous). (3-Triethoxysilylpropyl)menthylphenylphosphine (452 mg, 1 mmol) and the rhodium–cyclooctene complex (72 mg, 0·1 mmol) dissolved in toluene (20 ml) were ad-

ded to a mixture of porous glass (10 g) and the same solvent (20 ml). Toluene was almost completely removed by distillation, another portion of the solvent (20 ml) was added and the mixture was stirred for 0·5 h. The anchored complex was separated by filtration, washed thrice with 30 ml of toluene and dried (Rh content = 0·16%).

Glass—O—L* (nonporous, with low specific surface). A solution of the phosphine (452 mg, 1 mmol) and the rhodiumcyclooctene complex (72 mg, 0·01 mmol) in toluene (10ml) was added to a glass fabric (20 g) in benzene (500 ml). The mixture was allowed to stand at room temperature for 4 days, then approx. half the volume of benzene was distilled off, the glass fabric removed, washed thrice with 250 ml of benzene and dried *in vacuo* (Rh content = 0·03%).

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