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Metal controlled enantioselectivity in the catalytic asymmetric hydrosilylation

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Abstract

The asymmetric hydrosilylation of acetophenone with Ph_2SiH_2 has been investigated in the presence of (*S*)-amphos as the chiral ligand in combination with the cyclooctadiene-rhodium(I), -iridium(I), -palladium(II), and -platinum(II) chloride complexes.

High activity and optical yields up to 50% ee have been obtained. The product configuration induced by the rhodium system is (*S*), in all other cases it was (*R*).

Introduction

During the last fifteen years the catalytic asymmetric hydrosilylation of prochiral ketones has been studied intensively. As a standard method the addition of diphenylsilane to acetophenone has been introduced. To get a detailed insight into the origin of different enantioselectivities a large variety of chiral ligands and metals have been investigated.

P,P-, *N,N*-, and *P,N*-ligands were used in combination with transition metal olefin complexes [1–23]. Recently it could be shown by H. Brunner and W. Miehling that the noble metals can be replaced by copper if selected ligands are used [22].

One of the questions not clearly answered was that on the origin of the influence on the enantioselectivity of the reaction. In most cases the direct dependence of the product configuration on the ligand configuration has been shown. On the other hand, experiments have been described in which inversion takes place in the presence of a ligand excess [17]. The usual method of investigating the homogeneous

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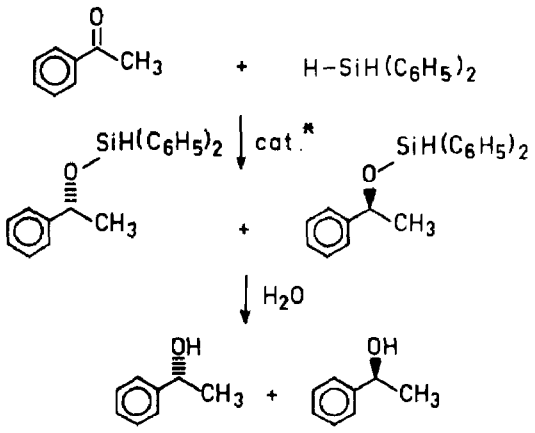


Scheme 1

catalytic asymmetric synthesis is the systematic variation of the catalytic system so as to optimize the activity and enantioselectivity. Thus, the structure of the chiral ligands is usually modified.

Here we describe an inverse strategy; we used the well-known ligand (*S*)-amphos in combination with cyclooctadiene-rhodium, -iridium, -palladium, and -platinum chloro complexes. As far as we know, this method of a constant ligand field influencing different metals has not before been applied in asymmetric hydrosilylation. Scheme 1 shows the investigated reaction.

Results and discussion

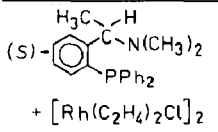
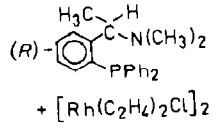
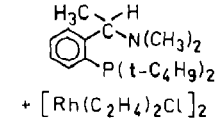
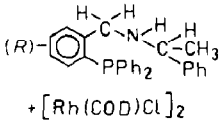
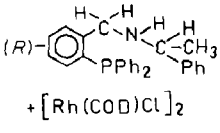
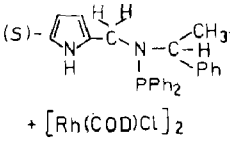
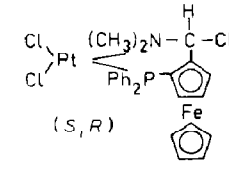
The amphos-RhCl catalyzed asymmetric hydrosilylation of acetophenone was investigated for the first time by N.C. Payne and D.W. Stephan in 1982 [16]. Used (*S*)-amphos as ligand resulted in 27% ee of (*S*)-1-phenylethanol, and similarly (*R*)-amphos gave 33% ee of the (*R*)-configurated product. About a 90% conversion was possible after a prolonged reaction time (72 h). For comparison, results obtained with similar ligands are listed in Table 1.

Our own results are compiled in Table 2. They demonstrate the high efficiency of the catalysts, except for the palladium system, which transforms only 12% of the acetophenone but with a 50% ee of (*R*)-1-phenylethanol. The amphos-$PdCl_2$ isolated does not catalyze the hydrosilylation reaction.

Variation of the ligand/metal ratio, studied in detail for amphos-RhCl, has shown that the optical yield is strongly dependent on the ligand concentration. The change in the ratio from 1 to 2.5 leads to an increase in the enantiomeric excess by 12 to 15%. The increase remains constant until the ratio exceeds 5. The optical yield decreases drastically when the ligand excess is 10-fold and the optical induction is almost neutralized. In the range from 0 to 25 °C the optical yield is practically independent of the temperature. Iridium and platinum catalyze the hydrosilylation with conversions as high as those of rhodium, however, the optical induction, accompanied by inversion, is clearly reduced.

Table 1

Asymmetric hydrosilylation of acetophenone with Ph_2SiH_2 in the presence of chiral *P,N*-ligands and Rh^I

Catalytic system	Chemical yield, %	Optical yield, %	Configuration	Ref.
	90.0	27.0	*S*	16
	90.0	33.0	*R*	16
	66.0	0	–	20
	88.0	33.6	*S*	17
	93.0	52.7 [a]	*S*	17
	98.7	19.3	*R*	18
	85.0	3.8	*S*	21

[a] Reaction at −10 °C

The inversion of the product configuration on going from rhodium to palladium, iridium, and platinum is an unexpected result and to our knowledge it represents the first example of a transition metal controlled, asymmetric hydrosilylation. Here we

Table 2

Asymmetric hydrosilylation of acetophenone with Ph_2SiH_2 in the presence of (*S*)-amphos-MCl_n Complexes

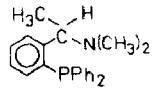
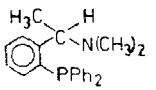
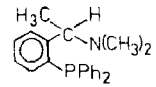
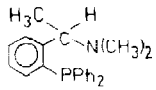
Catalytic system		Metal to ratio ligand	*T* (°C)	Solvent	Time (h)	Conversion (%)	Optical yield (% ee)	Method of (ee)-detection
Ligand	Complex							
	$[Rh(COD)Cl]_2$	1:1	25	toluene	7	76.5	32.0 (*S*)	GC
		1:2.5	0 → 25	toluene	7 → 23	96.0	46.5 (*S*)	opt. rotation
		1:2.5	25	toluene	7	91.0	44.0 (*S*)	GC, opt. rotation
		1:5	0 → 25	toluene	7 → 23	93.5	39.5 (*S*)	opt. rotation
		1:5	25	toluene	7	95.0	42.5 (*S*)	GC, opt. rotation
		1:5	25	toluene	3, 5	96.5	51.0 (*S*)	GC
		1:5	25	–	7	97.0	35.5 (*S*)	GC
		1:10	25	toluene	7	94.5	4.5 (*S*)	GC, opt. rotation
	$Pd(COD)Cl_2$	1:5	25	toluene	7	12.5	50.5 (*R*)	GC
	$[Ir(COD)Cl]_2$	1:5	25	toluene	7	89.5	16.5 (*R*)	GC
	$Pt(COD)Cl_2$	1:1	25	toluene	7	80.5	8.5 (*R*)	GC
		1:5	25	toluene	7	91.0	26.5 (*R*)	GC

Table 3

^{31}P NMR data for the investigated amphos complexes

Complex	Chem. shift δ (ppm) [a]	Coordination chemical shift Δ (ppm) [b]	J(M,P) (Hz)
amphos-IrCl	14,2 [c] (31,3) [d]	30,8	
amphos-$PdCl_2$	15,5 [c] (24,2) [d]	32,1	
amphos-$PtCl_2$	−6,4 [c] (9,1) [d]	10,2	
amphos-RhCl	20,4 [c]	37,0	146
$(amphos)_2$-IrCl [e]	–	–	
$(amphos)_2$-$PdCl_2$ [e]	14,9 [f]	32,1	
$(amphos)_2$-$PtCl_2$ [e]	−7,0 [f]	10,2	
$(amphos)_2$-RhCl [e]	20,2 [f]	37,4	145

[a] All chemical shifts are relative to external 85% H_3PO_4(capillary). [b] $\Delta = \delta\,^{31}P$(complex) $- \delta\,^{31}P$(amphos). [c] Recorded on a Bruker MSL-400 spectrometer, based on −16.6 ppm for amphos. [d] Second signal of smaller intensity. [e] Prepared in situ (amphos : cyclooctadiene-MCl = 2 : 1). [f] Recorded on a Varian CFT-20 spectrometer, based on −17.2 ppm for amphos.

can report only the facts, but the question of what happens during the configuration determining step remains open. More detailed investigations are necessary to get a better understanding of this phenomenon.

In 1985, T. Ikariya and coworkers described a similar effect during the asymmetric hydrogenation of amino acid precursors in the presence of the (Rh(−)BINAP)-ClO_4 complex and $(Ru_2Cl_4(-)(BIPAP)_2)NEt_3$ [24].

NMR spectra

With the exception of amphos-$PtCl_2$, the ^{31}P chemical shifts of the complexes were found between 14 and 20 ppm, and the calculated coordination chemical shifts were found to be between 31 and 37 ppm. As can be seen from Table 3, there is no significant difference in the chemical shifts on going from 1 : 1 to 2 : 1 complexes, which in all cases were prepared in situ in methylene chloride solution. It is noteworthy that all spectra with a 2 : 1 ratio also show the signals from the free ligand.

The exceptional position of amphos-$PtCl_2$ can be explained in terms of the observation made by S.O. Grim and R.L. Keiter [25] that ^{31}P(*cis*) appears at lower field than ^{31}P(*trans*) in palladium(II)chloro complexes, whereas the reverse is true of the platinum complexes. T.H. Brown and P.J. Green [26] have studied square planar rhodium(I) complexes of the Wilkinson type and have found the rhodium–phosphorus coupling to be larger for a phosphorus *trans* to a halogen ($J(Rh,P_A)$ 189 Hz for chlorine) than for phosphorus atoms *cis* to that halogen ($J(Rh,P_B)$ 142 Hz for chlorine). In view of our results we assume that the chlorine in amphos-RhCl is also in the *cis*-position (J(Rh,P) 146 Hz).

Experimental

(*S*)-Amphos was prepared by a procedure published by L. Horner and G. Simons [27]; $[\alpha]_D^{25}$ −67.2° ($c = 1.0$, C_6H_6), $[\alpha]_D^{25}$ −53.7° ($c = 4$, CH_2Cl_2). The cyclooctadiene complexes were prepared by the usual methods. All reactions were prepared by the usual methods. All reactions were carried out under argon in freshly distilled, dry solvent.

Diphenylsilane was prepared from chlorosilane by standard methods. Acetophenone was obtained commercially and was purified by distillation.

For the NMR spectra see the footnotes to Table 3. The optical yields were determined by use of a Polamat A polarimeter (Carl Zeiss, Jena) or by GLC on an HP 5800 A chromatograph equipped with 18 m glass capillary column coated with 0.3% XE 60-L-valine-t-butylamide after derivation of the phenylethyl alcohol with isopropylisocyanate [28]. The preparation of (−)-amphos-$PdCl_2$ has been described previously [29].

Hydrosilylation reaction

The catalysts were prepared in situ by reaction of 0.04 mmol of the relevant metal complex with (*S*)-amphos in 4 ml of degassed toluene at ambient temperature (for molar ratios, see Table 2). After stirring for 10 min diphenylsilane (12 mmol) was added and the mixture was stirred for a further 10 min. Then the solution was cooled to between −2 and 0 °C and after 10 min acetophenone (10 mmol) was added.

The mixture was kept at 0 °C for 10 min, and then warmed to 25 °C. In two cases the reaction was carried out for 7 h at 0 °C and afterwards for further 16 h at 25 °C, as specified in Table 2 by arrows.

When the reaction was carried out without toluene the catalyst was prepared in diphenylsilane. The work up, after hydrolysis was as described by J. Benes and J. Hetflejš [2].

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