Asymmetric Synthesis of Silanes with a Stereogenic Centre at Silicon *via* Hydrosilylation of Symmetric Ketones with Prochiral Diaryl Silanes Catalysed by binap–Rh^{I} Complexes†

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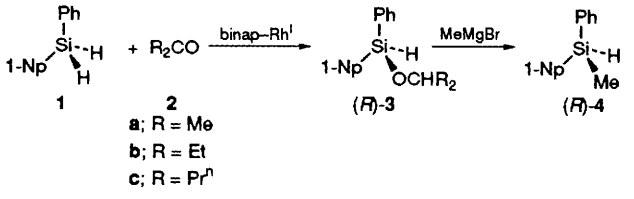
Reaction of (1-naphthyl)phenylsilane with symmetric aliphatic ketones catalysed by (*R*)-Cybinap–Rh^{I} gave the corresponding (*R*)-(alkoxy)(1-naphthyl)phenylsilane in >99% enantiomeric excess.

Although optically active silanes have attracted much interest, reports on the construction of a stereogenic centre at silicon are limited. Since trigonal silicon is too unstable for synthetic use, replacement of one of the two enantiotopic X groups in $R^1R^2SiX_2$ has mostly been used to obtain silanes which are chiral at silicon.[1] Asymmetric reaction of prochiral dihydrosilanes and various electrophiles catalysed by chiral transition metal complexes is a promising method for the synthesis of optically active organosilanes.[2] However only moderate enantiomeric excesses (up to 46% ee), have been attained with conventional chiral Rh^{I} catalysts.[3] We have found that the rhodium(I) complexes possessing Cybinap† as a chiral ligand[4] serve as excellent catalysts for the stereoselective construction of a stereogenic silicon centre, affording optically active alkoxysilanes in >99% ee.

Reaction of **1**[5] and a ketone was carried out in the presence of a catalytic amount of the binap–transition metal complex in a dry degassed solvent. Enantiomeric excesses of the products **3** were determined by HPLC analysis after purification by column chromatography on Florisil using hexane as eluent.‡ The absolute configurations of the products were determined based on the signs of the optical rotation of **4**[6] obtained by the reactions of **3** and MeMgBr, which are known to proceed with retention of configuration at silicon with slight loss of optical purity[1] (Scheme 1).

First, catalytic activities of several types of binap–metal complex, *e.g.* [RhCl(cod)]$_2$–binap, [IrCl(cod)]$_2$–binap, Ru(OAc)$_2$(binap), Ni(cod)$_2$–binap and Pd$_2$(dba)$_3$(CHCl$_3$)–



Scheme 1

Table 1 Reaction of (1-naphthyl)phenylsilane with symmetrical ketones catalysed by Cybinap– or binap–[RhCl(cod)]$_2$ systems[a]

Ketone	Ligand	S/C[b]	*t*/h	Yield[c] (%)	Ee (%) of **3**[d]	Config. of **3**[e]
2a	(*R*)-Cybinap	20	20	78	91	*R*-(+)
2a	(*R*)-binap	20	21	62	83	*S*-(−)
2a	(*R*)-Cybinap	100	20	81	>99	*R*-(+)
2a	(*S*)-Cybinap	100	24	79	>99	*S*-(−)
2b	(*R*)-Cybinap	20	18	97	>99	*R*-(+)
2b	(*R*)-binap	20	21	75	84	*S*-(−)
2c	(*R*)-Cybinap	20	21	95	98	*R*-(+)
2c	(*R*)-binap	20	25	74	95	*S*-(−)

[a] Reactions were carried out in THF (solvent/substrate 0.5–1.0) in a 20 ml Schlenk tube under argon at −20 °C. All conversions were >99% (GLC analysis) after the time given. [b] [Silane]/[Rh] ratio. [c] Isolated yield. [d] Determined by HPLC analysis with a chiral stationary column (Daicel Chiralcel OD, hexane, 1 ml min^{-1}) of alkoxysilane **3**. [e] Determined by the signs of optical rotation of **4** derived from **3** and MeMgBr. {Optically pure (*R*)-methyl(1-naphthyl)phenylsilane, $[\alpha]_D$ +35 (*c* 15.6, cyclohexane)[3b]}. The signs of the optical rotation of **3** are given in parentheses.

binap (cod = cyclooctadiene; dba = dibenzylideneacetone), have been investigated for the reactions of **1** and **2a** in THF. Among them, the neutral rhodium(I) complex derived from [RhCl(cod)]$_2$ and binap exhibited both the highest catalytic activity and enantioselectivity. Various binap derivatives, *e.g.* Cybinap, Tolbinap, and *p*-MeObinap† were then tested as ligands. When Cybinap was used for the reactions of **1** and **2a**, enantiomeric excesses were higher than those obtained with binap, Tolbinap, or *p*-MeObinap. Interestingly, the absolute configurations of the products obtained with (*R*)-Cybinap are opposite to those with the other (*R*)-binap derivatives.

Reaction conditions were also important for obtaining high enantiomeric excesses. Use of benzene, pyridine or acetone instead of THF as solvent led to lower ees. When the reaction was carried out in ethyl acetate or dichloromethane, a complex mixture was obtained. All the reactions were conducted at −20 °C since lower temperatures had no advantages. Some representative results are shown in Table 1. It is especially noteworthy that usually very low ees were obtained after prolonged reaction times. This indicates that considerable racemization of the products was induced in the absence of the substrates under the catalytic conditions. Thus, it is important to stop the reaction as soon as possible when conversions reached 99%.

When methyl(1-naphthyl)silane was allowed to react with acetone in the presence of [RhCl(cod)]$_2$–binap, the ee of methyl(1-naphthyl)phenylsilane derived from the product and PhMgBr was as low as 3%. Reaction of a more bulky silane, (9-anthryl)phenylsilane, resulted in formation of many unidentified products.

Chemical yields and enantiomeric excesses were also greatly influenced by the ketones used. Di(*n*-alkyl) ketones smoothly reacted with **1** to give **3** in high yields and in >98% ee, while diisopropyl ketone and benzophenone afforded **3** in low yields. Several trials using other substrates, such as alcohols, aldehydes, carboxylic acids, α,β-unsaturated ketones or esters, nitroalkanes, alkenes, and acetylenes, were unsuccessful, because the desired products were obtained with low ees and/or in low yields.

Thus, chiral alkoxysilanes **3** have been synthesized with high ees by the reaction of **1** and symmetrical di(*n*-alkyl) ketones catalysed by the [RhCl(cod)]$_2$–Cybinap system. This catalyst system differentiates efficiently between the two enantiotopic hydrogens attached to the silicon atom. Although many reactions of this kind could have been carried out through the biocatalytic approach,[7] few examples have been reported for transition metal catalysed asymmetric reactions.[8] These alkoxy silanes can be converted to various optically active silanes by nucleophilic substitution of alkoxy groups.[1,2]

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Footnotes

† *Abbreviations*: Cybinap = 2,2′-bis(dicyclohexylphosphino)-1,1′-binaphthyl; Tolbinap = 2,2′-bis[bis(4-methylphenyl)phosphino]-1,1′-binaphthyl; *p*-MeObinap = 2,2'-bis[bis(4-methoxyphenyl)phosphino]-1,1′-binaphthyl.

‡ The enantiomeric excess of **3** was carefully determined by HPLC (Daicel Chiralcel OD 4.6 × 250 mm) using hexane as eluent. Extensive racemization of **3** was observed in chloroform, and alcoholysis occurred when **3** was dissolved in alcohols.

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