Palladium-catalysed Asymmetric Hydrosilylation of Styrenes with a New Chiral Monodentate Phosphine Ligand

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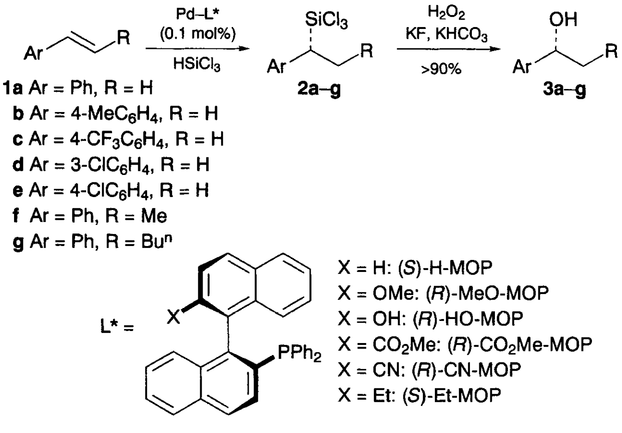
Asymmetric hydrosilylation of styrenes (ArCH=CHR) with trichlorosilane in the presence of a palladium catalyst (0.1 mol%) bearing a new chiral monodentate phosphine ligand, (*S*)-2-diphenylphosphino-1,1′-binaphthyl [(*S*)-H-MOP], followed by oxidation of the resulting 1-aryl-1-silylalkanes, gives optically active benzylic alcohols of up to 96% enantiomeric excess (e.e.).

Catalytic asymmetric hydrosilylation of alkenes is recognised as one of the important methods for the preparation of optically active alcohols.[1] Although simple terminal alkenes such as oct-1-ene[2] and cyclic alkenes such as norbornene[3] have been efficiently converted into the corresponding secondary alkyl alcohols with over 90% enantioselectivity by use of a palladium catalyst coordinated with 2-diphenylphosphino-2′-methoxy-1,1′-binaphthyl (MeO-MOP),[4] such high selectivity has not been observed in the hydrosilylation of styrene derivatives.[5,6] Here we report that a new monodentate phosphine ligand, (*S*)-2-diphenylphosphino-1,1'-binaphthyl (H-MOP),[7] which has the same basic skeleton as MeO-MOP but lacks the methoxy group, is particularly effective for the palladium-catalysed hydrosilylation of styrenes to give the corresponding benzylic alcohols with high enantiomeric purity, the enantioselectivity ranging from 89 to 96% e.e. (Scheme 1).

Asymmetric hydrosilylation of styrene **1a** with trichlorosilane was carried out without any solvents in the presence of 0.1 mol% of a H-MOP–palladium catalyst, generated *in situ* by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and (*S*)-H-MOP. Reaction at 0 °C for 12 h gave a quantitative yield of 1-phenyl-1-trichlorosilylethane **2a** as a single regioisomer, which was converted into (*R*)-1-phenylethanol **3a** in 97% yield by oxidative cleavage of the carbon–silicon bond[8] (entry 1, Table 1). The absolute configuration *R* was assigned by its optical rotation $\{[\alpha]_D^{22}$ +45.0 (*c* 1.80, CH_2Cl_2)$\}$,[9] and the enantiomeric excess was determined to be 93% e.e. by HPLC analysis of the (3,5-dinitrophenyl)carbamate ester of alcohol **3a** (ArNCO–pyridine–toluene), with a chiral stationary phase column (Sumichiral OA-4700, hexane:dichloroethane : ethanol = 50 : 15 : 1). The hydrosilylation carried out at −10 °C slightly raised the enantiomeric excess to 94% e.e. (entry 2).

Rather surprisingly, the MeO-MOP ligand, which is substituted with a methoxy group at the 2′-position on H-MOP and has been used successfully for the asymmetric hydrosilylation of other types of alkenes,[2,3] is much less effective than H-MOP for the present asymmetric hydrosilylation of styrene. Thus, the hydrosilylation of **1a** in the presence of a MeO–MOP–palladium catalyst under the same reaction conditions (0 °C, without solvent) gave (*R*)-**3a** with only 14% e.e. (entry 4). The enantioselectivity was greatly improved (71% e.e.) by the use of benzene as the solvent (entry 5),[5] but it is still much lower than that with H-MOP.



Scheme 1

Table 1 Asymmetric hydrosilylation of styrenes **1** with trichlorosilane catalysed by palladium–MOP complexes[a]

Entry	Styrene **1**	Ligand	Conditions *T*/°C	 *t*	Yield (%)[b] of **2**	E.e.(%)[c] of **3** (Config.)[d]	Specific rotation of **3**
1	**1a**	(*S*)-H-MOP	0	12 h	100	93 (*R*)	$[\alpha]_D^{22}$ + 45.0 (*c* 1.80, CH_2Cl_2)
2	**1a**	(*S*)-H-MOP	−10	32 h	92	94 (*R*)	
3[e]	**1a**	(*S*)-H-MOP	0	19 h	90	91 (*R*)	
4	**1a**	(*R*)-MeO-MOP	0	24 h	100	14 (*R*)	
5[e,f]	**1a**	(*R*)-MeO-MOP	5	44 h	100	71 (*R*)	$[\alpha]_D^{22}$ + 35.8 (*c* 0.96, CH_2Cl_2)
6	**1a**	(*R*)-HO-MOP	0	22 h	84	34 (*S*)	$[\alpha]_D^{22}$ − 15.6 (*c* 1.13, CH_2Cl_2)
7	**1a**	(*R*)-CO_2Me-MOP	0	12 h	100	30 (*S*)	$[\alpha]_D^{22}$ − 14.5 (*c* 1.83, CH_2Cl_2)
8	**1a**	(*R*)-CN-MOP	0	24 h	100	26 (*R*)	
9	**1a**	(*S*)-Et-MOP	0	12 h	100	18 (*R*)	
10	**1b**	(*S*)-H-MOP	0	15 h	94	89 (*R*)	$[\alpha]_D^{25}$ + 44.7 (*c* 1.27, $CHCl_3$)
11	**1b**	(*R*)-MeO-MOP	5	4 d	100	13 (*R*)	
12	**1c**	(*S*)-H-MOP	0	5 d	98	96 (*R*)	$[\alpha]_D^{21}$ + 27.9 (*c* 0.61, MeOH)
13	**1c**	(*R*)-MeO-MOP	5	5 d	84	10 (*R*)	
14	**1d**	(*S*)-H-MOP	0	36 h	68	95 (*R*)	$[\alpha]_D^{20}$ + 39.7 (*c* 1.02, $CHCl_3$)
15	**1e**	(*S*)-H-MOP	0	5 d	80	94 (*R*)	$[\alpha]_D^{21}$ + 36.6 (*c* 1.42, Et_2O)
16	**1f**	(*S*)-H-MOP	20	7 d	95	89 (*R*)	$[\alpha]_D^{20}$ + 40.0 (*c* 1.24, $CHCl_3$)
17	**1g**	(*S*)-H-MOP	20	4 d	89	92 (*R*)	$[\alpha]_D^{24}$ + 31.4 (*c* 1.03, $CHCl_3$)

[a] The hydrosilylation was carried out without solvent unless otherwise noted. The catalyst was generated *in situ* by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and a chiral phosphine ligand. The ratio of **1** : $HSiCl_3$: Pd : P is 1 : 1.2 : 0.001 : 0.002. [b] Isolated yield by distillation. [c] Determined by HPLC analysis of the (3,5-dinitrophenyl)carbamate esters of alcohols **3** with a chiral stationary phase column (Sumi- chiral OA-4700 or 4100). [d] Determined by measurement of the optical rotation. For (*R*)-**3a**, (*R*)-**3b**, (*R*)-**3d**, (*R*)-**3e** and (*R*)- **3f**, see ref. 9. For (*R*)-**3c**, see ref. 10. For (*R*)-**3g**, see ref. 11. [e] In benzene (1 mol dm^{-3} solution). [f] Reported in ref. 5.

Several MOP derivatives containing other substituents at the 2′-position[4,7] were also examined for their enantioselectivity in the hydrosilylation of styrene (entries 6–9). It was found that the electronic nature of the substituent is not a decisive factor in the enantioselection, all of the MOPs substituted with methoxy, hydroxy, carbomethoxy, cyano and ethyl groups showing low enantioselectivity irrespective of their electron-withdrawing or electron-donating character. It follows that the small size of the hydrogen at the 2′-position in H-MOP is important for the high enantioselectivity. The dihedral angle between the two naphthyl rings in the binaphthyl skeleton, which is controlled by steric bulkiness of the 2′-substituent, is presumably related to the enantioselectivity.

The H-MOP–palladium complex also catalysed the asymmetric hydrosilylation of styrene derivatives substituted on the phenyl ring **1b–e** and β-alkyl-substituted styrenes **1f** and **1g** to give the corresponding benzylic alcohols (*R*)-**3b–g**[9–11] of over 89% e.e. (entries 10, 12, 14–17). Interestingly, H-MOP–palladium catalyst was less enantioselective and/or less active than MeO-MOP–palladium for the hydrosilylation of non-styrene alkenes such as oct-1-ene and norbornene.

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