Chapter 7
Hydrosilylation of Carbon-Carbon Double Bonds

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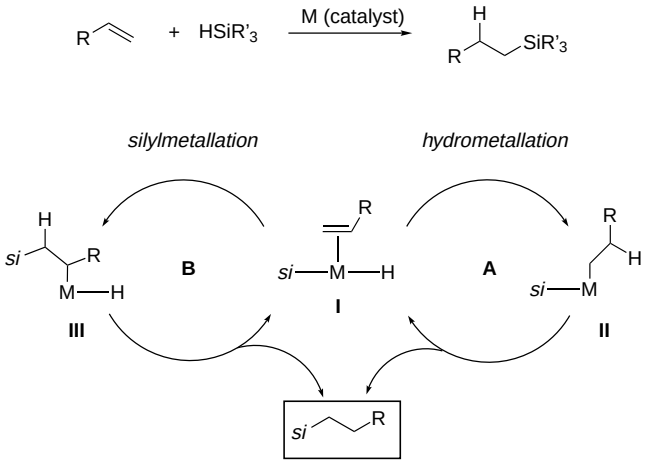
1
Introduction

It is well-documented that certain hydrosilanes undergo addition across the carbon-carbon multiple bonds under catalysis by transition metal complexes and the reaction is referred to as the hydrosilylation [1, 2, 3, 4]. Incorporation of chiral ligands into the metal catalyst can, in principle, make the hydrosilylation result in the formation of optically active alkylsilanes. Since an efficient oxidative cleavage of a carbon-silicon bond to furnish a carbon oxygen bond was found by Tamao [5, 6] in 1978, enantioselective hydrosilylation has been recognized to be a variant of the enantioselective hydration of olefins in general. Thus, optically active alkylsilanes are converted to the corresponding optically active alcohols by oxidation, which proceeds with retention of configuration at the stereogenic carbon center to give the alcohols without loss of their enantiomeric purity. The

asymmetric synthesis of optically active alcohols from alkenes has mainly been effected by asymmetric hydroboration with a stoichiometric amount of a chiral hydroborating agent [7]. Use of catalytic systems for asymmetric hydroboration has not always been successful in terms of enantioselectivity or catalytic activity [8]. Asymmetric hydrosilylation has thus become one of the most useful methods for the preparation of optically active alcohols from alkenes [9, 10]. Another important application of catalytic asymmetric hydrosilylation is the 1,4-hydrosilylation of 1,3-dienes which efficiently produces optically active allylic silanes.

2 Mechanism of Hydrosilylation of Olefins Catalyzed by Transition-Metal Complexes

A transition metal complex, ML_n (L=ligand), especially an electron-rich complex of a late transition metal such as Co(I), Rh(I), Ni(0), Pd(0), or Pt(0) as a precatalyst, activates both hydrosilanes, $HSiR_3$, and a variety of substrates, typically alkenes. A catalytic cycle is considered to involve further two steps as depicted in Scheme 1. The conventional hydrosilylation of alkenes catalyzed by $H_2PtCl_6 \cdot 6H_2O$/*i*PrOH (called the Speier catalyst [11]) is generally assumed to proceed by the Chalk-Harrod mechanism (Scheme 1, cycle A) [12, 13]. Oxidative addition of a hydrosilane gives a hydrido-silyl complex (**I**) which is coordinated with the substrate alkene (extremely rarely isolated at this stage). The complex **I** undergoes migratory insertion of the alkene into the M-H bond (*hydrometallation*) to give the alkyl-silyl species (**II**). Reductive elimination of the alkyl and silyl ligands from **II** forms the hydrosilylation product. Although the Chalk-Harrod mechanism accounts for an alkene isomerization, an H-D exchange between deuteriosilanes and alkenes, as well as the observed regioselec-



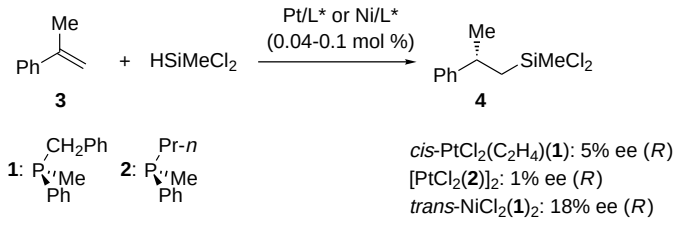
Scheme 1

tivity always associated with the catalytic hydrosilylation, an alternative mechanism has been proposed which involves preferentially an alkene insertion into the M-Si bond (*silylmetallation*) by using Rh(I) or Co(III) catalyst precursor to form the β-silylalkyl-hydrido intermediate (**III**), followed by reductive elimination to complete the hydrosilylation [14, 15, 16] (Scheme 1, cycle B). It is worthy of note that hydrosilanes exhibit a wide spectrum of reactivities in the oxidative addition depending on the substituents on the silicon atom and the nature of the metal catalyst. Thus, Pt complexes tolerate any hydrosilane, such as $HSiCl_nMe_{3-n}$ (n=1~3), $HSi(OR)_3$, or H_nSiR_{4-n} (n=1~3; R = alkyl or Ph) in the hydrosilylation, while, Pd complexes are applicable mostly to $HSiCl_nR_{3-n}$ (n=2, 3) and Rh complexes to preferably $HSiR_3$ [4].

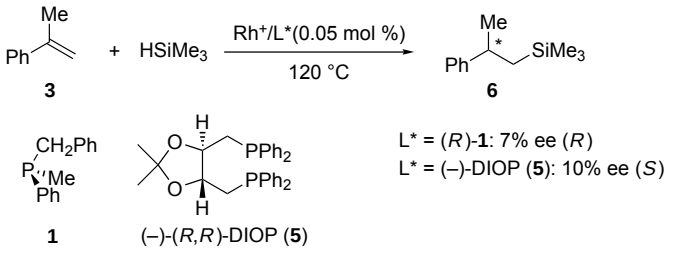
3
Hydrosilylation of 1,1-Disubstituted and Monosubstituted Olefins

Catalytic asymmetric hydrosilylation has been developed with the help of chiral phosphine ligands. In the initial stage, phosphine ligands with a sterogenic phosphorus atom were used. In the first report, a platinum complex coordinated with (*R*)-benzylmethylphenylphosphine (**1**), *cis*-$PtCl_2(C_2H_4)$ (**1**), was used for the reaction of 2-phenylpropene (**3**) with methyldichlorosilane at 40 °C to give (*R*)-1-(methyldichlorosilyl)-3-phenylpropane (**4**) with 5% ee [17, 18] (Scheme 2). On use of a platinum catalyst of (*R*)-methylphenylpropylphosphine (**2**) the enantioselectivity was lower (1% ee). Use of the nickel catalyst *trans*-$NiCl_2(\mathbf{1})_2$ bearing the chiral phosphorus ligand for the hydrosilylation of **3** improved the enantioselectivity, but the enantioselectivity was still not high (18% ee) [19, 20]. Cationic rhodium complexes coordinated with (*R*)-benzylmethylphenylphosphine (**1**) and (–)-DIOP (**5**) as ligand catalyzed the hydrosilylation of 2-phenylpropene (**3**) with trimethylsilane to give 1-(trimethylsilyl)-3-phenylpropane (**6**) in 7% and 10% ee, respectively (Scheme 3) [20].

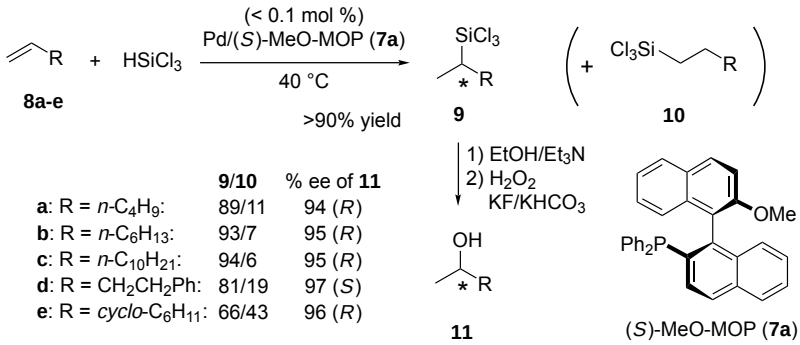
Recently, a palladium complex coordinated with an axially chiral, monodentate phosphine ligand, MeO-MOP (**7a**) or its analogs [21], has been reported to be highly effective for the enantioselective hydrosilylation of alkyl-substituted terminal olefins (Scheme 4) [22, 23]. Simple terminal olefins **8** were transformed efficiently into the corresponding optically active 2-alkanols **11** with enantioselectivities ranging between 94% and 97% ee by the catalytic hydrosilylation-ox-



Scheme 2

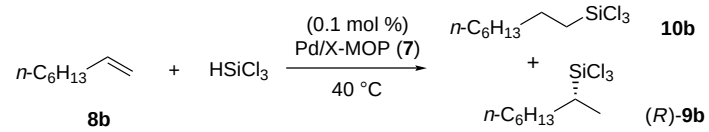


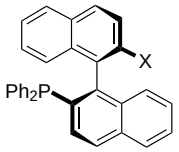
Scheme 3



Scheme 4

idation procedure.For example, the reaction of 1-octene (**8a**) with trichlorosilane in the presence of 0.1 mol % of a palladium catalyst generated from [PdCl(π-C_3H_5)]$_2$ and (*S*)-MeO-MOP (**7a**) at 40 ˚C for 24 h gave 2-octylsilane (**9a**) and 1-octylsilane (**10a**) in a ratio of 93 to 7. The branched isomer was oxidized into (*R*)-2-octanol (**11a**) with 95% ee. It is noteworthy that the reaction of simple terminal alkenes with the MeO-MOP ligand proceeds with high regioselectivity in favor of the branched isomer. No predominant formation of 2-silylalkanes from purely aliphatic 1-alkenes in hydrosilylation reactions has previously been observed with any transition-metal catalysts. Asymmetric hydrosilylation of 4-pentenyl benzoate and 1,5-heptadiene gave the corresponding 2-alkanols with 90% ee and 87% ee, respectively, the ester carbonyl and the internal double bond remaining intact [23]. High selectivity was also observed with the MOP ligands **7b**, **7c**, and **7d**, which have substituents other than methoxy at the 2' position [23] (Scheme 5). Thus, the hydrosilylation of 1-octene (**8b**) with MOP ligands substituted with benzyloxy or isopropoxy gave over 91% enantioselectivity and over 80% regioselectivity, suggesting that the steric bulkiness of the 2'-substituents has little influence on the present asymmetric hydrosilylation. The presence of an alkoxy group at the 2' position of 7 is not essential for high selectivity because replacement of the alkoxy group by an alkyl group did not affect the selectivity.





X-MOP (**7**)

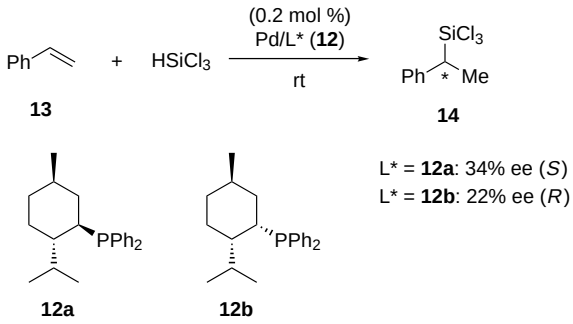
X-MOP	yield %	**9b : 10b**	% ee
(*S*)-MeO-MOP (**7a**)	83	93 : 7	95 (*R*)
(*S*)-PhCH$_2$O-MOP (**7b**)	85	80 : 20	95 (*R*)
(*S*)-*i*-PrO-MOP (**7c**)	88	90 : 10	91 (*R*)
(*R*)-Et-MOP (**7d**)	80	90 : 10	93 (*R*)

Scheme 5

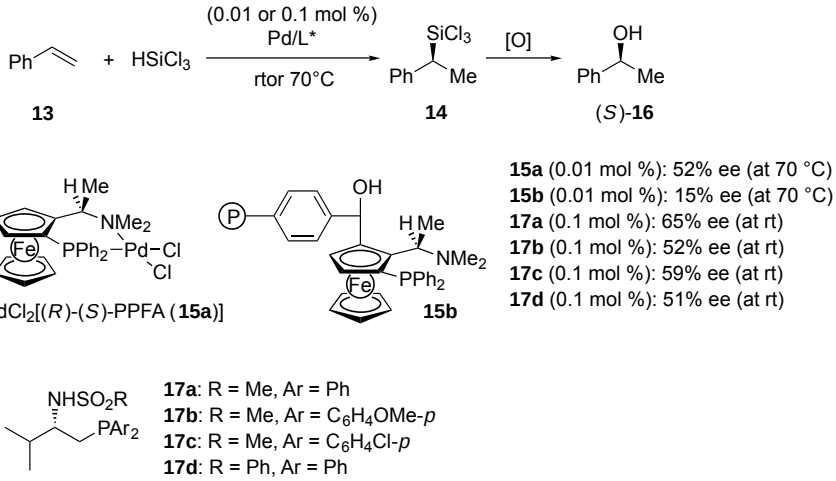
4 Hydrosilylation of Styrenes

Palladium-catalyzed hydrosilylation of styrene derivatives usually proceeds with high regioselectivity to produce benzylic silanes, 1-aryl-1-silylethanes, due to the participation of π-benzylic palladium intermediates [1, 2]. It is known that bisphosphine-palladium complexes are catalytically much less active than monophosphine-palladium complexes and hence asymmetric synthesis has been attempted by use of chiral monodentate phosphine ligands. In the first report, menthyldiphenylphosphine (**12a**) and neomenthyldiphenylphosphine (**12b**) [24, 25] were used for the palladium-catalyzed reaction of styrene (**13**) with trichlorosilane. These reactions gave 1-(trichlorosilyl)-1-phenylethane (**14**) in 34% and 22% ee, respectively (Scheme 6). Use of the ferrocenylmonophosphine (*R*)-(*S*)-PPFA (**15a**) [26, 27, 28] for the same reaction improved the enantioselectivity. In this case, the hydrosilylation product was oxidized to (*S*)-1-phenylethanol (**16**) with 52% ee (Scheme 7). The ferrocenylmonophosphine **15b** supported on Merrifield polystyrene has been also used for the hydrosilylation of styrene, although the enantioselectivity was lower (15% ee) [29]. Several chiral (β-*N*-sulfonylaminoalkyl)phosphines **17** were prepared from (*S*)-valinol and used for the asymmetric hydrosilylation of styrene and cyclopentadiene [30]. For styrene, phosphine **17a** which contains a methanesulfonyl group was the most effective giving (*S*)-1-phenylethanol (**16**) with 65% ee. Other amidophosphines **17b–c** are also fairly effective for this asymmetric hydrosilylation (Scheme 7).

The axially chiral, monophosphine ligand, MeO-MOP (**7a**), was not as effective for styrene derivatives as for simple terminal olefins [31]. The palladium-catalyzed hydrosilylation of styrene (**13**) with trichlorosilane in the presence of the (*R*)-MeO-MOP ligand (**7a**) under standard conditions (without solvent) followed by oxidation gave (*R*)-1-phenylethanol (**16**) with only 14% ee (Scheme 8). Use of benzene as solvent for the hydrosilylation reaction improved the enanti-

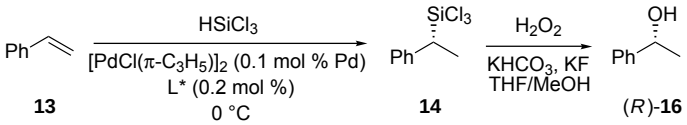


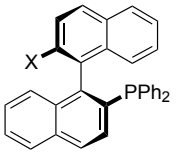
Scheme 6

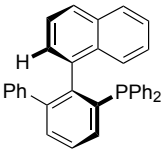


Scheme 7

oselectivity to 71%. For substituted styrenes such as *o*-chlorostyrene or β-methylstyrene, the enantioselectivity was around 80% with the MeO-MOP ligand. The substituents at the 2' position in the MOP ligands strongly affected the enantioselectivity [32]. The ligand H-MOP (**7f**), which has the same 1,1'-binaphthyl skeleton as MeO-MOP but lacks the methoxy group, is particularly effective for the palladium-catalyzed hydrosilylation of styrene giving (*R*)-**16** with 94% ee. On the other hand, the enantiomeric purities of alcohol **16** obtained with Et-MOP (**7d**) and CN-MOP (**7e**) were much lower, 18% ee (*R*) and 26% ee (*R*), respectively. The monophosphine (*S*)-**18** which was prepared through the catalytic asymmetric cross-coupling [33] was as effective as (*S*)-H-MOP (**7f**) for the hydrosilylation of styrene giving (*R*)-**16** with 91% ee. These results suggest that the small size of the hydrogen at the 2' position in H-MOP (**7f**) is important for high enantioselectivity and that the electronic nature of the substituent is not a deci-





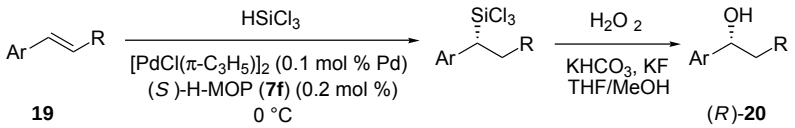


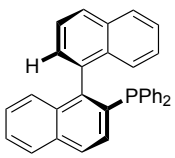
L*	% ee of **16**
(*R*)-MeO-MOP (**7a**)	14% ee
(*S*)-Et-MOP (**7d**)	18% ee
(*R*)-CN-MOP (**7e**)	26% ee
(*S*)-H-MOP (**7f**)	94% ee
(*S*)-**18**	91% ee

X = OMe: (*R*)-MeO-MOP (**7a**)
X = Et: (*S*)-Et-MOP (**7d**)
X = CN: (*R*)-CN-MOP (**7e**)
X = H: (*S*)-H-MOP (**7f**)

(*S*)-**18**

Scheme 8





(*S*)-H-MOP (**7f**)

Ar and R in **19**	% ee of **20**
Ar = 4-$CF_3C_6H_4$, R = H	96% ee
Ar = 4-ClC_6H_4, R = H	94% ee
Ar = 4-MeC_6H_4, R = H	89% ee
Ar = 4-$MeOC_6H_4$, R = H	61% ee
Ar = Ph, R = Me	89% ee (at 20 °C)
Ar = Ph, R = Bu-*n*	92% ee (at 20 °C)

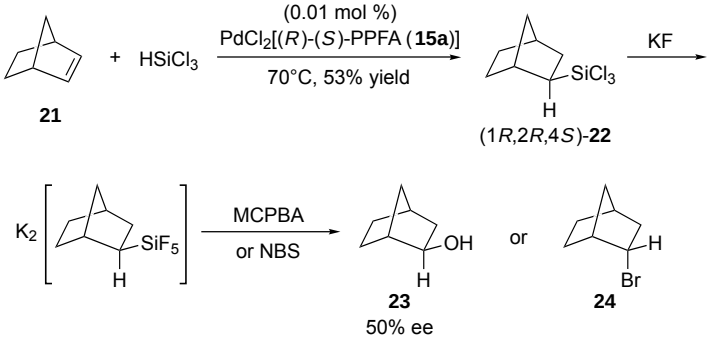
Scheme 9

sive factor in the enantioselection. Asymmetric hydrosilylation of styrenes **19** substituted on the phenyl ring or in the β-position catalyzed by palladium/H-MOP (**7f**) also proceeded with high enantioselectivity giving the corresponding optically active benzylic alcohols **20** in high enantiomeric purity (Scheme 9).

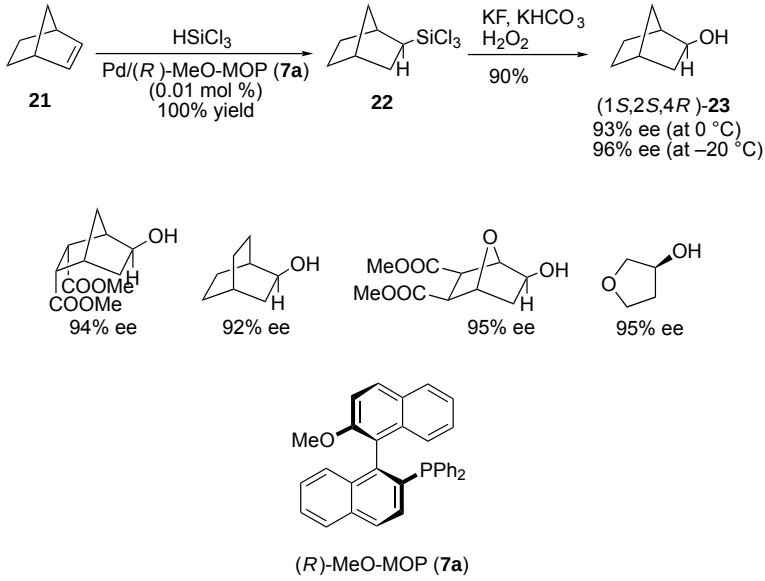
5
Hydrosilylation of Cyclic Olefins

Asymmetric synthesis through a selective monofunctionalization of enantiotopic positions is considered as being one of the most attractive strategies for the one-step construction of multiple chiral carbon centers [34, 35]. Asymmetric hydrosilylation of norbornene (**21**) was first attempted by use of a palladium catalyst coordinated with ferrocenylmonophosphine, (*R*)-(*S*)-PPFA (**15a**) [28]. The

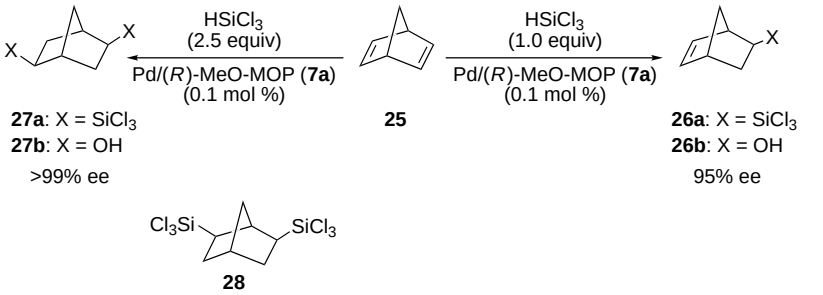
hydrosilylation of **21** with trichlorosilane gave (1*R*,2*R*,4*S*)-*exo*-2-(trichlorosilyl)norbornane (**22**) in about 50% ee (Scheme 10). Treatment of **22** with potassium fluoride followed by oxidation of the resulting pentafluorosilicate with MCPBA or NBS gave *exo*-2-norbornanol (**23**) or *endo*-2-bromonorbornane (**24**), respectively. The palladium-MeO-MOP complex (**7a**) showed much higher enantioselectivity and catalytic activity [36]. The hydrosilylation of norbornene (**21**) with trichlorosilane took place at 0 °C in the presence of 0.01 mol % of the MOP/palladium catalyst to give a quantitative yield of *exo*-2-(trichlorosilyl)norbornane (**22**) as a single product (Scheme 11). Direct oxidation of **22** with hydro-



Scheme 10



Scheme 11



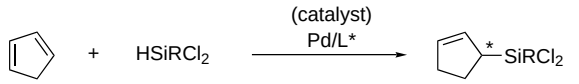
Scheme 12

gen peroxide in the presence of a large excess of potassium fluoride and potassium bicarbonate gave (1*S*,2*S*,4*R*)-*exo*-2-norbornanol (**23**) with 93% ee in high yield. Lowering of the temperature to –20 °C raised the enantiomeric excess to 96% ee. A bicyclo[2.2.2]octene, a diester of norbornenedicarboxylic acid, and 2,5-dihydrofuran derivatives [37] were also successfully subjected to asymmetric hydrosilylation-oxidation under similar reaction conditions to give the corresponding optically active alcohols with enantioselectivities in excess of 92%.

It is remarkable that the monofunctionalization of norbornadiene (**25**) giving *exo*-5-trichlorosilyl-2-norbornene (**26a**) is effected by the palladium-MOP catalyst with high chemo- and enantioselectivity [36] (Scheme 12). Thus, the reaction of **25** with 1.0 equivalent of trichlorosilane and the palladium/MeO-MOP catalyst followed by hydrogen peroxide oxidation gave (1*R*,4*R*,5*S*)-*exo*-5-hydroxy-2-norbornene (**26b**) with 95% ee. The reaction of **25** with 2.5 equivalents of trichlorosilane induced enantioselective hydrosilylation in both double bonds thus giving a 78% yield of chiral disilylnorbornane **27a** and the *meso* isomer **28** in a ratio of 18:1. Oxidation of **27a** gave the diol (1*R*,2*S*,4*R*,5*S*)-**27b** with >99% ee, the high enantiomeric purity being due to the coversion of the minor enantiomer of **26a** to the *meso* product **28**.

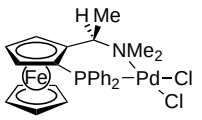
6 Hydrosilylation of 1,3-Dienes

Palladium-catalyzed hydrosilylation of 1,3-dienes is one of the important synthetic methods for allylic silanes, and considerable attention has been directed to the asymmetric synthesis of the latter by catalytic methods [9]. Optically active allylic silanes have been used as chiral allylating reagents in S_E' reactions with electrophiles, typically aldehydes [38, 39]. In the presence of Pd catalysts the reaction with hydrosilanes containing electron-withdrawing atoms or substituents on silicon usually proceeds in a 1,4-fashion giving allylic silanes [40, 41]. Asymmetric hydrosilylation of cyclopentadiene (**29**) forming optically active 3-silylcyclopentene (**30**) has been most extensively studied (Scheme 13). In the first report, hydrosilylation of cyclopentadiene (**29**) with methyldichlorosilane in the presence of 0.01 mol % of palladium-(*R*)-(*S*)-PPFA (**15a**) as a catalyst gave

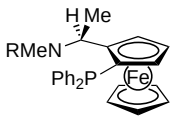


29

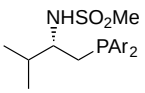
30a: R = Me
30b: R = Cl



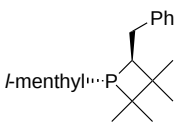
$PdCl_2$[(*R*)-(*S*)-PPFA (**15a**)]



(*S*)-(*R*)-**15c**: R = $CH_2C_3F_7$-*n*
(*S*)-(*R*)-**15d**: R = $CH_2C_8F_{17}$-*n*



17a: Ar = Ph
17b: Ar = C_6H_4OMe-*p*



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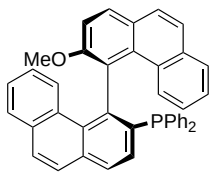
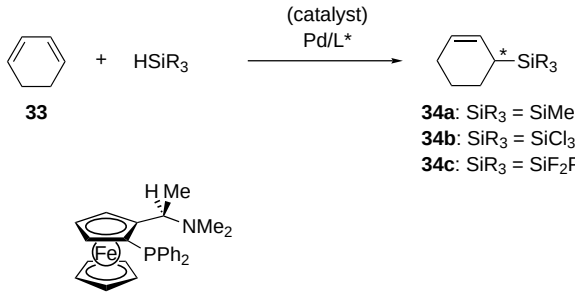


(*R*)-MOP-phen (**32**)

ligand L*	catalyst (mol %)	$HSiRCl_2$	temp (°C)	time (h)	yield (%)	% ee of **30**	ref
(*R*)-(*S*)-PPFA (**15a**)	0.01	$HSiMeCl_2$	30	20	87	25 (*S*)	42
(*S*)-(*R*)-**15c**	0.02	$HSiCl_3$	25	90	73	57 (*R*)	43
(*S*)-(*R*)-**15c**	0.02	$HSiCl_3$	0	20	7	60 (*R*)	43
(*S*)-(*R*)-**15d**	0.02	$HSiCl_3$	25	90	41	55 (*R*)	43
(*S*)-**17a**	0.1	$HSiCl_3$	0	–	82	61 (*S*)	30
(*S*)-**17a**	0.1	$HSiCl_3$	–20	–	35	71 (*S*)	30
(*S*)-**17b**	0.1	$HSiCl_3$	0	–	74	62 (*S*)	30
31	0.03	$HSiCl_3$	70	30	26	44 (*S*)	44,45
31	0.03	$HSiCl_3$	25-30	2	70	54 (*S*)	44,45
(*R*)-MOP-phen (**32**)	0.1	$HSiCl_3$	20	120	99	80 (*R*)	46
(*R*)-MOP-phen (**32**)	0.1	$HSiCl_3$	40	45	85	72 (*R*)	46
(*R*)-MeO-MOP (**7a**)	0.1	$HSiCl_3$	20	14	100	39 (*R*)	46

Scheme 13

allylsilane (*S*)-**30a** with 24% ee [42]. Use of the ferrocenylphosphines **15c,d** containing perfluoroalkyl groups on the side chain for the reaction of **29** with trichlorosilane increased the enantioselectivity (up to 60% ee) [43]. Some of the (β-*N*-sulfonylaminoalkyl)phosphines (**17**) [30] and phosphetane ligand **31**



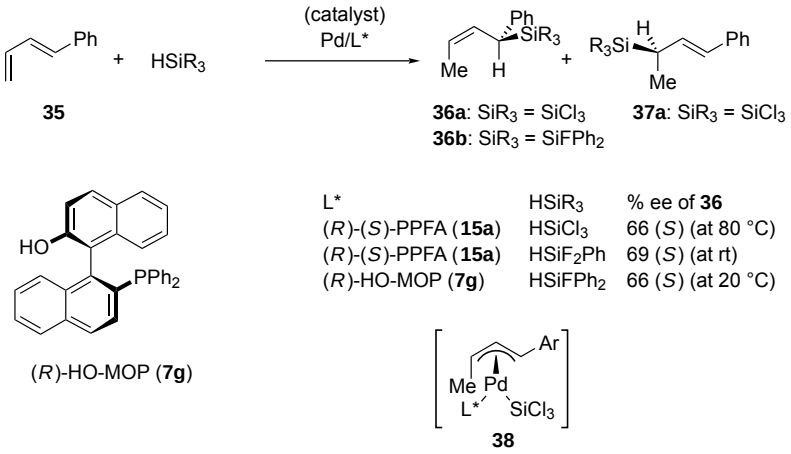
ligand L*	catalyst (mol %)	$HSiRCl_2$	temp (°C)	time (h)	yield (%)	% ee of **34**	ref
(*R*)-(*S*)-PPFA (**15a**)	0.01	$HSiMeCl_2$	30	20	95	2 (*S*)	42
(*R*)-MOP-phen (**32**)	0.1	$HSiCl_3$	20	150	99	51 (*R*)	46
(*R*)-(*S*)-PPFOAc (**15e**)	1	$HSiPhF_2$	rt	20	58	77 (*S*)	47, 48
(*R*)-(*S*)-PPFOMe (**15f**)	1	$HSiPhF_2$	rt	20	50	54 (*S*)	47, 48

Scheme 14

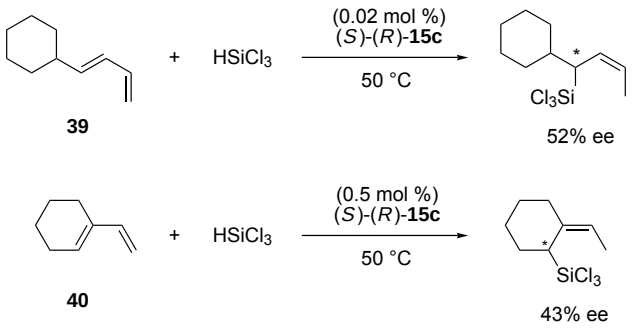
are also useful for the asymmetric hydrosilylation of **29** with trichlorosilane to give **30b** in 71% ee [44, 45]. The highest enantioselectivity so far reported for cyclopentadiene is 80% ee, which was obtained with MOP-phen ligand **32** [46].

For the asymmetric hydrosilylation of 1,3-cyclohexadiene (**33**) (Scheme 14) the enantioselectivity is higher in the reaction with phenyldifluorosilane than that with trichlorosilane or methyldichlorosilane. The reaction of **33** with phenyldifluorosilane in the presence of a palladium catalyst coordinated with ferrocenylphosphine **15e** gave the allylsilane (*S*)-**34c** with 77% ee [47, 48].

Linear 1,3-dienes have been also subjected to the palladium-catalyzed asymmetric hydrosilylation. Reaction of 1-phenyl-1,3-butadiene (**35**) with $HSiCl_3$ catalyzed by palladium-(*R*)-(*S*)-PPFA (**15a**) gave a mixture of the regioisomeric allysilanes **36a** and **37a** in a ratio of 94 to 6, the major isomer **36a** and the minor isomer **37a** having 66% ee (*S*) and 30% ee (*R*), respectively (Scheme 15) [49]. The π-allylpalladium intermediate **38** was postulated for this hydrosilylation. Use of phenyldifluorosilane in place of trichlorosilane slightly improved the enantioselectivity [47, 50]. Hydrosilylation of alkyl-substituted 1,3-dienes **39** and **40** in the presence of a ferrocenylmonophosphine-palladium catalyst also proceeded with high regioselectivity to give the corresponding 1,4-addition products with moderate enantioselectivity (Scheme 16) [43, 51].



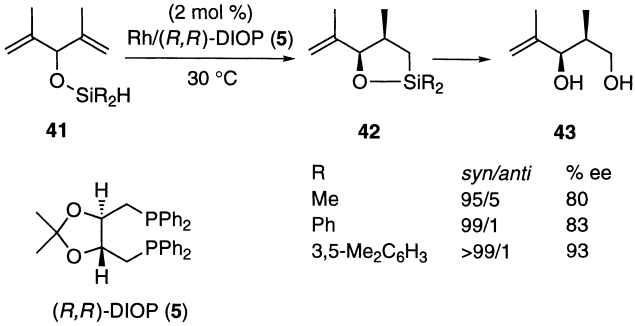
Scheme 15



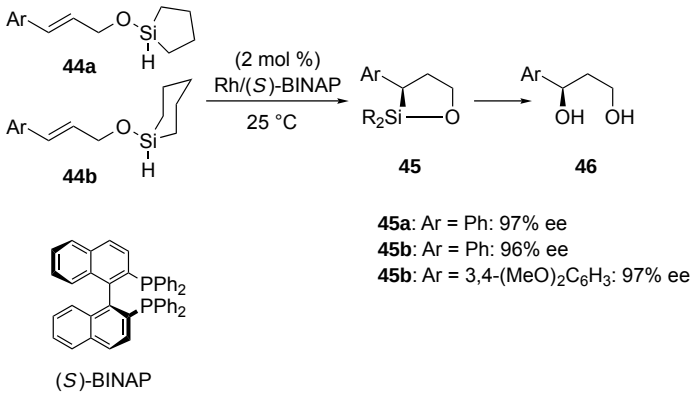
Scheme 16

7
Intramolecular Hydrosilylation

Intramolecular enantioselective hydrosilylation-oxidation of alkenyloxysilanes provides an efficient method for the preparation of optically active polyols from allylic alcohols. Cyclization of silyl ethers **41** of a *meso*-type allylic alcohol in the presence of rhodium-DIOP (**5**) as a catalyst proceeded with high diastereoselectivity and high enantioposition-selectivity. Oxidation of the carbon-silicon bond in the resulting sila-oxa-cyclopentane derivatives **42** gave *syn*-2,4-dimethyl-4-pentene-1,3-diol (**43**) in high enantiomeric excess (Scheme 17) [52]. The enantioselectivity was dependent on the alkyl groups on the silicon, the sterically crowded 3,5-dimethylphenyl group giving the highest selectivity (93% ee).



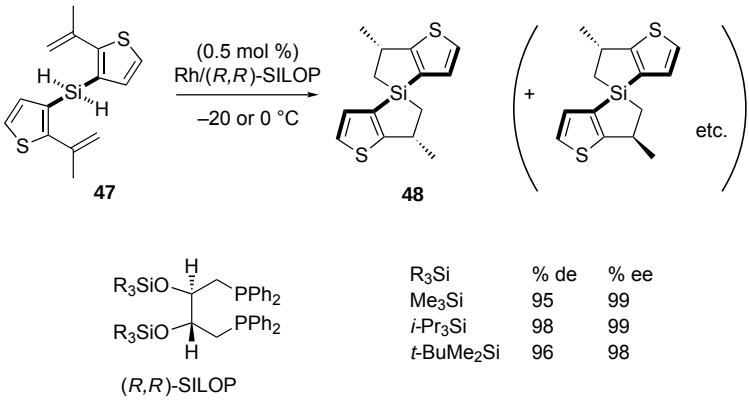
Scheme 17



Scheme 18

Enantioselective cyclization was also successful in the rhodium-catalyzed hydrosilylation of silyl ethers **44** derived from allylic alcohols. High enantioselectivity (up to 97% ee) was observed in the reaction of silyl ethers containing a bulky group on the silicon atom in the presence of a rhodium-BINAP catalyst (Scheme 18) [53]. The cyclization products **45** were readily converted to the 1,3-diols **46** by the oxidation. During studies on this asymmetric hydrosilylation, a silyl-rhodation pathway in the catalytic cycle was demonstrated by a deuterium scrambling method [54].

The axially chiral spirosilane **48** was efficiently prepared by double intramolecular hydrosilylation of bis(alkenyl)dihydrosilane **47**. By use of the SILOP ligand, a C_2 symmetric spirosilane which is almost enantiomerically pure was obtained with high diastereoselectivity (Scheme 19) [55]. The SILOP ligand is much more stereoselective for this asymmetric hydrosilylation than DIOP (**5**) that has an analogous structure.



Scheme 19

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