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Asymmetric Hydrosilylation of Cyclic 1,3-Dienes Catalyzed by an Axially Chiral Monophosphine–Palladium Complex[1]

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Abstract: Asymmetric hydrosilylation of cyclopentadiene and 1,3-cyclohexadiene with trichlorosilane in the presence of a palladium catalyst (0.1 mol %) bearing (*R*)-3-diphenylphosphino-3'-methoxy-4,4'-biphenanthryl [(*R*)-MOP-phen] gave a quantitative yield of the corresponding (*R*)-3-(trichlorosilyl)cycloalkenes of up to 80% ee. The allylation of benzaldehyde with the allylsilanes gave optically active homoallyl alcohols.

Palladium-catalyzed hydrosilylation of 1,3-dienes is one of the important methods for the preparation of allylic silanes,[2] and considerable attention has been paid to their catalytic asymmetric synthesis by use of chiral phosphine-palladium complexes.[3] We have previously reported that high enantioselectivity (over 90% ee) is attained in the palladium-catalyzed asymmetric hydrosilylation of simple terminal alkenes,[4] cyclic alkenes,[5] and styrene derivatives[6] by use of 2-diphenylphosphino-2'-methoxy-1,1'-binaphthyl (MeO-MOP)[7] or 2-diphenylphosphino-1,1'-binaphthyl (H-MOP),[8] but these chiral monophosphine ligands, whose basic skeleton is 1,1'-binaphthyl, are not so effective for the asymmetric hydrosilylation of 1,3-dienes. Here we report that (*R*)-3-diphenylphosphino-3'-methoxy-4,4'-biphenanthryl (MOP-phen),[9] which is 4,4'-biphenanthryl analog of MeO-MOP, is an efficient chiral ligand for the asymmetric hydrosilylation of cyclic 1,3-dienes to give the corresponding allylic silanes with high enantioselectivity.

Hydrosilylation of cyclopentadiene (**1a**) with trichlorosilane was carried out (Scheme 1) without any solvents in the presence of 0.1 mol % of palladium catalyst generated in situ by mixing [PdCl(π-C_3H_5)]$_2$ and a

Scheme 1

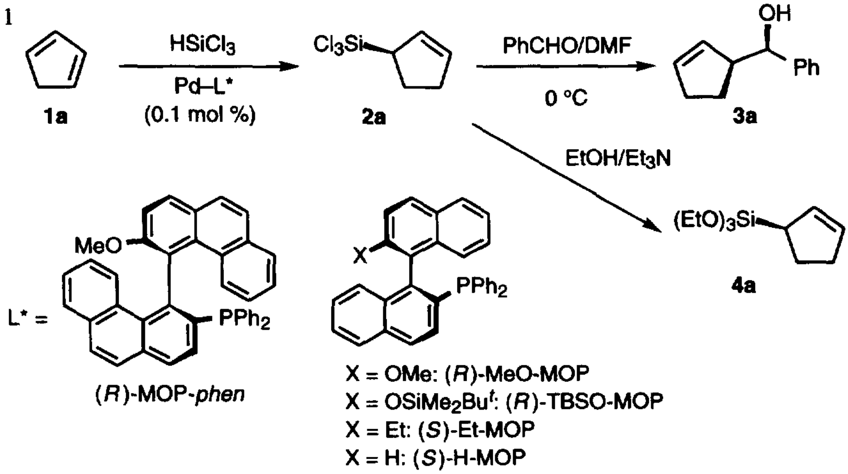


Table 1. Palladium-Catalyzed Asymmetric Hydrosilylation of Cyclic Dienes with Trichlorosilane[a]

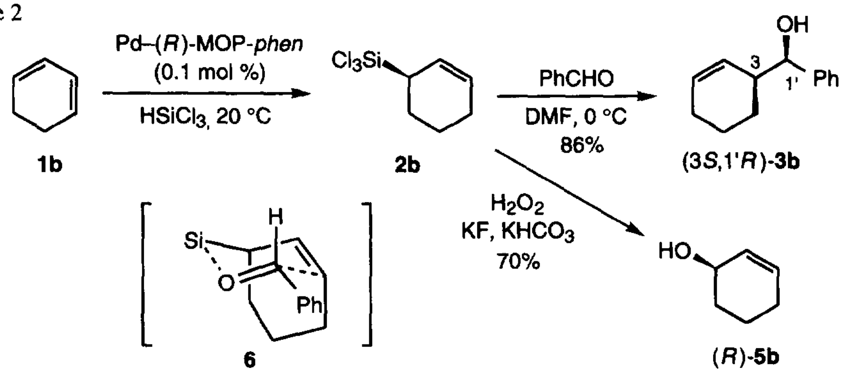
entry	diene	ligand	reaction conditions temp (°C)	time (h)	yield (%)[b] of 2	% ee[c] of 3 (config)[d]	specific rotation of 3 ($[\alpha]^{20}_D$)
1	**1a**	(*R*)-MOP-phen	20	120	99 (**2a**)	80 (*R*)	–27.0 (*c* 1.80, chloroform)
2	**1a**	(*R*)-MOP-phen	40	45	85 (**2a**)	72 (*R*)	
3	**1a**	(*R*)-MeO-MOP	20	14	100 (**2a**)	39 (*R*)	–12.4 (*c* 0.98, chloroform)
4	**1a**	(*R*)-TBSO-MOP	20	9	100 (**2a**)	49 (*R*)	
5	**1a**	(*S*)-Et-MOP	20	21	90 (**2a**)	43 (*R*)	
6	**1a**	(*S*)-H-MOP	20	3	91 (**2a**)	28 (*R*)	
7	**1b**	(*R*)-MOP-phen	20	150	99 (**2b**)	51 (*R*)	–6.8 (*c* 1.1, benzene)
8	**1b**	(*R*)-MeO-MOP	20	42	76 (**2b**)	16 (*R*)	–1.9 (*c* 2.0, benzene)
9	**1b**	(*S*)-H-MOP	20	9	77 (**2b**)	10 (*R*)	
10[e]	**1b**	(*R*)-MOP-phen	0	19	56[f]	30[g] (*R*)	

[a] The hydrosilylation was carried out without solvent. 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 1.0/1.2/0.001/0.002. [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 (Sumichiral OA-4700) unless otherwise noted. [d] Determined by the optical rotation of 3-(triethoxysilyl)cyclopentene (**4a**) (ref. 3c) or 2-cyclohexenol (**5b**) (ref. 14). [e] The reaction with $HSiF_2Ph$. [f] Yield of 3-(difluorophenylsilyl)cyclohexene. [g] Determined by HPLC analysis of the (3,5-dinitrophenyl)carbamate ester of alcohol **5b** with a chiral stationary phase column (Sumichiral OA-1100).

chiral phosphine ligand (Pd/P = 1/2). The reaction with (*R*)-MOP-phen ligand at 20 °C for 5 days (entry 1 in Table 1) gave a quantitative yield of 3-(trichlorosilyl)cyclopentene (**2a**), whose absolute configuration *R* was assigned by the specific rotation ($[\alpha]^{20}_D$ +62.3 (*c* 0.84, benzene)) of 3-(triethoxysilyl)cyclopentene (**4a**)[3c] obtained by treatment of **2a** with ethanol and triethylamine. The allyl(trichloro)silane **2a** was subjected to the S_E' reaction with benzaldehyde in DMF according to Kobayashi's procedures[10] to give 92% yield of 3-[hydroxy(phenyl)methyl]cyclopentene (**3a**) ($[\alpha]^{20}_D$ –27.0 (*c* 1.80, chloroform)) as a single diastereoisomer.[11] The enantiomeric purity was determined to be 80% ee by HPLC analysis of the (3,5-dinitrophenyl)carbamate ester of alcohol **3a** ($3,5\text{-}(NO_2)_2C_6H_3NCO$/pyridine), with a chiral stationary phase column (Sumichiral OA-4700, hexane/dichloroethane/ethanol = 50/15/1). The 80% ee of the homoallyl alcohol **3a** indicates that the enantioselectivity in the asymmetric hydrosilylation of cyclopentadiene is at least 80%, which is the highest value for the asymmetric hydrosilylation of 1,3-dienes.[3] Much lower enantioselectivity was observed with the MOP ligands,[7,8] MeO-MOP, TBSO-MOP, Et-MOP, and H-MOP, all of which have 1,1'-binaphthyl skeleton in place of 4,4'-biphenanthryl in MOP-phen[12] (entries 3–6).

For the asymmetric hydrosilylation of 1,3-cyclohexadiene (Scheme 2), the palladium catalyst coordinated with MOP-phen was also more effective than that coordinated with MeO-MOP or H-MOP. The reaction carried out with MOP-phen ligand at 20 °C gave (*R*)-3-(trichlorosilyl)cyclohexene (**2b**) of 51% ee (entry 7), while the reaction with MeO-MOP and H-MOP gave (*R*)-**2b** of only 16% ee and 10% ee, respectively (entries 8, 9). The absolute configuration *R* of allylsilane **2b** was determined by oxidation[13] into known (*R*)-(+)-2-cyclohexenol (**5b**) ($[\alpha]^{20}_D$ +55.8 (*c* 0.87, $CHCl_3$)).[14] Reaction of (*R*)-**2b** with benzaldehyde in DMF[10] gave (3*S*,1'*R*)-3-[hydroxy(phenyl)methyl]cyclohexene (**3b**) ($[\alpha]^{20}_D$ –6.8 (*c* 1.1, benzene))[15] in 86% yield. These stereo-

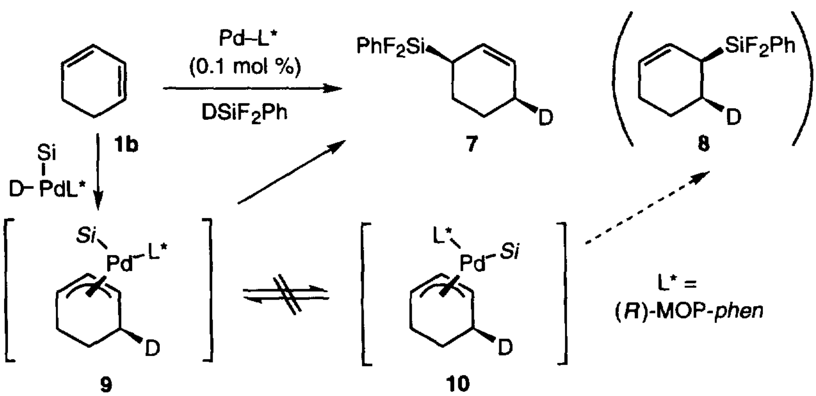
Scheme 2



chemical results confirm the cyclic mechanism proposed by Kobayashi[10] for the allylation with allyl(trichloro)-silanes in DMF, (*R*)-**2b** producing (3*S*,1'*R*)-**3b** by way of the six-membered cyclic transition state **6** in our system.[16] The absolute configuration of homoallyl alcohol (–)-**3a** obtained in the reaction of cyclopentenyl-(trichloro)silane **2a** with benzaldehyde (Scheme 1) is assigned to be (3*S*,1'*R*) by the cyclic transition state.

The use of phenyldifluorosilane[3k] in place of trichlorosilane did not improve the enantioselectivity in the present asymmetric hydrosilylation of **1b** (entry 10), but the reaction with deuterium-labeled silane, $DSiF_2Ph$,[17-19] gave us significant insight into the mechanism of hydrosilylation of 1,3-dienes. Thus, the reaction of 1,3-cyclohexadiene (**1b**) with $DSiF_2Ph$ gave *cis*-3-(phenyldifluorosilyl)-6-deuteriocyclohexene (**7**)[20] as a single isomer without any diastereo- or regioisomers such as **8** (Scheme 3), demonstrating that 1,4-*cis*-addition of hydrosilane to the 1,3-diene is an exclusive pathway. The π-allylpalladium intermediate **9**, which is formed by the addition of palladium-deuteride on a PdD(Si)L* species to the diene and has the silyl group located at the *trans* position to the π-allyl carbon next to the deuterated carbon, rapidly undergoes reductive elimination forming **7** before *trans-cis* isomerization to **10** which would produce **8**. It follows that the stereochemical outcome is determined at the enantioselective addition of palladium-hydride to the diene.

Scheme 3



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17. $^2H\{^1H\}$ NMR ($CHCl_3/CDCl_3$) δ 5.24 (t, J = 11 Hz). Prepared by dichlorination of D_3SiPh (ref. 18) with CuI and $CuCl_2$ in ether (ref. 19) followed by substitution of chlorides in $DSiCl_2Ph$ with fluorides by treatment with aq HF (ref. 3k).
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20. ^1H NMR ($CDCl_3$) δ 1.54-1.62 (m, 1 H), 1.67-1.82 (m, 1 H), 1.86-1.94 (m, 1 H), 1.98-2.06 (m, 2 H), 2.09-2.15 (m, 1 H), 5.71 (ddd, J = 1.8, 2.8, 9.9 Hz, CHD-CH=C*H*-CHSi, 1 H), 5.82 (ddd, J = 2.7, 3.5, 9.9 Hz, CHD-C*H*=CH-CHSi, 1 H), 7.37-7.75 (m, 5 H). $^2H\{^1H\}$ NMR ($CHCl_3/CDCl_3$) δ 1.97 (br d, J = 2.0 Hz).

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