Tetrahedron: *Asymmetry* 24 (2013) 418–420

Contents lists available at SciVerse ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Asymmetric hydrosilylation of cyclohexa-1,3-diene with trichlorosilane by palladium catalysts coordinated with chiral phosphoramidite ligands

Hoon Seo Park [a], Jin Wook Han [a,*], Ryo Shintani [b], Tamio Hayashi [b,c]

[a] *Department of Chemistry, College of Natural Sciences, Institute of Nanoscience and Technology, Hanyang University, Seoul 133-791, Republic of Korea*
[b] *Department of Chemistry, Faculty of Science, Kyoto University, Sakyo, Kyoto 606-8502, Japan*
[c] *Chemistry Department, Faculty of Science, King Abdulaziz University, PO Box 80203, Jeddah 21589, Saudi Arabia*

ARTICLE INFO

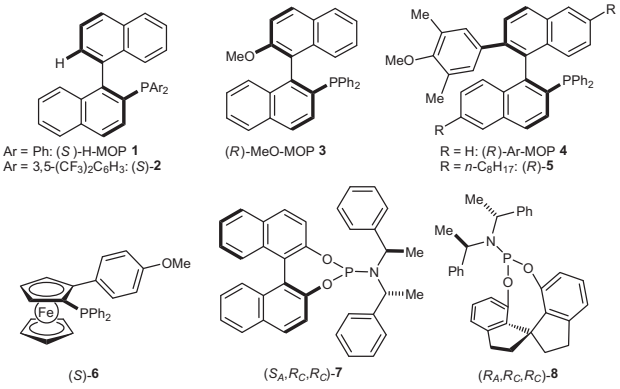
Article history:
Received 29 January 2013
Accepted 5 February 2013
Available online 27 February 2013

ABSTRACT

Chiral phosphoramidite ligands prepared from (*S*)-binaphthol and various secondary amines were examined for the palladium-catalyzed asymmetric hydrosilylation of cyclohexa-1,3-diene with trichlorosilane. With a sterically demanding phosphoramidite bearing bis(diphenylmethyl)amine, the high enantiomeric excess of 87% was achieved, which is the highest enantioselectivity in the hydrosilylation of cyclohexadiene reported to date. The catalytic activity in the present hydrosilylation was high with all of the ligands employed, while the enantioselectivities varied dramatically depending on the dialkylamine moiety of the phosphoramidite ligand.

1. Introduction

Palladium-catalyzed asymmetric hydrosilylations of carbon–carbon double bonds with trichlorosilane have been intensively investigated in order to achieve excellent regioselectivities and enantioselectivities with the aid of chiral monodentate ligands, represented by MOPs having an axially chiral binaphthyl moiety, from early 1990s to early 2000s.[1] During this period, the substrate scope of the hydrosilylation reaction has also been expanded to include styrenes, alkyl-substituted alkenes, and conjugated 1,3-dienes. With regard to the enantioselectivity, the highest values for the reaction of each olefinic substrate type have been obtained by choosing an appropriate chiral monophosphine ligand.[1] For example, chiral MOP ligands, which are readily changeable responding to the substrate types by substituting a suitable functional group at the 2′-position of the binaphthyl unit, have been developed to give the highest enantioselectivities for the catalytic hydrosilylation. For the hydrosilylation of styrenes and alkyl-substituted alkenes, the highest enantioselectivity has been reported with H-MOP ligands **1** and **2**[2] and MeO-MOP ligand **3**,[3] respectively. The MOP ligand has also been modified and optimized for the asymmetric hydrosilylation of 1,3-dienes, and Ar-MOP ligands **4** and **5** showed the highest enantioselectivity for cyclic 1,3-dienes.[4] Ferrocenylmonophosphines such as **6** have shown excellent enantioselectivities and catalytic activities in the reaction of styrene.[5]



On the other hand, chiral phosphoramidites, which are readily available from chiral diols and amines, have been reported to be effective as ligands for various catalytic asymmetric reactions.[6] Chiral phosphoramidites, such as **7** and **8**, have already been utilized in the palladium-catalyzed asymmetric hydrosilylation of styrenes and demonstrated excellent enantioselectivities and catalytic activities.[7] However, no reports concerning the application of chiral phosphoramidite ligands to the hydrosilylation of conjugated dienes have appeared in the literature, despite its synthetic utility. Palladium-catalyzed asymmetric hydrosilylations of 1,3-dienes with trichlorosilane, which proceed in a 1,4-addition fashion, produce enantiomerically enriched allylsilanes.[4a] The allylsilanes obtained are converted further without a loss of their enantiomeric purities into useful intermediates in stereospecific transformations,

* Corresponding author.
E-mail address: jwhan@hanyang.ac.kr (J.W. Han).

0957-4166/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetasy.2013.02.002

such as chiral allyl alcohols by Tamao oxidations[8] and chiral homoallyl alcohols via reaction with aldehydes.[9] Herein we report that a chiral phosphoramidite ligand derived from (*S*)-binaphthol and a secondary amine showed a higher enantioselectivity than **5** which has been until now the most enantioselective ligand in the palladium-catalyzed asymmetric hydrosilylation of cyclohexadiene.

2. Results and discussion

Chiral phosphoramidite ligands prepared from (*S*)-binaphthol and various secondary amines were examined for their catalytic activity and enantioselectivity in the palladium-catalyzed asymmetric hydrosilylation of cyclohexa-1,3-diene with trichlorosilane (Scheme 1). The reaction was carried out without solvent in the presence of 1.0 mol % of palladium catalysts formed in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ with 2.0 equiv (to palladium) of ligand **7** or **9**. The resulting 3-(trichlorosilyl)cyclohexene **10** was subsequently reacted with benzaldehyde in DMF to give the corresponding homoallyl alcohol **11**, which was subjected to HPLC analysis with a chiral stationary phase column for determination of the enantioselectivities. The results summarized in Table 1 show that the catalytic activities of the palladium complex with phosphoramidite ligands are high enough to complete the reaction within 22 h at 20 °C regardless of the ligand used, but the enantioselectivities varied dramatically according to the ligand.

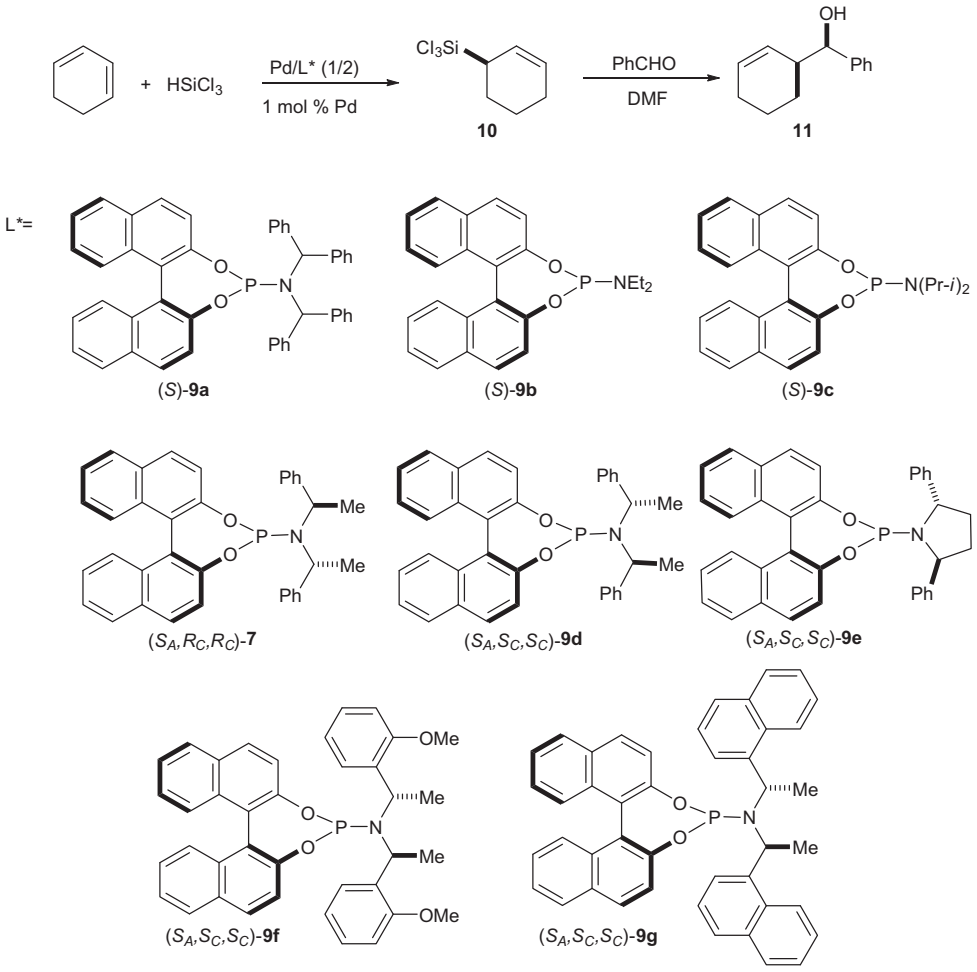
Among the chiral phosphoramidite ligands studied, the ligand of choice was the sterically demanding **9a**[10] which consisted of an axial chiral (*S*)-binaphthol and a bulky bis(diphenylmethyl)amine.

Table 1
Palladium-catalyzed asymmetric hydrosilylation of cyclohexa-1,3-diene with $HSiCl_3$[a]

Entry	L*	Temp (°C)	Time (h)	Yield[b] (%)	% ee[c] (abs config)
1	**9a**	20	20	82	87 (*R*)
2	**9a**	−10	84	97	87 (*R*)
3	**9b**	20	20	91	19 (*R*)
4	**9c**	20	22	93	34 (*R*)
5	**7**	20	22	93	57 (*R*)
6	**9d**	20	22	87	70 (*R*)
7	**9e**	20	22	79	6 (*S*)
8	**9f**	20	22	95	53 (*R*)
9	**9g**	20	20	80	47 (*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 ligand L*. The initial ratio of cyclohexa-1,3-diene/$HSiCl_3$/Pd/L* was 1.0/1.2/0.010/0.020.
[b] Isolated yields by bulb-to-bulb distillation.
[c] Determined by HPLC analysis of alcohol **11** with a chiral stationary column (Daicel Chiralpak OB-H).

Thus, the hydrosilylation proceeded at 20 °C for 20 h in the presence of the palladium/**9a** as a chiral catalyst to give (*R*)-3-trichlorosilylcyclohexene **10** with 87% ee, which is higher than the previously reported value of 83% ee obtained by the palladium/**5** catalyst at −10 °C for 168 h (entry 1).[4b,c] However, the enantioselectivity obtained by the palladium/**9a** catalyst was not improved upon by lowering the reaction temperature (entry 2). The steric bulkiness of the amine substituents plays a crucial role with regard to the enantioselectivity of this hydrosilylation. Thus, the enantioselectivities with the phosphoramidites from diethylamine **9b**[11]



Scheme 1. Pd-catalyzed asymmetric hydrosilylation of cyclohexa-1,3-diene with $HSiCl_3$.

and diisopropylamine **9c**[12] were only 19% and 34% ee, respectively (entry 3 and 4). A series of ligands with a stereogenic center on the amine substituents were also examined. Phosphoramidite **7**, which was one of the most enantioselective ligands in the asymmetric hydrosilylation of styrene,[7a] gave product **10** with a moderate enantiomeric excess of 57%, whereas its diastereomer **9d**[6] gave **10** with a higher ee than **7** but inferior to **9a** (entry 5 and 6). It should be noted that the product obtained from the hydrosilylation with both diastereomers **7** and **9d** had the same (*R*)-absolute configuration. Changing the phenyl group in **9d** to a 2-methoxyphenyl **9f**[13] or 1-naphthyl group **9g**,[14] caused the enantioselectivity to decrease to 53% and 47% ee, respectively. Ligand **9e**[15] bearing (*S*,*S*)-2,5-diphenylpyrrolidine, which is thought to be a cyclic version of (*S*,*S*)-bis(1-phenylethyl)amine, showed almost no enantioselectivity in the present reaction (entry 7). The results from electronic and steric tuning based on the chirality of diastereomer **9d** imply that the enantioselectivity of the hydrosilylation of cyclohexadiene is strongly dependent on the substituents on the nitrogen atom in the phosphoramidite ligands.

3. Conclusion

In conclusion, we have shown that chiral phosphoramidite ligand **9a** prepared from (*S*)-binaphthol and an achiral amine, bis(diphenylmethyl)amine is the most effective for the palladium-catalyzed asymmetric hydrosilylation of cyclohexa-1,3-diene with trichlorosilane, achieving a high enantioselectivity of 87% ee, which is the highest reported value so far in the hydrosilylation of cyclohexadiene.

4. Experimental

4.1. Palladium-catalyzed asymmetric hydrosilylation of cyclohexa-1,3-diene with $HSiCl_3$ and the subsequent reaction with benzaldehyde

The reaction conditions and results are summarized in Table 1. A typical procedure is given for the hydrosilylation reaction by the Pd/**9a** catalyst (entry 1). To a mixture of $[PdCl(\pi\text{-}C_3H_5)]_2$ (3.7 mg, 0.010 mmol), the phosphoramidite ligand **9a** (27 mg, 0.040 mmol), and cyclohexa-1,3-diene (160 mg, 2.0 mmol) was added dropwise $HSiCl_3$ (0.24 mL, 2.4 mmol) at 0 °C. The reaction mixture was stirred in a sealed tube at 20 °C for 20 h, and then distilled (bulb-to-bulb) under reduced pressure to give 354 mg (82% yield) of 3-(trichlorosilyl)cyclohexene **10**.[4b]

A mixture of 3-(trichlorosilyl)cyclohexene **10** (110 mg, 0.51 mmol) obtained above and benzaldehyde (21 mL, 0.2 mmol) in DMF (1 mL) was stirred at 0 °C for 2 h. Saturated aqueous sodium hydrogen carbonate was added to quench the reaction, and the aqueous layer was extracted with diethyl ether. The extract was dried over anhydrous $MgSO_4$, and the solvent was evaporated. The crude product was purified by preparative TLC on silica gel (hexane/ethyl acetate = 4:1) to give (*R*)-((*S*)-cyclohex-2-en-1-yl)(phenyl)methanol (*R*,*S*)-**11**.[4a,9a] The enantiomeric purity and absolute configuration of **11** were determined by HPLC analysis (Chiralpak OB-H, hexane/2-propanol = 9:1, flow 0.5 mL/min, 254 nm, t_1 = 10.7 min (*S*), t_2 = 16.3 min (*R*)) to be 87% ee of the (*R*,*S*)-isomer. It follows that allylsilane **10** is an (*R*)-isomer with 87% ee.

Acknowledgments

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (2011-0010550).

References

1. (a) Hayashi, T. *Acc. Chem. Res.* **2000**, *33*, 354; (b) Han, J. W.; Tokunaga, N.; Hayashi, T. *J. Am. Chem. Soc.* **2001**, *123*, 12915; (c) Yamamoto, K.; Hayashi, T. In *Transition Metals for Organic Synthesis (II)*; Beller, M., Bolm, C., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 2, p 167; (d) Tietze, L. F.; Ila, H.; Bell, H. P. *Chem. Rev.* **2004**, *104*, 3453; (e) Ogasawara, M.; Ito, A.; Yoshida, K.; Hayashi, T. *Organometallics* **2006**, *25*, 2715; (f) Hayashi, T.; Yamasaki, K. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier Ltd: Oxford, 2007; Vol. 10, p 815; (g) Han, J. W.; Hayashi, T. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed., 3rd ed.; Wiley-VCH: New York, 2009; p 771; (h) Han, J. W.; Hayashi, T. In *Stereoselective Synthesis 1: Stereoselective Reactions of Carbon–Carbon Double Bonds*; de Vries, J. G., Ed.; George Thieme: Stuttgart, 2011; p 923.
2. (a) Uozumi, Y.; Kitayama, K.; Hayashi, T. *Tetrahedron: Asymmetry* **1993**, *4*, 2419; (b) Kitayama, K.; Uozumi, Y.; Hayashi, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1533; (c) Uozumi, Y.; Tsuji, H.; Hayashi, T. *J. Org. Chem.* **1998**, *63*, 6137; (d) Hayashi, T.; Hirate, S.; Kitayama, K.; Tsuji, H.; Torii, A.; Uozumi, Y. *Chem. Lett.* **2000**, 1272; (e) Hayashi, T.; Hirate, S.; Kitayama, K.; Tsuji, H.; Torii, A.; Uozumi, Y. *J. Org. Chem.* **2001**, *66*, 1441; (f) Shimada, T.; Mukaide, K.; Shinohara, A.; Han, J. W.; Hayashi, T. *J. Am. Chem. Soc.* **2002**, *124*, 1584.
3. (a) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887; (b) Uozumi, Y.; Kitayama, K.; Hayashi, T.; Yanagi, K.; Fukuyo, E. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 713; (c) Hayashi, T. *Acta Chem. Scand.* **1996**, *50*, 259.
4. (a) Kitayama, K.; Tsuji, H.; Uozumi, Y.; Hayashi, T. *Tetrahedron Lett.* **1996**, *37*, 4169; (b) Hayashi, T.; Han, J. W.; Takeda, A.; Tang, J.; Nohmi, K.; Mukaide, K.; Tsuji, H.; Uozumi, Y. *Adv. Synth. Catal.* **2001**, *343*, 279; (c) Han, J. W.; Hayashi, T. *Chem. Lett.* **2001**, 976; (d) Han, J. W.; Hayashi, T. *Tetrahedron: Asymmetry* **2002**, *13*, 325; (e) Han, J. W.; Hayashi, T. *Tetrahedron: Asymmetry* **2010**, *21*, 2193.
5. (a) Pedersen, H. L.; Johannsen, M. *Chem. Commun.* **1999**, 2517; (b) Pedersen, H. L.; Johannsen, M. *J. Org. Chem.* **2002**, *67*, 7982.
6. (a) Feringa, B. L.; Pineschi, M.; Arnold, L. A.; Imbos, R.; de Vries, A. H. M. *Angew. Chem., Int. Ed.* **1997**, *36*, 2620; (b) Feringa, B. L. *Acc. Chem. Res.* **2000**, *33*, 346; (c) Alexakis, A.; Trevitt, G. P.; Bernardinelli, G. *J. Am. Chem. Soc.* **2001**, *123*, 4358; (d) Li, K.; Alexakis, A. *Chem. Eur. J.* **2007**, *13*, 3765; (e) Liu, W.-B.; He, H.; Dai, L. X.; You, S.-L. *Org. Lett.* **2008**, *10*, 1815; (f) Shintani, R.; Moriya, K.; Hayashi, T. *J. Am. Chem. Soc.* **2011**, *133*, 16440; (g) Fananas-Mastral, M.; Perez, M.; Bos, P. H.; Rudolph, A.; Harutyunyan, S. R.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2012**, *51*, 1922; (h) Shintani, R.; Moriya, K.; Hayashi, T. *Org. Lett.* **2012**, *14*, 2902.
7. (a) Jensen, J. F.; Svendsen, B. Y.; Cour, T. V. L.; Pedersen, H. L.; Johannsen, M. *J. Am. Chem. Soc.* **2002**, *124*, 4558; (b) Guo, X.-X.; Xie, J.-H.; Hou, G.-H.; Shi, W.-J.; Wang, L.-X.; Zhou, Q.-L. *Tetrahedron: Asymmetry* **2004**, *15*, 2231.
8. (a) Tamao, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985; p 231; (b) Tamao, K. In *Advances in Silicon Chemistry*; Larson, G. L., Ed.; JAI Press: London, 1996; p 1.
9. (a) Kobayashi, S.; Nishino, K. *J. Org. Chem.* **1994**, *59*, 6620; (b) Masse, C. E.; Pane, J. S. *Chem. Rev.* **1995**, *95*, 1293; (c) Kobayashi, S.; Hirabayashi, R. *J. Am. Chem. Soc.* **1999**, *121*, 6942.
10. Shintani, R.; Nakatsu, H.; Takatsu, K.; Hayashi, T. *Chem. Eur. J.* **2009**, *15*, 8692.
11. (a) Arnold, L. A.; Imbos, R.; Mandoli, A.; de Vries, A. H. M.; Naasz, R.; Feringa, B. L. *Tetrahedron* **2000**, *56*, 2865; (b) Shintani, R.; Park, S.; Duan, W.-L.; Hayashi, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 5901.
12. (a) de Vries, A. H. M.; Meetsma, A.; Feringa, B. L. *Angew. Chem., Int. Ed.* **1996**, *35*, 2374; (b) Duursma, A.; Pena, D.; Minnaard, A. J.; Feringa, B. L. *Tetrahedron: Asymmetry* **1901**, *2005*, 16.
13. (a) Tissot-Croset, K.; Polet, D.; Alexakis, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 2426; (b) Weihofen, R.; Tverskoy, O.; Helmchen, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 5546; (c) Shintani, R.; Park, S.; Shirozu, F.; Murakami, M.; Hayashi, T. *J. Am. Chem. Soc.* **2008**, *130*, 16174.
14. (a) Naasz, R.; Arnold, L. A.; Minnaard, A. J.; Feringa, B. L. *Angew. Chem., Int. Ed.* **2001**, *40*, 927; (b) Liu, L.; Ishida, N.; Murakami, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 2485.
15. (a) Choi, Y. H.; Choi, J. Y.; Yang, H. Y.; Kim, Y. H. *Tetrahedron: Asymmetry* **2002**, *13*, 801; (b) Trost, B. M.; Stambuli, J. P.; Silverman, S. M.; Schwoerer, U. *J. Am. Chem. Soc.* **2006**, *128*, 13328; (c) Shintani, R.; Ito, T.; Nagamoto, M.; Otomo, H.; Hayashi, T. *Chem. Commun.* **2012**, *48*, 9936.