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Supplementary Material Available: Full experimental and spectral details for this synthesis (10 pages). Ordering information is given on any current masthead page.

Catalytic Asymmetric Synthesis of Optically Active 2-Alkanols via Hydrosilylation of 1-Alkenes with a Chiral Monophosphine-Palladium Catalyst

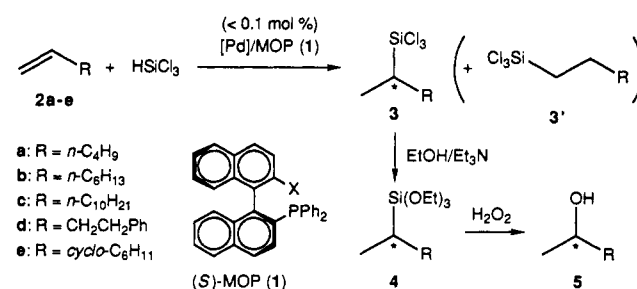
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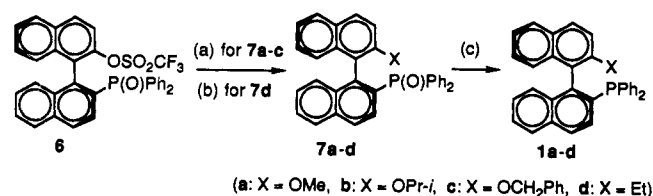
Catalytic asymmetric functionalization of simple prochiral olefins is an important goal in synthetic organic chemistry.^{1,2} We report here the first successful conversion of alkyl-substituted terminal olefins into optically active secondary alcohols (>94% ee),³ which is realized by palladium-catalyzed asymmetric hydrosilylation in the presence of a new chiral monodentate phosphine ligand (MOP, **1**) followed by oxidation of the carbon-silicon bond⁴ (Scheme I).

It is well-documented⁵ that the hydrosilylation of terminal olefins is catalyzed by platinum, rhodium, or nickel complexes to proceed with anti-Markovnikov selectivity leading to 1-silylalkanes. Rather surprisingly, only a little attention has been paid to the use of palladium catalysts for the hydrosilylation of 1-alkenes^{6,7} in spite of their frequent use for the reaction of 1,3-dienes

Scheme I



Scheme II^a



^a(a) (i) 3 N NaOH, 1,4-dioxane, methanol; (ii) MeI, *i*-PrI or PhCH₂Br (3–10 equiv), K₂CO₃ (2–4 molar equiv), acetone, reflux, 3–24 h (**7a**, 99%; **7b**, 92%; **7c**, 87%). (b) EtMgBr (1.1 equiv), NiCl₂(dppe) (2 mol %), Et₂O, reflux, 24 h (**7d**, 81%). (c) Et₃N (7–20 equiv), Cl₃SiH (5 equiv), xylene, 120 °C, 3–5 h (**1a**, 97%; **1b**, 84%; **1c**, 96%; **1d**, 79%).

and styrenes.^{5,6} In order to develop a catalyst possessed of high catalytic activity, high regioselectivity giving 2-silylalkanes, and high enantioselectivity in addition, we examined several types of phosphine-palladium catalysts for the reaction of 1-hexene (**2a**) with trichlorosilane. It was found that palladium complexes coordinated with a chelating bis(phosphine), dppb,⁸ chiraphos,⁹ or BINAP,¹⁰ did not catalyze the hydrosilylation at 80 °C, while the reaction took place at 40 °C with monodentate phosphine ligands.^{11,12} Among the monodentate phosphine ligands, (S)-2-(diphenylphosphino)-2'-methoxy-1,1'-binaphthyl (MOP, **1a**)¹³ turned out to be by far the best ligand, giving a high yield of 2-(trichlorosilyl)hexane (**3a**) with high regioselectivity¹⁴ as well as high enantioselectivity.

Chiral monophosphines (MOPs, **1**) are the ligands we have designed with a view to using them for the catalytic asymmetric reactions where a monophosphine ligand is required to generate a catalytically active species.¹⁵ The present palladium-catalyzed hydrosilylation is one of the cases. The phosphines **1a–d** were readily prepared in high yields starting with known optically active

(8) 1,4-Bis(diphenylphosphino)butane.

(9) (S,S)-2,3-Bis(diphenylphosphino)butane: Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* 1977, 99, 6262.

(10) (R)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl: Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumabayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem.* 1986, 51, 629.

(11) For example, the reaction in the presence of 0.1 mol % of a palladium-triphenylphosphine catalyst (P/Pd = 2/1) at 40 °C for 24 h gave a 12% yield of hexylsilanes consisting of 1- and 2-isomers in a ratio of 91/9, accompanied by isomerization of 1-hexene into internal olefins. See also ref 6.

(12) It is reasonable to expect that a monodentate phosphine ligand generates a palladium catalyst that is more active for the hydrosilylation than a chelating bis(phosphine) ligand. The former can form square-planar palladium(II) intermediate PdH(SiCl₃)L(CH₂=CHR) (L = monophosphine), which offers a coordination site for the activation of olefin.

(13) Preparation of (S)-**1a** from (S)-2'-methoxy-1,1'-binaphthyl-2-carboxylic acid has been reported: Hattori, T.; Shijo, M.; Kumagai, S.; Miyano, S. *Chem. Express* 1991, 6, 335.

(14) The high catalytic activity and regioselectivity of the palladium-MOP complex may be related to the reactivity of key intermediate Pd(2-alkyl)L(silyl). It seems that MOP ligand can accelerate the reductive elimination of 2-silylalkane and/or retard the β-hydrogen elimination forming 2-alkenes. Triphenylphosphine or tri-*o*-tolylphosphine caused the isomerization of a terminal olefin into internal olefins during the hydrosilylation while MOP did not (see footnote 11).

(15) An example for those reactions is nickel-catalyzed asymmetric cross-coupling: Hayashi, T.; Hayashizaki, K.; Kiyoi, T.; Ito, Y. *J. Am. Chem. Soc.* 1988, 110, 8153.

(1) For recent reviews on catalytic asymmetric reactions: (a) Brunner, H. *Synthesis* 1988, 645. (b) Brunner, H. *Top. Stereochem.* 1988, 18, 129. (c) Consiglio, G.; Waymouth, R. M. *Chem. Rev.* 1989, 89, 257. (d) Noyori, R.; Kitamura, M. *Modern Synthetic Methods*; Scheffold, R., Ed.; Springer-Verlag: New York, 1989; Vol. 5, p 115. (e) Ojima, I.; Clos, N.; Bastos, C. *Tetrahedron* 1989, 45, 6901.

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(3) Asymmetric synthesis of 1-arylethanol via palladium-catalyzed hydrosilylation or rhodium-catalyzed hydroboration of vinylarenes has been reported: (a) Hayashi, T.; Tamao, K.; Katsuro, Y.; Nakae, I.; Kumada, M. *Tetrahedron Lett.* 1980, 21, 1871. (b) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* 1989, 111, 3426. (c) Zhang, J.; Lou, B.; Guo, G.; Dai, L. *J. Org. Chem.* 1991, 56, 1670.

(4) (a) Tamao, K.; Ishida, N.; Tanaka, T.; Kumada, M. *Organometallics* 1983, 2, 1694. (b) Tamao, K.; Ishida, N. *J. Organomet. Chem.* 1984, 269, C37. (c) Tamao, K.; Nakajo, E.; Ito, Y. *J. Org. Chem.* 1987, 52, 4412. (d) Tamao, K. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, 1985; p 231.

(5) For reviews: (a) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley: Chichester, 1989; p 1479. (b) Speier, J. L. *Advanced Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1979; Vol. 17, p 407. (c) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. In *Journal of Organometallic Chemistry Library*; Seyferth, D., Davies, A. G., Fisher, E. O., Normant, J. F., Reutov, O. A., Eds.; Elsevier: Amsterdam, 1977; Vol. 5. (d) Ojima, I.; Kogure, T. *Rev. Silicon, Germanium, Tin Lead Compd.* 1981, 5, 7.

(6) It has been reported that reaction of 1-octene with HSiCl₃ catalyzed by Pd(PPh₃)₄ at 100 °C gives 1-octylsilane in 85% yield: Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* 1974, 30, 2143.

(7) Regioselective hydrosilylation of CF₃CH=CH₂ with HSiMeCl₂ or HSiCl₃ catalyzed by PdCl₂(PPh₃)₂ has been reported: Ojima, I.; Yatabe, M.; Fuchikami, T. *J. Organomet. Chem.* 1984, 260, 335.

Table I. Asymmetric Synthesis of 2-Alkanols through Catalytic Asymmetric Hydrosilylation of 1-Alkenes^a

entry	ligand (X in 1)	1-alkene (2)	reactn conditns: temp, °C; time, h	yield ^b of 3, %	ratio ^c of 3/3'	yield ^d of 5, %	% ee ^e (confgn)	[α] _D , deg (solvent) ^f
1	1a (OMe)	<i>n</i> -C ₄ H ₉ CH=CH ₂ (2a)	40; 24	91	89/11	70	94 (R)	-12.3 (c 5.06, EtOH) ^g
2	1a (OMe)	<i>n</i> -C ₆ H ₁₃ CH=CH ₂ (2b)	40; 24	83	93/7	71	95 (R)	
3 ^h	1a (OMe)	<i>n</i> -C ₆ H ₁₃ CH=CH ₂ (2b)	40; 72	97	87/13	70	94 (R)	-10.3 (c 5.59, EtOH) ^g
4 ⁱ	1a (OMe)	<i>n</i> -C ₆ H ₁₃ CH=CH ₂ (2b)	40; 24	97	88/12		91 (R)	
5	1a (OMe)	<i>n</i> -C ₆ H ₁₃ CH=CH ₂ (2b)	60; 16	93	89/11		86 (R)	
6	1b (OPr- <i>i</i>)	<i>n</i> -C ₆ H ₁₃ CH=CH ₂ (2b)	40; 24	88	90/10		91 (R)	
7	1c (OCH ₂ Ph)	<i>n</i> -C ₆ H ₁₃ CH=CH ₂ (2b)	40; 24	85	80/20		95 (R)	
8	1d (Et)	<i>n</i> -C ₆ H ₁₃ CH=CH ₂ (2b)	40; 24	80	90/10		93 (R)	
9	1a (OMe)	<i>n</i> -C ₁₀ H ₂₁ CH=CH ₂ (2c)	40; 72	90	94/6	75	95 (R)	-8.0 (c 8.10, EtOH) ^g
10	1a (OMe)	PhCH ₂ CH ₂ CH=CH ₂ (2d)	40; 24	90	81/19	68	97 (S)	+16.7 (c 2.40, CHCl ₃) ^g
11	1a (OMe)	<i>c</i> -C ₆ H ₁₁ CH=CH ₂ (2e)	40; 24	100	66/34	45 ^j	96 (R)	-7.79 (c 3.10, Et ₂ O) ^{j,k}

^aAll reactions were run without solvent in the presence of palladium catalyst prepared in situ by mixing [PdCl(π-C₃H₅)₂] and ligand (S)-MOP (1). The ratio of 2/HSiCl₃/Pd/1 is 1.0/1.2/0.001/0.002 unless otherwise noted. ^bIsolated yield of a mixture of 3 and 3' by distillation. ^cDetermined by GLC or ¹H NMR analysis of 3 (and 3') or 4 (and 4'). ^dIsolated yield (overall from 2) of regioisomerically pure alcohol 5. ^eDetermined by HPLC analysis of (3,5-dinitrophenyl)carbamate with a chiral column (see text). ^fLiterature rotations for optically pure (S)-5a, (S)-5b, (S)-5c, (S)-5d, and (S)-5e are [α]_D+12.70° (EtOH) (ref 21), [α]_D+9.79° (EtOH) (ref 21), [α]_D+7.94° (EtOH) (ref 21), [α]_D+17.2° (chloroform) (Pikard, R. H.; Kenyon, J. J. *Chem. Soc.* 1914, 105, 1115), and [α]_D+8.43° (Et₂O) (Levene, P. A.; Mikeska, L. A. *J. Biol. Chem.* 1927, 75, 587), respectively. ^gRotation at 25 °C. ^hReaction with 0.01 mol % of the catalyst. ⁱRatio of P/Pd is 1/1. ^jContaminated with 5% of 2-cyclohexylethanol. ^kRotation at 20 °C.

phosphinylbinaphthyl 6¹⁶ by a sequence of reactions shown in Scheme II.^{13,17}

The results obtained for the asymmetric synthesis of 2-alkanols 5 through the hydrosilylation of 1-alkenes 2 are summarized in Table I. All the olefins 2a-e were transformed efficiently into the corresponding optically active alcohols 5 with enantioselectivity ranging between 94% and 97% ee (entries 1, 2, and 9-11) by the catalytic hydrosilylation-oxidation procedure, the selectivity being highest for the enantioface selection of simple terminal olefins.¹ The regioselectivity forming 2-(silyl)alkanes is surprisingly high^{18,19} for the terminal olefins 5a-d substituted with a primary alkyl group. Lower regioselectivity was observed with vinylcyclohexane (2e), which is substituted with a sterically bulky group on the double bond (entry 11). Ligands 1b-d gave almost the same results as 1a, indicating that the substituents at the 2'-position on ligand 1 did not have significant effects on the catalytic activity or the selectivity (entries 6-8). It should be noted that the palladium-MOP complex is highly catalytically active, the hydrosilylation taking place with 0.01 mol % of the catalyst (entry 3).

A practical procedure is given for the reaction of 1-octene (2b) (entry 3). A mixture of 2b (2.81 g, 25 mmol), trichlorosilane (4.06 g, 30 mmol), [PdCl(π-C₃H₅)₂] (0.46 mg, 0.0013 mmol, 0.01 mol % Pd), and (S)-(-)-MOP-OMe (1a, 2.34 mg, 0.005 mmol, 0.02 mol %) was kept stirred at 40 °C for 72 h. The reaction mixture was distilled (bulb-to-bulb) under reduced pressure to give 6.20 g (97% yield) of (trichlorosilyl)octane consisting of 2-silyl and 1-silyl isomers (3b and 3'b, respectively) in a ratio of 87/13, which was converted quantitatively into (triethoxysilyl)octane 4b (contaminated with regioisomer 4'b) by treatment with ethanol (5 mL) and triethylamine (10 mL) in ether (600 mL). Oxidation of the triethoxysilane (H₂O₂/KF/KHCO₃/MeOH/THF) according to the procedure reported by Tamao⁴ followed by removal of a small amount of 1-octanol resulting from 3'b by the preferential complexation with calcium chloride²⁰ gave 2.28 g (70% from 2b) of isomerically pure (R)-2-octanol (5b)²¹ ([α]_D²⁵-10.3° (c 5.59, ethanol)). HPLC analysis of the (3,5-dinitrophenyl)carbamate

of 5b (ArNCO/pyridine/toluene) using a chiral stationary phase column (Sumichiral OA-1100, hexane/dichloroethane/ethanol = 100/20/1) demonstrated the enantiomeric purity to be 94%.

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Supplementary Material Available: Experimental details for the preparation of MOPs 1 and their analytical and spectroscopic data (3 pages). Ordering information is given on any current masthead page.

A Highly Stereoselective Olefination of Aldehydes Using New Zinc and Zirconium 1,1-Bimetallic Reagents

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The olefination of carbonyl derivatives by transition metal alkylidene complexes has been one of the most important applications of transition metal chemistry oriented toward organic synthesis.¹ One of the major drawbacks of this methodology has been the extension of the useful reactivity of the methylene transfer reagent Cl(Cp)₂TiCH₂AlMe₂^{1a-i} to more substituted heterobimetallics. We wish to report a general solution to this problem using new substituted and highly functionalized zinc and zirconium

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(17) (S)-1a: [α]_D²⁰-94.5° (c 0.27, chloroform), [α]_D¹⁶-59.7° (c 1.40, benzene) (ref 13); [α]_D¹⁶-59.3° (c 1.0, benzene). (S)-1b: [α]_D²⁰-90.0° (c 0.13, chloroform). (S)-1c: [α]_D²⁰-96.1° (c 0.12, chloroform). (S)-1d: [α]_D²⁰-85.1° (c 0.20, chloroform). Satisfactory spectral and elemental (±0.3% C, H) or MS analytical data were obtained for all compounds listed in Scheme II.

(18) The predominant formation of 2-alkylsilanes from aliphatic 1-olefins has never been observed with any transition-metal catalysts (ref 5).

(19) 3-Alkylsilanes, which would be produced by the hydrosilylation of internal olefins formed by isomerization, were not detected.

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