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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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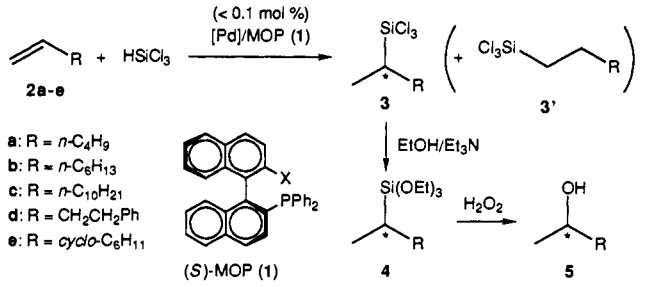
Catalytic asymmetric functionalization of simple prochiral olefins is an important goal in synthetic organic chemistry.[1,2] We report here the first successful conversion of alkyl-substituted terminal olefins into optically active secondary alcohols (>94% ee),[3] which is realized by palladium-catalyzed asymmetric hydrosilylation in the presence of a new chiral monodentate phosphine ligand (MOP, **1**) followed by oxidation of the carbon–silicon bond[4] (Scheme I).

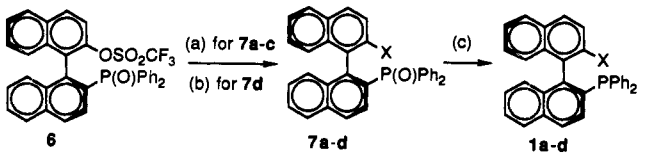
It is well-documented[5] that the hydrosilylation of terminal olefins is catalyzed by platinum, rhodium, or nickel complexes to proceed with anti-Markovnikoff selectivity leading to 1-silylalkanes. Rather surprisingly, only a little attention has been paid to the use of palladium catalysts for the hydrosilylation of 1-alkenes[6,7] in spite of their frequent use for the reaction of 1,3-dienes 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 regioselectivity[14] 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

Scheme I



Scheme II[a]



(a: X = OMe, b: X = OPr-*i*, c: X = OCH_2Ph, d: X = Et)

[a](a) (i) 3 N NaOH, 1,4-dioxane, methanol; (ii) MeI, *i*-PrI or $PhCH_2Br$ (3–10 equiv), K_2CO_3 (2–4 molar equiv), acetone, reflux, 3–24 h (**7a**, 99%; **7b**, 92%; **7c**, 87%). (b) EtMgBr (1.1 equiv), $NiCl_2$(dppe) (2 mol %), Et_2O, reflux, 24 h (**7d**, 81%). (c) Et_3N (7–20 equiv), Cl_3SiH (5 equiv), xylene, 120 °C, 3–5 h (**1a**, 97%; **1b**, 84%; **1c**, 96%; **1d**, 79%).

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(6) It has been reported that reaction of 1-octene with $HSiCl_3$ catalyzed by $Pd(PPh_3)_4$ at 100 °C gives 1-octylsilane in 85% yield: Tsuji, J.; Hara, M.; Ohno, K. *Tetrahedron* **1974**, *30*, 2143.

(7) Regioselective hydrosilylation of $CF_3CH{=}CH_2$ with $HSiMeCl_2$ or $HSiCl_3$ catalyzed by $PdCl_2(PPh_3)_2$ has been reported: Ojima, I.; Yatabe, M.; Fuchikami, T. *J. Organomet. Chem.* **1984**, *260*, 335.

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(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.; Kumobayashi, 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 $PdH(SiCl_3)L(CH_2{=}CHR)$ (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.

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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] (config)	$[\alpha]_D$, deg (solvent)[f]
1	**1a** (OMe)	n-$C_4H_9CH{=}CH_2$ (**2a**)	40; 24	91	89/11	70	94 (*R*)	−12.3 (*c* 5.06, EtOH)[g]
2	**1a** (OMe)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 24	83	93/7	71	95 (*R*)	
3[h]	**1a** (OMe)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 72	97	87/13	70	94 (*R*)	−10.3 (*c* 5.59, EtOH)[g]
4[i]	**1a** (OMe)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 24	97	88/12		91 (*R*)	
5	**1a** (OMe)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	60; 16	93	89/11		86 (*R*)	
6	**1b** (OPr-*i*)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 24	88	90/10		91 (*R*)	
7	**1c** (OCH_2Ph)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 24	85	80/20		95 (*R*)	
8	**1d** (Et)	n-$C_6H_{13}CH{=}CH_2$ (**2b**)	40; 24	80	90/10		93 (*R*)	
9	**1a** (OMe)	n-$C_{10}H_{21}CH{=}CH_2$ (**2c**)	40; 72	90	94/6	75	95 (*R*)	−8.0 (*c* 8.10, EtOH)[g]
10	**1a** (OMe)	$PhCH_2CH_2CH{=}CH_2$ (**2d**)	40; 24	90	81/19	68	97 (*S*)	+16.7 (*c* 2.40, $CHCl_3$)[g]
11	**1a** (OMe)	c-$C_6H_{11}CH{=}CH_2$ (**2e**)	40; 24	100	66/34	45[j]	96 (*R*)	−7.79 (*c* 3.10, Et_2O)[j,k]

[a] All reactions were run without solvent in the presence of palladium catalyst prepared in situ by mixing $[PdCl(\pi\text{-}C_3H_5)]_2$ and ligand (*S*)-MOP (**1**). The ratio of $2/HSiCl_3/Pd/1$ is 1.0/1.2/0.001/0.002 unless otherwise noted. [b] Isolated yield of a mixture of **3** and **3′** by distillation. [c] Determined by GLC or ^1H NMR analysis of **3** (and **3′**) or **4** (and **4′**). [d] Isolated yield (overall from **2**) of regioisomerically pure alcohol **5**. [e] Determined by HPLC analysis of (3,5-dinitrophenyl)carbamate with a chiral column (see text). [f] Literature rotations for optically pure (*S*)-**5a**, (*S*)-**5b**, (*S*)-**5c**, (*S*)-**5d**, and (*S*)-**5e** are $[\alpha]_D$ +12.70° (EtOH) (ref 21), $[\alpha]_D$ +9.79° (EtOH) (ref 21), $[\alpha]_D$ +7.94° (EtOH) (ref 21), $[\alpha]_D$ +17.2° (chloroform) (Pikard, R. H.; Kenyon, J. *J. Chem. Soc.* **1914**, *105*, 1115), and $[\alpha]_D$ +8.43° (Et_2O) (Levene, P. A.; Mikeska, L. A. *J. Biol. Chem.* **1927**, *75*, 587), respectively. [g] Rotation at 25 °C. [h] Reaction with 0.01 mol % of the catalyst. [i] Ratio of P/Pd is 1/1. [j] Contaminated with 5% of 2-cyclohexylethanol. [k] Rotation at 20 °C.

phosphinylbinaphthyl **6**[16] 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), $[PdCl(\pi\text{-}C_3H_5)]_2$ (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 ($H_2O_2/KF/KHCO_3/MeOH/THF$) according to the procedure reported by Tamao[4] followed by removal of a small amount of 1-octanol resulting from **3′b** by the preferential complexation with calcium chloride[20] gave 2.28 g (70% from **2b**) of isomerically pure (*R*)-2-octanol (**5b**)[21] ($[\alpha]^{25}_D$ −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.

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

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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 $Cl(Cp)_2TiCH_2AlMe_2$[1a-i] to more substituted heterobimetallics. We wish to report a general solution to this problem using new *substituted and highly functionalized* zinc and zirco-

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