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Catalytic Asymmetric Hydrosilylation of 1,3-Dienes with New Chiral Ferrocenylphosphine-Palladium Complexes

Tamio Hayashi* and Yonetatsu Matsumoto

Catalysis Research Center and Graduate School of Pharmaceutical Sciences, Hokkaido University, Kitaku, Sapporo 060, Japan

Ikutaro Morikawa and Yoshihiko Ito*

Department of Synthetic Chemistry, Kyoto University, Yoshida, Kyoto 606, Japan

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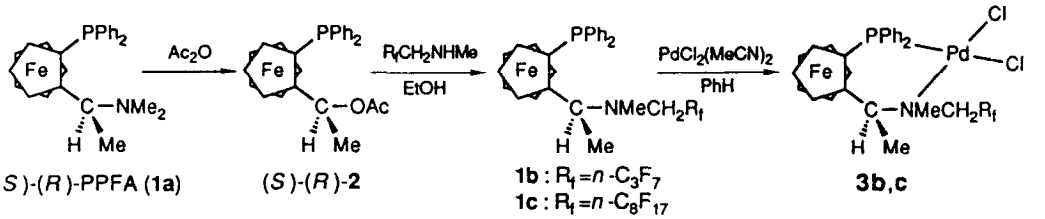
Abstract: A palladium catalyst coordinated with optically active ferrocenylmonophosphine ligand containing perfluoroalkyl group on the aminoethyl side chain was found to be highly catalytically active and stereoselective for the asymmetric hydrosilylation of several types of conjugated dienes with trichlorosilane to give optically active allylsilanes of over 60% ee.

We have previously reported the asymmetric hydrosilylation of conjugated dienes catalyzed by chiral ferrocenylphosphine-palladium complex $PdCl_2$[(*S*)-(*R*)-PPFA (**1a**)], where (*S*)-(*R*)-PPFA stands for (*S*)-*N*,*N*-dimethyl-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethylamine.[1,2] The chiral palladium catalyst was fairly effective for the hydrosilylation of 1-arylbutadienes with trichlorosilane producing optically active allylsilanes, (*Z*)-1-aryl-1-silyl-2-butenes and (*E*)-1-aryl-3-silyl-1-butenes, of up to 63% ee,[1] but was not so effective for the hydrosilylation of other types of dienes such as cyclopentadiene.[2] The inefficiency of the PPFA/Pd catalyst is due mainly to its low catalytic activity at a low reaction temperature, which may result from low solubility of the palladium catalyst in the reaction mixture consisting of a diene and trichlorosilane. Here we report the preparation of new chiral ferrocenylphosphine ligands containing perfluoroalkyl groups on the side chain, whose palladium complexes are highly soluble in the reactants and catalytically active for asymmetric hydrosilylation of several types of conjugated dienes under mild conditions producing optically active allylsilanes with high stereoselectivity.

N-Methylperfluoroalkylmethylamines ($HNMeCH_2Rf$: Rf = n-C_3F_7 or n-C_8F_{17})[3] were introduced on the side chain of ferrocenylmonophosphine by treatment of an excess of the amine with acetate (*S*)-(*R*)-2[4] in refluxing ethanol (Scheme 1). Optically active ferrocenylphosphines (*S*)-(*R*)-**1b** ($[\alpha]^{20}_D$ +249° (*c* 0.6, chloroform))[5] and (*S*)-(*R*)-**1c** ($[\alpha]^{20}_D$ +221° (*c* 0.5, chloroform))[5] obtained in around 70% yields were converted into palladium complexes **3b** and **3c** by the reaction with $PdCl_2(MeCN)_2$ in benzene.

Scheme 1



(*S*)-(*R*)-PPFA (**1a**) (*S*)-(*R*)-**2** **1b** : R_f = n-C_3F_7 **1c** : R_f = n-C_8F_{17} **3b,c**

Palladium complexes **3** were examined for catalytic activity and stereoselectivity in the hydrosilylation of cyclopentadiene with trichlorosilane (Scheme 2). The results are summarized in Table 1. Palladium complex **3b** which contains C_3F_7 group on the aminoalkyl side chain was found to be catalytically active at 25 °C to give 73% yield of 3-(trichlorosilyl)cyclopentene (**4**), whose optical purity was determined to be 57% by converting into known (*R*)-3-(trimethylsilyl)cyclopentene (**6**) ($[\alpha]^{20}_D$ +112° (*c* 1.1, benzene))[2,6] by way of (*R*)-3-(triethoxysilyl)cyclopentene (**5**) ($[\alpha]^{20}_D$ +43° (*c* 1.0, benzene)) (entry 2). The enantiomeric purity was confirmed (56.5% ee) by HPLC analysis of cyclopentanol derivative **7** with a chiral stationary phase column (Sumipax OA-2000, hexane/dichloroethane/ethanol = 250/20/1). At higher temperature the stereoselectivity was lowered (entry 1). Similar catalytic activity and stereoselectivity were observed with the palladium catalyst **3c** which has longer perfluoroalkyl group on the side chain (entries 4 and 5). On the other hand, **3a** which lacks the perfluoroalkyl group was completely inactive for the hydrosilylation with trichlorosilane under the standard conditions (entry 6), though it catalyzed the reaction with methyldichlorosilane giving 3-(methyldichlorosilyl)cyclopentene of lower enantiomeric purity (<25% ee).[2] The high catalytic activity observed with the perfluoroalkyl ligands is due, at least in part, to high solubility of the palladium catalysts **3b** and **3c** in the reactants at a low temperature.

Scheme 2

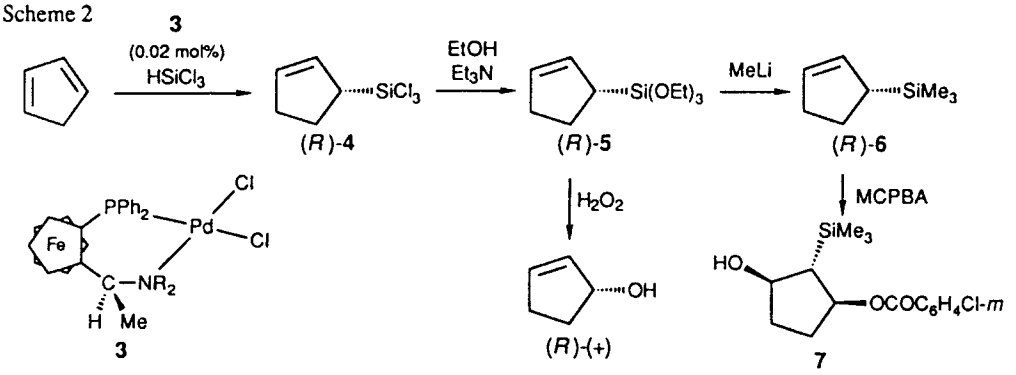


Table 1. Asymmetric Hydrosilylation of Cyclopentadiene with Trichlorosilane Catalyzed by Chiral Ferrocenylphosphine-Palladium Complexes **3**.[a]

entry	catalyst NR_2 in **3**	reaction conditions temp (°C)	time (h)	yield[b](%) of **4**	$[\alpha]^{20}_D$[c] of **5**	% op (config)
1	$NMeCH_2C_3F_7$ (**3b**)	80	20	73	+17°	22 (*R*)
2	$NMeCH_2C_3F_7$ (**3b**)	25	90	73	+43°	57 (*R*)
3	$NMeCH_2C_3F_7$ (**3b**)	0	20	7	+45°	60 (*R*)
4	$NMeCH_2C_8F_{17}$ (**3c**)	50	40	61	+33°	43 (*R*)
5	$NMeCH_2C_8F_{17}$ (**3c**)	25	90	41	+42°	55 (*R*)
6	NMe_2 (**3a**)	25	90	0	—	—

[a] A mixture of palladium catalyst **3** (0.0025 mmol), cyclopentadiene (16 mmol), and trichlorosilane (20 mmol) was kept at a given temperature in a sealed degassed glass tube. [b] Isolated yield by distillation. [c] (*c* 0.9-1.1, benzene).

The palladium complexes **3b** and **3c** were also effective for the asymmetric hydrosilylation of other types of conjugated dienes (Scheme 3). The results summarized in Table 2 show that all of 1-alkylbutadienes **8a-d** underwent the hydrosilylation with trichlorosilane at 30 or 50 °C to produce (*Z*)-2-butenylsilanes **9** substituted with alkyl groups at 1-position with high regio- and stereoselectivity. It should be noted that the reactions with $PdCl_2(PPh_3)_2$ as catalyst were much less regioselective. The regio- and stereochemical results may be illustrated by the catalytic cycle where a key intermediate is π-allylpalladium complex **14** substituted with *anti*-methyl and *syn*-alkyl groups, which is formed by regioselective hydropalladation of diene **8** in a *cisoid* conformation. The optically active allyl(trichloro)silanes **9**[7] were converted into optically active allyl alcohols **13** by oxidation of the carbon-silicon bond in allyl(triethoxy)silanes **12**[8,9] according to the procedure reported by Tamao.[10] The enantiomeric purities of the allyl alcohols were over 50% for **13a**, **13c**, and **13d**.

Scheme 3

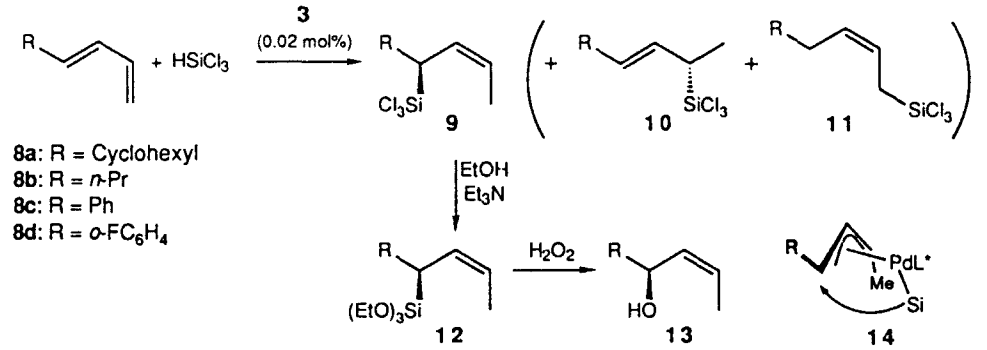


Table 2. Asymmetric Hydrosilylation of Dienes **8** with Trichlorosilane Catalyzed by Chiral Ferrocenylphosphine-Palladium Complexes **3b** or **3c**.[a]

diene R	catalyst	reaction conditions temp (°C)	time (h)	yield[b](%) of **9,10,11**	ratio[c] **9/10/11**	$[\alpha]^{20}_D$[d] of **12**	% ee[e]
cyclohexyl (**8a**)	**3b**	50	140	92	92/1/7	+3.82°	52[f]
cyclohexyl (**8a**)	$PdCl_2(PPh_3)_2$	80	120	92	77/5/18	—	—
n-propyl (**8b**)	**3b**	50	60	97	92/2/6	+10.5°	37[g,h]
phenyl (**8c**)	**3b**	30	90	91	93/7/0	−57.4°	63[i] (*R*)
phenyl (**8c**)	**3c**	80	20	64	81/19/0	−60.5°	66 (*R*)
phenyl (**8c**)	**3c**	30	90	94	91/9/0	−58.0°	63 (*R*)
o-FC_6H_4 (**8d**)	**3c**	50	90	78	91/9/0	−45.3°	56[j]
o-FC_6H_4 (**8d**)	$PdCl_2(PPh_3)_2$	80	90	64	74/26/0	—	—

[a] See footnote *a* in Table 1. [b] Isolated yield by distillation. [c] Determined by GLC analysis. [d] (*c* 0.9-1.2, benzene). [e] Determined by HPLC analysis of carbamates, obtained by the reaction of alcohols **13** with 3,5-dinitrophenyl isocyanate, with chiral stationary phase column OA-4100 or OA-4000. [f] **13a**: $[\alpha]^{20}_D$ +8.7° (*c* 1.1, benzene). [g] **13b**: $[\alpha]^{20}_D$ −6.3° (*c* 3.3, chloroform). [h] Determined by ^1H NMR analysis of alcohol **13b** in the presence of Eu(dcm)$_3$. [i] **13c**: $[\alpha]^{20}_D$ −137° (*c* 1.3, chloroform) [j] **13d**: $[\alpha]^{20}_D$ −149° (*c* 1.0, benzene).

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1 Hayashi, T.; Kabeta, K.; *Tetrahedron Lett.* **1985**, *26*, 3023.

2 Hayashi, T.; Kabeta, K.; Yamamoto, T.; Tamao, K.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*, 5661.

3 The *N*-methylperfluoroalkylmethylamines ($HNMeCH_2Rf$) were prepared starting with perfluoroalkanecarboxylic acids (RfCOOH) by amidation with methylamine ($MeNH_2$/MeOH/THF) followed by LAH reduction ($LiAlH_4/Et_2O$). ^1H NMR ($CDCl_3$) for $HNMeCH_2(n\text{-}C_3F_7)$: δ 1.46 (bs, 1 H), 2.57 (s, 3 H), 3.23 (t, J = 17 Hz, 2 H). ^1H NMR ($CDCl_3$) for $HNMeCH_2(n\text{-}C_8F_{17})$: δ 1.41 (bs, 1 H), 2.58 (s, 3 H), 3.24 (t, J = 16 Hz, 2 H).

4 (a) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, N.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138. (b) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* **1982**, *15*, 395, and references cited therein.

5 ^1H NMR ($CDCl_3$) for **1b**: d 1.46 (d, J = 6.8 Hz, 3 H), 1.96 (s, 3 H), 2.55 (bq, J = 17.1 Hz, 1 H), 3.04 (bq, J = 17.1 Hz, 1 H), 3.85-3.92 (m, 1 H), 3.95 (s, 5 H), 4.15-4.35 (m, 2 H), 4.38-4.45 (m, 1 H), 7.1-7.25, 7.3-7.43, 7.5-7.65 (m, 10 H). ^1H NMR ($CDCl_3$) for **1c**: d 1.46 (d, J = 6.8 Hz, 3 H), 1.96 (s, 3 H), 2.55 (bq, J = 17.1 Hz, 1 H), 3.05 (bq, J = 17.1 Hz, 1 H), 3.84-3.90 (m, 1 H), 3.95 (s, 5 H), 4.2-4.35 (m, 2 H), 4.39-4.45 (m, 1 H), 7.1-7.25, 7.33-7.43, 7.5-7.65 (m, 10 H).

6 The maximum rotation of (*R*)-(+)-**6** is calculated to be $[\alpha]^{20}_D$ 199° (*c* 0.9-1.1, benzene).

7 ^1H NMR (δ/$CDCl_3$). **9a**: 1.0-1.4 (m, 6 H), 1.65 (dd, J = 6.9, 1.8 Hz, 3 H), 1.6-2.0 (m, 5 H), 2.57 (dd, J = 11.5, 4.9 Hz, 1 H), 5.35 (ddq, J = 11.5, 10.8, 1.8 Hz, 1 H), 5.81 (dq, J = 10.8, 6.9 Hz, 1 H). **9b**: 0.91 (t, J = 7.1 Hz, 3 H), 1.1-1.9 (m, 4 H), 1.66 (dd, J = 6.8, 1.8 Hz, 3 H), 2.56 (td, J = 10.8, 2.8, 1 H), 5.16 (tq, J = 10.8, 1.8 Hz, 1 H), 5.76 (dq, J = 10.8, 6.8 Hz, 1 H). **9d**: 1.76 (d, J = 5.0 Hz, 3 H), 4.38 (d, J = 9.8 Hz, 1 H), 5.7-5.9 (m, 2 H), 6.9-7.5 (m, 4 H).

8 ^1H NMR (δ/$CDCl_3$). **12a**: 0.9-1.3 (m, 4 H), 1.21 (t, J = 7.0 Hz, 9 H), 1.4-1.9 (m, 7 H), 1.59 (dd, J = 6.2, 1.6 Hz, 3 H), 1.96 (dd, J = 10.9, 5.7 Hz, 1 H), 3.82 (q, J = 7.0 Hz, 6 H), 5.38 (tq, J = 10.9, 1.6 Hz, 1 H), 5.50 (dq, J = 10.9, 6.2 Hz, 1 H). **12b**: 0.86 (t, J = 7.0 Hz, 3 H), 1.0-1.6 (m, 4 H), 1.22 (t, J = 6.9 Hz, 9 H), 1.61 (dd, J = 6.6, 1.8 Hz, 3 H), 2.02 (ddd, J = 10.8, 10.6, 2.8 Hz, 1 H), 3.83 (q, J = 6.9 Hz, 6 H), 5.24 (tq, J = 10.8, 1.8 Hz, 1 H), 5.47 (dq, J = 10.8, 6.6 Hz, 1 H). **12d**: 1.15 (t, J = 7.0 Hz, 9 H), 1.70 (dd, J = 6.7, 1.7 Hz, 3 H), 3.76 (q, J = 7.0 Hz, 6 H), 3.80 (d, J = 10.7 Hz, 1 H), 5.52 (dq, J = 10.7, 6.7 Hz, 1 H), 5.77 (ddq, J = 10.7, 10.0, 1.7 Hz, 1 H), 6.9-7.2 (m, 3 H), 7.3-7.5 (m, 1 H).

9 Optically active allyl(triethoxy)silane **12c** has been used for stereochemical studies in the reaction of allylsiliconates with aldehyde: Hayashi, T.; Matsumoto, Y.; Kiyoi, T.; Ito, Y.; Kohra, S.; Tominaga, Y.; Hosomi, A. *Tetrahedron Lett.* **1988**, *29*, 5667.

10 Tamao, K.; Nakajo, E.; Ito, Y. *J. Org. Chem.* **1987**, *52*, 4412, and references cited therein.