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Catalytic Asymmetric Hydrosilylation of Ketones with New Chiral Ferrocenylphosphine-Imine Ligands

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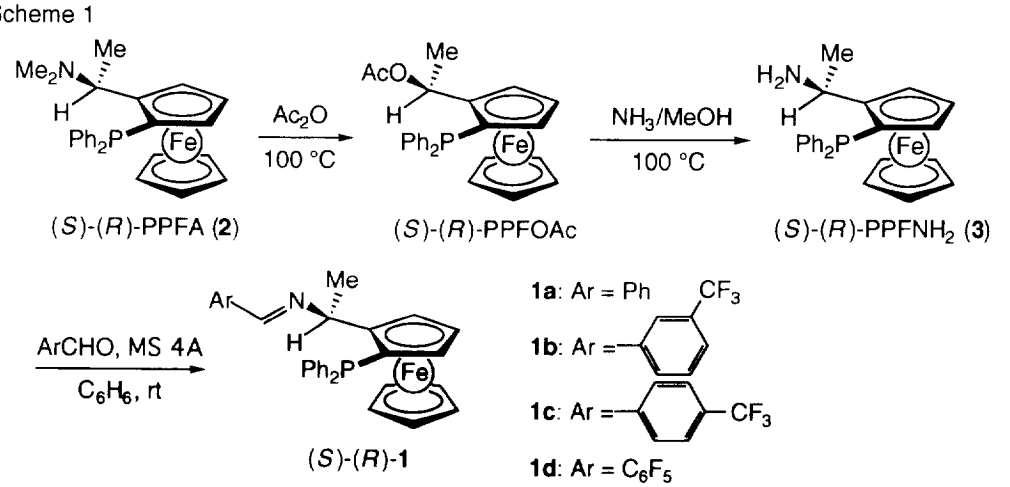
Abstract: New chiral ferrocenylphosphines containing an imino group on the side chain, (*S*)-*N*-alkylidene-1-[(*R*)-2-diphenylphosphinoferrocenyl]ethylamines, were prepared by condensation of (*S*)-1-[(*R*)-2-diphenylphosphinoferrocenyl]ethylamine with aromatic aldehydes. The imino-phosphine ligands were found to be very effective for rhodium-catalyzed asymmetric hydrosilylation of prochiral ketones with diphenylsilane to give optically active alcohols of up to 90% ee.

We have developed homochiral ferrocenylphosphines[1] which are effective as ligands for several types of asymmetric reactions catalyzed by transition metal complexes.[2] The ferrocenylphosphines have been demonstrated to be superior to others in that both monophosphines and 1,1'-bisphosphines can be readily prepared and structural modification can be readily made by introduction of a desired functional group on the side chain according to the demand of the reaction type. By this modification, the ferrocenylphosphines can bring about high enantioselectivity in a variety of catalytic asymmetric reactions, including rhodium(I)-catalyzed hydrogenation,[3] palladium(0)-catalyzed allylic substitution reactions,[4,5] and gold(I)- or silver(I)-catalyzed aldol-type reactions of isocyanocarboxylates.[6,7,8] Here we report that high enantioselectivity can be attained in the rhodium-catalyzed asymmetric hydrosilylation of ketones by use of new ferrocenylmonophosphines where an imino group was introduced on the ferrocenylmethyl position.

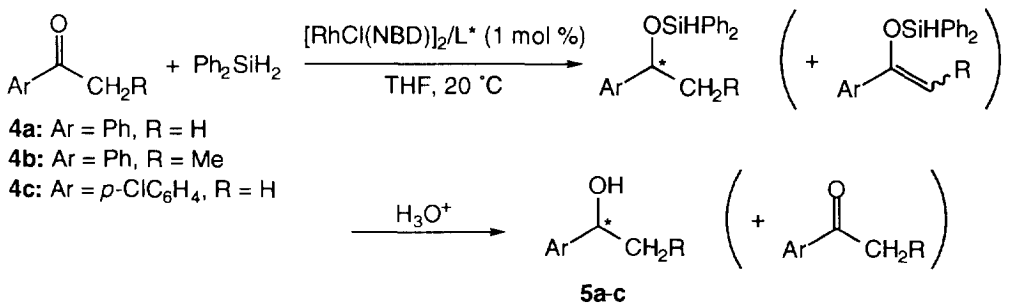
Scheme 1



Dedicated to the memory of Professor Hidemasa Takaya, deceased on 5 October 1995

A new ferrocenylmonophosphine, (*S*)-*N*-benzylidene-1-[(*R*)-2-diphenylphosphinoferrocenyl]ethylamine [(*S*)-(*R*)-**1a**] was prepared starting with (*S*)-(*R*)-PPFA **2** by a sequence of reactions shown in Scheme 1. The replacement of the dimethylamino group on (*S*)-(*R*)-PPFA **2** by an acetoxy group giving (*S*)-(*R*)-PPFOAc was previously reported to be effected by treatment with acetic anhydride at 100 °C.[1] The acetoxy group was substituted with an amino group by the reaction with a large excess of ammonia in methanol in an autoclave at 100 °C to give 80% yield of (*S*)-(*R*)-PPFNH$_2$ **3**.[9] The nucleophilic substitution reactions on the ferrocenylmethyl position are known to proceed with retention of configuration on the stereogenic carbon center.[1] Treatment of (*S*)-(*R*)-PPFNH$_2$ **3** with benzaldehyde in benzene in the presence of molecular sieves 4A at room temperature gave 85% yield of imine (*S*)-(*R*)-**1a**, which contains diphenylphosphino group and an imino group on the same cyclopentadienyl ring. A chelate coordination to a metal is expected with the phosphorus atom and the imino nitrogen. The condensation of amine **3** with 3-trifluormethylbenzaldehyde, 4-trifluormethylbenzaldehyde, and pentafluorobenzaldehyde, in a similar manner gave the corresponding imino-phosphines, (*S*)-(*R*)-**1b**, -**1c**, and -**1d**, respectively.[9]

Scheme 2



The ferrocenylphosphine-imine ligands prepared here were examined for their enantioselectivity in the rhodium-catalyzed asymmetric hydrosilylation of prochiral ketones with diphenylsilane[10] (Scheme 2). The results are summarized in Table 1, which also contains data obtained with some other chiral ferrocenylphosphine ligands. The imino-phosphine (*S*)-(*R*)-**1a** was found to be an effective chiral ligand for the hydrosilylation of acetophenone. Thus, to a catalyst (1 mol %) solution generated by mixing (*S*)-(*R*)-**1a** with [RhCl(NBD)]$_2$ (P/Rh = 1.5/1.0) in THF was added successively acetophenone **4a** and diphenylsilane at 20 °C. It was found by a GLC analysis that all of the ketone was consumed in 1 h. Hydrolysis of the reaction mixture with dilute hydrochloric acid in methanol gave 90% yield of (*S*)-1-phenylethanol **5a**, whose enantiomeric purity was determined to be 87% ee by an HPLC analysis with a chiral stationary phase column (entry 1). The reaction of propiophenone **4b** also took place in the presence of (*S*)-(*R*)-**1a**-rhodium catalyst to give (*S*)-1-phenylpropanol **5b** of 86% ee (entry 2). A slightly higher enantioselectivity was observed in the reaction with the imino-phosphine ligands, **1b**, **1c**, and **1d**, which were derived from aldehydes containing electron-withdrawing groups on the phenyl ring. The hydrosilylation was faster with those ligands (entries 3-5). Thus, the reaction of **4a** was completed in 10 min with the imine ligand (*S*)-(*R*)-**1b**, which has 3-trifluoromethyl group on the phenyl, to give (*S*)-1-phenylethanol of 90% ee. The importance of imino group on the asymmetric hydrosilylation is demonstrated by the reaction with (*S*)-(*R*)-PPFA[11] **2** or (*S*)-(*R*)-PPFNH$_2$ **3** ligand, which gave 1-phenylethanol **5a** with opposite configuration (*R*) in much lower enantioselectivity (entries 7-8). It is

Table 1. Asymmetric Hydrosilylation of Ketones **4** with Ferrocenylphosphine-Rhodium Catalysts[a]

entry	ketone **4**	ligand	reaction[b] time	ratio[c] of **5**/**4**	yield (%)[d] of alcohol **5**	% ee[e] (config)
1	PhCOMe (**4a**)	(*S*)-(*R*)-**1a** (Ar = Ph)	<1 h	>98/2	90	87 (*S*)
2	PhCOEt (**4b**)	(*S*)-(*R*)-**1a** (Ar = Ph)	<1 h	>98/2	97	86 (*S*)
3	PhCOMe (**4a**)	(*S*)-(*R*)-**1b** (Ar = *m*-$CF_3C_6H_4$)	<10 min	>98/2	90	90 (*S*)
4	PhCOMe (**4a**)	(*S*)-(*R*)-**1c** (Ar = *p*-$CF_3C_6H_4$)	<10 min	>98/2	94	89 (*S*)
5	PhCOMe (**4a**)	(*S*)-(*R*)-**1d** (Ar = C_6F_5)	<10 min	>97/3	86	89 (*S*)
6	*p*-ClC_6H_4COMe (**4c**)	(*S*)-(*R*)-**1b** (Ar = *m*-$CF_3C_6H_4$)	<1 h	>98/2	90	81 (*S*)
7	PhCOMe (**4a**)	(*S*)-(*R*)-PPFA (**2**)	<1 h	74/26	64	16 (*R*)
8	PhCOMe (**4a**)	(*S*)-(*R*)-PPF-NH_2 (**3**)	2 h	55/45	50	39 (*R*)

[a] The reaction was carried out in THF in the presence of 1 mol % of the rhodium catalyst at 20 °C under nitrogen: THF (2.0 mL), ketone (2.0 mmol), diphenylsilane (2.5 mmol), $[RhCl(NBD)]_2$ (0.01 mmol), ligand (0.03 mmol). [b] The reaction time in which all of the ketone was consumed. [c] The ratio of alcohol/ketone determined by ^1H NMR of the products after hydrolysis. [d] Isolated yield by distillation. [e] Determined by HPLC analysis of (3,5-dinitrophenyl)carbamates of the alcohols with Sumichiral OA-4700 for **5a,c** and with Sumichiral OA-4100 for **5b** (*n*-hexane/1,2-dichloroethane/alcohol = 50/15/1).

interesting that formation of a considerable amount of silyl enol ether, which gives the starting ketone by the acidic hydrolysis, was observed with these ligands lacking the imino group.

As described above, the ferrocenylphosphine-imines **1** are effective as chiral ligands for the rhodium-catalyzed asymmetric hydrosilylation of ketones. Further investigation is in progress to design more stereoselective ferrocenylphosphine ligands.

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9 ^{1}H (270 MHz, $CDCl_3$) and ^{31}P NMR (109 MHz, $CDCl_3$) spectra and specific rotations for (*S*)-(*R*)-PPFNH$_2$ (**3**) and imino-phosphines (*S*)-(*R*)-**1** are as follows: **3:** ^{1}H NMR δ 1.44 (d, J = 6.9 Hz, 3 H), 1.44 (br s, 2 H), 3.77 (br s, 1 H), 4.02 (s, 5 H), 4.21 (dq, *J* = 2.3, 6.9 Hz, 1 H), 4.28 (t, *J* = 2.3 Hz, 1 H), 4.43 (br s, 1 H), 7.25-7.57 (m, 10 H). ^{31}P NMR δ –23.7. $[\alpha]_D^{20}$ +296 (*c* 0.51, C_6H_6). **1a** ^{1}H NMR δ 1.65 (t, *J* = 6.6 Hz, 3 H), 3.75 (br s, 1 H), 4.07 (s, 5 H), 4.33 (t, *J* = 2.3 Hz, 1 H), 4.67 (br s, 1 H), 4.80 (dq, *J* = 2.3, 6.6 Hz, 1 H), 6.73-7.54 (m, 15 H), 8.00 (s, 1 H). ^{31}P NMR δ -23.1. $[\alpha]_D^{20}$ +387 (*c* 0.50, C_6H_6). **1b:** ^{1}H NMR δ 1.65 (t, *J* = 6.6 Hz, 3 H), 3.75 (br s,1 H), 4.08 (s, 5 H), 4.35 (t, *J* = 2.3 Hz, 1 H), 4.68 (br s, 1 H), 4.85 (dq, *J* = 2.3, 6.6 Hz, 1 H), 6.67-7.57 (m, 14 H), 8.02 (s, 1 H). ^{31}P NMR δ -23.7. $[\alpha]_D^{20}$ +372 (*c* 0.50, C_6H_6). **1c** ^{1}H NMR δ 1.68 (t, *J* = 6.6 Hz, 3 H), 3.76 (br s, 1 H), 4.07 (s, 5 H), 4.34 (t, *J* = 2.3 Hz, 1 H), 4.67 (br s, 1 H), 4.86 (dq, 2.3, 6.6 Hz, 1 H), 6.70-7.52 (m, 14 H), 8.05 (s, 1 H). ^{31}P NMR δ -23.5. $[\alpha]_D^{20}$ +352 (*c* 0.50, C_6H_6). **1d:** ^{1}H NMR δ 1.69.(t, *J* = 6.6 Hz, 3 H), 3.76 (br s, 1 H), 4.08 (s, 5 H), 4.35 (t, *J* = 2.6 Hz, 1 H), 4.66 (m, 1 H), 4.82 (m, 1 H), 6.58-8.13 (m, 10 H), 10.0 (s, 1 H). ^{31}P NMR δ -23.8. $[\alpha]_D^{20}$ +407 (*c* 0.50, C_6H_6).

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