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Asymmetric Hydroformylation of Olefins in Highly Crosslinked Polymer Matrixes

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When polymer-immobilized chiral phosphine-phosphite–Rh(I) complexes were used, the asymmetric hydroformylation of styrene gave 2- and 3-phenylpropanals with a substrate/catalyst ratio of 2000, *iso/normal* ratios of 84/16 to 89/11, and 89% *R* enantiomeric excess of 2-phenylpropanal; these results were at the highest level in catalytic activity, regio-, and enantioselectivities. Recovery-reuse of the catalyst was examined. Asymmetric hydroformylation of vinyl acetate, (*Z*)-2-butene, and 3,3,3-trifluoropropene was also successfully performed with the polymer-supported catalysts.

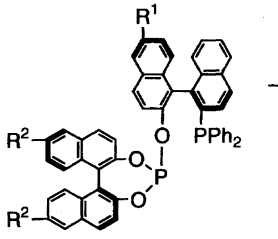
During the past four decades, asymmetric homogeneous catalysis has been developed as a convenient method for building chiral molecules in an asymmetric manner, and some of the achievements are now under industrial use.[1] However, homogeneous catalysts have some potential problems when applied to industrial processes. For example, the catalysts always are contaminated by products, and thus usually cannot be recovered for reuse or recycle. Thus, heterogeneous catalysts have many advantages over homogeneous ones; easy separation from products and facile recovery for recycling. Consequently, the industrial catalysts mostly employed are heterogeneous systems.

Polymer-support of a catalyst is a simple and effective method to switch homogeneous catalysts to heterogeneous ones. During the last two decades, intensive efforts have been devoted to the development of polymer-supported chiral catalysts.[2—4] Immobilization of catalysts on polymer-supports often causes significant decreases in catalytic activity or in selectivity of reactions due to slower diffusion of substrates into the polymer matrix.[5] Further decreases in catalytic activity or selectivity may arise by use of highly crosslinked polymer-supports, although these facilitate handlings.

We have studied the homogeneous asymmetric hydroformylation of a wide variety of substrates catalyzed by Rh(I) complexes of chiral phosphine-phosphite, (*R,S*)-BINAPHOS (**1a**).[6] This system is demonstrated to be the first example of the truly efficient catalysts of asymmetric hydroformylation for practical use. Here we report asymmetric hydroformylation of olefins using polymer-supported chiral phosphine-phosphite–Rh(I) complexes.[7] In the present study, we prepared vinyl-substituted BINAPHOS's **1b—d**, analogs of **1a**, immobilized their Rh complexes on polystyrenes with different crosslinking degrees, and examined asymmetric hydroformylation of several substrates (Chart 1).

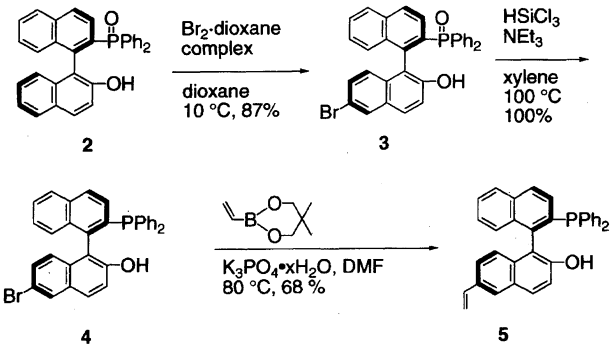
Synthesis of Polymer-Supported (*R,S*)-BINAPHOS–Rh Complexes

1 Preparation of Vinyl-BINAPHOS's. Syntheses of vinyl-BINAPHOS's **1b—d** were carried out as follows. Monovinylphosphine part **5** was prepared in a route outlined in Scheme 1. Bromination of (hydroxynbinaphthalenyl)diphenylphosphine oxide[8] **2** with a bromine–1,4-dioxane complex[9] gave **3**, which was then reduced to the corresponding phosphine **4**. The Suzuki–Miyaura reaction[10] was successfully applied to the cross-coupling of **4** with a vinylboronic acid ester to give **5**. Meanwhile, the divinyl-substituted



	R^1	R^2
1a:	H	H
1b:	-CH=CH$_2$	H
1c:	H	-CH=CH$_2$
1d:	-CH=CH$_2$	-CH=CH$_2$

Chart 1.



Scheme 1.

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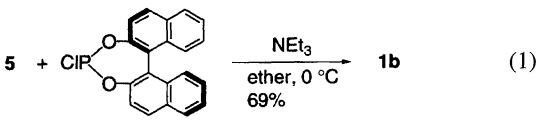
phosphite part **7** was prepared according to the route of Scheme 2 via the coupling between (tributyl)vinyltin and 6,6′-dibromo-1,1′-binaphthalene-2,2′-diol.[11] Mono-, di-, and trivinyl-BINAPHOS's **1b—d** were thus produced from **5** and/or **7** via the esterification described in Eqs. 1, 2, and 3.



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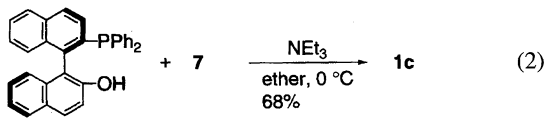

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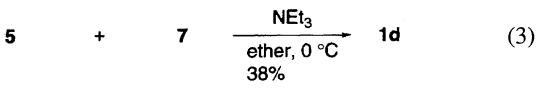
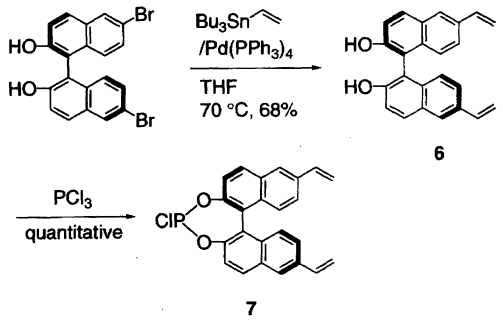


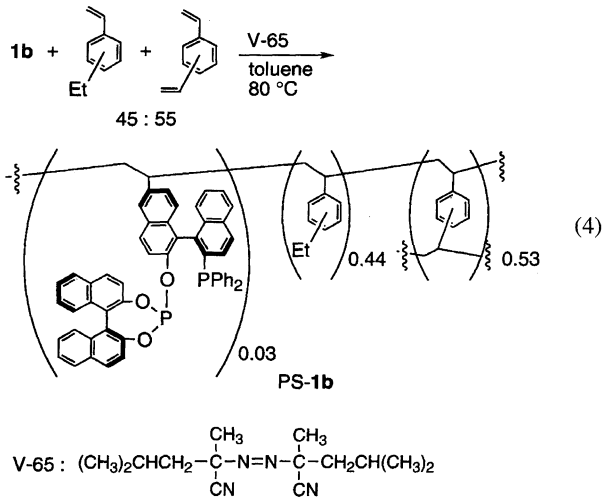
(3)

2 Copolymerization of Vinyl-BINAPHOS with Ethylstyrene and Divinylbenzene. Vinyl-BINAPHOS's **1b—d** were subjected to radical copolymerization with styrene in the presence of divinylbenzenes. Commercially available divinylbenzenes consist of 1, 2-, 1,3-, and 1,4-isomers as well as 3- and 4-ethylstyrenes. In this work, divinylbenzenes of 55 and 82% content were distilled under reduced pressure to remove stabilizers and then used. The ratios of divinylbenzenes/ethylstyrenes were retained through the purification. With 2,2′-azobis(2,4-dimethylpentanenitrile) (V-65) initiator, a 3 : 97 mixture of **1b** and the divinylbenzenes (55% content, 45% of ethylstyrenes are included as impurities) was copolymerized in toluene at 80 °C. The resulting polymer was washed successively with toluene and methanol. This polymer, abbreviated as PS-**1b**, contains an extremely high degree of crosslinking compared to the polystyrenes that are employed in most of the conventional studies (less than 10% of crosslinking).[2,4a—f] Other vinyl-BINAPHOS's were copolymerized in a similar manner.[12]

By IR analysis, absorption at 1630 cm^{-1} (corresponds to $-CH{=}CH_2$) suggested that PS-**1b** still contains a free vinyl group which may participate the hydroformylation reaction (vide infra).



Scheme 2.



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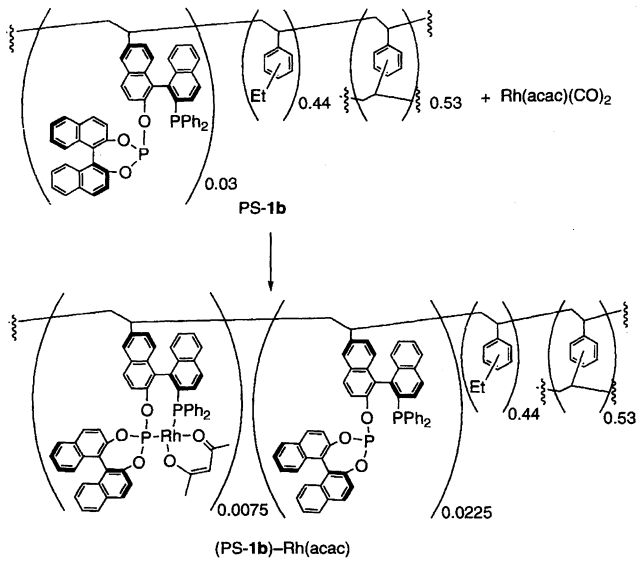
3 Preparation of Rh Complexes of Polymer-Supported BINAPHOS. The polymer-supported ligands were dispersed in benzene in the presence of $Rh(acac)(CO)_2$ and then the mixtures were freeze-dried. The resulting yellow solid was washed with methanol and dried in vacuo to afford (PS-**1b—d**)–Rh(acac), which was used as a catalyst.



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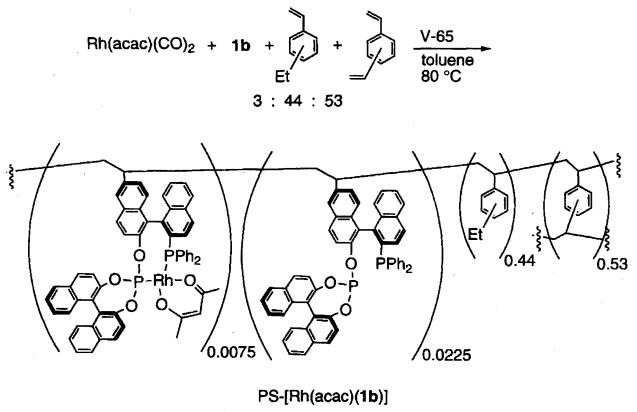
4 An Alternative Synthesis of Rh Complexes of Polymer-Supported BINAPHOS. The polymer-supported catalyst was alternatively prepared by polymerization of Rh(I) complexes of the ligands. Thus, at first, ligand **1b** was treated with $Rh(acac)(CO)_2$ to form Rh(acac)(**1b**). Copolymerization of Rh(acac)(**1b**) with divinylbenzenes (55 or 82% content) afforded the corresponding polymer-supported complex, PS-[Rh(acac)(**1b**)]. Similarly, PS-[Rh(acac)(**1c**)] and PS-[Rh(acac)(**1d**)] were synthesized.



(6)

Asymmetric Hydroformylation of Styrene

1 Asymmetric Hydroformylation with Polymer-Supported Monovinyl-BINAPHOS Complex. Asymmetric hydroformylation of styrene was examined under an atmosphere of carbon monoxide and hydrogen (total pressure of 20 atm, $CO/H_2 = 1/1$) employing the (PS-ligand)–Rh(acac) complexes as catalysts in benzene at 60 °C (Eq. 7). The results are summarized in Table 1, along with the result in homogeneous system (Run 1). All the runs were repeated at least three times to ensure the reproducibility of the data. Although the results heavily depended on the stirring speed of the reaction mixture, the reaction was completed after 12 h in all runs and the range of error for both the *i/n*- ratio and %ee was estimated to be $\pm<5\%$ when the stirring speed was kept at ca. 2000 rpm. The relation between the stirring speed and the reactivity and selectivities will be discussed later. With (PS-**1b**)–Rh(acac), 2-phenylpropanal and 3-phenylpropanal were obtained in an 84/16 ratio and the enantiomeric excess of the *iso*-aldehyde was 89% (*R*) (Run 2). The result is comparable to that obtained with the homogeneous system, Rh(acac)(**1a**) (Run 1). In addition to benzene, hexane could be used as a solvent (Run 3). Using (PS-**1c**)–Rh(acac), the regio- and enantioselectivities of the reaction were essentially the same as with Rh(acac)(**1a**) and (PS-**1b**)–Rh(acac) (Run 6). In contrast, however, lower ee was observed with (PS-**1d**)–Rh(acac) (Run 7).

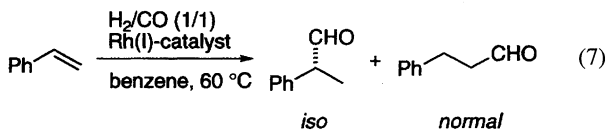
Table 1. Asymmetric Hydroformylation of Styrene Catalyzed by Polymer-Supported (*R,S*)-BINAPHOS's[a)]

Run	Catalyst	*i/n*	%ee
1	Rh(acac)(**1a**)	89/11	92
2	(PS-**1b**)–Rh(acac)	84/16	89
3[b)]	(PS-**1b**)–Rh(acac)	80/20	81
4[c)]	(PS-**1b**)–Rh(acac)	83/17	89
5[d)]	(PS-**1b**)–Rh(acac)	81/19	84
6	(PS-**1c**)–Rh(acac)	89/11	89
7	(PS-**1d**)–Rh(acac)	88/12	68
8	PS-[Rh(acac)(**1b**)]	85/15	90
9	PS-[Rh(acac)(**1c**)]	90/10	87
10	PS-[Rh(acac)(**1d**)]	87/13	85
11[d)]	PS-[Rh(acac)(**1b**)]	85/15	90

a) A solution of styrene (6.20 mmol) in benzene (0.35 mL) was allowed to react with carbon monoxide (10 atm) and hydrogen (10 atm) in the presence of a polymer catalyst (3.1×10^{-3} mmol Rh, Substrate/Catalyst = 2000) at 60 °C for 12 h. Conversion of styrene to aldehydes (>99% for all the runs) and *i/n* ratios were determined by ^{1}H NMR. Ee's were determined by GLC (Chrompack Cp-Cyclodex β-236M, 135 °C, He 2.0 kg cm^{-2}) after conversion into the corresponding carboxylic acid by the Jones oxidation of the product aldehyde. The absolute configuration of the *iso*-aldehyde was determined to be *R* for all runs. b) Hexane was used as the solvent. c) The polymer ligand was prepared from a 3 : 78 : 19 mixture of **1b**, styrene, and divinylbenzenes (55% content, 45% of ethylstyrenes are included as impurities) to make the crosslinking degree ca. 10%. d) The polymer ligand was prepared from a 3 : 97 mixture of **1b** and divinylbenzenes (82% content, 18% of ethylstyrenes are included as impurities).

2 Effect of Catalyst-Preparation Order. Asymmetric hydroformylation of styrene was examined with these PS-[Rh(acac)(ligand)] catalysts; the results are summarized in Table 1, Runs 8—11. Again, the activity and selectivity were comparable to the results with the corresponding homogeneous system. Note that the use of PS-[Rh(acac)-(**1d**)] showed higher enantioselectivity than that with (PS-**1d**)–Rh(acac) (compare Runs 7 and 10). The difference can be explained as follows. When the polymerization is carried out in the absence of Rh(I), ligand **1d** is frozen as a matrix of various conformations, some of which are not suitable to coordinate to Rh(I). This may result in the formation of a less stable Rh(I) complex, for example, with monodentate coordination. Coexistence of multiple active species could have caused the loss of selectivity. On the other hand, the conformation of **1d** should be fixed to a suitable form for the bidentate coordination to Rh(I), when **1d** is complexed with Rh(I) before polymerization. In this case, the catalyst can work in a manner similar to the way the homogeneous catalyst works. Indeed, such a difference is observed with **1d** in which both the phosphine site and the phosphite site are attached to the polymer. In contrast, with **1b** and **1c**, the ligands keep their flexibility in the polymer matrix, because only one of the two binaphthalenyl groups is bound to the polymer chain.

3 Effect of Crosslinking Degree. The cross-linking degree was decreased by employing additional styrene (Run 4) or increased by using 82% content divinylbenzene in place of 55% (Runs 5 and 11). As shown, the crosslinking degree does not appear to be influential on the selectivities.



(7)

4 Catalyst Recovery and Re-use. Because the present polymer catalyst hardly swells in benzene or hexane, easy handling and recovery-reuse have been achieved. After the reaction was completed in a glass-pressure bottle, the light yellow-polymer catalyst settled at the bottom of the vessel. The supernatant containing the products was simply removed via a syringe, and the remaining solid catalyst was charged with an olefin solution and H_2/CO.[13]

The stirring speed affected the productivity and the regio-

and enantioselectivities of the reaction. The results summarized in Table 2 are those when the reactions were stopped in a shorter reaction time (3 h) so that the conversions can be compared. Under the rapid-stirring conditions, the catalyst showed high reactivity and selectivities at the first runs (Conditions I—III). However, the polymer flakes were partly crushed by the stirring bar; so after the first runs, some of the powdery polymers were pulled out by a syringe. For example, fluorescent X-ray analysis or ICP emission spectrometry analysis of the drawn-out cloudy solution showed that ca. 50% of the initially charged Rh was removed after the first run under Conditions I. Due to such loss of the catalyst, much lower reactivities were observed in the second runs than the first ones under Conditions I—III. If one employs a larger amount of solvent and slow stirring conditions, the polymer breaking could be overcome, at the sacrifice of the reactivity and selectivities (Conditions V). In this case, the dissociation of Rh into the product solution was suppressed to 0.28% of initial content. Low reactivity with slow stirring may be interpreted as follows. The hydroformylation catalyzed by the insoluble polymer-supported catalyst is a three-phase reaction. Considering the low solubility of H_2 and CO gases to benzene (H_2 dissolves 0.38×10^{-2} mmol and CO dissolves 0.74×10^{-2} mmol to 1 mL of benzene at 60 °C, 1 atm.), one concludes that the delivery of H_2 and CO mostly takes place by the exposure of the polymer catalyst to the gas phase. Consequently, the slow stirring and use of larger volume of solvent inhibited enough access of H_2/CO to the Rh complex and resulted in low reactivity. In addition, the active species $RhH(CO)_2$(ligand) is unstable in an atmosphere with low H_2/CO concentration.[14] Thus, less selective new species may have arisen by the decomposition of $RhH(CO)_2$(ligand), which could cause the loss of selectivity. Conditions IV were chosen as optimized ones for recycling. The catalyst was used four times without any severe loss of selectivity.

5 Participation of Vinyl Group of Polymer Matrix in Hydroformylation. Polymer-supported catalyst PS-**1b** was treated with H_2/CO under the hydroformylation condition in the absence of substrate olefins. IR spectra of recovered PS-**1b** exhibited absorption at 1735 cm^{-1} (–CHO) at the expense of 1630 cm^{-1} (–CH=CH_2). Thus, it is suggested that the remaining –CH=CH_2 group in the polystyrene matrix was hydroformylated under the reaction conditions. Apparently, however, this did not cause any significant change of the selectivities of the catalyst as was observed in the recover-reuse experiments (vide supra).

Asymmetric Hydroformylation of Other Olefins

Asymmetric hydroformylation of other olefins was also examined using the polymer supported catalysts under the rapid (ca. 2000 rpm) stirring conditions (Eq. 8). The results are summarized in Table 3. For vinyl acetate, a total pressure of 100 atm was employed because hydrogenated by-products were produced under lower pressure. When the reaction was catalyzed by the polymer-supported catalysts, conversion of the reaction was variable (±20% range of error). However, *i*/*n*- ratios and %ee's were sufficiently reproducible (±<5%),

Table 2. Catalyst Recycle Process for Asymmetric Hydroformylation of Styrene Catalyzed by Rh–PS-**1b**[a]

Conditions	Run	Substrate /Catalyst	Stirring speed rpm	Time h	Conv. %	*i*/*n*	% ee
I	1st[b]	2000	1200	3	73	79/21	85
	2nd		1200	3	28	75/25	82
	3rd		1200	24	41	72/28	68
II	1st	1000	1000	3	75	86/14	86
	2nd		1000	3	20	79/21	80
	3rd		1000	16.5	12	72/28	66
III	1st	1000	800	3	87	74/26	80
	2nd		800	3	33	83/17	86
IV	1st	1000	600	3	77	73/27	74
	2nd		600	3	40	60/40	71
	3rd		600	3	23	65/35	71
	4th		600	17	74	65/35	71
V[c]	1st[d]	2000	200	3	23	66/34	74
	2nd		200	3	3	65/35	66
	3rd		800	14	20	64/36	61

a) A benzene (0.25 mL) solution of styrene (5.0 mmol) was allowed to react with H_2/CO (1/1, total pressure of 4.5 atm) at 60 °C in the presence of polymer-supported catalyst $Rh(acac)(CO)_2$–PS-**1b**. b) Dissociation of Rh from the polymer catalyst was ca. 50% of initial Rh content. c) For all of the runs, 0.5 mL of benzene was used. d) Dissociation of Rh from the polymer catalyst was 0.28% of initial Rh content.

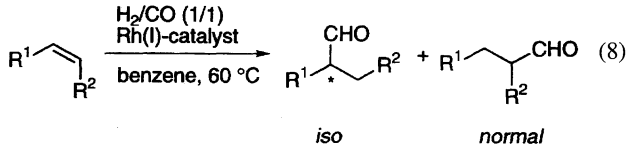
Table 3. Asymmetric Hydroformylatyion of Vinyl Acetate Catalyzed by Polymer-Supported (*R*,*S*)-BINAPHOS[a,b]

Run	Substrate	Catalyst	Conv. / %	TOF / h^{-1}	*i*/*n*	%ee[h]
1	CH_2=CHOAc	Rh(acac)(**1a**)	98	—	84/16	92 (*S*)
2		(PS-**1b**)–Rh(acac)	75	—	85/15	91 (*S*)
3		(PS-**1c**)–Rh(acac)	54	—	90/10	92 (*S*)
4		(PS-**1d**)–Rh(acac)	61	—	87/13	78 (*S*)
5		PS-[Rh(acac)(**1b**)]	67	—	87/13	92 (*S*)
6		PS-[Rh(acac)(**1c**)]	83	—	90/10	93 (*S*)
7		PS-[Rh(acac)(**1d**)]	78	—	90/10	89 (*S*)
8[c]	(*Z*)-2-Butene	Rh(acac)(**1a**)	—	4.6[d]	—	83 (*S*)
9[c]		PS-[Rh(acac)(**1b**)]	—	25[e]	—	81 (*S*)
10[c]	CH_2=$CHCF_3$	Rh(acac)(**1a**)	—	82[f]	94/6	82 (*S*)
11[c]		PS-[Rh(acac)(**1b**)]	—	351[g]	91/9	84 (*S*)

a) The reaction conditions are shown in the experimental part. b) All the runs were repeated at least twice to confirm the reproducibility. Ratio of *i*/*n* and %ee were always reproducible but the conversions in Runs 2—6 contained errors of ±20%. c) Large excess of substrate was employed for the reaction, the reactivity was estimated by turnover frequency (TOF) (= turnover number (TON) /h) instead of the conversion. d) TON was 97 after 21 h. e) TON was 450 after 18 h. f) TON was 1966 after 24 h. g) TON was 2460 after 7 h. h) The absolute configurations of the *iso*-aldehyde are shown in parentheses. Ee's were determined by GLC (Chrompack Cp-Cyclodex β-236M or Chrompack Chirasil-DEX CB) after conversion into the corresponding carboxylic acids by the Jones oxidation of the product aldehyde. See Ref. 6b for details.

varying in a range of 85/15—90/10 and 89—93% ee(*S*) (Runs 2, 3, 5, 6, and 7), respectively, similar values to those attained in the homogeneous system (Run 1). Again, slightly lower ee was observed when (PS-**1d**)–Rh(acac) was used as the catalyst (Run 4).

When (*Z*)-2-butene or 3,3,3-trifluoropropene was employed as a substrate, a large excess amount of olefin was used, and the reactivities were judged by turnover frequency (TOF) of the catalyst. With polymer-supported catalysts, both substrates gave selectivities similar to those with the homogeneous system (compare: Runs 8 and 9; Runs 10 and 11). It is noteworthy that TOF was even higher with the polymer-supported catalyst than with the homogeneous catalyst in these runs.



(8)

vinyl acetate: R^1 = AcO; R^2 = H
(*Z*)-2-butene: R^1 = CH_3; R^2 = CH_3
3,3,3-trifluoropropene: R^1 = CF_3; R^2 = H

Conclusion

Asymmetric hydroformylation of olefins using polymer-immobilized chiral phosphine-phosphite–Rh(I) complexes has been thus established. In the asymmetric hydroformylation of styrene, the highest level in catalytic activity, regio- and enantioselectivities was achieved with (PS-**1b**)–Rh(acac) and (PS-**1c**)–Rh(acac). The highly crosslinked polymer matrix was found to maintain the catalytic activity and/or enantioselectivity of the reaction. As a result, easy handling and recovery-reuse of the catalyst became possible. For further practical use of the system, however, mechanical properties of the catalyst polymers should be improved so that the polymer-crushing would be avoided under rapid stirring conditions. Modification of the engineering processes, for example, employing shaking instead of stirring and centrifuging the powdery catalyst, might be a possible solution. Asymmetric hydroformylation of vinyl acetate, (*Z*)-2-butene, and 3,3,3-trifluoropropene, was also successfully achieved with the polymer-supported catalysts. In view of the important roles played by the asymmetric catalysis in industry, such immobilization of asymmetric homogeneous catalysts should be a research target to be further explored.

Experimental

General Method. All manipulations of oxygen- and moisture-sensitive materials were conducted under purified argon atmosphere (BASF-Catalyst R3-11) by the use of the standard Schlenk techniques. Silica-gel chromatography was performed using Wakogel C-200.

Apparatus. Nuclear magnetic resonance spectra were taken with JEOL EX-270 (^{1}H 270 MHz; ^{13}C 68 MHz; ^{31}P 109 MHz) or Varian Mercury 200 (^{1}H 200 MHz; ^{31}P 81 MHz) spectrometer using tetramethylsilane as an internal standard, and coupling constants are given in Hertz. Optical rotation and melting points were measured on a JASCO DIP-360 and a Yanako MP-500D. GLC analyses were performed on a Shimadzu GC-15A gas chromatograph. Fluorescent X-ray spectrometry analysis was performed with a Kevex Inst. Inc. EDX-771. ICP emission spectrometry analysis was performed with a Seiko Inst. SPS1500VR.

Chemicals. Most of reagents were available from Wako Pure Chemical Industries Ltd. or Nacalai Tesque Ltd. All of solvents used for the reactions and recrystallizations were distilled under

argon after drying over an appropriate drying agent. For silica-gel column chromatography, Wako-gel C-200 was used.

Preparation of (*R*)-6-Bromo-2′-diphenylphosphinoyl-1,1′-binaphthalen-2-ol (3). A solution of bromine (1.8 mL, 34.0 mmol) in dioxane (20 mL) was added to a solution of (*R*)-2′-diphenylphosphinoyl-1,1′-binaphthalen-2-ol (**2**)[8] (4.0 g, 8.5 mmol) in dioxane (150 mL) at 5 °C. After being stirred at room temperature for 2 h, the mixture was quenched with aqueous $Na_2S_2O_3$, neutralized with aqueous $NaHCO_3$, and then extracted with $CHCl_3$. The organic layer was washed with brine and dried over $MgSO_4$ and Na_2SO_4. Evaporation of the solvents under reduced pressure, followed by column chromatography on silica gel (CH_2Cl_2 : AcOEt = 1 : 1) afforded product **3** as colorless crystals (4.1 g, 87% yield): Mp 160.4—162.8 °C (CH_2Cl_2–AcOEt), $[\alpha]_D^{23}$ −80° (*c* 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ = 9.05 (bs, 1H), 7.95—7.88 (m, 4H), 7.65—7.53 (m, 7H), 7.42—7.31 (m, 2H), 7.26—7.17 (m, 2H), 7.06—6.88 (m, 3H), 6.81—6.72 (m, 2H), 6.27 (d, *J* = 8.91, Hz, 1H); ^{31}P NMR ($CDCl_3$) δ = 31.26 (s). Calcd for $C_{32}H_{22}O_2PBr$: C, 69.96; H, 4.04%. Found: C, 69.78; H, 4.31%.

Preparation of (*R*)-6-Bromo-2′-diphenylphosphino-1,1′-binaphthalen-2-ol (4). Trichlorosilane (5.7 mL, 56 mmol) was added to a solution of **3** (3.1 g, 5.6 mmol) in xylene (40 mL) and triethylamine (16 mL, 110 mmol) at 0 °C. The reaction mixture was heated at 110 °C for 22 h and then slowly quenched with aqueous $NaHCO_3$ at 0 °C. The mixture was filtered through a Celite pad. The organic layer of the filtrate was separated, dried over Na_2SO_4 and $MgSO_4$, and concentrated. The residue was purified by column chromatography on silica gel (elute $CHCl_3$) to give the title product **4** as pale yellow solid material (1.94 g, 65% yield): Mp 91.4—93.6 °C ($CHCl_3$). $[\alpha]_D^{23}$ −57° (*c* 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ = 7.96—7.80 (m, 4H), 7.52—7.43 (m, 2H), 7.33—6.98 (m, 14H), 6.55 (d, *J* = 8.91 Hz, 1H), 4.62 (s, 1H); ^{31}P NMR ($CDCl_3$) δ = −12.82 (s). Calcd for $C_{32}H_{22}OPBr$: C, 72.06; H, 4.16%. Found: C, 72.02; H, 4.52%.

Preparation of (*R*)-2′-Diphenylphosphino-6-vinyl-1,1′-binaphthalen-2-ol (5). A mixture of **4** (1.0 g, 1.9 mmol), $Pd(PPh_3)_4$ (0.21 mg, 0.18 mmol), 2-vinyl-5,5-dimethyl-1,3,2-dioxaborinane[10] (0.40 mL, 2.9 mmol), and $K_3PO_4 \cdot H_2O$ (0.97 g, 4.5 mmol) in DMF (12 mL) was heated at 80 °C for 16 h. The resulting mixture was diluted with water and extracted with Et_2O. The organic layer was washed with brine, and then dried over Na_2SO_4 and $MgSO_4$. Evaporation of the solution and purification by silica-gel column chromatography ($CHCl_3$) gave **5** as colorless solid materials (0.62 g, 68% yield): Mp 93.6—95.4 °C ($CHCl_3$). $[\alpha]_D^{23}$ −28° (*c* 0.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ = 7.95—7.86 (m, 3H), 7.72 (bs, 1H), 7.54—7.01 (m, 16H), 6.79 (dd, *J* = 17.15 Hz, *J* = 10.55 Hz, 1H), 6.69 (d, *J* = 8.91 Hz, 1H), 5.70 (d, *J* = 17.15 Hz, 1H), 5.22 (d, *J* = 10.55 Hz, 1H), 4.53 (s, 1H); ^{31}P NMR ($CDCl_3$) δ = −13.01 (s). Calcd for $C_{34}H_{25}OP$: C, 84.98; H, 5.24%. Found: C, 84.35; H, 5.70%.

Preparation of (*R*)-2′-Diphenylphosphino-6-vinyl-1,1′-binaphthalen-2-yl (*S*)-1,1′-Binaphthalene-2,2′-diyl Phosphite (1b). Triethylamine (0.92 mL, 6.6 mmol) was added to a mixture of **5** (1.6 g, 3.2 mmol) and [(*S*)-1,1′-binaphthalene-2,2′-dioxy]chlorophosphine (2.5 g, 6.6 mmol) in Et_2O (25 mL) at 0 °C. The mixture was stirred for 24 h at room temperature and then quenched with cold water. The organic phase was separated; the aqueous phase was extracted with Et_2O. The combined organic phase was dried over $MgSO_4$. The residue was purified by silica gel chromatography (hexane : CH_2Cl_2 = 1 : 1) to give **1b** (1.8 g, 69%) as a colorless solid: Mp (hexane–CH_2Cl_2) >230°C (decomp). $[\alpha]_D^{23}$ 249° (*c* 0.45, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ = 8.06—7.87 (m, 5H), 7.74—7.71 (m, 2H), 7.57—7.91 (m, 24H), 6.78 (dd, 1H, *J* = 17.48, 10.89 Hz, 1H), 6.62 (d, *J* = 8.90 Hz, 1H), 5.99 (d, *J* = 8.9 Hz, 1H), 5.69 (d, *J* = 17.48 Hz, 1H), 5.25 (d, *J* = 10.89 Hz, 1H); ^{31}P NMR ($CDCl_3$) δ = 146.04 (d, *J* = 30.5 Hz), −13.21 (d, *J* = 30.5 Hz). HRMS Found: *m*/*z* 795.2194. Calcd for $C_{54}H_{37}O_3P_2$: M+H, 795.2215.

Preparation of (*S*)-6,6′-Divinyl-1,1′-binaphthalene-2,2′-diol (6). Vinyltributyltin (1.5 mL, 5.0 mmol) was added dropwise to a solution of (*S*)-6,6′-dibromo-1,1′-binaphthalene-2,2′-diol[15] (1.0 g, 2.3 mmol) and $Pd(PPh_3)_4$ (0.26 g, 0.23 mol) in THF (12 mL). The mixture was stirred at 70 °C for 36 h; THF was removed by a rotary evaporator. The residue was dissolved in Et_2O. To this solution was added a large excess of aqueous KF. The whole mixture was stirred vigorously; the organic layer was separated, washed with brine, and dried over $MgSO_4$. The solvent was removed in vacuo; the residue was roughly purified by silica-gel column chromatography (hexane/Et_2O = 1/20). Further purification by GPC and reprecipitation from hexane–ether gave product **6** in 68% yield as white solids that contained Bu_3SnF as an impurity. The impurity content was estimated to be 12.0 mol% by ^{1}H NMR. ^{1}H NMR ($CDCl_3$) δ = 5.01 (s, 2H, O*H*), 5.28 (d, *J* = 10.89 Hz, 2H, C*H*H=CH), 5.78 (d, *J* = 17.48 Hz, 2H, CH*H*=CH), 6.84 (dd, *J* = 17.48 and 10.89 Hz, 2H, CH_2=C*H*), 7.11 (d, *J* = 8.91 Hz, 2H, aromatic), 7.37 (d, *J* = 8.91 Hz, 2H, aromatic), 7.46 (dd, *J* = 1.65, 8.91 Hz, 2H, aromatic), 7.82 (d, *J* = 1.32 Hz, 2H, aromatic), 7.96 (d, *J* = 8.91 Hz, 2H, aromatic); ^{13}C NMR ($CDCl_3$) δ = 152.8, 136.5, 133.5, 133.0, 131.6, 129.5, 126.7, 124.9, 124.5, 118.1, 113.7, 110.7. Calcd for $(C_{24}H_{18}O_2)_{0.88}(Bu_3SnF)_{0.12}$: C, 80.91; H, 5.74%. Found: C, 80.90; H, 5.86%.

Preparation of [(*S*)-6,6′-Divinyl-1,1′-binaphthalene-2,2′-dioxy]chlorophosphine (7). A mixture of **6** (0.12 g, 0.35 mmol) and phosphorus trichloride (2.0 mL, 23 mmol) was heated at reflux under argon overnight. The excess PCl_3 in the reaction mixture was removed under reduced pressure. The last trace of PCl_3 in the residue was removed by azeotropic distillation with toluene (3 mL) under reduced pressure. This procedure was repeated three times. The crude product **7** was used for the next reaction without further purification. ^{1}H NMR δ = 5.35 (m, 2H), 5.85 (m, 2H), 6.87 (m, 2H), 7.18—8.00 (m, 10H); ^{31}P NMR ($CDCl_3$) δ = 179.0 (s).

Preparation of (*R*)-2′-Diphenylphosphino-1,1′-binaphthalen-2-yl (*S*)-6,6′-Divinyl-1,1′-binaphthalene-2,2′-diyl Phosphite (1c). To a solution of (*R*)-2′-Diphenylphosphino-1,1′-binaphthalen-2-ol[8] (0.11 g, 0.24 mmol) and **7** (0.35 mmol) in Et_2O (6 mL) was dropwise added a solution of triethylamine (0.06 mL, 0.43 mmol) in Et_2O (2 mL) at 0 °C. The resulting mixture was stirred at 0 °C for 1 h, and then at room temperature for 24 h. The reaction mixture was poured into cold water. The organic phase was separated; the aqueous phase was extracted with Et_2O. The combined organic phases was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica-gel column chromatography (hexane : CH_2Cl_2 = 2 : 1→1 : 1) to give **1c** (0.13 g, 68%) as a colorless solid. Mp (hexane–CH_2Cl_2) >220°C (decomp). $[\alpha]_D^{23}$ 316° (*c* 0.33, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ = 5.30 (m, 2H), 5.80 (m, 2H), 6.02 (d, *J* = 8.90 Hz, 1H), 6.70—8.05 (m, 33H); ^{31}P NMR ($CDCl_3$) δ = −13.3 (d, *J* = 30.5 Hz), 145.1 (d). HRMS Found: *m*/*z* 821.2426. Calcd for $C_{56}H_{39}O_3P_2$: M+H, 821.2373.

Preparation of (*R*)-2′-Diphenylphosphino-6-vinyl-1,1′-binaphthalen-2-yl (*S*)-6,6′-Divinyl-1,1′-binaphthalene-2,2′-diyl Phosphite (1d). Triethylamine (0.20 mL, 1.4 mmol) was added to a solution of **5** (0.94 mmol) and **7** (1.0 mmol) in Et_2O (20 mL) at 0 °C. The mixture was stirred at room temperature for 24 h and then quenched with cold water. The organic phase was separated; the aqueous phase was extracted with Et_2O. The combined

organic phase was dried over $MgSO_4$. The residue was purified by silica-gel column chromatography (hexane–CH_2Cl_2 = 1 : 1) to afford **1d** (0.302 g, 38%), Mp (hexane–CH_2Cl_2) >240°C (decomp). $[\alpha]_D^{23}$ 308° (*c* 0.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$) δ = 8.06—6.60 (m, 33H), 6.00 (d, 1H, *J* = 8.91 Hz, 1H), 5.84—5.23 (m, 6H); ^{31}P NMR ($CDCl_3$) δ = 146.0 (d, *J* = 30.5 Hz), −13.2 (d, *J* = 30.5 Hz). HRMS Found: *m/z* 847.2481. Calcd for $C_{58}H_{41}O_3P_2$: M+H, 847.2529.

Preparation of PS-1b. A solution of vinyl-BINAPHOS **1b** (0.13 g, 0.13 mmol), divinylbenzene (55% content, 45% of ethylstyrenes are included as impurities, total 0.53 g corresponding to 2.3 mmol of divinylbenzenes and 1.8 mmol of ethylstyrenes), and V-65 (0.020 g, 0.081 mmol) in toluene (1.5 mL) was placed in a 20-mL Schlenk tube and degassed by freeze-thaw cycles. The solution was heated at 70 °C for 5 h into induce solidification. To the mixture, methanol was added to afford a colorless precipitate. This was filtered, washed successively with methanol and toluene, and dried under reduced pressure to give 0.51 g of PS-**1b**. The polymer was insoluble in any organic solvent, and therefore, GPC analysis was impossible. Found: C, 88.45; H, 7.81%. Calcd for $[C_6H_4(CH_2CH_2)_2]_{53}[C_6H_5(CH_2CH_3)(CH_2CH_2)]_{44}[C_{54}H_{37}O_3P_2]_3$: C, 88.87; H, 8.98%. PS-**1c** and PS-**1d** were similarly prepared. PS-**1c**: 0.51 g. Found: C, 87.11; H, 7.88%. Calcd for $[C_6H_4(CH_2CH_2)_2]_{53}[C_6H_5(CH_2CH_3)(CH_2CH_2)]_{44}[C_{56}H_{39}O_3P_2]_3$: C, 88.88%; H, 8.97%. PS-**1d**: 0.48 g. Found: C, 86.79; H, 7.62%. Calcd for $[C_6H_4(CH_2CH_2)_2]_{53}[C_6H_5(CH_2CH_3)(CH_2CH_2)]_{44}[C_{58}H_{41}O_3P_2]_3$: C, 88.90; H, 8.97%.

Preparation of (PS-1b)–Rh(acac). A 20-mL Schlenk tube was charged with Rh(acac)$(CO)_2$ (2.3×10^{-2} mmol) and PS-**1b** (0.048 g, 0.10 mmol containing BINAPHOS). Degassed benzene (3.5 mL) was added to the mixture. After 1 d heating at 60 °C, the reaction mixture was freeze-dried. The resulting yellow solid was washed with methanol, dried in vacuo, and stored under argon. (PS-**1c**)–Rh(acac) and (PS-**1d**)–Rh(acac) were similarly prepared.

Preparation of PS–[Rh(acac)(1b)]. A solution of Rh(acac)-(**1b**) (Rh 1.6×10^{-2} mmol, containing 6.4×10^{-2} mmol of **1b**), divinylbenzene (0.29 mL, 2.0 mmol), and V-65 (5.1 mg, 2.1×10^{-2} mmol) in toluene (0.5 mL) was placed in a 20-mL Schlenk tube, and degassed by freeze-thaw cycles. The solution was heated at 80 °C for 13 h, while the mixture solidified. Methanol was added to the mixture to give yellow precipitates. These were filtered, washed successively with methanol and toluene, and dried under reduced pressure. The polymer complexes were used without further purification.

General Procedure for Asymmetric Hydroformylation of Styrene. In a 20 mL-Schlenk tube was placed a solution of styrene (0.71 mL, 6.2 mmol) in benzene (0.35 mL); the contents were degassed by freeze-thaw cycles. A polymer catalyst (3.1×10^{-3} mmol Rh) was placed in a 50-mL stainless autoclave, and the solution of styrene was transferred into the autoclave. Carbon monoxide (10 atm) and hydrogen (10 atm) were charged; the reaction mixture was heated at 60 °C. The reaction mixture was filtered and analyzed according to the method described in Ref. 6b. The results are summarized in Table 1.

Catalyst Recycling. In order to recycle the catalyst, the reaction was carried out in a glass-pressure bottle with a total pressure of 5 atm. After the reaction was completed, the liquid phase was removed with a syringe. The remaining solid catalyst was washed with benzene (5 mL×three times) and then charged with an olefin solution and H_2/CO for the next run. The results are summarized in Table 2. The discharged amount of rhodium after the first run was analyzed by the following process. The product-containing solution and the washes were concentrated, and the residues were analyzed by fluorescent X-ray spectrometry. When the Rh content was low, the samples were subjected to wet oxidation process | H_2SO_4–HNO_3 aq. | to remove all the organic materials. The remaining aqueous solution of the inorganic components were analyzed by ICP emission spectrometry. The results are also shown in Table 2.

General Procedure for Asymmetric Hydroformylation of Vinyl Acetate. A solution of vinyl acetate (6.23 mmol) in benzene (0.30 mL) was placed in a 20 mL-Schlenk tube and degassed by freeze-thaw cycles. A polymer (3.1×10^{-3} mmol Rh) was placed in a 50-mL stainless autoclave, into which the solution of styrene was transferred. Carbon monoxide (50 atm) and hydrogen (50 atm) were charged; then the whole was heated at 60 °C. The reaction mixture was filtered and analyzed according to the methods described in Ref. 6. The results are summarized in Table 3.

General Procedure for Asymmetric Hydroformylation of (*Z*)-2-Butene and 3,3,3-Trifluoropropene. In a 20 mL-Schlenk tube, benzene (0.50 mL) was placed and degassed by freeze-thaw cycles. To this, (*Z*)-2-butene in large excess was introduced. In a 50-mL stainless autoclave, a polymer (5.0×10^{-3} mmol Rh) and the solution of (*Z*)-2-butene were placed. Carbon monoxide (10 atm) and hydrogen (10 atm) were charged, and the whole was heated at 60 °C. The reaction mixture was filtered and analyzed according to the method described in Refs. 6 and 16. 3,3,3-Trifluoropropene was subjected to the reaction in a similar way. Both of the results are summarized in Table 3.

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