mixture set to a yellow gel. The mixture was cooled and treated with 100 mL of degassed hexane to shrink the gel. The insoluble material was filtered in the drybox and dried under reduced pressure to yield 2.36 g (92%) of **28** as a yellow powder. The elemental analysis for polymer **28** appears in Table III.

General Procedure for Asymmetric Hydrogenation Using Homogeneous Phosphinopyrrolidine–Rhodium(I) Catalysts. A typical hydrogenation was carried out as follows. To a glass-lined bomb were added 4 mg (0.01 mmol) of μ-dichloro-bis(1,5-hexadiene)dirhodium(I), 12 mg (0.022 mmol) of **22**, and 2 mmol of substrate. The bomb was brought into the drybox, and 15 mL of absolute ethanol and 8.3 μL of triethylamine were added. The bomb was sealed under argon and then pressurized to 800 psig with hydrogen. The bomb was placed in a constant-temperature bath maintained at 20 °C and stirred magnetically. The reactions were worked up as described previously.[15] The product was analyzed by ^{1}H NMR. The integration between product and starting material *N*-acetyl peaks was used to determine conversion. The optical yield was determined by polarimetry. Results are reported in Table I.

General Procedure for Asymmetric Hydrogenation Using Polymer-Supported Catalysts. A typical hydrogenation was carried out as follows. To an argon filled flask were added 68 mg (0.018 mequiv of diphosphine) of **27**, 2 mg (0.01 mmol of Rh) of μ-dichloro-bis(1,5-hexadiene)dirhodium(I), and 15 mL of ethanol. The mixture was stirred for 1 h and then filtered under argon to give the yellow polymer-bound catalyst. The catalyst was transferred under argon to a glass-lined bomb equipped with magnetic stirring. After addition of 0.5 mmol of substrate, 15 mL of ethanol, and 5.0 μL of triethylamine, the bomb was pressurized to 800 psig with hydrogen and stirred at 20 °C. The workup consisted of filtration to remove the catalyst and evaporation of the solvent. When the reaction solvent was ethanol, the residue was taken up in 10 mL of nitromethane and reevaporated. This removes the last trace of ethanol. The products were analyzed by ^{1}H NMR. The integration between product and starting material *N*-acetyl peaks was used to determine conversion. The optical yields were determined by polarimetry. The results are listed in Table II.

Acknowledgment. This work was supported by Grant DMR-77-14447 from the National Science Foundation. The ^{13}C and ^{31}P spectra were obtained at the Colorado State University Regional NMR Center, funded by the National Science Foundation (Grant No. CHE-78-18581). A fellowship for G.L.B. funded by the Phillips Petroleum Co. is greatly appreciated.

Registry No. **1**, 73300-49-9; **2**, 77429-64-2; **3**, 61478-28-2; **4**, 51-35-4; **5**, 33996-30-4; **6**, 37813-30-2; **7**, 61478-26-0; **8**, 61478-27-1; **9**, 77449-94-6; **10**, 2584-71-6; **11**, 37712-75-7; **12**, 77449-95-7; **13**, 77449-96-8; **14**, 77449-97-9; **15**, 3398-22-9; **15** ethyl ester HCl, 77449-98-0; **16**, 77449-99-1; **17**, 77450-00-1; **18**, 77450-01-2; **19**, 77450-02-3; **20**, 77450-03-4; **21**, 77450-04-5; **22**, 72598-03-9; **23**, 61478-29-3; **24**, 77450-05-6; **25**, 868-77-9; **26**, 97-90-5; **27**, 77429-62-0; **28**, 77429-63-1; **29**, 77429-65-3; (*R*)-**30a**, 10172-89-1; (*S*)-**30a**, 2018-61-3; (*R*)-**30b**, 61478-30-6; (*S*)-**30b**, 17355-23-6; (*R*)-**30c**, 19764-32-0; (*S*)-**30c**, 537-55-3; (*R*)-**30d**, 33043-31-1; (*S*)-**30d**, 31269-52-0; (*Z*)-α-acetamidocinnamic acid, 55065-02-6; (*Z*)-α-acetamido-*p*-acetyloxycinnamic acid, 64896-34-0; (*Z*)-α-acetamido-*p*-hydroxycinnamic acid, 64896-33-9; (*Z*)-α-acetamido-4-acetoxy-3-methoxycinnamic acid, 55739-56-5; μ-dichloro-bis(1,5-hexadiene)dirhodium(I), 12092-47-6; acryloyl chloride, 814-68-6; *N*,*N*-dimethylacrylamide, 2680-03-7.

(15) Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* **1972**, *94*, 6429.
(16) Knowles, W. S.; Sabacky, M. J.; Vineyard, B. D.; Weinkauff, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 2567.

Transition-Metal-Catalyzed Asymmetric Organic Synthesis via Polymer-Attached Optically Active Phosphine Ligands. 6.[1] Asymmetric Hydrogenation with Polymer Catalysts Containing Optically Active Pendent Alcohols

Gregory L. Baker, Scott J. Fritschel, and J. K. Stille*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

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Three acrylate comonomers, (*S*,*S*), (*R*,*R*) and racemic 1-methyl-2-hydroxypropyl acrylate (**7a–c**), were prepared from the corresponding isomers of 2,3-butanediol. The acrylates were copolymerized with ethylene dimethacrylate and *N*-acryloyl-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (**8**) to give cross-linked resins containing phosphinopyrrolidines and optically active alcohols. Polymers containing the 4,5-bis[(diphenylphosphino)methyl]-1,3-dioxolane unit (DIOP) were prepared by copolymerizing acrylates **7a–c** with ethylene dimethacrylate and 2-*p*-styryl-4,5-bis[(tosyloxy)methyl]-1,3-dioxolane (**1**) and treating the polymers with an excess of sodium diphenylphosphide. Exchange of Rh(I) onto these polymers provided catalysts that hydrogenated 2-acetamidoacrylic acid in tetrahydrofuran. The enantiomeric excesses obtained with the polymer-bound catalysts varied with the structure of the pendent alcohol, suggesting the participation of the polymer-bound alcohol at the catalyst site to provide an alcohol-like environment. A difference in enantiomeric excess (ee) was noted when catalysts containing either *R* or *S* alcohols were used.

One of the most challenging problems in preparing polymer-bound catalysts is the proper design of the polymer support. Previously we had prepared polymer-bound catalysts for asymmetric hydrogenation[2,3] and hydroformylation;[4] each catalyst was prepared with the solvent requirements of the reaction in mind. For the reduction of dehydroamino acids, a polar support obtained from copolymerization with hydroxyethyl methacrylate was synthesized, thus allowing the polymer-bound catalyst

(1) Part 5: Baker, G. L.; Fritschel, S. J.; Stille, J. K. *J. Org. Chem.*, preceeding paper in this issue.
(2) Takaishi, N.; Imai, H.; Bertelo, C. A.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 264.
(3) Masuda, T.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 268.
(4) Fritschel, S. J.; Ackerman, J. J. H.; Keyser, T.; Stille, J. K. *J. Org. Chem.* **1979**, *44*, 3152.

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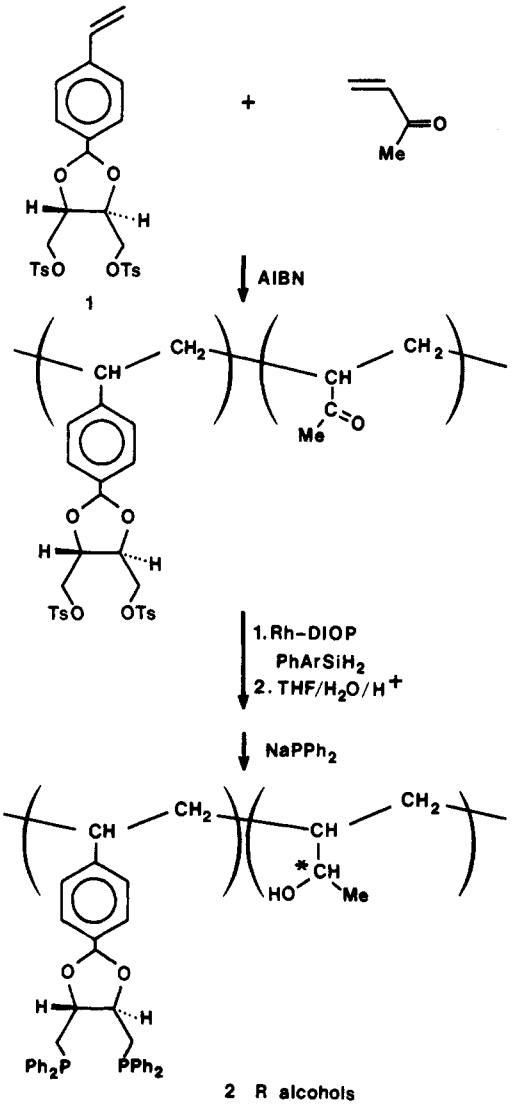
Scheme I. Polymer-Attached DIOP with Optically Active Alcohol Groups on the Polymer Chain

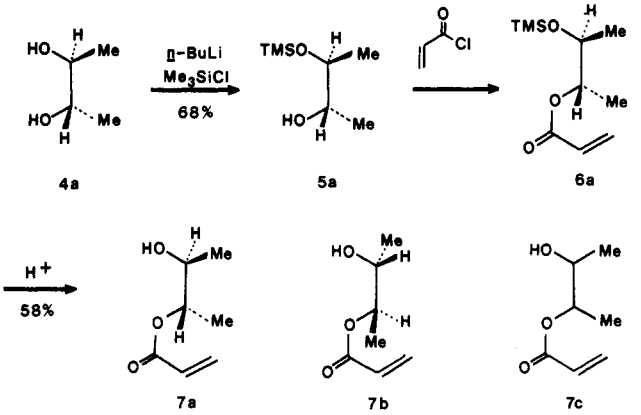


to swell in the polar solvents that are most suited for this reaction. For hydroformylations performed in nonpolar solvents, a styrene-based polymer was chosen. In both cases, the results obtained with the poylmer-bound catalysts mimicked those obtained with the analogous homogeneous catalysts.

In addition to providing desirable swelling characteristics, a polymer support must not interact with the catalyst in a way which reduces the catalyst enantioselectivity. A polymer-bound catalyst with a backbone derived from *N,N*-dimethylacrylamide was prepared,[1] but the catalyst enantioselectivity was inferior to that of the homogeneous analogue, even though the polymer swelled in the reaction solvent. These results either could be a result of unfavorable interactions of the support with the catalyst or a result of competition by the pendent amides for the metal, providing chiral catalyst sites.

Interactions between nonrhodium-bearing chiral sites in the polymer support and the catalyst may in principle lead to enhanced optical yields in asymmetric synthesis. This was in fact demonstrated with DIOP-containing polymers[3] that also contained optically active pendent alcohols. In this example (Scheme I), the chiral support was synthesized by reducing a copolymer of 1 and methyl vinyl ketone via asymmetric hydrosilylation. A 15% difference in optical yield was noted between reactions where polymers containing predominantly *R* alcohols and catalysts containing *S* alcohols were used. Unfortunately, the optical yields were lower than those obtained with the corresponding homogeneous catalyst.

Scheme II. Optically Active Acrylates of (*R,R*)- and (*S,S*)-2,3-Butanediol

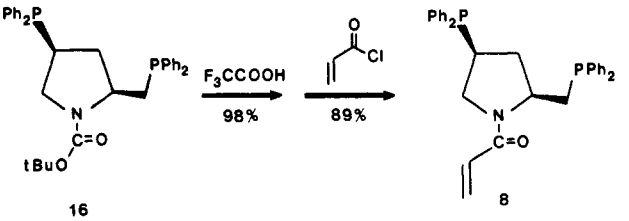


Although significant effects were observed when the ancillary chiral center was introduced, there were several drawbacks to this approach. The reduction of the methyl ketones is not stereospecific, although nonpolymeric ketones have been reduced in 60–80% ee.[5] In addition, it was possible that the polymer bound alcohol adjacent to the backbone did not have sufficient mobility to interact efficiently with the metal center.

In order to overcome these problems, we prepared a series of polymers containing optically pure alcohols. These alcohols were removed from the polymer backbone by several atoms (spacer effect) to ensure greater mobility.

Results and Discussion

Monomer and Polymer Synthesis. The synthesis of the optically active phosphinopyrrolidine and DIOP type ligand-containing monomers have been described.[1,2] Acrylamide 8 is readily prepared from BPPM (16) in two



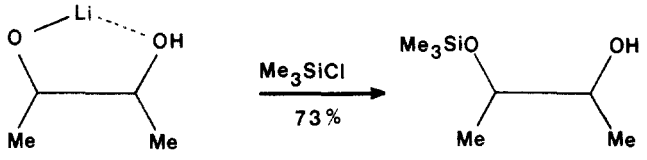
steps[1] and can be copolymerized with several comonomers. The styryl monomer 1 will also copolymerize with many comonomers, but a phosphination reaction on the polymer is required to prepare the polymer bound DIOP analogue.

An optically active comonomer suitable for use in preparing a polymer containing optically active pendent alcohols should be available in both the *R* and *S* enantiomers so that the chirality of the alcohol and that of the catalyst may be matched to provide any synergistic effect. A suitable starting material for the synthesis of optically active comonomers is 2,3-butanediol, since the *R,R* isomer is commerically available, and the *S,S* isomer can be synthesized in a straightforward manner from tartaric acid.[6]

(5) Dumont, W.; Poulin, J. C.; Dang, T. P.; Kagan, H. B. *J. Am. Chem. Soc.* **1973**, *95*, 8295. Poulin, J. C.; Dumont, W.; Dang, T. P.; Kagan, H. B. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1973**, *277*, 41.

(6) Schurig, V.; Koppenhoefer, B.; Buerkle, W. *J. Org. Chem.* **1980**, *45*, 538.

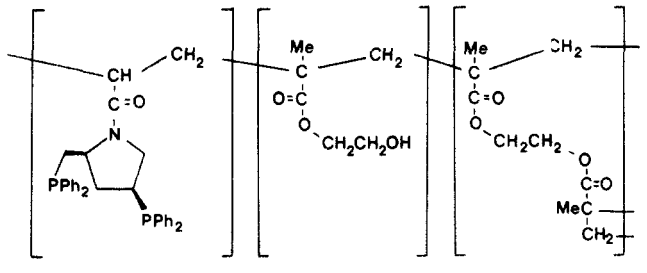
Optically active acrylates were prepared from the diols in three steps to give optically pure monomers (Scheme II). An inactive monomer prepared from racemic 2,3-butanediol was synthesized for use as a standard for comparison. Treatment of the diol (17) with 1 equiv of *n*-butyllithium at −98 °C followed by a slow addition of trimethylsilyl chloride gave the monoprotected diol (5) in as high as 73% yield. If the alcohols of the diol were independent of each other, a random statistical distribution would be expected, with the yield being 50%.



17 5

The free alcohol was converted to the acrylate ester by heating with acryloyl chloride, with the hydrochloric acid generated being efficiently removed by 3A molecular sieves. The protecting group was removed and the monomer distilled to give the optically pure monomers **7a,b** and racemic monomer **7c**. Although care was taken to prevent the polymerization of the acrylate during distillation, polymerization occasionally occurred in spite of the addition of free-radical inhibitors such as *tert*-butylcatechol and hydroquinone.

Phosphinopyrrolidine-containing polymers were prepared by the copolymerization of **8** with ethylene dimethacrylate and acrylates **7a–c** (Scheme III). This gave polymers **10–12** as white powders. Copolymerization of **1** with ethylene dimethacrylate and acrylates **7a–c** gave polymers **13a**, **14a**, and **15a** (Scheme IV) as white free-flowing powders. Treatment of the polymers with a large excess of sodium diphenylphosphide afforded the DIOP containing polymers **13b**, **14b**, and **15b**. Some loss of material was noted in this step, possibly due to partial hydrolysis of the polymer-bound esters. Polymers **18**



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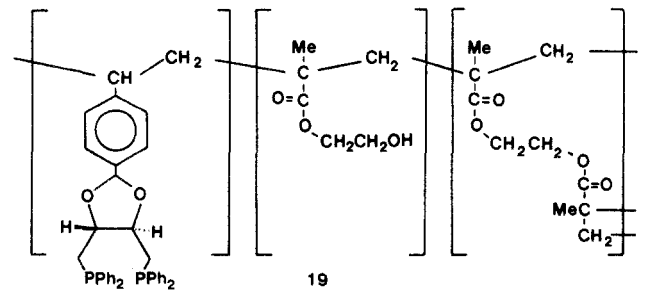

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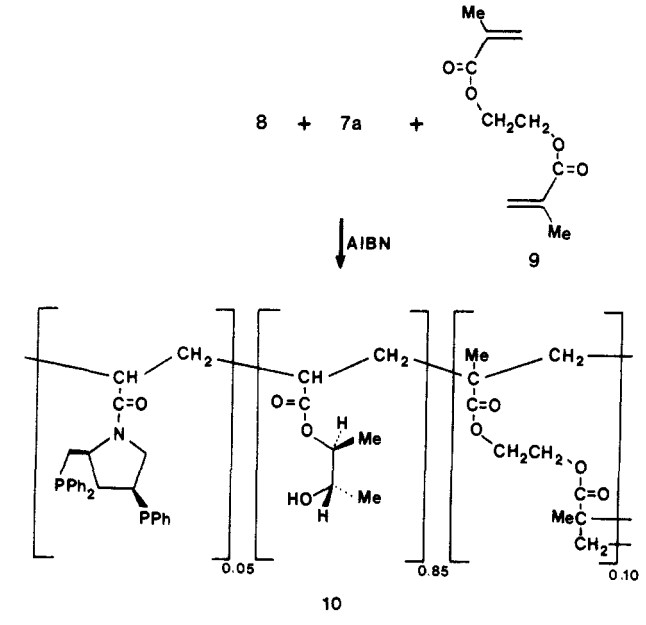
containing BPPM and hydroxyethyl acrylate units (see structure **27** in ref 2) and **19** containing DIOP and hydroxyethylmethacrylate units (see structure **5** in ref 1) were also used so that the effects of changing the polymer-bound alcohol from a primary to a secondary alcohol could be observed.

Scheme III. Polymers Containing Optically Active BPPM Ligand and Chiral Alcohol Sites



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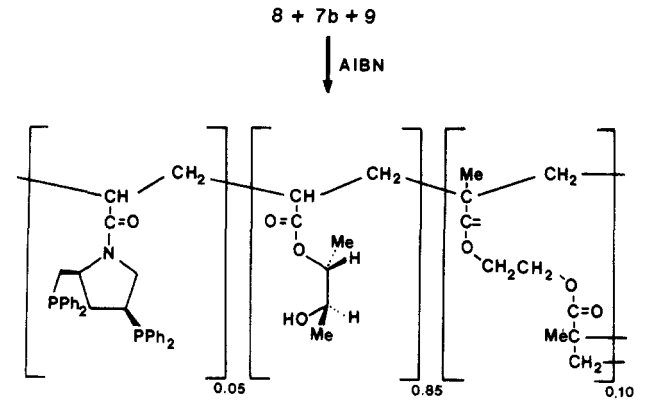

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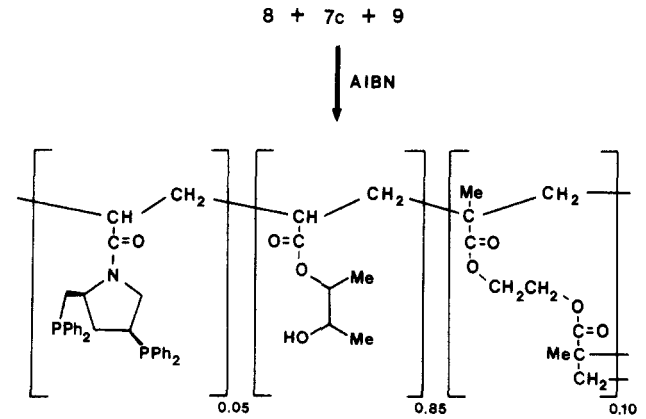
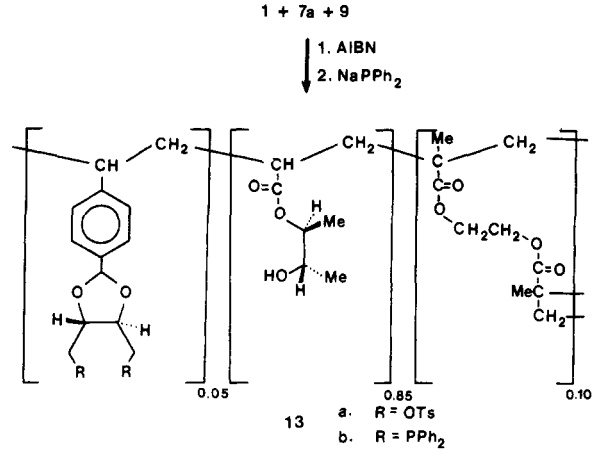


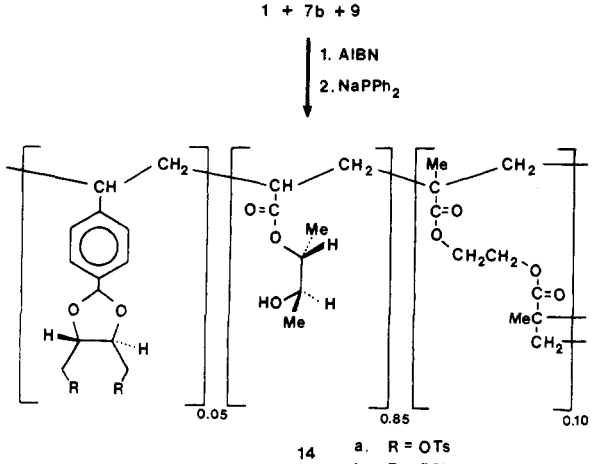
12

Hydrogenations with Polymer-Bound Optically Active Alcohols. All of the cross-linked polymers swelled in both THF and ethanol. Since ethanol would be expected to compete with the polymer-bound alcohols for sites at the catalyst, THF was chosen as the reaction solvent. The polymer-bound catalysts were prepared by stirring the polymer and μ-dichloro-bis(1,5-cyclooctadiene)dirhodium(I) in THF for several hours, and after

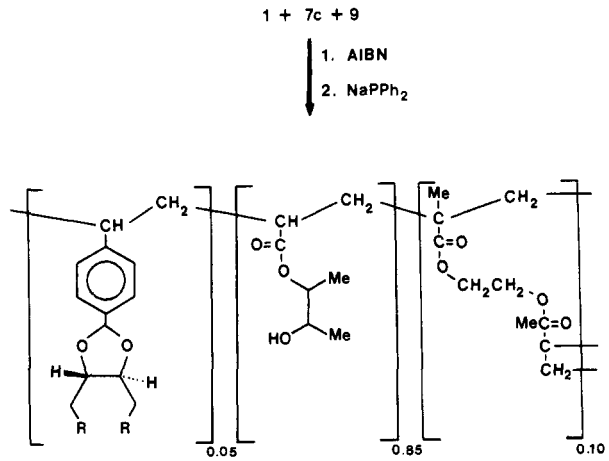
Scheme IV. Polymers Containing DIOP Ligand and Chiral Alcohol Sites



13 a. R = OTs
b. R = PPh_2



14 a. R = OTs
b. R = PPh_2



15 a. R = OTs
b. R = PPh_2

filtration, the yellow catalyst was then transferred under argon to the reaction vessel containing substrate. Solvent was added, and the reaction vessel was pressurized with hydrogen. Amines are known to increase the enantioselectivity of some catalysts, especially phosphinopyrrolidines.[7,8] Since amines could compete with the chiral alcohols for sites at the catalyst, they were not added,

(7) Achiwa, K. *J. Am. Chem. Soc.* **1976**, *98*, 8265.
(8) Ojima, I.; Kogure, T.; Yoda, N. *Chem. Lett.* **1979**, 495.

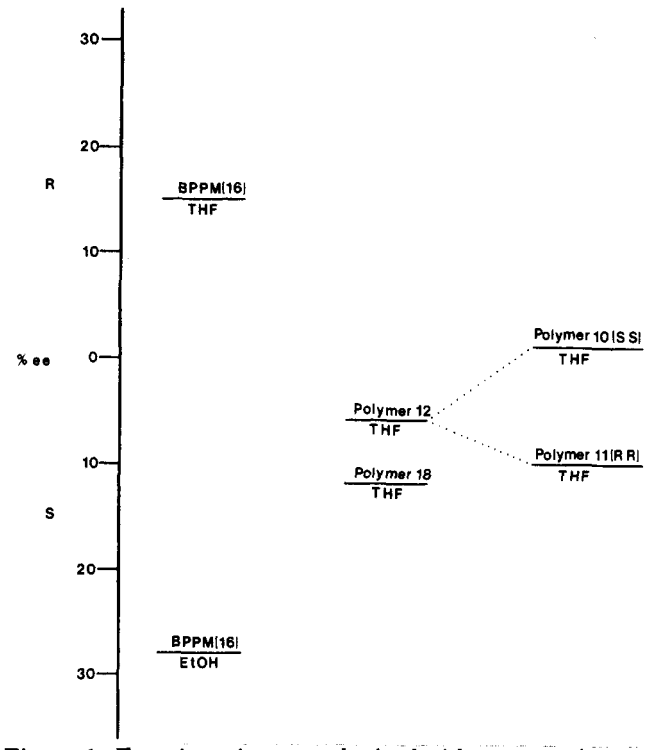


Figure 1. Enantiomeric excess obtained with asymmetric catalysts.

so that the full effect of the optically active alcohol might be observed.

The substrate chosen to probe the effects of the optically active alcohols was 2-acetamidoacrylic acid. The hydrogenation product, *N*-acetylalanine, was converted to the methyl ester by diazomethane and was then analyzed by GLC using a column containing a chiral stationary phase. This allows the direct, accurate determination of the enantiomeric excess from the reactions. This method is superior to analysis by optical methods since it is less sensitive to impurities and can be used to accurately determine enantiomeric excesses even when the product is nearly racemic.

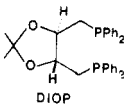
The hydrogenation of 2-acetamidoacrylic acid with phosphinopyrrolidine-containing polymers gave disappointing results. The schematic in Figure 1 is an interesting illustration of a polymer backbone influencing the behavior of a polymer-bound catalyst. The homogeneous hydrogenation in THF with BPPM (**16**) as the ligand proceeded in 15% ee. Switching to ethanol as the solvent led to a reversal of the predominant configuration from *R* to *S*. The use of alcohol-containing polymers in THF gave values intermediate between the two homogeneous results. A difference of 6% ee was noted when the alcohol structure was changed from secondary alcohols to primary alcohols (**12** vs. **18**), with the primary-alcohol-containing polymer more closely mimicking the homogeneous reaction in ethanol. A difference of 11% ee was noted between reactions carried out with polymers **10** and **11** that possess optically active pendent alcohols of opposite configuration.

If ethanol is considered to be a strongly interacting solvent and THF a relatively weakly interacting solvent, then the more bulky secondary alcohol would be expected to interact less efficiently with the catalyst site than primary alcohols as a result of steric interactions. The observed effect in the enantiomeric excess should be the ordering of the polymer catalysts from the weakly interacting pendent alcohols (**12**) to the more strongly interacting alcohols (**18**), with the weakly interacting support more closely resembling the reaction in THF. This is

Table I. Hydrogenation of 2-Acetamidoacrylic Acid with Polymer-Bound DIOP

phosphine	solvent	% ee[a] (config)
DIOP[b]	EtOH	67 (*R*)
DIOP	THF	59 (*R*)
19	THF	26 (*R*)
13b	THF	1 (*R*)
15b	THF	6 (*S*)
14b	THF	10 (*S*)

[a] All reactions were run with a diphosphine/rhodium ratio of 2:1, a substrate/rhodium ratio of 50:1, 15 mL of solvent, and 20 psig of hydrogen at 20 °C. Enantiomeric excesses were determined by GLC. [b] DIOP is



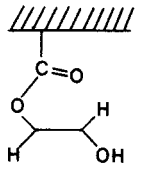
DIOP

consistent with the results.[1] The polymer containing alcohols of *R* chirality (**11**) apparently interact more efficiently with the catalyst site than polymer **10** which contains *S* alcohols, leading to an enantiomeric excess which is nearly that found when the primary-alcohol-containing polymer **18** is used.

Similar results were obtained when DIOP-containing polymers were used as catalysts (Table I). Again the gross effects of the alcohol structure were dominant, with a 16% difference in enantiomeric excess being noted when polymers **15b** and **19** were used. As expected, the result obtained by using polymer **15b**, containing racemic alcohols, fell between the results obtained with polymers containing optically active pendent alcohols (**13b** and **14b**).

Conclusions

The polymer support can have a profound influence on the performance of polymer-supported catalysts. The seemingly minor structural change of replacing **20** with **21**



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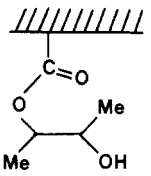

21

as the predominant support structure led to a change of as much as 19% in the observed enantiomeric excess. In addition, the use of the alcohol containing polymer with THF as the reaction solvent can result in enantiomeric excesses that differ by 42% from the results obtained with their homogeneous analogues. This is clear evidence that the pendent groups can act to provide a solvent environment around the catalyst site which is different from that which would be provided by the solvent alone.

The solvent interactions of chiral alcohols with the catalytic site have yet to be fully exploited. It is apparent that the number of phosphine–rhodium catalysts suitable for such an investigation would be limited to those which are relatively insensitive to changes in solvent from alcohol to THF. Unfortunately this insensitivity may indicate that few solvent–catalyst interactions occur at critical steps during the reduction, lessening the chance of significant synergistic interactions to be exploited.

Experimental Section

All reactions were routinely performed under an inert atmosphere of nitrogen or argon. Manipulations involving phosphines dissolved in solvents were carried out in a drybox or by Schlenk techniques. Inert gases were dried and deoxygenated by successive passage through a train of BASF De-ox catalyst and 4A molecular sieves. ^{1}H NMR spectra were obtained on a Varian EM360 spectrometer with tetramethylsilane as the internal standard. Infrared spectra were obtained on a Beckman AccuLab 3 or on a Perkin-Elmer 267 instrument as neat samples or potassium bromide pellets. Optical rotations were measured on a Perkin-Elmer Model 241 polarimeter. Melting points are uncorrected. Elemental analyses were determined by Micro-Tech Laboratories.

Monomers for Polymerizations. Ethylene dimethacrylate (**9**) was purchased and distilled prior to use. 2-*p*-Styryl-4,5-bis-[(tosyloxy)methyl]-1,3-dioxolane (**1**)[2] and *N*-acryloyl-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (**8**)[1] were prepared as described earlier.

(*S*,*S*)-2,3-Butanediol (4a). The diol was prepared as described[6] to yield 36 g (0.40 mol, 73%) of **4a**: bp 78–80 °C (10 mm) [lit.[6] bp 75 °C (10 mm)]; $[\alpha]_D$ +12.9° (neat) [lit.[6] $[\alpha]_D$ +13.2° (neat)].

(2*R*,3*R*)-*O*-(Trimethylsilyl)-2,3-butanediol (5b). A solution of 10.0 g (111 mmol) of (*R*,*R*)-2,3-butanediol in 50 mL of dry tetrahydrofuran was cooled with stirring under nitrogen to −98 °C, and 62.7 mL (1.77 M, 111 mmol) of *n*-butyllithium was added dropwise. To the alkoxide was added 12.1 g (111 mmol) of trimethylsilyl chloride. The mixture was allowed to warm to room temperature and was stirred for 10 h. The mixture was poured into a mixture of 50 mL of saturated sodium bicarbonate solution and 50 mL of brine. The layers were separated, and the aqueous layer was extracted with three 50-mL portions of ether. The combined organic layers were washed with 50 mL of brine and dried over magnesium sulfate. The solvents were removed under reduced pressure and the residue was distilled to yield 13.15 g (73%) of **5b** as a colorless liquid: bp 46–52 °C (12 mm); ^{1}H NMR ($CDCl_3$) δ 0.9 (s, 9 H), 0.9–1.1 (m, 6 H), 2.4 (br s, 1 H), 3.3–3.8 (m, 2 H); $[\alpha]^{25}_D$ −12.67° (*c* 1.7, $CHCl_3$), $[\alpha]^{25}_{546}$ −15.10°, $[\alpha]^{25}_{365}$ −41.09°.

(2*S*,3*S*)-*O*-(Trimethylsilyl)-2,3-butanediol (5a). The monoprotected diol was prepared from (*S*,*S*)-2,3-butanediol as described for the *R*,*R* isomer to yield 25 g (0.15 mol, 69%) of **5a**: bp 64–66 °C, (20 mm); ^{1}H NMR ($CDCl_3$) δ 0.9 (s, 9 H), 1.0–1.3 (m, 6 H), 2.4 (br s, OH), 3.2–3.6 (m, 2 H); $[\alpha]^{22}_D$ +33.7° (*c* 1.7, $CHCl_3$).

***O*-(Trimethylsilyl)-2,3-butanediol (5c).** The monoprotected diol was prepared from 2,3-butanediol as described for the *R*,*R* isomer to yield 24 g (0.15 mol, 68%) of **5c**: bp 66–68 °C (22 mm); ^{1}H NMR ($CDCl_3$) δ 0.9 (s, 9 H), 1.0–1.3 (m, 6 H), 2.4 (br s, OH), 3.2–3.6 (m, 2 H).

(1*R*,2*R*)-1′-Methyl-2′-hydroxypropyl Acrylate (7b). A mixture of 11.1 g (68.3 mmol) of **5b**, 7.8 g (86 mmol) of acryloyl chloride, 16 g of vacuum dried, powdered 3A molecular sieves, and 100 mL of carbon tetrachloride was heated to the reflux temperature for 20 h under nitrogen. The mixture was filtered, and the filter cake was washed well with carbon tetrachloride. After removal of the solvent under reduced pressure, the residue was taken up in 150 mL of tetrahydrofuran and treated with 100 mL of 2 N hydrochloric acid for 2 h at 0 °C. The mixture was poured into 100 mL of brine, and the layers were separated. The aqueous layer was extracted with three 100-mL portions of ether. The organic layers were washed with 50 mL of saturated sodium bicarbonate and 100 mL of brine and dried over potassium carbonate. The solvents were removed under reduced pressure, and the residue was distilled under reduced pressure to yield 4.15 g (42%) of **7b** as a clear liquid: bp 49–51 °C (0.1 mm); ^{1}H NMR ($CDCl_3$) δ 1.2 (d, J = 6 Hz, 3 H), 1.3 (d, J = 6 Hz, 3 H), 2.4 (br s), 3.7 (m), 4.9 (m), 5.6–6.7 (m); IR (neat) 3460, 1720, 1640, 1620, 1200 cm^{-1}; $[\alpha]^{25}_D$ 22.74 ° (*c* 2.7, $CHCl_3$), $[\alpha]^{25}_{546}$ 26.41°, $[\alpha]^{25}_{365}$ −57.05°.

Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 58.22; H, 7.92.

(1*S*,2*S*)-1′-Methyl-2′-hydroxypropyl Acrylate (7a). The *S*,*S* isomer **7a** was prepared as described for the *R*,*R* isomer **7b**: yield 11 g (75 mmol, 58%); bp 40 °C (0.01 mm); ^{1}H NMR ($CDCl_3$) δ 1.2 (d, 3 H, J = 4 Hz), 1.3 (d, 3 H, J = 4 Hz), 3.25 (s, 1 H), 3.5–4.0 (m, 1 H), 4.5–5.1 (m, 1 H), 5.5–6.5 (m, 3 H); $[\alpha]^{22}_D$ +22.9° (*c* 2.94, $CHCl_3$).

1′-Methyl-2′-hydroxypropyl Acrylate (7c). This ester was prepared as described for the *R*,*R* isomer **7b**: yield 9.9 g (69 mmol,

Table II. Elemental Analyses of Polymer-Bound Phosphines

polymer	% P	mmol of P_2/g
10	2.31	0.40
11	2.14	0.33
12	1.74	0.31
13b	2.84	0.44
14b	3.65	0.57
15b	0.99	0.15

Table III. Elemental Analyses of Polymers 13a-15a

polymer	% S	mol % of S_2	mmol of S_2/g
13a	2.93	6.92	0.48
14a	4.01	9.47	0.65
15a	3.01	7.11	0.50

53%); bp 40 °C (0.01 mm); ^{1}H NMR ($CDCl_3$) δ 1.2 (d, 3 H, J = 4 Hz), 1.3 (d, 3 H, J = 4 Hz), 3.3 (s, 1 H), 3.5–4.0 (m, 1 H), 4.5–5.1 (m, 1 H), 5.5–6.5 (m, 3 H).

Copolymerization of 8 with Optically Active Acrylates. Preparation of Polymers 10–12. The following procedure, as described for **10**, was also used for the synthesis of **11** and **12**. To a 50-mL resin kettle equipped with an efficient overhead stirrer, condenser, and nitrogen inlet was added 10 mL of dry deoxygenated benzene. An additional 5 mL of benzene was used to dissolve 0.669 g (4.64 mmol) of **7a**, 0.112 g (0.565 mmol) of ethylene dimethacrylate, and 0.139 g (0.274 mmol) of **8**. The benzene solution was added to the kettle, followed by 30 mg of AIBN dissolved in 2 mL of benzene. The mixture was stirred at 65 °C for 12 h. The resulting polymer was filtered under nitrogen and dried under reduced pressure for 48 h to give 0.78 g (85%) of **10** as a white powder. The elemental analyses are listed in Table II.

Copolymerization of 1 with Chiral Acrylate Comonomers. Preparation of 13a–15a. The following procedure, as exemplified for the synthesis of **13a**, was also used for **14a** and **15a**. Into a resin kettle equipped with an efficient overhead stirrer, condenser, and nitrogen inlet were charged 0.727 g (1.33 mmol) of **1** and 0.10 g of AIBN. To this were added 0.066 g (0.333 mmol) of ethylene dimethacrylate and 2.16 g (15.0 mmol) of **7a** as a solution in 5 mL of dry deoxygenated benzene. An additional 5 mL of benzene was added, and the kettle was heated with a 70 °C bath for 9 h. The polymer was then filtered and dried in vacuo to give 3.01 g (100%) of **13a** as a white powder. The elemental analyses of polymers **13a–15a** appear in Table III.

Phosphination of Polymers 13a–15a. Synthesis of 13b–15b. The following procedure, as exemplified for the synthesis of **13b**, was also used to prepare **14b** and **15b**. To a mixture of 2.22 g (1.07 mmol of tosyl functions) of **13a** in 20 mL of dry deoxygenated THF under a nitrogen atmosphere was added 15 mL of a 1 M solution of sodium diphenylphosphide. The reaction was stirred for 20 h and was then quenched by adding 10 mL of methanol dropwise. The polymer was filtered under nitrogen and dried in vacuo for 48 h to give 1.59 g (57%) of **13b**. The elemental analyses for polymers **13b–15b** appear in Table II.

Materials for Hydrogenation Reactions. Ethanol was dried and degassed by distillation from magnesium ethoxide under nitrogen. Tetrahydrofuran was distilled from sodium–benzophenone ketyl under nitrogen. Hydrogen was purchased from Airco and used as received. 2-Acetamidoacrylic acid was purchased from Aldrich and used as received.

General Procedure for Asymmetric Hydrogenation Using Polymer-Supported Phosphinopyrrolidine Catalysts. To a small-scale catalyst preparation tube[9] under nitrogen were added 140 mg (0.055 mmol of diphosphine) of **11**, 2 mg (0.008 mmol) of μ-dichloro-bis(1,5-cyclooctadiene)dirhodium(I), and 3 mL of dry THF. The mixture was stirred for 4 h and was then filtered. The polymer-bound catalyst was washed with THF and was then transferred to a drybox along with a glass-lined bomb containing 0.5 mmol of substrate. The catalyst was transferred to the bomb, and 15 mL of dry THF was added. The bomb was sealed and pressurized to 800 psig with hydrogen. The pressure was vented, and the bomb was repressurized to 800 psig. After the venting–repressurization procedure was repeated, the bomb was placed at 25 °C with magnetic stirring. The workup consisted of filtration to remove the catalyst and evaporation of the solvent. To the crude product was added an excess of diazomethane in an ether–methanol mixture. The solvent was evaporated to dryness and the product analyzed by GLC (10% SP-300 on Supelcoport 100/120, 6 ft × 0.025 in. stainless-steel column, 110 °C). The percent enantiomeric excess (configuration) of the products from hydrogenation of 2-acetamidoacrylic acid is listed in Figure 1 as follows (for THF): **16**, 15 (*R*); **10**, 1 (R); **12**, 6 (*S*); **11**, 10 (*S*); **18**, 12 (*S*); for THF, **16**, 28 (*S*).

General Procedure for Asymmetric Hydrogenation Using Polymer-Supported DIOP Catalysts. The procedure described for the use of polymer-bound phosphinopyrrolidines was followed, with the exception that the reduction was carried out in a Fischer–Porter low-pressure hydrogenation apparatus at 20 psig of hydrogen at 20 °C. The product was analyzed as before.

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Registry No. 1, 61085-15-2; **4a**, 19132-06-0; **5a**, 77429-75-5; **5b**, 77429-76-6; **5c**, 77481-19-7; **7a**, 77429-66-4; **7b**, 77429-68-6; **7c**, 77481-20-0; **8**, 73300-49-9; **9**, 97-90-5; **10**, 77429-67-5; **11**, 77429-69-7; **12**, 77519-28-9; **13a**, 77429-70-0; **13b**, 77429-71-1; **14a**, 77429-72-2; **14b**, 77429-73-3; **15a**, 77519-29-0; **15b**, 77519-30-3; **16**, 61478-28-2; **18**, 77429-62-0; **19**, 77429-74-4; (*R,R*)-2,3-butanediol, 24347-58-8; (*R,R*)-(±)-2,3-butanediol, 6982-25-8; acryloyl chloride, 814-68-6; 2-acetamidoacrylic acid, 5429-56-1; *N*-acetyl-L-alanine methyl ester, 19914-36-4; *N*-acetyl-D-alanine methyl ester, 3619-02-1; di-μ-chloro-bis(1,5-cyclooctadiene)dirhodium(I), 12092-47-6; DIOP, 37002-48-5.

(9) Glaser, R.; Geresh, S.; Blumenfeld, J. *J. Organomet. Chem.* **1976**, *112*, 355.