Transition-Metal-Catalyzed Asymmetric Organic Synthesis via Polymer-Attached Optically Active Phosphine Ligands. 4. Asymmetric Hydroformylation

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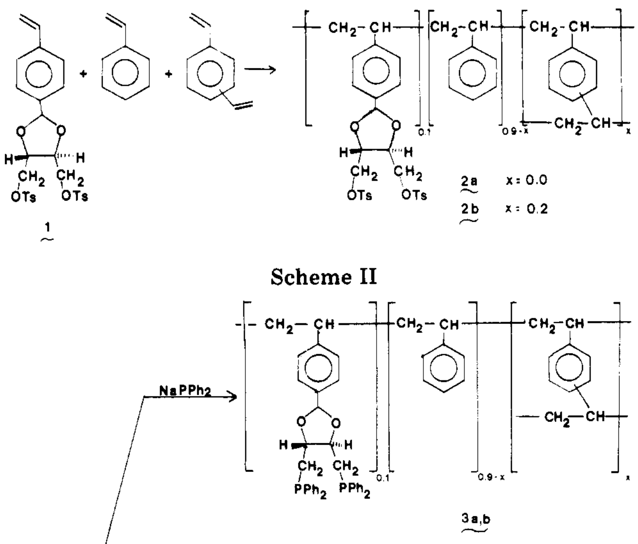
The suspension copolymerization of styrene, divinylbenzene, and 2-(*p*-styryl)-4,5-bis[(tosyloxy)methyl]-1,3-dioxolane (1) gave cross-linked beads containing a 10% incorporation of 1. Treatment of the copolymer with an excess of either sodium diphenylphosphide or the sodium salt of dibenzophosphole gave polymers containing the optically active 4,5-bis[(diphenylphosphino)methyl]-1,3-dioxolane (DIOP) (3) ligand or the corresponding dibenzophosphole (DIPHOL) derivative (4). Exchange of Rh(I)–carbonyl species onto the polymers gave polymer-attached catalysts for hydroformylation. The catalysts were characterized by ^{31}P NMR T_1 studies and by electron-induced X-ray emission analysis. Hydroformylation of various olefins using the polymer-supported catalysts showed unique selectivities and equivalent optical yields when compared to that for homogeneous counterparts. The catalysts could be reused via simple filtration with no loss in rate or selectivity.

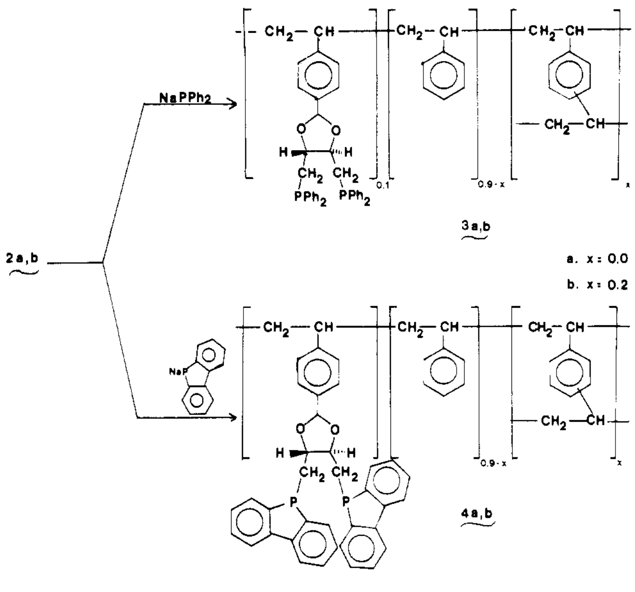
The most challenging problems in the design of polymer-supported homogeneous catalysts[1] lie in the selection of a polymer support compatible with the reaction solvent and the synthesis of ligands at controlled locations on the polymer. A suitably designed catalyst can retain the advantages of a homogeneous catalyst in terms of activity and mild reaction conditions while maintaining the ease of handling and recyclability of a heterogeneous catalyst.

Polymer support of homogeneous species is of particular interest in the field of asymmetric catalysis[2] since it is desirable to be able to recover and reuse both the transition metal and the optically active ligand. Only a few optically active polymer-attached ligands have been synthesized.[2-6] Cross-linked copolymers with polar backbones containing the 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP) ligand which swell in polar solvents have provided optical yields comparable to those of the homogeneous analogues in the hydrogenation of α-amino acid precursors.[2,3] Polystyrenes[4-6] containing the DIOP-type ligand have been used for Rh(I)-catalyzed asymmetric hydrogenation,[4,5] hydrosilylation,[4] and hydroformylation[6] reactions. Hydrogenation of α-substituted styrenes with the polymer-bound catalyst gave lower optical yields (1.5%) than the homogeneous catalyst (15%),[4] while hydrosilylation of acetophenone gave comparable optical yields (58%).[4] The hydroformylation of styrene[6] gave predominantly 2-phenylpropanal in an optical yield of only 2%. In view of the higher optical yields (up to 25% ee) reported for the homogeneous catalyst,[7-9] hydroformylation reactions with catalysts derived from using styrene–divinylbenzene copolymers with 2-(*p*-styryl)-4,5-bis[(tosyloxy)methyl]-1,3-dioxolane (1) were undertaken.

Scheme I



Scheme II



Results and Discussion

Catalyst Synthesis. The optically active styryl monomer 1[2] was copolymerized with styrene or with styrene and various amounts of divinylbenzene by suspension techniques to yield copolymers 2 containing 10 mol % of monomer 1 (Scheme I). Since 1 has been shown[2] to have a reactivity ratio near that of styrene, incorporation into the growing chain should occur randomly and the low percentage of 1 in the monomer feed should ensure isolation of ligand sites in the polymer backbone. Sulfur analysis on 2 confirmed 10 mol % incorporation of 1. Both soluble (**2a**) and 20% cross-linked (**2b**) polymers were prepared in order to determine any possible effect of polymer rigidity on the catalytic reactions. Due to the ease

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(1) For a recent review, see R. H. Grubbs, *CHEMTECH*, 512 (1977).

(2) N. Takaishi, H. Imai, C. A. Bertelo, and J. K. Stille, *J. Am. Chem. Soc.*, **100**, 264 (1978), and references cited therin.

(3) T. Masuda and J. K. Stille, *J. Am. Chem. Soc.*, **100**, 268 (1978).

(4) W. Dumont, J. C. Poulin, T. P. Dang, and H. B. Kagan, *J. Am. Chem. Soc.*, **95**, 8295 (1973).

(5) G. Strukl, M. Bonivento, M. Grazziani, E. Cernia, and N. Palladino, *Inorg. Chim. Acta*, **12**, 15 (1975).

(6) E. Bayer and V. Schurig, *CHEMTECH*, 212 (1976).

(7) G. Consiglio, C. Botteghi, C. Solomon, and P. Pino, *Angew. Chem., Int. Ed. Engl.*, **12**, 669 (1973).

(8) C. Solomon, G. Consiglio, C. Botteghi, and P. Pino, *Chimia*, **27**, 215 (1973).

(9) P. Pino, G. Consiglio, C. Botteghi, and C. Solomon, *Adv. Chem. Ser.*, **No. 132**, 295 (1974).

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Table I. Hydroformylations of Styrene and Vinylcyclohexane

substrate	catalyst	P, psi	T, °C	time, h	isomer ratio (b/n)	ee,[a] %
styrene	5b	1400	80	12	8.4	2.0
	5b	400	40	12	5.2	4.2
	5b[b]	400	40	12	4.8	3.8
	5b	45	25	72	2	11.4
	$Rh(H)(CO)(PPh_3)_3$ + 4DIOP[b,c]	16	40	192	2.2	25.2
	6b	1400	80	12	17	6.1
	6b	400	40	12	21	5.2
	$[Rh(CO)_2Cl]_2$ + DIPHOL[b,d]	1500	80	28	8.4	30.9
vinylcyclohexane	$Rh(H)(CO)(PPh_3)_3$ + 4DIOP[b]	16	50	168	0.025	
	5b	400	40	96	0.305	

[a] Calculated on the basis of optically pure (−)-(R)-hydratropaldehyde; $[\alpha]^{25}{}_D$ −213°.[8] [b] Recycled catalyst. [c] Homogeneous catalyst. [d] Reference 8. [e] Reference 10.

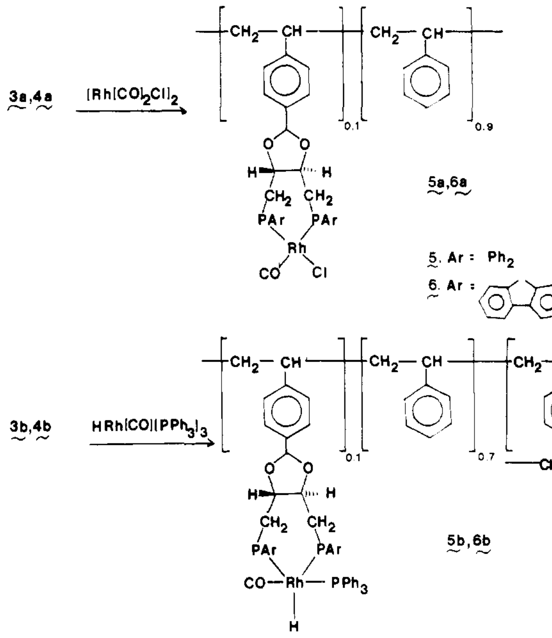
of filtration of the highly cross-linked polymers, the great majority of experiments were performed with these materials.

The polymers were phosphinated by treatment with an excess of sodium diphenylphosphide or the sodium salt of dibenzophosphole to afford polymer-bound ligands **3** (DIOP type) and **4** (DIPHOL type) (Scheme II). The phosphination reactions afforded virtually complete displacement of the tosylate functions as shown by phosphorus and sulfur analysis. Rhodium complexes of DIPHOL-type ligands have been reported[10] to provide high rates and optical yields for asymmetric hydroformylation.

The phosphinated copolymers were allowed to react with 50–75% of the theoretical amount of rhodium(I) species in order to ensure that the excess of phosphorus sites over rhodium would preclude any possibility of monophosphine sites containing rhodium. Cross-linked polymers **3b** and **4b** were treated with tris(triphenylphosphine)hydridocarbonylrhodium(I) while soluble polymers **3a** and **4a** were treated with μ-dichloro-tetracarbonyldirhodium(I) to avoid problems with the excess triphenylphosphine liberated from the hydridocarbonyl species. The resulting polymer-bound catalysts were used for the hydroformylation of a variety of olefinic substrates (Scheme III).

Catalyst Site Distribution. One of the most difficult problems encountered in working with highly cross-linked polymers as catalyst supports lies in the characterization of the nature and structure of the active species. The distribution of monomer **1** within the polymer is assumed to be random from the reactivity ratios. Elemental analysis on phosphinated polymers show essentially complete displacement of tosylate functions and effective phosphorus distribution in the polymer. Since only 75% of the theoretical amount of rhodium is exchanged onto the polymers, however, it is possible that sites deep within the particle are devoid of rhodium. A series of electron-induced X-ray analyses were conducted on whole and sectioned particles to determine whether the rhodium exchange reaction accessed the interior sites. To account for variations in surface roughness, all spectra were normalized to the phosphorus $K_{\alpha,\beta}$ emission. Average values obtained from replicate analyses were compared by using the t test. Results indicated no significant difference in rhodium to phosphorus ratio between data sets. Thus, rhodium is exchanged evenly throughout the polymer. Attempts at mapping the elemental distribution in polymer sections did not afford useful data. X-ray area scans performed with our energy-dispersive spectrometer cannot distinguish from background regions in which analyte concentration falls below 4%.

Scheme III



Hydroformylation Reactions. Styrene was chosen as a substrate for the initial hydroformylation studies since asymmetric hydroformylation of styrene with homogeneous DIOP-[7,9] and DIPHOL-Rh(I)[10] catalysts under a variety of conditions has been reported. Results of several typical runs using polymer-bound catalysts are presented in Table I. The selectivity to aldehydes was essentially complete; in no case were alcohols or reduced olefins detected in the reaction mixture. At higher temperatures polymerization of the substrate was a significant side reaction.

In no case was it possible to duplicate the literature optical yields for styrene. It is interesting to note, however, the trend shown in the ratio of branched to straight-chain aldehyde as a function of the catalyst used. The homogeneous species produces a branched to normal ratio of about 2. Catalyst **5b** causes the ratio to rise to about 6 while **6b** shows a branched to normal ratio of about 20.

The failure to duplicate the optical yields obtained in the literature probably is due to the extreme ease of racemization of the product hydratropaldehyde. Indeed, optically active aldehydes produced in the hydroformylation reaction, when placed back under the reaction conditions, slowly lost their optical activity.

Since the ease of racemization of hydratropaldehyde is due to the acidity of the α hydrogen, the asymmetric hydroformylation of a substrate with a less acidic α hydrogen, vinylcyclohexane, was carried out. Since no data

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(10) M. Tanaka, Y. Ikeda, and I. Ogata, *Chem. Lett.*, 1115 (1975).

Table II. Hydroformylation of Aliphatic Olefins

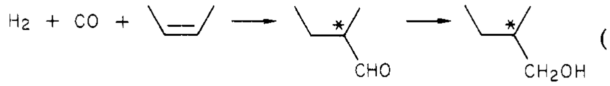
substrate	catalyst	*P*, psi	*T*, °C	time	isomer ratio (b/n)	ee, %
cis-2-butene	5b	45[a]	25	26 days		28.4[b]
	5b	45[a]	50	13 days		9.2[b]
	$Rh(H)(CO)(PPh_3)_3$ + 4DIOP[c]	16[a]	20	30 days		27[d]
trans-2-butene	5b	45[a]	25	21 days		7.2[b]
1-pentene	Rh(CO)(Cl)(DIOP)	400	75	22 h	0.43	
	5a	400	75	20 h	1.05	
	5b	400	75	20 h	0.95	
	5b[e]	400	75	20 h	0.98	
	5b[e]	400	75	20 h	0.94	
	Rh(CO)(Cl)(DIPHOL)	400	75	20 h	0.38	
	6a	400	75	20 h	1.05	
	6b	400	75	20 h	1.03	
	$Rh(H)(CO)(PPh_3)_3$ + 4DIOP[i]	16	25	*h*	0.074	
	f	400	80	21 h	1	
	g	400	80	*h*	0.18	

[a] Includes partial pressure of gaseous olefin. [b] Rotation measured on 2-methyl-1-butanol. [c] Reference 7. [d] Rotation measured on 2-methylbutanal. [e] Recycled catalyst. [f] Polymer-bound non-chiral-chelating diphosphine + $Rh(H)(CO)(PPh_3)_3$.[12] [g] Polymer-bound nonchiral monophosphine + $Rh(H)(CO)(PPh_3)_3$.[11] [h] Reaction time not specified. [i] Reference 9.

were available for the homogeneous asymmetric hydroformylation of vinylcyclohexane, the reaction was run initially by using a catalyst system described for the homogeneous asymmetric hydroformylation of styrene–tris(triphenylphosphine)hydridocarbonylrhodium(I) plus 4 equiv of DIOP. The reaction produced a high yield of straight-chain aldehyde. The amount of branched aldehyde obtained was too small to permit measurement of the optical yield.

One hydroformylation with polymer-bound catalyst **5b** was run to determine whether the changes in regioselectivity noted with styrene would be observed with vinylcyclohexane. A significant increase in the amount of branched aldehyde produced was noted, although the ratio was still greatly in favor of the straight-chain product.

In an effort to find a suitable substrate with which to demonstrate the asymmetric hydroformylation possible with polymer-bound catalysts, we hydroformylated *cis*-2-butene (Table II) (eq 1). This substrate had previously



(1)

been hydroformylated with tris(triphenylphosphine)hydridocarbonylrhodium(I) plus 4 equiv of DIOP to yield 2-methylbutanal in an optical yield of 27%.[7] Due to the volatility of the product aldehyde 2-methylbutanal, in situ reduction to the known 2-methyl-1-butanol with borane–methyl sulfide complex was performed before isolation. When the hydroformylation was carried out with catalyst **5b** under very mild conditions, the alcohol was obtained in an optical yield of 28%. This result clearly shows the polymer-bound Rh(I)–DIOP species are capable of performing as well as the homogeneous analogues for hydroformylation reactions.

Some other features of this reaction are apparent. First, the reaction rate at the temperatures and pressures required for maximum optical yields is extremely slow. Raising the temperature to increase the rates lowers the optical yields. Second, as was seen in the homogeneous studies,[7] the hydroformylation of *trans*-2-butene proceeds to give lower optical yield than that obtainable from the cis isomer. Both the cis and trans isomers are converted to a product of the same configuration. To determine whether changes in regioselectivity between homogeneous and polymer-bound species noted for styrene and vinylcyclohexane were general, we hydroformylated 1-pentene with various catalysts under a variety of conditions (Table II). Since the reactions were run under conditions that favor rapid reaction rates rather than high optical yields, no measurement of the optical yields of these reactions was made. The regioselectivity changes noted between homogeneous and polymer-supported catalysts are not limited to substrates containing cyclic or aromatic side chains. All the polymer-supported species showed a two- to threefold increase in the amount of branched aldehyde produced when compared to the amount obtained from homogeneous catalysts. This change in regioselectivity also has been noted in nonchiral polymer-bound chelating diphosphine catalyst.[12] Both a homogeneous Rh(I)–DIOP-type catalyst[7] at low temperatures and pressures and polymer-bound monophosphine–Rh(I) catalysts[11] at higher temperatures and pressures show much higher selectivity to straight-chain aldehydes than the polymer-supported chelating diphosphine-containing catalysts.

Table III. ^{31}P NMR Measurements

complex	T_1, s	approx line widths, Hz	$\delta(^{31}P)$
DIPHOL	10.5	1	−20.9
4a	1.75	22	−21.2
4b	1.27	140	−22.2
4b with $[Rh(CO)_2Cl]_2$	0.95	250	−22.4
DIOP	10.4	1	−22.3
3a	2.9	20	−23.1
3b	1.40	200	−23.5
3b with $[Rh(CO)_2Cl]_2$	0.95	200	−24.3

Only small changes were noted between either polymer-supported catalyst, whether cross-linked or soluble, in the hydroformylation of 1-pentene. This suggests that a factor other than chain rigidity is important in determining the changes in regioselectivity noted between homogeneous and polymer-supported catalysts.

Catalyst Site Mobility. A series of ^{31}P NMR T_1 measurements were performed on polymers **3a,b** and **4a,b** as well as monomeric DIOP and DIPHOL (Table III). The ^{31}P chemical shifts for all species studied are very

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(11) C. U. Pittman, Jr., and R. M. Hanes, *J. Am. Chem. Soc.*, **98**, 5402 (1976).

(12) C. U. Pittman, Jr., and A. Hirao, *J. Org. Chem.*, **43**, 640 (1978).

similar indicating nearly identical shielding. Considering the large range of ^{31}P chemical shifts (hundreds of ppm), this implies that the local environment about the phosphorus site does not change significantly in any of the ligands studied. Even complexation of Rh(I), presumably directly to the phosphorus ligands, is not reflected in large changes in the ^{31}P chemical shifts. These chemical shift values are similar to previously reported ^{31}P shifts of Rh(I)-bound phosphine complexes.[13]

Unlike the ^{31}P chemical shift, the resonance line widths varied greatly among the various species. Comparison with the T_1 values shows that the line widths are clearly not determined by spin–lattice processes. If the motion at the phosphorus site is slow enough, there could be broadening due to chemical shift anisotropy (CSA) and dipole–dipole (DD) interactions that are not completely motionally averaged. Both the CSA and DD interactions are described by second-rank tensors and thus may be circumvented by application of magic angle spinning (MAS) techniques under appropriate conditions.[14] A recent experiment has applied MAS techniques to ^1H NMR measurements on swollen cross-linked polystyrene in CCl_4 with significant narrowing of the resonance lines.[15] By analogy to this work, it seems resonable that CSA and DD interactions are a probable cause of the large ^{31}P line widths for the polymers.

On the basis of this interpretation, the line width should increase as the macromolecule becomes more rigid and thus its motion slows. For the free ligands in solution, the motion is very rapid and both the CSA and DD interactions average to zero. This produces a narrow ($\sim$1 Hz) isotropically averaged line. Upon polymerization, the motion becomes quite restricted and is not rapid enough to isotropically average CSA and DD effects. This accounts for the large increase in the observed line width. Motion is further restricted by the introduction of the higly cross-linked structure and then by complexation of Rh(I). Both modifications produce an expected increase in line width.

The ^{31}P spin-lattice relaxation times (T_1) are expected to be dominated by ^{31}P–^1H dipole–dipole interaction between ^{31}P and its nearest-neighbor protons. As the immediate electronic environment about the phosphorus site does not appear to change significantly for any of the species, changes in T_1 should primarily reflect motional changes. However, T_1 is not a monotonic function of molecular motion. As molecular motion slows from very rapid (extreme narrowing) to very slow (solid state), T_1 decreases, passes through a minimum, and then increases to a value which may be many minutes in the solid state.[16] Therefore, depending on which side of the minimum in T_1 one is dealing with, a slowing of molecular motion can cause either an increase or decrease in T_1. Both the T_1 and line width data in this study are consistent with a *decrease* in T_1 as molecular motion becomes more hindered. That is, as one proceeds through the series free ligand → soluble polymer → 20% cross-linked polymer → Rh(I)-complexed polymer, molecular motion slows. The greatest change in T_1 and thus in molecular motion occurs upon polymerization with much smaller, but significant, sequential decreases as cross-linking and the rhodium are introduced.

The observed changes in molecular motion may be correlated with the changes in regioselectivity observed in the hydroformylation reaction. Although intuitively it would seem that the polymer-bound catalyst should be more sterically hindered than the homogeneous species, the experimental results are in direct conflict with this view. In every case examined, the polymer-bound catalyst produces significantly higher amounts of branched aldehyde products when compared with those of the homogeneous species. This implies that the catalytically active species exhibits appreciably less steric hindrance around rhodium bound to the polymer, allowing a greater number of rhodium hydride additions to occur to place the more bulky rhodium moiety at the internal carbon of the substrate.

It appears that the restricted motion indicated in the ^{31}P NMR T_1 measurements is responsible, in that the volume swept by phosphine per second is greater for DIOP than polymer-attached DIOP, thereby making the active site in the polymer appear less bulky to the incoming substrate. Thus, the volume excluded from the incoming substrate is larger in the homogeneous catalyst than in the polymer-supported catalyst.

Experimental Section

All reactions were performed under an inert atmosphere, using Schlenk techniques, a glovebag, or a drybox. Benzene and tetrahydrofuran were freshly distilled from sodium–benzophenone ketyl before use. Styrene and vinylcyclohexane were washed with sodium hydroxide solution and water, dried, and distilled before use. *cis*-2-Butene (Matheson) was used as a received. 1-Pentene was passed through activated alumina and distilled before use. Synthesis gas (1:1 H_2–CO) was purchased as a custom mixture from Linde and used as received. ^1H NMR spectra were measured on Varian EM-360A or JEOL MH-100 spectrometers. Infrared spectra were measured on a Perkin-Elmer 267 instrument. Hydridocarbonyltris(triphenylphosphine)rhodium(I)[17] and 2-(*p*-styryl)-4,5-bis[(tosyloxy)methyl]-1,3-dioxolane (1)[2] were prepared by literature methods.

Polymerization Reactions. General procedures for soluble and cross-linked polystyrenes containing 1 are given below. Conversions were generally greater than 95%.

(1) Non-cross-linked Polymer (2a). To a well-stirred solution of 0.11 g of polyvinyl alcohol and 0.02 g of calcium carbonate in 110 mL of water heated to 50 °C was added a solution of 5.44 g (10.0 mmol) of 1, 9.27 g (90.0 mmol) of styrene, and 0.20 g of benzoyl peroxide. The temperature was raised to 95 °C for 12 h. The resulting beads were filtered, washed with water and methanol, and dried under reduced pressure. Anal. Calcd for 10% incorporation of 1: S, 4.32. Found: S, 4.46.

(2) Cross-linked Polymer (2b). To a well-stirred solution of 0.11 g of polyvinyl alcohol and 0.02 g of calcium carbonate in 110 mL of water heated to 50 °C was added a solution of 5.44 g (10.0 mmol) of 1, 7.22 g (70.0 mmol) of styrene, 2.60 g (20.0 mmol) of divinylbenzene, and 0.2 g of benzoyl peroxide in 10 mL of xylene. The temperature was raised to 95 °C and the reaction mixture was stirred vigorously for 12 h. The resulting beads were filtered and washed with 200 mL of water. Further washing with 50 mL each of 50:50 water–methanol, methanol, 50:50 methanol–dichloromethane, and dichloromethane followed by drying under reduced pressure at 65 °C afforded the desired copolymer. Anal. Calcd for 10% incorporation of 1: S, 4.17. Found: S, 3.99.

Phosphination Reactions. (1) Sodium Diphenylphosphide. Both copolymers **2a** and **2b** were phosphinated by stirring 4.0 g of copolymer (5.2 mmol of tosyl functions) with a solution of sodium diphenylphosphide (10.4 mmol) in tetrahydrofuran

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[13] K. S. Y. Lau, Y. Becker, F. Huany, N. Baenzinger, and J. K. Stille, *J. Am. Chem. Soc.*, **99**, 5664 (1977). Note that the chemical shift convention used in this reference is not as stated: in fact, negative chemical shifts are upfield (more shielded) from 85% H_3PO_4.

[14] M. Mehring, "High Resolution NMR Spectroscopy in Solids", P. Diehl, E. Fluck, and R. Kosfeld, Eds., Springer-Verlag, New York, N. Y., 1976.

[15] D. Doskocilova, B. Schneider, and J. Jakes, *J. Magn. Reson.*, **29**, 79 (1978).

[16] C. P. Slichter, "Principles of Magentic Resonance", Harper and Row, New York, N.Y., 1963, Chapter 5.

[17] N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, **15**, 59 (1974).

Table IV. Elemental Analysis of Phosphinated Polymers

polymer	% P calcd	% P found	polymer	% P calcd	% P found
3a	4.10	4.01	**4a**	4.11	4.23
3b	3.96	3.94	**4b**	3.97	3.84

prepared in the usual manner.[18] The reaction was allowed to proceed for 5 days at ambient temperature.

To the cross-linked polymer sample 5 mL of methanol was added to destroy the excess anion. The mixture was then poured into 200 mL of oxygen-free 50:50 acetone–water, stirred for 12 h under argon, and filtered under argon. The beads were then stirred for 12 h in 200 mL of oxygen-free benzene, filtered, and then stirred for 24 h in 200 mL of oxygen-free methanol. The beads were then filtered and dried under reduced pressure for 24 h.

The mixture containing the un-cross-linked polymer sample was poured into 400 mL of oxygen-free 50:50 acetone–water and was stirred for 12 h during which time the polymer precipitated as a tacky brown solid. The liquid was decanted and 400 mL of oxygen-free methanol was added to the residue. The mixture was stirred under argon for 3 days during which time the polymer became a free-flowing white powder. The powder was filtered and dried under reduced pressure for 48 h. The polymer was dissolved in benzene, filtered to remove a small amount of insoluble material, and precipitated with methanol. The resulting polymer was filtered and dried under reduced pressure.

(2) Lithium and Sodium Dibenzophosphole. The copolymers were phosphinated by stirring 2.0 g of copolymer (2.6 mmol of tosyl functions) at room temperature for 5 days under argon with lithium dibenzophosphole prepared by treating 1.39 g (5.40 mmol) of *P*-phenyldibenzophosphole[19] with 1.0 g of lithium wire in 25 mL of tetrahydrofuran for 5 h at room temperature. The excess lithium was removed with a forceps and 0.58 mL (5.4 mmol) of *tert*-butyl chloride was added to destroy the phenyllithium formed. The solution was heated to the reflux temperature for 10 min and allowed to cool to room temperature before the polymer was added. The reactions were worked up as described for the sodium diphenylphosphide phosphinations.

Alternatively, the copolymers were treated with an excess of the sodium salt of dibenzophosphole prepared by treating 5*H*-dibenzophosphole[20] with sodium in liquid ammonia as described previously.[18] The workup was the same as in the lithium case.

Exchange Reactions between Polymer-Bound Phosphines and Hydridocarbonyltris(triphenylphosphine)rhodium(I). Phosphinated polymers were exchanged with hydridocarbonyltris(triphenylphosphine)rhodium(I) such that the amount of rhodium exchanged onto the polymer was between 50 and 75% of the theoretical amount. A typical procedure is as follows.

Under an argon atmosphere were placed 0.31 g (0.34 mmol) of hydridocarbonyltris(triphenylphosphine)rhodium(I) and 1.00 g (0.68 mequiv of diphosphine) of **3b**. The solids were degassed by two vacuum/argon cycles, and 100 mL of degassed benzene was added. The mixture was stirred at 50 °C for 20 h and then filtered under nitrogen. The polymer was transferred to a Soxhlet thimble and extracted continuously under argon with benzene for 24 h. The polymer was dried under reduced pressure to yield 1.03 g (91%) of yellow powder. The polymer was kept either under vacuum or under argon until use.

Electron Microprobe. Qualitative analysis of polymer beads was accomplished by using a Hitachi HHS-2R scanning electron microscope equipped with a lithium-drifted silicon X-ray detector. Samples were prepared either by dusting polymer particles onto double-stick tape or by dispersing the particles in silver paint. Paint-mounted beads were polished with an aqueous alumina slurry to remove surface layers and permit examination of their interior. All samples were carbon coated to minimize charging.

Characteristic X-radiation was isolated with a single-channel analyzer and used to modulate oscilloscope brightness for elemental mapping. Since the probe beam and oscilloscope are rastered synchronously, sample composition can be determined as a function of position. Peak areas, for comparing internal and external rhodium concentrations, were calculated from display photographs by triangulation after background subtraction.

Hydroformylation Experiments. (1) Styrene and Vinylcyclohexane (Homogeneous Catalysts). A low-pressure carbonylation tube was immersed in concentrated nitric acid for 24 h, washed with distilled water, immersed in concentrated ammonium hydroxide for 24 h, washed with deionized water until the washings were neutral, and dried at 100 °C for 4 h. To the tube was added 0.498 g (1.00 mmol) of (+)-DIOP and 0.23 g (0.25 mmol) of hydridocarbonyltris(triphenylphosphine)rhodium(I). The solids were degassed by two vacuum/argon cycles, and a degassed solution of 5 mL of benzene and 3.0 mL (26 mmol) of styrene was injected through a septum. The tube was twice filled and evacuated with a 1:1 mixture of hydrogen and carbon monoxide (synthesis gas) and then pressurized to 45 psi with the gas mixture. The mixture was stirred at 25 °C for 72 h. The pressure was vented and the benzene was removed under reduced pressure. The remaining mixture was vacuum transferred to eliminate the catalyst and then analyzed by GC (20% Carbowax 20M, 10 ft, 180 °C) to determine conversion and isomer ratio. The ratios thus obtained were used to calculate the optical yield from the observed optical rotation. The hydroformylation of vinylcyclohexane was done in a similar manner.

(2) Styrene (Polymer-Supported Catalyst). Into a carbonylation tube treated as above and prefilled with argon was placed 0.25 g (0.11 mequiv of Rh) of **5b**. The tube was twice evacuated and filled with synthesis gas, and a degassed mixture of 3.0 mL (26 mmol) of styrene in 6 mL of benzene was injected through a septum. The mixture was placed under 45 psi of synthesis gas and stirred at room temperature for 72 h. The solution was filtered to remove the catalyst and the benzene was removed under reduced pressure. The remaining product was vacuum transferred to remove a small amount of colored impurities and analyzed as described above.

(3) *cis*-2-Butene (Polymer Catalyst). Into an argon-filled carbonylation tube treated as above was placed 0.30 g (0.15 mequiv of Rh) of **5b**. The tube was twice evacuated and filled with argon. Degassed benzene (10 mL) was then added. The tube was then pressurized to 1 atm with *cis*-2-butene and then 2 atm of synthesis gas was added (total pressure 3 atm). The pressure was maintained at 3 atm by periodic additions of synthesis gas as the mixture was stirred at room temperature for 26 days. The mixture was filtered to remove the catalyst, and to the filtrate were added 5 mL of anhydrous ether and 5 mL of anhydrous tetrahydrofuran. The solution was cooled to 0 °C and 0.7 mL (7 mmol) of borane–methyl sulfide complex was injected through a septum. The mixture was allowed to warm to room temperature and was stirred for 12 h. The mixture was hydrolyzed by dropwise addition of 10 mL of water followed by stirring at room temperature for 30 min. The layers were separated and the aqueous layer was extracted three times with 10 mL of ether. The combined organic layers were washed twice with 20 mL of brine and dried over magnesium sulfate. The solvents were removed under reduced pressure, and GC analysis (Carbowax 20M, 10 ft, 110 °C) on the residue confirmed production of the desired alcohol by comparison to an authentic sample. The sample for optical rotation was obtained by Kugelrohr distillation of the residue.

(4) 1-Pentene and Other Substrates at High Pressure. Reactions run at greater than 4 atm were performed in glass-lined Monel bombs. The reaction temperature was maintained by a stirred oil bath containing a Thermo-Watch, and the reaction mixtures were stirred with a magnetic stirrer. A typical procedure is given below.

Under an argon atmosphere 0.19 g (0.09 mmol of Rh) of **5b** was added to a glass-lined bomb. Benzene (10 mL), 1.0 mL (9.1 mmol) of 1-pentene, and 0.25 mL (2.1 mmol, internal standard) of *m*-xylene were added, and the bomb was closed. The bomb was then pressurized to 400 psi with synthesis gas for 5 min, and then the pressure was released. The bomb was repressurized to 400 psi and placed in an oil bath at 75 °C for 20 h. The bomb was removed from the bath and cooled to ice temperature before venting the pressure. The catalyst was filtered from the reaction mixture and the filtrate was analyzed by GC (Carbowax 20M, 10

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ft, 115 °C) to determine the isomer ratio.

Recycle Experiments. For experiments in which the polymeric catalyst was reused, the bomb containing the previous reaction was brought into an argon-filled drybox prior to venting the pressure. The catalyst was then removed from the reaction mixture by filtration and was washed well with deoxygenated benzene. The catalyst was placed in a fresh glass liner, and fresh substrate and solvent were added. The reaction and workup were carried out as previously described.

^{31}P NMR. All ^{31}P experiments were performed on a highly modified[21] Bruker HFX-90 spectrometer interfaced to a Nicolet 1180B data system, operating at 36.4 MHz. Samples were run in 15-mm tubes (active volume only) at ambient temperature, about 35 °C, under conditions of proton-noise decoupling. Field/frequency lock was maintained via a capillary of C_4F_8 external to the ^{31}P insert.[22]

The *i*th chemical shift is $\delta_i = (\nu_i - \nu_r)/\nu_r$, where ν_i is the resonant frequency of the *i*th spin isochromat and ν_r is the resonant frequency of the reference, an external sample of 85% H_3PO_4. When this convention is used, an increase in chemical shift is an increase in resonant frequency and a decrease in shielding.

Spin–lattice relaxation time (T_1) measurements were performed by using a modified form of the inversion recovery (IRFT)[23] often referred to as fast inversion recovery Fourier transfer (FIRFT).[24] Radio-frequency phase alternation was used to eliminate rf pulse defect errors and coherent noise.[25] T_1 data were analyzed by a three-parameter fit.[26]

All samples were run in 15-mm tubes prepared under an inert atmosphere. Free ligands and soluble polymers were run as solutions in degassed benzene. Cross-linked polymers were run swollen in degassed benzene. Rhodium was introduced as $[Rh(CO)_2Cl]_2$ to avoid interferences in the region of interest.

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Registry No. 1, 61085-15-2; **2a**, 70703-27-4; **2b**, 70703-28-5; styrene, 100-42-5; divinylbenzene, 1321-74-0; sodium diphenylphosphide, 4376-01-6; lithium dibenzophosphole, 70703-24-1; *P*-phenyldibenzophosphole, 1088-00-2; dibenzophosphole sodium salt, 70703-25-2; hydridocarbonyltris(triphenylphosphine)rhodium(I), 64665-44-7; *μ*-dichloro-tetracarbonyldirhodium(I), 14523-22-9; vinylcyclohexane, 695-12-5; (*R*)-hydratropaldehyde, 38235-74-4; DIPHOL, 70703-26-3; (+)-DIOP, 37002-48-5; (*Z*)-2-butene, 590-18-1; (*E*)-2-butene, 624-64-6; 1-pentene, 109-67-1.

Supplementary Material Available: Data from electron-induced X-ray emission analysis (3 pages). Ordering information is given on any current masthead page.

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Reactions of Esters with Phosphorus Ylides. 3.[1,2] Direct Conversion into Branched Olefins

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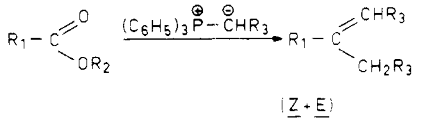
Aromatic and aliphatic esters can be directly converted into the corresponding isopropenyl compounds by reaction with methylenetriphenylphosphorane. In the case of aliphatic esters "salt-free" conditions are required to effect selective conversions. Reaction with other *n*-alkylidenetriphenylphosphoranes likewise affords the corresponding branched olefins as mixtures of *E* and *Z* isomers. *α*-Branched or stabilized phosphoranes do not react in this way. The reaction has also been extended to ylides containing (protected) functional groups. Examples are presented in which esters are reacted with ethoxycarbonyl-, carboxylate-, and ethylenedioxy-substituted phosphoranes and thereby converted into branched olefins containing these functional groups twice. The influence of ester structure and reaction conditions upon yield and product distribution is discussed.

Recently, the direct conversion of ester into isopropenyl groups by the action of methylenetriphenylphosphorane was described.[3] More generally this conversion can be depicted as the reaction in which an ester is allowed to react with an excess of alkylidenetriphenylphosphorane and thereby converted into a branched olefin in such a way that both oxygens in the original ester are replaced by the phosphorane alkyl moiety and that a double bond is introduced at the position of the original carbonyl group.



Under the conditions originally employed [excess of phosphorane in dimethyl sulfoxide (Me_2SO)] several aromatic esters afforded good yields of olefins, but with aliphatic esters appreciable amounts of acylated phosphoranes 4 (Scheme I) were also formed.[3] Further study led to a proposal for the mechanism of this ester–ylide reaction.[1] Inspection of this mechanism (vide infra) indicated several possibilities to improve the yield and to affect the product distribution of the reaction. The influence of solvent, temperature, the presence of dissolved

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