the anolyte solution consisted of 200 mL of dry acetonitrile containing 0.1 M tetra-*n*-butylammonium bromide as electrolyte. The catholyte consisted of 200 mL of the above solution plus 0.882 g (0.004 mol) of chlorodiphenylphosphine. The anolyte and catholyte solutions were circulated from separate flasks by ECO Model 920 Teflon pumps and were continuously flushed with dry nitrogen. Yields were calculated by adding triphenylphosphine as an internal standard and subjecting the resulting solution to gas chromatographic analysis on a 5 ft × $^1/_8$ in. 3% SE30 on 80–100 mesh Chromosorb WHP column at 215. The detector response had been calibrated by an authentic sample of tetraphenyldiphosphine.[18] Tetraphenyldiphosphine was isolated by removing the solvent in vacuuo, dissolving the resulting oil in benzene and running this solution through a short silica gel column to remove the electrolyte salt, followed by recrystallization from benzene–hexane: mp 121 °C (lit.[19] 122 °C); ^{31}P NMR −14.4 ppm (Me_2SO-d_6). The isolated material was compared with authentic tetraphenyldiphosphine by observing identical gas chromatographic retention times and by spiking the isolated sample with authentic material and observing only a single peak. This spiking technique was also used in ^{31}P NMR analysis with the observation of only one resonance.

Acknowledgment. Support of this work by the Office of Naval Research is gratefully acknowledged.

Registry No. Ia, 1079-66-9; Ib, 1079-65-8; Ic, 20472-53-1; Id, 13360-92-4; phenol, 108-95-2.

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Platinum-Catalyzed Asymmetric Hydroformylation with a Polymer-Attached Optically Active Phosphine Ligand

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A chiral ligand, analogous to 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(dibenzophospholyl)butane (DBP-DIOP) (**5**), attached to linear and to cross-linked polymer supports was obtained either by copolymerization of (4*R*,5*R*)-2-(*p*-styryl)-4,5-bis[(tosyloxy)methyl]-1,3-dioxolane (**2**) with styrene (or with styrene and divinylbenzene) followed by phosphination with lithium dibenzophosphole or directly by copolymerization of (4*R*,5*R*)-2-(*p*-styryl)-4,5-bis[(dibenzophospholyl)methyl]-1,3-dioxalane (**4**) with styrene (or with styrene and divinylbenzene). Exchange of Pt(II) onto the polymers followed by the addition of stannous chloride gave polymer-supported catalysts which were used for asymmetric hydroformylation of a variety of olefins. Hydroforymlations utilizing the polymer-supported catalysts showed comparable rates and gave nearly the same optical yields as the homogeneous analogue **5**. However, lower branched to normal ratios were obtained from the polymer-supported catalysts, especially with those which were cross-linked. The soluble polymer-supported catalyst could be recovered by precipitation with diethyl ether and filtration. Reuse of this catalyst showed no loss in rate or selectivity. Recycling of the cross-linked polymer was achieved by simple filtration with slight loss in rate but no loss in selectivity.

The successful development of chiral transition-metal complexes for asymmetric synthesis has been followed by attempts to attach such complexes onto an insoluble polymeric support. The primary advantage of a polymer-supported catalyst is the ability to recover and reuse both the transition metal and the chiral optically active ligand.[1,2] However, very few chiral, polymer-bound ligands have been synthesized.[3-22] Most of these polymer-supported catalysts have been used for asymmetric hydrogenations; the few asymmetric hydroformylations reported generally gave low optical yields.[10,17] The asymmetric hydroformylation of styrene promoted by a catalyst obtained by supporting [2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP)]-$PtCl_2$-$SnCl_2$ onto a Merrifield resin gave the corresponding hydrotropaldehyde in 29% ee.[4a] However, attempts to carry out the reaction in the presence of a similarly supported [2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(dibenzophospholyl)butane (DBP-DIOP)]-$PtCl_2$-$SnCl_2$ catalyst failed to give reasonable conversions to aldehydes.[22] We were able to carry out an asymmetric hydroformylation reaction of styrene with an [*N*-(*tert*-butoxycarbonyl)-(2*S*,4*S*)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (BPPM)]-$PtCl_2$-$SnCl_2$ catalyst bound to polystyrene beads.[3] Although branched to normal ratios were low (~0.5), the corre-

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Table I. Asymmetric Hydroformylation of Styrene[a]

run	cat.	time, h	convn, %	selectivity,[b] %	b/n[c]	ee,[d] %
1	[(−)-DBP-DIOP]$PtCl_2$ + $SnCl_2{\cdot}2H_2O$	16	100	80	3.4	64
2	[(−)-DBP-DIOP]$PtCl_2$ + $SnCl_2{\cdot}2H_2O$	3	54	82	3.4	64
3	[(−)-DBP-DIOP]$Pt(SnCl_3)Cl$	3	45	83	3.8	65
4	[(−)-DBP-DIOP]$Pt(SnCl_3)Cl$	18	100	83	3.8	64
5[e]	**8a** + $SnCl_2{\cdot}2H_2O$	24	62	81	1.6	65
6	**8b** + $SnCl_2{\cdot}2H_2O$	24	60	81	1.0	56
7[f]	**8b** + $SnCl_2{\cdot}2H_2O$	24	51	81.6	1.0	56
8[f]	**8b** + $SnCl_2{\cdot}2H_2O$	24	46	81.6	1.0	57
9[f]	**8b** + $SnCl_2{\cdot}2H_2O$	24	40	81.7	1.0	57

[a] $SnCl_2/Pt$ = 2.5; P_2/Pt = 1.7; H_2/CO = 1; T = 60 °C; P = 2600 psi. [b] Selectivity = hydroformylation products/total products. [c] Branched/normal ratio. [d] Determined by ^1H NMR using $Eu(hfc)_3$ as chiral shift reagent. The (*S*)-(+) enantiomer was obtained in excess. [e] Identical results were obtained upon three recycles of the catalyst with addition of $SnCl_2{\cdot}2H_2O$ each time. [f] The catalyst was recycled from the previous run, and $SnCl_2{\cdot}2H_2O$ was added.

Table II. Asymmetric Hydroformylation of Vinyl Acetate[a]

run	cat.	time, h	convn, %	vol ald,[b] %	b/n[c]	ee,[d] %
1	[(−)-DBP-DIOP]$PtCl_2$ + $SnCl_2{\cdot}2H_2O$	42	30	55	5.2	61
2	[(−)-DBP-DIOP]$Pt(SnCl_3)Cl$	42	30	22	3.3	60
3[e]	**8a** + $SnCl_2{\cdot}2H_2O$	42	22	21.7	1.0	58
4	**8b** + $SnCl_2{\cdot}2H_2O$	100	22	38	1.0	57
5[f]	**8b** + $SnCl_2{\cdot}2H_2O$	100	17	38	1.0	56
6[f]	**8b** + $SnCl_2{\cdot}2H_2O$	100	10	38	1.0	56
7[f]	**8b** + $SnCl_2{\cdot}2H_2O$	100	8	38	1.0	56

[a] $SnCl_2/Pt$ = 2.5; P_2/Pt = 1.7; H_2/CO = 1; T = 60 °C; P = 2700 psi. [b] % volatile aldehydes = acrolein + propanal/total aldehydes. [c] Branched/normal ratio. [d] Determined by ^1H NMR using $Eu(tfc)_3$ chiral shift reagent. The (*S*)-(+) enantiomer was obtained in excess. [e] Identical results were obtained upon three recycles of the catalyst with addition of $SnCl_2{\cdot}2H_2O$ each time. [f] The catalyst was recycled from the previous run, and $SnCl_2{\cdot}2H_2O$ was added.

sponding hydrotropaldehyde was obtained with the highest optical purity (>70%) that has been achieved with a polymer-supported chiral catalyst.[3]

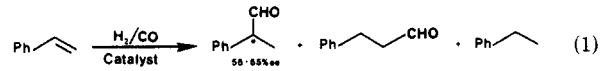
We wish to describe a method of supporting the [DBP-DIOP]–$PtCl_2$–$SnCl_2$ catalyst onto both soluble and cross-linked polystyrene structures and the use of these two supports in the asymmetric hydroformylation of some prochiral olefins.

Results and Discussion

Catalyst Synthesis. Copolymers **1** were synthesized by two different routes (Scheme I). The optically active styryl monomer **2**[14] was copolymerized with styrene in benzene solution or with styrene and divinylbenzene by suspension polymerization techniques. Polymers **3** were then phosphinated with an excess lithium dibenzophosphole to yield **1**. Alternatively, dibenzophosphole monomer **4** was obtained from the hydrolysis of enantiomerically pure (−)-DBP-DIOP (**5**)[23] (vide infra) to diol **6** in acidic medium followed by acetalyzation with *p*-vinylbenzaldehyde.[24] Copolymerization of enantiomerically pure **4** (vide infra) with styrene or styrene and divinylbenzene gave **1** in good yields. On the assumption that monomers **2** and **4** have reactivity ratios near that of styrene,[14] incorporation of the chiral monomers into the growing chain should occur randomly. Phosphorus analysis on **1a** and **1b** confirmed that charging 10 mol % of the monomer into the feed yielded a copolymer containing approximately 10 mol % incorporation of **2** and **4**, respectively.

The phosphole-containing copolymers were allowed to react with bis(dibenzonitrile)dichloroplatinum(II),[25] and the resulting polymer-supported catalysts **8** were used in the presence of stannous chloride dihydrate to catalyze the hydroformylation of a variety of olefinic substrates.

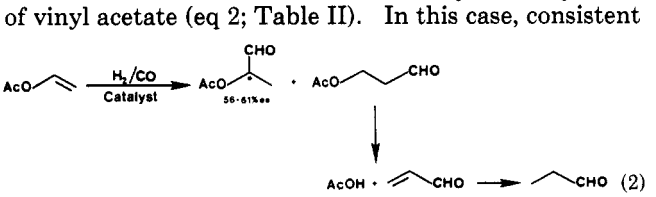
Hydroformylation Reactions. Initially the hydroformylation reactions were carried out by using the homogeneous catalyst [(−)-DBP-DIOP]$PtCl_2$ in the presence of excess stannous chloride in order to compare the results of hydroformylation of styrene with the polymer-supported analogues (eq 1).



(1)

High conversions of styrene were observed to yield predominantly the branched aldehyde in moderately good enantiomeric excess (ee) (Table I). No racemization of the branched product occurred under the reaction conditions. The use of preformed [(−)-DBP-DIOP]Pt-$(SnCl_3)Cl$ catalyst did not influence the course of the reaction significantly. High conversions also were obtained when the soluble polymer-supported catalyst **8a** was used, but the branched to normal ratio was considerably lower. Recycling this catalyst showed no changes in the reaction rate or selectivity. When cross-linked polymer **8b** was used, a further decrease of the branched to normal ratio was noticed, accompanied also by a slight decrease in the ee. A surprising result was that in this case, the reaction rate suffered a drop after each catalyst recycle. It is possible that changes in the polymer are responsible for such a decrease in activity (vide infra).

A similar trend was observed in the hydroformylation of vinyl acetate (eq 2; Table II). In this case, consistent



(2)

with the results obtained with a rhodium catalyst,[26] the linear aldehyde partially decomposed under the reaction conditions to give acetic acid and acrolein, which in turn

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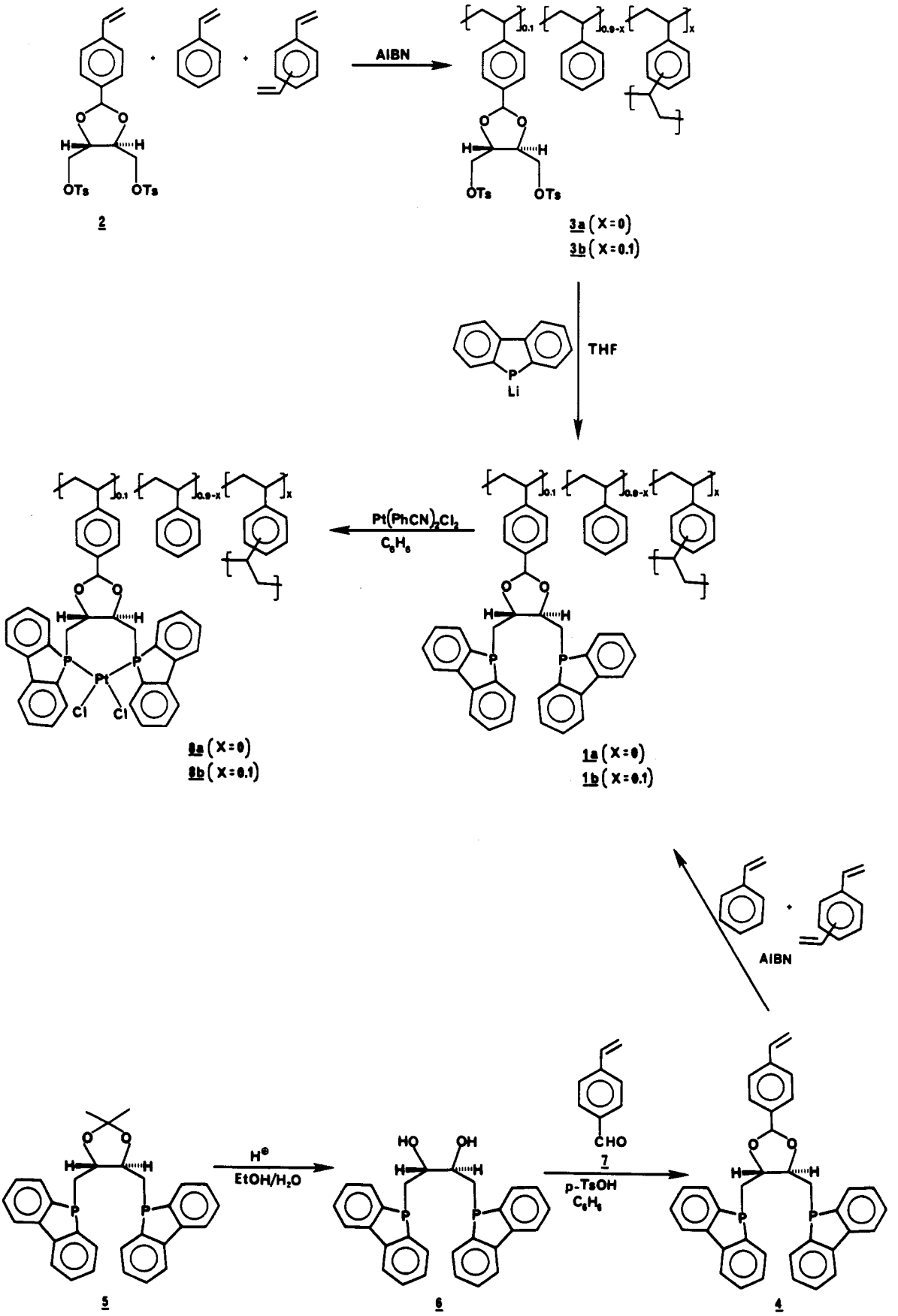
Scheme I



was partially hydrogenated to propanal. The reaction was slow even under homogeneous conditions, and use of the preformed [(−)-DBP-DIOP]Pt($SnCl_3$)Cl complex decreased the rate of decomposition of the linear aldehyde. Soluble polymer **8a** was recycled three times without loss of activity, whereas a decrease of activity upon recycle was recorded in the case of the cross-linked polymer **8b**. The 2-acetoxypropanal obtained had the highest enantiomeric

Table III. Asymmetric Hydroformylation of *N*-Vinylphthalimide[a]

run	cat.	time, h	convn, %	selectivity,[b] %	b/n[c]	ee,[d] %
1	[(−)-DBP-DIOP]$PtCl_2$ + $SnCl_2 \cdot 2H_2O$	60	60	37	6.0	68
2	[(−)-DBP-DIOP]$Pt(SnCl_3)Cl$	60	40	57	6.0	70
3[e]	**8a** + $SnCl_2 \cdot 2H_2O$	70	52	45	3.5	62
4	**8b** + $SnCl_2 \cdot 2H_2O$	100	30	40	2.4	60
5[f]	**8b** + $SnCl_2 \cdot 2H_2O$	100	24	39	2.5	58
6[f]	**8b** + $SnCl_2 \cdot 2H_2O$	100	18	40	2.5	58
7[f]	**8b** + $SnCl_2 \cdot 2H_2O$	100	10	40	2.5	58

[a] $SnCl_2/Pt$ = 2.5; P_2/Pt = 1.7; H_2/CO = 1; T = 60 °C; P = 2700 psi. [b] Selectivity = hydroformylation products/total products. [c] Branched/normal ratio. [d] Determined by ^1H NMR using $Eu(hfc)_3$ as chiral shift reagent. The (*S*)-(−) enantiomer was obtained in excess. [e] Identical results were obtained upon three recycles of the catalyst with addition of $SnCl_2 \cdot 2H_2O$ each time. [f] The catalyst was recycled from the previous run, and $SnCl_2 \cdot 2H_2O$ was added.

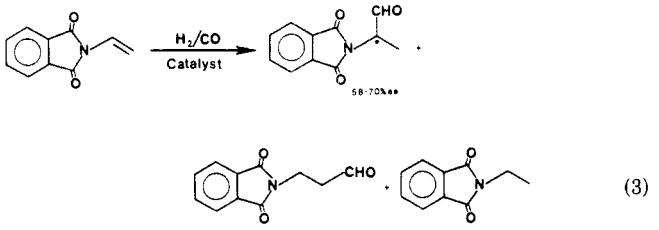
Table IV. Asymmetric Hydroformylation of Norbornene[a]

run	cat.	time, h	convn, %	selectivity,[b] %	ee,[c] %
1	[(−)-DBP-DIOP]$PtCl_2$ + $SnCl_2 \cdot 2H_2O$	3	100	88	26
2	[(−)-DBP-DIOP]$Pt(SnCl_3)Cl$	5	38	87	25
3[d]	**8a** + $SnCl_2 \cdot 2H_2O$	3	100	86	20
4	**8b** + $SnCl_2 \cdot 2H_2O$	4	100	87	20
5[e]	**8b** + $SnCl_2 \cdot 2H_2O$	4	85	86	19
5[e]	**8b** + $SnCl_2 \cdot 2H_2O$	4	78	86	20

[a] $SnCl_2/Pt$ = 2.5; P_2/Pt = 1.7; H_2/CO = 1; T = 60 °C; P = 2650 psi. [b] Selectivity = hydroformylation product/total products. [c] Determined by ^1H NMR using $Eu(hfc)_3$ as chiral shift reagent. The (1*R*,2*R*,4*S*)-(−) enantiomer was obtained in excess. [d] Identical results were obtained upon three recycles of the catalyst with addition of $SnCl_2 \cdot 2H_2O$ each time. [e] The catalyst was recycled from the previous run, and $SnCl_2 \cdot 2H_2O$ was added.

excess achieved by asymmetric catalysis and showed no racemization under the reaction conditions.

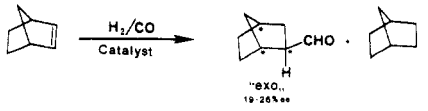
N-Vinylphthalimide has been reported to undergo hydroformylation at a very low rate (~50% conversion in 5 days) in the presence of Rh(I)/(−)-DBP-DIOP[27] providing the branched product almost exclusively but in low enantiomeric excess (~30%). Use of the [(−)-DBP-DIOP]$PtCl_2$–$SnCl_2$ catalyst allowed a faster reaction with better enantiomeric excess (eq 3; Table III). Even though



(3)

the linear product was obtained in small amounts, large amounts of hydrogenation product were observed. A higher aldehyde selectivity was achieved in the presence of the preformed catalyst [(−)-DBP-DIOP]$Pt(SnCl_3)Cl$ and with the polymer-supported catalyst. In the latter case a lower *b*/*n* ratio was observed.

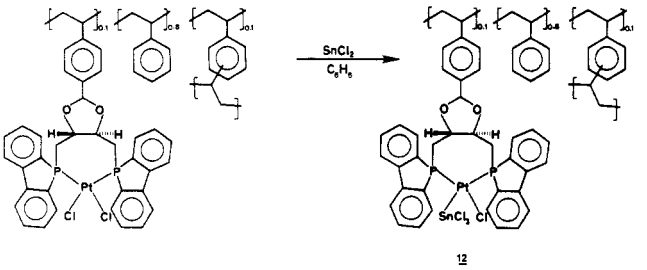
Norbornene was hydroformylated very rapidly (eq 4; Table IV). The reaction affored only the "exo" aldehyde but low asymmetric induction was achieved.



(4)

The hydroformylation of these four substrates shows a common pattern in the change of activity and selectivity when the catalyst is supported on a polymeric backbone. Regioselectivity changes between the homogeneous and heterogeneous catalysts have already been reported for other chiral[10] and nonchiral[28] polymer-bound chelating diphosphines in the presence of rhodium(I). This is indicative that a steric effect due to the polymer chain is important in influencing the regiospecificity of the olefin insertion step in the catalytic cycle.

Scheme II



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The decrease in the reaction rate observed upon recycle of the polymer-supported catalyst is not entirely due to mechanical loss during the recycle, amounting to 13 wt % after four recycles. Possible leaching of the platinum out of the cross-linked polymer could be responsible for some of the rate loss. However, platinum elemental analysis of the catalyst recovered after four recycles (3.29% Pt, calculated; 3.22% Pt, found) showed that such a loss of platinum does not occur. This result was supported by solid-state CP/MAS ^{31}P NMR experiments. Polymer **8b** was treated with a 2.5-fold excess of stannous chloride (Scheme II), and the solid-state ^{31}P NMR spectrum of the product **12** was obtained (Figure 1). Polymer **12** was used to catalyze the hydroformylation of styrene under the conditions described in Table I. After two recycles, the spectrum of the recovered catalyst showed that the ratio of the peaks of the coordinated and uncoordinated ligands remained unchanged. This confirms that no decomplexation of platinum occurred during the hydroformylation reaction and that the drop in rate upon recycle must be attributed primarily to other changes in the polymer.

A microscopic analysis of the polymer after recycle showed that some of the beads crumbled into small powder-like particles, and the extent of this process increases as the polymer is submitted to further recycles (Figure 2). This result suggests that a decrease of the catalytic sites per unit surface areas may account for the loss in activity.

Hydroformylation Reactions Using Ligands of Opposite Configuration. An attractive feature in asym-

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Table V. $^{31}P\{^1H\}$ and Selected ^1H NMR Chemical Shifts of Phosphine Ligands 5 and 4 and Their Adducts with Compound 9 (Scheme III)[a]

	^{31}P, δ			^1H, δ			
				(−)-(*R*,*R*)[b]		(+)-(*S*,*S*)[b]	
compd	(−)-(*R*,*R*)[b]		(+)-(*S*,*S*)[b]	ketal/acetal[c]	CMe[d]	ketal/acetal[c]	CMe[d]
5		−20.82		1.57 (s)		1.57 (s)	
10	26.99		24.70	1.36 (s)	1.82 (d, 13.5 Hz)	1.31 (s)	1.59 (d, 13.5 Hz)
4		−20.90		5.90 (s)		5.90 (s)	
		−21.07					
11	25.75		23.39	5.95 (s)	1.46 (d, 8.1 Hz)	6.20 (s)	1.22 (d, 5.4 Hz)
	25.39		21.78		1.79 (d, 8.1 Hz)		1.45 (d, 5.4 Hz)

[a] The spectra were obtained on 0.1 M solutions in $CDCl_3$. A 1:1 ratio of **9** to ligand was used. [b] Configurations of the chiral centers in the free phosphine ligands. [c] Chemical shifts of the ketal methyls or the acetal protons on the ligands. [d] Chemical shifts of the methyl groups on the chiral auxiliary **9**.

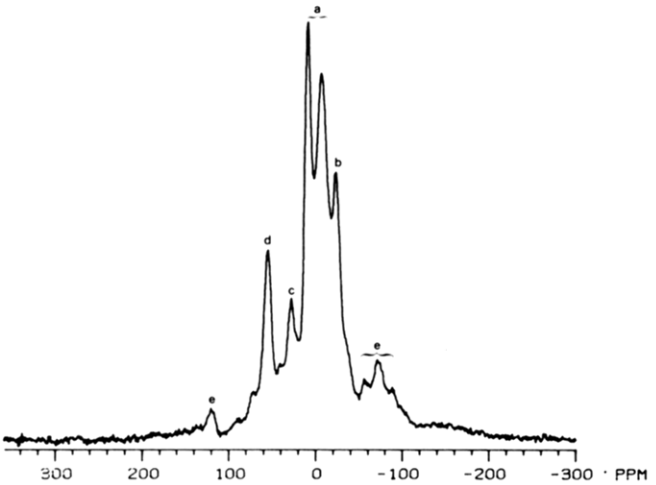
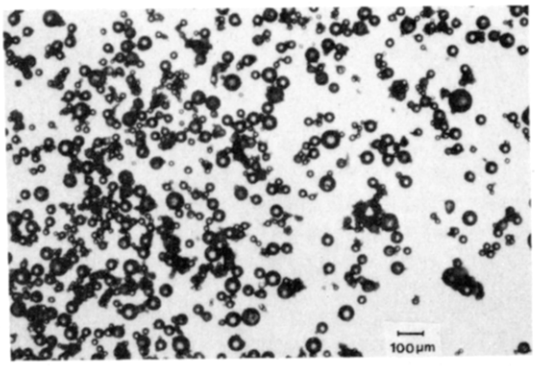
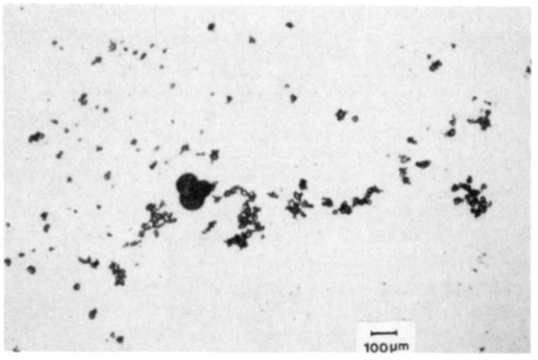


Figure 1. Solid-state ^{31}P NMR (CP/MAS) spectrum of polymer **12**: (a) phosphorus coordinated to $Pt(SnCl_3)Cl$; (b) uncoordinated phosphorus; (c) Pt satellite of peaks a; (d) phosphorus coordinated to excess $SnCl_2$; (e) spinning side bands.



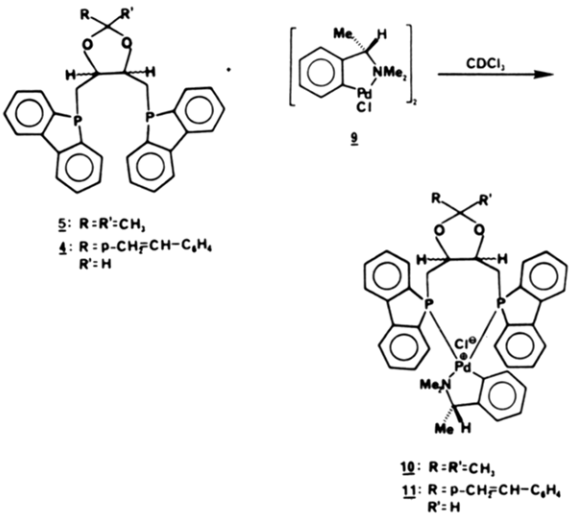
(a)



(b)

Figure 2. (a) Beads of polymer **1b**. (b) Beads of polymer **1b** recovered from a hydroformylation reaction.

Scheme III



metric syntheses is the potential of selective production of either enantiomer of the chiral product. In asymmetric catalysis, producing a certain enantiomer in excess should be related to the particular configuration of the chiral ligand employed.

For establishment of the general validity of the catalytic system described, the hydroformylation of styrene in the presence of [(+)-DBP-DIOP]$PtCl_2$–$SnCl_2$ under the conditions described above was carried out. The results were identical with those reported in Table I for the [(−)-DBP-DIOP] except that in the case (−)-2-phenylpropanal was obtained in excess.

Determination of the Optical Purity of the Phosphine Ligands. In the design of an asymmetric synthesis, it is of paramount importance that the chiral auxiliaries employed are enantiomerically pure. In most reports of asymmetric catalysis, it has always been assumed that the asymmetric ligands used are enantiomerically pure. This assumption is usually justified by the fact that the ligands are synthesized from naturally occurring precursors. Through a number of chemical reactions, assumed to occur without racemization, these precursors are transformed into the desired ligands. However, all of these assumptions are not necessarily obvious and the optical purity of a chiral compound can be determined only by using a method that can differentiate between the two enantiomers.

For determination of the enantiomeric purity of the chiral ligands used in the course of this research, a spectroscopic method suggested by a recent report[29] was especially useful. Reactions of either enantiomers of ligand **5** or **4** with equimolar amounts of (−)-bis(μ-chloro)bis-

(29) Kyba, E. P.; Rines, S. P. *J. Org. Chem.* **1982**, *47*, 4800.

[(*R*)-dimethyl(α-methylbenzyl)aminato-C^2,*N*]dipalladium-(II) (**9**) were carried out by dissolving the reactants in deuteriochloroform to provide diastereomeric complexes **10** or **11**, respectively (Scheme III). The resulting solutions were submitted to ^{31}P and ^{1}H NMR analysis to obtain the chemical shift data (Table V). Although a differentiation in the chemical shifts of some protons of the enantiomers was observed, a better differentiation was obtained from the ^{31}P chemical shifts. The base-line separation between the peaks of diastereomers **10** and **11** provided an accurate method for the determination of the optical purity of phosphine ligands **5** and **4**. For both ligands **5** and **4** it was possible to detect the presence of 2% of the minor enantiomer in a prepared 98:2 mixture (^{31}P spectra available as supplementary material). With these results, it is possible to establish that ligands **5** and **4** were at least 98% enantiomerically pure and that no racemization took place during the transformation of **5** to **4** (Scheme I). Another advantage in using this method of evaluating the enantiomeric purity of a ligand is that the free phosphine ligand can be recovered quantitatively.[30]

Experimental Section

All reactions involving the synthesis of the catalyst supports were performed under an inert atmosphere of nitrogen or argon. Manipulations involving phospholes in solution were carried out in a glovebag or by Schlenk techniques. ^{1}H NMR spectra (270 MHz) were recorded on an IBM WP 270 spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard. ^{31}P NMR spectra (81 MHz) were recorded on an IBM WP 200 spectrometer in $CDCl_3$ with 85% H_3PO_4 as an external reference. Optical rotations were measured on an Autopol III automatic polarimeter. Melting points are uncorrected. Elemental analyses were obtained from Micro-Tech Laboratories, Inc., Skokie, IL. Pt elemental analyses were obtained from Analytische Laboratorien, D-5250 Engelskirchen, West Germany. Synthesis gas (1:1, H_2:CO) was purchased as a custom mixture from SGP Inc. and was used as received. Styrene, vinyl acetate, and norbornene were purchased from Aldrich, freshly distilled, and stabilized with *p*-methoxyphenol before use as hydroformylation substrates. *N*-Vinylphthalimide was purchased from Monomer-Polymer and Dajac Laboratories Inc. and used as received. Gas chromatographic analyses were carried out on a Varian Model 3700 using a 10% OV-101 Chromosorb W-HP, 80/100 (2m × $^1/_8$ in.), with a thermal conductivity detector or a DB1 fused silica capillary columns (30 m length × 0.25 mm i.d.) with a flame ionization detector and helium as the carrier gas. The chromatograph was interfaced with a Varian Chromatographic Data System IIIC for determining relative peak areas by electronic integration.

Solid-State NMR Spectra. The solid-state ^{31}P NMR spectra were obtained on a Nicolet NT-150 spectrometer at a phosphorus frequency of 60.745 MHz with a cross-polarization magic-angle spinning (CP/MAS) unit, including the probe built in house. The decoupling field was 50 kHz. The spinner system is a modified version of Wind's,[31] with a sample volume of 0.4 cm^3. The samples were spun at 3200 rps (52 ppm). The CP contact time was 1 ms, and the repetition time was 2 s. A total of 2K points were collected with a spectrum width of 20 kHz and an acquisition time of 26 ms. The 30-Hz line broadening was added to improve the signal-to-noise ratio. Chemical shifts are relative to external 85% phosphoric acid, with (−)-(2*S*,3*S*)-bis(diphenylphosphino)butane ("chiraphos") as a secondary standard, with the more shielded signal at −14 ppm.

Viscosity/Molecular Weight Determination. The intrinsic viscosity of the soluble polymer **1a** was determined with a Cannon Ubbelohde microdilution viscosimeter Nos. 50 in chloroform at 25 °C. Gel permeation chromatography (GPC) was done in chloroform at a flow rate of 1.0 mL/min with a Waters GPC equipped with a 6000-A pump, U6K injector, R401 RI detector, 730 data module, and 10^3, 10^4, and 10^5 Å μ-Styragel columns. The system was calibrated with polystyrene standards of known molecular weight.

(2*R*,3*R*)-2,3-Dihydroxy-1,4-bis(dibenzophospholyl)butane (6). A flask equipped with a Vigreux column surmounted by a distillation head was flushed with argon and charged with 2.5 g (5.0 mmol) of (−)-DBP-DIOP (**5**),[23] 150 mL of ethanol, 10 mL of water, and 3 mL of concentrated hydrochloric acid. The suspension was heated in order to achieve a very slow distillation. After 2 h the solution was cooled and the solvent was removed under reduced pressure to yield a yellow semisolid material. This was triturated with water, and the resulting white powder was filtered and dried under reduced pressure. Flash chromatography[32] (1:1 ethyl acetate/hexane) afforded 2.2 g (96%) of white solid which was sufficiently pure for preparative purposes. A pure analytical sample was obtained by recrystallization from chloroform/hexane: mp 128–130 °C; $[\alpha]^{24}_D$ −12° (*c* 0.75, $CHCl_3$); ^{1}H NMR δ 1.7–2.2 (m, 4 H), 3.2 (br s, 2 H, disappeared by shaking with D_2O), 3.6–3.7 (m, 2 H), 7.2–8.1 (m, 16 H); ^{31}P NMR δ −20.62 (s, 2 P). Anal. Calcd for $C_{28}H_{24}O_2P_2$: C, 73.99; H, 5.32; P, 13.63. Found: C, 73.81; H, 5.42; P, 13.48.

4-Vinylbenzaldehyde (7). This compound was obtained in 78% yield by the coupling reaction of 4-bromobenzaldehyde with vinyl tributyltin in the presence of tetrakis(triphenylphosphine)palladium(0):[24] bp 53 °C at 0.25 mm (lit.[33] 75–78 °C at 1 mm); ^{1}H NMR δ 5.4 (d, *J* = 10.9 Hz, 1 H), 5.9 (d, *J* = 17.6 Hz, 1 H), 6.7 (dd, *J* = 17.6, 10.9 Hz, 1 H), 7.5 (d, *J* = 8.2 Hz, 2 H), 7.8 (d, *J* = 8.2 Hz, 2 H), 10.0 (s, 1 H).

(4*R*,5*R*)-2-(*p*-Styryl)-4,5-bis[(dibenzophospholyl)-methyl]-1,3-dioxolane (4). A flask containing 60 mg of *p*-toluenesulfonic acid and equipped with a Soxhlet extractor containing 4A molecular sieves was flushed with argon and charged with a deoxygenated solution of 800 mg (1.76 mmol) of **6**, 206 mg (1.56 mmol) of 4-vinylbenzaldehyde, and a few crystals of *p*-methoxyphenol in 50 mL of benzene. The solution was heated at reflux for 13 h. The reaction mixture was cooled to room temperature and purified by flash chromatography[32] (silica, 10% hexane/benzene). Removal of the solvent under reduced pressure afforded an oil. The oil was dissolved in a minimum amount of chloroform and precipitated as white crystals upon addition of hexane to yield 600 mg (67%) of **4**: mp 118 °C; $[\alpha]^{24}_D$ −43.1° (*c* 1.0, C_6H_6); ^{1}H NMR δ 1.7–2.1 (m, 4 H), 4.0 (p, *J* = 6.3 Hz, 1 H), 4.1 (p, *J* = 6.3 Hz, 1 H), 5.3 (d, *J* = 10.9 Hz, 1 H), 5.8 (d, *J* = 17.6 Hz, 1 H), 5.9 (s, 1 H), 6.7 (dd, *J* = 17.6, 10.9 Hz, 1 H), 7.2–8.0 (m, 20 H); ^{31}P NMR δ −20.7 (s, 1 P), −20.9 (s, 1 P). Anal. Calcd for $C_{37}H_{30}O_2P_2$: C, 78.13; H, 5.28; P, 10.91. Found: C, 77.88; H, 5.44; P, 10.98.

Soluble Polymer 1a. A solution of 382.2 mg (0.67 mmol) of phosphole monomer **4**, 630.9 mg (6.05 mmol) of freshly distilled styrene, and 25 mg of azobis(isobutyronitrile) (AIBN) in 6 mL of benzene was degassed by two freeze–pump–thaw cycles and transferred into a flask equipped with a mechanical stirrer and a reflux condenser. The solution was stirred at 60 °C under argon. After 10 h, a degassed solution of 25 mg of AIBN in 2 mL of benzene was added. After 14 h (total 24 h) the solution was concentrated to half the volume by evaporating the solvent under a stream of argon and transferring the solution into a flask containing 200 mL of methanol. The suspension was stirred at room temperature for 3 h and then filtered. The white solid was washed with methanol and dried under reduced pressure to yield 805 mg (79.5%) of polymer: ^{31}P ($CDCl_3$) δ −20.8 (s, 1 P), −21.01 (s, 1 P); $[\eta]$ = 0.093 dL/g (by Cannon Ubblelohde viscosimeter at 25 °C in chloroform); $[\eta]$ = 0.147 dL/g; $\bar{M}_n$ 23 635; $\bar{M}_w$ 147 65 (by GPC at 20 °C in chloroform). Anal. Calcd: P, 4.12. Found: P, 4.99.

Cross-Linked Polymer 1b. A solution of 500 mg of polyvinylpyrrolidone (M_r 40 000) in 60 mL of water was degassed by two freeze–pump–thaw cycles, transferred to a 250 mL Morton creased flask containing a variable speed stirrer, and heated to 65 °C under argon. A mixture of 441.5 mg (0.77 mmol) of phosphole monomer **4**, 648.2 mg (6.22 mmol) of styrene, 101.1 mg (0.77 mmol) of divinylbenzene, 50 mg of AIBN, and 2 mL of toluene was deoxygenated and added to the flask. The suspension was stirred for 20 h, cooled, treated with 30 mL of methanol, and

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stirred for 30 min. The beads were filtered in a glovebag, washed with 50 mL of methanol, 50 mL of tetrahydrofuran, 50 mL of benzene, and 50 mL of methanol, and dried under reduced pressure to afford 972.2 mg (80%) of 20–60-μm beads: solid-state ^{31}P NMR (CP/MAS) δ −24.8 (broad signal with a shoulder at δ −18.8). Anal. Calcd: P, 4.01. Found: P, 4.18.

Polymers 3a and 3b. Polymers **3a** and **3b** were obtained by copolymerization of monomer **2** with styrene and divinylbenzene using the methods described for the synthesis of polymers **1a** and **1b** from phosphole monomer **4**.

Reaction of 3a and 3b with Lithium Dibenzophosphole. These reactions were carried out following previously reported procedures.[10]

[(−)-DBP-DIOP]PtCl$_2$. This complex was prepared following a literature procedure;[34] ^{31}P NMR δ 0.94 (^1J(Pt,P) = 3490 Hz).

[(−)-DBP-DIOP]Pt(SnCl$_3$)Cl. A mixture of 150 mg (0.19 mmol) of [(−)-DBP-DIOP]PtCl$_2$ and 74.6 mg (0.39 mmol) of anhydrous stannous chloride was stirred in 80 mL of dichloromethane at room temperature under argon for 7 h. The suspension was filtered to eliminate the excess stannous chloride. The solution was concentrated to 10 mL, and 20 mL of hexane was added. The precipitate (145 mg, 77.5%) was filtered, washed with hexane, and dried under reduced pressure: ^{31}P NMR (CH_2Cl_2/$CDCl_3$) δ(P$_1$) 8.4, δ(P$_2$) 8.6 (^1J(Pt,P$_1$) = 2289 Hz, ^1J(Pt,P$_2$) = 2710 Hz, ^2J(P$_1$,P$_2$) = 21 Hz, ^2J(Sn,P$_1$) = 2998 Hz, ^2J(Sn,P$_2$) = 3082 Hz; average of ^{117}Sn and ^{119}Sn coupling = 198 Hz).

Exchange of Platinum onto 1a. A degassed solution of an amount of polymer **1a** containing 0.24 mmol of dibenzophosphole ligand in 10 mL of benzene was added to a refluxing solution of 0.14 mmol of bis(benzonitrile)dichloroplatinum(II)[25] in 10 mL of benzene. Reflux was continued under argon for 20 h. The solution was concentrated to about 8 mL, and 30 mL of diethyl ether was added. The yellow solid was filtered, washed with diethyl ether, and dried under reduced pressure to yield 270 mg (80%) of catalyst.

Exchange of Platinum onto 1b. A solution of 0.12 mmol of bis(benzonitrile)dichloroplatinum(II)[25] in 10 mL of benzene was added to a refluxing suspension of an amount of polymer **1b** containing 0.21 mmol of dibenzophosphole ligand in 5 mL of benzene. Reflux was continued for 40 h under argon. The mixture was filtered in a glovebag, washed with 10 mL of dichloromethane and 10 mL of benzene, and dried under reduced pressure to afford the polymer-supported catalyst **8b** in 98.6% yield: solid-state ^{31}P NMR (CP/MAS) δ −2.0 (^1J (Pt,P) = 3549 Hz), −24.7 (uncoordinated ligand). Anal. Calcd: Pt, 6.99. Found: Pt, 5.96.

Polymer 12. A suspension of 100 mg of polymer **1b** and 30 mg of anhydrous stannous chloride in 15 mL of benzene was stirred at 40 °C under argon for 10 h. The solid was filtered, washed with benzene, and dried under reduced pressure to yield 110.5 mg of orange beads: solid-state ^{31}P NMR (CP/MAS) (Figure 1) δ(P$_1$) −8.3, δ(P$_2$) 7.26, δ −24.3 (uncoordinated ligand), 53.7 (ligand coordinated to excess $SnCl_2$).

Homogeneous Hydroformylations. A 125-mL Parr Monel bomb was charged with 0.02 mmol of Pt catalyst and 0.04 mmol of stannous chloride dihydrate. The bomb was brought into an argon-filled glovebag and charged with 8.7 mmol of olefinic substrate dissolved in 3 mL of benzene. The bomb was sealed, pressurized, and vented three times with the synthesis gas mixture (1:1, H_2:CO) and then pressurized (usually to 2400 psi at room temperature) and heated with stirring in an oil bath at 60 °C. At the end of the reaction, the bomb was quenched in a dry ice bath, the pressure was vented, and the solvent was removed by distillation. The product mixture was vacuum transferred (in the case of styrene and vinyl acetate) or flash chromatographed (in the case of norbornene and *N*-vinylphthalimide) from the catalyst and analyzed by GLC or by ^{1}H NMR to determine the conversion and the product composition. The ee's were determined with an accuracy of ±3% by ^{1}H NMR by using Eu(hfc)$_3$ or Eu(tfc)$_3$ chiral shift reagents.

Typical Experiment for the Determination of Enantiomeric Excess. Approximately 0.1 mL of the reaction mixture containing 2-phenylpropanal was diluted with deuteriochloroform and placed in an NMR tube. Eu(hfc)$_3$ was added in small portions until a neat splitting of the peak of the formyl proton (doublet at 9.6 ppm) was observed in the ^{1}H NMR spectrum. The integration of the two peaks (14.46 ppm for the (+) and 14.34 ppm for the (−)-enantiomer) was used to calculate the enantiomeric excess according to

$$\% \text{ ee} = \frac{(+) - (-)}{(+) + (-)} \times 100$$

Hydroformylations with Catalyst 8. The procedure for hydroformylation in the presence of soluble (**8a**) and cross-linked (**8b**) polymer-supported catalysts was the same as that followed in the homogeneous case except that at the end of the reaction, the bomb was opened in a glovebag. Catalyst **8b** was recovered by filtration and **8a** by precipitation with diethyl ether followed by filtration. In both cases, 0.04 mmol of stannous chloride dihydrate was added to the catalyst on each recycle.

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Registry No. **1a**, 71206-64-9; **1b**, 71206-28-5; **4**, 71206-27-4; **5**, 57221-96-2; **6**, 104322-96-5; **7**, 1791-26-0; **9**, 34424-15-2; **10** (isomer 1), 104267-70-1; **10** (isomer 2), 104321-48-4; **11** (isomer 1), 104267-71-2; **11** (isomer 2), 104418-79-3; PhCH=CH$_2$, 100-42-5; (*S*)-PhCH(CHO)CH$_3$, 33530-47-1; PhCH$_2$CH$_2$CHO, 104-53-0; (*S*)-AcCH(CHO)CH$_3$, 66875-70-5; AcOCH$_2$CH$_2$CHO, 18545-28-3; [(+)-DBP-DBP-DIOP]PtClSnCl$_3$, 104267-72-3; [(−)-DBP-DIOP]Pt(SnCl$_3$)Cl, 104371-27-9; [(−)-DBP-DIOP]PtCl$_2$, 104293-04-1; SnCl$_2$, 7772-99-8; AcOCH=CH$_2$, 108-05-4; 4-bromobenzaldehyde, 1122-91-4; vinyltributyltin, 7486-35-3; tetrakis(triphenylphosphine)palladium, 14221-01-3; (*S*)-2-phenylpropanol, 37778-99-7; bis(benzonitrile)dichloroplatinum (II), 14873-63-3; *N*-vinylphthalimide, 3485-84-5; (*S*)-*N*-(1-formylethyl)phthalimide, 51482-36-1; *N*-(2-formylethyl)phthalimide, 2436-29-5; *N*-ethylphthalimide, 5022-29-7; 2-norbornene, 498-66-8; (1*R*,2*R*,4*S*)-2-formylnorbornane, 104418-69-1.

Supplementary Material Available: ^{31}P spectra of diastereomers of **10** and **11** and of diastereomeric mixtures (2 pages). Ordering information is given on any current masthead page.

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