Styrene Hydroformylation Catalyzed by Homogeneous and Polymer-Anchored Rhodium Complexes. The Effect of Cis-Chelating Phosphine

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The selectivity in styrene hydroformylations was studied for the homogeneous catalysts RhH(CO)(PPh$_3$)$_3$ and RhH(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(PPh$_3$) and their polymer-anchored analogues (Ⓟ-C$_6$H$_4$PPh$_2$)$_x$RhH(CO)(PPh$_3$)$_{3-x}$ and [Ⓟ-C$_6$H$_4$P(Ph)CH$_2$CH$_2$PPh$_2$]RhH(CO)L, respectively. Temperatures of 60, 80, and 120 °C were employed at pressures of 100, 400, and 800 psi using 1:1 H$_2$/CO. The *b/n* product ratio decreased as temperature was increased. As pressure was raised the *b/n* ratio increased. The selectivity was also studied as a function of P/Rh ratio and, for the polymer-anchored catalysts, as a function of the ligand loading within the resin's matrix. Only at 120 °C and low pressures did the normal product (3-phenylpropanal) predominate. These results are discussed in terms of equilibria among rhodium complexes based on the hydroformylation mechanisms postulated by Wilkinson.

In order to employ homogeneous catalysts as fixed beds and to facilitate the separation of products from expensive homogeneous catalysts, many groups have turned to polymer anchoring of the catalyst complexes.[1-3] This approach has been used for rhodium complexes in the oxo reaction[4-7] and very high terminal selectivities have been achieved when polymer matrices are used containing high phosphine concentrations and high P/Rh ratios.[8,9] By anchoring a catalyst to a swellable resin, the catalyst can operate, mechanistically, as if it were in solution. Thus, the ability to tailor its selectivity, using ligand and solvent changes, is maintained. Several advantages, in addition to ease of catalyst recovery, have been reported for polymer-bound systems. These include: enhanced hydrogenation activity of immobilized titanocene[10] and Ir(CO)Cl(PPh$_3$)$_2$,[11] greater positional selectivity in both hydrogenations[12] and hydroformylations,[8,9] as well as increased selectivity based on substrate size considerations.[13]

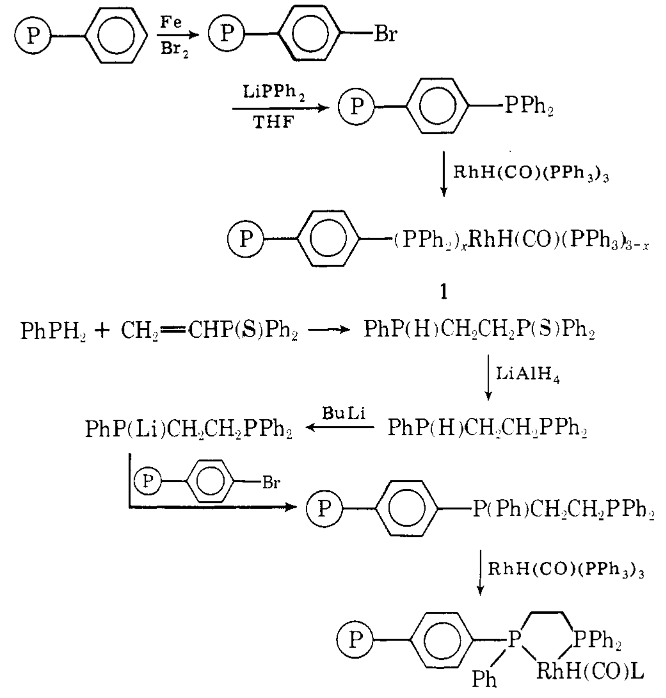
In some cases, the leaching of catalyst from the polymer bed over a period of time becomes an important consideration. One way to reduce the leaching rate is to employ a chelating ligand to bind the metal to the polymer.[14] Thus, Ⓟ-C$_6$H$_4$P(Ph)CH$_2$CH$_2$PPh$_2$ has been used to anchor rhodium complexes, such as Ⓟ-C$_6$H$_4$P(Ph)CH$_2$CH$_2$PPh$_2$)RhH(CO)L, to polymers for use in hydroformylations.[14] However, the use of such cis-chelating ligands modified catalyst selectivity and reactivity in the hydroformylation of aliphatic olefins.[14] Only one study has appeared in which the selectivities of homogeneous vs. polymer-anchored catalysts were compared where the catalyst is cis chelated by a bidentate phosphine.[14]

We were interested in how the normal/branched selectivity in styrene hydroformylations would respond to the use of 1,2-bis(diphenylphosphine)ethane as a ligand and to the use of this ligand as part of a polymer matrix. Styrene is known to be a more reactive substrate than terminal aliphatic olefins in rhodium-catalyzed hydroformylations.[15,16] It has also been shown that the branched product, 2-phenylpropanal, is the major product formed when rhodium catalysts are used.[17] However, studies of the selectivity as a function of ligand, temperature, pressure, and catalyst immobilization have not appeared for styrene.[18] Thus, in this report, we describe the selectivity of styrene hydroformylations, catalyzed by rhodium in the presence of PPh$_3$ and Ph$_2$PCH$_2$CH$_2$PPh$_2$ ligands, as well as their matrix-anchored analogues, Ⓟ-C$_6$H$_4$PPh$_2$ and Ⓟ-C$_6$H$_4$P(Ph)CH$_2$CH$_2$PPh$_2$, respectively.

Results and Discussion

Polystyrene–1% divinylbenzene resins (200–400 mesh) were functionalized with diphenylphosphino and diphos groups as shown in Scheme I. This route randomly distributes phosphine sites (on a macro level) throughout the swollen resin. The resins were then reacted with RhH(CO)(PPh$_3$)$_3$ to incorporate rhodium by ligand exchange. Triphenylphosphine, displaced in this manner from RhH(CO)(PPh$_3$)$_3$, was removed by continuous extraction. The resulting polymers are summarized in Table I. Resins with a range of ligand concentration levels (expressed as ligand loading levels) and P/Rh ratios were prepared in order to study the dependence of hydroformylation selectivity on these variables. The percentage of the polymer's styrene units which have been functionalized with a phosphine ligand is referred to as the ligand loading of that resin.

Scheme I



Hydroformylation reactions were carried out in benzene at pressures of 100, 400, and 800 psi and at temperatures of 60, 80, and 120 °C. In each case, a 1:1 H$_2$/CO ratio was employed. The polymer-anchored catalysts were compared to their homogeneous analogues which were studied over the same range of conditions. RhH(CO)(PPh$_3$)$_3$ (plus added PPh$_3$ in some cases) was the homogeneous analogue of resin 1, while RhH(CO)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(PPh$_3$) (plus added Ph$_2$PCH$_2$CH$_2$PPh$_2$) was the homogeneous analogue of resin 2.

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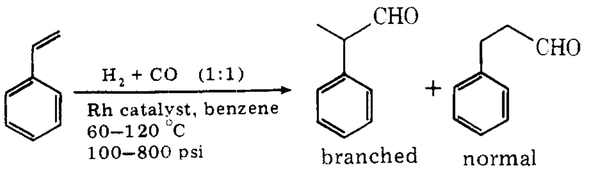
Table I. Summary of Resin Catalysts (Ⓟ-$C_6H_4PPh_2$)$_x$-$RhH(CO)(PPh_3)_{3-x}$, 1, and (Ⓟ-$C_6H_4P(Ph)CH_2CH_2PPh_2$)-RhH(CO)L, 2, Prepared and Used in Styrene Hydroformylations

resin	% P	% Rh	% ligand loading	P:Rh
1A	1.78	2.69	7.2	2.2
1B	4.68	4.75	40	3.3
1C	4.74	1.10	40	14.3
2A	1.36	1.64	1.4	2.8
2B	7.16	7.28	21.6	3.3
2C	6.97	2.55	21.6	9.1
2D	6.64	1.32	21.6	16.7

When 1 and 2 were compared to their homogeneous analogues, the P/Rh and styrene/Rh ratios of the respective reactions were held equal. The branched and normal products (2-phenylpropanal and 3-phenylpropanal, respectively) from each reaction were quantitatively analyzed by GLC using electronic integration and internal standard techniques. The selectivity is defined as the branched/normal (i.e., *b/n*) ratio.



(1)

The selectivities of styrene hydroformylations catalyzed by resins **1A–C** ((Ⓟ-$C_6H_4PPh_2$)$_x$$RhH(CO)(PPh_3)_{3-x}$) are summarized in Table II. Table III summarizes the corresponding reactions catalyzed by the homogeneous analogue, $RhH(CO)(PPh_3)_3$. In every case at 60 and 80 °C, the branched product predominates. Only at 120 °C and at lower pressures did the normal product predominate. The response of selectivity to reaction variables, using resins **1A–C**, shows the following trends. At 60 °C, the *b/n* ratio increased as the ligand loading increased from 7.2 to 40% at low P/Rh ratios at both 100 and 800 psi. However, increasing the P/Rh ratio from 3.3 to 14.3 (while holding ligand loading constant at 40%) caused a slight decrease in the *b/n* ratio at both 100 and 800 psi. At 120 °C, the *b/n* ratio increased from 1.29 to 5.16 as the ligand loading increased from 7.2 to 40%. At all pressures, there was a decrease in the *b/n* ratio as temperature was raised from 60 to 120 °C while holding both ligand loading and P/Rh constant. In all cases, the *b/n* ratio increased as the pressure was increased. In summary, high ligand loading, high pressure, and low temperature gave larger *b/n* ratios.

The same trends observed in the resin-catalyzed reactions were observed using $RhH(CO)(PPh_3)_3$ homogeneously (see Table III). Thus, the highest *b/n* ratios were observed at high pressures and lower temperatures. However, when the homogeneous catalyst was used, the selectivity was not very sensitive to the P/Rh ratio (when pressure and temperature were held constant). The *b/n* ratio, again, was sharply dependent upon temperature, decreasing rapidly as temperature increased at all pressures. However, high *b/n* ratios (i.e., 5.5) are still possible at 120 °C and 800 psi as long as P/Rh is high (i.e., 14.3). In summary, the dependence of selectivity on temperature, pressure, ligand concentration, and P/Rh ratio was about the same for the polymer-anchored catalysts (**1A–C**) as for $RhH(CO)(PPh_3)_3$, although at equivalent conditions the resin selectivities were somewhat lower.

The generally sited mechanism of olefin hydroformylation is that of Wilkinson.[19-21] As shown in Scheme II, loss of phosphine from $RhH(CO)(PPh_3)_3$ gives $RhH(CO)(PPh_3)_2$, **3**, which in turn coordinates carbon monoxide giving

Scheme II

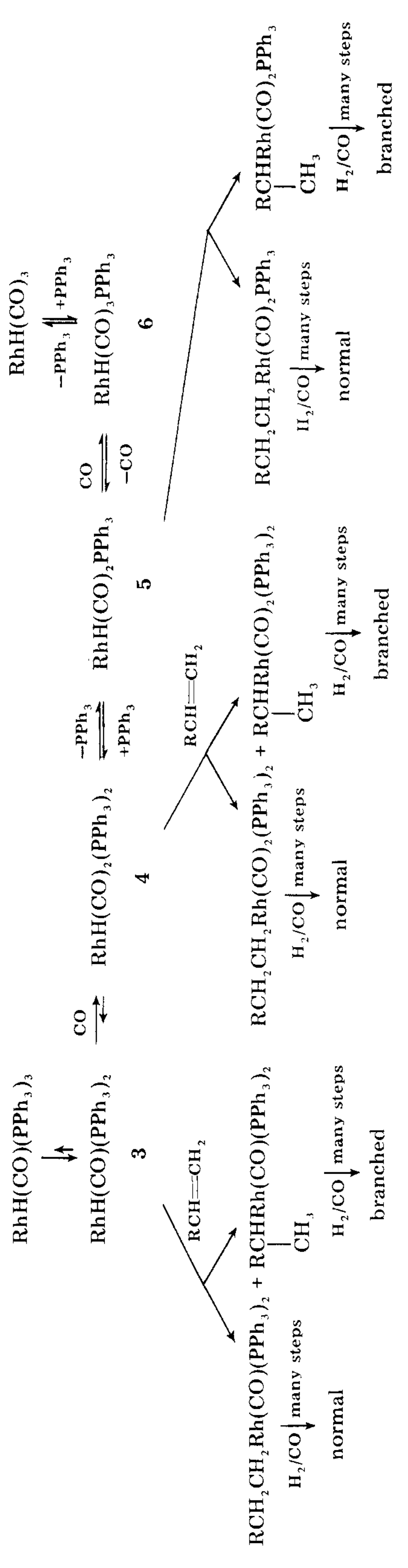


Table II. Selectivities (*b*/*n*) in Hydroformylations of Styrene Catalyzed by Resins 1A–C, (Ⓟ-$C_6H_4PPh_2)_xRhH(CO)(PPh_3)_{3-x}$[a]

resin (ligand loading, P/Rh)	pressure, psi	*b*/*n*, yield, % 60 °C	80 °C	120 °C
1A (7.2, 2.2)	100	1.5, 43.9	—	0.66, 59.7
	400	—	2.1, 100	—
	800	9.5, 98.4	—	1.3, 100
1B (40, 3.3)	100	8.8, 99.3	—	—
	800	12.9, 97.6	—	—
1C (40, 14.3)	100	5.5, 51.2	4.2, 97.8	1.1, 100
	800	8.6, 48.3	6.9, 99.9	5.2, 100

[a] Each reaction contained 0.044 mmol of Rh, 1 mL of styrene, 8 mL of benzene and employed 1:1 H_2/CO.

Table III. Selectivities (*b*/*n*) in Hydroformylations of Styrene Catalyzed by $RhH(CO)(PPh_3)_3 + PPh_3$[a]

P/Rh	pressure, psi	*b*/*n*, yield, % 60 °C	80 °C	120 °C
3	100	11.0, 100	2.7, 100	0.6, 97.7
	400	13.9, 100	8.0, 98.9	1.7, 100
	800	15.0, 96.9	10.6, 96.4	4.6, 100
5.3	100	5.4, 95.8	1.1, 100	0.6, 100
	400	11.4, 100	6.3, 100	0.8, 100
	800	14.7, 100	10.2, 100	4.8, 100
14.3	100	8.7, 100	4.4, 100	0.8, 100
	400	11.7, 100	9.0, 100	
	800	13.0, 100	10.4, 100	5.5, 100

[a] Each reaction contained 0.044 mmol of Rh, 1 mL of styrene, 8 mL of benzene and employed 1:1 H_2/CO.

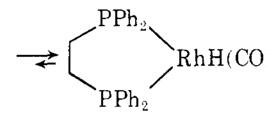
$RhH(CO)_2(PPh_3)_2$, **4**. Complex **4** is in equilibrium with $RhH(CO)_2PPh_3$, **5**, by further phosphine dissociation. Both **3** and **5** may complex olefin followed by the usual steps (rhodium hydride addition, CO insertion, hydrogen oxidative addition, and reductive elimination) to produce aldehydes via the "dissociative" process. Complex **4** (an 18-electron complex) must give aldehyde via an "associative" process. For both electronic and steric reasons,[19–21] the bisphosphine complexes **3** and **4** would give higher selectivity to the normal product with aliphatic olefins, while **5**, by comparison, would give more branched product. However, when styrene is the substrate, the addition of rhodium hydride prefers the Markovnikov direction. Electronically, the addition of CO to rhodium makes $L_xRh–H$ more acidic which should favor Markovnikov addition. Based only on electronic arguments,[22] Markovnikov addition should follow the order **5** > **4** > **3**. At higher CO partial pressures one would expect the proportion of **4** and **5** at equilibrium would increase relative to **3**, thereby favoring Markovnikov addition and a higher *b*/*n* product ratio. This change in selectivity is just what is observed.

Finally, it is conceivable that **5** could undergo reversible loss of phosphine. Also, addition of CO to **5** might produce $RhH(CO)_3(PPh_3)$, **6**, at higher CO pressures. Complex **6** then might catalyze hydroformylation (associatively). The rhodium hydride addition of **6** (or $RhH(CO)_3$) would occur with even greater Markovnikov selectivity than **5** based on electronic considerations.

The *b*/*n* ratio would be expected to decrease at higher temperatures because, as temperature increases, the relative values of association constants of phosphine and CO with rhodium favor the formation of the phosphine–rhodium complexes vs. rhodium–carbonyl complexes.[7] Thus, as temperature increases, **3** and **4** would be favored over **5** and a shift to more terminal product (anti-Markovnikov rhodium hydride addition) should be observed (and it is). Furthermore, this effect should be sensitive to CO partial pressure. Thus, at lower CO pressure the shift to more terminal product (as temperature is raised) should be more pronounced than at higher CO pressures. This is exactly the trend observed in Tables II and III.

The hydroformylation of 1-pentene, catalyzed by rhodium in the presence of the cis-chelating ligand $Ph_2PCH_2CH_2PPh_2$, exhibited far lower *n*/*b* selectivities than analogous reactions in the presence of PPh_3.[14] Furthermore, the $Ph_2PCH_2CH_2PPh_2$–rhodium complexes were more active isomerization catalysts and internal hydroformylation catalysts.[14] Thus, we extended these studies to styrene. The preparation of complex **7** was carried out according to eq 2.

$Ph_2PCH_2CH_2PPh_2 + RhH(CO)(PPh_3)_3$



(2)

7

To the degree that the hydroformylation mechanisms of reactions catalyzed by **7** resemble those catalyzed by $RhH(CO)(PPh_3)_3$ (i.e., Scheme I), one would suggest the involvement of the equilibria shown in Scheme III. Species **8** and **10** could catalyze the reaction via a dissociative process while **9** and **11** would require an associative process. The acidity of

Scheme III

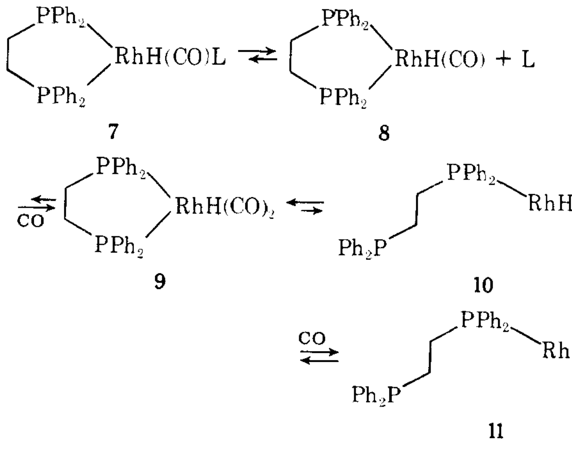


Table IV. Selectivities (*b/n*) in Hydroformylations of Styrene Catalyzed by $RhH(CO)(Ph_2PCH_2CH_2PPh_2)(PPh_3)$

P/Rh	pressure, psi	*b/n*, yield, % 60 °C	80 °C	120 °C
3	100	1.4, 24.1	0.9, 72.8	0.7, 69.4
	400	9.0, 100	6.4, 100	1.3, 100
	800	11.9, 100		3.6, 100
16.7	100	25.8, 53.1	20.1, 7.32	4.3, 90.5
	400	26.5, 54.9	21.8, 72.0	12.3, 100
	800	28.1, 30.4	21.5, 23.1	14.8, 100

[a] Each reaction contained 0.044 mmol of Rh, 1 mL of styrene, and 8 mL of benzene and employed 1:1 H_2/CO.

Table V. Selectivities (*b/n*) in Hydroformylations of Styrene Catalyzed by Resins 2A–D, Ⓟ-$C_6H_4P(Ph)CH_2CH_2PPh_2)$-$RhH(CO)L$[a]

resin (ligand loading, P/Rh)	pressure psi	*b/n*, yield, % 60 °C	80 °C	120 °C
2A (1.4, 2.8)	100	6.4, 100	—	0.8, 94.4
	400	—	8.3, 100	—
	800	12.9, 100	—	3.5, 100
2B (21.6, 3.3)	100	5.4, 97	1.5, 100	0.7, 85
	400	12.0, 100	7.2, 100	1.1, 100
	800	12.2, 100	8.9, 100	1.8, 100
2C (21.6, 9.1)	100	3.2, 49.3	2.1, 95.2	0.96, 98.5
	400	7.0, 50.7	4.5, 81.0	2.0, 100
	800	7.9, 34.6	7.3, 100	3.0, 100
2D (21.6, 16.7)	100	4.7, 83.1	1.7, 32.4	0.8, 33.9
	400	—	3.2, 100	—
	800	6.0, 15.2	5.3, 59.4	4.4, 100

[a] Each reaction contained 0.044 mmol of Rh, 1 mL of styrene, and 8 mL of benzene and employed 1:1 H_2/CO.

these complexes should follow the order **11** > **10** > **9** > **8**. On that basis, the *b/n* selectivity should follow the same order since increasing acidity would favor increased Markovnikov addition of rhodium hydride to styrene. Sterically, terminal rhodium addition should be favored more for the addition of **8** than **10** and **9** than **11**. The steric effects of cis phosphines (**8** and **9**) are presumed to be less than that of two trans PPh_3 groups. Overall, higher CO pressures would shift the equilibria in Scheme III from **8** toward **9–11**. Due to the chelate effect, the equilibrium constant of **9** $\rightleftharpoons$ **10** must be very small.

Hydroformylations of styrene were carried out using **7** at pressures of 100, 400, and 800 psi and temperatures of 60, 80, and 120 °C. Using **7** the P/Rh ratio was 3. By adding excess $Ph_2PCH_2CH_2PPh_2$ reactions were also carried out at P/Rh = 16.7. These reactions are summarized in Table IV. Similarly, reactions catalyzed by the resin-anchored catalysts **2A–D** were carried out over the same range of conditions. These are summarized in Table V.

The selectivities of the homogeneous reactions (Table IV) exhibit the following trends. Increasing the temperature lowers the *b/n* ratio at all pressures and both P/Rh ratios. Increasing pressure from 100 to 800 psi causes large increases in *b/n* selectivity. At all temperatures, the *b/n* ratio increased when the P/Rh ratio increased from 3 to 16.7 at constant pressure. The first two trends parallel those observed using $RhH(CO)(PPh_3)_3$ as the catalyst. However, the dependence of the *b/n* ratio on P/Rh was much more pronounced using the chelating ligand than PPh_3. When high P/Rh ratios (i.e., 16.7), higher pressures (800 psi), and lower temperatures (60 °C) are combined, remarkably high selectivities were observed. Thus, *b/n* = 28.1 at these conditions.

These results are in accord with the equilibria outlined in Scheme III. Higher CO pressures did, indeed, lead to higher *b/n* ratios as predicted by a general equilibrium shift from **8** toward **11**. Higher temperatures should favor bisphosphine complexes **8** and **9** relative to **10** and **11**. Thus, a decrease in *b/n* ratio with increasing temperature (as observed) is expected. The reason for the increase in *b/n* ratio with increased P/Rh ratios (Table IV), however, is unclear.

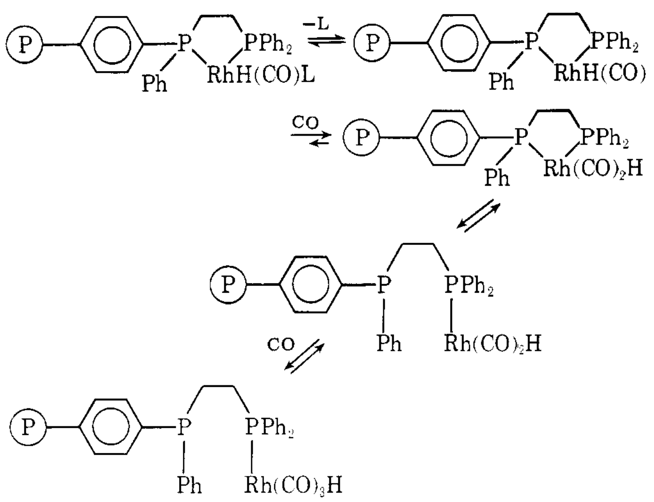
Using resins **2A–D**, the variation of selectivity follows these same trends (see Table V). Increasing temperature again lowers the *b/n* ratio, and increasing pressure again raises this ratio (although not nearly as markedly as was the case in the homogeneous reactions (Table IV). However, one sharp difference is noted. At constant ligand loading (21.6%) there is no clear trend in the *b/n* selectivity as the P/Rh ratio is raised from 3.3 to 9.1 to 16.7 (resins **2B–D**, Table V). This should be compared to the large increase in *b/n* ratio as P/Rh increased in the homogeneous reactions. This effect may be the manifestation of the matrix isolation of most anchored diphos ligands from a given rhodium atom. Thus, the resin-anchored catalysts were not able to achieve *b/n* ratios as high as those observed for the homogeneous systems.

The equilibria depicted in Scheme IV show possible paths involved. If only these equilibria are involved, one would predict selectivity would not depend strongly on the P/Rh ratio, as was the case (Tables IV and V). The strong dependence of the *b/n* ratio on the P/Rh ratio in the homogeneous reactions, however, remains unexplained. Perhaps two phosphorus atoms from different diphos molecules can coordinate rhodium to generate a trans bisphosphine species. Such a trans species presumably would tend to undergo anti-Markovnikov rhodium hydride addition (sterically more favorable) to styrene.

The selectivities did not change as a function of conversion. Thus, the *b/n* ratios remained constant during the course of these reactions whether the catalyst was $RhH(CO)(PPh_3)_3$ or **7**. This was also true for the resin-bound catalysts **1** and **2**. This observation was expected since no double bond isomerization can take place with styrene as the substrate. The selectivity, using these same catalyst systems, also remained constant during the hydroformylation of 1-pentene.[14]

The leaching of rhodium from chelating polymers **2C** and **2D** was studied by (1) examining the resins after five recycles

Scheme IV



at 100°C and 400 psi and (2) extensive extraction with a toluene solution under 1 atm of carbon monoxide. No change in percent of Rh was noted by atomic absorption analyses.

A reviewer requested that an explanation be offered for why the *b/n* selectivities of resins **1A–1C** were somewhat lower than those of the homogeneous analogues (realizing that the responses of selectivity to changes in temperature, pressure, and P/Rh were virtually identical). While a definitive response is unwarranted, we suggest two reasons be considered. The competition between carbon monoxide and phosphine within the resin beads involves different phosphine concentrations at the average Rh site because the phosphine has limited mobility on a polymer chain. Also, the concentration of carbon monoxide dissolved inside the resin beads may not be identical to that in bulk solution.

Experimental Section

Benzene was dried over CaH_2 for 24 h and distilled under nitrogen. Nitrogen, hydrogen, and carbon monoxide were obtained commercially (99+%) and used as received. $RhH(CO)(PPh_3)_3$ and $Ph_2PCH_2CH_2PPh_2$ were used as received from Strem Chemical Co. $RhH(CO)\ (Ph_2PCH_2CH_2PPh_2(\ (PPh_3)$, **7**, was prepared as described previously.[14]

Preparation of $PhP(H)CH_2CH_2PPh_2$. This compound was prepared by the base-catalyzed addition of phenylphosphine across the double bond of diphenylvinylphosphine sulfide followed by $LiAlH_4$ reduction of the sulfide as described by King.[23] A 40% yield, bp 210–215 °C (0.2 torr), was obtained and the product has an NMR spectrum identical to that previously reported.[24]

Preparation of Resins 1A–C. These resins were prepared according to published methods.[5,25]

Preparation of Resins 2A–D. A dry THF solution (100 mL) containing $PhP(H)CH_2CH_2PPh_2$ (5.2 g, 16.3 mmol) was added slowly to a suspension of potassium metal (4.7 g, 120 mmol) in dry THF (100 mL) under nitrogen. A yellow precipitate appeared immediately. Stirring was continued 2 days at 22 °C and unreacted potassium was then removed. The solution was transferred, under nitrogen, to a rapidly stirred deoxygenated THF slurry of brominated styrene–1% divinylbenzene resin beads (2.1 g, 20.8% Br, 34% of the resin's phenyl rings were brominated). This reaction was stirred under nitrogen for 72 h after which the unreacted $K^+[PhPCH_2CH_2PPh_2]^-$ was hydrolyzed in deoxygenated acetone–water (3:1, 500 mL). The resulting resin beads were washed successively in 500 mL each of the following nitrogen-purged solvents: acetone, water, benzene, and methanol. The beads were dried at 22 °C (0.1 mm) for several days. Analysis found 7.73% P which corresponded to 21.6% of the phenyl rings containing an attached Ⓟ-$C_6H_4P(Ph)CH_2CH_2PPh_2$ group. Aliquots of this polymer were then swollen in benzene and reacted with the desired amount of $RhH(CO)(PPh_3)_3$ to effect phosphine exchange. Using various ratios of polymer to $RhH(CO)(PPh_3)_3$, the P/Rh of the resin could be varied. The resulting polymers (i.e., **2B–D**) were then extracted (soxhlett) with benzene for 3 days and dried in vacuo. Resin **2A** was prepared in the manner similar to that described above.

Hydroformylations. Hydroformylations of styrene were carried out in 150 cm^3 stainless steel pressure bombs which had been dried at 120 °C overnight and purged with nitrogen while cooling. The appropriate amount of resin catalyst (0.044 mmol of Rh) or its homogeneous analogue (0.044 mmol) was added with benzene (8 mL) and styrene (1 mL). The bomb was cooled in an ice bath, pressurized to 200 psig with carbon monoxide and allowed to equilibrate 5 min before venting to atmospheric pressure. This procedure was repeated twice. The bomb was then pressurized to the desired pressure with equal amounts of hydrogen and carbon monoxide. The reaction was conducted at constant pressure using apparatus already described.[14] The bomb was placed in a pre-equilibrated oil bath at the proper temperature and shaken, vigorously, with a wrist-action shaker for the desired reaction time. Upon completion, the bomb was cooled and gases were then vented. The reaction solution was analyzed, quantitatively, by GLC ($\frac{1}{8}$ in × 7 ft, 15% OV-17 on Chromosorb W, isothermol (180 °C, He carrier gas)) to determine the percent conversion and branched to normal aldehyde ratio.

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Registry No.—$PhP(H)CH_2CH_2PPh_2$, 33355-58-7; $K^+[PhPCH_2CH_2PPh_2]^-$, 64611-28-5; styrene, 100-42-5; $RhH(CO)(PPh_3)_3$, 17185-29-4; $RhH(CO)(Ph_2PCH_2CH_2PPh_2)(PPh_3)$, 64611-33-2; $Ph_2PCH_2CH_2PPh_2$, 1663-45-2.

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