Colloidal Pt supported on poly(vinyl alcohol) ($n = 1500$) was prepared according to Rampino's procedure.[7]

Hydrogen Generation. In a typical photochemical hydrogen producing experiment, 8 mL of an aqueous solution containing $ZnT_{SO_3Na}PP$ (7.7×10^{-5} M), AsA (1.0×10^{-1} M), MeV^{2+} (1.0×10^{-2} M), and Pt colloid (Pt, 1.15×10^{-4} M) was placed in a 10-mL test tube and was carefully deareated by flushing with N_2. The test tube was then closed, and into the tube was introduced 1.00 mL of Ar as an internal standard with a syringe through a rubber seal. The tube was irradiated, with ice cooling, with a National RF-110 V 500-W tungsten lamp. A filter to cut off light below 430 nm (Toshiba VY 43) was used. After irradiation a small amount of gas present in the tube was removed by use of a 50-μL microsyringe through a rubber seal, and the amount of hydrogen produced was determined by gas chromatography (Shimadzu GC-3BT) with a molecular sieve 13X column (Yanagimoto MFG Co. Ltd.) with N_2 as carrier gas at room temperature. Control experiments were carried out in a similar manner.

Quantum Yield Determination. The quantum yield was determined for 428 ± 30-nm irradiation, selected by simultaneous application of a Toshiba T-44 cut off filter and an aqueous crystal violet solution (0.25 mM). A ferrioxalate (0.15 M) chemical actinometer was employed to measure photon quanta.

Emission Spectra. The emission spectra from $ZnT_{SO_3Na}PP$ in nondegassed aqueous solutions were recorded with a Union FS-301 high-sensitivity fluorescence spectrometer. In water were dissolved $ZnT_{SO_3Na}PP$ (3.3×10^{-7} M) and an appropriate quencher

(AsA or MeV^{2+}), and the solution was irradiated at the maximum absorbance of $ZnT_{SO_3Na}PP$ (422 nm). The emission intensities were monitored from 550 to 750 nm. No correction was necessary, since MeV^{2+}, AsA, or CTAB shows no appreciable absorption in the visible region. The relative intensities of the emission at 607 nm relative to the $ZnT_{SO_3Na}PP$ emission in the absence of the above quencher (100%) are as follows. In the absence of CTAB: 5×10^{-1} M MeV^{2+}, negligible; 5×10^{-5} Me MeV^{2+}, 24; 1×10^{-1} M AsA, 98. In the presence of 3.3×10^{-3} M CTAB: 5×10^{-3} M MeV^{2+}, 75; 1×10^{-1} M AsA, 29.

Reaction of Chemically Generated $ZnT_{SO_3Na}PP^{+\cdot}$ with AsA. An aqueous solution of $ZnT_{SO_3Na}PP$ (3 mL, 1×10^{-4} M) was rapidly stirred with an excess amount of bromine dissolved in dichloromethane. The violet $ZnT_{SO_3Na}PP$ solution turned to green and the generation of $ZnT_{SO_3Na}PP^{+\cdot}$ was confirmed with a broad absorption of 500–750 nm (disappearance at 558 nm) by electronic spectrum. After the addition of 50 μL of 0.1 M AsA to the solution of the cation radical, the color of the solution turned to slightly turbid violet within a few seconds, and $ZnT_{SO_3Na}PP$ was regenerated, judging from the electronic spectrum and other characteristic spectra. From the absorption at 558 nm the amount of regenerated $ZnT_{SO_3Na}PP$ amounted to 90%, based on the $ZnT_{SO_3Na}PP$ initially used.

1-Pentene Hydroformylation Catalyzed by Polymer-Bound Ruthenium Complexes

Charles U. Pittman, Jr.,* and Gary M. Wilemon

Department of Chemistry, The University of Alabama, University, Alabama 35486

Polymer-bound ruthenium hydroformylation catalysts were prepared by reacting diphenylphosphinated styrene–1% divinylbenzene resins with $Ru(CO)_3(PPh_3)_2$ under a carbon monoxide atmosphere. Resins with 29% and 5% ring-substitution loading levels of phosphine were prepared, and resins with P/Ru ratios of 3.1, 6.7, and 11.3 were made with the 29% phosphine loading. These resins functioned as 1-pentene hydroformylation catalysts and were compared to the homogeneous use of $Ru(CO)_3(PPh_3)_2$ as the catalyst. No olefin isomerization occurred. The resin catalysts with P/Ru ratios of 3.1 and 6.7 at 29% loading gave higher n/b aldehyde selectivities (3.5–3.8) than the homogeneous catalyst when employed at P/Ru ratios of 20 but not as high as was achieved by using $Ru(CO)_3(PPh_3)_2$ in molten PPh_3 (5.1). The n/b selectivity was discussed in terms of the equilibrium between (polymer–$PPh_2)_2RuH_2$(alkene)(CO) and polymer–PPh_2RuH_2(alkene)$(CO)_2$ within the resin matrix where phosphine loading, P/Ru, ligand mobility, and swelling play contributing roles. The novel 1,1'-bis(diphenylphosphino)ferrocene ligand induced higher n/b selectivities than PPh_3 in homogeneous Ru-catalyzed reactions.

Extensive studies of olefin hydroformylation[1] have been conducted by using cobalt[2] and rhodium[3] complexes as catalysts. Ruthenium complexes have been far less extensively studied.[1] Wilkinson et al. examined the activity of several ruthenium phosphine complexes,[4-6] using 1-hexene as the substrate in benzene at 120 °C and 1400 psi. $Ru(CO)_3(PPh_3)_2$, $RuH_2(CO)_2(PPh_3)_2$, $RuH(NO)(PPh_3)_3$,
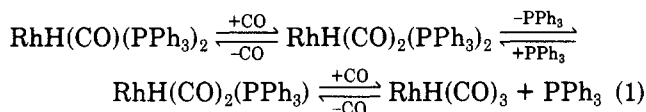
and $RuH_4(PPh_3)_3$ were found to be effective catalysts. Hexene conversions ranged from 79 to 88% and the normal to branched aldehyde ratios (n/b) varied from 2.0 to 2.9. Products from competing hydrogenation or isomerization reactions (i.e., alkanes, internal alkenes) were not observed. The recovered metallic species in each case was $Ru(CO)_3(PPh_3)_2$, suggesting the same active species could have operated in each case. Wilkinson proposed $RuH_2(CO)_2PPh_3$ was the active catalytic species.

We have previously employed polymer-supported cobalt and rhodium complexes for hydroformylation catalysts.[7-15]

(1) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1–60.
(2) Falbe J. In "Carbon Monoxide in Organic Synthesis"; Springer-Verlag: New York, 1970; pp 3–77.
(3) Marko, L. In "Aspects of Homogeneous Catalysis"; Ugo, R., Ed.; Reidel Publishing Co.: Boston, 1974; Vol. 2, pp 3–55.
(4) Evans, D.; Osborn, J. A.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3133.
(5) Sanchez-Delgado, R. A.; Bradley, J. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 399.
(6) Evans, D.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *Nature (London)* **1965**, *208*, 1203.
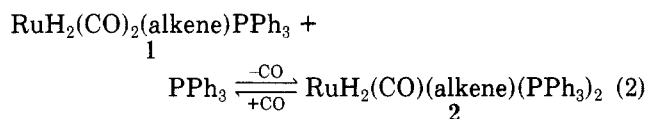
(7) Evans, G. O.; Pittman, C. U., Jr.; McMillan, R.; Beach, R. T.; Jones, R. *J. Organomet. Chem.* **1974**, *67*, 295.
(8) Pittman, C. U., Jr.; Smith, L. R.; Hanes, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 1742.
(9) Pittman, C. U., Jr.; Hanes, R. M. *J. Am. Chem. Soc.* **1976**, *98*, 5402.

Remarkably high normal/branched (n/b) aldehyde selectivities were found by using hydridocarbonylrhodium complexes supported on diphenylphosphinated styrene/divinylbenzene.[9,12] The observed n/b ratios were far higher than those obtained, at equivalent P/Rh ratios and phosphine concentrations, by using the corresponding homogeneous RhH(CO)(PPh$_3$)$_3$ catalyst system.[12] These remarkable selectivities were related to the equilibria between the rhodium species depicted below which, apparently, differ significantly when the phosphine groups are resin bound vs. when the PPh$_3$ molecule is free in solution[10,12] (see eq 1).

$$RhH(CO)(PPh_3)_2 \xrightleftharpoons[-CO]{+CO} RhH(CO)_2(PPh_3)_2 \xrightleftharpoons[+PPh_3]{-PPh_3}$$

$$RhH(CO)_2(PPh_3) \xrightleftharpoons[-CO]{+CO} RhH(CO)_3 + PPh_3 \quad (1)$$

Since Wilkinson found the rate and selectivity of ruthenium-catalyzed hydroformylation depended upon such variables as P/Ru, H$_2$/CO, phosphine concentration, and temperature,[4-6] the possibility existed that polymer-anchored ruthenium catalysts might exhibit modified selectivities relative to their homogeneous analogues. Furthermore, resin-attached ruthenium catalysts might be used as fixed catalyst beds, permitting their use in flow systems or their use in batch reactions where catalyst/product separations would be simplified. Thus, polystyrene/divinylbenzene resins were phosphinated and the ruthenium complex, Ru(CO)$_3$(PPh$_3$)$_2$, was attached. These supported catalysts were studied in hydroformylations of 1-pentene.

In order to compare the behavior of polymer-anchored and homogeneous ruthenium catalyst systems, the major trends from Wilkinson's results with homogeneous ruthenium catalysts will be mentioned now.[4-6] At 120 °C, 1400 psi, and a H$_2$/CO ratio of 1/1, Wilkinson found that increasing the hydrogen partial pressure (holding total pressure constant) increased the rate. Increasing the carbon monoxide pressure decreased rate, a result consistent with rate-determining oxidative addition of hydrogen subsequent to dissociation of carbon monoxide. The n/b aldehyde ratio was not very sensitive to the total or partial pressures. However, the addition of excess PPh$_3$ increased the n/b selectivity and lowered the rate. In molten PPh$_3$, the n/b ratio was approximately 5, but the yield was less than 10% in 20 h, suggesting a mechanism involving phosphine dissociation. The mechanism proposed by Wilkinson is shown in eq 2. Since the orientation

$$RuH_2(CO)_2(alkene)PPh_3 +$$
$$\mathbf{1}$$

$$PPh_3 \xrightleftharpoons[+CO]{-CO} RuH_2(CO)(alkene)(PPh_3)_2 \quad (2)$$
$$\mathbf{2}$$

of Ru–H addition to the olefin determines the n/b selectivity, the regiospecificity of this step is critical. Wilkinson[5] proposed that the intermediate which adds to olefin was RuH$_2$(CO)$_2$(alkene)PPh$_3$ (1), which at high PPh$_3$ concentrations would undergo the equilibrium shown in eq 2. Thus, either 1 or 2 undergoes intramolecular olefin insertion into the Ru–H bond. Compound 2 would be ex-

pected to add ruthenium more selectively to the terminal position (leading to higher n/b ratios) due to the greater steric bulk of its two PPh$_3$ ligands.

Experimental Section

Dichlorodicarbonylbis(triphenylphosphine)ruthenium(III) [RuCl$_2$(CO)$_2$(PPh$_3$)$_2$] and ruthenium(III) trichloride hydrate (RuCl$_3$·xH$_2$O) were purchased from Strem Chemical Co. and used as received. Other reagents purchased and used without further purification were chlorodiphenylphosphine (Ph$_2$PCl) (Pressure Chemical Co.), bis(1,2-diphenylphosphino)ethane (Ph$_2$PCH$_2$CH$_2$PPh$_2$) (Organometallics, Inc.), 1-pentene (Chemical Samples Co.), hydrogen, nitrogen, and carbon monoxide. Benzene and THF were continually refluxed over CaH$_2$ under nitrogen and distilled immediately prior to use.

Infrared spectra (IR) were obtained on a Beckman IR-33 instrument. Proton nuclear magnetic resonance (NMR) spectra were obtained on a Hitachi Perkin-Elmer R-20B 60-MHz instrument. Olefin conversions and product distributions were determined via gas–liquid chromatography (GLC) using a Hewlett-Packard Model 5710A or Varian Model 3700 gas chromatograph with $1/8$ in. × 6 ft copper columns packed with 15% Carbowax 20M on Chromosorb W. GLC data was processed via electronic integration with a Hewlett-Packard Model 3380A reporting integrator. Internal-standard and area-normalization calibration techniques were used to determine yields and product distributions. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories.

Washing of Styrene–Divinylbenzene Copolymer. Cross-linked polystyrene beads (100 g, 0.95 mmol, 200–400 mesh, 1% divinylbenzene, 14 000 molecular weight exclusion limit; Bio-Rad Laboratories) were washed successively in 1 L of the following solutions at 60–80 °C: 1 N NaOH (1 h), 1 N HCl (1 h), 1 N NaOH (1 h), 1 N HCl (1 h), H$_2$O (24 h), DMF (1 h), 1 N HCl (1 h), and H$_2$O (24 h). The following solutions were then used at room temperature: CH$_3$OH (1 h), CH$_2$Cl$_2$/CH$_3$OH (2/3, 1 h), CH$_2$Cl$_2$/CH$_3$OH (3/1, 1 h), CH$_2$Cl$_2$/CH$_3$OH (9/1, 1 h), and CH$_2$Cl$_2$ (24 h). The resin was then filtered and dried in vacuo (0.05 torr, 25 °C). In most cases, the washing was accompanied by a loss in weight of 5–10%.

Bromination of Styrene–Divinylbenzene Copolymer. In a typical preparation, cross-linked polystyrene beads (20 g, 0.19 mol) were swelled in CCl$_4$ (300 mL) at 0 °C in the dark. Iron powder (2 g) was added to this slurry and vigorous stirring initiated. Bromine (6.5 g, 0.041 mol) in CCl$_4$ (75 mL) was added dropwise over 1 h. The reaction was then warmed to room temperature. HBr was vented into an aqueous AgNO$_3$ trap. The slurry was stirred for 24 h, the solvent was removed by filtration on a coarse glass frit funnel, and unreacted iron powder was removed with a magnet. The resin was then washed by stirring successively in 1 L each of 5% sodium thiosulfate (1 h), 5% aqueous sodium carbonate (1 h), acetone (6 h), benzene (6 h), benzene/methanol (7/3, 6 h), and methanol (6 h). The beads were then dried in vacuo for 24 h (25 °C, 0.05 torr). Bromine analysis indicated 10.59% Br.

Reaction of Brominated Resin with Lithiodiphenylphosphine. To a stirred THF (75 mL) suspension of lithium (5 g, 0.7 mol) was added a THF solution (50 mL) containing chlorodiphenylphosphine (40 g, 0.182 mol) dropwise under nitrogen. Formation of lithiodiphenylphosphine was indicated by the appearance of a bright red color. After 24 h, unreacted lithium metal was removed, and the solution was slowly added to a rapidly stirring THF slurry of the brominated beads (20 g, 10.59% Br, 0.026 mol of Br.) This mixture was allowed to stir overnight (longer when higher percentage Br resins were used) under nitrogen. The slurry was then hydrolyzed by being added to 2 L of nitrogen-saturated acetone/water (3/1) and stirred for 1 h. The beads were then filtered and washed by being stirred successively in 1 L each of the following nitrogen-saturated solvents: water (2 h), acetone (2 h), benzene (24 h), benzene (2 h), benzene/methanol (2 h), methanol (2 h). The beads were then dried in vacuo (80 °C, 0.05 torr) for 24 h and analyzed for 3.60% P which corresponds to 15.3% of the polystyryl rings substituted with the diphenylphosphine moiety. Bromine analysis showed almost quantitative replacement of bromide (0.07% Br).

(10) Pittman, C. U., Jr.; Hirao, A.; Jones, C.; Hanes, R. M.; Ng, Q. *Ann. N.Y. Acad. Sci.* **1977**, *295*, 15.
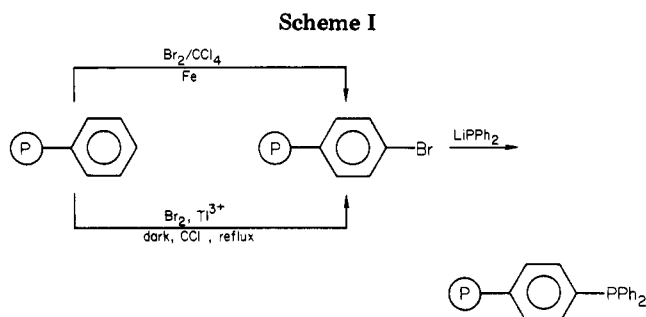
(11) Pittman, C. U., Jr.; Hirao, A. *J. Org. Chem.* **1978**, *43*, 640.

(12) Pittman, C. U., Jr. *Colloq. Int. CNRS* **1977**, *No. 281*, 4.

(13) Pittman, C. U., Jr.; Lin, C. C. *J. Org. Chem.* **1978**, *43*, 4928.

(14) Pittman, C. U., Jr.; Honnick, W. D.; Yang, J. J. *J. Org. Chem.* **1980**, *45*, 684.

(15) Pittman, C. U., Jr.; Honnick, W. D. *J. Org. Chem.* **1980**, *45*, 2132.

Scheme I

Preparation of Ru(CO)₃(PPh₃)₂.[16] Triphenylphosphine (2.37 g, 9 mmol) and 90 mL of 2-methoxyethanol were placed in a three-necked, 500-mL, round-bottomed flask. Stirring was initiated, and the contents were heated to refluxing temperatures. Then solutions of RuCl₃·xH₂O (0.39 g, 1.5 mmol) in 30 mL of 2-methoxyethanol, 30 mL of aqueous formaldehyde (40% w/v), and KOH (~0.6 g) in 30 mL of 2-methoxyethanol were added rapidly and succesively to the flask. The reaction solution was refluxed for 1 h and then cooled to room temperature. The resultant yellow precipitate was filtered on a glass frit, washed with ethanol (50 mL), water (50 mL), ethanol (50 mL), and n-hexane (100 mL), and dried in vacuo (0.05 torr, 25 °C) for 1 h; yield 0.9 g (84%). Infrared spectral analysis shows a single strong band at 1900 cm⁻¹ (C=O).

Anal. Calcd for C₃₉H₃₀O₃P₂Ru: C, 66.0; H, 4.26; P, 8.73; Ru, 14.2. Found: C, 66.15; H, 4.31; P, 8.56; Ru 14.22.

Anchoring of Ru(CO)₃(PPh₃)₂ to Polymeric Ligands. In a typical preparation, phosphinated resin (3.3 g, 5.60% P, 6.00 mmol of P) and Ru(CO)₃(PPh₃)₂ (1.0 g, 1.41 mmol) were placed in a flask previously purged with carbon monoxide and containing toluene (100 mL) saturated with carbon monoxide. The resulting slurry was refluxed under carbon monoxide for 24 h to accomplish ligand exchange. The resin was then recovered by filtration (glass frit) and extracted with benzene under carbon monoxide in a Soxhlet extractor for 24 h to remove all soluble catalyst and ligand. The polymer-bound catalyst was then dried in vacuo (0.05 torr, 25 °C) for 30 min and stored in a sealed tube under a positive pressure of carbon monoxide. Elemental analysis showed 5.89% P and 2.87% Ru, which corresponds to a P/Ru ratio of 6.70.

Hydroformylation of 1-Pentene with Ru(CO)₃(PPh₃)₂ or Polymer-Bound Ru(CO)₃(PPh₃)₂. Hydroformylations were carried out in 75 cm³ stainless-steel pressure bombs. The bombs were dried in a 120 °C oven overnight before use and flushed with nitrogen while cooling. The appropriate amount of catalyst (0.1 mmol of Ru, polymer-bound or soluble) was added, along with benzene (10 mL) and 1-pentene (2.2 mL, 20.1 mmol). The bomb was flushed three times with ~400 psig of hydrogen and then pressurized to the desired pressure and ratio of hydrogen and carbon monoxide. The bomb was then placed in an oil bath preequilibrated at the proper temperature and shaken with a wrist-action shaker for 20 h. (Some reactions were outfitted with a sampling device which enabled aliquots of the reaction to be obtained without interrupting the reaction. These reactions were run until ~80% of the 1-pentene had been consumed.) The bomb was then cooled, the gases were vented, and the resin was recovered by filtration. Products were isolated by preparative GLC in example cases and analyzed by ¹H NMR and IR. Spectra were identical with those of commercial samples.

Hexanal: IR (KBr) 2820 and 2720 (aldehyde C–H), 1725 (aldehyde C=O) cm⁻¹; NMR (CDCl₃) δ 9.8 (t, 1, CHO), 2.4 (t, 2, C₂H), 1.7 (t, 2, C₃H), 1.4 (m, 4, C₄H and C₅H), 0.9 (t, 3, CH₃). 2-Methyl-1-pentanal: IR (KBr) 2860 and 2710 (aldehyde C–H), 1715 (aldehyde C=O), 1380 (pendant CH₃) cm⁻¹; NMR (CDCl₃) δ 9.6 (d, 1, CHO), 2.3–2.5 (m, 1, C₂H), 1.3–1.8 (m, 4, C₃H and C₄H), 1.1 (d, 3, C₂CH₃), 0.9 (t, 3, CH₃).

Results and Discussion

**Preparation of Phosphinated Resins.** The phosphinated polymeric ligands were prepared from 200–400-

Table I. Elemental Analysis, Composition, and Swelling Data for Resin-Bound Ruthenium Catalysts, (Polymer-PPh₂)₂Ru(CO)₃

resin	%P	%Ru	P/Ru	PL, %[a]	swelling factor[b]
1	5.57	5.81	3.1	29.2	1.6
2	5.89	2.87	6.7	29.2	1.8
3	5.25	1.52	11.3	29.2	2.4
4	7.05	1.59	14.5	5.3	2.2

[a] PL is the percentage of the resin's phenyl rings substituted with PPh₂ groups. [b] The swelling factor is the volume of the swollen resin divided by the volume of the equivalent amount of dry resin. This was measured in a graduated cylinder by noting the number of milliliters of a given quantity of dry resin and then determining (after 8 h) the expansion of the resin when excess benzene was added.

mesh styrene–1% divinylbenzene resin beads, as shown in Scheme I. Prior to use, these commerically available resins were washed thoroughly to remove impurities left behind from the commerical polymerization process.[17] Then, the resins were brominated either by iron-catalyzed Friedel–Crafts bromination (Experimental Section) or according to the procedure described by Farrall and Fréchet.[18] Almost quantitative replacement of the bromine was achieved through treatment with lithiodiphenylphosphine. Resins were prepared with 5.3 and 29.2% phosphine loadings (the percentage of the resin's phenyl rings substituted with PPh₂ groups) corresponding to analyses of 1.45 and 5.60% P, respectively.

Anchoring of Homogeneous Ruthenium Catalysts to Polymeric Ligands. The ruthenium complexes used in this study were bound to phosphinated polystyrene resins through ligand displacement. Ru(CO)₃(PPh₃)₂ was refluxed with phosphinated resin in toluene for 24 h under an atmosphere of carbon monoxide to prevent catalyst decomposition (eq 3). The resins were filtered, extracted with benzene, and dried in vacuo.
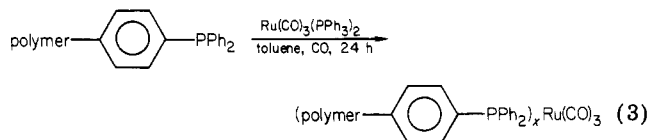
For examination of the effects of both phosphine loading and P/Ru ratios (at constant loading) within a polymer matrix during a catalytic process, both the 5.3% and 29.2% phosphine loaded resins were used, and the 29.2% load resin was used to make three different P/Ru ratios (i.e., 3.1, 6.7, and 11.3). The 5.3% phosphine-loaded resin was converted to a P/Ru ratio of 14.5. The phosphine loading levels, P/Ru ratios, and elemental analyses of the polymer-bound catalysts are summarized in Table I. Polymers prepared in this fashion exhibited colors similar to the starting complexes.[19] Resins with anchored Ru(CO)₃(PPh₃)₂ were yellow, as was the soluble catalyst. All polymer-bound catalysts exhibited infrared absorptions in the carbonyl stretching region similar to their respective soluble complexes. (Polymer-PPh₂)₂Ru(CO)₃ exhibited a broad carbonyl stretch centered around 1910 cm⁻¹ while Ru(CO)₃(PPh₃)₂ exhibited a lone broad band at 1900 cm⁻¹.

Matrix swelling allows reagents to access catalytic sites throughout the volume of the resin beads. Thus, swelling is an important consideration in the use of microporous

(16) Ahmad, N.; Levison, J. J.; Robinson, J. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 50.

(17) Rolles, H. M.; Schluenz, R. W. *J. Am. Chem. Soc.* **1974**, *96*, 6469.
(18) Farrall, J. Jean; Fréchet, Jean M. J. *J. Org. Chem.* **1976**, *41*, 3877.
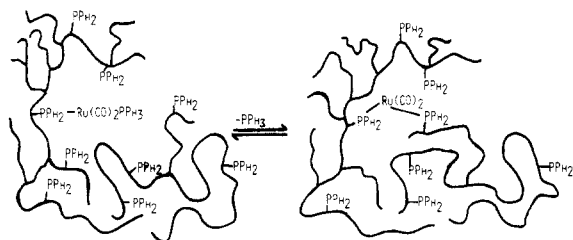(19) Hanes, R. M. Ph.D. Dissertation, The University of Alabama, Universtiy, AL, 1976.

Figure 1. Polymer cross-linking by complete phosphine ligand exchange at ruthenium sites within the matrix.

Table II. Homogeneous Hydroformylations of 1-Pentene with $Ru(CO)_3(PPh_3)_2$ [a]

reaction	temp, °C	pressure, psig	H_2/CO ratio	P/Ru[c] ratio	% conv	n/b[b]
1	140	1000	1/1	0	99	2.3
2	140	1000	1/1	3	99	2.4
3	140	1000	1/1	10	99	3.3
4	140	1000	1/1	20	90.5	3.4
5	140	1000	2/1	0	99	2.6
6	140	1000	9/1	0	99	2.4
7	140	1000	1/2	0	88.5	3.0
8	140	1000	1/9	0	69.5	3.1
9	140	1500	1/1	0	99	2.5
10	140	300	1/1	0	14.4	3.1
11	100	1000	1/1	0	66.8	2.5
12	100	1000	1/1	3	18.1	3.2
13	140	1000	1/1	10[d]	5.2	3.1
14	140	1000	1/1	26[d]	0	

[a] All reactions were run with 0.1 mmol of Ru complex and 20.1 mmol of 1-pentene in 10 mL of benzene. [b] n/b is the mole ratio of hexanal to 2-methyl-1-pentanal obtained. [c] No excess phosphine was added when P/Ru = 0. [d] Instead of PPh_3, the ligand 1,1'-bis(diphenylphosphino)-ferrocene was employed.

resin supports for catalysts. Diffusional restrictions into the beads are a function of swelling. Thus, the degree of swelling after 2 h in benzene at ambient temperature was determined for each of the polymer-bound catalysts. These data are also given in Table I. All of the catalysts used in this study were swellable in benzene but to a lesser extent than the starting polystyrene-1% divinylbenzene resin beads which swelled to 5.4 times their dry volume. Resins catalysts 1–4 only swelled to from 1.6 to 2.4 times their dry volume. Changes in the swelling properties of the polymers are probably caused by two factors. First, since phosphine substitution results in the placement of large organometallic complexes within a polymer matrix, the polymer's ability to return to its original volume upon the drying may be retarded. Thus, 1 mL of a polymer-bound catalyst sample contains less polymer than 1 mL of the original resin beads. Thus, it will not swell as much when exposed to a solvent. Second, the ruthenium atoms present in the polymer matrix become cross-links when two phosphine groups coordinate to a ruthenium (see Figure 1). These cross-links would serve to hold the metal onto the polymer, but they would also inhibit the internal mobility of the resin and, thus, its swelling ability.

Limited swelling of polymer-bound catalysts could result in slower reaction rates when diffusion of reactants into the polymer-anchored metal sites is made more difficult. It is not known if the swelling factors remain the same at reaction conditions. For example, at higher temperatures under H_2/CO atmospheres, phosphine dissociation within the resin might be facilitated, and some fraction of the cross-links present in the swollen resin at ambient conditions might be removed. Swelling factors for a few polymeric catalysts used in this study were determined at 100 °C and found to be identical with those obtained at room temperature; but swellabilities at 120 or 150 °C under high pressures of hydrogen or carbon monoxide were not obtained. Since the relative association constants of carbon monoxide and PPh_3 for ruthenium are not known at reaction temperatures, the density of metal cross-links during a catalytic reaction cannot be estimated.

1-Pentene Hydroformylations with Homogeneous and Polymer-Bound $Ru(CO)_3(PPh_3)_2$. Since Wilkinson[5] had previously shown that adding excess triphenylphosphine to $Ru(CO)_3(PPh_3)_2$ increased the n/b ratio, the selectivities of the analogous polymer-bound $Ru(CO)_3(PPh_2Ph–polymer)_2$ species at varying phosphine loading levels and at different P/Ru ratios were of interest. These resins should then serve as catalysts in the same manner as the homogeneous complex, $Ru(CO)_3(PPh_3)_2$. The normal to branched aldehyde ratio (n/b) should reflect the effects of phosphine loading and P/Ru as well as the internal mobility of the polymer backbone. Second, it was hoped that the polymer-anchored catalysts might give higher n/b ratios than those reported by Wilkinson[5] for the soluble catalyst where n/b ratios as high as 3.8 (at a P/Ru ratio of 100 in benzene) and 5.1 (in molten PPh_3) were found. Since steric considerations are important, it

was hoped that polymeric phosphines might produce larger increases in the n/b ratios than those observed by Wilkinson for PPh_3. Furthermore, Pittman and Hanes[9] have shown that the n/b selectivities in 1-pentene hydroformylations are remarkably high when polymer-bound rhodium catalysts were employed at high phosphine loadings and high P/Rh ratios.

1-Pentene was chosen as the substrate since its hydroformylation products were easily separated by GLC. Homogeneous reactions were conducted by using $Ru(CO)_3(PPh_3)_2$ at temperatures ranging from 100 to 140 °C and at pressures ranging from 300 to 1500 psig of 1/1 H_2/CO in order to compare the results with those of the resin catalysts. All homogeneous reactions were run for 2 h, and their results are tabulated in Table II. The n/b selectivities, with 1-pentene, were very similar to those reported for 1-hexene by Wilkinson.[5] No isomerization was observed for any of the reactions, indicating that n/b selectivity was entirely due to reaction of the terminal alkene. With $Ru(CO)_3(PPh_3)_2$ (1000 psig of 1/1 H_2/CO, 140 °C) the n/b ratio increases from 2.3 to 3.4 as P/Ru is increased from 0 to 20. Furthermore, as the H_2/CO ratio varies from 1/9 to 1/1 to 9/1, the selectivity decreases from 3.1 to 2.5 (at a H_2/CO ratio of 1/1) and then remains constant (1000 psig, 140 °C). Lowering the temperature from 140 to 100 °C decreased the rate but did not significantly alter the n/b ratio.

When equimolar amounts of 1,1'-bis(diphenylphosphino)ferrocene were added to homogeneous hydroformylations (100 psig of 1/1 H_2/CO, 140 °C), the n/b improved (from 2.3 with no added ligand to 3.1), but the rate is much lower than that for $Ru(CO)_3(PPh_3)_2$. Wilkinson[5] observed the same trends when using $Ru(CO)_3$(diphos) as the catalyst (1400 psig of 1/1 H_2/CO, 120 °C) and suggested that the concentration of coordinatively unsaturated intermediates decreased, thus producing a decrease in rate.

For comparison of hydroformylation selectivities of homogeneous $Ru(CO)_3(PPh_3)_2$ with the resin-bound catalysts, hydroformylations were conducted by using the polymeric catalysts at 1000 psig of 1/1 H_2/CO and 140 °C. Aliquots of the reactions were taken periodically and analyzed to determine their n/b ratios. The results of these reactions are shown in Figure 2 and tabulated in Table III. None of the polymeric catalysts gave n/b ratios higher than were observed with $Ru(CO)_3(PPh_3)_2$ in molten PPh_3.

Table III. Polymer-Bound Catalysts and Their
Selectivities in the
Hydroformylation of 1-Pentene[a]

resin	PL, %[b]	P/Ru	% conv	n/b[c]
1	29.2	3.1	19.6	3.6
1	29.2	3.1	31.9	3.7
1	29.2	3.1	44.8	3.5
1	29.2	3.1	64.4	3.7
2	29.2	6.7	2.4	3.5
2	29.2	6.7	9.6	3.5
2	29.2	6.7	28.1	3.6
2	29.2	6.7	47.7	3.8
3	29.2	11.3	27.4	2.8
3	29.2	11.3	35.6	2.7
3	29.2	11.3	42.7	2.8
3	29.2	11.3	72.4	3.2
4	5.3	14.5	10.8	1.4
4	5.3	14.5	15.6	1.6
4	5.3	14.5	20.4	1.6
4	5.3	14.5	27.2	1.6
4	5.3	14.5	67.4	2.0

[a] All reactions employed the amount of resin necessary to have 0.1 mmol of Ru complex present and 20.1 mmol of 1-pentene in 10 mL of benzene. Each reaction was carried out at 140 °C and 1000 psig (1/1 H_2CO). [b] See footnote a in Table I. [c] See footnote b in Table II.
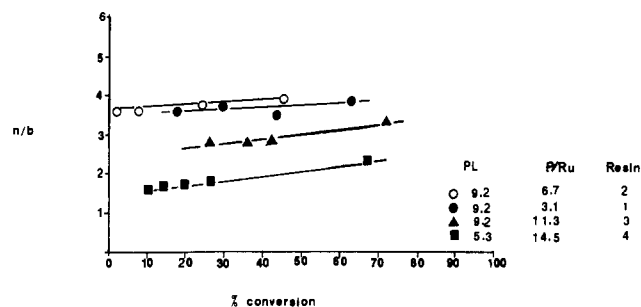

Figure 2. The n/b selectivity of resin-anchored ruthenium catalysts in 1-pentene hydroformylations as a function of conversion (reactions were conducted in benzene at 1000 psig, 1/1 H_2/CO, and 140 °C).

Resins 1 and 2 (PL = 29.2%, P/Ru ratios of 3.1 and 6.7, respectively) gave the highest n/b selectivities (3.5–3.8 over all conversions studied). This selectivity is high when one remembers that the homogeneous reactions required a P/Ru ratio of 100 to achieve an n/b = 3.8. Thus a modest selectivity enhancement induced by the polymer matrix is evident.

Surprisingly, resin 3 (PL = 29.2%, P/Ru ratio of 11.3) gave consistently lower n/b selectivities than either resin 1 (PL = 29.2%, P/Ru ratio of 3.1) or resin 2 even though resin 3 had the largest P/Ru ratio, and all three resins had the same phosphine loading. Since resin 3 has a higher concentration of uncoordinated phosphine sites than either resin 1 or 2 and since it also has greater chain mobility [i.e., it has a larger swelling factor (2.4) than either resin 1 (1.6) or resin 2 (1.8)], resin 3 might be expected to give the highest selectivities. This expectation is based on shifting the equilibrium, shown in eq 2 for homogeneous species, to the right to generate more (polymer–PPh₂)₂RuH₂(alkene)(CO) within the resin, thereby giving more 1-hexanal. While greater chain mobility should facilitate the formation of the diphosphine complex, it should also be noted that the more a resin swells, the further apart the phosphine sites become. Resin 3 swells more than resins 1 or 2. Therefore the local concentration of phosphine within
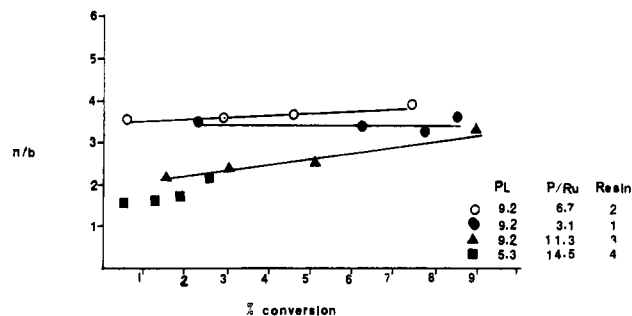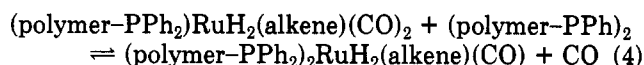

Figure 3. The n/b selectivity of resin-anchored ruthenium catalysts in 1-pentene hydroformylations under a 1/2 H_2/CO atmosphere (reactions were conducted in benzene at 1000 psig and 140 °C).

3 is lower than that in resins 1 or 2 under these reaction conditions, and this would operate to favor the formation of (polymer–PPh₂)RuH₂(alkene)(CO)₂. This explanation is consistent with the lower n/b ratio observed with resin 3. Apparently, the dilution of phosphine due to the swelling of resin 3 negates the increase in selectivity caused by resin 3's higher P/Ru ratio (relative to those of resins 1 and 2).

The substantially lower selectivities of resin 4 (phosphine loading 5.3%, P/Ru ratio of 14.5), relative to resins 1 and 2, can be similarly explained. Resin 4 has a lower phosphine loading (5.3% vs. 29.2% for 1 and 2), and its internal phosphine concentration is substantially lower. Consequently the intraresin equilibrium shown in eq 4 would lie more to the left for resin 4 than for resins 1 and 2.

$$(polymer–PPh_2)RuH_2(alkene)(CO)_2 + (polymer–PPh_2)_2$$
$$\rightleftharpoons (polymer–PPh_2)_2RuH_2(alkene)(CO) + CO \quad (4)$$

An effort was made to boost the selectivities of the polymeric catalysts by increasing the partial pressure of carbon monoxide (i.e., H_2/CO ratio of 1/2) at 1000 psig and 140 °C. The results are displayed in Figure 3. As can be seen by carefully comparing Figure 3 with Figure 2 (reductions using a H_2/CO ratio of 1), the increased partial pressure of carbon monoxide had no noticeable effect on the n/b ratios of any of the resin-catalyzed reactions. Increasing the partial pressure of carbon monoxide in the same manner had increased the n/b ratio from 2.3 to 3.0 for the homogeneous process (entries 1 and 7, Table III).

In conclusion, this work demonstrates that tailoring the phosphine loading and the P/Ru ratio within a resin matrix can be used to modify the selectivity of the resin-bound ruthenium hydroformylation catalysts in predictable ways. The knowledge gained from homogeneous mechanistic studies has been used to understand the activity and selectivity of the resin catalysts. This is only the second polymer-bound ruthenium catalyst where the effects of the resin matrix, loading, and P/Ru have been studied.[20]

Registry No. 1-Pentene, 109-67-1; Ru(CO)₃(PPh₃)₂, 14741-36-7.

(20) Pittman, C. U., Jr.; Wilemon, G. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 67.