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Catalytic Reactions Using Polymer-Bound vs. Homogeneous Complexes of Nickel, Rhodium, and Ruthenium

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Abstract: A series of styrene–divinylbenzene resins were diphenylphosphinated and then complexed with the homogeneous catalysts $(PPh_3)_2Ni(CO)_2$, $(PPh_3)_3RhCl$, $(PPh_3)_3RhH(CO)$, and $(PPh_3)_2RuCl_2(CO)_2$. Reactions catalyzed by the polymer-anchored catalysts were compared with the same reactions carried out with the corresponding homogeneous catalyst. Butadiene cyclooligomerization to 4-vinylcyclohexene, **6**, (*Z,Z*)-1,5-cyclooctadiene, **7**, and (*E,E,E*)-1,5,9-cyclododecatriene, **8**, was effected using $(PPh_3)_2Ni(CO)_2$ and its anchored analogs. Selective hydroformylation of the exocyclic double bond of **7** to a mixture of normal and branched aldehydes **14** and **15** was carried out over $(PPh_3)_3RhH(CO)$ and its anchored analogs as was the hydroformylation of 1-pentene. The rates of hydroformylation as a function of the polymer-bound $-PPh_2/Rh$ ratio, cross-link density, resin particle size, and diffusion effects are discussed. The hydrogenation of **6**, **7**, and **8** by $(PPh_3)_3RhCl$ and its anchored analogs gave ethylcyclohexane, cyclooctane, and cyclodecane. The effect of catalyst anchoring on rates was discussed. Selective hydrogenation of **6**, **7**, and **8** to ethylcyclohexene, (*Z*)-cyclooctene, and (*E*)-cyclododecene was effected using $(PPh_3)_2RuCl_2(CO)_2$ homogeneously and anchored, in the presence of excess PPh_3. Excess anchored phosphine units could not promote the selectivity of these hydrogenations. A comparison of homogeneous vs. anchored catalysts in terms of rates, diffusion, internal polymer mobility, and product selectivity is made where possible.

In recent years the discovery and utility of homogeneous hydrogenation,[1] isomerization,[2] hydrosilation,[3] oligomerization,[4,5] and carbonylation[6] reactions have expanded enormously. Commercial processes based on homogeneously catalyzed routes are becoming increasingly important as evidenced by the Wacker[7] process and others.[8] However, homogeneous catalysis can exhibit the problems of product contamination and catalyst loss, where the products are not readily separated from the catalyst. Anchoring homogeneous catalysts to polymers or other supports effectively "heterogenizes" them, allowing their use in fixed beds and simplifying catalyst recovery. Thus, the anchoring of homogeneous catalysts has recently been the object of several groups.[9]

When a homogeneous catalyst is heterogenized in such a way that it can react, mechanistically, in the same manner as its homogeneous counterpart, the greater selectivity and activity of the homogeneous catalyst is preserved. However, the distinction between homogeneous and heterogeneous catalysis can become difficult to distinguish,[10] especially when highly cross-linked resins or glass or metal surfaces are used to anchor the catalyst.[9c] Where reactants must diffuse into a swollen polymer matrix to reach a bound catalyst site, reaction rates may be lowered because diffusion becomes a rate limiting effect. This was noted by Grubbs[11] in hydrogenations over bound Wilkinson's catalyst, by Pittman, et al.[12] for hydroformylation reactions over polymers to which $Co_2(CO)_8$ was bound by phosphine replacement of

Table I, Elemental Analyses of Polymer-Bound Catalysts[a]

Polymeric catalyst	% P	mmol of P g^{-1}	% metal	mmol of metal g^{-1}
1a	2.39	0,771	2.10 Ni	0,358
1b	1.75	0.564	1.82 Ni	0.310
2	1.83	0.590	1.70 Rh	0.165
3a	1.34	0.432	1.92 Rh	0.187
3b	3.57	1.150	1.87 Rh	0.182
3c	2.01	0.647	1.44 Rh	0,140
4a	1.88	0.605	1.27 Ru	0.126
4b	5.03	1.62	0.98 Ru	0.194

[a] All polymers are SX-1 except **1b** which is SX-2. Infrared spectra of the polymer-bound catalysts showed the same metal–carbonyl and metal–hydride absorptions as the free metal complexes.

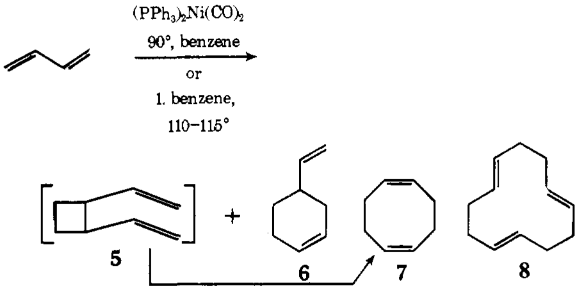
the terminal carbonyls, and by Pittman and Hanes[13] for hydroformylations over bound $(PPh_3)_3RhH(CO)$. Another related, but distinct, factor is that the concentration of reactants at the catalytic site can be different for polymer-bound systems than it is when the catalyst is simply dissolved in solution. This occurs because there are differences in solvation energies between the bulk solution and the inside of the swollen polymer matrix.[13,14] This leads to different concentration gradients into the matrix for various reactants.[14] Finally, where a catalyst is anchored to glass or ceramic surfaces, the reactants and catalyst may interact with the surface in, as yet, undefined ways to induce changes in rates, product distributions, and molar turnover ratios.[15]

Because polymer-bound catalysts appear to offer great promise for practical application[14-20] in specific and selective chemical transformations at mild conditions, we have explored some model butadiene oligomerization, reductions, and hydroformylations over homogeneous catalysts and their polymer-bound counterparts. The reactions described here were not chosen because of great novelty or commercial value. Instead these studies represent part of an extensive program[9b,12,13,21,22] to define the role swollen polymers play in reactions employing anchored catalysts.

Results

Transition metal-complexed polymers **1–4** were prepared as outlined in Scheme I. Styrene–divinylbenzene resin beads with 1 and 2% divinylbenzene (Bio Rad Laboratories SX-1 and SX-2 resins with molecular weight permeation exclusion limits of 14,000 and 2700, respectively) were employed. The phosphinations were carried out as previously reported,[12] and the metals were bound via simple triphenylphosphine exchange. It had previously been shown that resins, with either 1 or 2% divinylbenzene and excess bound phosphine moieties, were sufficiently mobile to coordinate more than one phosphine to the metal being anchored.[11-14,18] The lack of metal leaching upon catalyst recycling through several reactions[23] and analytical data confirmed that multiple chelation had occurred in polymers, **1–4**. The composition of polymer-anchored catalyst systems **1–4** are summarized in Table I.

Cyclooligomerizations. Homogeneous cyclooligomerization, catalyzed by $(PPh_3)_2Ni(CO)_2$ gave 4-vinylcyclohexene, **6**, (*Z*,*Z*)-1,5-cyclooctadiene, **7**, (*E*,*E*,*E*)-1,5,9-cyclododecatriene, **8**, and when stopped short of completion the intermediate *cis*-1,2-divinylcyclobutane, **5**, was formed (eq 1). It underwent a subsequent Cope rearrangement to produce (*Z*,*Z*)-1,5-cyclooctadiene as the reaction continued. The product distribution was close to that previously reported for this reaction.[4] Using either 1 or 2% cross-linked resins, the cyclooligomerization reactions, employing anchored catalyst **1** swollen in benzene, gave the same product distribution, Furthermore, the molar turnover limit for both the homogeneous and two anchored systems was 1100–1200. Catalyst **1** could be repeatedly recycled giving high product yields until this limit was reached or a 1500 mol excess of butadiene could be charged and allowed to react until no further reaction would occur (i.e., at 1100–1200). These reactions are summarized in Table II. The major difference between the bound and homogeneous catalyst system was rate. The anchored catalyst required 115° to achieve the same rate of butadiene disappearance given by $(PPh_3)_2Ni(CO)_2$ at 90°, when equal volumes of solutions and the same butadiene concentrations were employed.



(1)

No nickel was lost during the recycling process for either SX-1 or SX-2 systems. For one deactivated system, analysis gave 2,29% P and 1.97% Ni vs, 2.32% P and 2.01% Ni originally. The deactivated catalyst no longer exhibited carbonyl absorptions at 1997 and 1943 cm^{-1}. This result is similar to the loss of carbonyl groups from **1** during its deactivation in ethynylferrocene oligomerizations where a 1:1 Ni to ferrocene complex was formed.[24] Repressurizing with CO at this point did not regenerate an active catalyst.

Hydrogenations. Hydrogenation of oligomers **6**, **7**, and **8** was carried out using homogeneous and anchored (i.e., **2**) $(PPh_3)_3RhCl$. Grubbs[11,14] showed that anchored catalysts similar to **2** could be used to hydrogenate small olefins in the presence of large ones. Such size selectivity could be modified by varying solvent which, in turn, varied the de-

Table II. Results of 1,3-Butadiene Cyclooligomerization by Homogeneous and Polymer-Bound $(Ph_3P)_2Ni(CO)_2$[a]

Run	Catalyst	mmol of catalyst	mmol of butadiene	Overall yield	Products **5**	6	7	**8**
1	$(Ph_3P)_2Ni(CO)_2$[b]			100	0	26.6	64.3	8.9
2	$(Ph_3P)_2Ni(CO)_2$	0.156	188.5	100	0	25.3	63.2	11.5
3	Resin **1a**	0.179	185.0	26.0[c]	33.6	34.2	20.0	11.2
4	Resin 1c	0.155	185.0	21.9[c]	22.6	33.1	32.9	11.4
5	Resin **1b**	0.171	115.0	90.0	0	33.3	55.6	11.1
6	Recycle	0.171	115.0	42.3	0	31.8	57.9	11.3
7	Resin **1b**	0.171	55.5	92.0	0	28.7	61.2	10.0
8	Recycle	0.171	55.5	90.8	0	31.7	56.4	11.9
9	Recycle	0.171	55.5	81.7	0	29.2	59.7	11.1
10	Recycle	0.171	55.5	11.2	0	27.6	61.5	10.9

[a] All reactions are run 24 hr in benzene (20 ml), 90° for homogeneous reactions, 110–115° for polymer-bound catalysts, conducted in sealed bombs under 1,3-butadiene pressure. [b] Wilke's results.[12] [c] Reaction stopped short of equilibrium to analyze for divinylcyclobutane.

Scheme I

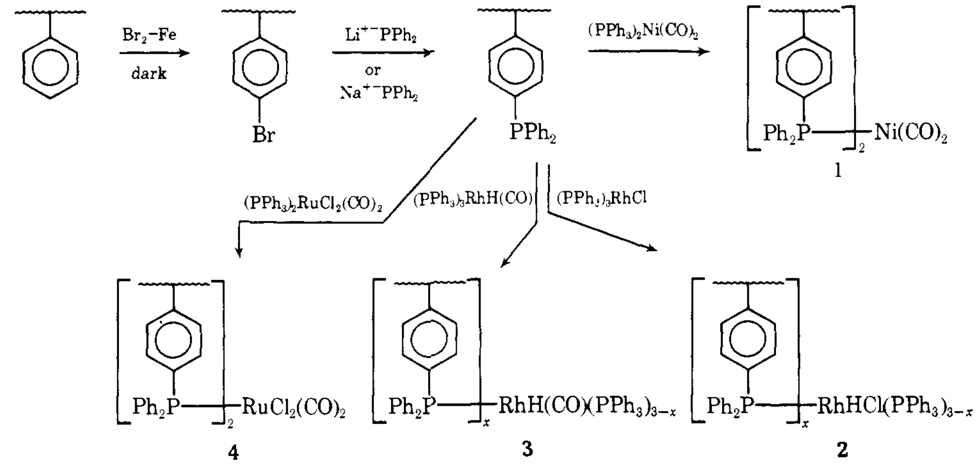
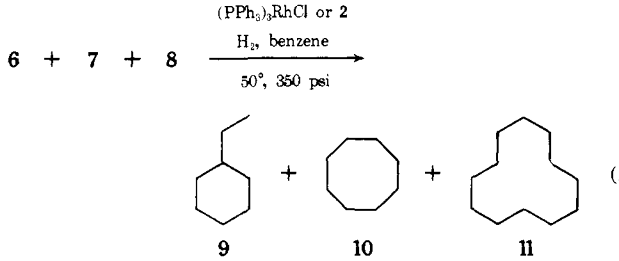


Table III, Results of Hydrogenation of 1,3-Butadiene Cyclooligomers by Homogeneous and Polymer-Bound $(Ph_3P)_3RhCl$[a]

Run	Catalyst	mmol of catalyst	Olefin	mmol of olefin	% alkane
1	$(Ph_3P)_3RhCl$	0.100	6	23.6	100
2	$(Ph_3P)_3RhCl$	0.100	7	24.1	100
3	$(Ph_3P)_3RhCl$	0.100	8	27.8	100
4	**2**	0.083	6	23.6	100
5	Recycle 2	0.083	6	23.6	100
6	Recycle **2**	0.083	6	23.6	100
7	2	0.083	7	24.1	100
8	2	0.083	8	27.8	100

[a] Reactions at 50°, 350 psi of H_2 for 4 hr.

gree of swelling. Thus, it was not surprising that the three small olefins, 4-vinylcyclohexene, 1,5-cyclooctadiene, and 1,5,9-cyclododecatriene, were quantitatively hydrogenated (eq 2) using $(PPh_3)_3RhCl$ or **2** under mild conditions (50°,



(2)

350 psi H_2, 2 hr). No loss of Rh from resin **2** occurred even after repeated recycling. Table III summarizes selected results.

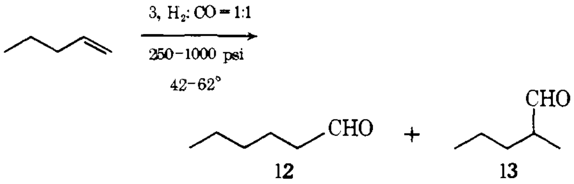
It is interesting to note that the rate of hydrogenation using **2** was 0.8 as fast as $(PPh_3)_3RhCl$ under these conditions. On the other hand, Grubbs found bound $(PPh_3)_3RhCl$ was only 0.06 times as active using this reagent homogeneously. The explanation for this difference lies in the greater retardation of rate due to diffusion in Grubbs' polymers. He employed a 2% cross-linked resin whereas polymer **2** was only 1% cross-linked. Furthermore, Grubbs employed resins with a 74–149 μ partical diameter whereas polymer **2** was more finely divided (i.e., 37–74 μ). Both these effects led to a smaller rate reduction using **2** relative to employing the catalyst homogeneously. Finally Grubbs' reactions were carried out at 25° and 15 psi vs. the 50° and 350 psi used in this work. At this lower temperature, **2** was 0.5 times as active as homogeneous $(PPh_3)_3RhCl$. One purpose of conducting these hydrogenations was to provide experience with catalyst **2** for subsequent use in reactions where two homogeneous catalysts were used sequentially, on the same resin, to carry out multistep synthesis.[25]

Table IV, Effects of Recycling Catalyst 3a and Exposing It to Water on the Hydroformylation of Pentene. Reactions Conducted Batchwise

Run	Temp, °C	Pressure (psig)	Time, hr	Pentene consumed %	Total yield of aldehydes[a]	Ratio of hexanal/ 2-methylpentanal[a]
1[b]	50	800	4.5	97.1	97.1	2.72
2	50	500	4.8	81.5	81.5	2.51
3	30	500	4.5	8	8	
4	50	800	4.5	96.5	96.5	2.65
5	40	250	4.5	29	29	3.46
6[c]	50	800	4.5	8.3	8.3	d
7[e]	40	250	4.5	27	27	3.48
8[f]	40	250	4.5	20	20	2.75
9[f]	50	800	4.5	61.7	61.7	2.38
10[f]	50	800	4.5	53.0	53.0	2.17
11[f]	50	800	4.5	11.3	11.3	2.8
12[f]	50	800	4.5	25.8	25.8	1.8
13	40	800	4.5	13	13	1.9
14	40	250	4.5	7.5	7.5	

[a] Yields were determined by GLC. No alcohol or pentane was obtained. [b] Fresh catalyst 3a introduced. The runs 1–6 were carried out by recycling this batch. [c] 2-Pentene used in this reaction. [d] Only 2-methylpentanal was observed. [e] Fresh catalyst 3a used and this sample was repeatedly recycled through run 17. [f] Catalyst was exposed to water and is less active at 50° than dry catalyst.

Hydroformylations. The extremely active hydroformylation catalyst $(PPh_3)_3RhH(CO)$[26] was anchored to give bound catalyst **3**. This system readily catalyzed the hydroformylation of 1-pentene to high yields of both normal and branched aldehydes **12** and **13** (eq 3). The catalyst could be



(3)

repeatedly recycled and even exposed to water[27] without drastic loss of activity. These results are summarized in Tables IV, V, and VI. Two polymers **3a** and **3b** differed in their bound $-PPh_2$ to Rh ratio (**3a**, 2.3 and **3b**, 4.4) although the total percent of Rh was about the same. Rhodium was not lost upon repeated recycling of either poly-

Table V. Catalysis of the Hydroformylation of Pentene by Homogeneous $(PPh_3)_3RhH(CO)$ and by Resin **3b**. Effects of Recycling **3b** and Exposing It to Moisture

Run	Catalyst	Temp, °C	Pressure (psig)	Time, hr	Pentene[a] consumed (%)	Total yield[a] of aldehydes	Ratio of hexanal/ 2-methylpentanal[a]
1	$(PPh_3)_3RhH(CO)$[b]	40	250	3.0	73.8	73.8	2.85
2	$(PPh_3)_3RhH(CO)$[b]	40	250	4.5	83.8	83.8	2.88
3	$(PPh_3)_3RhH(CO)$[b]	60	800	4.5	100[c]	92.9[c]	2.69
1	**3b**	23	1000	12.5	10.3	10.3	Only normal aldehyde detected
2[d]	**3b**	28	250	12.5	11.3	11.3	
3	**3b**	40	500	12.5	68.8	68.8	4.34
4[e]	**3b**	53	1000	12	56.5	56.5	4.26
5	**3b**	62	1000	12.8	83.0	83.0	4.44
6[f]	**3b**	40	250	22.5	63.8	63.8	3.95
7[g]	**3b**	40	250	12.5	41.6	41.6	5.2
8[g]	**3b**	40	250	17	44.5	44.5	4.73
9[g]	**3b**	40	250	36.5	>80	>80	3.6
10[h]	**3b**	40	250	4.5	7.1	27.1	4.2
11[h,i]	**3b**	40	250	4.5	Trace	Trace	All 2-methylpentanal
12[h,j]	**3b**	22	250	64	64	64	3.46

[a] Yields measured by GLC. [b] Concentration of catalyst was 1.8×10^{-2} mol l.$^{-1}$ and the olefin was 1.53 mol. l.$^{-1}$ in each run. [c] About 5% pentane was found. [d] This reaction employed catalyst which had previously been used in a 40°, 17 hr hydroformylation. [e] Run 4 was performed with catalyst which had previously been used fresh in run 5. [f] Run 6 was performed with the catalyst which had just been isolated from run 1 (i.e., its third recycling). [g] Runs 7–9 performed sequentially with the catalyst sample used in run 6. Note; it is active after six recycling procedures. [h] Catalyst had been exposed to water. [i] Run 11 performed with catalyst recycled from run 10 and the substrate was 2-pentene. [j] Run 12 was performed with catalyst recycled from run 11.

mer. In fact a small increase in the percent of Rh was noted due to continued displacement of PPh_3 groups from the bound catalyst until essentially all three were replaced by bound $-PPh_2$ moieties. This conclusion was substantiated by analytical results. The P/Rh ratio in **3b** steadily approached 4.4 indicating all the original PPh_3 moieties were replaced with anchored PPh_2 units.

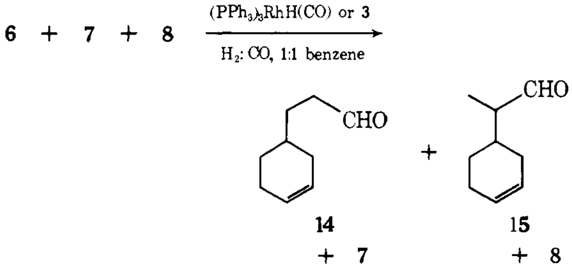
High yields of aldehydes were obtained at 50-60° and 500-1000 psi. Under these conditions the normal to branched product ratio was 2.5-2.85 using **3a**. After exposure of the catalyst to water, **3a** was still active, but the rate of hydroformylation decreased and was erratic from run to run. Also the normal to branched ratio dropped after continued water exposure to about 1.8.

The catalytic activity decreases as the bound $-PPh_2$ to Rh ratio increases (see Table VI). At temperatures from 50 to 62° catalyst **3a** ($P/Rh = 2.3$) was appreciably more active than **3b** ($P/Rh = 4.4$) even at lower total H_2-CO pressures. As the temperature was lowered to 40° this reactivity difference decreases. The polymer's greater internal mobility at higher temperatures apparently permits excess bound phosphine groups to contact catalytic sites. Thus, the concentration of coordinatively unsaturated rhodium intermediates is decreased leading to lower catalytic activity. Thus, in this case, excess bound $-PPh_2$ is acting to decrease the rates, just as added PPh_3 does with $(PPh_3)_3RhH(CO)$ when employed homogeneously.[26]

The effect of the bound $-PPh_2$/Rh ratio on the normal to branched product ratio was remarkable. In a series of resins where the PPh_2/Rh ratio increased from 2.3 to 4.4, the normal to branched ratio went from 2.6 to 4.4 at 60° and 800 psi (1/1 H_2/CO). A sharp increase in this ratio occurred when the $-PPh_2$ to Rh ratio exceeded 3. At 200-400 psi and 40-55°, the product ratios were temperature and pressure dependent while from 60 to 80° they were largely temperature independent. While difficult to interpret, these results suggest diffusion plays a role in the final product ratios at lower temperatures and pressures.

Comparisons of the activity of **3a** and **3b** with $(PPh_3)_3RhH(CO)$, employed homogeneously, were carried out at identical temperatures, pressures, and times. The olefin concentrations in benzene and the ratio of olefin to Rh were also held constant. Fresh catalyst **3a** had approximately the same reactivity as the homogeneous catalyst. At 40° and 250 psig, **3a** was 0.22 times as active as $(PPh_3)_3RhH(CO)$. At 60° and 800 psig, **3a** was 1.08 times as active. This increase in reactivity of the anchored relative to the homogeneous catalyst with an increase in temperature again suggests diffusion to the catalyst sites plays a rate limiting role at lower temperatures where diffusion is slower.

Hydroformylations of the cyclooligomers of butadiene, produced over **1**, were also conducted using bound catalyst **3c**. Only the exocyclic double bond of 4-vinylcyclohexene was hydroformylated (see Table VII). The internal double bonds of this compound, (*Z*,*Z*)-1,5-cyclooctadiene and (*E*,*E*,*E*)-1,5,9-cyclododecatriene, were unchanged (eq 4).



(4)

Exactly the same selectivity was obtained using $(PPh_3)_3RhH(CO)$. Quantitative yields of 3-(cyclohex-3-enyl)propanal and 2-(cyclohex-3-enyl)propanal were obtained using both catalysts. Furthermore the normal to branched ratio was the same (4.3) with both bound and homogeneous catalysts.

Catalyst **3** could be readily recycled with little loss of reactivity. In contrast to 1-pentene hydroformylations at 60°, the rate of hydroformylation of 4-vinylcyclohexene over **3c** was about 0.3 that of the rate using $(PPh_3)_3RhH(CO)$ at identical conditions. The $-PPh_2$ to Rh ratio in **3c**, used in these reactions, was 1.7. This is lower than in **3a**, thus rate retardation by excess internal phosphine cannot be invoked to explain the difference.[28]

Selective Polyene to Monoene Hydrogenations. Recently, Fahey[29,30] demonstrated that polyenes can be hydrogenated to their corresponding monenes with remarkably high selectivity using $(PPh_3)_2RuCl_2(CO)_2$. Thus, this catalyst was

Table VI, Effect of the $-PPh_2$/Rh Ratio, in 1-Pentene Hydroformylations, on Both the Activity of Polymer-Bound Catalysts and the Normal to Branched Product Ratio

Run	Catalyst[a]	Temp, °C	Pressure[b] (psig)	Time, hr	1-Pentene[c] consumed (%)	Ratio of hexanal/ 2-methyl-pentanal[c]
1	3a	60	800	18	100	2.84
2[d]	3a	61	800	10.5	100	2.64
3[d]	3a	62	800	4.5	98.1	2.9[g]
4	3a	50	800	4.5	97.1	2.2[g]
5[e]	3a	50	500	4.8	81.5	2.51
6	3a	40	500	8.0	69.2	2.69
7	3b	62	800	6.5	31.2	4.40
8	**3b**	62	1000	12.8	83.0	4.44
9	**3b**	51	800	4.5	23.1	4.57
10[f]	3b	53	1000	12.0	56.5	4.26
11	**3b**	40	500	12.5	68.7	4.34

[a] The ratio of bound PPh_2 to Rh in 3a was 2.3 while in 3b it was 4.4. [b] In each case the H_2:CO ratio was 1 : 1. [c] Determined by GLC measurements. [d] The catalyst used in run 1 was reused in run 2 and again recycled in run 3. [e] This catalyst was recycled from run 4. [f] This catalyst was recycled from run 9. [g] Chromatogram peaks were broadened and these values are approximate.

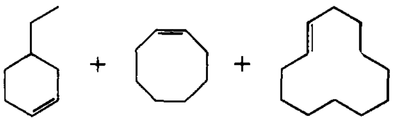
Table VII, Results of Hydroformylation of 1,3-Butadiene Cyclooligomers by Homogeneous and Polymer-Bound $(Ph_3P)_3RhH(CO)$[a]

Run	Catalyst	mmol of catalyst	Ole-fin	mmol of olefin	% yield of alde-hydes	Primary/ secondary
1	$(Ph_3P)_3RhH(CO)$	0.109	**6**	14.8	100	4.29
2	$(Ph_3P)_3RhH(CO)$	0.109	7	15.1	0	
3	$(Ph_3P)_3RhH(CO)$	0.109	**8**	15.9	0	
4	3c	0.140	**6**	14.8	100	4.35
5	Recycle 3**c**	0.140	**6**	14.8	96.4	4.28
6	Recycle 3c	0.140	**6**	14.8	95.2	4.30

[a] Reactions in benzene (20 ml), 65–70°, H_2:CO 1 : 1, total pressure 500 psi. Homogeneous reactions run 4 hr, polymeric catalysts 12–18 hr.

anchored (resin **4**) and selective hydrogenations of cyclooligomers **6**, **7**, and **8** to 4-ethylcyclohexene, **16**, (*Z*)-cyclooctene, **17**, and (*E*)-cyclododecane, **18**, respectively, were carried out to compare the bound and homogeneous use of this catalyst. These results are summarized in Table VIII and eq 5. Using $(PPh_3)_2RuCl_2(CO)_2$ in benzene at 145° and 150 psi with a large excess of PPh_3, Fahey's results were essentially repeated. Furthermore, the product yields and distributions were similar using resin **4** with excess PPh_3. The bound catalyst was recycled with no loss of ruthenium or of catalytic activity.

$$\mathbf{6} + \mathbf{7} + \mathbf{8} \xrightarrow[H_2,\ \text{benzene},\ PPh_3]{4\ \text{or}\ (PPh_3)_2RuCl_2(CO)_2}$$



16 **17** **18** (5)

An 18-20 mol excess of PPh_3 was employed with **4** and with $(PPh_3)_2RuCl_2(CO)_2$ as in Fahey's studies.[29,30] The ability to repeatedly recycle **4** without detectable loss of Ru, in the presence of excess PPh_3, suggests that "homogeneous" $(PPh_3)_2RuCl_2(CO)_2$ is not formed as the active agent. If it was formed it would be expected to leach during repeated reactions. It is interesting to note that the selectivity in converting **8** to **18** dropped only slightly, from 97.1 to 90.2%, going from $(PPh_3)_2RuCl_2(CO)_2$ to **4.** This loss of selectivity on anchoring was minor compared with the decrease in triene to monoene selectivity which Bailar observed upon heterogenizing $(PPh_3)_2PdCl_2$ to polymers.[18,31] Moreover, the drop in selectivity using **4** was probably the result of the higher temperature employed using resin **4** (165-170° and 15 hr) relative to the homogeneous reactions (145° and 5 hr). The rate of hydrogenation was much slower employing resin **4.**

In order to obtain selective hydrogenation to monoenes using $(PPh_3)_2RuCl_2(CO)_2$, a large excess of PPh_3 had to be present[29,30] (PPh_3/Ru ratios from 11 to 20 were optimum). In order to determine if the internal mobility of excess bound phosphine groups on 1% cross-linked resins was sufficient to promote this selectivity, Ru was anchored in one sample of **4** such that the P to Ru ratio in the polymer was 14.8. Then 1,5-cyclooctadiene reductions were conducted in benzene at 165°, 150 psi of H_2, for 15 hr without added PPh_3. The cyclooctene to cyclooctane ratio dropped sharply from 90:5 to 55:45. Thus, excess anchored phosphine sites could not promote high monoene selectivity. Apparently, these bound phosphine moieties do not encounter the bound catalyst at a rate fast enough to influence the mechanism in the manner that excess added PPh_3 did. Thus, while excess bound $-PPh_2$ groups could retard the rate of hydroformylation using **3**, they could not increase hydrogenation selectivity using **4.** At temperatures below 0°, Regen showed nitroxide spin labels bound to swollen 1% cross-linked polystyrene resins had correlation times of at least 1×10^{-10} sec. Similar values were found for those bound to uncross-linked polystyrene.[32] Thus, rotational motion was not markedly restricted when the matrix was highly swollen in benzene. However, even at 165°, the translational motion of bound phosphines must be significantly restricted relative to free dissolved PPh_3 which has diffused into the resin.

Summary

It appears that resin-bound catalysts **1–4** each act, mechanistically, the same as their homogeneous counterparts, This is apparent from the similar product distributions obtained in a variety of reactions, the response to excess PPh_3, temperature changes, and changes in hydrogen and carbon monoxide pressures. Diffusion and internal translational mobility effects account for differences between the anchored and homogeneous systems that were observed. Anchored $(PPh_3)_2Ni(CO)_2$, $(PPh_3)_3RhCl$, $(PPh_3)_3RhH(CO)$, and $(PPh_3)_2RuCl_2(CO)_2$ respectively catalyze cyclooligomerizations, hydrogenations, hydroformylations, and selective hydrogenations more slowly than do their homogeneous counterparts. As the temperature is raised, as the resin particle size is decreased, and as the resin's cross-link density is lowered, the anchored/homogeneous rate ratios increase. This is in accord with a diffusion retardation of rate with anchored catalysts. The internal mobility of resin anchored-PPh_2 moieties was demonstrated by multiple chelation of the catalyst, the increase in hydroformylation selectivity (normal/branched) as the anchored -P/Rh ratio increased, and the decrease in hydroformylation rates as the anchored -P/Rh ratio increased. However, anchored $-PPh_2$ moieties cannot be considered as mobile as dissolved PPh_3. Excess anchored $-PPh_2$ could not enhance hydrogenation selectivity as readily as dissolved PPh_3 did in selective reductions employing anchored $(PPh_3)_2RuCl_2(CO)_2$.

It is possible that an anchored catalyst such as (Ⓟ-$PPh_2)_3RhH(CO)$ could be more active than its homogeneous counterpart if, upon dissociation of a single Ⓟ-PPh_2

Table VIII, Results of Hydrogenation of 1,3-Butadiene Cyclooligomers by Homogeneous and Polymer-Bound $(Ph_3P)_2RuCl_2(CO)_2$

Run	Catalyst	mmol	Polyene	mmol	% alkane	% alkene	% diene	% triene
1[a]	$(Ph_3P)_2RuCl_2(CO)_2$	0.130	**8**	1.10	1.9	97,1	0.3	0.3
2[a]	$(Ph_3P)_2RuCl_2(CO)_2$	0.130	7	1.10	6.1	93.4	0.8	
3[b]	$(Ph_3P)_2RuCl_2(CO)_2$	0.090	**8**	12.3	1.8	97.1	0.6	0.5
4	$(Ph_3P)_2RuCl_2(CO)_2$	0.090	7	16.3	3.9	93.8	3.3	
5	$(Ph_3P)_2RuCl_2(CO)_2$	0.090	**6**	16.3	5.7	87.7	6.8	
6[c]	4a	0.053	7	16.3	5.7	90.2	4.1	
7	Recycle 4a	0.053	7	16.3	5.4	90.5	4.1	
8	Recycle 4a	0.053	7	16.3	5.5	90.6	3.9	
9	4a	0.053	6	16.3	5.4	88.2	6.6	
10	4a	0.053	8	12.3	2.1	95.1	2.0	1.8
11[d]	4b	0.097	7	16.3	45.9	54.1	0.0	
12[d]	Recycle 4b	0.097	7	16.3	43.8	56.2	0.0	

[a] Fahey's results, [b] Homogeneous reactions at 145°, 5 hr. [c] Polymer-bound reactions at 165–170°, 15 hr. [b,c] Reactions conducted at 150 psi of H_2, 0.262 g (1.0 mmol) of PPh_3 added in 20 ml of benzene. [d] No excess PPh_3 added, except the excess bound to the polymer.

ligand, a higher concentration of coordinatively unsaturated sites (relative to homogeneously employed $(PPh_3)_3$-RhH(CO)) was generated. This is feasible because, once dissociated, the Ⓟ-PPh_2 moiety might find it difficult to recombine due to entropy or enthalpy considerations resulting from its polymer attachment. We are currently investigating this as a potential explanation for some large anchored/homogeneous rate ratios observed at higher temperatures.

Experimental Section

Benzene, THF, and toluene were dried over CaH_2 for at least 24 hr and then distilled under nitrogen. Similar care was taken to dry all solvents. Nitrogen, hydrogen, and carbon monoxide were obtained commercially (99+%) and used as received. Organometallic complexes were obtained from Strem or Pressure Chemical Co. GLC separations were done on a Varian Model 90-P gas chromatograph using Carbowax 20-M or SE-30 (15% on 100-120 N chromasorb P, 6 ft × ¼ in.). The ir, ^1H NMR, uv, and mass spectra were obtained on a Beckman Ir-33, Perkin Elmer R20B or Varian Ha-100, Cary 14, and Perkin-Elmer Hitachi RMU-6M instruments respectively.

Anchoring Catalysts to Diphenylphosphinated Polystyrene Resins, The diphenylphosphinated resins were swollen in a stirred toluene solution at 100° under nitrogen. A toluene solution of the homogeneous catalyst to be anchored was then added, and the reaction was conducted at 100° for 24 hr. The solvent was decanted, and the polymer beads were extracted (Soxhlet) for 24 hr with benzene under nitrogen to remove any unbound catalyst and free PPh_3 from the resin. The total phosphine and metal contents were controlled as described in detail elsewhere.[33]

Homogeneous Reaction of 1,3-Butadiene with Bis(triphenylphosphine)nickel Dicarbonyl, Into a dry, nitrogen purged stainless steel bomb were placed bis(triphenylphosphine)nickel dicarbonyl (0.10 g, 0.156 mmol), and dry benzene (10 ml, nitrogen saturated). After degassing by several freeze–thaw cycles, 1,3-butadiene (10.2 g, 188.5 mmol) was condensed in at −78°. The bomb was then warmed to 90°, shaken for 24 hr, cooled, and then vented to a −78° trap. No 1,3-butadiene was recovered. GLC of the reaction mixture showed 4-vinylcyclohexene (25.3%), (*Z,Z*)-1,5-cyclooctadiene (63.2%), and (*E,E,E*)-1,5,9-cyclododecatriene (11.5%). The products were collected by preparative GLC and their ir, NMR, and mass spectra were found to be identical with commercially available samples (Aldrich Chemical Co.).

Reaction of 1,3-Butadiene with Polymer-Bound Bis(triphenylphosphine)nickel Dicarbonyl, Into a dry, nitrogen purged stainless steel bomb were placed polymer-bound bis(triphenylphosphine)-nickel dicarbonyl (0.50 g, 0.179 mmol of Ni), and dry benzene (10 ml, nitrogen saturated). The system was degassed by several freeze–thaw cycles, 1,3-butadiene (10.4 g, 193 mmol) was added at −78°, and the bomb was warmed to 110–115° and shaken for 24 hr. After cooling to 25° and venting in a −78° trap, 1.03 g (9.9%) of the 1,3-butadiene was recovered. GLC of the reaction mixture gave *cis*-1,2-divinylcyclobutane (15.2%), 4-vinylcyclohexene (31.7%), (*Z,Z*)-1,5-cyclooctadiene (41.2%), and (*E,E,E*)-1,5,9-cyclododecatriene (11.9%). The products were collected by preparative GLC, and their ir, NMR, and mass spectra were found to be identical with commercially available samples.

Reactions which had reached completion gave no divinylcyclobutane. The polymer-bound catalysts were recycled after filtration under nitrogen, washed with dry, nitrogen saturated benzene, vacuum dried, and then carried through an identical reaction procedure again.

Reaction of Cyclooligomers 6, 7, and 8 with Homogeneous and Polymer-Bound $(Ph_3P)_3RhCl$, Into a dry, nitrogen purged stainless steel bomb were placed tris(triphenylphosphine)rhodium chloride (0.0925 g, 0.1 mmol), 4-vinylcyclohexene (2.55 g, 23.6 mmol), and dry benzene (10 ml, nitrogen saturated). Dissolved gases were removed by several freeze–thaw cycles; the bomb was flushed with hydrogen, pressurized to 350 psi with hydrogen, and heated at 50°, with shaking for 4 hr. After cooling to 25°, a pressure of 225 psi was noted. Analytical GLC showed only ethylcyclohexane, **9**, Samples were collected by preparative GLC. The ir spectrum showed no =C—H or C=C bands but now exhibited a band at 1380 cm^{-1} (terminal methyl). The mass spectrum was identical with an authentic sample of **9** as was the NMR spectrum. Similar reactions with 1,5-cyclooctadiene and 1,5,9-cyclododecatriene also resulted in complete hydrogenation to cyclooctane and cyclododecane.

Analogous reactions using polymer-bound tris(triphenylphosphine)rhodium chloride (0.50 g, 0.083 mmol of Rh) also resulted in complete hydrogenation. The polymeric catalyst was recycled by filtering under nitrogen, washing with dry benzene, and being carried through the reaction procedure again. The resin catalyst could be stored dry in air for extended periods.

Hydroformylations of 1-Pentene Over 3a and 3b, The hydroformylation reactions were carried out in 150-cm^3 stainless steel pressure bombs. The bombs were thoroughly washed, scrubbed, rinsed with acetone, oven dried at 120–140° before use, and flushed with nitrogen for 30 min while cooling. The appropriate amount of the swollen resins **3a** or **3b** (0.187 mequiv of bound Rh) was then added with dry, nitrogenated benzene and 1-pentene (18.3 mequiv). The bomb was pressurized to 400 psig at 0° with carbon monoxide, allowed to equilibrate 10 min, and then vented back to atmospheric pressure. This procedure was repeated two more times, and the bomb was then pressurized to the desired pressure with equal pressures of carbon monoxide and hydrogen. The reaction was heated at the desired temperature and shaken for the appropriate time. Products analyzed quantitatively by GLC. The resin was filtered, and the products were isolated in example cases, by preparative GLC and analyzed by ir and mass spectral analysis. The recovered 1-pentene, hexanal, and 2-methylpentanal gave ir and mass spectra identical with purified commercial samples.

Reaction of Cyclooligomers 6, 7, and 8 with Homogeneous and Polymer-Bound $(Ph_3P)_3Rh(H)(CO)$, Into a dry, nitrogen purged stainless steel bomb were placed hydridocarbonyltris(triphenylphosphine)rhodium (0.10 g, 0.109 mmol), **6** (1.6 g, 14.8 mmol), and dry benzene (10 ml, nitrogen saturated). Dissolved gases were removed by several freeze–thaw cycles. The bomb was flushed with hydrogen, pressurized with 250 psig of hydrogen and 250 psi of carbon monoxide, and heated, with shaking, at 60° for 4 hr. After cooling to 25°, a pressure of 370 psig was noted. Analytical GLC showed only a trace (less than 1%) of unreacted **6**, Two products were seen, one of 18.9% and the other 81.1% (4.3:1). Samples were collected by preparative GLC. The major product was identified as 3-(cyclohex-3-enyl)propanal: parent ion (60 eV) *m/e* 138; ir (KBr) 3000 (s), 2910–2810 (b, s), 2699 (s), 1725 (b, s), 1650 (m), 1457 (s), 1439 (s), 1145 (m), 840 (m), 740 (m), and 651 (s), cm^{-1}; NMR ($CDCl_3$) δ 9.74 (triplet, 1 H, J = 2 Hz, aldehyde proton), 3.64 (m, 2 H, olefinic protons), and 1.52–2.65 (complex, 11 **H**, saturated protons). The minor product was identified as 2-(cyclohex-3-enyl)propanal: parent ion *m/e* 138; ir (KBr) 3000 (s), 2950–2820 (s), 2690 (s), 1755 (s), 1650 (w), 1457 (m), 1439 (m), 1380 (m), 1145 (m), 922 (m), 840 (w), 725 (m), and 655 (s) cm^{-1}.

No hydroformylation of the cyclohexenyl double bond was found. Similar reactions using 1,5-cyclooctadiene and cyclododecatriene gave no hydroformylation products. When the reaction was heated past 90°, hydroformylation of secondary double bonds occurred, and a complex mixture of mono- and dihydroformylation products results.

Analogous reactions using polymer-bound hydridocarbonyltris(triphenylphosphine)rhodium (1.00 g, 0.140 mmol of Rh) and **6** (1.6 g, 14.8 mmol) gave quantitative conversion to 3-(cyclohex-3-enyl)propanal (81.3%) and 2-(cyclohex-3-enyl)propanal (18.7%). Recycling of the bound catalyst was accomplished by filtration of the polymer from the reaction solution, washing with dry, nitrogen saturated benzene, and carrying the polymer through the reaction procedure again.

Hydrogenation of 6, 7, and 8 by Homogeneous and Polymer-Bound $(Ph_3P)_2RuCl_2(CO)_2$. Into a dry, nitrogen purged stainless steel bomb were placed dichlorodicarbonylbis(triphenylphosphine)ruthenium (0.070 g, 0.09 mmol), triphenylphosphine (0.262 g, 1 mmol), **7** (1.76 g, 16.3 mmol), and dry benzene (20 ml, nitrogen saturated). Dissolved gases were removed by several freeze-thaw cycles, the bomb was flushed with hydrogen, pressurized to 150 psig with hydrogen, and both were heated and shaken at 145° for 5 hr. After cooling to 25° a pressure of 100 psig was noted. Analytical GLC showed three peaks. These were collected by preparative GLC, giving unreacted 1,5-cyclooctadiene (2.5%), (*Z*)-cyclooctene (93.7%) (parent ion *m/e* 110; ir (KBr) 3000 (s), 2910 (vs), 2840 (vs), 1655 (m), 1475 (s), 1455 (s), 900 (s), 755 (vs), 705 (s) cm^{-1}; NMR ($CDCl_3$) δ 5.61 (m, 2 H, olefinic protons), 1.54 (s, 4 H, saturated ring protons) and 1.5 (m, 4 H, saturated ring protons)) and cyclooctane (3.94%) (parent ion *m/e* 112; ir no C=C or =C—H; NMR ($CDCl_3$) δ 1.54, singlet).

When **6** was the substrate, GLC of the reaction mixture showed unreacted **6** (2.9%), 4-ethylcyclohexene (85.3%) (parent ion *m/e* 110; ir 3020 (m), 2940–2820 (s), 1660 (w), 1450 (s), 1380 (m), 1140 (m), 1005 (m), and 810 (s) cm^{-1}; NMR ($CDCl_3$) δ 4.76–5.38 (complex, 2 H, olefinic protons), 1.97–1.14 (complex, 9 H, methylene protons), and 0.72 (t, 3 H, J = 7.2 Hz, $-CH_3$)) and ethylcyclohexane (11.8%) (parent ion *m/e* 112; ir and NMR spectra were identical to an authentic sample).

Analogous reactions using polymer-bound $(Ph_3P)_2RuCl_2(CO)_2$ (0.5 g, 0.053 mmol of Ru) also gave the same selective hydrogenation reactions when conducted at 165–170°. The polymeric catalyst was recycled by filtration under nitrogen from a reaction solution, washed with benzene, vacuum dried (25°, 0.05 Torr), and carried through the reaction procedure again.

Reactions using the catalysts with excess bound phosphine groups but no added PPh_3 (1.0 g, .10 mmol Ru) and 1,5-cyclooctadiene (1.76 g, 16.3 mmol) gave cyclooctane 45.9%, cyclooctene 54.1%, and no 1,5-cyclooctadiene. Recycling was accomplished as described above.

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