Sequential Multistep Reactions Catalyzed by Polymer-Anchored Homogeneous Catalysts

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Abstract: The first examples of sequential multistep organic reactions carried out over polymer-anchored homogeneous catalysts are reported where two such catalysts are bound to the same cross-linked polymer. Also, sequential catalytic reactions where two catalysts, each anchored to a separate resin, are mixed together in the same reactor were conducted. Sequential cyclooligomerization of butadiene to 4-vinylcyclohexene (7), (Z,Z)-1,5-cyclooctadiene (8), and (E,E,E)-1,5,9-cyclododecatriene (9), followed by hydrogenation to ethylcyclohexane (10), cyclooctane (11), and cyclododecane (12), was accomplished using a single styrene–divinylbenzene resin to which $(PPh_3)_2Ni(CO)_2$ and $(PPh_3)_3RhCl$ had been anchored. The same reaction sequence was effected by a mixture of two resins to which $(PPh_3)_2Ni(CO)_2$ and $(PPh_3)_3RhCl$ were individually attached. Cyclooligomerization of butadiene to 7, 8, and 9 followed by selective hydroformylation of the exocyclic double bond of 7 was accomplished using a resin catalyst to which both $(PPh_3)_2Ni(CO)_2$ and $(PPh_3)_3RhH(CO)$ were anchored. Similarly, the same reaction series was catalyzed by a mixture of resins to which these species were individually anchored. Cyclooligomerization was also followed sequentially by selective hydrogenation of the oligomers 7, 8, and 9 to the monoenes ethylcyclohexene (15), (Z)-cyclooctene (16), and (E)-cyclododecene (17) using a mixture of resins containing anchored $(PPh_3)_2Ni(CO)_2$ and $(PPh_3)_2RuCl_2(CO)_2$. The bound catalysts were readily recovered by filtration and were active to repeated recycling with the exception of anchored $(PPh_3)_2Ni(CO)_2$ used with the Ru catalyst. In this case the high temperature necessary for employing $(PPh_3)_2RuCl_2(CO)_2$ causes degradation of the nickel system. These reactions were compared to those using the homogeneous analogs of the bound catalysts.

In the preceding paper[1] the synthesis of styrene–divinylbenzene resins, to which the homogeneous catalysts $(PPh_3)_2Ni(CO)_2$, $(PPh_3)_3RhCl$, $(PPh_3)_3RhH(CO)$, and $(PPh_3)_2RuCl_2(CO)_2$ had been anchored, was described. These bound catalysts were compared with their homogeneous counterparts in butadiene cyclooligomerizations, hydrogenations, and hydroformylation reactions. Some of the advantages of polymer-bound homogeneous catalysts, such as ease of separation from products, reagent size selectivity, and their ability to be recycled were discussed along with the potential effects of internal mobility and diffusion which cause differences between bound and homogeneously catalyzed reactions. The distinction between homogeneous and heterogeneous catalysis has not always been clearly defined in these areas, and this point has been made with increasing frequency.[2-5]

In addition to advantages of heterogenized homogeneous catalysts just discussed,[1] several other potential advantages could be explored. Binding a transition metal complex, with an open coordination site, to a polymer might permit this molecule to be isolated, thus avoiding further complexation. Such a catalyst should be significantly activated by such attachment. Reductive elimination from a bound catalyst complex could produce coordinatively unsaturated species. Grubbs et al.[6] anchored titanocene dichloride and reduced this with 2 equiv of butyllithium in an attempt to prepare a "matrix isolated" titanocene. The resulting polymer was 6.7 times more active a hydrogenation catalyst than reduced benzyltitanocene dichloride. Attempts to make a five-coordinate Fe(porphyrin)imidazole, using a resin-bound imidazole, initially failed because the mobility of these ligands was sufficient to permit two ligands to reach the iron atom giving only the six-coordinate species.[7a] However, ambient temperature reversible oxygenation of a Co^{II} porphyrin, anchored to a resin via an imidazole, has now been reported, suggesting a five-coordinate species was achieved.[7b]

Patchornik and Krause have bound two reagents, an enolizable and a nonenolizable carboxylic acid, to chloromethylated styrene resins and effected selective intrapolymeric condensation to give increased yields of β-keto acids.[8] *No studies have appeared where more than one transition metal catalyst complex has been anchored to the same polymer and then used to effect sequential multistep reactions in the same reactor.* However, this concept has been applied in enzyme immobilization studies by Mosbach.[9] He bound both hexokinase and glucose 6-phosphate isomerase to the same polystyrene support and then converted glucose, sequentially, to glucose 1-phosphate and then glucose 6-phosphate. Thus, the product from the first enzymatic reaction became the substrate for the second. The studies reported in this paper detail our extension of this concept to "heterogenized" homogeneous transition metal catalysts.

Results and Discussion

Binding two, or more, catalysts to the same substrate raises several questions. Will each catalyst react as it does individually or will the catalysts interfere with one another? Can such systems be recycled? Where catalysts do react or interfere with each other, can this be avoided by anchoring in such a way that contact between them is prevented? Finally, will one catalyst intervene in the reaction path, or be destroyed by the reaction, which the second catalyst promotes?

Diphenylphosphinated polystyrene resins were synthesized as reported previously.[1,10-12] The metal complexes $(PPh_3)_2Ni(CO)_2$, $(PPh_3)_3RhCl$, $(PPh_3)_3RhH(CO)$, and $(PPh_3)_2RuCl_2(CO)_2$ were then anchored by thermal phosphine exchange reactions in toluene as described.[1,10] Scheme I outlines the anchored catalysts used in this work. The preparation and use in single reactions of resin catalysts 1, 2, 4, and 6 were described in the preceding paper.[1] Catalyst sites of one metal complex cannot come into contact with those of another complex when two or more of these resins are mixed together and swollen in the same reactor. On the other hand, 3 and 5 each contain two different catalysts bound to the same polymer, and the internal mobility of such swollen resins would allow these sites to come in contact. Attempts to carry out the cyclooligomerizations, hydrogenations, and hydroformylations, described in the preceding paper, in a joint sequence within the same reactor were successful and are now described. The synthesis of 3 and 5 is described in the Experimental Section.

Scheme I
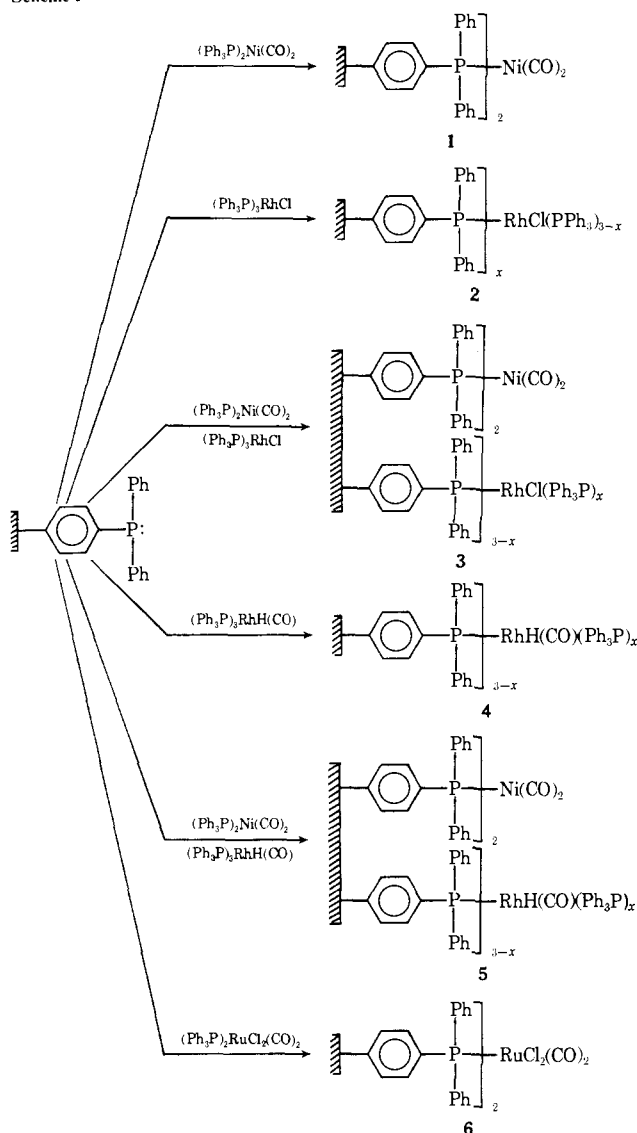
Sequential Cyclooligomerization and Hydrogenation. Butadiene was cyclooligomerized to 4-vinylcyclohexene (**7**), (*Z,Z*)-cyclooctene (**8**), and (*E,E,E*)-1,5,9-dodecatriene (**9**), and then, sequentially, these oligomers were quantitatively reduced to their saturated analogs, **10**, **11**, and **12** (eq 1).
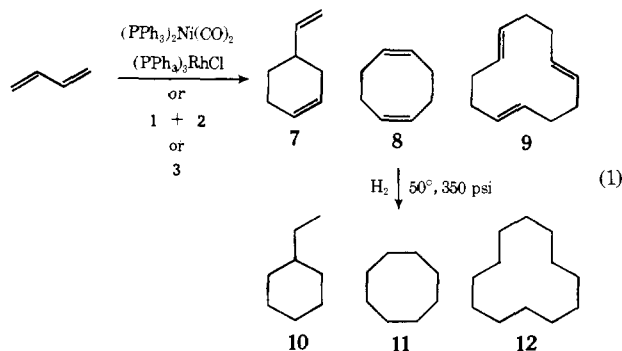

These sequential reactions were effected in three ways (1) using both $(PPh_3)_2Ni(CO)_2$ and $(PPh_3)_3RhCl$ in the same solution, (2) using a mixture of anchored catalysts **1** and **2**, and (3) employing resin **3** to which the two catalysts were anchored. Butadiene was oligomerized in benzene for 24 hr at 90° using the homogeneous catalysts or 110–115° using the anchored catalysts. The reaction bomb was then cooled to 50° and pressurized to 350 psi with hydrogen for 24 hr.

High yields of alkanes (see Table I) were obtained from the cyclooligomers in all cases (85–89%), and the overall yields from butadiene were high until the molar turnover limit of $(PPh_3)_2Ni(CO)_2$ was reached (about 1100).[1,13] The mixed anchored catalysts **1** and **2** and **3** could be recycled without substantial loss of activity until this turnover limit was reached. This limit was defined as the point where the rate fell sharply to a point where further conversion was impractical. Separate experiments demonstrated that $(PPh_3)_2Ni(CO)_2$ does not catalyze hydrogenation, nor does $(PPh_3)_3RhCl$ catalyze oligomerization under the conditions employed. These catalysts do not interfere with each other when employed homogeneously or bound to the same polymer (i.e., **3**).

The homogeneous reactions exhibited faster hydrogen pressure drops. Using equal molar amounts of catalyst and cyclooligomers in the same volume of benzene, the hydrogenation using **2** was about 0.8 as fast as the homogeneous reaction while the rate using **3** was about 0.15 as fast. These results compare to Grubbs' observation that $(PPh_3)_3RhCl$ bound to 2% cross-linked styrenedivinylbenzene resins were only 0.06 as active as using the homogeneous catalyst. The reason that **3** exhibited slower rates than **2** is due to the fact the mole fraction of metal in the polymer was higher. Since Ni was almost completely dicoordinated and Rh di- and tricoordinated with polymer-bound phosphine groups, the effective cross-link density of resin **3** was greater than **2** since the chelated metals now become cross-linking sites. This was substantiated by examining the P/Ni + Rh ratio in the polymer and by recovering displaced PPh_3 (as PPh_3O) from resin preparations. Both **2** and **3** were prepared from 1% divinylbenzene resins while Grubbs employed 2% divinylbenzene resins. Furthermore, we employed a smaller particle size distribution (37–74 μ) than did Grubbs (74–149 μ). Thus, diffusion retardation of rate would be expected to be greater in Grubbs' work.

Sequential Cyclooligomerization and Hydroformylation. Butadiene was sequentially cyclooligomerized to **7, 8,** and **9** and **7** was then selectively hydroformylated at the exocyclic double bond to 3-(cyclohex-3-enyl)propanal (**13**) and 2-(cyclohex-3-enyl)propanal (**14**) (see eq 2). Three catalyst
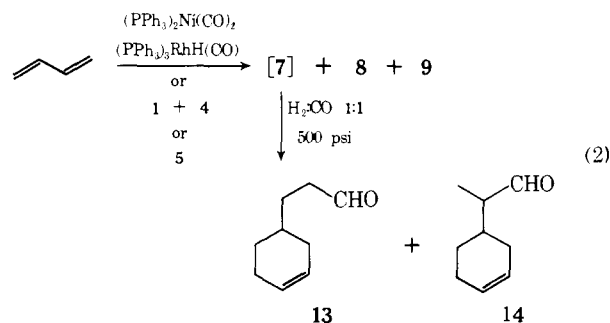
systems were employed: (1) homogeneous $(PPh_3)_2Ni(CO)_2$ and $(PPh_3)_3RhH(CO)$, (2) a mixture of resins **1** and **4**, and (3) resin **5** containing both catalysts anchored to the same polymer. The cyclooligomerizations were conducted in benzene for 24 hr (90° for the homogeneous systems and 110–115° for the anchored catalysts). The reactor was then cooled and pressurized with a 1:1 mixture of H_2–CO to effect the hydroformylation of **7** to **13** and **14**. The hydroformylation retained its selectivity in these reactions as all endocyclic double bonds were inert under these conditions. High yields in both steps were obtained using all three catalyst systems (see Table II). Furthermore, the differences in yields and product distributions using the three different systems varied only a few percent. The polymeric catalyst systems were easily recovered by filtration under nitrogen

Table I. Sequential Reactions of 1,3-Butadiene with Homogeneous and Polymer-Bound $(Ph_3P)_2Ni(CO)_2$ and $(Ph_3P)_3RhCl$

Run	Catalyst	mmol	Catalyst	mmol	mmol of butadiene	% conversion	% 7	% 8	% 9	% alkane[d]
1	$(Ph_3P)_2Ni(CO)_2$	0.157					23.6[a]			0
2[e]			$(Ph_3P)_3RhCl$	0.054	128	0	0	0	0	0
3	$(Ph_3P)_3Ni(CO)_2$[b]	0.157	$(Ph_3P)_3RhCl$[c]	0.108	187	98.3	20.8	66.4	12.8	99.3
4	Resin 1[f]	0.179	Resin 2[f]	0.083	181	84.7	22.3	54.9	20.5	86.4
5	Resin 1[f]	0.179	Resin 2[f]	0.083	55	92.2	22.7	61.3	16.0	86.3
6	Recycle	0.179	Recycle	0.083	55	91.8	23.1	60.8	16.1	84.5
7	Recycle	0.179	Recycle	0.083	55	81.3	22.8	59.7	17.5	83.2
8	Recycle	0.179	Recycle	0.083	55	21.6	23.9	58.6	17.5	81.9
9	Resin 3[f]	0.413	Resin 3[f]	0.300	55	92.3	24.9	60.7	14.4	84.1
10	Recycle	0.413	Recycle	0.300	55	92.1	25.1	60.5	14.5	82.8

[a] mmol of 7 added to reaction at 350 psi H_2. [b] Homogeneous oligomerizations 90°, 24 hr, polymer-bound oligomerizations 110–115°, 24 hr. [c] Hydrogenations at 50°, 350 psi H_2. [d] Total percent of the cyclooligomerization products which were hydrogenated to alkanes. [e] No H_2 pressure. [f] Polymer 3 analyzed for 2.49% Ni and 3.09% Rh while 2 contained 1.83% P and 1.70% Rh and 1 analyzed for 2.39% P and 2.10% Ni.

Table II. Sequential Reactions of 1,3-Butadiene with Homogeneous and Polymer-Bound $(Ph_3P)_2Ni(CO)_2$ and $(Ph_3P)_3RhH(CO)$

No.	Catalyst	mmol	Catalyst[a]	mmol	mmol of butadiene	Total Yield	% 7	% 8	% 9	% aldehydes[e]	Primary/secondary
1	$L_2Ni(CO)_2$	0.157					14.8[b]			0	
2			$L_3RhH(CO)$[h]	0.109	55	0	0	0	0	0	
3	$L_2Ni(CO)_2$[c]	0.157	$L_3RhH(CO)$[d]	0.109	185	96.1	22.2	57.5	20.3	85.9	4.21
4[f,g]	Resin 1[i]	0.179	Resin 4[i]	0.140	105	89.5	28.5	45.0	26.5	89.3	4.18
5[f,g]	Recycle	0.179	Recycle	0.140	55	38.1	27.2	49.6	23.2	88.7	4.27
6[f,g]	Resin 1[i]	0.179	Resin 4[i]	0.140	55	96.7	23.1	58.2	19.7	91.1	4.22
7[f,g]	Recycle	0.179	Recycle	0.140	55	92.1	24.1	57.9	18.0	89.3	4.31
8[f,g]	Recycle	0.179	Recycle	0.140	55	42.6	27.1	50.4	22.5	86.2	4.58
9[f,g]	Resin 5[i]	0.186	Resin 5[i]	0.137	75	88.4	24.7	57.4	17.9	84.1	5.81
10[f,g]	Recycle	0.186	Recycle	0.137	75	74.3	25.1	59.1	15.8	83.2	5.72

[a] L represents (Ph_3P) ligand. [b] mmol of 7 added at 500 psi, H_2:CO 1:1. [c] Homogeneous oligomerizations for 24 hr at 90°. [d] Homogeneous hydroformylations 70°, 6 hr. [e] Aldehydes resulting from 4-vinylcyclohexene. [f] Polymer-bound oligomerizations at 110–115°, 24 hr. [g] Polymer-bound hydroformylations at 70°, 18 hr. [h] No H_2–CO pressure. [i] Polymer 4 analyzed for 2.01% P and 1.44% Rh. Polymer 5 analyzed for 4.06% P, 1.09% Ni, and 1.41% Rh. Polymer 1 analyzed for 2.39% P and 2.10% Ni.

and then recycled with no loss of activity until the maximum turnover ratio of the nickel species was reached.

The normal to branched (13/14) aldehyde ratio was about 4.3 when the homogeneous catalysts or the combination of resin catalysts 1 and 4 was employed. This agrees well with normal to branched ratios observed by Wilkinson[14] in the hydroformylation of other terminal olefins by $(PPh_3)_3RhH(CO)$ under similar conditions. In resin 4 the ratio of excess bound $-PPh_2$ to Rh was 1.7. When the dual catalyst resin 5 was used the 13/14 ratio was markedly increased to 5.8 from 4.3. This increase is presumably the result of the effect of excess bound $-PPh_2$ units in resin 5. The ratio of excess bound $-PPh_2$ to Rh in this resin was 6.1. This result was in accord with the observation[1] that the linear to branched ratio in 1-pentene hydroformylation increased from 2.6 to 4.4 using a series of polymer-bound $(PPh_3)_3RhH(CO)$ catalysts with excess $-PPh_2$ to Rh ratios varying from 2.3 to 4.4. In a more detailed study[15] of this phenomena, the bound $-PPh_2$/Rh ratio was varied from 1.7 to 44. At large ratios normal to branched product ratios of 10 to 1 could be obtained.

Separate experiments showed that $(PPh_3)_2Ni(CO)_2$ and its polymer analogs could not effect hydroformylation of 4-vinylcyclohexene and that $(PPh_3)_3RhH(CO)$ or 4 could not promote oligomerization of butadiene under the conditions employed. Thus each catalyst was inert with respect to the function of the second catalyst, making sequential multistep synthesis in a single reactor possible. Elemental analysis confirmed that no nickel or rhodium was leached from resins 1 or 4. Similarly neither metal was lost from resin 5 after several recycles. The ir spectrum of 4 and 5 after several recycles exhibited the Rh–H stretch at 2000 cm⁻¹ and carbonyl absorption at 1952 cm⁻¹. The intensity of these bands was only slightly weaker than those in the starting polymers. However, the nickel-bound carbonyl absorptions at 1997 and 1943 cm⁻¹ in resin 1 and 5 were almost entirely gone at the point indicating this catalyst became inactive. The final nickel species formed is unknown, but the same behavior of anchored $(PPh_3)_2Ni(CO)_2$ was observed in ethynylferrocene cyclooligomerization studies.[16]

When both catalysts were present in the same reaction (i.e., using 1 + 4, or homogeneous catalysts, or using 5) the yield of aldehyde obtained from the hydroformylation of 7 dropped to about 85% from 100% when 4 was used alone. The same results were noted upon recycling the catalyst. Several explanations were considered. It was conceivable that 7 was being isomerized in the presence of both catalysts, thus lowering the aldehyde yields. However, this was ruled out by recovering the appropriate amount of 7 in each case (about 10–15%). Secondly, it was possible that small concentrations of PPh_3 might be dissociated from the nickel complex during the hydroformylation step and this might retard the reaction rate. To test this, pure 7 was hydroformylated by 4 and $(PPh_3)_3RhH(CO)$ in the presence of a 0.2 M excess of dissolved PPh_3. In the presence of the excess phosphine, the hydroformylation over 4 was markedly slower. The period of the H_2–CO pressure drop increased from 4 to 8 hr when PPh_3 was added. Significantly, the aldehyde yield, after 12 hr, was 90.7% when the added PPh_3 was present vs. 100% without added PPh_3. Thus, it is possible that small amounts of PPh_3 from 1 might have effected the rates of hydroformylation using 1 + 4 in the same reac-

Table III. Sequential Reaction of 1,3-Butadiene with Homogeneous and Polymer-Bound $(Ph_3P)_2Ni(CO)_2$ and $(Ph_3P)_2RuCl_2(CO)_2$

| No.	Catalyst[a]	mmol	Catalyst	mmol	mmol of butadiene	Total Yield	% 7	% 8	% 9	% 15[d]	% 16[d]	% 17[d]
1[b]			$L_2RuCl_2(CO)_2$	0.090	100	0	0	0	0	0	0	0
2[c]	$L_2Ni(CO)_2$	0.157	$L_2RuCl_2(CO)_2$	0.090	162	97.2	21.8	68.8	9.4	85.3	89.1	98.2
3	$L_2Ni(CO)_2$	0.157	$L_2RuCl_2(CO)_2$	0.090	55	98.1	23.6	64.1	13.3	86.1	88.7	94.6
4	Recycle	0.157	Recycle	0.090	55	91.2	22.9	65.3	11.8	85.8	84.9	91.7
5	Recycle	0.157	Recycle	0.090	55	56.2	23.9	62.8	13.3	86.4	87.2	92.2
6[e]	Resin 1[f]	0.079	Resin 6[f]	0.053	55	92.3	24.1	56.8	19.1	84.2	88.9	91.8
7	Recycle	0.179	Recycle	0.053	55	0	0	0	0	0	0	0

[a] L represents Ph_3P. [b] No hydrogen pressure. [c] Homogeneous oligomerization at 90°, 24 hr, hydrogenations at 140°, 4 hr, 150 psi of H_2, in 20 ml of benzene with 0.262 g of Ph_3P added. [d] Percent of respective polyene hydrogenated to monoene; 15 is 4-ethylcyclohexene, 16 is Z-cyclooctene, and 17 is E-cyclododecene. [e] Polymer-bound oligomerization at 115°, 24 hr, hydrogenation at 165°, 18 hr. [f] Polymer 1 analyzed for 2.39% P and 2.10% Ni while 6 analyzed for 1.88% P and 1.27% Ru.

tor. The normal to branched aldehyde ratio also increased from 4.3 using only resin **4** to 5.0 using **4** plus a 0.2 M excess of dissolved PPh_3.

Finally it was thought that aldehydes **13** and **14** might be decarbonylated to a small extent by the nickel catalyst (or a combination of the nickel and rhodium catalysts). Thus, **13** and **14** were resubjected to $(PPh_3)_2Ni(CO)_2$ and to both $(PPh_3)_2Ni(CO)_2$ plus $(PPh_3)_3RhH(CO)$ at the conditions employed before (H_2/CO, 1/1, 500 psi, 70° 24 hr). GLC analyses of the products showed that **7** or **10** or ethylcyclohexene had not been formed. Thus, no decarbonylation had occurred with either $(PPh_3)_2Ni(CO)_2$ or the combination $(PPh_3)_2Ni(CO)_2$ plus $(PPh_3)_3RhH(CO)$ present. From these results it appears that the less than quantitative yields observed during hydroformylation in systems with **1** + **4** present were the result of small amounts of PPh_3 present in solution during those reactions.

Sequential Cyclooligomerization Plus Selective Hydrogenation to Monoenes. Fahey[17,18] demonstrated **8** and **9** were selectively hydrogenated to (Z)-cyclooctene (**16**) and (E)-cyclododecene (**17**) in 92 and 97% yields using $(PPh_3)_2RuCl_2(CO)_2$ homogeneously with excess PPh_3 present. We extended these studies to polymer anchored systems[1] and achieved similar results. However, excess resin anchored –PPh_2 groups (up to a 15 mol excess) were not able to enhance selectivity to monoene in the manner that PPh_3 could.[1,19] Studies were undertaken to demonstrate that selective hydrogenation could be effected sequentially with cyclooligomerization.

Butadiene was efficiently converted to cyclooligomers **7**, **8**, and **9** followed by sequential selective hydrogenation (eq 3) to monoenes **15**, **16**, and **17**. The sequential reactions

(3)
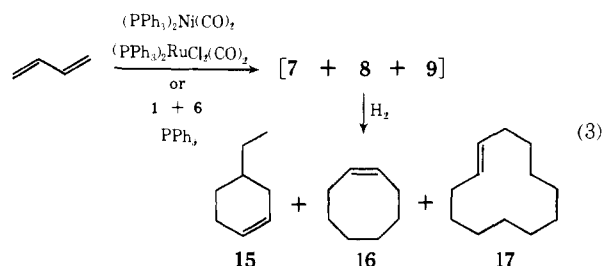
could be carried out (1) using $(PPh_3)_2Ni(CO)_2$ and $(PPh_3)_2RuCl_2(CO)_2$ together homogeneously, (2) using a mixture of resins **1** and **6** and, (3) using a resin to which both the nickel and ruthenium species were anchored. The latter system was not pursued in detail because the nickel catalyst was destroyed at the temperature which the resin-anchored ruthenium complex was used.[20] Thus studies were concentrated on the first two modes. As summarized in Table III, high yields of the monoenes **15**, **16**, and **17** were obtained from butadiene in all cases in which a large molar excess (15–20) of PPh_3, relative to Ru, was added to the

reaction solutions. Furthermore, the product distribution in the sequential homogeneous and sequential resin catalyzed reactions were very similar (Table III).

The homogeneous and resin catalyzed oligomerizations were carried out at 90° for 24 hr and 115° for 24 hr, respectively. The homogeneous hydrogenations were conducted at 140°, 4 hr, and 150 psi of hydrogen while those employing anchored catalyst (i.e., **6**) were performed at 165°, 18 hr, and 150 psi. Thus butadiene was first oligomerized and then the reactor temperature was raised and a hydrogen pressure applied. The slower rates observed for the heterogeneous selective hydrogenations are probably a diffusion effect. Comparison to homogeneous hydrogenations is complicated because, in addition to hydrogen and polyene diffusion into the catalyst sites, one must consider the concentration of PPh_3 within the resin's matrix. Using 165° in the hydrogenation step caused $(PPh_3)_2Ni(CO)_2$ or its bound analog to decompose. Thus, a mixture of catalysts **1** and **6** could not be recycled because of the decomposition of **1** during hydrogenation. However, **1** + $(PPh_3)_2RuCl_2(CO)_2$ or the all homogeneous system could be recycled, after product removal by vacuum distillation, because 140° was employed in the hydrogenation step in those cases. As with all systems employing $(PPh_3)_2Ni(CO)_2$ (**1**), or dual anchored catalysts, recycling was possible until the maximum molar turnover ratio (1100–1200) of the nickel complex was reached. It should be noted that independent hydrogenation experiments showed **6** or $(PPh_3)_2RuCl_2(CO)_2$ had very high (>15,000) turnover numbers.

In conclusion, the application of more than one resin-bound transition metal catalyst in multistep sequential synthesis has been successfully demonstrated. Extension of this concept throughout the field of homogeneous catalysis should be possible. For example, single pot, multistep, homogeneously catalyzed, syntheses of styrene and (E)-1,9-non-4-endial from butadiene are under study in this laboratory using resin anchored catalysis such as **4**, (P-$PPh_2)_2Pd(C_4H_2O_3)$, (P-$PPh_3)_2RuCl_2(PPh_3)$, and (P-$PPh_2)_2IrCl(CO)$.[21]

Multistep catalysts are well known in heterogeneous catalyses. One only need consider zeolites or hydrocracking catalysts (such as $Co-Mo-Al_2O_3-silica$). The dual "heterogenized" homogeneous enzyme studies of Mosbach[9] represent the thrust of these ideas into biochemistry. In dual anchored catalysts some critical considerations include: proximity effects of the two catalysts, catalyst compatibility when heterogenized, ability to operate the sequential reactions simultaneously (i.e., low intermediate concentration) to give rate enhancements, and rate enhancement via the generation of a high concentration of coordinatively unsaturated active sites. The studies described above did not achieve sequential or consecutive reactions simultaneously (low intermediate concentrations), but studies are in progress to reach that goal.[21]

Table IV. Elemental Analyses of Polymer-Bound Catalysts[a]

Polymeric catalyst	% P	mmol of P g^{-1}	% Ni	mmol of Ni g^{-1}	% Rh	mmol of Rh g^{-1}	% Ru	mmol of Ru g^{-1}
1	2.39	0.771	2.10	0.358				
2	1.83	0.590			1.70	0.165		
3	9.22	2.980	2.49	0.424	3.09	0.300		
4	2.01	0.647			1.44	0.140		
5	4.06	1.310	1.09	0.186	1.41	0.137		
6	1.88	0.605					1.27	0.126

[a] All polymers are SX-1 beads. Infrared spectra of the polymer-bound catalysts exhibited the same metal–hydride and metal–carbonyl absorptions as the free complexes.

Experimental Section

Solvents and reagents were obtained and purified as described.[1] GLC, ir, NMR, uv, and mass spectral studies were performed as described.[1] The preparation of resins 1, 2, 4, and 6 has been given.[1] The resins containing two metal complexes were prepared similarly. The diphenylphosphinated resin was swollen in toluene and a solution of both metal complexes, in the desired stoichiometry, was added under nitrogen. The reaction was heated at 100° for 24 hr after which the metal complexes were quantitatively complexed to the resin (provided the resin contained an equivalent of bound phosphine per equivalent of metal-complexed PPh$_3$ groups originally charged). Thus, both complexes were added in one step, and the stoichiometry was readily controlled. The analytical data for polymers 1–6 are given in Table IV.

Butadiene Cyclooligomerization and Sequential Hydrogenation with Homogeneous and Polymer-Bound (PPh$_3$)$_2$Ni(CO)$_2$ and (PPh$_3$)$_3$RhCl. Into a dry, nitogen purged stainless steel bomb were placed (PPh$_3$)$_2$Ni(CO)$_2$ (0.10 g, 0.156 mmol), (PPh$_3$)$_3$RhCl (0.10 g, 0.108 mmol), and dry benzene (10 ml, nitrogen saturated). After degassing, 1,3-butadiene (10.0 g, 187 mmol) was added at −78°, and the reaction was maintained at 100° with shaking for 24 hr. After cooling no unreacted 1,3-butadiene was recovered. Aliquots of solution were removed for analyses. A nitrogen purge was used in some cases to remove traces of unreacted 1,3-butadiene. The reactor was flushed with hydrogen, pressurized to 500 psig, heated to 60°, and shaken for 24 hr. Analytical GLC of the 1 ml of solution from the first step showed 4-vinylcyclohexene (17.3%), (Z,Z)-1,5-cyclooctadiene (66.7%), and (E,E,E)-1,5,9-cyclododecatriene (15.9%), identified as reported.[1] Only traces (less than 1%) of unreacted 1,3-butadiene were found. After cooling to 25°, a pressure of 95 psig was noted, and the excess hydrogen was vented. Analytical GLC showed three products which were collected by preparative GLC. Using ir, MS, and NMR, and products were identified as ethylcyclohexane, cyclooctane, and cyclododecane.[1]

Similar reactions using polymer-bound bis(triphenylphosphine)nickel dicarbonyl (0.5 g, 0.179 mmol of Ni) and polymer-bound tris(triphenylphosphine)rhodium chloride (0.5 g, 0.083 mmol of Rh) gave the same products but in somewhat lower yields. Oligomerization of butadiene resulted in recovery of unreacted butadiene (17.3%) with the products (82.7%) being 4-vinylcyclohexene (20.3%), (Z,Z)-1,5-cyclooctadiene (51.9%), and (E,E,E)-1,5,9-cyclododecatriene (26.5%). The hydrogenation yield was approximately 85%, giving a complex mixture of ethylcyclohexane (18.1%), cyclooctane (48.), and cyclododecane (21.6%), along with small amounts of various mono-, di-, and trienes.

Analogous reactions using resin (1.0 g) containing both catalysts on the same beads, bis(triphenylphosphine)nickel dicarbonyl (0.424 mmol of Ni g^{-1}) and tris(triphenylphosphine)rhodium chloride (0.30 mmol of Rh g^{-1}), gave yields almost identical with the catalysts on separate resin beads.

Butadiene Cyclooligomerization and Sequential Hydroformylation of 7 with Homogeneous and Polymer-Bound (Ph$_3$P)$_2$Ni(CO)$_2$ and (Ph$_3$P)$_3$RhH(CO). Into a dry, nitrogen purged stainless steel bomb were placed (PPh$_3$)$_2$Ni(CO)$_2$ (0.15 g, 0.235 mmol), (PPh$_3$)$_3$RhH(CO) (0.10 g, 0.109 mmol), and dry benzene (15 ml, nitrogen saturated). After thorough degassing, 1,3-butadiene (10.0 g, 185 mmol) was added at −78°, and the reaction was heated, with shaking, at 100° for 24 hr. No unreacted butadiene was recovered upon venting into a cold trap. About 1 ml of solution was removed for analysis. The remaining solution was nitrogen purged

to remove any traces of dissolved, unreacted butadiene. Then the reactor was flushed with hydrogen, pressurized to 250 psig with hydrogen and on to 500 psig with carbon monoxide, and heated with shaking at 60° for 4 hr. Analytical GLC of the 1-ml sample from the first step showed a trace of unreacted butadiene along with 4-vinylcyclohexene (21.9%), (Z,Z)-1,5-cyclooctadiene (57.8%), and (E,E,E)-1,5,9-cyclododecatriene (20.3%).[1]

After cooling to 25°, a pressure of 405 psig was noted and the excess gases vented. Analytical GLC of the reaction solution showed no detectable loss of 1,5-cyclooctadiene or 1,5,9-cyclododecatriene. Only 14.4% of the original 4-vinylcyclohexene remained unchanged. The branched hydroformylation product, 2-(cyclohex-3-enyl)propanal, accounted for 16.5% and the terminal product, 3-(cyclohex-3-enyl)propanal, accounted for 69.1% of the original amount of 4-vinylcyclohexene. These samples were identical with those reported.[1]

Similar reactions using polymer-bound bis(triphenylphosphine)nickel dicarbonyl (0.5 g, 0.179 mmol of Ni) and polymer-bound (PPh$_3$)$_3$RhH(CO) (0.5 g, 0.07 mmol of Rh) gave the same product distribution, though in only 89% total conversion of 1,3-butadiene. The polymeric catalysts were recycled by filtering under nitrogen, washing with benzene, and being carried through the reaction procedure again. The resin catalysts could be exposed to, or stored in, the air.

An 89% conversion of 1,3-butadiene was also obtained when using a polymer with both catalysts, (Ph$_3$P)$_2$Ni(CO)$_2$ and (Ph$_3$P)$_3$RhH(CO), bound to the same beads (1.0 g, 0.1866 mmol of Ni, and 0.137 mmol of Rh).

Butadiene Cyclooligomerization and Sequential Selective Hydrogenation to Monoenes with Homogeneous and Polymer-Bound (Ph$_3$P)$_2$Ni(CO)$_2$ and (Ph$_3$P)$_2$RuCl$_2$(CO)$_2$. Into a dry, nitrogen purged stainless steel bomb were placed (PPh$_3$)$_2$Ni(CO)$_2$ (0.10 g, 0.157 mmol), (PPh$_3$)$_2$RuCl$_2$(CO)$_2$ (0.10 g, 0.13 mmol), triphenylphosphine (0.262 g, 1 mmol), and dry benzene (20 ml, nitrogen saturated). After degassing, 1,3-butadiene (6.6 g, 122 mmol) was added at −78° and the reaction was heated 24 hr at 100° with constant shaking. After cooling unreacted butadiene (1.02 g, 15.5%) was recovered by venting into a cold trap. A 1-ml aliquot was removed and a nitrogen purge was employed to remove any dissolved, unreacted butadiene. The reactor was flushed with hydrogen, pressurized to 150 psig with hydrogen, and heated with shaking at 140° for 14 hr. Analytical GLC of the 1-ml sample from the first step found 4-vinylcyclohexene (21.8%), (Z,Z)-1,5-cyclooctadiene (68.8%), and (E,E,E)-1,5,9-cyclododecatriene (9.4%). These were identified as described previously.[1]

After cooling to 25°, the hydrogen pressure was 81 psi. Analytical GLC of the reaction mixture now found ethylcyclohexane (2.6%), 4-ethylcyclohexene (18.5%), 4-vinylcyclohexene (0.6%), cyclooctane (3.2%), (Z)-cyclooctene (61.4%), 1,5-cyclooctadiene (4.2%), cyclododecene (9.3%), and only traced of cyclododecane, cyclododecadiene, and 1,5,9-cyclododecatriene.

The system was recycled by distilling off solvent and products under vacuum, reintroducing dry benzene (20 ml, nitrogen saturated), condensing in 1,3-butadiene at −78°, and beginning the reaction procedure over again. A temperature of 145° must not be exceeded or the (Ph$_3$P)$_2$Ni(CO)$_2$ will decompose, giving black, finely divided nickel.

Analogous reactions using the catalysts, bis(triphenylphosphine)nickel dicarbonyl (0.5 g, 0.179 mmol of Ni) and dichlorodicarbonylbis(triphenylphosphine)ruthenium (0.5 g, 0.053 mmol of Ru), bound to separate batches of resin gave overall results only slightly lower than the homogeneous reaction. Recovery of the

polymer was accomplished by filtration; however, the $(Ph_3P)_2Ni(CO)_2$ had decomposed during the period of hydrogenation when a temperature of 165° was employed.

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Tin-119 Chemical Shifts of Ortho, Meta, Para, 2,6-, and Polysubstituted Aryltrimethyltin Derivatives and Related Organotin Compounds[1a]

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Abstract: Tin-119 chemical shifts for 15 meta and para, 10 ortho, 7 2,6-disubstituted, and seven miscellaneous polysubstituted aryltrimethyltin compounds along with the shifts of 15 additional aliphatic organotin compounds have been recorded by direct observation at 37.27 MHz in the continuous wave mode. Although the chemical shift response of the ten nuclei which have thus far been incorporated into various series of phenyl compounds with respect to electron withdrawal is mixed, i.e., about half the series studied fail to change in the expected downfield direction with electron withdrawal, the tin chemical shifts show excellent correlations ($r > 0.97$) with σ_I and $\sigma_R{}^\circ$ values, with the shifts changing in the anticipated manner. The shift differences, $\Delta\delta$, imposed by moving the substituent from the para to the ortho position range from the small changes induced by the halogen and trifluoromethyl groups to $\Delta\delta = -16.3$ ppm for the dimethylamino group. These changes are accentuated in the 2,6-derivatives. Upfield shifts of the alkyl group-bearing substituents are interpreted in terms of steric compression and angular distortion produced in the bonds to tin, while dispersion forces may account for the downfield shifts of the ortho and 2,6-disubstituted halo derivatives. Small tin-119m Mössbauer quadruple splittings, observed for these derivatives are also found for the para compounds and are interpreted in terms of electronegativity. $|J(^{119}Sn-^{19}F)|$ coupling constants for the ortho, meta, and para derivatives have similar small values, and large upfield shifts characteristic of higher coordination at tin are lacking. The observed effects of introducing saturated carbon atoms in aliphatic derivatives α, β, and γ to tin on the shifts are similar to those for carbon-13 and the heavier nuclei, with α- and β-substitution producing a downfield shift and γ-substitution producing an upfield shift, suggesting a similar mechanism governing the shifts in each case. The shift of the *syn*-7-trimethyltinnorbornene lies 14.3 ppm to lower field than in the anti isomer suggesting interaction with the double bond. Large downfield shifts are also seen when the tin atom is incorporated into a small ring. Unsaturated groups induce large upfield shifts when directly attached to tin.

Since the first publication by Burke and Lauterbur[2] in 1961, there have been over 40 research papers reporting tin-119 NMR chemical shift data,[3] and an excellent review.[4] Tin chemical shifts are now known to range from -1712 for SnI_4 in a 1:1 mixture with $SnCl_4{}^2$ to $+199$ ppm for diethyltin thioglycolate,[5] with respect to tetramethyltin as a standard, or 1911 ppm overall (or to -662 for $CH_3SnBr_5{}^{2-}$ in water,[6] for a range of 861 ppm for organotin derivatives, or to -282 for triethyltin hydride,[3] for a range of 481 ppm for four-coordinated organotin species). Yet there is no satisfactory answer to the question of the effect of electron withdrawal on tin chemical shifts.

In an attempt to settle this question, we report in this paper tin chemical shifts for 15 meta and para, 10 ortho, 7 2,6-disubstituted, and 7 miscellaneous and polysubstituted aryltrimethyltin compounds, along with the shifts of 15 additional organotrimethyltin species.

Results

The reader of the tin chemical shift literature is cautioned to note carefully the sign convention used in tabulating the data. While the use of tetramethyltin as a standard dates from the early work of Hunter and Reeves,[7] it is only recently that the shift sign conventions of the heavier nu-