

1,3-Butadiene Oligomerization Catalyzed by Polymer-Attached Palladium Complexes. Comparison with Homogeneous Catalysis

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Palladium chloride, tetrakis(triphenylphosphine) palladium, and palladium acetate have been anchored to diphenylphosphinated styrene-divinylbenzene resins to provide resin catalysts with from 1.1 to 10.9% Pd loadings and P:Pd ratios from 2.1 to 25.7. Butadiene was oligomerized to product mixtures of E-1-acetoxy-2,7-octadiene, **6**; 3-acetoxy-1,7-octadiene, **7**; E-1,3,7-octadiene, **8**; E-1-acetoxy-2-butene, **9**; and 3-acetoxybutene, **10**; in THF-HOAc at 100°C in the presence of these anchored catalysts. The product distribution was essentially unchanged as the percentage Pd in the resin was varied at constant P:Pd. The product distribution varied modestly as P:Pd was changed. The product distribution for reactions catalyzed by such resins was the same as those homogeneously catalyzed by PPh₃ plus Pd(OAc)₂ when compared at equal P:Pd ratios. These observations rule out a mechanism involving a bridged bimetallic intermediate in Pd(OAc)₂ catalyzed reactions because the resin matrix effectively isolates Pd sites from one another. Palladium leaching was serious for anchored PdCl₂ and Pd(PPh₃)₄ but less so for Pd(OAc)₂. The effect of the P:Pd ratio on leaching is discussed. In the presence of triethylamine, metallic palladium was precipitated in the resin.

INTRODUCTION

Recently palladium complexes have been found to catalyze a large number of organic reactions, including olefin oxidation, oligomerization of olefins, dienes, and alkynes, carbonylation, acetoxylation, isomerization, and hydrogenation (1). Commercial homogeneous catalytic reactions (2), such as the Wacker process, are becoming increasingly important. However, homogeneous catalysts can be lost and products can be contaminated where reaction products and catalysts are not easily separated. Catalysts which are chemically attached to cross-linked polymers [for reviews, see Ref. (3)], or other supports (4), are effectively "heterogenized" and may be used in fixed or fluidized catalyst beds, thereby simplifying product recovery and catalyst recycle. Reported chemical advantages which polymer-bound catalysts exhibit in certain cases,

include (a) enhanced size and positional selectivity (5), (b) ability to carry out sequential catalytic reactions (6), (c) the matrix-like isolation of reactive catalytic species from one another (7), and (d) a different response of reaction rate to ligand concentration than that observed in homogeneous systems (8). For the reasons listed above we undertook the synthesis of polymer-attached palladium catalysts including PdCl₂, Pd(PPh₃)₄, and Pd(OAc)₂. These complexes were attached to swellable styrene-divinylbenzene resin beads by polymeric triphenylphosphine moieties. The linear dimerization-acetoxylation of 1,3-butadiene was the reaction used to study the catalytic behavior of the attached catalysts. Sequential oligomerization-hydrogenation studies are also reported where both (PPh₃)₂PdCl₂ and (PPh₃)₃RhCl were attached to the same resin. These studies

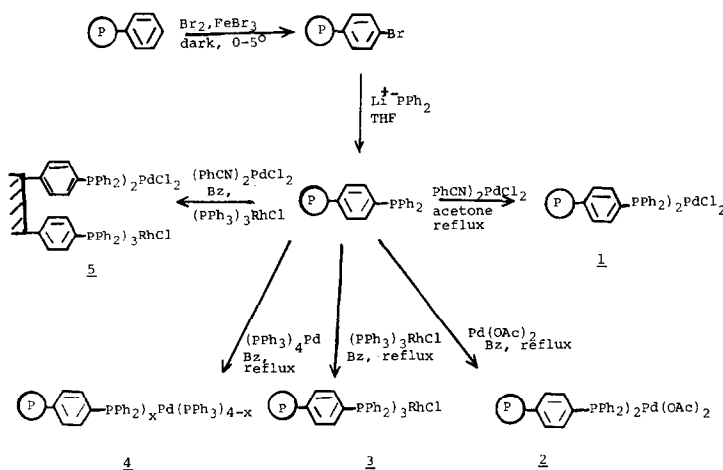
constitute part of an extensive exploration of the role swollen polymers play in reactions of resin-anchored catalysts (6, 8-12).

RESULTS AND DISCUSSION

The palladium(II) catalyzed reaction of butadiene with carboxylic acids to give octadienyl esters was reported to be a slow reaction accompanied by the formation of large quantities of 1,3,7-octatriene and butenyl esters (13). Addition of tertiary amines greatly increased the rate of this reaction and its selectivity to octadienyl acetates (14). In order to expose catalyst

sites on swellable resins to triethylamine and acetic acid, we chose tetrahydrofuran (THF) as a standard solvent since THF is capable of swelling catalytic styrene-divinylbenzene resins, thus allowing diffusion of the substrates into the catalyst. When comparing polymer-attached catalysts to the corresponding palladium complex, employed homogeneously, equivalent solvent volumes and reagent concentrations were employed.

Catalyst preparation. Polymer-anchored PdCl_2 , $\text{Pd}(\text{PPh}_3)_4$, and $\text{Pd}(\text{OAc})_2$ catalysts were prepared as outlined in Scheme 1.



SCHEME 1

Styrene-divinylbenzene resin beads (1% divinylbenzene, Bio Rad Labs SX-1, 200-400 mesh) with a molecular weight permeation exclusion limit of 14,000 (15) were employed. The resin was brominated (Br_2 , FeBr_3 , dark, cold) and phosphinated (THF, LiPPh_2 excess) as previously reported. $\text{Pd}(\text{PPh}_3)_4$ and $(\text{PPh}_3)_3\text{RhCl}$ were attached to the polymer by a room temperature exchange of the coordinated PPh_3 groups for the polymer attached phosphine groups (i.e., Poly- PPh_2) in benzene. The anchoring of PdCl_2 was accomplished by displacement of benzonitrile from $(\text{PhCN})_2\text{PdCl}_2$ by Poly- PPh_2 moieties in refluxing acetone, ac-

ording to the method of Bruner and Bailar (16). Palladium acetate was reacted with the phosphinated resin at room temperature in benzene to give resin 2 in a manner similar to Stephenson and co-workers' (17) preparation of $(\text{PPh}_3)_2\text{Pd}(\text{OAc})_2$.

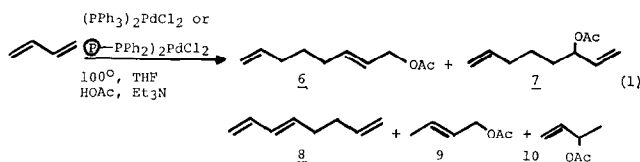
$\text{Rh}(\text{PPh}_3)_3\text{Cl}$ and $(\text{PhCN})_2\text{PdCl}_2$ were simultaneously reacted with the same phosphinated resins in acetone, using the appropriate ratio of complex to anchored phosphine to give the dual catalyst 5. Also, each complex was anchored to separate batches of resin. The rhodium and palladium catalyst sites cannot come into contact with each other when samples of resins 1 and 3

are mixed together and swollen in the same reactor. On the other hand, when the two complexes are anchored to the same polymer, **5**, the internal mobility of the resin might allow a fraction the sites to come into contact. Other studies employing two homogeneous catalysts or two polymer-bound complexes in the same reactor have been previously reported by us (6).

Analyses for % P, % Pd, and % Rh established the catalyst loading and the P: Pd ratios of the anchored catalysts. These are summarized in Table 1 together with analytical results after cycling the catalyst through dimerization reactions. PdCl₂ was attached at two different P: Pd ratios (3.8 and 1) and polymers containing Pd(OAc)₂, with P: Pd ratios of 2.1, 4.8, 4.9, 5.3, 9.1, 12.5, and 25.4, were prepared. This permit-

ted a study of product selectivity as a function of the P: Pd ratio.

Dimerization-acetoxylation catalyzed by resin-anchored PdCl₂ and Pd(PPh₃)₄. 1,3-Butadiene (6 g) was reacted with acetic acid (3 g) in the presence of catalytic amounts of (PPh₃)₂PdCl₂ (homogeneous) or its resin-anchored equivalent. Triethylamine (3.3 g) was used as a promoter. The reactions [Eq. (1)] were carried out in sealed bombs, in the absence of oxygen, using THF as the solvent at 100°C. The products included E-1-acetoxy-2,7-octadiene, **6**, (60–80%), 3-acetoxy-1,7-octadiene, **7**, (15–30%), E-1,3,7-octatriene, **8**, (3–10%) as well as small amounts of E-1-acetoxy-2-butene, **9** (<5%) and 3-acetoxybutene, **10** (<2%). Representative product distributions and reaction conditions are summarized in Table 2.



Resin **1a** (P: Pd = 3.8) and **1b** (P: Pd = 1) could be recycled with a decrease in activity noted after several recycles. Palladium leaching was significant in both resins. For example, the Pd content of resin **1a** dropped from 1.74 to 1.29% after two recycles and to 1.05% after five recycles. The palladium content of **1b** dropped from 5.43 to 4.46% in three cycles. Palladium loss was much slower in the absence of triethylamine. In addition to the loss of palladium from the resin, palladium metal was deposited in the polymer matrix due to catalyst decomposition during the reaction. Resin **1b** was black after the first cycle while **1a**, with a larger P: Pd ratio (3.8), slowly turned darker over several cycles. After five cycles, **1a** was a greenish-brown, apparently similar to the greenish-brown color observed by Bruner and Bailar

(16) with anchored PdCl₂ catalysts which had been used in hydrogenation reactions. Both **1a** and **1b** exhibited a sharp decrease in the intensity of their $\nu(\text{Pd-Cl}) = 340 \text{ cm}^{-1}$ bands during the reactions in accord with the observed drop in the chlorine content of the resin (2.58 to 0.23% in **1a** after five recycles).

The combined effect of leaching Pd and depositing metallic Pd is to decrease the number of active catalyst sites. Since the number of phosphine sites remains constant, this leads to an increase in the P: Pd ratio in the resin as a function of time. This could be the cause of the increased selectivity to product **6** as resin **1a** was recycled. The ratio of **6**: **7** increased from 2.1 to 6.4 (Table 2) after several recycles. These observations suggested that a polymer with a high phosphine loading and a large P: Pd

TABLE 1
 Elemental Analyses of Polymer-Bound Catalysts

Polymeric catalyst	P/Pd	% P	% Pd	% Cl	% Rh	After several reactions			
						% P	% Pd	% Cl	% Rh
1a	3.8	1.93	1.74	2.58	—	2.18 ^a	1.05	0.23	
1b	1	1.36	5.43	—	—	1.46 ^b	4.46		
1c	26.4	9.40	1.22			9.59	1.05		
3		2.01	—	—	1.44	1.99			1.49
4	5.9	1.99	1.16	—	—	1.90 ^c	0.68		
						1.93 ^d	0.50		
5		1.36	1.75	—	1.50	1.26	1.37		1.65
2a	2.1	6.75	10.90	—	—	5.39 ^b	9.34		
2b	4.8	7.42	5.31	—	—	6.36 ^b	2.17		
2c	9.1	7.90	2.97	—	—	6.47 ^e	2.29		
2d	12.5	7.76	2.22	—	—	6.57 ^e	2.69		
2e	4.9		2.34						
2f	25.4	8.12	1.10	—	—	5.64 ^e	1.34		
2g	5.3		1.31						

^a After 5 cycles.^b After 3 cycles.^c No added Et₃N, 2 cycles.^d After 2 cycles.^e After 4 cycles.
 TABLE 2
 Linear Oligomerization of 1,3-Butadiene Catalyzed by Polymer-Bound
 (PPh₃)₂PdCl₂ (1) and Pd(PPh₃)₄ (4)^a

Run	Catalyst	Time (hr)	Catalyst (mmol)	P/Pd ratio	Overall yield	Products					6/7 ratio
						6	7	8	9	10	
1	Resin 1a	24	0.144	4	100	59	28	10	2	1	2.1
2	Recycle	5	0.144	4	100	68	26	4	1	1	2.6
3	Recycle	24	0.144	4	72	79	17	4	0	0	4.7
4	Recycle	24	0.144	4	40	83	13	4	0	0	6.4
5	Recycle ^c	24	0.144	4	30	80	13	5	2	0	6.2
6	Resin 1b ^d	24	0.144	1	85	77	20	3	0	0	3.8
7	Recycle	24	0.144	1	80	73	25	2	0	0	2.9
8	Recycle	24	0.144	1	75	72	25	3	0	0	2.9
9	Resin 4 ^e	24	0.087	6	100	62	30	3	5	0	2.1
10	Recycle ^f	24	0.087	6	85	60	21	3	15	1	2.9
11 ^b	Resin 4	24	0.087	6	100	62	28	5	4	1	2.2
12	Recycle	24	0.087	6	8	65	30	5	0	0	2.2

^a Effect of redycling. Reactions were run in THF (20 ml), acetic acid (3.0 g), triethylamine (3.3 g) at 100°C in sealed bombs under 1,3-butadiene (6 g) pressure.^b No added triethylamine.^c Initial % Pd = 1.74, % Cl = 2.58, % P = 1.93, final Pd = 1.05, % Cl = 0.23, % P = 2.18.^d Initial % Pd = 5.43, % P = 1.36, final % Pd = 4.46, % P = 1.46.^e Initial % Pd = 1.16, % P = 1.99, final % P = 1.90, % Pd = 0.68.^f Initial % Pd = 1.16, % P = 1.99, final % Pd = 0.50, % P = 1.92.

TABLE 3
Linear Oligomerization of 1,3-Butadiene Catalyzed by Homogeneous and Polymer-Bound
(PPh₃)₂PdCl₂ and Pd(PPh₃)₄^a

Run	Catalyst	Catalyst (mmol)	P/Pd ratio	Overall yield	Products					6/7 ratio
					6	7	8	9	10	
1	PdCl ₂ ^b	0.144	1	74	67	14	3	13	2	4.8
2	(PPh ₃) ₂ PdCl ₂	0.144	2	100	65	25	6	4	0	2.6
3	(PPh ₃) ₂ PdCl ₂	0.144	3	100	56	31	10	3	0	1.8
4	(PPh ₃) ₂ PdCl ₂	0.144	6	100	59	29	6	4	1	2.0
5	(PPh ₃) ₂ PdCl ₂	0.144	10	100	49	25	20	3	3	2.0
6	Pd(PPh ₃) ₄	0.087	4	100	64	26	7	1	0	2.5
7	Resin 1b ^c	0.144	1	85	82	14	4	0	0	5.9
8	Resin 1a	0.144	3.8	100	59	28	10	1	2	2.1
9	Resin 4	0.087	5.9	100	62	28	5	4	1	2.2

^a Reactions were run in THF (20 ml), acetic acid (3.0 g), triethylamine (3.3 g) at 100°C in sealed bombs under 1,3-butadiene (6 g) pressure.

^b One mole of PPh₃ added to PdCl₂.

^c All polymer-bound oligomerization data is for the first cycle.

ratio would better resist palladium leaching and give a high selectivity to product 6. Thus, resin 1c was prepared (9.4% P, P: Pd = 26.4). After eight recycles the % Pd dropped only slightly from 1.22 to 1.05%. Throughout these runs the 6:7 product ratio remained in the 7.2 to 7.8 range in accord with expectation. However, the reaction rate (18) was slower.

Dimerization-acetoxylation of 1,3-butadiene were carried out homogeneously (PdCl₂, PPh₃) for comparison with the resin catalysts (Table 3). An increase from 1 to 10 in the P: Pd ratio, in the homogeneously catalyzed reactions, did not result in an increase in selectivity to 6. The product distribution obtained using resin 1a (first cycle) was the same as that obtained with its homogeneous equivalent (runs 3 and 4 vs 8, Table 3).

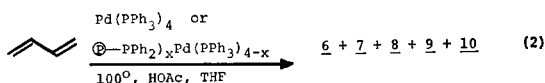
The homogeneous catalyst system was more stable to reaction conditions. When the P: Pd ratio is 1 or more, no deposition of Pd metal was noted, in agreement with the observations of Smutny (19). However, the resin catalysts were more stable to cyanide poisoning. After samples of 1a and 1b (0.2 g) were twice refluxed for 24 hr in

ethanol with a large excess of KCN (0.3 g), followed by washing with hot water, ethanol, acetone, and ether, they still exhibited catalytic activity. This treatment was previously employed by Bruner and Bailar (16) in a test of Pd²⁺ as the active species in anchored hydrogenation catalysts. The KCN treatment did cause the disappearance of the $\nu_{\text{Pd-Cl}}$ ir band at 340 cm⁻¹ and the extensive removal of Pd from the polymer. Fresh 1a lost 60% of its original Pd on treatment with KCN, while 1a, which had already been through two oligomerization reaction cycles, lost 45% of its Pd. After KCN treatment, the product distributions obtained in the dimerization-acetoxylation resembled that given by that same resin after many recycles (i.e., 1a 6:7 = 6.6 after KCN treatment). This is in accord with partial Pd removal by CN⁻ which, in turn, increases the P: Pd ratio within the matrix.

Palladium tetrakis(triphenylphosphine), Pd(PPh₃)₄, has been reported to be an active homogeneous catalyst for the telomerization of 1,3-butadiene without need for an amine co-catalyst (19). We confirmed

this observation [Table 3, Eq. (2)] and found the product distribution was similar to that obtained with $\text{PdCl}_2 + 4\text{PPh}_3$ under the same conditions. When anchored catalyst **4** (P:Pd = 5.9) was employed, the

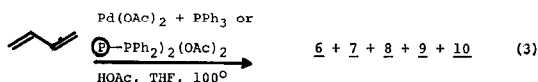
product distribution was only slightly different (runs 9 vs 6, Table 3). The great similarity of all these reactions implicates $(\text{PPh}_3)_x\text{Pd}^0$ as the active species in the catalytic process.



Resin **4** was only active for one cycle, however. Considerable palladium leaching was observed (% Pd dropped from 1.99 to 0.68 on the first cycle) a brownish solution containing $\text{Pd}(\text{OAc})_2$ (via ir) appeared. A major fraction of the catalysis might be promoted by dissolved Pd species in this case. Production of metallic palladium was not observed and the resin remained light yellow. However, in the presence of triethylamine as a co-catalyst, the polymer could be recycled, but extensive deposition of metallic palladium occurred on the resin.

Dimerization-acetoxylation catalyzed by resin-anchored $\text{Pd}(\text{OAc})_2$. The problems of leaching and deposition of metallic palladium appeared to rule out the use of

anchored PdCl_2 or $\text{Pd}(\text{PPh}_3)_4$ in continuous or batch processes. Anchored $\text{Pd}(\text{OAc})_2$ was found to leach far less at equivalent P:Pd ratios. Therefore, it was studied more extensively. The importance of the counterion in oligomerization-addition reactions, catalyzed by palladium, has been increasingly recognized (20). Palladium complexes with organic acids, such as $\text{Pd}(\text{OAc})_2$, are easily prepared, and they are ideal oligomerization-addition catalysts for reactions which employ a common nucleophile such as acetate because co-catalysts, such as triethylamine or sodium phenoxide, are unnecessary. Thus a series of resins, **2a-g**, containing anchored $\text{Pd}(\text{OAc})_2$, was prepared and used to catalyze 1,3-butadiene dimerization-acetoxylation [Eq. (3)].



The product distributions resembled those obtained with anchored PdCl_2 and $\text{P}(\text{PPh}_3)_4$. The major products **6** (56–66%) and **7** (19–28%) were produced in amounts similar to those obtained using resins **1a** and **1b**, (Table 4). Products **8–10** were also produced in minor amounts. The ratio of **6**:**7** varied only slightly (2.3 to 2.5) as the P:Pd ratio varied from 2.1 to 25.4. Thus, the P:Pd ratio does not play a major role in the product distribution. As the P:Pd ratio increased, the yield of **9** increased (2 to 15%), however. Most striking was the fact that the product distribution was es-

entially the same for the homogeneous and anchored $\text{Pd}(\text{OAc})_2$ systems. This suggests both proceed by the same pathway (21). This point is illustrated comparing runs 1 vs 2, 3 vs 4, 5 vs 6, and 9 vs 10 in Table 4. Finally, the quantity of 1,3,7-octatriene produced was found sensitive to temperature, reaction time, and changes in solvent.

The reproducibility of the product distribution was less when using resin catalysts **2a**, **b**, **e**, and **g** with low P:Pd ratios (P:Pd = 2.1–5.3) than when using **2c**, **d**, and **f** (P:Pd = 9.1–25.4). Representative examples using **2d** and **f** are shown in

TABLE 4
Product Distributions in Butadiene Oligomerizations Catalyzed Both by Resin-Anchored and Homogeneous $\text{PPh}_3 + \text{Pd}(\text{OAc})_2$ in THF-HOAc^a

Run no.	Catalyst ^b	% Pd by Wt on resin	Pd/P	Time (hr)	Product yields (%)				
					6	7	8	9	10
1	Resin 2a	10.90	2.1	18	64	28	5	2	1
2	Homogeneous	—	2.0	18	63	27	7	2	1
3	Resin 2b	5.31	4.8	20	66	26	4	2	2
4	Homogeneous	—	4.0	8	63	28	4	3	2
5	Resin 2c	2.97	9.1	20	58	21	5	11	5
6	Homogeneous	—	9.0	10	56	20	8	10	3
7	Resin 2d	2.22	12.5	20	58	21	3	12	6
8	Resin 2e	2.34	4.9	20	65	27	5	2	1
9	Resin 2f	1.10	25.7	24	52	21	6	14	8
10	Homogeneous	—	25.0	2	53	19	7	15	6
11	Resin 2g	1.31	5.3	20	63	27	5	3	2
12	Homogeneous	—	0	23	62	33	0	3	1
13	Homogeneous	—	0.2	24	62	31	3	4	1
14	Homogeneous	—	1.0	21	63	27	7	2	1

^a In all reactions 0.134 mmol of Pd, 20 ml THF, 3 g HOAc, and 6 g 1,3-butadiene were reacted in sealed bombs at 100°C. The P/Pd ratio was varied by addition of PPh_3 (homogeneous runs) or by incorporation of $-\text{PPh}_2$ groups into the resin.

^b The resins contained the following percentages (by wt) of phosphorous **2a**, 6.75; **2b**, 7.42; **2c**, 7.90; **2d**, 7.76; **2e**, 3.41; **2f**, 8.12; **2g**, 7.21. The overall butadiene conversion was 100% in each reaction and the reported values are the averages of three runs each.

Table 5. The rate of 1,3-butadiene conversion remained about the same upon recycling these resins. The resins with low P:Pd ratios slowly became black due to the deposition of some metallic palladium, while resins with high P:Pd ratios appeared stable. Reaction solutions filtered from polymers **2d** and **2f** were colorless, indicating that no leaching occurred. A yellow tint was always observed in the reaction solutions filtered from **2a** and **2b**. No decomposition of $\text{Pd}(\text{OAc})_2$ to Pd metal was seen during homogeneous catalyst use as long as the $\text{PPh}_3/\text{Pd}(\text{OAc})_2$ ratio was above 0.5. When no PPh_3 was present, decomposition to metallic palladium occurred. This agrees with the observations of Smutny (19). The presence of phosphine preserves the integrity of the catalyst system. However, far higher P:Pd ratios were needed in resin

systems to achieve this effect. This may be due to the limited mobility of the polymer-bound phosphines versus dissolved PPh_3 . The limitation in mobility requires the observed higher P:Pd ratio for stability in the resin. A similar difference in homogeneous versus anchored ligand mobility was previously related to unusual rate effects observed using polymer bound $\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2$ (8).

The anchored $\text{Pd}(\text{OAc})_2$ catalysts were less active than the homogeneous system by factors of 4 to 20 when compared at equal P:Pd ratios at 100°C (18). This could be due to diffusion effects and reagent gradient effects in the resin, or it might result from a difference in solvation effects when employing the resin. The catalyst efficiency was in excess of 5000 for resins **2c**, **2d**, and **2f**. This is higher than the 1200

TABLE 5

Product Distributions Obtained in Dimerization-Acetoxylation of 1,3-Butadiene Catalyzed by Resin-Attached Pd(OAc)₂ upon Recycling

Run	Catalyst	P/Pd ratio	6	7	8	9	10
1	Resin 2d	12.5	57	20	9	13	1
2	Recycle	12.5	56	22	5	14	2
3	Recycle	12.5	62	25	1	10	2
4	Recycle	12.5	54	21	11	11	3
5	Resin 2f	25.7	52	21	5	15	8
6	Recycle	25.7	50	20	9	14	7
7	Recycle	25.7	51	20	7	10	4

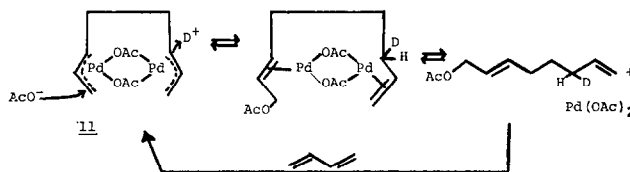
mol of product/mol of Pd(OAc)₂ observed by Smutny in homogeneous reactions (19).

The Pd(OAc)₂ complex with 1,2-diphenylphosphinoethane has been found to give only 1:1 adducts in the catalytic reactions of 1,3-butadiene and active methylene compounds (22). This contrasts with the production of dimer products in the presence of monodentate phosphines. The lack of dimerization when bidentate phosphines are used has been attributed to the decrease in the number of coordination sites at palladium available to the diene. The resin-anchored palladium catalysts are also chelated species (two or more phosphine moieties in the polymer bind to the metal)

(8, 9, 23). Despite this chelation by the resin, the resulting product distribution agrees with that exhibited when using Pd(OAc)₂+PPh₃. Thus, the phosphine-palladium association equilibrium, within the swollen resin, more resembles that taking place in the presence of dissolved PPh₃ than in the presence of 1,2-diphenylphosphinoethane. That is, the "chelation effect" (an unusually small concentration of coordinatively unsaturated Pd due to small dissociation constant) does not operate within the resins.

The ir spectrum of resins **2a-g** were similar to (PPh₃)₂Pd(OAc)₂: $\nu(\text{COO})_{\text{asym}} = 1634$ and 1630 cm^{-1} , respectively. After the first cycle, the resins acquired bands at 1700 and 1950 cm^{-1} . The 1700 cm^{-1} absorption corresponds to un-ionized and uncoordinated -COO stretching bands (24). These are apparently due to acetic acid which is hydrogen bonded to coordinated acetate. The observation of a broad OH band is in accord with this suggestion. No noticeable intensity change occurs on subsequent cycles.

Smutney (19) proposed a mechanism for linear dimer formation in which bridged bimetallic palladium intermediates, such as **11**, were formed (Scheme II). Complex **11**

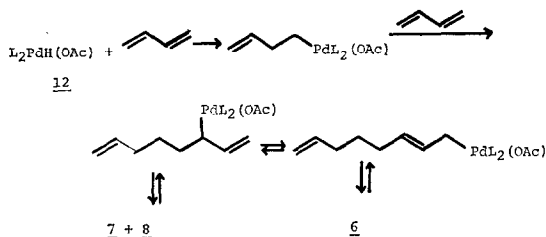


SCHEME II

was isolated (19) from oligomerization reactions, and the incorporation of deuterium agreed with such a pathway (19, 25). Maitlis (1), on the other hand, suggested a step-

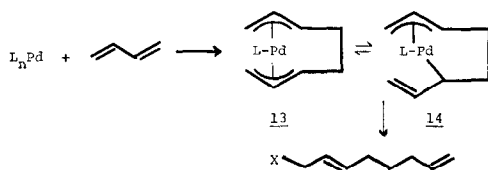
wise mechanism which involved the formation of a Pd(II) hydride complex, **12**, by oxidative addition of acetic acid. Bimetallic intermediates were not necessary in this

path (Scheme III). Mononuclear bis-(π -allyl)-palladium intermediates, such as



SCHEME III

13 and **14** shown in Scheme IV, have been advocated by Wilke *et al.* (26), Heimbach



SCHEME IV

et al. (27), and Takahashi *et al.* (28) to explain Pd-catalyzed linear dimerizations.

Bonds and Brubaker (7) have demonstrated that resins have the ability to isolate catalytic sites from one another within the crosslinked matrix. This concept of active site isolation should be able to allow a choice between a mechanism involving bridged bimetallic intermediates (Scheme II) or monometallic intermediates (Schemes III or IV). The formation of bimetallic intermediate **11** on a resin-anchored palladium acetate catalyst would not be a likely event unless the resin were highly mobile internally and unless the loading of palladium in the resin was very high. The reaction of two phosphine-complexed palladium atoms, within the resin, to form bridged complexes, would be prevented unless the polymer could readily deform in such a way that two sites would encounter one another. In resins where the palladium loading is below 3% and the P: Pd ratio is >6 , the palladium sites are essentially isolated from one another.

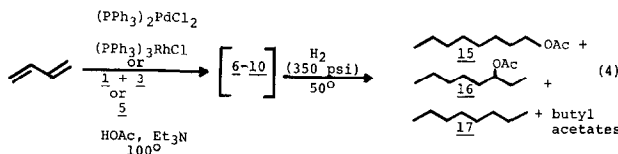
Since the product distribution was essentially unchanged as the percentage Pd in the resin varied from 10.90 to 1.10% at

P: Pd ratios of 2–6 (see runs 1, 3, 8, 11 in Table 4), the bridged bimetallic intermediate appears unlikely. Furthermore, only small changes in selectivity were found with large changes in the P: Pd ratio. This is clear when one compares runs 1, 3, 8, and 11 with runs 5, 6, and 9 in Table 4. These results strongly implicate a mechanism which does not involve a bridged bimetallic intermediate when resin-anchored catalysts are employed. This does not rule against a bimetallic intermediate, such as **11** in homogeneous oligomerizations. However, the fact that the product distributions were essentially the same for both the homogeneous and anchored palladium acetate catalyzed reactions, when compared at equivalent P: Pd ratios, suggests both reactions proceed by the same pathway (21). Thus, paths, such as those shown in Schemes II or III are favored over a path involving an intermediate such as **11**.

When a resin-anchored $Pd(OAc)_2$ catalyst was employed, the site of catalytic action was within the resin matrix. One way in which this was demonstrated involved the use of a three-phase test (30).

Palladium did not migrate from the catalyst resin (P:Pd > 3.5) to phosphinated resin beads (without metal) when both were refluxed in the same solution, separated only by a coarse glass frit. Thus, Pd(OAc)₂ or other palladium complexes were not being dissociated from the polymer and moving into solution. Furthermore, the Pd(OAc)₂ catalysts could be recycled several times without loss of activity unlike polymer-anchored PdCl₂ in the presence of amines. Resin **2c** exhibited a catalyst efficiency greater than 5000 mol of product/mol of Pd. Finally, resin-anchoring permitted the products to be separated from the reactor by flushing through a screen whereupon the reactor could immediately be recharged with solvent and reactants.

Sequential oligomerization-acetoxylation



The mixture of anchored catalysts **1** and **3** could be repeatedly recycled. Palladium leaching from **1a** or **1b** employed in the sequential reactions followed the same pattern discussed previously for oligomerization-acetoxylation. Resin **5** could also be recycled. Analyses of **5**, after four cycles, indicated some palladium leaching (% Pd = 1.75 dropped to 1.37) but no loss of rhodium (% Rh = 1.50 increased to 1.65% due to weight loss of resin as Pd leached).

Unsuccessful attempts were made to oligomerize butadiene to octadienyl acetates **6** and **7** and then selectively hydrogenate the terminal double bond of **6** using (PPh₃)₃RuCl₂ (*31*). Homogeneous reactions using PdCl₂+2PPh₃ and (PPh₃)₃RuCl₂ produced oligomers but extensive double bond isomerization was promoted by the ruthenium complex. No hydrogenation occurred below 80°C. Apparently (PPh₃)₃RuCl₂ was deac-

and hydrogenation. Palladium catalyzed oligomerization-acetoxylation could be followed by hydrogenation in the presence of (PPh₃)₃RhCl or its resin analog **3**. Similarly, this sequence could be conducted in the presence of resin **5** containing both palladium and rhodium complexes [Eq. (4)]. The saturated acetates **15** and **16**, octane, and butyl acetates were obtained quantitatively from their unsaturated precursors **6-10**. 1,3-Butadiene was heated for 24 hr at 100°C in THF in the presence of catalyst, acetic acid and triethylamine. This was followed by cooling to 40-50°C and pressurizing the reactor to 350 psi with hydrogen for 4 hr. Separate experiments demonstrate measurable hydrogenation did not occur in the presence of (PPh₃)₂PdCl₂ or resin **1** alone below 70°C.

tivated during the oligomerization sequence. Above 80°C the palladium complex was known to effect hydrogenation and complete hydrogenation occurred. Therefore, this dual catalyst combination was not pursued further.

EXPERIMENTAL METHODS

Benzene and THF were dried (CaH₂) and distilled under nitrogen. Similar care was taken to dry all solvents. Nitrogen, hydrogen, and butadiene were obtained commercially (99 + %) and used as received. Organometallic complexes were obtained from Strem or Pressure Chemical Co. The glc separations were done on a Varian Model 90-P for preparative work, a Hewlett-Packard Model 5710 A gas chromatograph for analytical work using OV-17 (8% on DMCS Chromosorb W, 6 ft × 1/8 in). The ir, ¹H nmr, and mass spectra were obtained

on a Beckman IR-33, Perkin-Elmer R20B, and Perkin-Elmer Hitachi RMU-6M instruments, respectively. All elemental analyses were performed by Schwarzkopf Micro-analytical Laboratories, Woodside, N. Y., 11377.

Anchoring catalysts to diphenylphosphinated polystyrene resins. The PdCl_2 was anchored by reacting $(\text{PhCN})_2\text{PdCl}_2$ with phosphinated resin in refluxing acetone according to the method of Bruner and Bailar (16). The solvent was decanted, and the polymer beads were extracted (Soxhlet) for 24 hr with acetone to remove unbound catalyst and free benzonitrile from the catalyst. $\text{Pd}(\text{OAc})_2$ was reacted with the phosphinated resin in benzene at room temperature, analogous to the homogeneous preparation of $\text{Pd}(\text{PPh}_3)_2(\text{OAc})_2$ by Stephenson *et al.* (17). When warmed, the yellow polymer became red and then black, apparently due to the deposition of palladium metal on the polymer. The resin was washed repeatedly with cold THF. Extended Soxhlet extraction (THF) resulted in some decomposition to black palladium metal on the polymer. The polymer-anchored $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ was prepared by phosphine exchange with the phosphinated resin in toluene at 100°C , as described before (11b). The total phosphine and metal contents were controlled as described elsewhere (6).

Homogeneous reaction of 1,3-butadiene with bis(triphenylphosphine) palladium dichloride. Into a dry, nitrogen purged stainless steel reactor bomb were placed bis(triphenylphosphine) palladium dichloride (0.10 g, 0.144 mmol), acetic acid (3.0 g, 50 mmol), triethylamine (3.3 g, 33 mmol), a controlled molar excess of PPh_3 , and dry THF (20 ml, nitrogen saturated). After degassing by several freeze-thaw cycles, 1,3-butadiene (4 g, 74 mmol) was condensed into the reactor at -195°C . The reactor was warmed to 100°C , shaken for 24 hr, cooled and then vented to a -78°C trap. No butadiene was recovered. Gas-liquid

chromatography of the reaction mixture found E-1-acetoxy-2,7-octadiene (67%), **6**; 3-acetoxy-1,7-octadiene (27%), **7**; and E-1,3,7-octadiene (6%), **8**. The products were collected by preparative glc. For **6** ir 1745 (s), $\nu_{(\text{C}=\text{O})}$, 1670 (m), 1645 (m), $\nu_{(\text{C}=\text{C})}$; and 985 (sh), 965 (s), 910 (s) cm^{-1} ; nmr (CDCl_3) δ 1.55 (m, 2, $-\text{CH}-$), 2.0 (5, 3, COCH_3), 1.9-2.3 (m, 4, allylic CH_2), 4.45 (d, 2, $\text{OCH}_2\text{C}=\text{}$), 5.7 (m, 3, $=\text{CH}$); Anal.: found: C, 71.20; H, 9.33; calcd: C, 71.45; H, 9.55; **7** ir 1744 (s) $\nu_{(\text{C}=\text{O})}$, 1645 (m) $\nu_{(\text{C}=\text{C})}$, 990 (s), 910 (s); nmr (CDCl_3) δ 1.75 (m, 2, $-\text{CH}_2-$), 2.0 (s, 3, COCH_3), 1.8-2.4 (m, 4 $=\text{CH}-\text{CH}_2\text{CH}_2\text{CH}=\text{}$), 2.9-3.4 (m, 1 proton), 4.8-6.1 (m, 6 $=\text{CH}-$ and $=\text{CH}_2$); Anal.: found: C, 71.61; H, 9.76; calcd: C, 71.45; H, 9.55. They agree well with reported spectra of **6** and **7** (31). For **8** ir 1640 (s), 1600 (s), 1000 (s), 965 (s), 910 (s) cm^{-1} ; nmr (CDCl_3) δ 2.0 (m, 4, $-\text{CH}_2$), 4.6-5.2 (m, 4, $=\text{CH}_2$), 5.2-6.5 (m, 4, $=\text{CH}-$); parent ion m/e 108. This is in accord with reported spectra (32).

Reaction of 1,3-butadiene with polymer-bound bis(triphenylphosphine) palladium dichloride. Into a dry, nitrogen purged stainless steel reactor were placed polymer-bound bis(triphenylphosphine) palladium dichloride resin **1a** (0.87 g, 0.144 mmol Pd), acetic acid (3.0 g, 50 mmol), triethylamine (3.3 g, 33 mmol), and dry THF (20 ml, nitrogen saturated). The system was degassed (three freeze-thaw cycles), 1,3-butadiene (4 g, 74 mmol) was added at -78°C , the reactor was warmed to 100°C and shaken for 24 hr. After cooling to 25°C and venting in a -78°C trap, no 1,3-butadiene was recovered. Gas-liquid chromatography of the reaction mixture gave **6** (59%), **7** (27%), **8** (10%), **9** (1%) and **10** (2%). For **9** ir 1740 (s), $\nu_{(\text{C}=\text{O})}$; 1670 (m), $\nu_{(\text{C}=\text{C})}$ and 920 (w), 960 (s), cm^{-1} $\nu_{(\text{C}-\text{H})}$; nmr (CDCl_3) δ 1.55 (d, 3H, CH_3), 2.2 (s, 3H, OOCCH_3), 4.5 (d, 2H, $\text{OCH}_2\text{C}=\text{}$), 5.3-6 (m, 2H, $-\text{CH}=\text{CH}-$); Anal.: found: (%) C, 63.4; H, 9.80; calcd: C, 63.3; H, 9.70. For **10** ir 1740 (s) $\nu_{(\text{C}=\text{O})}$; 1640 (m)

$\nu_{(C=C)}$ and 925 (s), 945 (s), 990 (s) cm^{-1} ; nmr (CDCl_3) δ 1.30 (d, 3H, CH_3), 2.0 (s, 3H, OOCCH_3) 4.8–6.2 (m, 4H, remaining protons); Anal.: found: C, 63.11; H, 9.60, calcd: C, 63.3; H, 9.70. The polymer-bound catalysts were recycled after filtration in air, washing with dry, nitrogen-saturated THF, drying *in vacuo*, and again carried through an identical reaction.

Reaction of 1,3-butadiene with homogeneous and polymer-anchored bis(triphenylphosphine) palladium diacetate. Into a dry, nitrogen purged stainless steel bomb were placed palladium acetate (0.03 g, 0.134 mmol) acetic acid (3.0 g, 50 mmol), the appropriate molar excess of PPh_3 , and dry THF (20 ml, nitrogen saturated). After degassing by several freeze-thaw cycles, 1,3-butadiene (6 g, 11.1 mmol) was added at -78°C , and the bomb was warmed to 80°C and shaken for 6–10 hr. After cooling to 25°C and venting in a -78°C , trap, no 1,3-butadiene was recovered.

Equivalent amounts of anchored and homogeneous $\text{Pd}(\text{OAc})_2$ were employed at 100°C for 24 hr. The quantities of reagents were the same as the homogeneous case.

Reaction of 1,3-butadiene with homogeneous and polymer-bound palladium tetrakis(triphenylphosphine). Into a dry, nitrogen purged stainless steel reactor were placed $\text{Pd}(\text{PPh}_3)_4$ (0.10 g, 0.087 mmol), acetic acid (3.0 g, 50 mmol) and THF (20 ml, nitrogen saturated). After degassing, 1,3-butadiene (4 g, 74 mmol) was added at -196°C and the reaction was maintained at 100°C with shaking for 24 hr. No butadiene was recovered. Gas-liquid chromatography of the reaction mixture found **6** (64%), **7** (26%), **8** (7%), **9** (1%), and no **10**.

Analogous reactions with polymer-bound palladium tetrakis(triphenylphosphine) resin **4** (0.80 g, 0.087 mmol) resulted in a complete oligomerization for the first cycle, and a dark brown solution due to palladium acetate. Also, no activity was obtained on recycling. Reactions were also performed

with polymer-bound palladium tetrakis(triphenylphosphine) with added Et_3N co-catalyst. The polymer turned black on the first cycle with considerable leaching of palladium. However, on subsequent re-cycles using the triethylamine co-catalyst significant activity was retained.

Butadiene linear oligomerization and sequential hydrogenation with homogeneous and polymer-bound (PPh_3)₂ PdCl_2 and (PPh_3)₃ RhCl . Into a dry, nitrogen purged stainless steel reactor were placed $(\text{PPh}_3)_2\text{PdCl}_2$ (0.10 g, 0.144 mmol), $(\text{PPh}_3)_3\text{RhCl}$ (0.10 g, 0.108 mmol), acetic acid (3.0 g, 50 mmol), triethylamine (3.3 g, 33 mmol) and dry THF (20 ml, nitrogen saturated). After degassing, 1,3-butadiene (4 g, 74 mmol) was added at -196°C and the reaction was maintained at 100°C with shaking for 24 hr. After cooling, 91% of the 1,3-butadiene was recovered. Aliquots of solution were removed for analysis after a nitrogen purge was used to remove traces of unreacted 1,3-butadiene. The reactor was flushed with hydrogen, pressurized to 300 psig, heated to 50°C , and shaken for 4 hr. Analytical glc of a 1 ml aliquot from the first step found **6** (63%) and **7** (37%). After cooling to 25°C (150 psig noted) the excess hydrogen was vented. Analytical glc showed two products which were collected by preparative glc. The ir, nmr, and elemental analyses were identical with commercially available samples (Aldrich Chemical Co.) of 1-acetoxy octane, **15**, and 3-acetoxy octane, **16**. The ir spectrum of both isomers showed no C=C bonds or olefinic protons in the nmr.

Similar reactions using polymer-bound bis(triphenylphosphine) palladium dichloride, resin **1b** (0.5 g, 0.144 mmol of Pd), and polymer-bound tris(triphenylphosphine) rhodium chloride, **3** (0.5 g, 0.108 mmol of Rh), gave the same products in slightly different distributions and yields. Oligomerization of butadiene resulted in recovery of unreacted butadiene (30%) with the products: 1-Acetoxy-2,7-octadiene (84%)

6 and 3-acetoxy-1,7-octadiene (16%) **7**. The hydrogenation yield was 100% giving 1-acetoxy octane (82%) and 3-acetoxy octane (18%). Analogous reactions using resin **5** (1.0 g), containing both catalysts on the same beads, bis(triphenylphosphine) palladium dichloride (0.144 mmol Pd) and tris(triphenylphosphine) rhodium chloride (0.073 mmol Rh), gave yields and product distributions similar to the homogeneous case.

Butadiene oligomerization and sequential hydrogenation with homogeneous and polymer-bound $(PPh_3)_2PdCl_2$. Resin **1a** (0.87 g, 0.144 mmol Pd) was used to first effect the oligomerization at 100°C (as above) for 24 hr then cooling to 25°C. No butadiene was recovered. A sample was removed for analytical glc. The reactor was flushed with hydrogen, pressurized to 200 psig for 3 hr at 65°C. Quantitative hydrogenation to 1-acetoxy octane and 3-acetoxy octane was obtained.

The homogeneous use of $(PPh_3)_2PdCl_2$ first oligomerized the butadiene at 100°C for 24 hr. The solution was cooled to 25°C and a sample was removed for analytical glc. The reactor was pressurized to 200 psig for 3 hr at 75–80°C to effect the quantitative hydrogenation to octyl acetates.

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