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USE OF POLYMER MATRICES TO ACTIVATE PALLADIUM(0) CATALYSTS AND REDUCE CATALYST AGGLOMERATION

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Summary

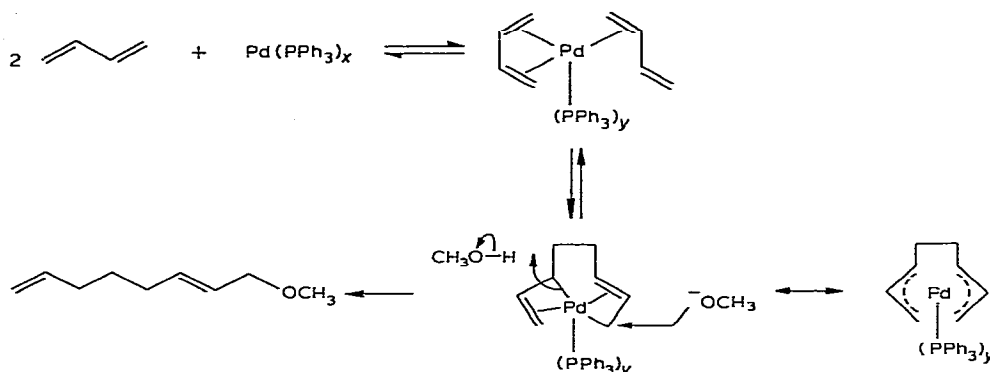
The dimerization—alkylation of butadiene to 1-methoxy-3,7-octadiene and 3-methoxy-1,7-octadiene has been studied in benzene at 100°C using both homogeneous and resin-attached palladium(0) catalysts. Pd(PPh₃)₄ was used as the homogeneous catalyst. Styrene-divinylbenzene (1% crosslinked) resins, functionalized with diphenylphosphine groups, were treated with Pd(PPh₃)₄ to give the resin-bound catalysts by ligand exchange. The rates of the homogeneously catalyzed reactions reach a limiting value as the catalyst concentration reaches 4×10^{-3} to 6×10^{-3} M due to equilibrium processes which limit the concentration of active species. The concentration of palladium in the resins is far higher (0.5×10^{-1} to 7×10^{-1} M), yet at similar P/Pd ratios the rates are greater per Pd using the resins. Furthermore, much larger catalyst charges may be employed, with the resin catalysts, without reaching limiting rates. Apparently, the resin retards the ability polymer-attached phosphines to highly coordinate (i.e., 3 or 4) palladium(0) relative to the corresponding situation in homogeneous solution. The resin matrix appears to retard the tendency, exhibited in the homogeneous reactions, for the catalyst to agglomerate and precipitate from solution as an inactive material.

Introduction

Heterogeneous metal and metal oxide catalysts have played an enormous role in organic synthesis for 100 years [1]. More recently homogeneous transition metal complexes have been found to catalyze a wide range of reactions [2] including oxidations [3], hydrogenations [4], oligomerizations [5], carbonylations [6], and decarbonylations [7]. Due to the difficulty in separating products from homogeneous catalysts in certain situations, the concept of attaching homogeneous catalysts to substrates has been envisioned as a way to make “fixed-beds” of homogeneous catalysts. One promising route is to attach

Halpern studied the analogous dissociation of $\text{Pt}(\text{PPh}_3)_4$ and found the first dissociation constant was very large and the second was $1.6 \times 10^{-4} M$ [24]. Berger [22] showed that the maximum reaction rate of the palladium-catalyzed dimerization—alkoxylation occurred when $\text{P/Pd} = 2$. At high phosphine concentrations and high P/Pd ratios the rate of reaction 1 becomes very slow. At low

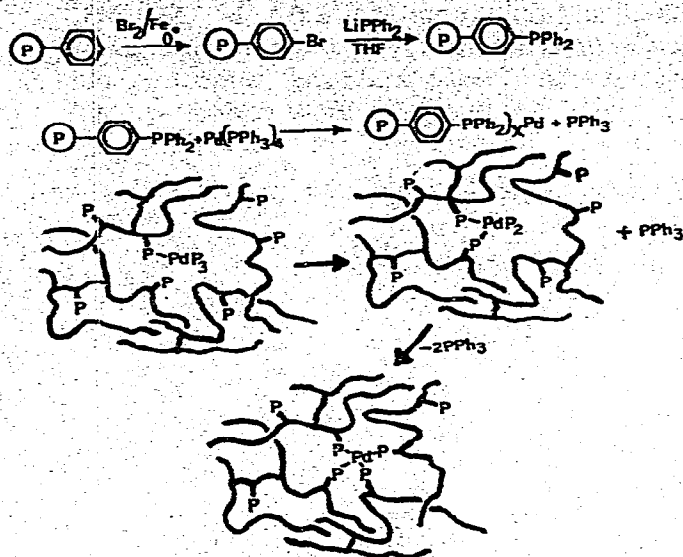
SCHEME 1



P/Pd ratios, butadiene competes more successfully for coordination sites than at higher ratios. However, at low P/Pd ratios the homogeneous catalyst system becomes unstable and palladium agglomeration occurs, particularly at higher catalyst concentrations. Also, our studies showed that the rate does not increase as the catalyst concentration is raised beyond from 4 to $6 \times 10^{-3} \text{ mol l}^{-1}$ (see Fig. 2).

We reasoned that a phosphinated styrene-divinylbenzene resin could be used to anchor palladium(0) complexes within the resin matrix. In particular, it seemed likely that up to two anchored phosphines would readily coordinate with palladium. However, further coordination of a third and fourth anchored phosphine site to a given palladium atom should become highly unfavorable, relative to the equivalent homogeneous solution equilibria shown in Scheme 1. The coordination of three or four anchored phosphine sites to a given palladium, during the ligand exchange reaction which fixed the palladium complex to the polymer, would require a great increase in the density of polymer chain segments in the vicinity of the metal atom. This should result in steric crowding and entropically unfavorable chain conformations. This concept is outlined in Scheme 2. Even if three or four phosphines did coordinate to palladium swelling the polymer in the presence of butadiene should cause the dissociation of one or two of the coordinated phosphines. Such dissociations should be strongly favored (see Fig. 1) relative to the same situation in the homogeneous solution. The net effect should be to generate a more coordinatively unsaturated palladium within the resin matrix than would be found using the corresponding homogeneous catalyst. This would be the case even though the phosphine concentration within the resin is very high. Lower phosphine coordination could result in faster catalytic rates, per palladium atom, using the resin-anchored catalyst.

SCHEME 2



The polymer should also act to "matrix isolate" palladium atoms from one another within the polymer in contrast to the high agglomeration tendency in homogeneous solutions. While chain mobility is significant [25,26], and metal migration within the resin would certainly be expected, the encounter rate of such anchored metal sites is expected to be far slower than similar processes in solution [27,28]. Therefore, one would expect the polymer-anchored palladium catalysts would not only be more active, but also would be more

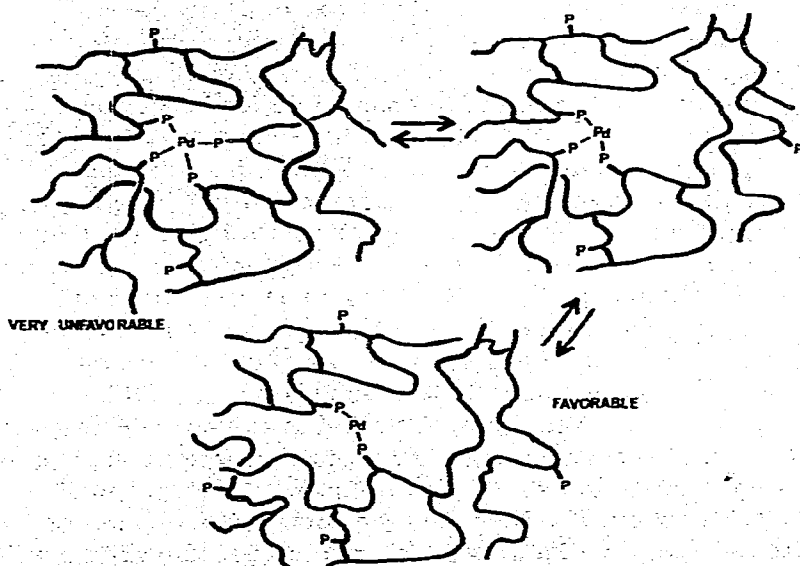


Fig. 1. The possible effect of steric crowding and unfavorable chain conformations on the phosphine-palladium equilibria within the resin matrix.

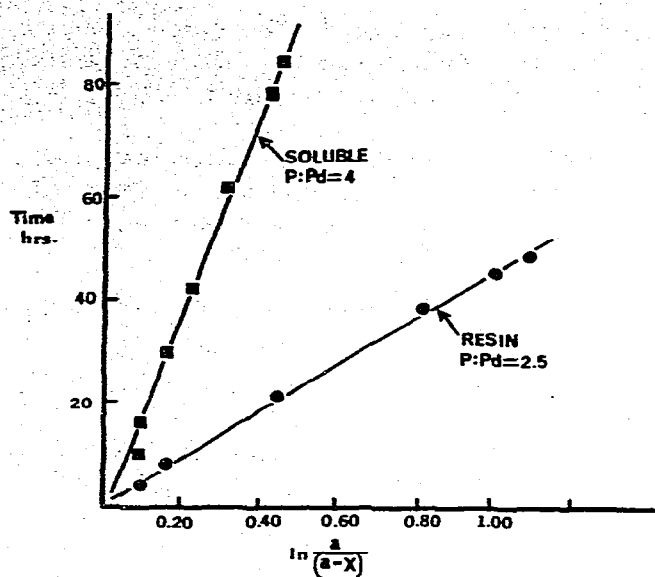


Fig. 2. Sample kinetic plots for the dimerization—methoxylation of butadiene at 100°C. (a represents the original concentration of methanol and X represents either the methanol consumed or the dimeric product formed).

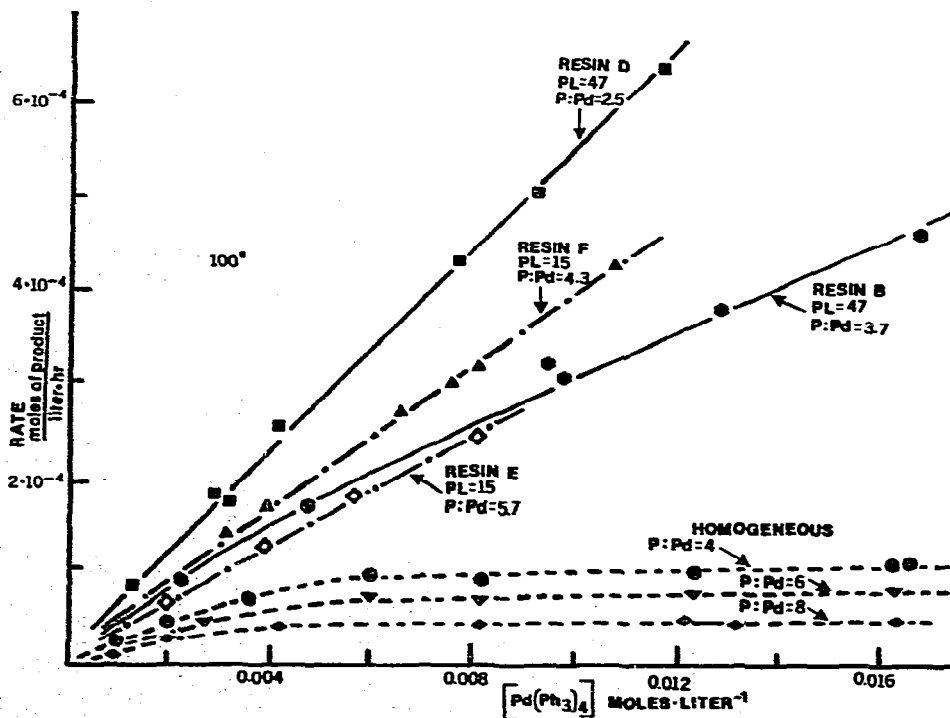


Fig. 3. Variation of dimerization—methoxylation rate as catalyst concentrations is increased. Comparison of homogeneous and polymer anchored palladium(0) catalysts.

stable than the corresponding homogeneous complexes. Further, they should be able to be used in far higher concentrations in the reaction solutions. Overall, this should permit the use of smaller reaction vessels and facilitate longer catalyst lifetimes.

Kinetic studies of the homogeneous dimerization—methoxylation reaction were carried out using excess butadiene to determine the order in methanol and in palladium complex. The disappearance of methanol and the appearance of dimers were monitored by GLC (internal standard technique). Plots of $t =$

$(1/k) \ln \frac{[\text{CH}_3\text{OH}]}{[\text{CH}_3\text{OH} - X]}$, where X is the amount of methanol consumed at time t ,

were straight lines. Rates were evaluated as the reciprocal of the slope over the first 10% conversion. Figure 2 illustrates two sample kinetic plots. One is for a homogeneous reaction and one is for a resin-anchored catalyst.

The pseudo first order rate constants from this treatment (i.e., such as Fig. 2) were then plotted as a function of the concentration of $\text{Pd}(\text{PPh}_3)_4$ for the homogeneous reactions. These plots are summarized in Fig. 3 for P/Pd ratios of 4, 6, and 8 as dashed curves. When P/Pd is 8, an additional 4 mol of PPh_3 has been added. As the concentration of homogeneous $\text{P}(\text{PPh}_3)_4$ is increased above 0.004 M , the rate rapidly levels off in all three homogeneous cases. This is characteristic of an equilibrium-limited upper concentration limit of the active catalytic species. It was observed throughout these studies for the homogeneous use of palladium(0) catalysts. Figure 3 also illustrates that the limiting homogeneous catalyst concentration is increased somewhat as the P/Pd ratio is lowered. As expected, the rates were higher as the P/Pd ratio was lowered. Finally, the rates exhibited by several polymer-anchored catalysts as a function of the amount of catalyst added are also shown in Fig. 3.

A series of polymer-anchored catalysts, $(\text{P})-\text{PPh}_2)_X\text{Pd}$, was prepared according to Scheme 2. Three different diphenylphosphinated styrene-divinylbenzene resins were prepared by this bromination—phosphination procedure. Resin beads (200—400 mesh) which were 1% crosslinked were employed. The levels of phosphine substitution were determined by analyses. Specifically, phosphine loading levels of 15, 47, and 74% were used in this study (where phosphine loading (PL) is defined as the percentage of the polymers' phenyl rings which

TABLE 1
RESIN-ANCHORED PALLADIUM CATALYSTS EMPLOYED IN THE DIMERIZATION—METHOXYLATION OF BUTADIENE

Catalyst No.	Phosphorous loading	Analysis			Swelling factor ^a
		Pd (%)	P (%)	P/Pd	
A	74	8.1	6.2	4.5	1.1—1.2
B	47	7.7	7.1	2.7	1.8
C	47	7.2	7.9	3.1	
D	47	5.7	7.8	2.5	
E	15	3.0	1.8	5.7	
F	15	2.9	2.4	4.3	2.7

^a The ratio of the swollen resin's volume in benzene to its dry volume.

have been substituted by diphenylphosphine substituents). The phosphinated resins were then treated with $\text{Pd}(\text{PPh}_3)_4$, prepared by the method of Coulson [30], in refluxing benzene to anchor palladium by phosphine exchange. A range of P/Pd ratios from 2.5 to 5.7 was employed. The catalytic resins used in this work are summarized in Table 1.

The uptake of palladium introduces further crosslink sites into the resin and thereby further restricts chain mobility. After bromination, phosphination, and uptake of palladium, the swelling ability of the resins decreased. The higher the phosphine loading became, the less swellable the resins were (see Table 1). For example, the swelling factor in benzene for resin A (PL = 74, P/Pd = 4.5) was only 1.1–1.2 versus 2.7 for resin F (PL = 15, P/Pd = 4.3). The slow rates exhibited by reactions catalyzed by resin A may reflect its very low swelling ability.

At 100°C the rates of these reactions, catalyzed both by homogeneous and anchored catalysts were all quite slow. These conditions were purposely chosen to allow the kinetics to be conveniently followed and to avoid complications due to diffusion limitations of the reaction rates. Resin F was shattered by abrupt cooling in liquid nitrogen followed by grinding. Electron microscopic investigation revealed a large increase in surface area occurred. When a sample of the ground resin was used in reaction 1, the rate plot was almost identical to that shown in Fig. 3, showing that diffusion was not a complication at 100°C.

It is interesting to consider the actual concentration of palladium complexes within the swollen resin. Calculations, which have corrected the volume of the swollen beads based on the appropriate packing factors, indicate the concentration of palladium within resin A is about 6.1×10^{-1} molar. For resins B and F these concentrations are 3.6×10^{-1} and 0.9×10^{-1} molar, respectively. Therefore, the actual concentrations of palladium complexes within the resins are a factor of ten to several hundred times greater than those in homogeneous solution.

To compare the catalytic behavior of the anchored catalysts to homogeneous $\text{Pd}(\text{PPh}_3)_4$, dimerization—methoxylation reactions were carried out using the resins A–F over the same range of conditions and stoichiometries employed for homogeneous runs. Again, the rates were first order in methanol (see Fig. 2 for an example kinetic plot). Rate constants were then determined in the same manner as for the homogeneous reactions for several different amounts of resin charged to each reaction. However, it is not proper to think of the catalyst concentration as specifically increasing when more resin is added, because the palladium complex is present at a constant concentration within the swollen resin matrix. As more resin is added, the amount of palladium complex catalyst available within the same reactor volume goes up, but its concentration remains the same within the resin. These studies are summarized in part, in Fig. 3. The abscissa in Fig. 3 plots the concentration of homogeneous $\text{Pd}(\text{PPh}_3)_4$. In Fig. 3 the concentration read from the abscissa does not apply directly to the resin catalysts. Instead, one simply should note that the total amount of palladium within the 50 ml reaction solution was the same for the homogeneous and resin catalysts at any point along the abscissa.

Figure 4 shows the increases in rate which were obtained as more resin catalyst was added to the reaction (holding other variables constant). The

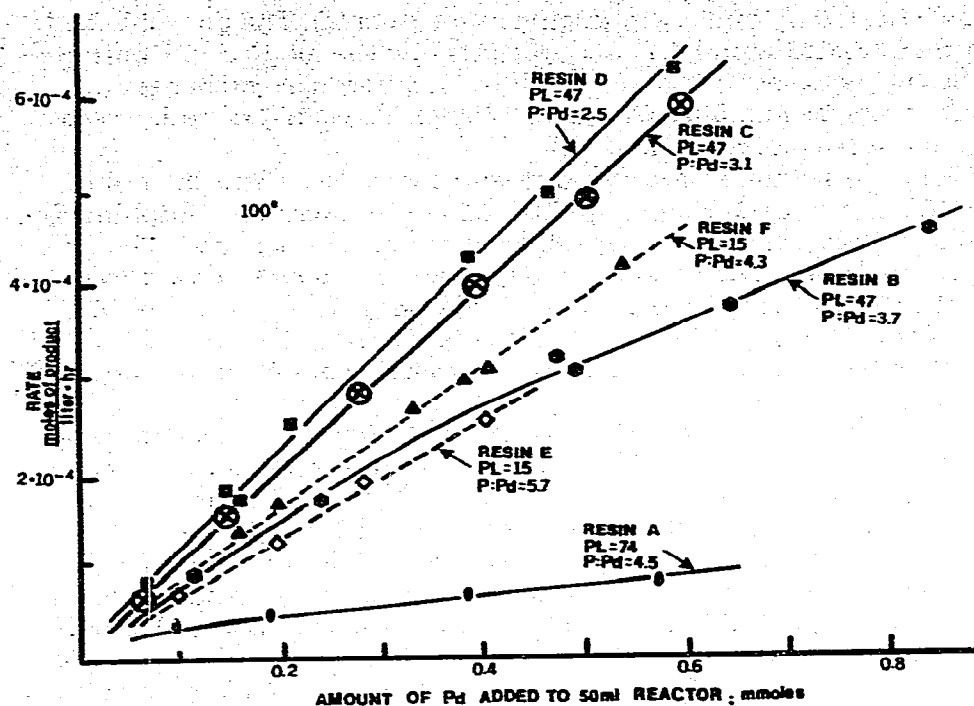


Fig. 4. Variation of dimerization—methoxylation rate as the amount of polymer-anchored catalysts is increased. The effect of phosphine loading and P/Pd ratio.

linear plots show the lack of fluid-phase mass transport resistance (at conditions where diffusion control was ruled out for resin F). In Fig. 4, the same abscissa scale is used as in Fig. 3, but the total amount of palladium complex is expressed as the mmol of Pd present in the 50 ml reaction volume.

Several features of the reactions catalyzed by the anchored catalysts differ distinctly from the homogeneous reactions. At all concentrations, the resin-anchored catalysts were more active than their homogeneous counterparts at comparable P/Pd ratios. Rate enhancements were obtained by adding more anchored catalyst, even when large amounts of catalyst were already present. For example, resins C, D, E, and F can be added until more than 1.2×10^{-2} mol of Pd are present in the reaction solution without loss of rate enhancement as more catalyst is added. This contrasts sharply with the homogeneous reactions where limiting rates are reached when from 4 to 6×10^{-3} mol l^{-1} of catalysts has been added. This is even more remarkable when one considers that the actual concentrations of palladium complex within the resin are much higher than those in any of the homogeneous studies.

The rates are lowered as the phosphine loading (PL) in the resins is increased. Figure 4 illustrates this principle. For example at PL = 74% the rate is very slow compared to PL = 47 or 15%. The P/Pd ratios also play a major role in the rate. As P/Pd increases in the resins (holding PL constant) the rate decreases. This is shown in Fig. 4 by comparing P/Pd ratios of 2.5, 3.1, and 3.7 (solid lines) at 47% phosphine loading. Furthermore, at 15% phosphine loading (dashed lines)

the rate decreases as P/Pd is raised from 4.3 to 5.7. Finally, the rate is faster at PL = 15% when Pd/P is 4.3 than when P/Pd is 3.7 for the higher phosphine loading of 47%.

Another difference between anchored and homogeneous catalyst systems is the far greater stability of the anchored catalysts. For example, resin D could be recycled despite the fact it had a low (2.5) P/Pd ratio. The use of a 2.5 P/Pd ratio in homogeneous reactions leads to the formation of a black precipitate during the reactions. This coincides with a decrease in catalytic activity during the reaction. Another resin (PL = 47%, P/Pd = 4.0) was recycled twice and remained yellow-brown. After these reactions, the rate at which the recycled resin-catalyzed dimerization was, within experimental error, the same as that of a fresh aliquote of the same resin. Apparently, site isolation is occurring in the resins which, in turn, allows a higher fraction of the palladium to remain active, even after long reaction periods. Recycle lifetimes and molar turnover limits have not been established for these catalysts, but even cursory observations clearly established that these limits are far higher using the resin catalysts.

Short term leaching studies have been performed by subjecting the resin catalysts to reaction conditions in the presence of excess phosphinated resin which has no metal complexed to it. The two resin batches were placed in the same reactor, connected by a solvent bridge but physically separated from each other. Within the limits of analytical detection (<0.2%), no palladium was found to migrate from the catalyst resin to the metal-free resin. For example, when a gram of resin A was subjected to reaction conditions for 96 h at 100°C, no palladium migration or uptake occurred into a metal-free resin sample with 47% phosphine loading.

The rate enhancements achieved by anchoring palladium(0) to resins are actually more dramatic than it appears in Fig. 3 and 4. This follows from a consideration of the actual palladium and phosphine concentrations inside the resin beads. The same solution volumes were employed using both homogeneous and polymeric catalysts, but the swollen polymer always occupies less than 10% of the solution volume. Thus, the concentration of palladium and phosphine within the swollen resin spheres is a minimum of ten times greater than is indicated on the abscissas of Fig. 3. Therefore, resins C, D, E, and F show no curvature at real catalyst loadings of at least 0.12 mol l^{-1} (0.6 mmol per 50 ml in Fig. 4). The importance of this observation is that very high catalyst concentrations remain active when anchored to polymer matrices. This fact will permit the use of smaller reactors for this process.

The product selectivity (ratio of 1-methoxy-2,7-octadiene to 3-methoxy-1,7-octadiene) remained constant at about 3.5 as the catalyst concentration was increased in the homogeneous runs. This was true over the catalyst concentration range from 1×10^{-3} to $16 \times 10^{-3} \text{ M}$. Selectivity did not change as the P/Pd ratio was increased from 4 to 8. However, the selectivity was substantially higher using resin catalysts E and F which had a 15% PL and P/Pd ratios of 5.7 and 4.3, respectively. In these cases, the selectivity was in the range of 5.7 to 7. As the phosphine loading was increased in the resin, the selectivity decreased. For example, at PL = 47% the selectivity was 3 to 4 when P/Pd was 2.5 or 3.1 (resins C and D) and selectivity decreased to 2.5–3.0 at 47% PL when P/Pd reached 3.7 (resin B). Finally, using highly phosphine loaded resin A (PL = 74,

P/Pd = 4.5), the selectivities were lowered to about 1.8. It therefore appears possible to use the resin anchoring to modify catalyst selectivity. Selectivity increases as the resin's phosphine loading decreases and it increases as the P/Pd ratio decreases.

Conclusions

The ability to continue to achieve rate enhancements upon incremental catalyst addition, to reactions having high catalyst loadings, is unique to the resin-anchored catalyst system. Clearly, this argues for a repression of the phosphine-palladium equilibria (shown in Scheme 1 for the soluble catalyst) in the anchored catalysts. This phenomenon is portrayed in Fig. 1. It is possible to avoid an upper limit on the rate with incremental catalyst addition using resin catalysts. Since the actual concentration of palladium and phosphine within the resins was far higher than that present in the homogeneous solutions, the faster rates (per palladium atom) exhibited with several of the resin catalysts was particularly striking. The only logical explanation appears to be that shown in Fig. 1 (i.e., a higher fraction of the palladium is more coordinatively unsaturated in the resin relative to that in solution). Diffusion effects would slow down the reactions catalyzed by the resin. Differences in solubility of the reagents the solvent (benzene) and the swollen resin are not expected to be major in this case.

The ability to recycle the anchored catalysts and their ability to achieve higher turnover numbers, indicate that the deposition of metallic palladium within the resins is a slow process. Even at low P/Pd ratios (i.e., 2.5 for resin D) this process is slow and the resin may be recycled, provided oxygen is carefully excluded. Mazur [28] showed that polymer-attached benzyne moieties survive for periods of up to several minutes when attached inside styrene-divinylbenzene resins. This kinetic stability may be contrasted to the diffusion-controlled rate of benzyne dimerization in homogeneous solutions. Without doubt, site isolation occurred. Recently, Grubbs [31] presented convincing evidence for site isolation of titanocene molecules which had been chemically attached to styrene-divinylbenzene macroreticular resins. Thus, it is not unexpected that we find the resin-bound palladium(0) catalysts were able to be recycled despite the propensity of palladium(0) to undergo agglomeration and precipitation of catalytically inactive palladium metal from homogeneous solution. We conclude that palladium complexes, indeed, are isolated to some degree from one another within the resin matrix.

Experimental

General. $(\text{Ph}_3\text{P})_4\text{Pd}$ was purchased from Strem Chemical Company and used as received. 1-Pentene was purchased from Chemical Samples Corporation and analyzed by GLC for isomeric purity (99%). Butadiene (>99%) was obtained commercially and used as received. Benzene and THF were continually refluxed over CaH_2 in a nitrogen atmosphere and distilled immediately prior to use. Similar care was taken to dry all solvents.

Infrared, nuclear magnetic resonance (NMR), and mass spectra were obtained on Beckman IR-33, Varian Associates HA-100, and Perkins-Elmer-Hitachi

RMU-6M instruments, respectively. Analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, New York. Analytical GLC was performed on a Hewlett-Packard model 5501A gas chromatograph using $1/8'' \times 10'$ copper columns packed with 12% OV-210 on DMCS Chromosorb W support. Quantitative GLC data were obtained via electronic integration with a Hewlett-Packard Model 3380A reporting integrator. Area normalization (with response factor correction) internal standard calibration techniques were used to determine yields and product distributions. Preparative GLC runs were done on a Prep-Master and a Varian Model 90-P.

Bromination of styrene-divinylbenzene resin. Brominations were carried out similar to previous reports [15,27]. Complete details are published elsewhere [32].

Preparation of diphenylphosphine-substituted copolymer. The brominated resins were treated with LiPPh_2 [31] in a manner similar to previous descriptions [15,27]. The details are available elsewhere [32].

Preparation of copolymers containing $(\text{Ph}_2\text{P})_4\text{Pd}$. In a typical preparation, phosphinated resin (10 g, P, 3.53%, 15% of the resin's phenyl rings are substituted with Ph_2P , 11.4 mol P) and $(\text{PPh}_3)_4\text{Pd}$ (3.5 g, 3.0 mmol) were added into a nitrogen-purged 100 ml round bottom flask along with benzene (50 ml). The resulting slurry was stirred under nitrogen and refluxed for 3 days to remove soluble catalysts and ligand. The brownish colored polymer-attached catalyst, resin F, was then dried under vacuum (25°C , 0.05 torr) for 2 days. Analysis showed P, 2.94; Pd, 2.35%, corresponds to a P/Pd ratio of 4.3 to 1.

Dimerization-methoxylation of 1,3-butadiene. Reactions were conducted in 3 oz. Fischer-Porter pyrex aerosol compatibility tubes equipped with shut-off valves and stainless steel "dip-needles" and valving for periodic sample removal while reacting under pressure. The reactor vessels were dried at 120°C for 24 h and flushed with nitrogen while cooling. The resin catalyst (0.5 g, 0.23 mmol Pd, PL = 47%, P/Pd = 3.7) was charged to the tube along with sodium phenoxide (0.12 g, 1.0 mmol), mesitylene (5.0 mmol) for use as a GLC internal standard, and benzene (25 ml) containing 25 mmol of methanol. After three liquid nitrogen freeze-thaw degassing cycles, 1,3-butadiene (8.1 g, 150 mmol) was condensed into the tube. The contents were brought to 25°C where the total solution volume was 50 ml. The reaction was heated at 100°C and stirred magnetically. At intervals of 5–10 h, 0.3 ml aliquotes were withdrawn for GLC analysis (OV-17, 8% on DMCS Chromosorb W, $6' \times 1/8''$, temperature programmed from 60°C for two minutes to 120°C at $16^\circ\text{C}/\text{min}$, using mesitylene as the internal standard). After the run was completed, products were collected by preparative GLC (OV-17, 10% on DMCS Chromosorb W, $6' \times 1/4''$, isothermal, 120°C). For 1-methoxy-2,7-octadiene: IR (cm^{-1}), 3080, 3020, 1650, 1385, 1130, 990, 970, and 914; NMR (CDCl_3) δ (ppm) 1.5 (m, 2, CH_2), 2.1 (m, 4, $\text{CH}_2-\text{CH}=\text{CH}_2$), 3.3 (s, 3H, CH_3O), 3.9 (d, 2, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.0 (m, 2H, $\text{CH}=\text{CH}_2$), 5.6 (m, 3, $\text{CH}_2=\text{CH}$); mass spectrum, parent ion, m/e 140. For 3-methoxy-1,7-octadiene: IR (cm^{-1}) 3080, 3020, 1640, 1450, 1100, 990, 910 (no internal *trans* double bond, i.e. 970 cm^{-1}); mass spectrum, parent ion m/e 140. These spectra agree with published spectra of the two isomers [18,19,21,22].

Recycle reactions were conducted using resin B and another resin having PL = 47% and P/Pd 4.0. Initially the resins were yellow to orange-brown. After two

reactions recycling the catalyst the color was orange-brown and not black. The rate of dimer formation after two recycles with this catalyst was the same as that exhibited by fresh aliquotes of the same resin.

An example leaching study. Resin A (1 g) was placed in a glass dispersion tube with sintered glass walls and this was, in turn, placed in an aerosol compatibility tube. A sample of phosphinated resin without metal (1 g; P, 3.5%, PL = 47%) was then added into the tube so that it was around outside of the dispersion tube containing resin A. Then a solution containing 1 mmol of methanol per each ml of benzene (total 50 ml) was added along with sodium phenoxide (0.3 g). After three freeze-thaw degassing cycles, the contents were heated to 100°C for 96 h while being magnetically stirred. The solution was cooled, decanted and the resins were analyzed for palladium. No palladium was detected in the original metal-free resin (limit of detection 0.2%). Similar experiments were conducted in the presence of butadiene (100 mmol) and no palladium migration to the metal-free resin was noted.

Acknowledgements

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References

- 1 M. Boudart, *Advan. Catalysis*, **20** (1969) 153.
- 2 P.N. Rylander, *Organic Syntheses with Noble Metal Catalysts*, Academic Press, New York, 1973.
- 3 C.W. Bird, *Transition Metal Intermediates in Organic Synthesis*, Academic Press, New York, 1967.
- 4 B.R. James, *Homogeneous Hydrogenation*, Wiley, New York, 1973.
- 5 G. Lefebvre and Y. Chauvin, in R. Ugo (Ed.), *Aspects of Homogeneous Catalysis*, Vol. 1, Manfredi Publ., Milan, 1970, p. 107.
- 6 M. Orchin and W. Rupilius, *Catalysis Rev.*, **6** (1972) 85.
- 7 J. Tsuji and K. Ohno, *Synthesis*, (1969) 157.
- 8 C.U. Pittman, Jr. and G.O. Evans, *Chemtech*, (1973) 560.
- 9 J.C. Ballar, *Catalysis Rev.*, **10** (1974) 17.
- 10 B. Delmon and G. Jannes (Eds.), *Catalysis, Heterogeneous and Homogeneous*, Elsevier, Amsterdam, 1975.
- 11 R.H. Grubbs, C. Gibbons, L.C. Kroll, W.D. Bonds, Jr. and C.H. Brubaker, Jr., *J. Amer. Chem. Soc.*, **96** (1974) 2373.
- 12 C.U. Pittman, Jr., S.E. Jacobson and H. Hiramoto, *J. Amer. Chem. Soc.*, (1975) 4774.
- 13 R.H. Grubbs, E.M. Sweet and S. Phisanbut, in P. Rylander and H. Greenfield (Eds.), *Catalysis in Organic Synthesis*, Academic Press, New York, 1976, p. 153.
- 14 C.U. Pittman, Jr. and R.M. Hanés, *J. Amer. Chem. Soc.*, **98** (1976) 5402.
- 15 C.U. Pittman, Jr. and L.R. Smith, *J. Amer. Chem. Soc.*, **97** (1975) 341.
- 16 W.O. Whitehurst and W. Haag, *Second North American Meeting of the Catalysis Society*, Houston, TX., February 1971; *Belgium Pat.*, 721,686 (1968). Also See H. Heinemann, *Chemtech.*, (1971) 286.
- 17 C.U. Pittman, Jr., S.K. Wu and S.E. Jacobson, *J. Catalysis*, **44** (1976) 87.
- 18 E.H. Smutny, *Ann. N.Y. Acad. Sci.*, **214** (1973) 125.
- 19 S. Takahashi, T. Shibano and N. Tagihara, *Tetrahedron Lett.*, (1967) 2451 and *Bull. Chem. Soc. Japan*, **46** (1973) 600.
- 20 J. Tsuji, M. Hara and Y. Mori, *Tetrahedron*, **29** (1972) 3721.
- 21 T.C. Shields and W.E. Walker, *J. Chem. Soc. Chem. Commun.*, (1971) 193.
- 22 V.J. Berger and H. Reichel, *J. Prakt. Chem.*, **315** (1973) 1067.
- 23 P.M. Maitlis, *The Organic Chemistry of Palladium*, Vol. II, Academic Press, New York, 1971, p. 46.
- 24 J.F. Birk, J. Halpem and A.L. Pickard, *Inorg. Chem.*, **7** (1968) 2672.
- 25 J.I. Crowley and H. Rapoport, *Acc. Chem. Res.*, **9** (1976) 135.

- 26 L.T. Scott, J. Rebek, L. Ovsyanko, and C.L. Sims, *J. Amer. Chem. Soc.*, 99 (1977) 625.
- 27 C.U. Pittman, Jr. and L.R. Smith, *J. Amer. Chem. Soc.*, 97 (1975) 1749.
- 28 P. Jayalekshmy and S. Mazur, *J. Amer. Chem. Soc.*, 98 (1976) 6710.
- 29 G. Gubitosa, M. Boldt and H.H. Brintzinger, *J. Amer. Chem. Soc.*, 99 (1977) 5174.
- 30 D.R. Coulson, *Inorganic Synthesis*, Vol. XIII, McGraw Hill, New York, 1972, p. 121.
- 31 R.H. Grubbs, C.P. Lau, R. Cukier and C.H. Brubaker, Jr., *J. Amer. Chem. Soc.*, 99 (1977) 4517.
- 32 Q.Y. Ng, Ph.D. Thesis University of Alabama, 1977.
- 33 C. Tamborski, F.E. Ford, W.L. Lehn, G.J. Moore and E.J. Soloski, *J. Org. Chem.*, 27 (1962) 619.