Palladium/Phosphinated Polystyrene as a Catalyst in the Heck Arylation. A Comparative Study

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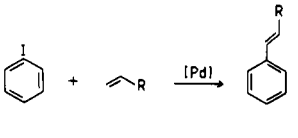
Palladium anchored to phosphinated polystyrene with a Pd/P ratio of 1/1 gives very high activity in the arylation of methyl acrylate and styrene with iodobenzene. A comparative study shows that this catalyst is considerably more efficient than Pd/C, $Pd(OAc)_2$, $PdCl_2$, $Pd(OAc)_2/2PPh_3$, or $Pd(PPh_3)_4$. ESCA and X-ray studies have been used to determine that the active state of the catalyst is metallic palladium. This is further supported by a study of the product distribution of two reactions that are very sensitive to the type of catalyst employed, namely, the arylation of butyl vinyl ether and trimethylallylsilane, as well as by the fact that iodo- but not bromobenzene reacts with this catalyst. The polymer-bound catalyst with a Pd/P ratio of 1/5 was unable to bring about any arylation starting from iodobenzene, after 3 h. During the same time the catalyst with a ratio Pd/P of 1/1 gave full conversion. Nevertheless the former catalyst resulted in the highest activity when bromobenzene was used as the reagent. This suggests that a comparatively stable palladium(0) phosphine complex is the reacting species in this special case. Addition of triphenylphosphine to Pd/C gives, in contrast to plain Pd/C, a similar product pattern as $Pd(OAc)_2/2PPh_3$ on arylation of butyl vinyl ether and trimethylallylsilane, respectively.

The palladium-catalyzed arylation of olefins has found wide application in organic synthesis. In this reaction, extensively studied by Heck,[1] homogeneous catalytic systems have been proven to be highly efficient,[2] although heterogeneous catalysts are sometimes preferred.[3] In order to make homogeneous catalysts generally more attractive from an industrial point of view, the technique of complex immobilization has been developed,[4] and polystyrene-supported palladium catalysts have successfully been used for a variety of organic reactions.[5] Pittman et al. have immobilized palladium on phosphinated polystyrene and used this catalyst for the oligomerization of butadiene. In this case palladium metal was observed in the matrix.[5b] Teranishi and co-workers have studied different carbon–carbon bond forming reactions, such as the Heck arylation,[5e] using similarly prepared catalysts. They propose that the polymer-bound species are reduced to a heterogeneous analogue of tetrakis(triphenylphosphine)palladium(0) by hydrazine reduction in the presence of phosphine. The type of species formed in polymer matrices, as well as their fate in the catalytic cycle, is a matter of controversy. Recent reports suggest that metal particle formation is very common.[6] Usually, the polymer-bound phosphine ligands tend to be less efficient than phosphines in solution in stabilizing the metal ion toward reduction to the metallic state. The difficulty in distinguishing between metal particle and metal complex catalysis is not restricted to supported catalysts but has also been found in nonsupported systems.[7]

This work has been devoted to a study of the influence of different catalysts, or catalyst precursors, on the substitution of vinylic hydrogens by aryls. The aim has been twofold; first, to study phosphinated polystyrene/palladium(II) as catalyst precursor, and second, to compare and evaluate the most commonly used systems, i.e. palladium(0)/phosphine complexes,[2] palladium(II) salts (acetate, chloride),[8] palladium metal,[9] and palladium on charcoal.[3] In this study we focused on *catalyst activity* and *catalyst selectivity*, as these are the essential features pertaining to a catalyst.

Results and Discussion

The catalytic activities of a series of different palladium catalysts, e.g. palladium(II) on phosphinated polystyrene (four different types, P_1, P_2, P_3, and P_5 with palladium/phosphorus ratios of 1:1, 1:2, 1:3, and 1:5, respectively), Pd/C, $Pd(OAc)_2/2PPh_3$, $Pd(OAc)_2$, $Pd(PPh_3)_4$, and $PdCl_2$, with iodobenzene and methyl acrylate or styrene as substrates, are presented in Figures 1–3. All reactions were carried out in acetonitrile, using triethylamine as the base (eq 1).



(1)

Two conclusions are apparent. First, the arylation of styrene is the slower reaction, independent of the type of catalyst used. The same observation was reported by

(1) (a) Heck, R. F. *Org. React. (N.Y.)* **1982**, *27*, 345. (b) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146.

(2) (a) Dieck, H. A.; Heck, R. F. *J. Am. Chem. Soc.* **1974**, *96*, 1133. (b) Dieck, H. A.; Heck, R. F. *J. Org. Chem.* **1975**, *40*, 1083.

(3) Hallberg, A.; Westfelt, L. *J. Chem. Soc., Perkin Trans. 1* **1984**, 933.

(4) For recent reviews, see: (a) Lieto, J.; Milstein, D.; Albright, R. L.; Minkiewicz, J. V.; Gates, B. C. *Chemtech* **1983**, 46. (b) Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *8*, 109. (c) Whitehurst, D. D. *Chemtech* **1980**, 44. (d) Hartley, F. R.; Vezey, P. N. *Adv. Organomet. Chem.* **1977**, *15*, 189. (e) Chauvin, Y.; Commereuc, D.; Dawands, F. *Prog. Polym. Sci.* **1977**, *5*, 95.

(5) For phosphine-ligated palladium(0) and palladium(II) complexes, see: (a) Bruner, H.; Bailar, J. C., Jr. *Inorg. Chem.* **1973**, *12*, 1465. (b) Pittman, C. U., Jr.; Wuu, S. K.; Jacobson, S. E. *J. Catal.* **1976**, *44*, 87. (c) Pittman, C. U., Jr.; Ng, Q. *J. Organomet. Chem.* **1978**, *153*, 85. (d) King, R. B.; Hanes, R. M. *J. Org. Chem.* **1979**, *44*, 1092. (e) Terasawa, M.; Kaneda, K.; Imanaka, T.; Teranishi, S. *J. Organomet. Chem.* **1978**, *162*, 403. (f) Kaneda, K.; Kurosaki, H.; Terasawa, M.; Imanaka, T.; Teranishi, S. *J. Org. Chem.* **1981**, *46*, 2356. (g) Trost, B. M.; Warner, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6112. (h) Trost, B. M.; Warner, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 5940. For bipyridyl-ligated palladium(II), see: (i) Card, R. J.; Neckers, D. C. *Inorg. Chem.* **1978**, *17*, 2345. (j) Card. R. J.; Liesner, C. E.; Neckers, D. C. *J. Org. Chem.* **1979**, *44*, 1095. (k) Drago, R. S.; Nyberg, E. D.; El A'mma, A. G. *Inorg. Chem.* **1981**, *20*, 2461. For ionically bound palladium(II), see: (l) Holy, N. L.; Shelton, S. R. *Tetrahedron* **1981**, *37*, 25.

(6) (a) Neuberg, M. Dissertation, Stanford University, 1979, and references therein. (b) Bergbreiter, D. E.; Chen, B.; Lynch, T. J. *J. Org. Chem.* **1983**, *48*, 4179.

(7) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.

(8) Heck, R. F.; Nolley, J. P., Jr. *J. Org. Chem.* **1972**, *37*, 2320.

(9) (a) Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 581. (b) Mizoroki, T.; Mori, K.; Ozaki, A. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1505.

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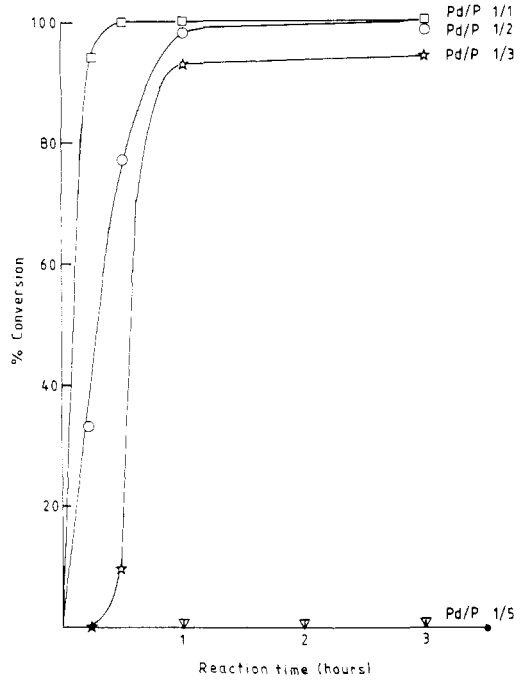


Figure 1. Conversion as a function of time for the arylation of methyl acrylate with iodobenzene at 100 °C: polymer-bound catalysts (corresponding to 1 mol % palladium); (□) P_1, (○) P_2, (☆) P_3, (▽) P_5.

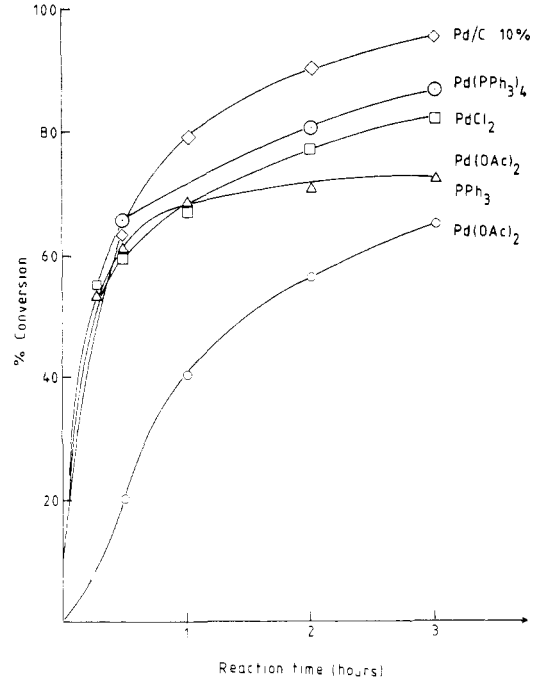


Figure 2. Conversion as a function of time for the arylation of methyl acrylate with iodobenzene at 100 °C: common palladium catalysts (corresponding to 1 mol % palladium).

Heck[10] using phenylmercuric chloride and $LiPdCl_3$ as the catalyst.

The second conclusion is that the rate of reaction is strongly dependent on which type of palladium is introduced to catalyze the reaction. By comparing the reaction rate of iodobenzene and methylacrylate, using different catalysts while holding the concentration of palladium at 1 mol %, the catalysts can be arranged in the following order of increasing time for 50% conversion: P_1 < Pd-

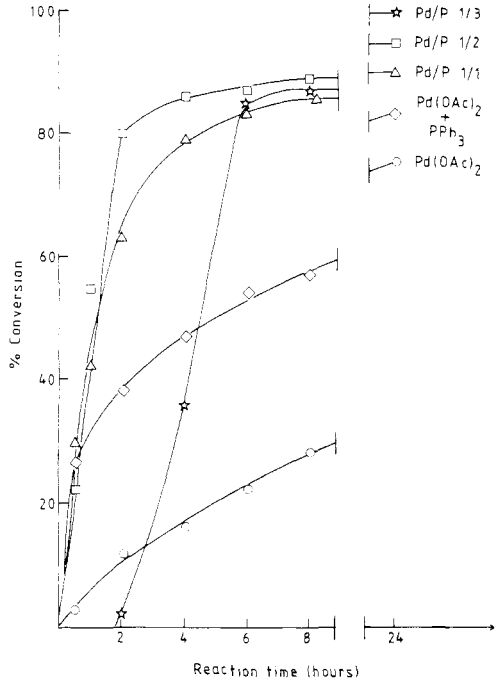
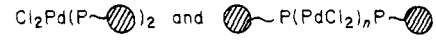


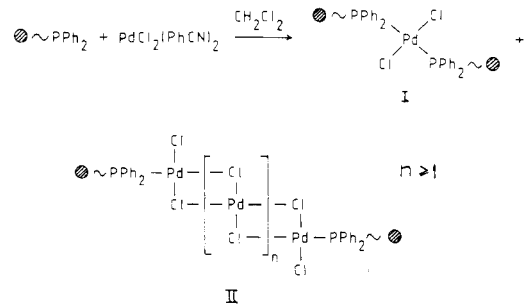
Figure 3. Conversion as a function of time and total yield after 24 h for the arylation of styrene with iodobenzene at 100 °C: catalysts corresponding to 1 mol % palladium; (△) P_1, (□) P_2, (☆) P_3. (Apart from *trans*-stilbene, minor amounts of 1,1-diphenylethylene were formed.)

$(OAc)_2/2PPh_3 \sim Pd(PPh_3)_4 < P_2 < Pd/C \sim Pd/C/2PPh_3 \ll P_3 \ll Pd(OAc)_2 <<< P_5$. If the homogeneous systems studied are excluded from the reactivity series given above, Pd/C shows activity between the most and the least active of the polymer-bound catalysts. With respect to catalyst selectivity a resemblance between the polymer-bound systems and Pd/C was found (vide infra).

The decrease in catalytic activity observed for the matrix-bound catalysts (Figure 1) when going from a high Pd/P ratio (P_1, 1/1) to a low ratio (P_5, 1/5) was explained for the case of hydrogenation, as a function of the constitution of the polymer-bound catalysts in a previous paper.[11] In that paper it was shown that two different species, viz.,



are formed in the resin during preparation as shown in eq 2.



(2)

The relative proportions of these species varied with metal incorporation in the resin. For the highest metal loading, the chloride-bridged complex (II) was dominant while at the lowest metal loading the bisphosphine complex (I) was the sole, or at least the dominant, component.

Thus at high metal loadings corresponding to P_1 the catalytic action will be predominantly due to II, while at

(10) Heck, R. F. *J. Am. Chem. Soc.* **1968**, *90*, 5518.

(11) Andersson, C.; Larsson, R. *J. Catal.* **1983**, *81*, 179.

concentration P_5 complex I will be the catalyst precursor.

The Heck arylation reaction is generally believed to involve an oxidative addition of the aryl halide to a palladium(0) complex[1,2] or a palladium metal particle.[12] Thus, an initial reduction of palladium(II) is a prerequisite for the arylation to take place. Since the ease of reduction of the two species present in the resin differs considerably with ordinary reducing agents such as H_2 or CO,[13] it is interesting to note that the observed trend in catalytic activity follows the same trend in reducibility. The polymer with the highest content of II, which is easily reduced, also shows the highest activity. Polymers with increased content of I show a decrease in the catalytic activity.

The reduction of the polymer-bound catalysts could be followed visually by the change in color of the polymer, from yellow to dark brown-black. We also used the same techniques as reported earlier[13] to determine the actual state of palladium in our spent catalysts (P_1–P_5). For all except P_5, the X-ray diffraction lines Pd(100) and Pd(200) of palladium metal were observed. ESCA analyses of the catalysts also revealed that palladium metal was formed in the polymers during the reaction, though some palladium(II) remained in polymer P_3. Thus, under the reaction conditions employed, part of the original palladium(II) was reduced to the metallic state. The most likely way by which this occurred was via olefin reduction.[8] This hypothesis is supported by an independent experiment where catalyst P_2 was heated to 100 °C in acetonitrile in the presence of methyl acrylate. The change in color of the polymer which accompanies reduction of palladium(II) to palladium(0) was observed.

With respect to total conversion there is a rather close resemblance between Pd/C and the polymers P_1, P_2, and P_3 as shown in Figures 1 and 2. This, together with the observed formation of palladium metal in these polymers during the reaction, suggests that metallic palladium plays an important role in making these polymer-bound catalysts highly active for the arylation reaction.

It is well-known that the shape of metal phases (the size and form of crystallites and/or metal dispersion) is important in determining their catalytic activity.[14] The high activity of polymers P_1 and P_2 suggests that the metal phase formed here differs from the metal phase of the Pd/C catalyst. The importance of the metallic surface was apparent from a separate experiment in which a Pd/C (10% Pd) catalyst was treated with H_2 (760 torr) at room temperature for 24 h followed by evacuation at 100 °C. The activity was markedly increased compared to the untreated catalyst. This treatment of the catalyst is effective in reducing surface oxides on the metal particles.[15] Thus a fresh metal surface increases the catalytic activity. Although we have not determined the crystallite size of the polymer-bound catalysts, we find it reasonable to suggest that in situ reduction of discrete molecular complexes bound to the polymer network can create clean metal particles of a very small size and thus with a high degree of metal dispersion. Moreover, trapping effects in the polymer can prevent the metal particles from agglomeration. Such effects have been reported in another study of polymer-bound palladium.[6b]

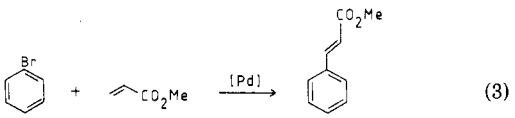
In the reaction of styrene and iodobenzene, qualitatively the same order of catalyst activity was found. Catalysts P_1 and P_2 gave about 90% conversion in 5 h (Figure 3), while P_3 required about 8 h to reach the same amount of conversion. We additionally noted that catalyst P_3 showed only traces of the product after 2 h of reaction, while P_1 and P_2 had both reached about 50% conversion after the same amount of time. Obviously P_3 needs time to develop full catalytic capacity. The same effect, though less pronounced, can be observed in the arylation of methyl acrylate with all three catalysts. This induction period for P_3 is probably due to the presence of only a small amount of the complex II (eq 2). Since (I) is more stable against reduction, a relatively long time is needed for P_3 to develop the catalytically active metallic palladium compared to P_1 and P_2.

The initial activity for $Pd(OAc)_2/2PPh_3$ was comparable to that of the polymer-supported catalysts P_1 and P_2 for both substrates tested (Figures 2 and 3). However, this system is deactivated during reaction so that in the case of methyl acrylate, only about 60% conversion was reached. In the styrene case a more than fourfold longer reaction time was needed to give the same yield as with P_1 or P_2.

The duration of the high activity period for $Pd(OAc)_2/2PPh_3$ is of the same order (~20 min) for styrene as for methyl acrylate. One possible explanation for the deactivation is a time-dependent decomposition of the highly active original species to one of low activity. Temperature-induced decomposition to palladium metal has been observed in a similar system,[16] and palladium black was always observed in the end of each run in the present study. In that case, however, the metal phase must be of a different kind than that formed in our polymers which maintained a very high activity throughout the reaction. The primary particles formed in solution upon reduction have a tendency to agglomerate to form larger metallic particles. This is probably not the case for reduction on the surface of, or inside of, a polymer gel (vide supra).

We conclude from our results on iodobenzene reacting with either methyl acrylate or styrene that the formation of palladium metal from palladium(II) can give a highly active catalyst for the Heck arylation, provided that the primary particles formed are supported in such a fashion so that extensive agglomeration does not occur. This does not imply, though, that the entire catalytic cycle is necessarily operating on the metallic phase (vide infra).

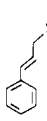
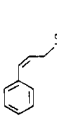
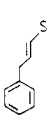
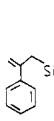
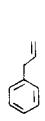
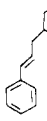
Literature reports indicate that arylations using bromobenzene are generally difficult if catalysts other than palladium(0) phosphine complexes are used.[1,17] This contrasts with the reaction of activated bromobenzenes, where examples of reactions using Pd/C can be found.[3] In their study on polymer-bound palladium, Teranishi et al.[5e] tried to react bromobenzene with styrene using what they claimed to be a polymer-bound tetrakis(triphenylphosphine)palladium analogue as the catalyst. Only traces of stilbene were found in that study. This prompted us to test our polymer-bound systems P_1–P_5 in the arylation of methyl acrylate with bromobenzene (eq 3). Methyl



(3)

(12) Klabunde, K. J.; Low, J. Y. F. *J. Am. Chem. Soc.* **1974**, *96*, 7674.
(13) Andersson, C.; Larsson, R. *J. Catal.* **1983**, *81*, 194.
(14) Andersson, J. R. "Structure of Metallic Catalysts"; Academic Press: London, 1975.
(15) Lam, Y. L.; Boudart, M. *J. Catal.* **1977**, *47*, 393.
(16) Fitton, P.; Rick, E. A. *J. Organomet. Chem.* **1971**, *28*, 287.
(17) Reports on successful arylations starting from bromobenzene, omitting phosphine ligand, have occurred. The reactions have in these cases been effected with bases such as Na_2CO_3, $NaHCO_3$, KOH, KOAc, or TMEDA. Examples are: (a) Davison, J. B.; Simon, N. M.; Sojka, A. S. *J. Mol. Cat.* **1984**, *22*, 349. (b) Chalk, A. J.; Magennis, S. A. *J. Org. Chem.* **1976**, *41*, 273.

Table I. Distribution (GLC Yields) Resulting from the Arylation of Trimethylallylsilane with Iodobenzene at 100 °C[a]

							
P_2	12	33	2	8	16	11	15
Pd/C	26	24		5	17	14	12
$Pd/C/2PPh_3$		62	4	7	20	5	
$Pd(OAc)_2/2PPh_3$		62	4	9	17	6	

[a] 1 mol % catalyst; reaction time, 8 h.

acrylate was chosen as the olefin because of its higher reactivity toward iodobenzene (vide supra). In this case (Figure 4) our catalysts may be arranged in the following order of decreasing activity $P_5 \gg P_3 > P_2 > P_1$, with P_5 giving 80% conversion after 6 days of reaction. This order is quite the opposite of that found for arylation using iodobenzene. Moreover, this sequence is opposite to the tendency of these polymers to form palladium metal. Thus our results strongly indicate that metallic palladium cannot promote the coupling of bromobenzene with olefins. This is in accordance with the literature reports on ordinary catalyst systems.

The nature of the resin-bound species, which affects the reaction of bromobenzene is, however, not easily determined. Catalyst P_5, which is superior to the others, did not change its color during the reaction. This suggests that a complex analogous to $Pd(PPh_3)_4$, which is pale yellow, was formed in the resin under the reaction conditions. Moreover, in synthetic methods used to prepare the homogeneous $Pd(PPh_3)_4$ complex, P/Pd ratios ranging from 3 to 10 times excess have to be used.[18] This resembles the situation in catalyst P_5 in which the P/Pd ratio is 5. The observation that the catalytic activity of our polymers is dependent on the P/Pd ratio, with a high ratio enhancing the activity, is thus in support of the formation of a $Pd(PPh_3)_4$ type of complex in the resin. Furthermore, the supported complex seemed to be comparatively stable, as it maintained catalytic capacity even after several days under the reaction conditions.

We have applied the ESCA technique to determine the actual oxidation state of palladium in catalyst P_5 after reaction with bromobenzene. However, on the basis of earlier experiences on ESCA studies of polymer-bound palladium phosphine complexes we believe that measured binding energies for such systems should be interpreted with caution.[13] Either charging effects of the isolating polymer or the possible presence of palladium in different oxidation states may make a safe assignment difficult.

The evidences for the existence of a $Pd(PPh_3)_4$ analogue in catalyst P_5 could not be fully confirmed by our ESCA data. With catalyst P_5 we found a Pd $3d_{5/2}$ binding energy of 336.9 eV (Table III), which is lower than that found for palladium(II) on phosphinated polystyrene gels but which is also higher than that found for palladium metal on such gels.[13] It is also 0.7 eV higher than that reported for $Pd(PPh_3)_4$.[5e] Thus, in light of our measured Pd $3d_{5/2}$ binding energy we cannot unambiguously state that the palladium in the active catalyst P_5 is an analogue to $Pd(PPh_3)_4$. Teranishi and co-workers[15e] found an even greater difference (1.5 eV) between $Pd(PPh_3)_4$ and what they claim to be a polymer-bound palladium(0) phosphine complex. Their failure to affect the conversion of bromobenzene, while iodobenzene reacted smoothly, together with the green color they report for their catalyst strongly suggests

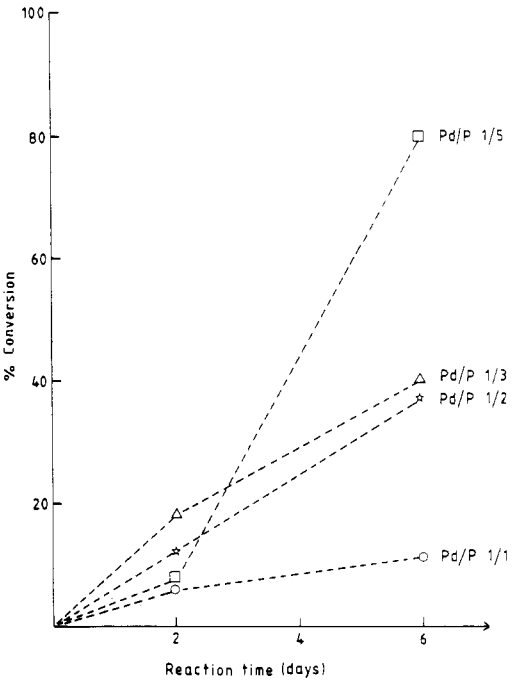


Figure 4. Conversion as a function of time for the arylation of methyl acrylate with bromobenzene at 100 °C: polymer-bound catalysts (corresponding to 1 mol % palladium); (○) P_1, (☆) P_2, (△) P_3, (□) P_5.

that the active species in their catalyst is in fact a mixture of metallic palladium and palladium(II).

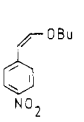
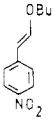
Methyl acrylate and styrene, which give predominantly methyl cinnamate and *trans*-stilbene respectively upon arylation, are not useful starting materials to probe selectivity of the different catalytic systems. In connection with a proceeding study of the arylation of vinylsilane[19] and allylsilane,[20] we have recently found that the outcome of the latter reaction is very sensitive to the catalyst employed. While the homogeneous catalyst $Pd(OAc)_2/2PPh_3$ mainly gives arylation of allylsilane, this reaction is accompanied to a high degree by cleavage of the silicon–carbon bond when Pd/C is employed (Table I). We interpret this result by assuming that the dissociation of the hydridopalladium halide is favored in presence of a good ligand such as triphenylphosphine, while the readdition, which eventually leads to desilylation, occurs more frequently in the absence of phosphine.[20]

It is apparent from Table I that the phosphinated polystyrene catalyst P_2 is very similar to Pd/C, when the overall product distribution is considered. This further supports the hypothesis that metallic palladium is the active component in catalyst P_2. The catalysts can be divided into two groups, based on the product patterns,

(18) Hartley, F. R. "The Chemistry of Platinum and Palladium"; Applied Science Publishers: London, 1973.

(19) Hallberg, A.; Westerlund, C. *Chem. Lett.* **1982**, 1993.
(20) Karabelas, K.; Westerlund, C.; Hallberg, A. *J. Org. Chem.*, following paper in this issue.

Table II. Influence of Catalysts on the E/Z Ratio in the Arylation of Butyl Vinyl Ether with p-Nitrobromobenzene at 100 °C[a]

		
P_1	10	10
Pd/C	11	10
Pd/C/2PPh_3	4	10
$Pd(OAc)_2$/2PPh_3	4	10

[a] 1 mol % catalyst; reaction time, 8 h.

Table III. Data for Polymer-Bound Palladium Catalysts

catalyst	% Pd	Pd:P ratio	binding energy Pd $3d_{5/2}$,[a] eV	color of catalyst before reacn	color of catalyst after reacn
P_1	5.0	1:1	337.0 ± 0.1	brown-red	greyish-black
P_2	2.8	1:2	337.5 ± 0.1	orange	brown-black
P_3	1.8	1:3	337.7 ± 0.1	yellow	brown-red
P_5	1.0	1:5	336.9 ± 0.1	pale-yellow	yellow

[a] Spent catalysts.

one consisting of the heterogeneous systems where the metallic phase is supported and the other containing the systems where PPh_3 is present. This can be further substantiated by examining the E/Z ratio of 1-(2-butoxyethenyl)-4-nitrobenzene, formed via palladium-catalyzed arylation of butyl vinyl ether with 1-bromo-4-nitrobenzene. While the Heck arylations discussed above predominantly give the thermodynamically most stable products, we have recently found that the outcome of the arylation of alkyl vinyl ethers is sensitive to the catalyst system, Pd-$(OAc)_2$/2PPh_3 and Pd/C giving characteristic E/Z ratios. Again, the catalysts can be divided into the two groups as depicted in Table II.

The fact that Pd/C in the presence of PPh_3 behaves like $Pd(OAc)_2$/2PPh_3 is very interesting. In the arylation of allylsilane we noticed that a considerable amount of palladium covered the inside of the reaction vessel as a mirror. Thus the metal had been transferred from the charcoal to the glass, apparently via a soluble palladium intermediate. We think that the insertion of palladium into the aryl iodide occurs at the Pd metal surface and, after formation of a ligated arylpalladium iodide, coupling occurs. After reductive elimination, a part of the palladium employed is deposited as metal on the glass.

The catalytic cycle can apparently operate via a complex, giving the same product pattern as $Pd(OAc)_2$/2PPh_3. A dissolution of palladium metal has been observed in similar systems.[21] We therefore suggest that the catalytic cycle is extended to include a connection between palladium metal and ligated arylpalladium halide complex as outlined in Scheme I.

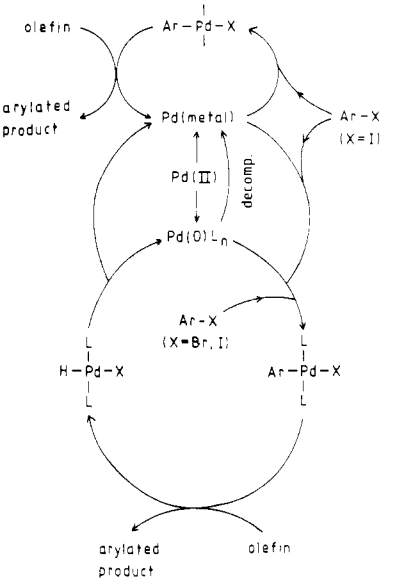
It should be stressed that the observations supporting this idea were made only in two specific systems using allylsilane and butyl vinyl ether as substrates. However, it is reasonable to assume that a similar transformation from palladium metal to a ligated complex occurs when other olefins are employed.

Experimental Section

General Comments. ESCA spectra were recorded on an AEI ES200 spectrometer using AlKα radiation. Mass spectra were obtained by using a Finnigan 4021 (Data System Incos 2100) gas chromatograph–mass spectrometer. Quantitative gas chromatographic analyses were performed on a Varian 3700 instrument equipped with a 2-m column of 5% NPGS on Chromosorb W or, for the analyses of (*E*)- and (*Z*)-1-(2-butoxyethenyl)-4-nitrobenzene, a 2.5-m glass column of 3% OV 1 on Gaschrom Q to avoid decomposition of the product during chromatography and a flame ionization detector. Elution band areas were determined electronically by using a Varian 4270 integrator. 2-Methylnaphthalene was used as an internal standard. The triethylamine and methyl acrylate were distilled, and the triethylamine was stored over (3 Å) molecular sieves until use. The catalysts, palladium on charcoal (10% Pd, 700–800 m^2/g; Riedel de Haën), palladium acetate (Fluka AG), and palladium chloride (Johnson-Matthey Chemicals), were all used as received. Tetrakis(triphenylphosphine)-palladium was prepared according to the method described by Coulson.[22] The polymer-bound catalysts were prepared by the procedure described previously,[11] using a Merrifield resin with 2% divinylbenzene (Merck). Iodobenzene (Fluka AG), bromobenzene (Janssen), and all other chemicals were used without further purification.

General Procedure. The aryl halide (10 mmol), triethylamine (10 mmol), and the internal standard (2-methylnaphthalene, 400 mg) were mixed in a 100-mL heavy-walled, thin-necked Pyrex tube fitted with a Teflon stopcock. The catalyst (corresponding to 1 mol % Pd) and, when present, phosphine ligand were dissolved/dispersed in 10 mL of acetonitrile and added to the mixture. The olefin (10 mmol of methyl acrylate, styrene, trimethylallylsilane, or butyl vinyl ether) was added, the stopcock closed, and the mixture heated at 100 °C in an oil bath. Samples of ~0.2 mL were collected periodically, partitioned between diethyl ether and water, and the organic phase was analyzed by GC–MS.

Scheme I



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Registry No. CH_2=$CHCH_2SiMe_3$, 762-72-1; $BuOCH$=CH_2, 111-34-2; PhI, 591-50-4; p-$NO_2C_6H_4Br$, 586-78-7; Pd, 7440-05-3; PPh_3, 603-35-0; $Pd(OAc)_2$, 33571-36-7; (*E*)-$PhCH$=$CHCh_2SiMe_3$, 19752-23-9; (*Z*)-p-$NO_2C_6H_4CH$=$CHOBu$, 97826-85-2; (*E*)-p-$NO_2C_6H_4CH$=$CHOBu$, 97826-86-3; PhBr, 108-86-1; methyl acrylate, 96-33-3; styrene, 100-42-5.

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