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A COORDINATIVELY UNSATURATED, POLYMER-BOUND PALLADIUM(0) COMPLEX. SYNTHESIS AND CATALYTIC ACTIVITIES

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Summary

A coordinatively unsaturated palladium(0) complex was prepared by the reduction of a polymer-bound palladium(II) chloride complex, which was prepared by the reaction of poly-4-diphenylphosphinomethylstyrene with palladium chloride, with hydrazine in ethanol in the presence of triphenylphosphine. Catalytic activities of the polymer-bound palladium(0) complex were examined for three representative types of palladium(0)-induced reactions involving oxidative addition of halides to the metal: (i) vinylic hydrogen substitutions with aryl halides, (ii) acetylenic hydrogen substitutions with aryl halides, (iii) vinylic halogen substitutions with Grignard reagents. Use of the catalyst resulted in formation of corresponding products in good yields. The catalytic activity is comparable to that of analogous homogeneous catalysts, yet is not remarkably lowered on being recycled.

Introduction

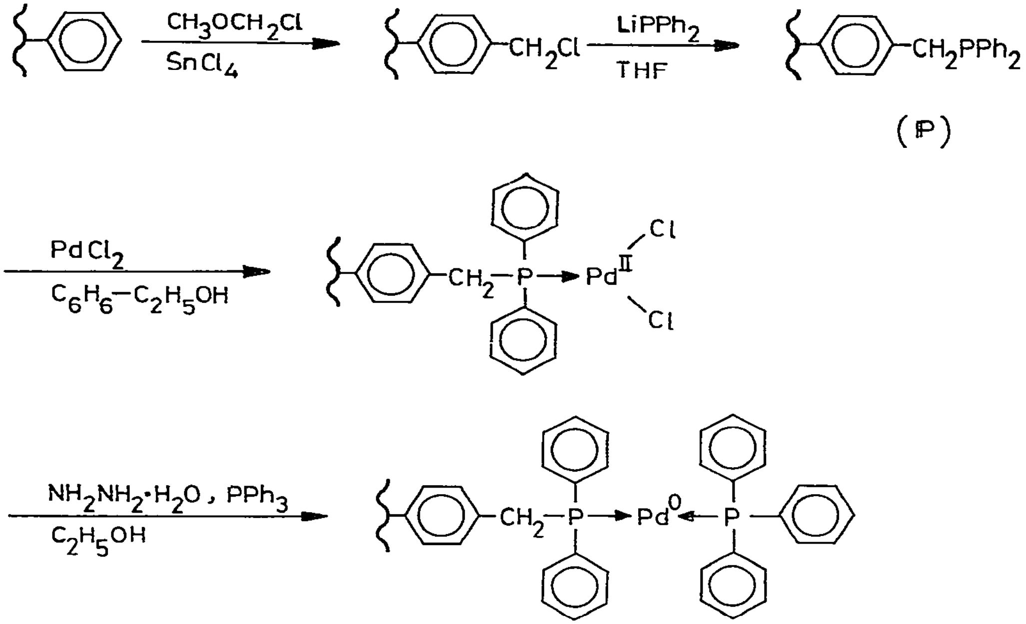
Previously we reported that coordinatively unsaturated metal complexes which are very stable in the atmosphere are easily available by the reaction of poly-4-diphenylphosphinomethylstyrene with rhodium chloride or palladium chloride. This stability results from polymer effects [1, 2].

It is well-known that zero-valent palladium complexes show unique reactivity in various organic reactions [3]. It, however, is very difficult to use the palladium(0) complexes as practical catalysts because of their instability to air and moisture, and because of difficulties in their separation from a reaction mixture. These difficulties might be overcome by using a polymeric unsaturated palladium(0) complex which is more stable than a comparable soluble palladium(0) complex. We have found that a phosphinated polystyrene-bound and three-coordinate palladium(II) chloride complex can be reduced smoothly with hydrazine hydrate in the presence of triphenylphosphine to give an unsaturated, polymer-bound palladium(0) complex, Ⓟ-Pd^0-$(PPh_3)_n$ (Ⓟ is the polymeric ligand). The isolated palladium(0) complex is very stable to air and moisture and is an efficient and recoverable catalyst for various carbon-carbon bond formation reactions which are known to be induced by palladium(0) complexes.

Recently, Pittman et al. reported butadiene oligomerizations and dimerization-alkoxylations catalyzed by polymer-bound palladium(0) complexes. The palladium(0) complexes were prepared by two methods: the direct ligand-exchange reaction of a polymeric ligand with $Pd(PPh_3)_4$, and *in situ* conversion of polymer-bound palladium(II) complexes to palladium(0) species [4]. In the former procedure, coordinatively unsaturated complexes, (Ⓟ -$PPh_2)_{2\&3}Pd^0$ were generated by varying the P/Pd ratio and the P-loading in the polymer [4d].

Results and Discussion

The polymer-bound palladium(0) complex was prepared as outlined in Scheme 1. Polystyrene with no-crosslinking



SCHEME 1

was chloromethylated, followed by phosphination to give a diphenylphosphinomethylated resin in which ca. 74% of phenyl rings contained a phosphine substituent. The reaction of the phosphinated resin with palladium chloride in benzene-ethanol generated the polymer-bound palladium(II) complex. In ethanol solution containing two moles excess of triphenylphosphine, the polymeric Pd(II) complex was easily reduced with hydrazine hydrate to give a dark-green, polymeric complex which contained (by elemental analysis) one atom of palladium, one mole of the polymeric phosphine, and one mole of triphenylphosphine.* Phenyllithium also

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* Reduction with hydrazine hydrate in the absence of triphenylphosphine gave a very air-sensitive complex.

could be used as a reductant. Leaching of the metal was not observed during the reduction.

Table 1 shows the results of X-ray photoelectron spectroscopic studies of the two polymer-bound palladium complexes and of some soluble palladium complexes. The palladium $3d_{3/2}$ and $3d_{5/2}$ binding energies for the polymer-bound palladium(0) complex $\Delta E_b = -1.4$ and -1.0 eV, are lower than those of the starting polymer-bound palladium(II) complex, respectively. From the results for the three soluble palladium(0) complexes, it is clear that the palladium 3d binding energies depend strongly on the nature of the ligands. Consequently, it is impossible to identify the reduced complex as a zerovalent one on the basis of its palladium 3d binding energies only. It, however, is evident that the shifts show that reduction of the starting

TABLE 1

PALLADIUM 3d AND PHOSPHORUS 2p BINDING ENERGIES (in eV)[a] FOR POLYMER-BOUND PALLADIUM COMPLEXES AND SOLUBLE PALLADIUM COMPLEXES

Complex	Pd $3d_{3/2}$	Pd $3d_{5/2}$	P 2p
Ⓟ-Pd-PPh$_3$	342.6	337.6	132.3
Ⓟ-PdCl$_2$	344.0	338.6	132.0
$PdCl_2(PPh_3)_2$[b]	343.6	338.3	132.0
$PdCl_2$[b]	343.6	338.1	
$Pd(PPh_3)_4$	341.4	336.2	131.2
$Pd(CO)(PPh_3)_3$	343.2	337.9	132.4
$Pd(dba)_2$	342.4	337.0	

[a] The binding energies are referenced to carbon 1s (285.0 eV), and the energy differences were determined with an accuracy of ±0.2 eV.

[b] We reported priviously (see Ref. 2).

palladium(II) complex to the lower valent state has taken place . Fig. 1 shows the palladium 3d spectrum of the reduced complex: sharp lines, with 2.7 and 2.5 eV palladium $3d_{3/2}$ and $3d_{5/2}$ energy widths at half-maximum intensity,

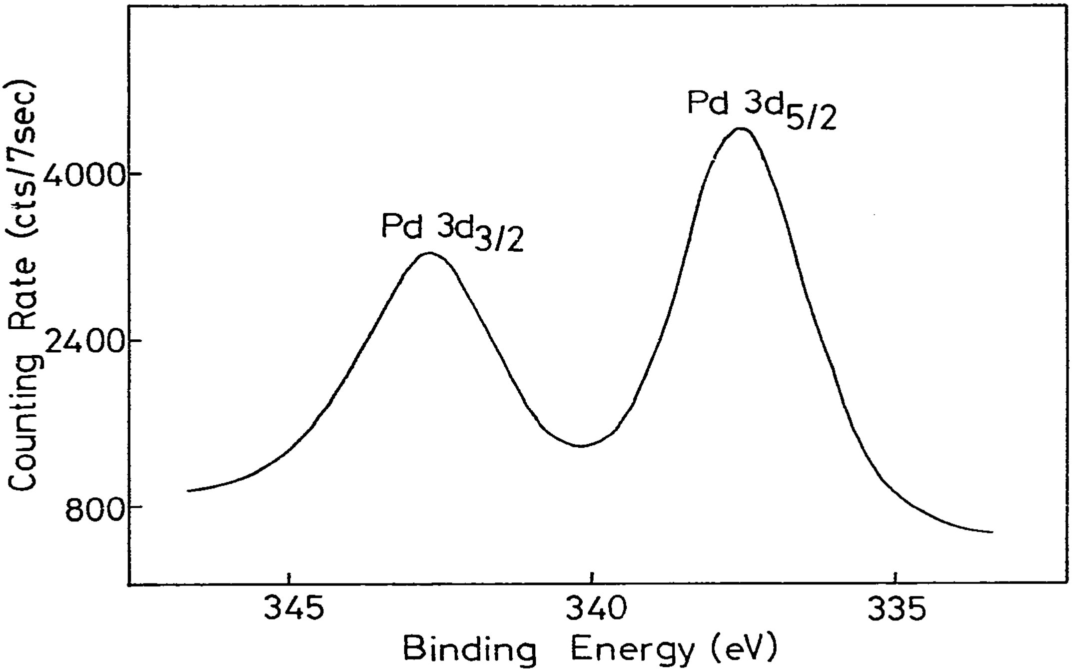

Fig. 1 Palladium 3d photoelectron spectrum of a polymer-bound palladium(0) complex (Ⓟ-Pd-PPh_3).

respectively. This shows the reduced complex to be composed of one species. Also, the palladium is not metallic, because if it was, the energy widths would be broader. Furthermore, no ESR signal assignable to a palladium(I) species was observed. Therefore, it is probable that the polymer-bound complex is an unsaturated, two-coordinate palladium(0) complex with two vacant sites as shown in Scheme 1.

However, mixtures of one-, two-, and three-coordinate palladium(0) complexes may exist. Also, Pittman et al. obtained coordinatively unsaturated and polymer-bound palladium(0) complexes, $(\text{Ⓟ}-PPh_2)_{2\&3}Pd^0$ by the ligand-exchange reaction of a polymeric phosphine, Ⓟ, with $Pd(PPh_3)_4$ [4d]. These results suggest that polymer chains sterically hinder the coordination of a sufficient number of phosphine ligands to form a coordinatively saturated complex and that they stabilize the unsaturated complex. The facile formation of unsaturated complexes using polymeric ligands is one of the advantages over homogeneous systems [5].

In order to test the catalytic activities of the polymer-bound palladium(0) complex, three representative types of palladium(0)-induced reactions, all of which involve the oxidative addition of halides to the metal, were studied: (i)vinylic hydrogen substitutions with aryl halides [6a], (ii) acetylenic hydrogen substitutions with aryl halides [6b], (iii) vinylic halogen substitutions with Grignard reagents [6c].

The results are listed in Table 2. Most reactions were carried out under conditions similar to those used in the corresponding homogeneous reactions. Although the starting polystyrene used in the preparation of the polymer-bound palladium(0) complex was not crosslinked, the polymeric complex was not soluble in the reaction mixtures and was easily separated from the mixtures by filtration or centrifugation. The polymeric complex displayed efficient catalytic activities in these reactions. In the reaction of styrene with iodobenzene (Run 1), stilbenes were formed in 86% yield and (E)-stilbene could be easily isolated in 70% yield by recrystallization from the filtrate. The molar

TABLE 2

REACTIONS OF OLEFINS OR ACETYLENES WITH HALIDES

Run	Olefin or Acetylene (mmol)	Halide (mmol)	Catalyst (mmol)	Conditions[a]	Products (Yield %)[b]	
1	Styrene (25)	Iodobenzene (28)	(0.14)	A	(E)-Stilbene (78)	(Z)-Stilbene (8)
2	Styrene (25)	Iodobenzene (28)	Recycle-1	A	(E)-Stilbene (74)	(Z)-Stilbene (8)
3	Styrene (25)	Iodobenzene (28)	Recycle-2	A	(E)-Stilbene (61)	(Z)-Stilbene (7)
4	Styrene (25)	Iodobenzene (28)	Exposed to air. (0.14)	A	(E)-Stilbene (63)	(Z)-Stilbene (9)
5	Methylacrylate (25)	Iodobenzene (28)	(0.14)	A	(E)-Methyl-cinnamate (68)	(Z)-Methyl-cinnamate (13)
6	Phenylacetylene (25)	Iodobenzene (28)	(0.14)	B	Diphenylacetylene (63)	
7	1-Pentyne (5)	Iodobenzene (5)	(0.14)	C	1-Phenyl-1-pentyne (59)	
8	(Z)-β-Bromostyrene (2.1)	Methylmagnesium iodide (5.4)	(0.035)	D	(Z)-β-Methyl-styrene (98)	(E)-β-Methyl-styrene (2)
9	(E)-β-Bromostyrene[c] (2.1)	Methylmagnesium iodide (5.4)	(0.035)	D	(E)-β-Methyl-styrene (72)	(Z)-β-Methyl styrene (3)

[a] A = tri-n-butylamine (4.7 ml), 100°C, 2 hr; B = tri-n-butylamine (4.7 ml), 40°C, 20 hr; C = piperidine (1.5 ml), sodium methoxide (5 mmol), 50°C, 5 hr; D = benzene (20 ml), room temperature, 24 hr. [b] Yields were based on the starting olefin or acetylene, and determined by GLC. [c] Containing 12% (Z)-isomer.

turnover numbers of 125 are much larger than those of 75 in the corresponding homogeneous reaction reported by Heck et al. [6a]. Bromobenzene and chlorobenzene were used in place of iodobenzene in this study, but the corresponding stilbenes were obtained in only trace yield. The polymeric complex was effective in catalyzing the acetylenic substitutions (Run 6, 7). Generally, it is preferable to carry out these reactions at higher temperatures [6b]. However, the starting acetylenes were more rapidly polymerized at higher temperature when this catalyst system was used. Consequently, these reactions had to be carried out at lower temperatures and, consequently, only moderate yields resulted. The reactions of the isomeric β-bromostyrenes with methylmagnesium iodide proceeded quantitatively and showed high stereospecificity (Run 8, 9). The polymeric complex, which was separated from the reaction mixture by centrifugation in air, could be reused with some loss of activity (Run 1, 2, 3). However, it seems that the loss of activity is not due to the lowering of the catalytic activity itself, but to the loss of polymer in the separation process. Even after the catalyst had been exposed to air for 6 days, its activity did not remarkably decrease (Run 4).

In conclusion, the polymer-bound palladium(0) complex catalyst has not only the same reactivities in the carbon-carbon bond formation reactions as the analogous soluble palladium(0) complex catalysts, but offers practical advantages such as easy handling, separation, and reuse.

Experimental

General

Gas-liquid chromatography (GLC) measurements were made using a Shimadzu GC-4BPF chromatograph and a 5-m column of silicone KF 96. X-ray photoelectron spectra were taken on an Hitachi 507 photoelectron spectrometer using Al K_α radiation. All solvents were rigorously dried and distilled. (Z)-β-Bromostyrene was prepared by the method of Cristol and Norris [7]. Methylmagnesium iodide was prepared by the reaction of methyl iodide with magnesium in ether and titrated. Tetrakis(triphenylphosphine)palladium [8], carbonyltris(triphenylphosphine)palladium [9], and bis(dibenzylideneacetone)palladium [10] were prepared by methods reported in the literatures. Hydrazine hydrate and sodium methoxide were of commercial grade and used without purification. All other materials were obtained commercially, dried, and purified. Triphenylphosphine was recrystallized from ethanol under a nitrogen atmosphere before use. Carbon-carbon bond formation products were collected by recrystallization or preparative GLC, and were identified by comparison (retention time in GLC, mixed melting point, IR and NMR spectra) with authentic samples.

Preparation of Poly-4-diphenylphosphinomethylstyrene

The chloromethylated resin [2] was treated with $LiPPh_2$ in a manner similar to a previous report [2]. Analysis showed C, 82.42; H, 6.25; Cl, 0.54; P, 8.71%.

Preparation of Polymer-Bound Palladium(II) Complex

The polymer-bound palladium(II) complex was prepared by the reaction of the phosphinated resin with palladium chloride in the manner reported previously [2]. Analysis showed C, 55.90; H, 4.25; Cl, 11.00; P, 7.09%, corresponds to a P/Pd ratio of 1.1 to 1, where the palladium content was calculated by difference.

Preparation of Polymer-Bound Palladium(0) Complex

The polymer-bound palladium(II) chloride complex (7.0 g, 14.8 mgatom of Pd) was added to ethanol (50 ml) containing triphenylphosphine (9.1 g, 34.7 mmol). The mixture was stirred at room temperature for 3 hr. Then hydrazine hydrate (6.0 g, 0.12 mol) was added to the mixture and stirring was continued for 2 hr. The resulting polymer was filtered, washed with ethanol and ether, and dried under vacuum to give the drak-green, polymeric complex. All the above procedures were carried out under an argon atmosphere. Anal. Found: C, 69.55; H, 5.11; Cl, 1.81; P, 8.41%. Calcd. for Ⓟ-Pd-PPh$_3$: C, 69.92; H, 5.14; Cl, 1.72; P, 8.57%.

Vinylic and Acetylenic Hydrogen Substitution Reactions

The reaction of styrene with iodobenzene is typical. Styrene (2.60 g, 25 mmol), iodobenzene (5.70 g, 28 mmol), and tri-n-butylamine (4.7 ml) were placed in a reaction bottle equipped with a magnetic stirrer bar and a condensor. The polymer-bound palladium(0) complex (0.10 g, 0.14 mgatom of Pd) was added and the bottle was flushed with argon. Then the mixture was stirred at 100°C for 2 hr. The polymeric catalyst was separated from the reaction mixture by centrifugation, washed several times with ether in air, and reused for the same reaction. GLC analysis of the separated solution showed that (E)- and (Z)-stilbene had been produced in 78 and 8% yield, respectively, and that unreacted styrene remained. The solution was concentrated under reduced pressure to give a white solid. The latter was recrystallized from benzene-ethanol to give 3.15 g of (E)-stilbene (70%). Other reactions were carried out in the same manner.

Vinylic Halogen Substitution Reactions

(Z)-β-Bromostyrene (0.38 g, 2.1 mmol), the catalyst (0.025 g, 0.036 mgatom of Pd), and benzene (20 ml) were placed in a reaction bottle. The bottle was flushed with argon. Then a titrated ethereal solution of methylmagnesium iodide

(4.5 ml, 5.4 mmol) was added and the mixture was stirred at room temperature for 24 hr. The solution was directly analyzed by GLC. The starting bromostyrene was consumed completely to give (Z)- and (E)-β-methylstyrene in 98 and 2% yield, respectively. Similarly, the reaction of (E)-β-bromostyrene was carried out to give (E)- and (Z)-β-methylstyrene in 72 and 3% yield, respectively.

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