

Poly(styryl)bipyridinepalladium Complexes as Heterogeneous Catalyst for Hydrogenation of Alkenes and Alkynes

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Poly(styryl)bipyridinepalladium(II) acetate is a useful catalyst for the hydrogenation of alkenes and alkynes though differing selectivity is observed in the two reactions. More substituted or sterically bulky olefins appear to be reduced less rapidly than less hindered olefins, while there are only relatively minor differences in the rate of hydrogenation of a variety of alkynes. Alkynes are reduced preferentially to the alkenes, and the resulting alkenes can be obtained in good yield without significant isomerization if the reaction is stopped after consumption of 1 equiv of hydrogen. In each case examined the consumption of the first equivalent of hydrogen is indicated by a significant change in rate of hydrogen consumption. This rate change appears to be unique for the use of catalysts based on polystyrene-2% divinylbenzene copolymer.

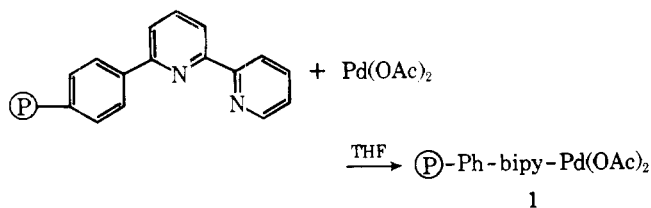
As part of our continuing activity in the development of useful polymer-bound reagents,¹⁻³ we have recently reported the preparation of poly(styryl)bipyridine, a generally useful support for the preparation of polymer-bound transition metal catalysts.⁴ Among the catalysts which we have developed, for example, are those for isomerization of strained hydrocarbons,⁵ for olefin metathesis,⁷ and for the mild hydrogenation of dienes to monoenes.⁸ The latter work led us to explore the hydrogenation of other substrates.

Since the hydrogenation of various functional groups is among the most common and useful organic reactions, a great deal of effort has been invested in the development of improved catalysts and part of that effort has involved polymer-bound transition metal catalysts.⁹⁻¹⁵ Grubbs, for instance, has prepared a polymer-bound titanium-cyclopentadienyl complex which is 10-25 times more active as a catalyst for the hydrogenation of olefins than its nonpolymer-bound analogue, mainly because polymer binding minimizes dimerization of the active catalytic species.¹¹ Grubbs has also shown that a rhodium catalyst bound to phosphinated polystyrene-2% divinylbenzene resulted in resin-controlled rate of olefin hydrogenation.¹² And Pittman has used polymer-bound hydrogenation catalysts as part of a catalyzed multistep sequence of reactions.¹³

In this report we show that poly(styryl)bipyridinepalladium species exhibit a selectivity of olefin hydrogenation similar to that of Grubbs' rhodium catalyst¹² and a novel selectivity in alkyne hydrogenation.

Results and Discussion

Catalyst Synthesis. Poly(styryl)bipyridinepalladium(II) acetate (**1**) is readily prepared from the reaction of palladium



acetate with poly(styryl)bipyridine in tetrahydrofuran (THF) under ambient conditions. The polymer **1** is isolated by filtration through fritted glass and thoroughly washed. The IR spectrum of **1** contains bands at 1550 and 1560 cm^{-1} , indicating the presence of the acetate ligands.¹⁶ Poly(styryl)bipyridinepalladium(II) acetate is converted to poly(styryl)bipyridinepalladium(0) upon interaction with slightly more than 0.5 mol equiv of lithium aluminum hydride in THF at room temperature. (The structure of this material is under investigation. It is not yet clear whether there is any palla-

dium-bipyridine interaction or whether the material is composed of small, entrapped metal clusters.)

Hydrogenation. In a typical hydrogenation reaction, 10 mmol of substrate, 100 mg of **1**, and 10 mL of dry tetrahydrofuran are added to a round-bottom flask which is then attached to an atmospheric hydrogenation apparatus, purged with hydrogen, and stirred under ~ 1 atm of hydrogen at room temperature. The hydrogen uptake is monitored as a function of time. When the hydrogenation is terminated, the polymer is removed by filtration through fritted glass, the tetrahydrofuran is removed by distillation at reduced pressure, and the resulting solution is examined by NMR spectroscopy.

The hydrogenation of alkenes has already been presented^{4b} and will only be summarized here. In all cases studied except 1-octene, the consumption of hydrogen occurs at a constant rate for at least the initial 80% of the reaction. The relative rates are reproducible over several polymer batches, and the polymer can be reused with only small differences in activity. In the case of 1-octene the rate decreases with time. The behavior of 1-octene is due to competing olefin isomerization. After consumption of 0.5 equiv of hydrogen, only internal octenes and octane are observed by NMR. The rate of hydrogenation decreases as reduction of the internal olefins becomes important.

The hydrogenation of 1-hexene was conducted under different conditions and followed by GLC (Figure 1). In this case, the hydrogenation was catalyzed by poly(styryl)bipyridinepalladium(0) (0.16 mequiv Pd/g). The data demonstrate that isomerization is more rapid than hydrogenation, and 2-hexene rapidly becomes the major species in solution.

Olefin isomerization does not occur in the absence of hydrogen, but does occur in the presence of a limited amount of hydrogen. Poly(styryl)bipyridinepalladium(0) was added to THF, and the mixture was stirred under hydrogen for 20 min. 1-Hexene was then introduced, and the flask was removed from the source of hydrogen and stoppered. The solution was stirred for 1 h in this hydrogen environment. GLC analysis indicated 50% 2-hexene, 25% 1-hexene, 12% 3-hexene, and 12% hexane.

A turnover number of greater than 2800 is observed in the hydrogenation of 3-methyl-3-buten-2-ol. A lower turnover is observed when there is competing olefin isomerization; a turnover number of ~ 800 is observed in the reduction of 1-octene. The polymer **1** is not effective for the reduction of nitrobenzene, benzophenone, chlorobenzene, or benzyl alcohol after 24 h at 50 psi.

The catalyst recovered from these and the alkyne hydrogenations contains only Pd(0). This is concluded from two observations. First, the recovered catalyst has an IR spectrum nearly identical with that of independently prepared

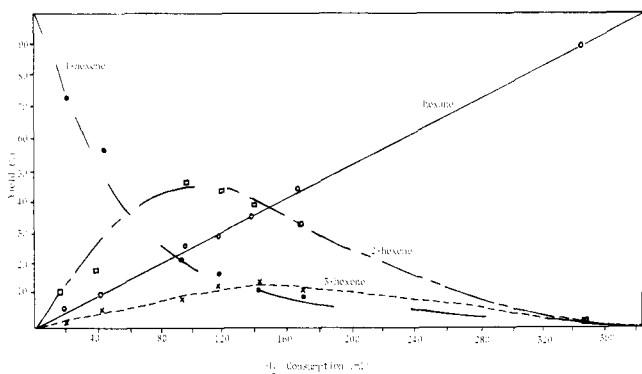


Figure 1. Progress of hydrogenation of 1-hexene.

poly(styryl)bipyridinepalladium(0). Also, the recovered catalyst can be used to catalyze the isomerization of quadricyclene to norbornadiene. This reaction has been shown to be catalyzed by poly(styryl)bipyridinepalladium(0), but not by poly(styryl)bipyridinepalladium(II) acetate.⁵

In our hands, it is not possible to differentiate hydrogenations catalyzed by the initial addition of poly(styryl)bipyridinepalladium(0) from those of polymer-bound palladium(II) acetate.⁶ Although the role of Pd(II) in the hydrogenation is not fully understood, it is clear that Pd(II) is reduced to Pd(0) during the hydrogenation and that the resulting polymer-palladium(0) system is an efficient hydrogenation catalyst. Therefore, the uniqueness of this system is perhaps best evaluated by comparisons with Pd/C (Figures 2 and 3).

The hydrogenation of alkynes over poly(styryl)bipyridinepalladium species generally proceeds with a constant rate of hydrogen consumption until 1 equiv of hydrogen has been consumed, at which time a discreet change in rate is observed. This behavior appears to be unique to poly(styryl)bipyridinepalladium species based on 2% cross-linked resin (Figures 2 and 3). Figure 2 allows comparison of the hydrogenation of 4-octyne in the presence of poly(styryl)bipyridinepalladium(II) acetate and in the presence of palladium on carbon. Figure 3 allows comparison of the hydrogenation of diphe-

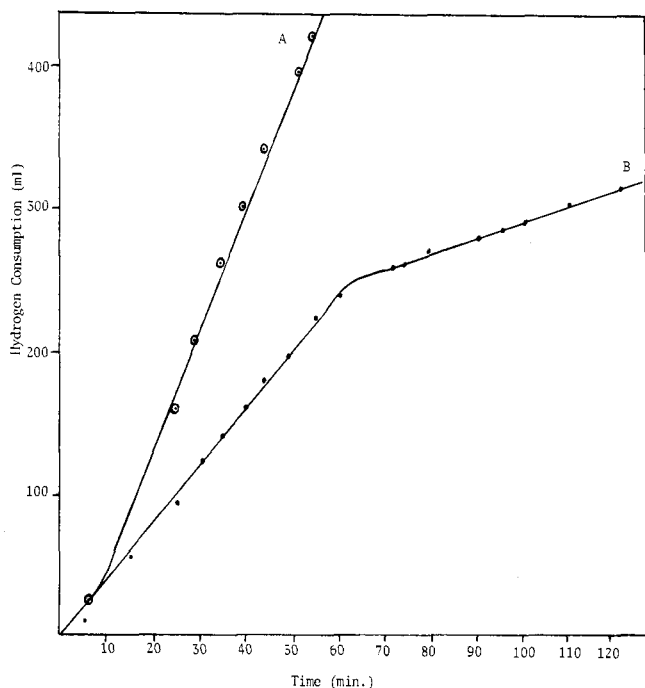


Figure 2. Effect of catalyst on hydrogenation of 4-octyne: (A) 10% Pd/C; (B) poly(styryl)bipyridinepalladium(II) acetate. A 250-mL amount of hydrogen is 1 equiv.

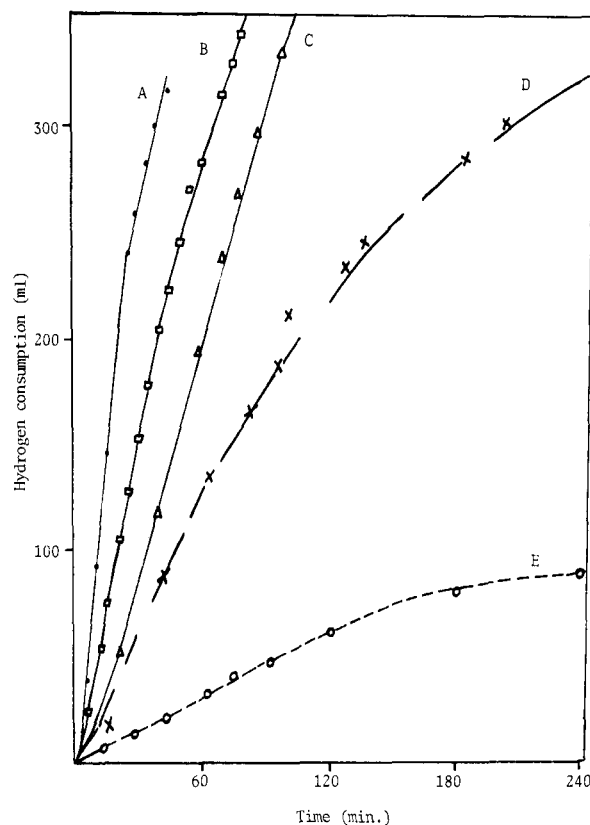


Figure 3. Effect of catalyst on the hydrogenation of diphenylacetylene in dry THF: (A) poly(styryl)bipyridinepalladium(II) acetate on 2% cross-linked resin; (B) poly(styryl)bipyridinepalladium(0) on 2% cross-linked resin; (C) 10% Pd/C; (D) poly(styryl)bipyridinepalladium(II) acetate on 20% cross-linked resin; (E) bipyridinepalladium acetate (240 mL = 1 equiv of H₂).

nylacetylene in the presence of a variety of catalytic species. The importance of the amount of cross-linking is apparent from these data.

Similar results are observed for other alkynes, though the rate of hydrogenation may either increase or decrease after consumption of the first equivalent of hydrogen. For example, in the case of 2-methyl-3-butyne-2-ol an initial rate of 4.3 mL/min is followed by a rate of 5.4 mL/min. Although the alkene is hydrogenated more rapidly, the alkyne is reduced preferentially in a mixture. For example, 5 mmol each of 2-methyl-3-butyne-2-ol and 2-methyl-3-buten-2-ol was added to 10 mL of dry THF and 100 mg of poly(styryl)bipyridinepalladium(II) acetate. After consumption of ~0.7 equiv of hydrogen, 72% 2-methyl-3-buten-2-ol and 28% 2-methyl-3-butyne-2-ol were observed by NMR. The corresponding alkane was not present in more than trace quantities.

The relative rates of hydrogenation of a number of alkynes are presented in Table I. The rate of hydrogenation of 2-methyl-3-butyne-2-ol (4.3 mL/min) was arbitrarily set at 1.0, and the same catalyst was used in all cases. In each case, except for propynoic acid, a rate change was observed after the consumption of 1 equiv of hydrogen. Propynoic acid hydrogenation was slow and was not carried out past 2 h (~20% conversion to propenoic acid).

The rate of hydrogenation of alkyne is much less sensitive to molecular size than the hydrogenation of olefins. 2-Methyl-3-buten-2-ol is hydrogenated at a rate of ~7 times that of either 4-octene or dimethyl fumarate (maleate), yet the analogous alkynes are hydrogenated at approximately equal rates.

The alkenes can be obtained in reasonably good yield from the hydrogenation of the alkyne. In one example, the hydrogenation of diphenylacetylene was terminated after the rate

Table I. Relative Rates of Alkyne Hydrogenation^a

alkyne	registry no.	relative rates		
		yne	ene	ane
phenylacetylene	536-74-3	3.3	1.0	
2-octyne	2809-67-8	1.6	0.4	
2-methyl-3-butyn-2-ol	115-19-5	1.0	2.1	
4-octyne	1942-45-6	1.0	0.3	
1-octyne	629-05-0	0.9	1.3	
diphenylacetylene	501-65-5	0.9	0.6	
dimethyl acetylenedicarboxylate	762-42-5	0.9	0.3	
propynoic acid	471-25-0	0.1		

^a Alkyne (10 mmol) was hydrogenated in 10 mL of THF in the presence of 100 mg of poly(styryl)bipyridinepalladium(II) acetate (0.69 mequiv/g) at 25 °C, 1 atm hydrogen.

change was observed. A 90% yield of stilbene was observed by NMR.

Mechanistic Considerations. It appears from the following observations that selectivity in hydrogenation of a mixture of substrates is controlled by formation of the thermodynamically more stable palladium-substrate complex rather than by kinetic factors. (1) Although the rate of hydrogenation of 2-methyl-3-buten-2-ol is twice as rapid as the rate of hydrogenation of 2-methyl-3-butyn-2-ol, the alkyne is preferentially hydrogenated in a mixture. (2) Isomerization of 2-hexene does not occur in the presence of equimolar 1,5-hexadiene.⁸ (3) Although the hydrogenation of *cis*- and *trans*-stilbene occurs separately at the same rate, the *cis* isomer is preferentially hydrogenated in a mixture. *Cis*-*trans* isomerization is not important under the reaction conditions. (4) The hydrogenation of 1-octyne results in 1-octene as the major, if not exclusive, product after consumption of 0.9 equiv of hydrogen, in spite of the efficiency of olefin isomerization in the absence of the alkyne.

Observations 1, 2, and 4 are accounted for by the preferential complexation of an alkyne or a diene relative to an alkene, an often observed phenomenon.¹⁷ Observation 3 must be due to a preference for the complexation of *cis*- over *trans*-stilbene. As expected, the selectivity in this case is less complete than in the other cases. The partial hydrogenation of a 53:47 *cis*-/*trans*-stilbene mixture results in a product distribution of 33:29:38 for bibenzyl and *cis*- and *trans*-stilbene.

The relative rates of substrate hydrogenation do not always correlate with the selectivity of hydrogenation of a mixture of substrates (see example 1 above). Therefore, factors other than thermodynamic stability of the palladium-substrate complex must control the actual rate of hydrogenation.

We suggest that the initial step in polymer palladium catalyzed hydrogenation involves molecular shuffling of the polymer backbone during approach of the substrate to the metal. The symmetry of the alkyne moiety allows minimum geometrical and steric constraint upon complexation. The acetylene moiety and connected groups form a linear system with a 360° surrounding π system. Therefore, the molecular shuffling of the backbone should be similar in all cases, unless there is an unusually bulky substituent, predicting only minor rate differences. Alkenes, on the other hand, must approach with the π cloud facing the metal since there are, in alkenes, four different spatially oriented groups. The molecular shuffling of the backbone will depend on the steric bulk and placement of those substituents, consistent with the relative rate effects observed.

This explanation is also consistent with the observation that a discreet change in rate of hydrogen consumption observed after the first equivalent of hydrogen has been added to an

alkyne occurs with the 2% cross-linked polymer, but not with the more rigid 20% cross-linked polymer.¹⁸

The abnormally slow hydrogenation of propynoic acid is probably due to repulsion of the polar carboxylic acid moiety and the nonpolar polymer surface.

Conclusions

Either poly(styryl)bipyridinepalladium(II) acetate or poly(styryl)bipyridinepalladium(0) may be used for the efficient hydrogenation of alkenes or alkynes under ambient conditions. Catalysts based on polystyrene-2% divinylbenzene show a unique change in the rate of hydrogenation after 1 equiv of hydrogen has been added to an alkyne. The hydrogenation of alkynes may be stopped after the addition of 1 equiv of hydrogen to yield the alkene in ~90% yield or allowed to continue to the alkane.

Hydrogenation of olefins may be accompanied by olefin isomerization. Isomerization of the olefins resulting from alkyne hydrogenation is not observed if the reaction is stopped prior to consumption of the first equivalent of hydrogen.

The overall process of hydrogenation appears to be controlled by the formation of a substrate-palladium complex. Steric interaction between the substrate and the polymer backbone on approach of the substrate to the metal center plays a significant role in determining the relative rate of olefin hydrogenation. Steric factors are less important for alkyne hydrogenation. The relative stability of metal-substrate complexes controls the selectivity of reduction observed when a mixture of substrates is present.

The catalyst recovered from the hydrogenation involves palladium(0). It is possible, however, that the polymer-bound palladium(II) complex does play some role during the hydrogenation.

Experimental Section

Proton magnetic resonance spectra were obtained on either a Varian Associates CFT-20 or A-60 nuclear magnetic resonance spectrometer and the infrared spectrum on a Perkin-Elmer 337 grating infrared spectrophotometer. GLC analyses were obtained on a Hewlett Packard 5710 A gas chromatograph with flame ionization detectors and an Omniscrite recorder with disc integration. Elemental analyses of solid samples were performed by Spang Microanalytical Laboratory.

Commercial samples were inspected by NMR and GLC for purity before use. Benzene and tetrahydrofuran were distilled over calcium hydride and stored over molecular sieves prior to use as solvents for the hydrogenation reactions.

Poly(styryl)bipyridine was prepared as previously described.^{4b} The resulting polymer was subjected to Soxhlet extraction with dimethylformamide and benzene before use. **Poly(styryl)bipyridinepalladium(0)** was prepared by the lithium aluminum hydride reduction of poly(styryl)bipyridinepalladium(II) acetate as previously described.^{4b} The material was subjected to Soxhlet extraction with acetone prior to use. Elemental analysis indicated 1.74% Pd and 1.19% N. This material was used for all hydrogenations. **Poly(styryl)bipyridinepalladium(II) acetate** was also prepared as previously described.^{4b}

Olefin Hydrogenation. In a typical procedure, 3-methylbuten-3-ol (0.86 g, 10 mmol) and 100 mg of 1 (0.07 mmol of Pd) were added to 10 mL of dry THF in a 100-mL round-bottom flask. The flask was attached to a 1-atm hydrogenation apparatus, the system was purged with hydrogen, and the solution was stirred under 1 atm of hydrogen. The hydrogen consumed was measured as a function of time, and the reaction was stopped when no further uptake of hydrogen was observed. The catalyst was separated by filtration through fritted glass, the solvent removed by distillation at reduced pressure, and the product identified by NMR spectroscopy: (DCCl₃, δ) 2.4 (s, 1), 1.48 (m, 2), 1.23 (s, 6), and 0.91 (m, 3). Complete conversion to 2-methyl-2-butanol was observed.

In all cases studied, except 1-octene and 1-hexene, the rate of hydrogen uptake was constant throughout at least the first 80% of the reaction. The rates of hydrogen consumption are reproducible to less than $\pm 10\%$ error in all cases. In the case of 1-octene, the data from three runs indicate an initial rate of 4.8 ± 0.2 mL/min. On third reuse

of the catalyst, data from two runs indicate an initial rate of hydrogen uptake of 4.6 ± 0.3 mL/min, within experimental error of the data from the fresh catalyst.

Elemental analysis for palladium of the polymer before reduction showed 7.30% palladium compared with 7.27% after the hydrogenation. The results are from a single determination in each case.

Hydrogenation of 1-octene was conducted as described above. After consumption of 125 mL of H_2 (0.5 equiv), the reaction was removed from the hydrogenation apparatus, worked up in the normal manner, and analyzed by NMR: ($CDCl_3$, δ) 5.7–5.4 (m, 10), 2.2–1.8, 1.8–1.2, and 1.2–0.75 (m, 168 total). No absorption was observed at δ 5.7–6.25, so only small amounts of 1-octene may be present.

Hydrogenation of 1-hexene was conducted as described above with the exception that 100 mg (0.02 mmol of Pd) of poly(styryl)-bipyridinepalladium(0) was used as the catalyst. The reaction was followed by GLC using a $2\text{ m} \times \frac{1}{8}$ in. column packed with 15% ethylene glycol saturated with silver nitrate on Chromosorb P at 25 °C. The products were identified on the basis of retention time and peak enhancement. This column allows clean separation of the 1-hexene and trans internal olefins. Any cis olefins formed would lie under the peak assigned to 1-hexene and must be minor on the basis of the rapid disappearance of this material. The data are presented in Figure 1.

Isomerization of 1-Hexene. A round-bottom flask containing 100 mg (0.02 mmol of Pd) of poly(styryl)bipyridinepalladium(0) and 10 mL of THF was purged with hydrogen. 1-Hexene (10 mmol) was added, and the flask was removed from the source of hydrogen and stoppered. The solution was stirred for 1 h under this hydrogen environment and examined by GLC: 50% 2-hexene, 25% 1-hexene, and 12% hexane.

This sequence was repeated with the exception that 1-hexene (5 mmol) was added together with 1,5-hexadiene (5 mmol). After 1 h, GLC indicated 90% 1-hexene, 6% 2- and 3-hexenes, and 4% hexanes. (The internal hexenes probably result from ~10% hydrogenation of the diene.)

Hydrogenation of stilbene isomers was conducted as described above. Pure *cis*- or *trans*-stilbene undergoes hydrogenation at equal rates. In each case, samples were removed from the hydrogenation solution after consumption of ~0.5 equiv of hydrogen and examined by NMR. In neither case was the data consistent with competing *cis*-*trans* isomerization. Hydrogenation of 10 mmol of a 53:47 *cis/trans* mixture (determined by NMR ($DCCl_3$, δ) 7.8–7.2 (m, 137), 7.19 (s, 11.5), and 6.60 (s, 13)) was conducted. After consumption of 80 mL of H_2 , the NMR spectrum included ($DCCl_3$, δ) 7.8–7.0 (m, 132), 6.60 (s, 7), and 2.9 (s, 16), consistent with a 33:29:38 ratio of *bibenzyl/cis/trans*-stilbenes, respectively.

Hydrogenation of alkynes was conducted as described above for the hydrogenation of alkenes. In each case at least two runs were performed. One run was stopped after consumption of ~0.8 equiv of hydrogen, and the products were examined by NMR. In each case the product resulting from clean 1,2-hydrogen addition was observed, with no indication of rearrangement or isomerization.

Hydrogenations over other catalysts were conducted in the same manner except that 100 mg of the desired catalyst was used instead of poly(styryl)bipyridinepalladium(II) acetate.

Hydrogenation of Diphenylacetylene. Diphenylacetylene (0.178 g, 0.01 mol) and 100 mg of poly(styryl)bipyridinepalladium(II) acetate (0.07 mmol of Pd) were added to 25 mL of THF. The solution was purged with hydrogen and then stirred under hydrogen at room temperature and atmospheric pressure. After 40 min, a decrease in the rate of hydrogen uptake was observed and the reaction was terminated. The solution was filtered and the solvent removed at reduced pressure. The NMR showed ($DCCl_3$, δ) 7.24–7.0 (m, 90 units), 6.50 (s, 10), and 2.85 (s, 3), consistent with a 32:59:9 mixture of *trans*-stilbene, *cis*-stilbene, and *bibenzyl*, respectively.

This reaction was repeated in the presence of 150 mg (0.02 mmol of Pd) of poly(styryl)bipyridinepalladium(0). The NMR showed

($DCCl_3$, δ) 7.4–7.0 (m, 154), 6.6 (s, 13), and 2.85 (35), consistent with a 43:57 mixture of *cis*-stilbene and *bibenzyl*, respectively. Only a trace of *trans*-stilbene could be present.

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Registry No.—Poly(styryl)bipyridine, 68965-74-2; palladium, 7440-05-3.

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