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A Polymer-Bound Bidentate-Phosphine−Palladium Complex as a Catalyst in the Heck Arylation

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Polymer-supported 1,2-bis(diisopropylphosphino)benzene Pd(II) complex **2** shows a higher level of catalytic activity than the structurally analogous monomeric Pd(II) complex **1** in the Heck arylation of methyl acrylate by iodobenzene. The polymer-supported Pd(II) complex has a much higher turnover number (by more than 1 order of magnitude) than either **1** or $Pd(OAc)_2/PPh_3$ at synthetically useful concentrations of reagents. The reaction rate of the monomeric Pd(II) complex **1** is enhanced by electrochemical prereduction of Pd(II) to Pd(0). Deactivation in homogeneous solution via aggregation of the reactive complex to insoluble palladium metal clusters or by equilibration to a sterically blocked tetraphosphino complex is proposed to explain the higher catalytic activity of the polymer-supported Pd(II) complex than of its structurally analogous soluble monomer.

Introduction

Recent recognition of the importance of using recyclable metal catalysts in environmentally-benign synthesis has evoked a renewed interest in evaluating the catalytic efficiencies and turnover numbers of polymer-immobilized catalysts that maintain high activity and selectivity. In particular, anchored multidentate ligands may permit stabilization of catalytically active complexes without precipitous drops in induced reactivity. In this paper, we describe a new polymeric catalyst that immobilizes a bidentate phosphine ligand to which palladium coordinates, producing a catalytic site with high turnover number toward a Heck arylation reaction.

Olefin arylation promoted by palladium complexes has found wide application in organic synthesis.[1,2] For the past twenty years, the kinetics and mechanism of the Heck reaction have been studied[3] and considerable effort has been expended to optimize yields of palladium-catalyzed carbon−carbon bond formation.[4−14] Although homogeneous phosphine complexes are easily prepared *in situ* and are highly efficient chemically,[4,5] their catalytic activities are often plagued by low catalytic turnover caused by precipitation and aggregation of the metal or by formation of other catalyst decomposition products, particularly at high catalyst concentrations. For example, Haag and Whitehurst[15] have reported formation of inactive black metallic precipitates during the carbonylation of allylic chloride when catalyzed by $Pd(NH_3)_4Cl_2$.

Immobilization of the active catalyst onto a polymeric support can be used, in principle, to address this problem, since polymer-bound catalysts can (a) produce enhanced size and positional selectivity; (b) carry out sequential catalytic reactions; (c) attain matrix-like isolation of the catalytically reactive species; and (d) exhibit a kinetically different response to ligand concentration than is observed in homogeneous solution.[16] Although they are often less active, heterogeneous catalysts are often very durable and are readily separated from the reactants and products.

Several polymer-supported palladium catalysts have been used for the Heck arylation, but the identity of the catalytically active species remains controversial. For example, in their study of the Heck arylation with polystyrene-supported tetrakis(triphenylphosphine)palladium, Teranishi and co-workers found higher activity upon reduction with hydrazine[17] and Hallberg and co-workers[18] have suggested that the active state in the arylation of methyl acrylate with iodobenzene on polystyrene-supported palladium catalysts is metallic palladium. In contrast, Liu and co-workers[19] have proposed a Pd(0) complex as the active site with silica-supported polymeric palladium catalysts. Thus, the catalytically active species to be anticipated in a polymer matrix, as well as its fate in the catalytic cycle, is unclear.

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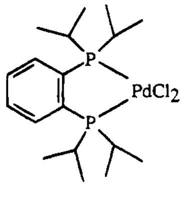
The catalysts studied heretofore have been monodentate-phosphine polymeric palladium complexes.[17,18] Despite restrictions imposed by the metal-coordination number and catalyst geometry,[20] multidentate ligands have been reported to suppress catalyst deactivation because a chelated five-membered (or larger) ring stabilizes the complex. In previous work,[21] we have shown that a polymer-bound bidentate phosphine ligand can stabilize a nickel(0) complex during the cross-coupling between two aryl halides, producing a moderate turnover number (40–600). This work compares the catalytic efficiency among monomeric and polymeric catalysts (**1** and **2**), catalyst precursors (a bidentate-phosphine Pd(0) complex), and $Pd(OAc)_2/PPh_3$ in the Heck arylation of methyl acrylate with iodobenzene, eq 1. The polymer-supported catalyst offers the following advantages: (1) high turnover number; (2) easy separation from products; (3) recyclability; (4) high thermal stability; and (5) moderate catalytic efficiency.



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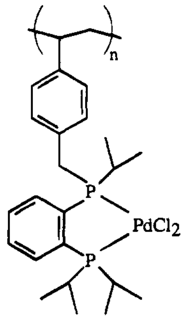

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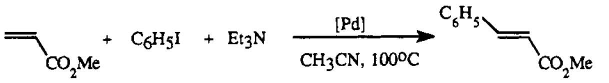


(1)

Experimental Section

General. All manipulations involving phosphines were conducted under an Ar or N_2 atmosphere. Elemental analyses were obtained from the Galbraith Laboratories.

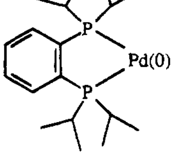
Materials. Pd $(OAc)_2$ (Strem) and PPh_3 (Aldrich) were used as supplied.

Bis[1,2-bis(diisopropylphosphino)benzene]palladium(0), 2:1 Pd(0) Complex. In a 50 mL round-bottom flask were combined 32 mg of dichloro-[1,2-bis(diisopropylphosphino)benzene]palladium(II)[22] (0.066 mmol) and 21 mg of 1,2-bis(diisopropylphosphino)benzene (0.066 mmol) in 20 mL of MeOH. To this solution was added, by syringe, 7.5 mg of $NaBH_4$ (0.20 mmol) in 2 mL of water. The resulting solution was stirred for 2 h at room temperature before being brought to reflux for 20 h. A bright yellow compound, collected after cooling to −15 °C, was washed with 100 mL of MeOH and vacuum-dried: 24 mg (50%). ^{31}P-NMR (C_6D_6): 43.3 ppm (s). UV (benzene): λ_{max} = 366 nm (sh). HRMS (EI): P^+. Calcd for $C_{36}H_{64}P_4Pd$ 727.307156, found 727.308711. Anal. Calcd C, 59.48%; H, 8.81%; P, 17.06%; Pd, 14.65. Found: C, 59.44%; H, 8.53%; P, 18.75%; Pd, 14.07%.

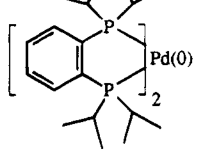
Dichloro-[1-[(polyvinylbenzyl)isopropylphosphino]-2-(diisopropylphosphino)benzene]palladium(II) (2). This compound was prepared according to literature method.[21] From the elemental analysis (calcd for $(C_{24}H_{34}P_2)_n$: C, 74.98; H, 8.91; P, 16.11; found: C, 71.08; H, 8.08; P, 14.50), the polymer is better represented as $[(C_{24}H_{34}P_2)_{0.78}-(C_9H_9Cl)_{0.22}]_n$, where $C_{24}H_{34}P_2$ represent phosphinated polyvinylbenzyl chain and C_9H_9Cl represents the unreacted polyvinylbenzyl chloride chain. In a 250 mL round-bottom flask, 200 mg of 1-[(polyvinylbenzyl)isopropylphosphino]-2-(diisopropylphosphino)benzene[21] (0.5 mmol) was suspended in 120 mL of acetone under Ar. To this mixture was added 198 mg $(PhCN)_2PdCl_2$ (0.5 mmol) in 50 mL of acetone. The resulting mixture was heated under reflux for 72 h. After having been cooled to rt, a pale yellow solid was washed with 100 mL of THF and with 150 mL of acetone before being taken up by Soxhlet extraction with acetone (26 h). The insoluble residue (i.e., material insoluble in DMSO, DMF, MeOH, or C_6H_6) was then vacuum-dried: 233 mg, 80% yield. Anal. Calcd for 100% palladium loading $(C_{20.7}H_{28.5}P_{1.56}Pd_{0.78}Cl_{1.78})_n$: C, 52.66; H, 6.08; P, 10.23; Pd, 17.58. Found: C, 51.18%; H, 6.25%; P, 9.21%; Pd, 16.27%. The ratio of P/Pd = 2.0 indicates a 100% Pd loading onto each polymer-bound phosphino ligand and the absence of phosphine oxide impurity. (Phosphine oxide will not bind to Pd(II) and the ratio of P/Pd would be higher if the phosphino coordinating ligand had been partially oxidized.)

Electrochemical Measurements. Coulometric Characterization of the Reduction Wave of Dichloro[1,2-bis(diisopropylphosphino)benzene]palladium(II) (1). Electrochemical data were obtained on a Princeton Applied Research Model 175 universal programmer. All experiments were performed with tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. A two-compartment electrochemical cell with $Ag/AgNO_3$ in MeCN as reference electrode, carbon cloth as the counterelectrode, and Pt wire as the working electrode was equipped with a stir bar. Electrolyte (25 mL of 0.1 M TBAP in MeCN) having been added to under a 15 min Ar purge, a blank electrolysis at −1.8 V was conducted until the initial current (100 μA) had decayed to 44 μA (background current). To the cathodic compartment was then added 16 mg of **1** (0.03 mmol). A constant potential of −1.8 V was applied while the solution was rapidly stirred. The electrolysis was disconnected when the initial current (7 mA) had decreased to 95 μA. The total current passed was 94% of the theoretical value for a 2-e^- reduction.

Controlled Potential Bulk Electrolysis. A two-compartment electrochemical cell was rendered free of air and moisture by flushing with argon while externally heating the vessel with a heat gun. The cell was equipped with carbon cloth cathode, a platinum anode, and a $Ag/AgNO_3$ reference electrode. The cell was filled with 30 mL of 0.2 M TBAP in MeCN. After purging with Ar, a potential of −1.7 V was applied for ca. 5 min in order to eliminate impurities from the working electrode. To the cathodic compartment was added 50 mg of **1** (0.1 mmol) with or without 31 mg of 1,2-bis(diisopropylphosphino)benzene (0.1 mmol), thus producing either the 1:1 or 2:1 complexes shown. The electrolysis was conducted at −1.7 V until the initial current had decayed to 200 μA.



"1:1 Pd(0) complex"



2:1 Pd(0) complex

Spectroelectrochemistry. *In situ* measurements were made during both the thermal Heck reaction and during electrolysis of **1** (as conducted as described above) within an electrochemical cell equipped with parallel optical flats. The extent of reaction was monitored by following changes in intensity in the absorption spectra of the metal catalyst.

Sample Preparation for X-ray Photoelectron Spectroscopy (XPS). The polymer **2** (before and after 200 catalytic reaction cycles) was mounted on 1 cm^2 sample mounting stub by dusting the powder onto the electrically

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conductive adhesive transfer tape (Scotch Brand 9703). Photoionization of the core-orbital electrons was accomplished with Mg Kα X-rays (1253.6 eV) at an incident power of 264 W. The plane of the sample was normal to the analyzer entrance aperture and the X-rays were incident at 50° to the sample plane. A Vacuum Generators ESCALAB Mark I Spectrometer, equipped with a hemispherical analyzer operated at a constant pass energy of 50 eV, was used to analyze the photoelectrons. The dimensions of the analyzer entrance aperture were 10 × 4 mm with an Einzel magnification ration of 1:1. The channel width in the spectra was 0.05 eV per channel with a dwelling time of 1.2 s per channel. Calibration of the energy scale was accomplished with a sputter-cleaned Cu(111) crystal on the binding energy scale of Cu $2P_{3/2}$ = 932.60 eV and Cu L_3VV = 334.70 eV. All binding energies were corrected by normalizing the adventitious C 1s to 284.6 eV.

Kinetic Studies of Carbon–Carbon Coupling. Relative Catalytic Activity of Different Pd Catalysts in the Heck Reaction. The iodobenzene (10 mmol), triethylamine (12 mmol), methyl acrylate (12 mmol), and the internal standard (dodecane, 75 mg) in 5 mL of MeCN were mixed in a 50 mL round-bottom flask equipped with a condenser. To this solution was added 49 mg of **1** (0.1 mmol), 56 mg of **2** (0.1 mmol), $Pd(OAc)_2$ (0.1 mmol)/PPh_3 (0.2 mmol), or the electrochemically prereduced 1:1 and 2:1 Pd(0) complexes derived from **1** (ca. 0.1 mmol). The resulting mixtures were brought to reflux at 100 °C under N_2. Samples were collected periodically and eluted with ether through a short silica gel column before being analyzed by gas chromatography (GC). Products were identified by coinjection with authentic samples.[18] The initial rates of catalyzed carbon–carbon coupling were calculated from the slope of a plot of the dependence of ln[ArI] on time. Since catalyst deactivation was observed during the course of the reactions catalyzed by $Pd(OAc)_2/PPh_3$ and by **1**, the initial reaction rates were calculated from data obtained at less than 25% consumption of starting material.

Determination of Ccatalyst Turnover Number of the Polymer-Supported Pd(II) Complex 2. To a 500 mL round-bottom flask was added 33 mL of iodobenzene (0.30 mol), 33 mL of methyl acrylate (0.37 mol), 52 mL of triethylamine (0.47 mol), 1.5 mL of dodecane (8.8 mmol), and 8.4 mg of **2** (ca. 0.01 mmol) in 50 mL of MeCN. The resulting mixtures were heated to reflux at 100 °C under N_2 for more than 247 h. When the iodobenzene has been completely consumed, the reaction vessel was recharged with the same concentration of iodobenzene, methyl acrylate, and triethylamine. The resulting mixtures were again heated to reflux at 100 °C under N_2. The initial rates of disappearance of starting material was determined as described above, before the sequence was repeated with a fresh injection of additional iodobenzene and methyl acrylate.

Results and Discussion

Electrochemical Behavior of 1 and 2. The cyclic voltammogram of the monomeric Pd(II) complex **1** in DMSO exhibits an irreversible reduction wave at −1.9 V (Figure 1). Coulometry shows this wave to be a two-electron reduction. This complex **1** exhibits electrochemical behavior very different from the analogous Ni(II) complex,[21] where two one-electron reductions of equal area at −1.31 V and −2.03 V are observed. The invariance of the observed peak areas with scan rate indicates that neither dimerization nor disproportionation takes place during the reduction of the Ni(II) complex. On the other hand, the absence of a discrete observable reduction wave for the conversion of Pd(II) to Pd(I) in **1** is an indication that disproportionation or dimerization of the Pd(I) complex occurs during the reduction.

This behavior is typical of Pd(II) phosphine complexes. DuBois and co-workers[23] have reported similar electrochemical behavior when Pd(II) is coordinated with other bidentate phosphine ligands, e.g., bis(diphenylphosphino)methane or bis(diphenylphosphino)ethane. Amatore[24] has also reported that a two-electron reduction occurs in $(PPh_3)_2PdCl_2$. In general, a wave for the Pd(II)/Pd(I) reduction is not observed in phosphine complexes because of a relatively fast dimerization or disproportionation.

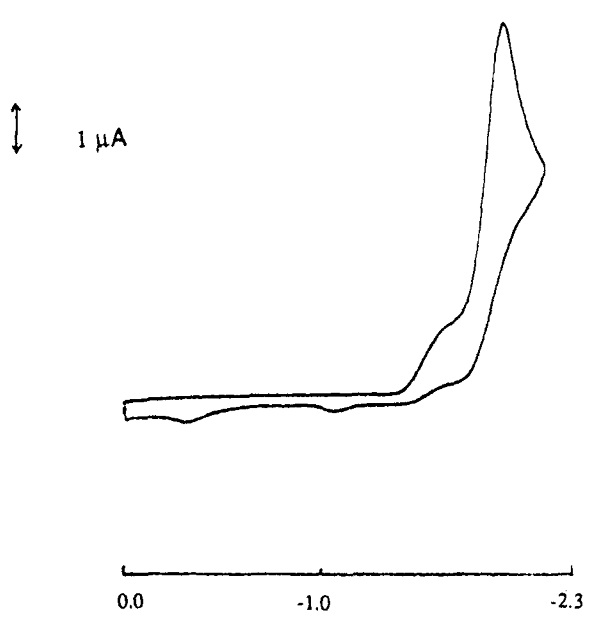

Figure 1. Cyclic voltammogram of dichloro-[1,2-bis(diisopropylphosphino)benzene]palladium(II) (**1**). As a 0.01 M solution in DMSO at a Pt electrode, 25 °C, 0.1 M TBAP, scan rate = 100 mV/s.

Because the polymer-supported Pd(II) complex **2** is insoluble in organic solvents, its electrochemical properties were explored by formulating a carbon paste electrode coating.[25] With a composite graphite electrode, a irreversible reduction wave at −1.9 V in DMSO was observed (Figure 2). The reduction wave at −1.3 V is assigned to residual polyvinybenzyl chloride, since polyvinylbenzyl chloride itself shows a reduction wave at −1.3 V in THF. Thus, the monomeric and polymer-supported palladium(II) complexes are reduced to the corresponding Pd(0) complexes at about the same potential. The reduction of $Pd(OAc)_2/PPh_3$ takes place at −1.5 V and is irreversible.

Zero-valent palladium complexes have been suggested as effective catalysts in the Heck reaction. More reactive species Pd(0) complexes can be generated by either chemical[26] or electrochemical reduction.[24] For example, Amatore has shown that "$Pd(0)(PPh_3)_2$" produced by electrochemical reduction of $(PPh_3)_2PdCl_2$ is coordinatively unsaturated and more reactive than $Pd(0)(PPh_3)_4$. In this study, we have generated a highly catalytically active "[1,2-bis(diisopropylphosphino)benzene]palladium(0)" complex by controlled potential bulk electrolysis reduction of the corresponding Pd(II) complex **1**, eq 2.

Catalysis of the Heck Reaction by Polymer 2. The Heck arylation is generally believed to involve an oxidative addition of the aryl halide to a palladium(0) com-

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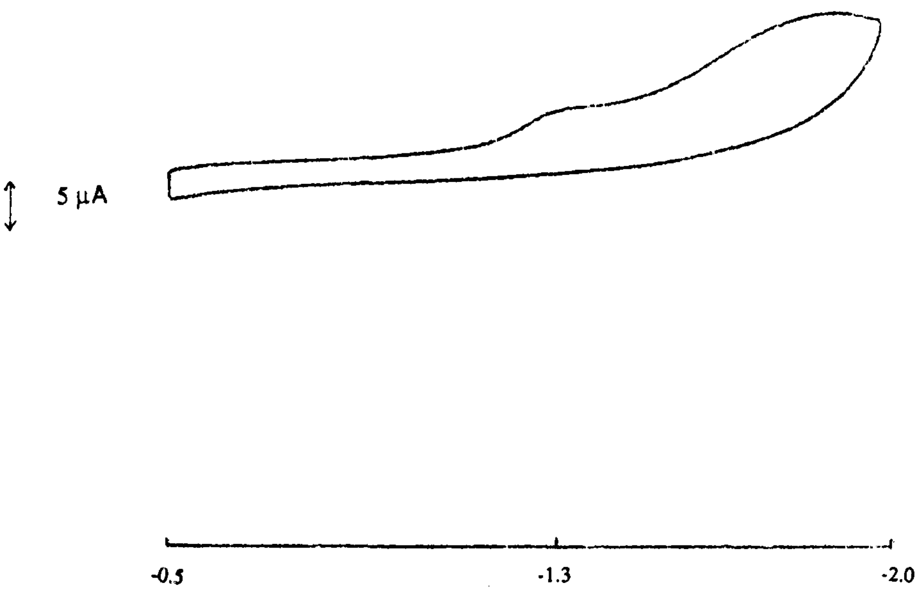
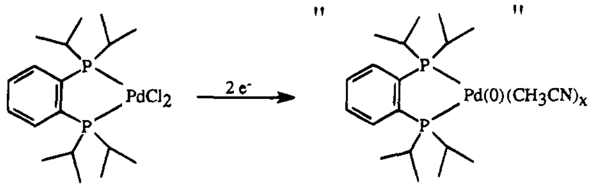


Figure 2. Cyclic voltammogram of dichloro-[1-[(polyvinylbenzyl)isopropylphosphino]-2-(diisopropylphosphino)benzene]palladium(II) (**2**). As a 0.01 M solution in DMSO at a graphite electrode, 25 °C, 0.2 M TBAP, scan rate = 100 mV/s.



(2)

1 "1:1 Pd(0) complex"

plex[3,4,27] or to a palladium metal cluster.[28] Thus, an initial reduction of the palladium(II) catalyst is a prerequisite for the arylation. Although the initial reduction in the mixture of a Pd(II) phosphine complex with iodobenzene and methyl acrylate remains unclear, the previously proposed oxidative addition, insertion, and reductive elimination sequence does regenerate Pd(0) after a complete turn of the cycle.[3c] The relative initial rates of coupling of iodobenzene with methyl acrylate catalyzed by a series of different palladium catalysts, **1**, **2**, prereduced **1**, and $Pd(OAc)_2/PPh_3$ are presented in Table 1. All reactions were carried out in CH_3CN with triethylamine as base. The data observed upon Heck catalysis with **1**, **2**, and $Pd(OAc)_2/PPh_3$ lead to the following generalizations:

(1) The reaction rate is strongly dependent on the identity of the palladium catalyst. The observed initial catalytic activity decreases in the following order: prereduced (Pd(0) oxidation state) of **1** ~ $Pd(OAc)_2/PPh_3$ > polymer-supported **2** > monomeric Pd(II) complex **1**. No catalytic activity is observed with $Pd(OAc)_2$ in the absence of triphenylphosphine. The monomeric Pd(II) complex **1** has not only the slowest reaction rate but also the longest induction time. Of special significance is the observation that the polymer-supported Pd(II) complex **2** has higher activity than the analogous monomeric Pd(II) complex **1**. The longer induction time and slower reaction rate of **1** than of **2** indicates that the catalytically active species are deactivated under the homogeneous conditions (*vide infra*).

(2) Electrochemical prereduction is effective in increasing catalyst activity, for the prereduced, sterically accessible Pd(0) complex **1** has a higher initial reaction rate than either the monomeric Pd(II) complex **1** (by a factor of 165) or the polymer-supported Pd(II) complex **2** (by a factor of 5).

Table 1. Comparisons of Catalytic Activities[a] of Various Palladium Catalysts in the Heck Arylation (eq 1)

	relative rate (time⁻¹)	turnover no.[b]	induction period (h)
monomer-Pd(II) **1**	0.007	13	8.5
polymer-Pd(II) **2**	0.2	780	0
prereduced 1:1 Pd(0) complex	1.1	120	0
prereduced 2:1 Pd(0) complex	0	0	0
$Pd(OAc)_2/2PPh_3$	1.0	50	0

[a] Reaction conditions: iodobenzene (10 mmol), Et_3N (12.5 mmol), methyl acrylate (12.5 mmol), internal standard (dodecane, 75 mg), and catalyst (0.1 mmol), heated in 5 mL of CH_3CN at 100 °C under N_2. Initial reaction rates were calculated from $d[ArI]/dt = k_{obs}[ArI]$ from a plot of the dependence in ln[ArI] on reaction time. [b] Turnover number is defined as the ratio of number of moles of aryl halide converted to arene to the number of moles of catalyst when catalytic activity was reduced to <5% of its initial rate.

(3) The initial rate of coupling upon repeated recharging of reagents is constant for polymeric complex **2**. In contrast, the initial rates of reaction catalyzed by the monomeric palladium complex **1** and by $Pd(OAc)_2/PPh_3$ rapidly decreased with time. These catalysts were, thus, gradually rendered inactive upon attempts at repeated cycling under the reaction conditions.

(4) Although the initial coupling rate catalyzed by the polymer-supported Pd(II) complex **2** is lower than that by $Pd(OAc)_2/PPh_3$ (by a factor of about 4), its recyclability is much better than for $Pd(OAc)_2/PPh_3$. A large turnover number (780) is easily achieved with **2** at higher catalyst concentrations (10 mM), where the catalyzed reaction is fast, whereas **1** and $Pd(OAc)_2/PPh_3$ have average turnover numbers of only about 13 and 50, respectively, under the same conditions. At lower catalyst concentrations (0.06 mM), higher turnover numbers are attained for both catalysts, but with a concommitant decrease in reaction rate.

(5) The polymer-supported Pd(II) complex **2** can be recycled, and products can be easily separated from the heterogeneous catalyst by simple filtration. The recycled polymer-supported catalyst is stable to the air and retains

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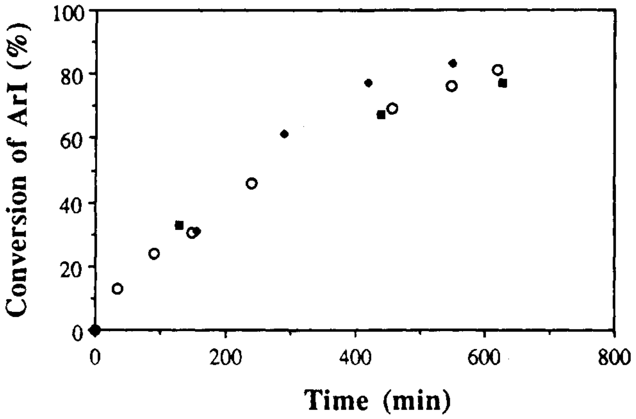
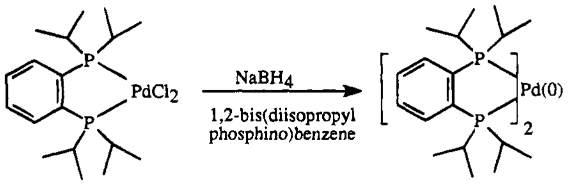


Figure 3. Recyclability of polymer-supported Pd(II) complex **2** toward the Heck reaction. Reaction conditions: **2** (56 mg, 0.1 mmol), iodobenzene (10 mmol), methyl acrylate (10 mmol), triethylamine (10 mmol), dodecane as internal standard (0.2 mL) in 50 mL of CH_3CN heated to reflux under N_2. Iodobenzene, methyl acrylate, and triethylamine at these same concentrations were recharged into the reaction vessel after every catalytic cycle: (a) ◆ the first catalytic cycle; (b) ○ the third catalytic cycle; (c) ■ the fifth catalytic cycle.

its original catalytic activity after many turnovers (Figure 3). It is therefore a convenient catalyst for Heck coupling reactions.

Relative Catalytic Activity. It is unusual to find a heterogeneous catalyst with higher catalytic activity than the structurally correspondent homogeneous catalyst as is observed here for **1** and **2**. Absorption spectra of **1** as a monomeric Pd(II) complex and in its prereduced form are shown in Figure 4. Upon electrochemical reduction to Pd(0), the absorption of the monomeric Pd(II) complex **1** at 318 nm totally disappears and is replaced by a new band at 285 nm. Because the Heck reaction is associated with a Pd oxidation state change, the progress of the catalytic coupling can be monitered, in principle, under homogeneous conditions by absorption spectroscopy. In a solution containing **1** in the presence of iodobenzene and methyl acrylate, a transient absorption at 360 nm (sh) that could not be assigned to either a Pd(II) and Pd(0) complex was observed (Figure 5), eventually being replaced by a final absorption at 390 nm after 24 h. This intermediate cannot be observed in the presence of **2** or in the presence of prereduced **1** or $Pd(OAc)_2$ lacking a coordinating phosphine ligand. It is possible therefore that catalyst **1** may suffer a reaction-retarding side reaction, accounting for its lower catalytic activity.

This side product can be assigned from its exact spectral match with bis(1,2-bis(diisopropylphosphino)benzene)palladium(0) prepared as in eq 3 by a procedure



(3)

1 **2:1 Pd(0) complex**

similar to that reported by Chatt et al. in the preparation of bis[1,2-bis(diethylphosphino)benzene]palladium(0).[29]

There are also several other potential explanations for structurally dependent catalytic activity that could be offered based on extrapolations from data available in the literature. First, because higher activity is observed with the prereduced **1** than with **1** in the Pd(II) oxidation state, one might reasonably expect correlation of catalytic activity with the ease of electrochemical reduction. This argument has been made for other catalytic conversions: for example, Andersson has rationalized the higher activity of a polymer-supported Pd(II)–phosphine complex in the hydrogenation of olefins by invoking the complexes' easy electrochemical reducibility.[30] If electroreduction of **2** were easier than that of **1** because of a structurally enforced less negative reduction potential, the observed order of reactivity might be anticipated. However, as shown above, all Pd(II) complexes examined here show the same irreversible reduction peak potential by cyclic voltammetry, making this effect unlikely as a cause of enhanced catalytic reactivity in **2**. These same effects would also be problematic if oxidative addition were the rate-determining step.

Second, Hallberg et al. have proposed the possibility that Pd metal clusters, rather than the reduced Pd(0) complex itself, might be the reactive site for catalyzed Heck coupling.[18] Because well-dispersed palladium clusters might have higher activity than aggregated palladium metal, trapping of isolated clusters within the polymer backbone might accelerate the catalyzed reaction compared with reactivity observed under conditions where clusters can freely grow further. This explanation would remain viable if it could be shown that cluster formation takes place within the polymer but without precipitation.[16a] Fortunately, a Pd metal cluster and a Pd(0) complex can be easily distinguished by X-ray photoelectron spectroscopy (XPS).[31] For example, palladium metal has a 3 $d_{5/2}$ absorption at 335.2 eV, while the tetrakis(triphenylphosphine) Pd(0) has the 3 $d_{5/2}$ absorption at 336.2 eV. An XPS characterization analysis of the polymer-supported Pd(II) complex **2** after 200 catalytic cycles (retaining >95% of its original catalytic activity) shows no X-ray diffraction lines for palladium metal (Table 2). This contrasts with results reported by Hallberg,[18] who did observe palladium metal in the phosphinated polystyrene-supported palladium. Therefore, with our catalysts, palladium metal clusters are not required for the arylation under our reaction conditions, and the high activity coupled with high turnover number that we observe for **2** may derive from a balance between stable complex formation as a consequence of bidentate ligation within the polymer and the inhibition of metal cluster formation and precipitation as a consequence of complex immobilization. The XPS analysis also indicates that the recycled polymer-supported catalyst **2** may separate as iodobenzene oxidative adduct or olefin coordination adduct and remain in the Pd(II) state.

Third, the polymer-supported catalyst **2** might be expected to have higher catalytic activity than the analogous monomeric catalyst **1** if metal leaching to produce an inactive non-phosphine ligated salt were a major deactivation pathway. Metal decomplexation in homogeneous solution lacking an excess of complexing ligand would result in the loss of catalytic activity. In the presence of excess ligand, further complexation to a sterically hindered tetrakisphosphino complex may also

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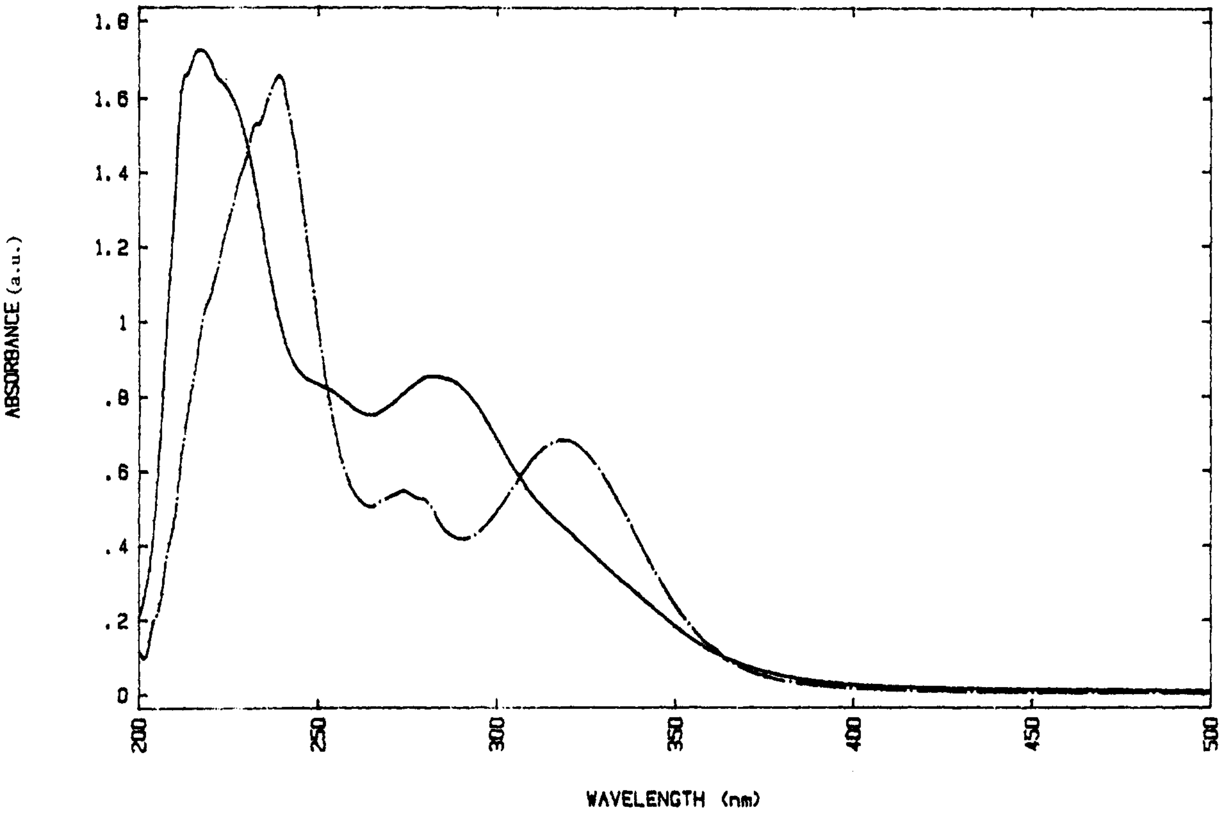


Figure 4. Absorption spectra of 0.001 M solutions of dichloro-[1,2-bis(diisopropylphosphino)benzene]palladium(II) **1** (–·–) and the corresponding Pd(0) complex (—) in deaerated CH_3CN.

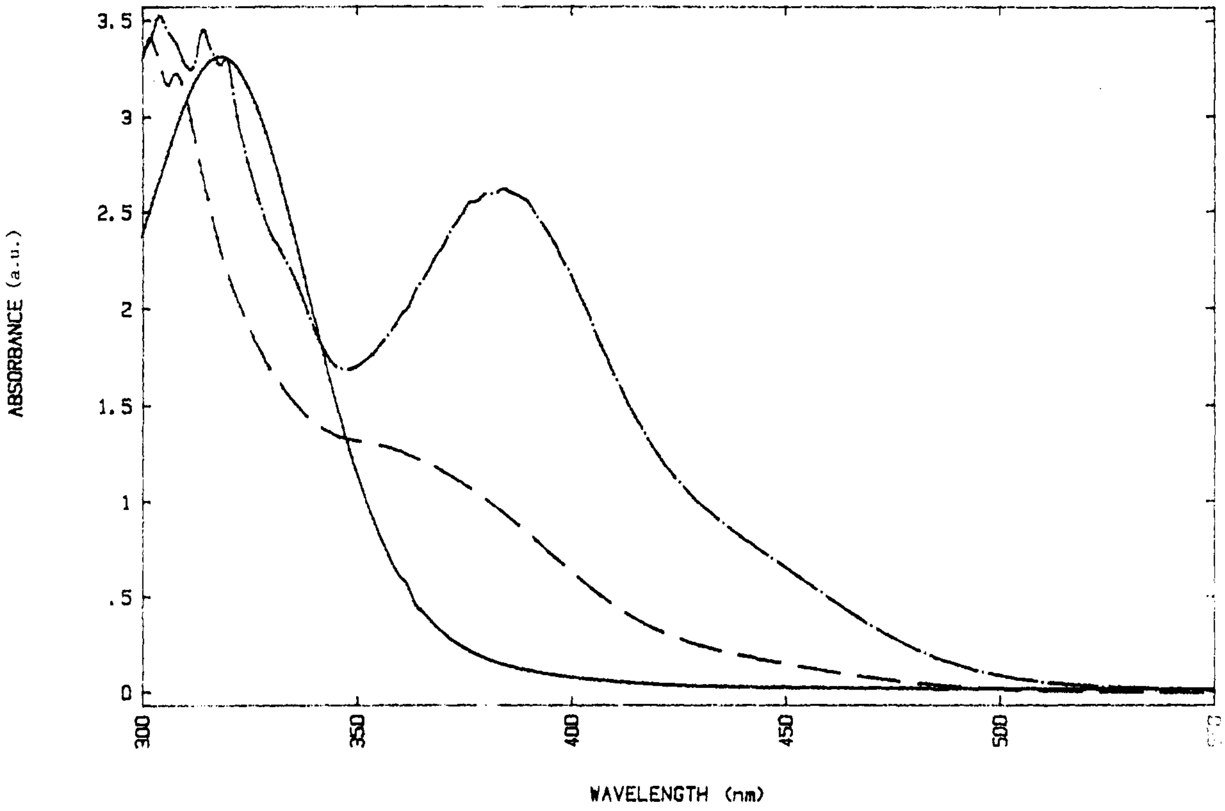


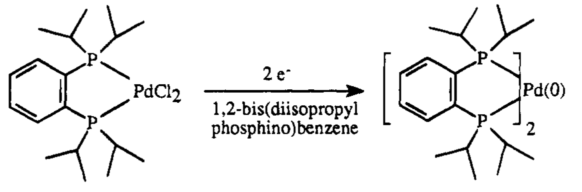
Figure 5. Changes induced in the absorption spectrum of **1** after 10 cycles of Heck reaction catalysis. Initial absorption (—); after 4 h (– –); after 24 h (–·–).

take place. The bis[1,2-bis(diisopropylphosphino)benzene]palladium(0) generated by electrochemical reduction of 1 equiv of **1** in the presence of 1 equiv of 1,2-bis(diisopropylphosphino)benzene (eq 4) is at least a thousand times less catalytically active than **1** in either its Pd(II) or Pd(0) oxidation state. The loss of catalytic activity in the 2:1 Pd(0) complex may be attributed to steric inhibition,[32] with the highly sterically hindered

Table 2. XPS Analyses of Polymer-Supported Pd(II) Catalyst 2

	3 $d_{5/2}$ (eV)
polymer-supported Pd(II) catalyst (before the Heck arylation)	337.8
polymer-supported Pd(II) catalyst (after 200 catalytic cycles)	337.7
Pd metal	335.2[a]
$(Ph_3P)_2PdCl_2$	335.2[a]
$(Ph_3P)_4Pd(0)$	336.2[a]

[a] From ref 31.



(4)

1 2:1 Pd(0) complex

bisphosphine ligands effectively blocking Pd from attack by the aryl halide.

Loss of Catalytic Activity of Monomeric Pd(II) Complex 1. One possible explanation for the observed differences in turnover number between these catalysts is the ease of deactivation (by disproportionation and/or dimerization) of the catalytic metal complex under homogeneous conditions. The irreversibility of the cyclic voltammograms shown in Figure 1 imply that the Pd(0) complexes are not chemically stable in the absence of a redox-mediated reaction. Aggregation and precipitation of palladium metal is known to deactivate $Pd(OAc)_2/PPh_3$ during the Heck reaction.[18] The weak coordination ability of the monodentate triphenylphosphine ligand may contribute to this instability. In contrast, the stronger coordination by the bidentate ligand 1,2-bis(diisopropylphosphino)benzene when attached to a rigid polymer backbone obviates this problem. This suggestion also explains the observed concentration dependence of catalytic turnover number, with aggregation becoming a proportionately more serious problem for the homogeneously dispersed catalysts at higher concentrations. Similarly, a slow diffusion rate for association of the reactants with the catalytically active site under heterogeneous conditions may contribute to the initial slow reaction rate for polymer-supported Pd(II) catalyst **2**.

This deactivation probably involves the aggregation of reactive Pd(0) complexes, either by disproportionation or dimerization, because strong interaction between these unsaturated Pd(0) complexes can be expected under homogeneous conditions. Aggregation may involve formation of a highly sterically hindered, less reactive 2:1 Pd(0) complex between 2 equiv of 1:1 Pd(0) complex (eq 5). The resulting Pd(0) cluster, lacking ligand stabilization, readily precipitates.[33] Strong evidence to support this dimerization derives from the observation, based on ultraviolet absorption, of the formation of $(L_2)_2Pd(0)$ during the reaction. Thus, two coordinatively unsaturated Pd(0) complexes can interact strongly with each other under homogeneous conditions, whereas this intermolecular interaction is greatly diminished by immobilization onto the matrix-like polymer backbone under heterogeneous conditions, where the movement of the Pd(0) complex is frozen and the interaction between two activated palladium species is avoided. This deactivation pathway (eq 5) inhibits the formation of catalytically active species under homogeneous conditions and causes a long induction period and a slow reaction rate with the monomeric Pd(II) complex **1**.

$$2L_2Pd(0) \rightleftharpoons (L_2)_2Pd(0) + \text{"Pd(0)"} \qquad (5)$$

L = 1,2-bis(diisopropylphosphino)benzene

Conclusions

By incorporating a bidentate phosphine ligand onto a polystyrene backbone, we have developed a Heck catalyst which has the following characteristics: (1) high turnover number; (2) easy recyclability without loss of catalytic activity; (3) moderate efficiency (reaction rate is somewhat slower than with $Pd(OAc)_2/PPh_3$); (4) easy separation of product from the catalyst; and (5) a stability sufficient enough for handling in air. Dimerization of the reactive Pd(0) sites, which may occur during coupling under homogeneous conditions, is suppressed with the polymer-supported palladium catalyst.

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