Fluorous Phase Soluble Palladium Nanoparticles as Recoverable Catalysts for Suzuki Cross-Coupling and Heck Reactions

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1,5-Bis(4,4′-bis(perfluorooctyl)phenyl)-1,4-pentadien-3-one stabilizes palladium(0) nanoparticles (transmission electron microscopy) formed in the reduction of palladium dichloride with methanol. These palladium colloids are soluble in perfluorinated solvents, and they are efficient recoverable catalysts for Suzuki cross-couplings and Heck reactions under fluorous biphasic conditions.

Introduction

Many efforts have been devoted in the past decade to the preparation, structure determination, and possible applications of metal nanoparticles.[1] One important application is as catalysts due to their large surface area. Several approaches have been reported[1] for their preparation, such as chemical reduction, thermal decomposition, metal vapor deposition, UV photolysis, sonochemical decomposition, and electrochemical synthesis. Among them, the most generally used is the reduction of metal salts by a suitable reducing agent in the presence of stabilizers, which adsorb to the particle surface, control the particle size, and prevent agglomeration. In the case of monometallic or bimetallic nanoparticles involving palladium, several reducing agents (hydrazine, β-cyclodextrine, hydrogen, alcohols, polymethylhydrosiloxane, sodium borohydride, tetraalkylammonium hydrotriorganoborates) and stabilizing agents (ionic and nonionic surfactants, polymers, dendrimers, β-cyclodextrines and thiolated β-cyclodextrines, solvents such as ethers and thioethers, other nitrogen, phosphorus, and sulfur based ligands) have been reported (vide infra). These colloidal particles, with varying sizes ranging from 0.9 to 120 nm, have been used mainly in hydrogenation reactions.[2] The reduction of hydrogen carbonate to formate,[3] several oxidative processes,[4] and hydrosilation[5] have also been reported. Concerning palladium-catalyzed carbon–carbon bond formation reactions, some articles appeared in the last five years on Heck reaction[6] and Suzuki cross-coupling.[6b,f,7] In general the colloidal catalyst was not recycled, with some exceptions on heterogeneous catalysis by

supported[2f,p,4c,5,6g,h] (charcoal, mesoporous silica, alumina, titanium dioxide, lyotropic liquid crystal polymer) palladium nanoparticles. Recently the first report on recyclable palladium nanoparticles on homogeneous catalysis has appeared.[2r] It concerns dendrimer-encapsulated fluorous phase soluble palladium nanoparticles

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active in the hydrogenation of alkenes. To enhance solubility of the catalyst-carrying poly(amidoamine) dendrimers in fluorous solvents, the terminal dendrimer amine groups were reacted with carboxylic acid end groups of perfluoropolyethers.

Fluorous biphasic solvent systems (FBS) hold promise in the field of recoverable metallic catalysts.[8] Several catalytic reactions have been achieved[8] in FBSs such as hydroformylation, hydrogenation, hydride reduction, hydroboration, hydrocarbon oxidations, alkene epoxidations, and more recently, conjugate additions under nickel catalysis.[9] Wacker oxidation of alkenes has been performed[10] in the presence of a palladium(II) bis-(diketonate) bearing perfluorinated chains. Palladium-catalyzed cross-coupling of organozinc bromides with aryl iodides,[11] palladium-catalyzed allylation reactions,[12] and palladium-catalyzed Heck reactions[13] involved the use of Pd(dba)$_2$ or palladium(II) acetate and polyfluorinated phosphines. Since phosphine ligands are readily oxidized to their corresponding oxides, the development of phosphine-free palladium catalysts would be worthwhile. Some years ago we reported the phosphine-free Suzuki cross-coupling between cinnamyl bromides and arylboronic acids catalyzed by Pd(dba)$_2$.[14] More recently, we have described[15] the catalytic properties of a 15-membered macrocyclic triolefin palladium complex, which can be successfully used and recovered in Suzuki couplings without addition of phosphines.

We present here the first fluorous phase soluble phosphine-free recoverable catalytic material involving palladium nanoparticles active in the Suzuki cross-coupling and Heck reactions.

Results

Our first idea was to develop a phosphine-free fluorous phase soluble Pd(0) catalytic system based on a dibenzylideneacetone derivative featuring perfluori-

Table 1. Molar Ratios of PdCl$_2$:1 and Analytical Data of the Materials

batch	PdCl$_2$:1	% C	% H	% Cl	% Pd[a]	mean particle size (nm)[b]	mp (°C)
1	0.53	32.15	1.17	<0.5	9.94	3.95	140–145
		32.19	1.09				
2	0.54	34.64	0.93	<1	6.03		158–163
		34.63	0.86				
3	4.65	27.42	0.72	<1	30.08	5.1	170
		27.50	0.76				
4	4.65	20.37	0.45	<0.8	37.64	4.52	166–172
		20.50	0.46				

[a] Determined by ICP. [b] Determined by TEM (see Figures 2 and 3).

nated chains. The ligand 1,5-bis(4,4′-bis(perfluorooctyl)-phenyl)-1,4-pentadien-3-one (dba-R$_f$), **1**, was prepared by aldol condensation[16] of 4-perfluorooctylbenzaldehyde[17] with acetone. Preparation of the complex Pd(dba-R$_f$)$_2$ was attempted following a procedure similar to that described[18] for the preparation of Pd(dba)$_2$, the classical dibenzylideneacetone complex of palladium(0). However, no Pd(dba-R$_f$)$_2$ was obtained. Instead a black solid (batch 1) was formed from ligand **1** and palladium dichloride using methanol as the reducing agent. Spectroscopic data (^{1}H NMR, IR) of this solid, in sharp contrast with that of Pd(dba)$_2$,[19] did not show the expected changes in the ligand signals due to metal complexation (olefinic signals should be shifted to higher fields and carbonyl stretching band should be shifted to lower frequency). These facts indicate the absence of metal coordination to the carbon–carbon double bonds. However, the material was soluble in perfluorinated solvents and showed catalytic activity. These observations led us to the idea that we had generated palladium nanoparticles stabilized by the fluorinated ligand, which renders them soluble in fluorous media. Transmission electron microscopy (TEM) confirmed the presence of such nanoparticles (4–5 nm).

Some other batches were prepared in a similar way, but using different molar ratios of palladium(II) chloride: **1**, as indicated in Table 1. If all the carbon content of the materials is due to compound **1**, we can calculate from elemental analyses the expected percentages of fluorine and oxygen. The sum of all percentages (C, H, F, Pd, O) gives approximately 100 (96.96 for batch 1; 99.40 for batch 2; 104.14 for batch 3; and 92.66 for batch 4), which is in accordance with our assumption that **1** is the only species stabilizing the palladium nanoparticles. From these data we can calculate the molar ratio **1**/palladium: 0.87 for batch 1; 1.53 for batch 2; 0.25 for batch 3; 0.15 for batch 4.

These materials were tested as catalysts in Suzuki[20] and Heck[21] reactions (Scheme 1). The conditions and yields for five consecutive runs are collected in Table 2.

Mixtures of organic-perfluorinated solvent were used in each case, in such a way that they are miscible when

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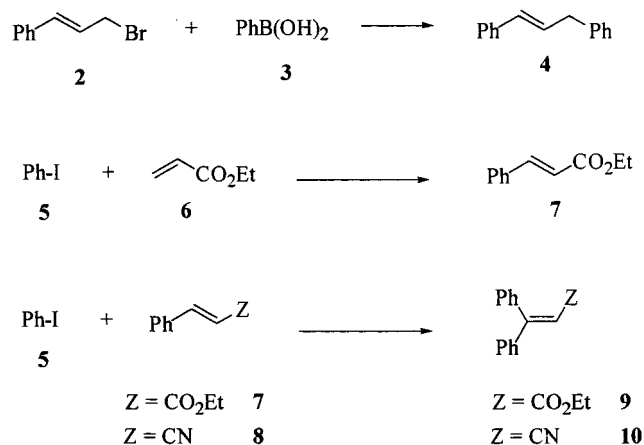(18) (a) Takahashi, Y.; Ito, T.; Sakai, S.; Y. Ishii, Y. *Chem. Commun.* **1970**, 1065–1066. (b) Rettig, M. F.; Maitlis, P. M. *Inorg. Synth.* **1990**, *28*, 110–111.
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Table 2. Experimental Conditions and Results for Suzuki and Heck Reactions of Scheme 1

catalyst	base	solvent	% mol of Pd	t (°C)	time (h)[a]	product (%)[b]
batch 1	K_2CO_3	$C_6H_6-C_8F_{17}Br$	9.2	reflux	15/7/7/7/7	**4** (90/80/76/75/78)
batch 2	Et_3N	$CH_3CN-C_8F_{17}Br$	4.3	80	24/48/48/72/48	**7** (49/65/70/71/67)
batch 3	Et_3N	CH_3CN-Galden HT 135	31.8	80	6/7/5/6/7	**7** (77/78/86/85/81)
batch 3	Et_3N	$CH_3CN-C_8F_{17}Br$	63.5	140	96/96/96/120/96	**9** (48/69/51/47/50)[c]
batch 4	Et_3N	$CH_3CN-C_8F_{17}Br$	39.5	140	96/120/120/120/168	**10** (58/60/64/30/25)[d]

[a] Reaction times for five consecutive runs. [b] Yields of isolated product for five consecutive runs. [c] The compound was isolated in the last run by column chromatography; the yields for the four precedent runs were determined by GC using 4-nitroveratrole as internal standard. [d] Yields of isolated product by column chromatography, **8** being also recovered (28/17/19/49/56%).

Scheme 1.   Suzuki and Heck Reactions Tested[a]

Ph⌒⌒Br + PhB(OH)₂ ⟶ Ph⌒⌒Ph

2   **3**   **4**

Ph-I + ⫶CO₂Et ⟶ Ph⌒CO₂Et

5   **6**   **7**

Ph-I + Ph⌒Z ⟶ (Ph)(Ph)C=Z

5

| Z = CO₂Et | **7** | | Z = CO₂Et | **9** |
| Z = CN | **8** | | Z = CN | **10** |

[a] See Table 2 for experimental conditions and results.

heated at the reaction temperature, but they form two layers at room temperature. The phases were separated by decantation after reaction, the organic phase containing the product was washed with water (Suzuki reaction) or 1 M HCl (Heck reactions), and the fluorinated phase containing the catalyst was reused directly four more times. In the Suzuki reaction leading to 1,3-diphenylpropene, **4**, and in the monoarylation of ethyl acrylate with iodobenzene to give ethyl cinnamate, **7**, the crude obtained from the organic phase after usual workup contained only the desired compound, which was identified by comparison of ^{1}H NMR and GC data with those of authentic samples. The reactions of ethyl cinnamate or cinnamonitrile with excess iodobenzene did not go to completion, and the desired final product (**9**[22] or **10**[23]) was accompanied by the departure alkene (**7** or **8**) and minor amounts of biphenyl. The products were separated by column chromatography, or in some cases the yields were determined by GC using an internal standard.

For the Suzuki reaction between cinnamyl bromide **2** and phenylboronic acid **3** we used potassium carbon-

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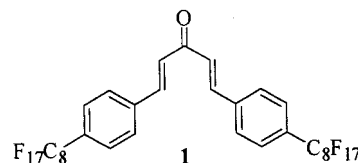
Figure 1. 1,5-Bis(4,4′-bis(perfluorooctyl)phenyl)-1,4-pentadien-3-one, **1**.
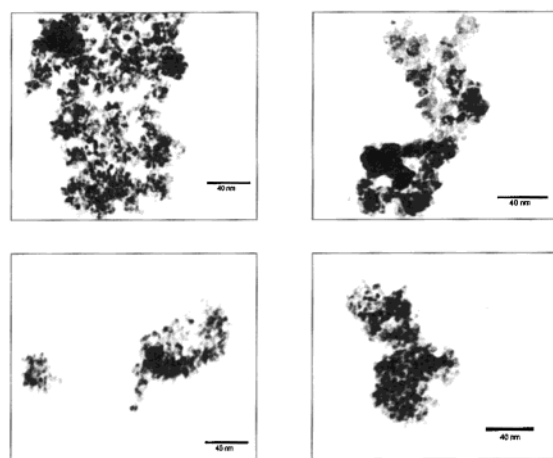
Figure 2. TEM images. Top left: batch 3; top right: batch 4; bottom left: batch 1; bottom right: batch 1 recovered after five cycles of Suzuki coupling. Bar is equivalent to 40 nm.

ate as base and catalytic material corresponding to batch 1. The weight of the catalyst introduced in the reaction corresponds to 9.2% molar palladium with respect to the limiting reagent. The Heck reaction between iodobenzene and ethyl acrylate was performed using triethylamine as base, a mixture of acetonitrile-perfluorooctyl bromide as solvent, and batch 2 catalytic material (the weight of material introduced in the reaction corresponds to a 4.3% molar palladium with respect to the limiting reagent). Better yields of ethyl cinnamate **7** were obtained in shorter times when we used the mixture acetonitrile−Galden HT 135 as solvent and batch 3 as catalytic material (the weight of material introduced in the reaction corresponds to a 31.8% molar palladium with respect to the limiting reagent). Heck reactions on 1,2-disubstituted olefins ethyl cinnamate and cinnamonitrile were also achieved with triethylamine and acetonitrile−perfluorooctyl bromide at higher temperature (140 °C), with partial recovery of the olefin. Batch 3 and batch 4 catalysts were used respectively, with % molar of palladium higher than before (63.5 and 39.5, respectively).

Preliminary results informed us that batch 3 produced compound **4** (Suzuki cross-coupling) in 60% yield with a turnover number (TON) of 206. The same batch
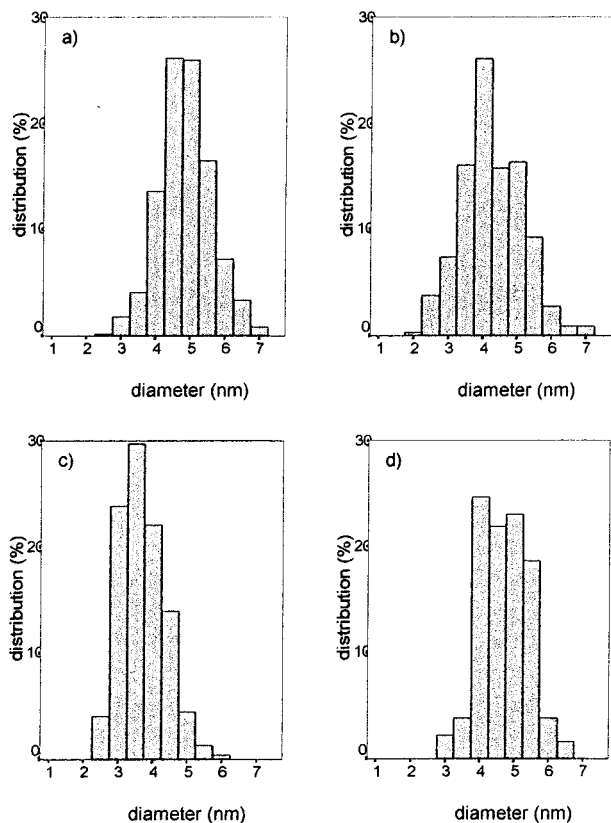
Figure 3. Particle size distributions: (a) batch 3 (296 particles); (b) batch 4 (163 particles); (c) batch 1 (111 particles); (d) recovered batch 1 after five cycles of Suzuki coupling (90 particles).

3 at 110−120 °C produced ethyl cinnamate, **7**, in 92% yield with a TON of 914.

Figure 2 shows TEM images for batches 1, 3, and 4 and also for the recovered material of batch 1 after five cycles of Suzuki coupling (mean particle size 4.94 nm). The particle size distributions are compared in Figure 3.

The possibility of stabilizing palladium nanoparticles by more simple fluorinated compounds is under study.[24]

Conclusion

We have developed a method to prepare new materials based on Pd nanoparticles soluble in perfluorinated solvents. They act as recoverable catalysts under fluorous biphasic conditions (five runs) in the Suzuki reaction between phenylboronic acid and cinnamyl bromide and in Heck reactions of ethyl acrylate, ethyl cinnamate, and cinnamonitrile with iodobenzene. To our knowledge this is the first case of the use of fluorinated compounds as stabilizers of palladium nanoparticles and also the first case of recoverable nanoparticle palladium catalysts under homogeneous conditions for the mentioned reactions leading to carbon−carbon bond formation.

(24) Under the specific experimental conditions above-described *p*-bisperfluorooctylbenzene and 1H,1H-perfluorooctylamine stabilize palladium nanoparticles, but perfluorooctylbenzene, *o*-bisperfluorooctylbenzene, *m*-bisperfluorooctylbenzene, *p*-perfluorooctylbenzaldehyde, 1H,1H,2H-perfluoro-1-decene, sodium perfluorononanoate, perfluorononanoic acid, and potassium perfluorooctylsulfonate do not.

Experimental Section

General Procedures. HRMS (FAB$^+$) was obtained at "S.C.A.I. Unidad de Espectrometría de Masas de la Universidad de Córdoba" using *m*-nitrobenzyl alcohol as matrix. Elemental analyses were determined at "Servei d'Anàlisi Química de la Universitat Autònoma de Barcelona". The % (w/w) of palladium in the batches of catalytic material was determined by inductively coupled plasma (ICP) at "Serveis Cientifico-Tècnics de la Universitat de Barcelona". The average of two determinations are given. The samples (0.050 g) were digested with nitric and perchloric acid in 250 mL Pyrex tubes equipped with condensers, then treated with warm *aqua regia* and diluted to 50 mL with deionized water (Milli-Q quality). For the determination the samples were diluted 1/100 with 2% HCl. Transmission electron microscopy (TEM) was carried out in "Servei de Microscopia Electrònica de la Universitat Autònoma de Barcelona" with an electronoptical magnification of 200 000:1 or 100 000:1. The colloidal material was placed on a specially produced structureless carbon support film with a thickness of 4−6 nm. The colloidal material was suspended in perfluorooctyl bromide, and a drop of this suspension was placed on the support film and dried in air.

4,4′-Bis(perfluorooctyl)dibenzylidenacetone (1). 4-Perfluorooctylbenzaldehyde[16] (1.227 g, 2.34 mmol) and acetone (0.070 g, 1.20 mmol) were added to a stirred solution of sodium hydroxide (0.234 g, 5.85 mmol) in water (15 mL) and ethanol (15 mL). The mixture was stirred at room temperature for 12 h, then it was partitioned between water and perfluorooctane. The fluorous phase was evaporated, affording **1** as a white solid (1.072 g, 1.002 mmol, 86% yield): mp 112−115 °C; IR (film) 1655, 1627, 1593, 1208, 1147, 985, 655 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.15 (d, J = 15.3 Hz, 2H), 7.66−7.83 (m, 10H); ^{1}H NMR (250 MHz, DMSO-d_6) δ 7.35 (d, J = 16.0 Hz, 2H), 7.66−7.79 (m, 10H); MS (70 eV, EI) *m/z* 1071 (M + 1, 1), 651 (M + 1-C$_7$F$_{15}$, 15), 166 (54), 152 (100), 151 (40), 141 (86); HRMS (FAB$^+$) calcd for C$_{33}$H$_{12}$F$_{34}$O 1070.0423; found 1071.0347 (corresponding to M + 1).

Preparation of Colloidal Palladium Catalysts. Batch 1 (Typical Procedure). A mixture of palladium(II) chloride (0.106 g, 0.598 mmol), sodium chloride (0.085 g, 1.453 mmol), and methanol (6 mL) was stirred at room temperature for 24 h. The solution was filtered through a plug of cotton, then diluted with methanol (total volume of 90 mL), and heated to 60 °C. 4,4′-Bis(perfluorooctyl)dibenzylidenacetone (**1**, 1.217 g, 1.138 mmol) was added to the warm and stirred solution and the stirring continued at this temperature for 15 min. Then sodium acetate (1.37 g, 16.7 mmol) was added, and the stirred mixture was left at room temperature for 1 h. The formed precipitate was filtered, and it was washed with methanol, water, and acetone, affording a black solid (0.518 g): mp 140−145 °C; IR (KBr) 1656, 1626, 1596, 1299, 1203, 1148, 1114, 1090, 653 cm^{-1}. Anal. Found: C 32.15 and 32.19, H 1.17 and 1.09, Cl <0.5, Pd 9.94.

All other batches were prepared by the same procedure under the palladium(II) chloride:**1** molar ratios of Table 1.

Suzuki Reaction Leading to 1,3-Diphenylpropene, 4. A solution of phenylboronic acid (0.074 g, 0.609 mmol) in benzene (5 mL) was added under nitrogen atmosphere to a stirred mixture of cinnamyl bromide (0.100 g, 0.508 mmol), anhydrous potassium carbonate (0.620 g, 4.49 mmol), batch 1 catalyst (9.94% w/w of Pd) (0.050 g, 0.0467 mmol of Pd), benzene (5 mL), and perfluorooctyl bromide (5 mL). The reaction mixture was refluxed until cinnamyl bromide was not detected by GC, then it was cooled to room temperature, and the two phases were separated by decantation. The organic layer was diluted with diethyl ether, it was washed with water and dried with anhydrous sodium sulfate, and the solvent was evaporated, affording **4** as an oil (0.089 g, 90% yield), which was characterized by comparison of GC and ^{1}H NMR data with those of an authentic sample. The perfluorous phase contain-

ing the catalyst was reused in the next reaction. This procedure is repeated four times more, with the results given in Table 2. At the end of the last cycle the fluorous phase is washed with water to remove suspended inorganic salts, then the catalyst separates as a solid at the interphase between aqueous and fluorous phases, and it is recovered by filtration.

Heck Reaction Leading to Ethyl Cinnamate, 7, with Batch 2 Catalyst and Acetonitrile−Perfluorooctyl Bromide as Solvent. A stirred mixture of ethyl acrylate (0.054 mL, 0.049 g, 0.497 mmol), iodobenzene (0.037 mL, 0.067 g, 0.33 mmol), triethylamine (0.092 mL, 0.067 g, 0.665 mmol), batch 2 catalyst (6.03% w/w of Pd) (0.025 g, 0.014 mmol of Pd), acetonitrile (4 mL), and perfluorooctyl bromide (4 mL) was heated at 80 °C in a closed reactor under nitrogen atmosphere (GC monitoring). After 24 h the reaction mixture was cooled to room temperature and the two phases were separated by decantation. The organic phase was washed with 1 M hydrochloric acid and dried with anhydrous sodium sulfate, and the solvent was evaporated, affording **7** as an oil (28 mg, 49% yield), which was identified by comparison of GC and ^{1}H NMR data with those of an authentic sample. The fluorous phase containing the catalyst was reused in the next reaction. The procedure was repeated four times more, with the results indicated in Table 2.

Heck Reaction Leading to Ethyl Cinnamate, 7, with Batch 3 Catalyst and Acetonitrile−Galden HT 135 as Solvent. A stirred mixture of ethyl acrylate (0.109 mL, 0.100 g, 1.00 mmol), iodobenzene (0.075 mL, 0.136 g, 0.667 mmol), triethylamine (0.185 mL, 0.135 g, 1.33 mmol), batch 3 catalyst (30.08% w/w of Pd) (0.075 g, 0.212 mmol of Pd), acetonitrile (4 mL), and Galden HT 135 (4 mL) was heated at 80 °C in a closed reactor under nitrogen atmosphere (GC monitoring). After 6 h the reaction mixture was cooled to room temperature, and the two phases were separated by decantation. The organic phase was washed with 1 M hydrochloric acid, it was dried with anhydrous sodium sulfate, and the solvent was evaporated, affording **7** as an oil (90 mg, 77% yield), which was identified by comparison of GC and ^{1}H NMR data with those of an authentic sample. The fluorous phase containing the catalyst was reused in the next reaction. The procedure was repeated four times more, with the results indicated in Table 2.

Heck Reaction between Ethyl Cinnamate and Iodobenzene with Batch 3 Catalyst. A stirred mixture of ethyl cinnamate (0.095 mL, 0.100 g, 0.57 mmol), iodobenzene (0.064 mL, 0.116 g, 0.57 mmol), triethylamine (0.236 mL, 0.173 g, 1.71 mmol), batch 3 catalyst (30.08% w/w of Pd) (0.128 g, 0.362 mmol of Pd), acetonitrile (4 mL), and perfluorooctyl bromide (4 mL) was heated at 140 °C in a closed reactor under nitrogen atmosphere (GC monitoring). After 48 h more iodobenzene was

added (0.064 mL, 0.116 g, 0.57 mmol), and the mixture was stirred at 140 °C for an additional 48 h. Then, it was cooled to room temperature and the two phases were separated by decantation. The organic phase was washed with 1 M hydrochloric acid and dried with anhydrous sodium sulfate, and the solvent was evaporated to afford a mixture of ethyl cinnamate, compound **9**, and a minor quantity of biphenyl. The yield of **9** determined by GC (4-nitroveratrol as internal standard) was 48%. The fluorous phase containing the catalyst was reused in the next reaction. The procedure was repeated four times more, with the results indicated in Table 2. In successive experiments 2 equiv of iodobenzene with respect to ethyl cinnamate was used from the very beginning. The crude mixture obtained from the organic phase after the last cycle was chromatographed through silica gel (230−400 mesh) with hexane and then 9:1 hexane−ethyl acetate as eluent to afford **9**[22] as an oil (0.073 g, 50% yield): IR (film) 1723, 1618 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.10 (t, $J = 7.3$ Hz, 3H), 4.04 (q, $J = 7.3$ Hz, 2H), 6.36 (s, 1H), 7.34 (m, 10H).

Heck Reaction between Cinnamonitrile and Iodobenzene with Batch 4 Catalyst. A stirred mixture of cinnamonitrile (0.14 mL, 0.145 g, 1.12 mmol), iodobenzene (0.239 mL, 0.437 g, 2.13 mmol), triethylamine (0.464 mL, 0.338 g, 3.35 mmol), batch 4 catalyst (37.64% w/w of Pd) (0.125 g, 0.442 mmol of Pd), acetonitrile (4 mL), and perfluorooctyl bromide (4 mL) was heated at 140 °C in a closed reactor under nitrogen atmosphere (GC monitoring). After 4 days it was cooled to room temperature, and the two phases were separated by decantation. The organic phase was washed with 1 M hydrochloric acid and dried with anhydrous sodium sulfate, and the solvent was evaporated to give a mixture of cinnamonitrile, compound **10**, and a minor quantity of biphenyl. Column chromatography through silica gel (230−400 mesh) with 19:1 hexane−ethyl acetate as eluent afforded **10** as an oil (133 mg, 58% yield) and cinnamonitrile (0.041 g, 28% recovery). The fluorous phase containing the catalyst was reused in the next reaction. The procedure was repeated four times more with the results indicated in Table 2. Compound **10**:[22b,23] IR (film) 2213, 1592, 1568 cm^{-1}; ^{1}H NMR (250 MHz, CDCl$_3$) δ 5.74 (s, 1H), 7.40 (m, 10H).