

MVS-derived palladium nanoparticles deposited on polydimethylphosphazene as recyclable catalysts for Heck-type reactions: Preparation, structural study, and catalytic activity

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Received 14 November 2006; revised 21 December 2006; accepted 21 December 2006

Available online 25 January 2007

Abstract

Palladium nanoparticles, obtained by the metal vapor synthesis (MVS) technique, were deposited on polydimethylphosphazene (PDMP). The Pd/PDMP system showed high catalytic activity in the Heck C–C coupling of iodobenzene and methyl acrylate, with greater activity than commercially available catalysts such as Pd(OAc)₂ and Pd on carbon. The Pd/PDMP is soluble in the reaction solvent, 1-methyl-2-pyrrolidinone, and can be quantitatively recovered at the end of the reaction by precipitation without loss of metal. When reused, the recovered Pd/PDMP retains its catalytic activity. A multinuclear (³¹P, ¹³C, ¹⁵N) solid-state NMR study identified and characterized the strong structural and dynamic modifications induced by Pd nanoparticles on PDMP. Moreover, solid-state NMR studies and HRTEM analyses, performed on the pristine catalyst and on the catalyst recovered after the reaction, highlighted the almost complete structural invariability of the Pd/PDMP, pointing out the high stability toward agglomeration of the palladium nanoparticles in such a system. Pd/PDMP in the presence of triphenylphosphine was also active in the alkylative cyclization of 7-octen-1-yne, an important C–C coupling reaction to obtain substituted 1,2-bis(alkylidene)cyclohexanes, which are valuable building blocks in fine chemistry.

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Keywords: Heck reaction; Alkylative cyclization; Palladium; Polydimethylphosphazene; Metal vapor synthesis; ³¹P, ¹³C, ¹⁵N solid-state NMR; HRTEM

1. Introduction

The arylation/vinylation of alkenes promoted by palladium-based catalysts, independently discovered by Mizoroki [1] and Heck [2] in the early 1970s and often reported as the Heck reaction, is one of the most important ways to form C–C bonds in organic synthesis [3]. For this reason, there currently is much interest in the Heck reaction in both academic and industrial groups.

Palladium compounds (i.e., Pd(acetate)₂, PdCl₂) with phosphines and palladium complexes (i.e., PdCl₂(PPh₃)₂, Pd(PPh₃)₂) are the catalysts generally used for this reaction [3]. In such systems, the phosphine ligands serve to stabilize the palladium zero species, generally considered the catalytically active form, and avoid the precipitation of palladium black [3,4]. They operate in the homogeneous phase and, to overcome the problems with such catalysts, especially for applications in large-scale synthesis (i.e., difficulty recovering products, catalyst instability, palladium metal present in the reaction mixture), numerous heterogeneous palladium catalysts have been prepared, including supported palladium compounds [5] and stabilized colloidal palladium [3c,6]. However, it was demonstrated that in many cases, the heterogeneous catalysts lose the palladium, which

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leaches in the reaction conditions from the surface into solution as highly active soluble palladium species [7]. Recently, it also has been proved that Pd in solution at the ppm level can catalyze the Heck reaction [8].

Only a few examples of heterogeneous palladium catalysts that do not leach have been reported in the literature. They concern palladium salts on zeolites, which resulted truly heterogeneous catalysts only in dependence on the catalyst pretreatment and on the base and solvent used [9], and palladium nanoparticles deposited on particular layered double hydroxides [10] or on suitable functionalized zeolites containing primary amino [11] and SH [12] groups. Recently, a catalyst consisting of palladium deposited on commercial polyvinylpyridine, prepared according to the metal vapor synthesis (MVS) technique, has been found to exhibit an appreciable catalytic activity in the Heck reaction with a possible partial contribution from supported active palladium species [13]. Thus, at present it appears to be of relevance to continue research into the preparation of new palladium-based catalysts, which ideally should combine high catalytic activity with easy separation of the products from the reaction mixture and complete recovery of the metal without contamination of the products.

In a recent paper [14], we reported new heterogeneous catalysts formed by depositing ruthenium nanoparticles on polyorganophosphazenes (POP). The POPs are polymers of general formula $[N=PR_2]_n$ that have an inorganic backbone composed of alternating nitrogen and phosphorus atoms. POPs are very attractive supports for metals because of their particular physical and chemical properties [15]. In fact, they show high stability toward strong acids, bases, and aggressive chemicals; high thermal stability and flame resistance; and unusual flexibility, biocompatibility, and photosensitivity. The nitrogen atoms in the main chain are very basic and can bind metals [16]. The Ru on POP catalysts exhibited high catalytic activity in the hydrogenation of a wide range of unsaturated substrates under mild conditions [14]. In that study, the importance of POPs as supports was pointed out. Depending on the dispersing liquid, POPs can act as either insoluble or soluble supports, so it was possible to work in both the heterogeneous and homogeneous phases. Interestingly, in the latter case, the catalysts could be completely recovered by precipitation and reused without loss of activity. High-resolution transmission electron microscopy (HRTEM) analyses demonstrated high stability of the catalysts toward agglomeration [14].

Encouraged by these results, in this paper we have used polydimethylphosphazene (PDMP), the first member of the series of the polyalkylphosphazenes, as support for nanoparticles of palladium, obtained by the MVS technique. MVS involves vaporization in high vacuum of metals in presence of a large excess of weakly stabilizing organic solvents (e.g., aromatic hydrocarbons, olefins, THF, acetone) [17]. This technique allows the preparation of metal nanoparticles in the 2–8 ppm range, which can be considered “ligand-free” [18]. The particles can be deposited on organic and inorganic supports under very mild conditions (–40 °C to room temperature), thus avoiding the formation of large particles, which are generally less catalytically active, and giving rise to catalysts that do not need further ac-

tivation processes [18–20]. The resulting palladium on PDMP system (Pd/PDMP) was used as a catalyst in Heck reactions. The catalytic activity of such system was compared with that of some of the most commonly used supported and unsupported Pd catalysts, as well as other Pd catalysts prepared by the MVS technique. Solid-state NMR studies and HRTEM analyses also were performed on Pd/PDMP both before and after the catalytic tests, to investigate the stability of the system during the reactions.

2. Experimental

2.1. Materials and apparatus

All operations involving the MVS products were performed under a dry argon atmosphere. The co-condensation of palladium and the appropriate solvent was carried out in a static reactor as described previously [21]. The solvated Pd atom solutions were worked up under argon atmosphere using standard Schlenk techniques. The amount of palladium in the above solutions was determined by atomic absorption spectrometry (AAS) in a electrochemically heated graphite furnace with a Perkin–Elmer 4100ZL instrument. The limit of detection (lod) calculated for palladium was 2 ppb. Solvents were purified by conventional methods, distilled, and stored under argon. Iodobenzene, methyl acrylate, and palladium acetate were supplied from Aldrich and used as received. Triethylamine (from Aldrich) was distilled and stored over KOH pellets before use. Commercial carbon (Monarch 880, Cabot) with surface area 220 m²/g was used. Samples of palladium on carbon, 1 wt% Pd, were supplied by Chemi and Enghelard. Polydimethylphosphazene (PDMP) [14], 1-bromo-3-methyl-1,2-pentadiene [22], and 4-pentenyl magnesium bromide [23] were prepared according to procedures described in the literature.

The GLC analyses were performed on a Perkin–Elmer Auto System gas chromatograph, equipped with a flame ionization detector (FID), using a SiO₂ column (BP-1, 12 m × 0.3 mm, 0.25 μm) and helium as carrier gas. ¹H and ¹³C NMR spectra were measured on a Varian Gemini 200 spectrometer at 200 and 50.3 MHz, respectively, using chloroform-*d* as a solvent; chemical shifts are relative to internal Si(CH₃)₄.

All of the high-resolution solid-state NMR experiments were performed on a Varian InfinityPlus 400 double-channel spectrometer operating at Larmor frequencies of 399.89 MHz for ¹H, 161.88 MHz for ³¹P, 100.56 MHz for ¹³C, and 40.52 MHz for ¹⁵N. The spectrometer was equipped with two CP-MAS probes for rotors with an outer diameter of 3.2 and 7.5 mm. For all of the nuclei, the 90° pulses were 4.0–5.0 μs for the 7.5-mm probes and 2.0–2.5 μs for the 3.2-mm probes. All of the spectra were recorded by spinning the sample about an axis forming an angle of 54.74° with respect to the external magnetic field (MAS) at a frequency of 5500 Hz and using proton high-power decoupling conditions. The ¹H X cross-polarization (CP) spectra were recorded using a recycle delay of 5 s and contact times of 500 μs for X = ³¹P, 1 ms for X = ¹³C, and 2 ms for X = ¹⁵N. ¹H T₂-selective CP spectra were recorded with a 100-μs delay inserted between the ¹H 90° pulse and the

contact time, thus allowing the magnetization of proton nuclei with very short spin–spin relaxation times to dephase completely [24]. Direct excitation (DE) spectra were recorded by single pulse excitation for ^{31}P , whereas for ^{13}C , a depth pulse sequence [25] was used to suppress probe and rotor background signals; recycle delays of 3 and 60 s were used for ^{13}C and ^{31}P , respectively, which were found to allow the full recovery of nuclear magnetization equilibrium between two successive scans, thus giving quantitative spectra. The chemical shifts were referenced to 85% H_3PO_4 (^{31}P), TMS (^{13}C) and glycine (^{15}N) through the use of suitable external standards. All the spectra were recorded at $20.0 \pm 0.2^\circ\text{C}$.

Electron microscopy was done with a JEOL 2000EX microscope. Before being introduced into the instrument, the samples, in the form of film, were cooled to 77 K and crushed at this temperature. The obtained powders were ultrasonically dispersed in *n*-heptane, and a drop of the suspension was deposited on a copper grid covered with a lacy carbon film. Histograms of the particle size distribution were obtained by counting at least 300 particles onto the micrographs; the mean particle diameter (d_m) was calculated from the formula $d_m = \sum d_i n_i / \sum n_i$, where n_i is the number of particles of diameter d_i . The counting was carried out on electron micrographs obtained at 300,000 magnification, where Pd particles well contrasted with respect to the support were clearly detected. The graduation of the particle size scale was 1 nm.

2.2. Preparation of palladium catalysts

2.2.1. Preparation of the solvated Pd atoms

In a typical experiment, Pd vapor generated at 10^{-4} Pa by resistive heating of the metal (500 mg) in an alumina-coated tungsten crucible was co-condensed at liquid nitrogen temperature with a 1:1 mixture of mesitylene and 1-hexene (40 ml) in a glass reactor as described elsewhere [21]. The reactor chamber was heated to the melting point of the solid matrix (-40°C), and the resulting red-brown solution was siphoned and handled at low temperature ($-30/-40^\circ\text{C}$) with the Schlenk tube technique. The metal content of the solution was assessed by AAS. The metal-containing mesitylene/1-hexene solution (1 ml) was heated over a heating plate in a porcelain crucible, in the presence of *aqua regia* (2 ml), four times. The solid residue was dissolved in 0.5 M aqueous HCl, and the solution was analyzed by AAS. The palladium content of the solvated metal solution was 1.9 mg/ml.

The 1-methyl-2-pyrrolidinone Pd atom solution (palladium, 2.5 mg/ml) was likewise prepared by co-condensation of palladium and 1-methyl-2-pyrrolidinone vapors.

2.2.2. Preparation of palladium on polydimethylphosphazene, Pd/PDMP (1 wt% Pd)

The aforementioned brown mesitylene/1-hexene Pd atom solution (1.3 ml, 2.47 mg Pd) was added to a suspension of PDMP (247 mg) in mesitylene (20 ml). The mixture was stirred for 12 h at room temperature. The colorless solution was removed, and the light-brown solid was washed with pentane and dried under reduced pressure. The metal content of the Pd on

a PDMP catalyst (1 wt% Pd) was determined by AAS analysis, as reported in Section 2.2.1.

2.2.3. Preparation of palladium on carbon catalysts, Pd/C (1 wt% Pd)

First, the mesitylene/1-hexene Pd atom solution (1.5 ml, 2.85 mg Pd) was added to a suspension of carbon (285 mg) in mesitylene (20 ml). The resulting mixture was stirred for 48 h at room temperature and worked-up as reported in Section 2.2.2, furnishing the Pd on carbon catalyst containing 1 wt% Pd, as determined by AAS analysis.

Then, the 1-methyl-2-pyrrolidinone Pd atom solution (1 ml, 2.5 mg Pd) was added to a suspension of carbon (250 mg) in 1-methyl-2-pyrrolidinone (20 ml), and the resulting mixture was stirred for 4 days at room temperature. The colorless solution was removed, and the black solid was washed with toluene and successively with pentane and dried under reduced pressure. The metal content of the Pd on carbon catalyst (1 wt% Pd) was determined by AAS analysis, as reported in Section 2.2.1.

2.3. Catalytic reactions

2.3.1. Heck reaction between iodobenzene and methyl acrylate: General procedure

1-Methyl-2-pyrrolidinone (NMP) (5 ml), methyl acrylate (1 ml, 10 mmol), iodobenzene (0.63 ml, 5 mmol), anhydrous triethylamine (0.78 ml, 5 mmol), and the catalyst (containing 5×10^{-3} mg atom of Pd) were introduced under argon atmosphere into a 25-ml round-bottomed, two-necked flask equipped with a stirring magnetic bar, a bubble condenser, and a silicon stopper. The reaction mixture was magnetically stirred at 75°C . When needed, small samples of the reaction mixture were taken from the stoppered side neck. For GC analysis, the samples were treated with either water or 0.5 M aqueous HCl. The organic products were then extracted with diethyl ether, dried over dry sodium sulfate, and analyzed by GLC. The reaction was interrupted at the time reported in Table 1.

2.3.2. Recovering the Pd/PDMP catalyst and checking the activity of the liquid phase

In some cases, the Pd/PDMP catalyst was recovered at the end of the reaction by adding an excess of THF or diethyl ether at the cooled reaction mixture. The solid was separated by filtration (0.2- μm Teflon filter) and analyzed by AAS. The metal content was 1 wt% Pd, the same of the starting material, within the interval $\pm 2\%$. AAS analysis of the filtrate did not show the presence of palladium ($\text{lod} = 2$ ppb). The presence of active homogeneous species in the liquid phase was further checked. The filtrate was concentrated to the initial volume under reduced pressure, and fresh methyl acrylate (1 ml, 10 mmol), iodobenzene (0.63 ml, 5 mmol), and anhydrous triethylamine (0.78 ml, 5 mmol) were added to the resulting solution. The mixture was stirred for 24 h at 75°C . No reaction occurred, as shown by GLC analysis of the mother liquor.

Table 1
Reaction between iodobenzene and methyl acrylate to *trans*-methyl cinnamate, **3**, catalyzed by palladium on polydimethylphosphazene, Pd/PDMP, and other palladium catalysts^a

Run	Catalyst	Time (h)	Conversion (%) ^b	Specific activity ^c
1	Pd/PDMP 1%	1	78	780
		4	>95	
2	Pd/PDMP 1%	1	75	750
	Recovered from run 1	4	>95	
3 ^d	Pd/C 5%	5	69	138
4 ^e	Pd/C 5%	2	67	335
5 ^f	Pd/C 1%	2	62	310
	MVS			
6 ^g	Pd/C 1%	2	76	380
	MVS			
7	Pd(OAc) ₂	1	50	500
8 ^h	Pd/MH	3	49	16
9 ⁱ	Pd/NMP	2	61	305

^a Reaction conditions: iodobenzene 0.63 ml (5 mmol); methyl acrylate 1 ml (10 mmol); triethylamine 0.78 ml (5 mmol); 1-methyl-2-pyrrolidinone, NMP; (5 ml); catalyst 5×10^{-3} mg-atom Pd (unless otherwise stated); $T = 75^\circ\text{C}$.

^b GC conversion of iodobenzene.

^c Calculated as moles of iodobenzene converted/g-atom of metal per hour.

^d CHEMI product.

^e ENGHELARD product.

^f Catalyst obtained depositing metallic Pd from the mesitylene/1-hexene Pd atom solution, prepared by MVS technique, on carbon.

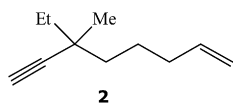
^g Catalyst obtained depositing metallic Pd from the 1-methyl-2-pyrrolidinone Pd atom solution, prepared by MVS technique, on carbon.

^h Mesitylene/1-hexene Pd atom solution, prepared by MVS technique; catalyst 5×10^{-2} mg-atom Pd.

ⁱ 1-Methyl-2-pyrrolidinone (NMP) Pd atom solution, prepared by MVS technique.

2.3.3. Alkylative cyclization of 3-ethyl-3-methyl-7-octen-1-yne

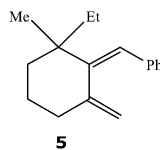
2.3.3.1. Synthesis of 3-ethyl-3-methyl-7-octen-1-yne, 2 4-Pentenylmagnesium bromide, 0.36 N in THF (37 mmol), was added to a stirred solution of ZnCl₂ (5.1 g, 37 mmol) in THF (20 ml) at 0 °C. The mixture was stirred for 30 min at room temperature, then treated (at -10 °C) with a solution of 5.6 mmol of CuCN 2LiCl prepared from LiCl (0.48 g, 11.2 mmol) and CuCN (0.50 g, 5.6 mmol) in THF (25 ml). Stirring was continued at 0 °C for 30 min, after which the reaction mixture was cooled at -70 °C, and 1-bromo-3-methyl-1,2-pentadiene (4.0 g, 25 mmol) was added over a period of 5 min. The cooling bath was removed, and the mixture was allowed to warm to room temperature while being monitored for completion by GLC. On completion (1 h), the reaction was quenched with saturated ammonium chloride. A standard ethereal workup and bulb-to-bulb distillation (10⁻² mm Hg) provided the pure enyne (2.98 g, 79%):



¹H NMR, δ : 0.97 (3H, t, $J = 7.4$ Hz, CH_3CH_2); 1.14 (3H, s, CH_3); 1.20–1.65 (6H, m, CH_2); 2.06 (2H, m, $\text{CH}_2\text{CH}=\text{CH}_2$); 2.07 (1H, s, $\text{HC}\equiv$); 4.98 (2H, m, $\text{CH}=\text{CH}_2$); 5.70–5.93 (1H, ddt, $J_{\text{trans}} = 17.1$, $J_{\text{cis}} = 10.2$, $J_{\text{vic}} = 6.6$ Hz, $\text{CH}=\text{CH}_2$).

¹³C NMR, δ : 9.0, 24.1, 25.9, 34.1, 34.2, 35.1, 40.5, 68.7, 90.9, 114.5, 138.8.

2.3.3.2. Reaction between iodobenzene and 3-ethyl-3-methyl-7-octen-1-yne promoted by Pd(OAc)₂: General procedure In a sealed Carius tube, the appropriate solvent (toluene or NMP, 10 ml), triphenylphosphine (3:1 regarding palladium) and triethylamine (10 ml) were added to Pd(OAc)₂ (5–10 mol% to the acetylenic substrate) and the mixture was magnetically stirred, under argon atmosphere, for 30 min at room temperature and for 5 min at 100 °C. After cooling at room temperature, the mixture was treated, under argon, with iodobenzene (0.45 ml, 4 mmol) and 3-ethyl-3-methyl-7-octen-1-yne (300 mg, 2 mmol). The mixture was stirred at 100 °C for the required time and monitored by GLC and ¹H NMR; when needed, small samples of the reaction mixture were taken from the stoppered side neck. The mixture was subsequently cooled, extracted with hexane, and filtered on celite. The organic layer was washed with water up to neutrality, dried over dry sodium sulfate, and analyzed by GLC and GC-MS. After concentration under vacuum, the crude product was analyzed by ¹H NMR then purified by column chromatography on silica gel (*n*-pentane as an eluent), affording (Z)-1-benzylidene-2-methylidene-6-ethyl-6-methylcyclohexane, **5**, as a colorless oil:



¹H NMR, δ : 0.77 (3H, t, $J = 7.4$ Hz, CH_3CH_2); 1.08 (3H, s, CH_3); 1.15–1.30 (2H, m, $\text{CH}_2\text{—CH}_3$); 1.44–1.84 (4H, m, $\text{CH}_2\text{—CH}_2$); 2.20–2.50 (2H, m, $\text{CH}_2\text{C}=\text{}$); 4.46 (1H, dd, $J = 2.5$ and 1.2 Hz, $=\text{CH}_2$); 4.78 (1H, m, $=\text{CH}_2$); 6.14 (1H, s, $=\text{CHPh}$); 7.05–7.40 (5H, m, Ph).

¹³C NMR, δ : 7.97 (CH_3CH_2); 23.01 (CH_3); 24.38 (CH_2); 29.29 (CH_2CH_3); 31.39 (Cq); 37.33 ($\text{CH}_2\text{C}=\text{}$); 40.05 (CH_2); 112.68 ($=\text{CH}_2$); 121.74 ($=\text{CH}$); 125.67 (Ph); 127.66 (Ph); 128.88 (Ph); 138.80 (Ph); 145.82 ($\text{C}=\text{CHPh}$); 150.17 ($\text{C}=\text{CH}_2$).

IR, ν : 3078; 3021; 2962; 2875; 1633; 1494; 1459; 890.

MS, m/z (int. rel. %): 226 (M^+ , 6); 211 (15); 197 (100); 183 (11); 169 (57); 155 (53); 141 (55); 128 (32); 115 (41); 105 (10); 91 (32); 77 (17); 55 (17); 39 (39).

2.3.3.3. Reaction between iodobenzene and 3-ethyl-3-methyl-7-octen-1-yne promoted by supported palladium catalysts: General procedures

(a) *Pd/C as a catalyst.* In a sealed Carius tube, a mixture of iodobenzene (4 mmol), triethylamine (10 ml), Pd/C (1%), obtained depositing on carbon Pd nanoparticles from the 1-methyl-2-pyrrolidinone Pd atom MVS solution (0.1 mmol) and eventually triphenylphosphine (0.3 mmol) in NMP as a solvent (10 ml), was magnetically stirred under argon atmosphere for 1 h at 100 °C. After cooling at room temperature, the mixture was treated under argon with 3-ethyl-3-methyl-7-octen-1-yne (2 mmol), stirred at 100 °C for the required time, monitored by GLC and ¹H NMR, and worked up as reported above.

(b) *Pd/PDMP as catalyst.* In a sealed Carius tube, the catalyst (0.02 mmol) in NMP (10 ml) was stirred at room temperature until it was dissolved (30 min). Iodobenzene (4 mmol), triethylamine (10 ml), 3-ethyl-3-methyl-7-octen-1-yne (2 mmol), and eventually triphenylphosphine (0.06 mmol) were successively added under argon atmosphere to the catalyst solution. The obtained mixture was magnetically stirred at 100 °C for the required time, monitored by GLC and ¹H NMR, and worked up as specified earlier.

3. Results and discussion

3.1. Preparation of the polydimethylphosphazene supported palladium catalyst, Pd/PDMP

The polydimethylphosphazene-supported palladium catalyst, Pd/PDMP, was prepared by deposition of Pd nanoparticles, obtained by the MVS technique [17,18], on PDMP. Palladium atoms, produced by resistance heating of the metal under high vacuum, were co-condensed at low temperature (−196 °C) with a 1:1 (v/v) mixture of 1-hexene and mesitylene on the cooled wall of the reactor. On warming until the solid matrix melted (ca. −30 °C), a brown solution known as a solvated palladium atoms solution, containing palladium atoms and/or palladium nanoclusters, which are soluble and stabilized by the excess of the organic solvents acting as weakly coordinating ligands [17], was obtained. The solvated palladium atoms solution behaved as a source of metal nanoparticles. When the solution was allowed to warm to ambient conditions in the presence of PDMP, the nanoclusters agglomerated with subsequent deposition of palladium nanoparticles on PDMP (Scheme 1).

3.2. Palladium on polydimethylphosphazene, Pd/PDMP, as a catalyst in Heck-type reactions

3.2.1. Reaction between iodobenzene and methylacrylate

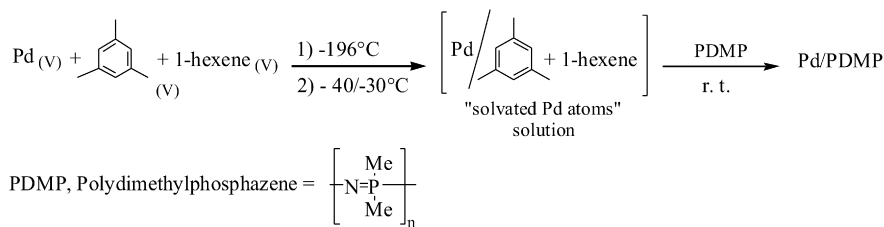
The catalytic activity of the Pd/PDMP system was examined in the C–C coupling reaction of iodobenzene, **1**, and methyl acrylate, **2**, used as a standard reaction (Scheme 2). Its catalytic

activity was also compared with that of commercially available catalysts, such as palladium on carbon and palladium acetate, that are widely used in the Heck reaction [3], as well as with that of homogeneous and carbon-supported palladium systems suitably prepared using the MVS technique.

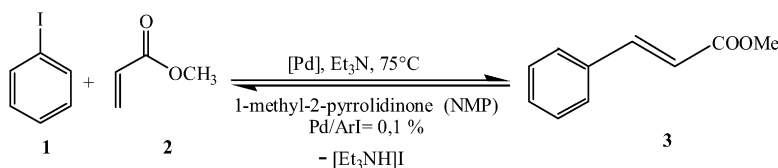
The reaction was performed at 75 °C in 1-methyl-2-pyrrolidinone (NMP), using an excess of **2** with respect to **1** (molar ratio **2**/**1** = 2) to avoid the formation of twofold coupling byproducts [3a]. Triethylamine was used as a base; it reacts with the hydriodic acid formed in the course of the reaction, thus shifting the equilibrium toward the products. *Trans*-methyl cinnamate, **3**, was formed selectively. The results obtained are reported in Table 1.

Because the PDMP is soluble in NMP, the catalyst dissolved completely, and the reaction proceeded in a phase that appears homogeneous. The reaction was very fast; in fact, the conversion was 78% after 1 h (run 1) and became almost quantitative after 4 h (≥95%, run 1). The catalyst can be recovered from the reaction mixture by precipitation with diethyl ether or THF and reused, with the catalytic activity remaining unchanged (run 2). The recycle test was repeated four times, and no significant reductions in catalyst activity and selectivity were observed. Interestingly, Pd/PDMP was more active than commercially available samples of Pd on carbon, which were insoluble in the reaction mixture (runs 3 and 4), as well as of other Pd on carbon samples prepared through the deposition of Pd nanoparticles, obtained by the MVS technique from mesitylene- or 1-methyl-2-pyrrolidinone palladium atom solutions, on the support (runs 5 and 6, respectively). Pd/PDMP is also more active than soluble catalysts, such as the commercially available palladium acetate (run 7), widely used in Heck reactions [3], and the MVS-derived mesitylene/1-hexene palladium atom solution (Pd/MH) and 1-methyl-2-pyrrolidinone palladium atom solution (Pd/NMP) (runs 8 and 9). Thus the high catalytic activity of the Pd/PDMP system is evident.

It is now well established that a key feature of supported palladium catalysts used in the Heck reaction is the leaching of metal into the reaction mixture [7]. Consequently, from a catalytic standpoint, the process becomes homogeneous, and from a practical standpoint, catalyst separation and recycling become



Scheme 1.



Scheme 2.

inconvenient problems. For these reasons, we have examined the leaching of the metal from the Pd/PDMP catalyst at the end of the reaction. AAS showed that the metal content of the solid obtained by precipitation with diethyl ether (Scheme 3, step a) was 1 wt% Pd, the same as that the starting material, within the interval $\pm 2\%$. The behavior of the mother liquor was also examined (Scheme 3, step b). First, AAS revealed no palladium content. In addition, as a further test for the presence of active metal in the recovered solution, no reaction was observed on adding fresh iodobenzene, methyl acrylate, and triethylamine and heating at 75 °C, for up to 24 h (Scheme 3, step c).

These results appear to be particularly important for the use of the Pd/PDMP catalyst in Heck reactions considering the high catalytic activity of such a system and the complete recovery of the metal during the precipitation process. In contrast, according to Ref. [7], we observed that the carbon-supported catalysts used in runs 3–6 release into the liquid phase substantial amounts of the metal as soluble palladium species that are not recaptured from the support at the end of the reaction. For example, in the reaction catalyzed with Pd/C 1% derived from the MVS 1-methyl-2-pyrrolidinone Pd atom solution (run 6), we found that the leaching started immediately and that 40% of the total palladium was present in solution after 2 h and 60% at the end of the reaction (after 4 h).

3.2.2. Alkylative cyclization of 3-ethyl-3-methyl-7-octen-1-yne

The foregoing results prompted us to use the Pd/PDMP catalyst in C–C coupling reactions of particular relevance in

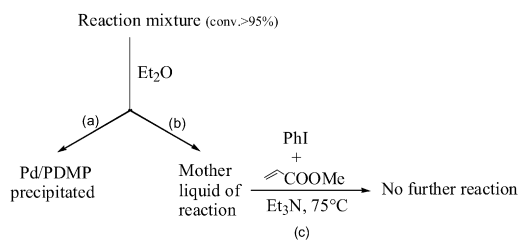
organic chemistry, such as 6-exo-trig alkylative cyclization of 1,7-enynes, which provide a simple strategy to substituted 1,2-bis(alkylidene)cyclohexanes possessing the R substituent stereospecifically Z (Scheme 4) [26,27]. 1,2-Bis(alkylidene)cycloalkanes are valuable building blocks for further structural elaboration as in the construction of steroids and related compounds [27,28].

The reaction of iodobenzene, **1**, with 3-ethyl-3-methyl-7-octen-1-yne, **4**, was chosen to be the reaction test. The enyne **4**, characterized by side chains in the α position next to the triple bond, was obtained via a cross-coupling process between 1-bromo-3-methyl-1,2-pentadiene and 4-pentenyl zinc chloride in the presence of 15 mol% of CuCN·2LiCl, according to the general procedure for the synthesis of α, ω -enyne reported earlier by us (Scheme 5) [23].

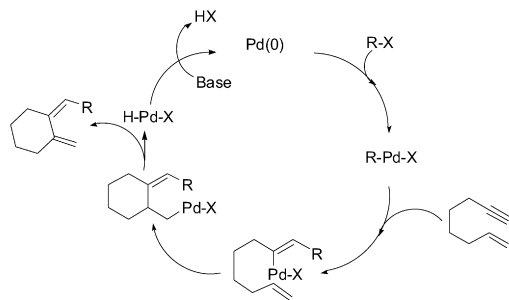
At first, to establish the feasibility of the alkylative cyclization, we subjected a mixture of the enyne **4** and excess iodobenzene to 10 mol% Pd(OAc)₂ and 30 mol% triphenylphosphine in 1:1 toluene-triethylamine at 100 °C, in accordance with the Trost protocol [27], as reported in Table 2. The reaction, carefully monitored by GC, gave a complete substrate conversion after 6 h, affording the desired alkylative cycloadduct **5** in 61% yield (run 10), together with a complex mixture of byproducts deriving mainly from the isomerization and oligomerization of **5**, as shown by GC-MS analysis. Compound **5**, which appeared to be very sensitive toward decomposition during the reaction and workup, was obtained pure by elution on silica gel column (*n*-pentane as eluent) and fully characterized by spectroscopic methods; the Z stereochemistry was assigned by NOE ¹H NMR experiments.

The nature of the solvent exerted a dramatic influence on the reaction rate and, consequently, on the reaction selectivity. In fact, replacing toluene by NMP led to a considerable increase in the reaction rate, giving 87% conversion after 30 min at 100 °C, even when the run was carried out with lower amounts of the Pd(OAc)₂/PPh₃ catalytic system (run 11 vs run 10). In this case, **5** also was formed with high selectivity (93%); such selectivity decreased with increasing reaction time, probably for the instability of **5**, as evidenced earlier (run 11).

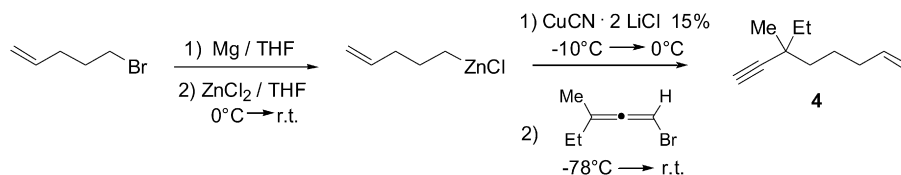
Performing the reaction with NMP as solvent, Pd/PDMP gave analogous satisfactory results as Pd(OAc)₂ in the same experimental conditions (run 12). Also in this case, compound **5** was obtained with very high selectivity (92%), although a 75% substrate conversion took 4 h. In principle, this slower reaction rate can be related to the smaller amounts of the Pd-catalyst used in the run (run 12 vs run 11). Once again the Pd/PDMP catalyst, recovered by precipitation with pentane, washed with toluene to remove PPh₃, and dried, was recycled, with unchanged catalytic activity. However, the presence of PPh₃ in



Scheme 3.



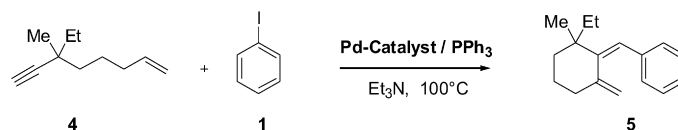
Scheme 4.



Scheme 5.

Table 2

Reaction between iodobenzene and 3-ethyl-3-methyl-7-octen-1-yne, **4**, catalyzed by palladium on polydimethylphosphazene, Pd/PDMP, and other palladium catalysts^a



Run	Catalyst (%) ^b	PPh ₃ (%) ^b	Solvent	Time (h)	Conversion (%) ^c	Selectivity (%) ^d
10	Pd(OAc) ₂ (10)	30	Toluene	6	100	61
11	Pd(OAc) ₂ (5)	15	NMP	0.5	87	93
12	Pd/PDMP 1% (1)	3	NMP	1	100	70
				4	75	92
13	Pd/PDMP 1% (1)	–	NMP	22	100	62
				22	12	12
14 ^e	Pd/C 1% (5)	15	NMP	24	96	65
15 ^e	Pd/C 1% (5)	–	NMP	5	33	85
				24	60	73

^a Reaction conditions: Iodobenzene 0.45 ml (4 mmol); compound **4** 300 mg (2 mmol); triethylamine 10 ml; solvent 10 ml.

^b Mol% with respect to the enyne **4**.

^c GC conversion of compound **4**.

^d Calculated by GC and ¹H NMR analyses.

^e Catalyst obtained depositing metallic Pd from the 1-methyl-2-pyrrolidinone Pd atom solution, prepared by MVS technique, on carbon.

the reaction mixture is probably essential to stabilize the catalytic species; as previously reported for Pd(OAc)₂ [26,27], the lack of phosphine dramatically slowed the reaction, with only 12% conversion after 22 h and very low selectivity obtained in compound **5** (run 13).

Samples of MVS Pd/C catalysts used for comparison as supported systems slowly promoted the reaction, giving in NMP and in the presence of PPh₃ an almost complete substrate conversion with 65% selectivity in compound **5** after 24 h (run 14). Interestingly, without phosphine, the reaction rate decreased further, but the selectivity remained satisfactory (>70%) during the run (run 15).

The results obtained indicate that Pd/PDMP is a very promising catalyst for use in such types of reaction, also considering the very low concentration of metal sufficient to produce high catalytic activity. This catalyst was much more active than the analogous MVS heterogeneous system in which the palladium is deposited on carbon. With respect to the soluble catalyst Pd(OAc)₂, Pd/PDMP was less active but could be easily recovered at the end of the reaction and reused with the same catalytic activity.

4. Structural studies of the Pd/PDMP catalyst

To obtain information on the structural features and the catalytic behavior of the Pd/PDMP catalyst, solid-state NMR studies and HRTEM analyses were performed on the starting catalyst as well as on the catalyst recovered after the catalytic runs.

4.1. Solid-state NMR studies

High-resolution solid-state NMR techniques were applied to explore the structural and dynamic modifications induced by the deposition of Pd atoms on PDMP. Given the nature of the

polymer, ¹³C, ³¹P, and ¹⁵N nuclei were investigated, providing information on the conformation and mobility of methyl side groups (¹³C) and the backbone (³¹P and ¹⁵N). In particular, selective techniques, based on either different pulse sequences or values of several acquisition parameters, were used to highlight the presence of phases with differing dynamic behaviors in the polymer. In this regard, it must be noted that, for instance, direct excitation (DE) spectra were recorded to give a quantitative answer (i.e., the integrals of the signals being proportional to the number of the corresponding nuclei). In cross-polarization (CP) spectra, the signals of nuclei in a rigid environment are usually enhanced, whereas in the “¹H T₂-selective” CP spectra, the signals arising from rigid phases are strongly reduced or completely suppressed.

4.1.1. ³¹P spectra

The ³¹P DE-MAS spectrum of PDMP (Fig. 1a) clearly arose from the superimposition of several peaks, corresponding to different chemical environments for the phosphorous nuclei, despite the presence of a single phosphorous atom per molecular unit. This behavior was previously reported for other polyphosphazenes and was ascribed to the coexistence of amorphous, crystalline, and/or interfacial phases [29–31]. Application of a spectral deconvolution procedure revealed the presence of four peaks resonating at 11.1, 14.2, 17.7, and 21.2 ppm (Table 3).

Several experimental observations concur in attributing the peaks at 14.2, 17.7, and 21.2 ppm to rigid phases (i.e., signal enhancement in CP spectra (Fig. 1b), larger chemical shift anisotropy, and short ¹H ³¹P CP time) and the one resonating at 11.1 ppm, the only peak not suppressed in the ¹H T₂-selective ³¹P CP-MAS spectrum (Fig. 1c), to a phase with a much higher molecular mobility [32]. A glass transition temperature of about –46 °C has been reported for PDMP [31], in agreement with the presence of a mobile amorphous phase at ambient temper-

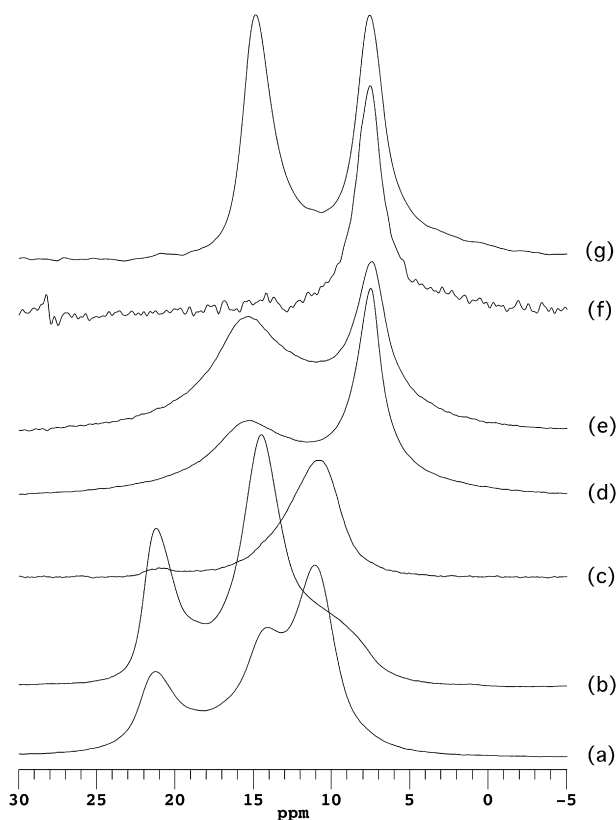


Fig. 1. Solid-state ^{31}P NMR spectra. DE-MAS spectra of (a) PDMP, (d) Pd/PDMP, (g) Pd/PDMP recovered after the catalytic run; CP-MAS spectra of (b) PDMP, (e) Pd/PDMP; ^1H T_2 -selective CP-MAS spectra of (c) PDMP, (f) Pd/PDMP.

Table 3
Results of the spectral deconvolutions of ^{31}P DE-MAS NMR spectra

Sample	Chemical shift (ppm)	Linewidth (Hz)	Intensity (%)	Type of phase
PDMP	11.1	465	43.5	Amorphous
	14.2	440	19.9	Crystalline (a)
	17.7	1120	22.9	Interfacial
	21.2	355	13.7	Crystalline (b)
Pd/PDMP	7.6	550	43.0	Amorphous
	15.0	1160	57.0	Rigid
Pd/PDMP recovered	7.6	385	40.7	Amorphous
	14.9	375	59.3	Rigid

ature. Moreover, two different crystalline modifications were clearly identified for PDMP by X-ray [33]. Combining these results, assignment of the four peaks present in the ^{31}P spectrum of PDMP can be attempted; the peak at 11.1 ppm undoubtedly arose from the amorphous phase, whereas those at 14.2 and 21.2 ppm, exhibiting a small line width, should correspond to two crystalline phases, referred to herein as “a” and “b,” respectively. The broader peak resonating at 17.7 ppm could be ascribed to a rigid interfacial phase, in agreement with previous studies on polyphosphazenes [34]. The percentage of ^{31}P nuclei belonging to the four different phases can be calculated from the sum of the integrals of the central peaks and the corresponding spinning sidebands of the ^{31}P DE-MAS spectrum, as reported in Table 3.

The ^{31}P DE-MAS spectrum of Pd/PDMP (Fig. 1d) indicates a drastic change in the chemical environments of all of the ^{31}P nuclei. Indeed, only two peaks can be seen present in the spectrum, resonating at 7.6 and 15.0 ppm. From the ^{31}P CP-MAS- and ^1H T_2 -selective CP-MAS spectra (Figs. 1e and 1f, respectively), the peak at 7.6 ppm can be easily assigned to a mobile amorphous phase, and the peak at 15.0 ppm can be assigned to a rigid one. Thus, the introduction of Pd nanoparticles in the polymer strongly affected the structural properties of the amorphous phase, with the corresponding ^{31}P peak experiencing a shift of 3.5 ppm toward lower frequencies, already observed for Ru-doped PDMP [31], and attributable to an increase of the conformational disorder of the amorphous phase [29,35]. Moreover, the rigid phases were strongly modified by the presence of Pd nanoparticles; a single rigid phase was now observed, with a chemical shift much more similar to the PDMP crystalline phase a but with a larger line width, similar to that of the PDMP peak previously assigned to an interfacial phase. On the other hand, the total amount of amorphous and rigid phases did not change with respect to the pristine polymer (see Table 3). In this regard, it is noteworthy that the increase in the intensity ratio between the CP signal due to the mobile phase and those arising from the rigid phases, observed in passing from PDMP to Pd/PDMP, can be attributed to a change in the nuclear parameters affecting the CP process (^1H ^{31}P CP time and ^1H spin-lattice relaxation time in the rotating frame) [32].

Finally, comparing the ^{31}P DE-MAS spectra of Pd/PDMP and the sample recovered after the catalytic run (Figs. 1d and 1g, respectively) indicates that no sensible structural changes occurred for the polymer during the catalytic reaction. Two peaks remained in the spectrum of the recycled sample resonating at 7.6 and 14.9 ppm, with integrals very similar to those of Pd/PDMP. However, the dynamic environments of the two phases likely experienced a sensible change, as suggested by the observed line narrowing, which was particularly noticeable for the rigid phase (see Table 3).

4.1.2. ^{15}N spectra

Natural abundance ^{15}N CP-MAS spectra were also recorded for PDMP and Pd/PDMP samples (see Figs. 2a and 2b, respectively). Solution-state ^{15}N NMR was recently used to investigate the metal-ion complexation of ^{15}N -labeled polyphosphazenes [36], but to the best of our knowledge, the present work is the first report of ^{15}N solid-state NMR spectra of polyphosphazenes in the literature.

The very low sensitivity of ^{15}N nuclei precludes obtaining spectra with a good signal-to-noise ratio even with very long acquisition times (3–5 days for the spectra of Fig. 2). However, some signals could be clearly distinguished; the spectrum of PDMP showed an intense signal at 55.2 ppm and two smaller peaks at about 48 and 37 ppm with intensity only slightly larger than noise. In Pd/PDMP, similar signals could be recognized; now the most intense peaks were at 38.5 and 47.4 ppm, whereas that at 55.2 ppm was almost null. Even though a detailed interpretation of these data is probably premature at this stage, it is clear that the spectral differences indicate a noticeable change in the structural properties of PDMP due to interaction

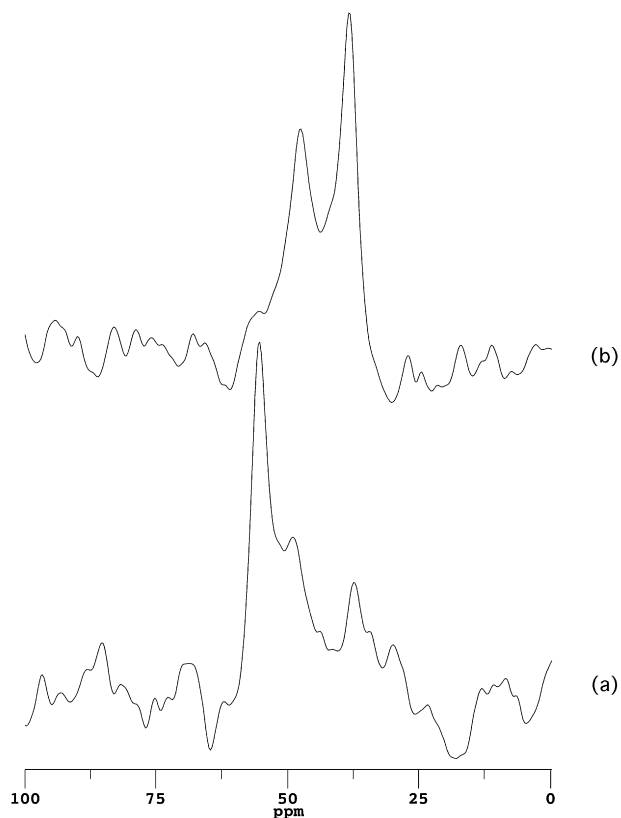


Fig. 2. Solid-state ^{15}N CP-MAS NMR spectra of (a) PDMP, (b) Pd/PDMP.

with Pd nanoparticles, in full agreement with the ^{31}P observations. The ^{15}N peak at 38.5 ppm possibly can be assigned to the amorphous phase, because its intensity sensibly increased when passing from PDMP to Pd/PDMP, in agreement with what was observed in the corresponding ^{31}P CP-MAS spectra (see Figs. 1b and 1e), whereas the peaks at about 47 and 55 ppm could be ascribable to the two crystalline phases *a* and *b*. Unfortunately, in this case, the extremely low sensitivity of ^{15}N nuclei prevents the acquisition of quantitative DE-MAS spectra.

4.1.3. ^{13}C spectra

The ^{13}C DE-MAS spectrum of PDMP, reported in Fig. 3a, comprised two signals, resonating at about 23 ppm and separated by 90 Hz, due to the J-coupling between the methyl carbons and the neighboring ^{31}P nuclei. It must be noted that, in contrast to what was observed in the ^{31}P DE-MAS spectrum, here no ^{13}C signals can be distinguished for the different phases, indicating that the chemical environments, and thus the conformational properties, of the methyl groups were very similar in the different amorphous and crystalline phases in PDMP. This disagrees somewhat with the observation reported by Meille et al. [37] of two different ^{13}C doublets for PDMP. In that case, however, no ^{31}P spectra were reported, and thus the polymorphism of the two samples, which depend strongly on their thermal history [33], cannot be directly compared.

The ^{13}C DE-MAS spectrum of Pd/PDMP was more complex (Fig. 3b); application of a deconvolution procedure revealed the presence of an additional doublet, characterized by the same

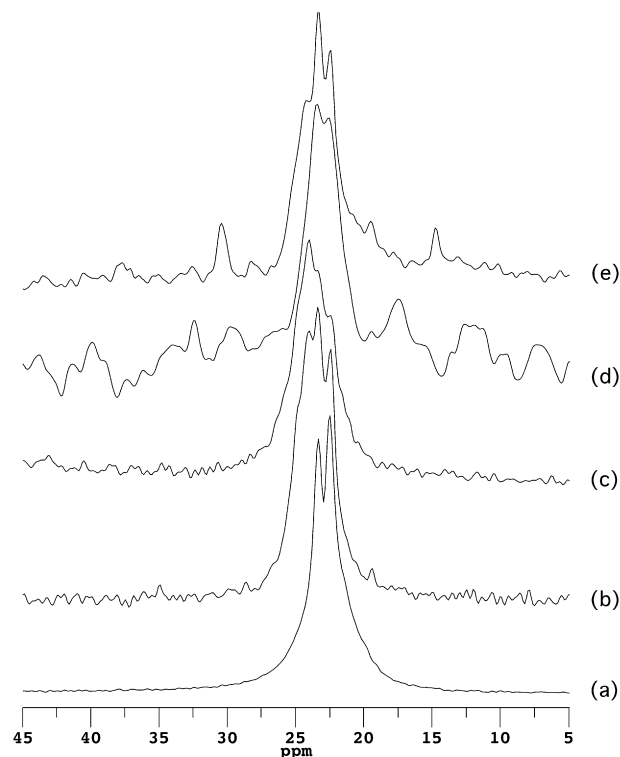


Fig. 3. Solid-state ^{13}C NMR spectra. DE-MAS spectra of (a) PDMP, (b) Pd/PDMP, (e) Pd/PDMP recovered after the catalytic run; (c) CP-MAS spectrum of Pd/PDMP; (d) ^1H T_2 -selective CP-MAS spectrum of Pd/PDMP.

J-coupling, and shifted by about 1.6 ppm toward higher chemical shifts with respect to the doublet already observed for PDMP. Thus, this additional doublet must be assigned to methyl carbons experiencing a slightly different chemical environment due to the presence of Pd nanoparticles. Moreover, the doublets at about 23 and 24.6 ppm can be assigned to methyl groups experiencing, respectively, fast and hindered motions, on the basis of ^{13}C CP-MAS (Fig. 3c) and ^1H T_2 -selective ^{13}C CP-MAS spectra (Fig. 3d). From the intensities of the peaks in the ^{13}C DE-MAS spectrum of Pd/PDMP (Fig. 3b) obtained from spectral deconvolution, the percentage of methyl groups experiencing a restricted motion was found to be 55%, in very good agreement with the percentage of rigid phase found from the ^{31}P DE-MAS spectrum.

No strong differences were observed between the ^{13}C DE-MAS spectra of Pd/PDMP (Fig. 3b) and of the sample recovered after the catalytic run (Fig. 3e), apart from a slightly lower intensity for the higher-frequency doublet. This indicates that the catalytic reaction did not substantially alter the structural and dynamic properties of the PDMP methyl groups.

4.2. HRTEM analyses

HRTEM was applied to investigate the size of Pd nanoparticles and their distribution on the support. In particular, the polymer was sufficiently transparent to the electron beam to allow the observation of metal particles as small as 1.0 nm, whereas those of smaller size escaped detection [38]. TEM (Fig. 4) revealed an image representative of the material be-

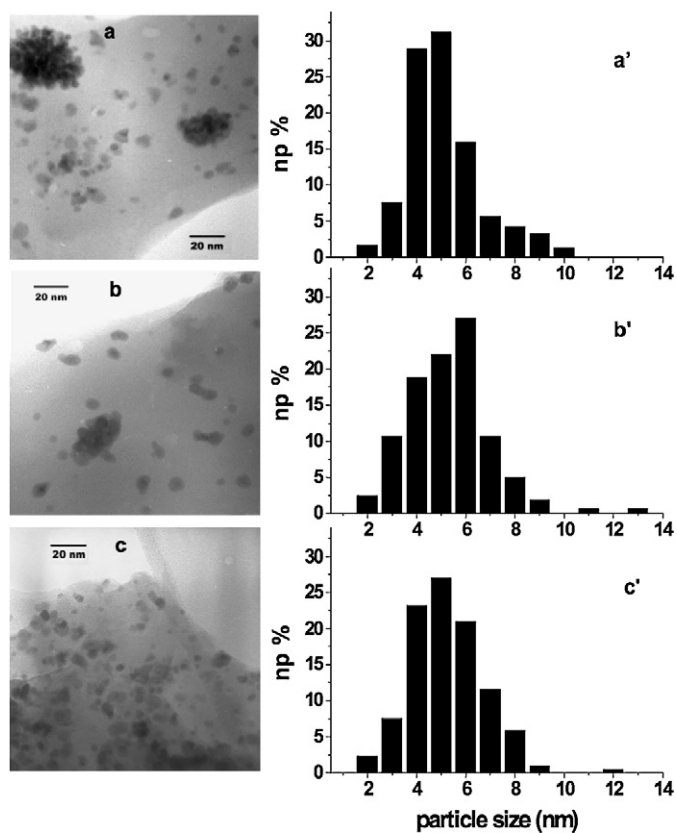


Fig. 4. HRTEM images representative of the Pd/PDMP catalyst and corresponding histograms of Pd particle size distribution in the following forms: (a, a') fresh; (b, b') after reaction; (c, c') after reaction in blank conditions.

for the reaction (panel a), with the corresponding histogram of the distribution of Pd primary particles (panel a'), that is, single particles or particles merged with other particles for less than 1/4 of their profile, contributing most of their surfaces to the total metal surface exposed to the reactants. It can be seen that most of the Pd particles, exhibiting roughly circular profiles, were quite well distributed on the support, although with some nonhomogeneity, whereas in some cases they were gathered in dense aggregates. In both forms, the particle size was 1.0–10 nm (mean, ca. 4.5 nm).

After the reaction of iodobenzene and methyl acrylate in NMP and subsequent reprecipitation, Pd particles still appeared mostly widely distributed on the polymer, with a decreased occurrence of dense aggregates (panel b), likely due to the dissolution/reprecipitation process of the material. With respect to the fresh catalyst, the metal particle size distribution exhibited a slight shift of the maximum and of the mean value (5.0 nm) toward larger values, as well as a slight broadening in the same direction (panel b'). Such features indicated the occurrence, in a quite limited way, of some sintering of the metal particles as a consequence of the reaction and/or the dissolution/reprecipitation process.

HRTEM also was performed on the sample recovered from a test of simulated reaction in the so-called "blank conditions." These measurements were performed without the reagents (iodobenzene and methylacrylate) by dissolution of Pd/PDMP in NMP at 75 °C and by precipitation with THF or diethyl ether.

The distribution of Pd particles on the support (panel c) appeared very similar to that obtained for the catalyst recovered from the actual reaction (panel b). Interestingly, the features of their size distribution (panel c') appeared to be intermediate between those of the catalyst before and after reaction in NMP, indicating also that the dissolution/reprecipitation process itself is able to promote some sintering of the metal particles.

5. Conclusions

The MVS technique has proven to be a simple and useful method for depositing palladium nanoparticles on PDMP under mild experimental conditions. Solid-state NMR showed that in the Pd/PDMP system, strong interactions are present between Pd nanoclusters and the polymer, giving rise to modifications in either conformational or dynamic properties of both the amorphous and crystalline phases of the polymer. HRTEM analyses showed that the Pd nanoparticles were generally well dispersed on the support, with a mean diameter of ca. 4.5 nm.

The Pd/PDMP system, used in the Heck C–C coupling of iodobenzene and methyl acrylate, exhibited very good catalytic activity, with greater activity than either the commercial soluble catalyst Pd(OAc)₂ or supported palladium on carbon catalysts commercially available or prepared by the MVS technique. In addition, the Pd/PDMP system, quantitatively recovered at the end of the reaction, retained its catalytic activity when reused. The high activity of Pd/PDMP probably arises from the ready dissolution of the polymeric system in the reaction solvent (1-methyl-2-pyrrolidinone), allowing the catalytic process to occur in a phase that appears to be homogeneous, in which the Pd nanoparticles can optimally exhibit their catalytic activity. The dissolution–precipitation processes of the catalyst before and after the catalytic reaction did not cause a substantial change in the NMR spectra and HRTEM analysis, demonstrating this catalyst's high stability toward agglomeration. These results also suggest that during the catalytic process, the Pd nanoparticles remained close to the polymer, probably interacting with the basic nitrogen atoms of the PDMP; in this way, after the precipitation process, a structural situation for the recovered catalyst similar to that for the pristine catalyst was obtained. The almost-complete structural invariability of the catalyst before and after the dissolution–precipitation processes appears to be of particular relevance considering that many heterogeneous catalysts, which leach in solution mononuclear Pd species, show a strong restructuring of the metal particles in recycled catalysts [6b,7b,39].

Pd/PDMP in presence of triphenylphosphine showed good catalytic properties in the alkylative cyclization of 3-ethyl-3-methyl-7-octen-1-yne. The alkylative cyclization of 7-octen-1-yne is an important C–C coupling reaction to get substituted 1,2-bis(alkylidene)cyclohexanes, which are valuable building blocks in the preparation of steroids and related compounds [27,28]. Even if it is less active than the system Pd(OAc)₂/PPh₃, Pd/PDMP is easily recovered from the reaction mixture and can be reused with the same catalytic activity. Moreover Pd/PDMP is considerably more active than the supported Pd/C catalyst prepared by MVS.

All of these results seem to be of relevance, and further studies are in progress to extend such reactions to other substrates to get compounds of relevance in fine chemistry. It is also worth highlighting the value of the polymeric support. In fact, the properties of polyorganophosphazenes can be easily modulated, changing the nature of the R groups bonded to the phosphorus in the $-\text{[N=PR}_2\text{]}_n-$ chain [15] with the possibility of obtaining supports with high solubility in other solvents generally used in Heck reactions [3].

Acknowledgments

The authors thank Dr. Emanuela Pitzalis (IPCF-CNR, Pisa, Italy) for AAS analyses, and Dr. Mario Gleria (ISTM-CNR, Padova, Italy) and Professor Maria Carla Gallazzi (Politecnico di Milano, Italy) for helpful discussions on PDMP properties. G.M. and L.B. thank the San Paolo Institute (Torino, Italy) for financial support. Partial support from the Ministero dell'Istruzione, Università e Ricerca (MIUR, Italy) is also acknowledged.

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