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Synthesis and characterization of functionalized titania-supported Pd catalyst deriving from new orthopalladated complex of benzophenone imine: catalytic activity in the copper-free Sonogashira cross-coupling reactions at low palladium loadings

Kazem Karami,*^a Sedigheh Abedanzadeh,^a Pablo Hervés,^b

^aDepartment of Chemistry, Isfahan University of Technology, Isfahan 84156/83111, Iran. E-mail: karami@cc.iut.ac.ir ^bDepartamento de Quimica Fisica, Universidade de Vigo, 36310 Vigo, Spain. E-mail: jherves@uvigo.es

Abstract

The present work describes the preparation of organically modified TiO₂-supported Pd catalyst originated from the new bezophenone imine-derived CN-palladacycle. The heterogeneous organic-inorganic hybrid catalyst system has been characterized by FT-IR, XRD, SEM, EDX, TEM and XPS techniques and exhibited good catalytic activity in the Sonogashira cross-coupling reactions of phenylacetylene with aryl halides under copper-, amine- and phosphine- free conditions, in conjunction with the ultra low catalyst Pd-loading. Significantly, the heterogeneous Pd catalyst allowed the reaction of phenylacetylene with aryl iodides to improve in excellent yields under very mild conditions using green solvent. Finally, the reusability of the supported Pd-complex was investigated by multiple reuses of the supported catalyst in subsequent Sonogashira cross-couplings.

Keywords: palladacycle, TiO₂, Sonogashira, catalyst, heterogeneous

1. Introduction

Nitrogen-containing palladacycles have received growing interest due to their applications in many areas including organic synthesis, optical resolution, design of new metallomesogens and antitumoral drugs, asymmetric synthesis, intermolecular aromatic C-H bond activation, synthesis and reactivity of organometallic complexes with biologically important ligands and drug delivery.¹⁻¹⁰ They show promising catalytic activities as a new family of homogeneous and heterogeneous palladium catalyst precursors,¹¹⁻¹⁵ due to the fact that N-donor ligands strongly donate electrons to the metal center, stabilizing various oxidation states of metals and subsequently influencing their reactivity.^{16, 17}

The Sonogashira coupling reaction of terminal alkynes with aryl halides is one of the most important methods which has been widely applied for the synthesis of natural products, pharmaceutical compounds and polymeric materials.¹⁸⁻²³ This reaction is generally catalyzed by homogeneous Pd complexes in the presence of toxic phosphine ligands, using copper salts as co-catalysts and amine as a solvent or base, under inert condition which has so many drawbacks.²⁴⁻²⁹ Consequently, there have been many efforts to introduce highly active and easily reusable catalysts through convenient Cu-, amine and phosphine- free methods under environmentally friendly conditions.

Supported palladium catalysts with high dispersion and narrow size distribution of palladium particles would address the limited practical application of homogeneous palladium catalysts and exhibit high activity, recyclability, low palladium loading and promising performances in the synthetic and industrial chemistry. In this regard, a wide variety of solid materials as heterogeneous Pd supports including active carbon,³⁰ mesoporous silica,³¹ metal oxides,³² zeolites,³³ magnetic materials,³⁴ hydrotalcites,³⁵ hydroxyapatite,³⁶ and organic–inorganic hybrid³⁷ have been investigated. However, many heterogeneous catalytic systems suffer from high palladium loading and/or low catalytic activities due to the palladium agglomeration and catalyst deactivation.³⁸

In this study, we report the synthesis and characterizations of a nitrogen-containing orthopalladated complex driving from bis[4-(dimethylamino)phenyl]methaniminium chloride (Auramine-O). In continuation of our interest in developing new supported catalysts,³⁹⁻⁴² herein we use

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a strategy to convert a homogeneous catalyst into a heterogeneous one through the stabilization of active Pd sites onto the large surface area of inorganic support by an organic spacer to create organicinorganic hybrid catalyst. A simple route is described to prepare a supported CN-palladacycle catalyst based on functionalized TiO_2 as a very suitable inorganic support. The resulting ultra Pd-loaded material was investigated as a catalyst for copper- and amine- free Sonogashira coupling reactions of phenylacetylene with aryl halides which were carried out in the absence of phosphine ligands under air. In the context of green chemistry, heterogeneous catalysis of Sonogashira coupling reactions of phenylacetylene with aryl iodides carried out in ethanol as a green solvent.

2. Results and discussions

2.1. Synthesis and characterization of chloro-bridged CN-palladacycle

Nitrogen-derived palladacycles, have attracted much attention as exciting catalyst precursors for cross coupling reactions due to their accessibility, thermal stability, slow decomposition and high catalytic activity. ^{11,43}

New dinuclear CN-palladacycle was synthesized through the reaction of palladium (II) acetate with bis[4-(dimethylamino)phenyl]methaniminium chloride (Auramine-O) in 1:1 molar ratio. The green orthopalladated chloro-bridged complex could be produced directly from the refluxing reaction of $Pd(OAc)_2$ with Auramine-O ligand in toluene for one 24 hours (method **A**). However, during the second method (**B**), the reaction of $Pd(OAc)_2$ with Auramine-O ligand was carried out in THF, at room temperature for higher reaction time of 72 hours to afford the pure product in higher yield. The dinuclear CN-palladacycle was characterized by IR and NMR spectroscopies. The elemental analysis result of the prepared compound was in good agreement with the calculated values.

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Auramine-O Dimeric Palladacycle (ADP)

Scheme 1 Synthetic method for new orthometallated compound. (i) toluene, Δ , 24 h; (ii) THf, 72 h.

As illustrated in Fig. 1, the FT-IR spectrum of Auramine-O ligand shows the peak at 1685 cm⁻¹ due to the C=N stretching vibration.⁴⁴ This band appears at the lower energies (1606 cm⁻¹) in the spectrum of synthesized dinuclear complex (Fig. 1b) indicating the coordination of the ligand to the metal. As clearly shown in Fig. 1a, the iminium salt displays strong, broad N-H stretching absorptions in the 2250 to 3000 cm⁻¹ region, where overlap with C-H absorption occurs. The lower frequency region of FT-IR spectrum shows the characteristic bands at 674 and 416 cm⁻¹ related to the v(Pd-C) and v(Pd-N) vibrations in the dinuclear complex, respectively (Fig 1b).^{45,46} These vibrational bands confirm the successful coordination of the CN-orthopalladation of Auramine-O ligand to the palladium(II) center by covalent interaction.

In the ¹H NMR spectrum, the signal related to the methyl protons of cyclometallated Auramine-O appears at 3.00 ppm. All of the ¹H NMR signals for the aromatic protons of the complex are shifted with respect to the parent iminium salt confirming the coordination of Auramine-O.



Fig. 1 FT-IR spectra of: (a) Auramine-O ligand, (b) dinuclear palladium complex (ADP) (c) TiO₂, (d) fresh TiO₂-supported Pd catalyst.

2.2. Synthesis and characterization of functionalized TiO₂- supported Pd catalyst

Organic-inorganic hybrid catalysts simultaneously have the advantage of easy separation and recovery of the heterogeneous catalysts in addition to homogeneous reaction conditions. They are composed of three components including support, organic spacer and an active center.^{47,48}

In order to design heterogeneous catalysts, solid supports containing nitrogen as donor atoms have been achieved special interest. Since N-donor ligands are air stable, less expensive and nontoxic, they can be used to replace phosphine groups and coordinate to the various transition metal complexes.

Due to the fact that inorganic supports like TiO_2 show advantages such as mechanical stability and resistance against solvent, chemical reagents and high temperature,⁴⁹ a general rout has been designed to support a CN-palladacyclic complex onto the organically modified-TiO₂ surface to prepare an efficient heterogeneous pre-catalyst. The synthetic procedure is illustrated in Scheme 2.

TiO₂ usually shows pH-dependent surface charges in the aqueous solution because of the existence of Ti-OH on the surface. The absorption property of TiO₂ greatly changes with environment of different pH value. Considering that the catalytic properties of supported catalysts depend on their preparation conditions, we tried to prepare the ligand functionalized TiO₂ using the pH-dependent procedure.^{50,51} To obtain the TiO₂-supported Pd catalyst, a mixture of chloro-bridged orthopalladated complex (**ADP**) and a functionalized TiO₂ were refluxed in acetone for 24 hours.



TiO₂ -supported Pd nanocatalyst

Scheme 2 Synthetic method and proposed route for the synthesis of new TiO₂- supported catalyst. (i) dry

toluene, 12 h, reflux (ii) acetone, 24 h.

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The stabilization of CN-palladacycle onto the functionalized TiO_2 is due to donation of an electron lone pairs on the nitrogen groups of 3-aminopropyltrimethoxysilane (APTES) into the unoccupied orbital of the palladium atoms in continuous of the bridge cleavage reaction of the dimeric compound **ADP** (Scheme 2).

Fig. 1 shows the FT-IR spectra of Auramine-O ligand, Auramine-O dimeric palladacycle (**ADP**), TiO₂ and fresh TiO₂-supported Pd catalyst. Corresponding to the FT-IR spectrum of TiO₂-supported catalyst illustrated in Fig. 1d, the broad band centered at 500-600 cm⁻¹ is likely due to the vibration of the Ti-O bonds in the TiO₂ lattice.⁵² The peak at 1627cm⁻¹ and the broad peak appearing at 3451cm⁻¹ are assigned to vibrations of hydroxyl groups.^{45,52-53} In modified sample these peaks overlap with broad bands of the stretching and deformation modes of NH₂ groups.^{45, 54} The stretching vibrations of aliphatic groups are appeared at 2951 cm⁻¹. The bands at 1124 and 1383 cm⁻¹ are attributed to the characteristic absorptions of the Si-CH₂ and Si-O groups, respectively.⁵⁵ Also, the presence of several bands with medium intensity in the 2839–3062 cm⁻¹ regions is allocated to C-H stretching of groups (symmetric and asymmetric stretching).

The elemental analysis further proved the existence of C, H, and N atoms in the prepared TiO₂supported Pd catalyst.

Powder X-ray diffraction (XRD) analysis for fresh catalyst exhibits the sharp reflections belonging to the TiO_2 nanoparticles in the anatase phase. Although no Pd species could be detected by XRD pattern due to the low amount of Pd content or its high dispersion on the solid surface, the presence of Pd species was clearly evidenced by X-ray photoelectron spectroscopy (XPS) verifying the orthopalladetd complex **ADP** coated on the TiO_2 .



Fig. 2 Powder XRD pattern of TiO₂-supported Pd catalyst.

Fig. 3 shows high resolution XPS spectra of TiO₂-supported Pd catalyst. The Pd 3d spectrum in Fig. 3a related to the fresh catalyst, shows the characteristic Pd $3d_{5/2}$ and $3d_{3/2}$ doublet peaks, with a peak separation of 5.26 eV. The fitted $3d_{5/2}$ peaks are located near the expected positions for the Pd⁰ and Pd²⁺ species at around 335.3⁵⁶⁻⁵⁸ and 337.6 eV⁵⁶⁻⁵⁷, respectively. The fitting indicates that Pd in the fresh catalyst is a mixture of Pd^{2+} and Pd^{0} states. After the first run, Pd^{0} is observed in higher proportions, which indicates that after the catalytic cycle Pd^{2+} cations were transformed into Pd^{0} (Fig. 3b). According the Pd 3d spectrum of Pd catalyst after the forth catalytic cycle (Fig. 3c), presence of the characteristic Pd 3d_{5/2} and 3d_{3/2} doublet peaks related to the Pd⁰ species confirming the conversion of the whole Pd^{2+} ions to Pd^{0-} . In fact, the percentage of Pd^{2+} decreases from 53% for fresh catalyst to 36% from first run and approximately 0% for the fourth run as we can see in figure 3. According to the XPS data of Pd catalyst before and after the recycle, the Si 2p spectrum shows only one component, with the Si 2p peak position around 103.3 eV, assigned to Si-O bonds.⁵⁸ The Ti 2p spectrum shows the characteristic Ti $2p_{3/2}$ and $2p_{1/2}$ doublet peaks, with a peak separation of 5.54 eV. The characteristic shake-up peaks for TiO_2 are also observed. The fitted $2p_{3/2}$ peak is located near the expected positions for the TiO₂ species at around 458.7 eV.⁵⁸ The HR-XPS N 1s spectra of the fresh Pd catalyst shows two components, one at around 400.0 eV attributed to C-N bonds⁵⁸ and another minor component at around 401.9 eV attributed to N⁺-H bonds.⁵⁹ The N 1s fitted spectrum after the first recycle shows one component at around 400.0 eV attributed to C-N bonds⁵⁸ and after the forth recycle, the nitrogen presented a very low signal and the peak was not possible to fit. The Cl 2p spectrum of the fresh Pd catalyst shows the characteristic Cl $2p_{3/2}$ and $2p_{1/2}$ doublet peaks, with a peak separation of 1.6 eV. After the recycle, no chlorine signal is detected which indicate that after the catalytic cycles Pd²⁺ species were transformed into Pd⁰ and the ligand was removed from palladacycle.

As illustrated in the similar investigations⁶⁰ the formation of TiO_2 -supported Pd(0) nanoparticles are possibly due to the donation of an electron lone pairs on the nitrogen groups into an unoccupied orbital of the palladium nanoparticles. Moreover, the presence of ethanol as e solvent, possibly leads to the reduction of Pd(II) to Pd(0).

XPS analysis showed that the palladium content of fresh catalyst was about 1.5 %. The palladium content of catalyst after the reaction cycle was considerable, according to the XPS analysis. Further information about homogeneous or heterogeneous nature of the catalyst was obtained by hot filtration test which were in accordance with the results obtained from XPS analysis and confirmed that using this catalyst reaction proceeds mostly under heterogeneous conditions.



Fig. 3 XPS spectra of high resolution Pd 3d of (a) fresh TiO₂-supported Pd catalyst, (b) after the first run and (C)

after the forth run.

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To obtain the morphology and particle size of the catalyst, FE-SEM images of the catalyst were carried out (Fig. 4). Furthermore, energy-dispersive X-ray spectroscopy (EDX) obtained from SEM shows the presence of Pd atoms as well as Ti, Si, N, and O atoms in the structure of fresh TiO₂-supported Pd catalyst (Fig. 5).



Fig. 4 FE-SEM image of fresh TiO₂-supported Pd catalyst.



Fig. 5 EDX spectrum of the fresh TiO₂-supported Pd catalyst

According to the TEM images, the Pd nanoparticles are formed and well dispersed through the supported inorganic surface. It was verified that synthesis of catalyst through the pH adsorption method played an important role in the distribution of nanoparticles. The size distribution of fresh TiO₂-supported Pd catalyst is shown in Fig. 6. The histogram could be fitted to a Gaussian function, yielding a mean size of 2.24 nm based on the sizes of 90 particles (Fig. 6a). According o the TEM

images after the first run, the average particle size of Pd^0 in supported Pd catalyst was 2.61 nm. The average particle size of Pd^0 after the forth run was 3.31 nm.



Fig. 6 TEM images of (a) fresh TiO₂-supported Pd catalyst, (b) after the first run and (C) after the forth run: The histograms illustrate the size distribution of Pd catalyst.

2.3. Sonogashira reactions catalyzed by Pd NPs

There are several disadvantages in the earlier reported methods for the Sonogashira coupling reactions such as employing expensive, toxic and air/moisture sensitive phosphine ligands, long reaction times, low yields, inert conditions and environmental pollution caused by the formation of side products and use of large amount of amines as organic solvents or bases.⁶¹ In the copper-mediated Sonogashira coupling reactions, the Glaser-type oxidative dimerization of the terminal alkynes cannot be avoided⁶² which produce undesired side products (diynes) that are generally difficult to separate. Consequently, in our screening experiments, the realization of a Sonogashira reaction catalyzed by the low Pd-loading of TiO₂-supported Pd catalyst in the absence of copper, amine and phosphine ligands was our goal.

The effectiveness of supported Pd catalyst for the Sonogashira cross-coupling reaction of iodobenzene with phenylacetylene was initially investigated. First we investigated the effect of solvent in the Sonogashira reaction of iodobenzene with phenylacetylene (Table 1, entry 1-7). The yield was significantly decreased when H_2O was used as the solvent (Table 1, entry 5); this may be due to the insolubility of the substrate and catalyst in water. However, application of 1: 1 aqueous EtOH improves the yield to some extent (Table 1, entry 6). On the other hand inferior results were obtained with solvents like THF, CH₃CN, toluene and DMF (Table 1, entries 1-4). As shown in Table 1 better performance of the catalytic system was observed when EtOH was used and based on the above we have considered EtOH for further optimization. A very low Pd-loading of 0.005 mol % was found to be the optimum amount of catalyst. To investigate the effect of the base which plays a crucial role in the overall performance of a catalytic system in a Sonogashira reaction, several inorganic and organic bases were tested (Table 1, entry 7-10). K_2CO_3 was found to be reactive in our catalytic system and we have considered it for further optimization. The preliminary investigation for reaction optimization was performed with 0.005 mol% of Pd catalyst and two equivalent of K₂CO₃ in EtOH (4 mL) at 85°C under aerobic condition. The results obtained are highlighted in Table 1. The turnover frequency of the catalyst was defined to be 5880, which was regarded as a factor to show the high efficiency of the catalyst.

Table 1

To demonstrate the versatility of the catalytic system, we investigated the reaction using a variety of aryl iodide with phenylacethylene under the optimized conditions. It was observed that aryl iodides underwent cross coupling within a short reaction time at very low catalyst Pd-loading of 0.005 mol%, with excellent yields (Table 2). They may produce very high TOFs in such catalytic reactions.

Table 2

To study the performance of TiO₂-supported Pd catalyst for the Sonogashira cross-coupling reaction of aryl bromide with phenylacethylene, optimization of the reaction conditions with various solvents and catalyst dosages were applied for bromobenzaldehyde in different range of time reactions and temperatures (Table 3). Among the different reaction conditions, maximum conversion was observed when we have considered the reaction in DMF (4 mL), in the presence of 0.02 mol% of Pd catalyst at 110 °C, under aerobic condition for 8 hours.

Table 3

The generality of the current system has been investigated with several electronically diverse aryl bromide and phenylacetylene (Table 4, entries 1-8). Different functionality at the phenyl ring of the aryl halide moiety affects the reaction conditions. When the reactions of activated aryl bromides containing electron deficient phenyl rings with phenylacetylene were carried out in DMF at 110 °C for 8 h, excellent yields of desired cross-coupling products were observed . However, the electron donating groups at the *para* position of aryl bromides couple smoothly with phenylacetylene to give good to excellent yield of cross coupling products. Considering the steric effect, aryl bromides with ortho substituents, provided the corresponding products in high yields (Table 4, entry 4).

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Table 4

Finally Sonogashira reactions of phenylacetylene and aryl chlorides were also investigated in our present system, under the optimized condition used for the case of aryl bromides. To check the effectiveness of our protocol, phenylacetylene was reacted with electron rich 4-aminorobenzene and electron deficient nitrochlorobenzene. Although aryl chlorides are not so reactive and are employed less in palladium-catalyzed coupling reactions,⁶³⁻⁶⁵ modest to good yield of desired cross coupling products was observed in all cases (Table 4, entries 9-12).

A possible catalytic reaction cycle for the Sonogashira reaction has been shown in Scheme 3, over the active Pd-sites present in the TiO_2 - supported heterogeneous catalyst. At first, oxidative addition of aryl halide to the Pd catalyst takes place, followed by transmetallation of alkyne and lastly, reductive elimination of the final product.

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Scheme 3 Possible catalytic cycle of the heterogeneously catalyzed Cu-free Sonogashira reaction over TiO₂supported Pd catalyst.

Aryl halides containing electron-withdrawing groups improve the oxidative addition of C-X to the Pd catalyst, as an activated halo derivatives.²⁵ However, electron-rich aryl halides require harsher experimental conditions to give acceptable results. Although, the mechanism of the Sonogashira reactions has not yet been established clearly, we assume that the lower tendency of electron-rich aryl halides towards metallo-oxidative insertions could be responsible for this diminished reactivity.^{66,67}

Although, there is no second metal in the copper-free Sonogashira reaction, the second step is conventionally called transmetallation. Several studies have attempted to understand how the alkyne is transferred to the Pd catalyst through the transmetallation step. Amines generally used in the Sonogashira reaction, appreciably deprotonated the alkyne in solution. But despite the fact that the

Sonogashira reaction is occurred in the amine-free condition in this study, we cannot have the deprotonation of the alkyne in solution. Therefore, deprotonation is hypothesized to occur on the Pd center. Initially, the alkyne coordinates to the Pd center in the η^2 -fashion, pulling electron density away from the acetylene. This makes the terminal proton more acidic, enabling deprotonation by weaker bases (Scheme 3).⁶⁸⁻⁷⁰ Importantly, the electronic properties of the terminal alkyne have considerable effects the on the deprotonation mechanism: electron withdrawing groups (EWG) decrease and electron donating groups (EDG) increase the energy required for deprotonation.⁶⁸ The base initially forms the more reactive species of the type Pd⁰L₂ in the oxidative addition step lead to accelerate the overall reaction.⁷⁰ Using of stronger bases, an excess amount of phenylacetylene and more acidic phenylacetylenes considerably increase the rate by affecting the deprotonation step.⁷¹

Furthermore, the reaction kinetics of Sonogashira reaction of phenylacetylene with iodobenzene with 0.02 mol% catalyst was investigated and the result is shown in Fig. 7. A control experiment indicated that the coupling reaction did not occur smoothly in the absence of a catalyst. The yield of the product increased quickly with reaction time until it reached 96% at the 30 minutes.



Fig. 7 Kinetic profiles of the Pd catalyst in the Sonogashira reaction. (a) Normal reaction kinetics in the presence of catalyst; (b) Reaction kinetics in the absence of catalyst. Reaction conditions: iodobenzene (1.0 mmol), phenylacetylene (1.2 mmol), K₂CO₃ (2.0 mmol), EtOH (4 ml), catalyst (0.02 mol% Pd), 85 °C, 30 min.

2.4. Comparison with the other studies

To further evaluate the catalytic performance of catalyst, a comparison was made with several literature-reported supported catalysts (Table 5). The reactions of iodobenzene with phenylacetylene were taken as the standard reactions and the results are listed in Table 5. It can be clearly seen that for the Sonogashira reaction of iodobenzene with phenylacetylene, the current catalyst is superior to others in terms of catalytic efficiency. Moreover, this catalyst also proved to be the most efficacious in activity for the Sonogashira reaction, as reflected from its high TOF value. It should be noted that the supported-Pd catalyzed Sonogashira reactions of iodobenzene with phenylacetylene were carried out in EtOH in the absence of organic solvents, which makes this catalytic capacity more impressive. Thus this catalytic system provides a simple and green method for the Sonogashira reaction of aryl iodides. Compared to previous research,⁷²⁻⁷⁷ this catalytic system requires a very small amount of catalyst Pd-loading and can be run under relatively mild reaction conditions.

Table 5

2.5. Recyclability

The reusability of the catalysts is a very important theme and makes them useful for commercial applications. After the catalytic reactions, the recovery and reusability of TiO_2 -supported Pd catalyst were initially investigated in the Sonogashira reaction of iodobenzene with phenylacethylene under the same condition. Before running another cycle, the solid was separated by simple filtration and washed with acetone, water and then dried. The catalyst is reusable and used for four runs. The results are shown in Fig. 8.

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Fig. 8 A recyclability test for catalyst Sonogashira cross-coupling reaction of iodobenzene with phenylacethylene (reaction condition are the same as given in Table 2).

3. Experimental

3.1. General

¹H NMR spectra were recorded at room temperature on a 400 MHz Bruker spectrometer. Chemical shifts (δ) are reported relative to internal TMS. C, H and N elemental analysis were performed using a PE 2400 series analyzer. Fourier transform infrared (FT-IR) spectra were obtained in KBr pellets with a Jasco FT/IR 680 plus instrument. Scanning electron microscopy (SEM) studies were carried out at 15 kV using a HITACHI S-4160 instrument (Japan). Energy dispersive X-ray analysis (EDX) results were obtained at 20 kV using Philips (Model XL-30) instrument. Transmission electron micrographs (TEM) were obtained with a JEOL JEM 1010 microscope operating at an accelerating voltage of 100 kV. The X-ray powder diffraction (XRD) pattern was recorded using a Scintag X-ray diffractometer with a 1.54 °A (Cu Ka) X-ray radiation source. The XPS experiments were performed in a SPECS Sage HR 100 spectrometer with a non-monochromatic X-ray source (Magnesium K α line of 1253.6 eV energy and a power applied of 250 W), placed perpendicular to the analyzer axis and calibrated using the 3d_{5/2} line of Ag with a full width at half maximum (FWHM) of 1.1 eV. An electron flood gun was used during measurements to neutralize charging effects. The selected resolution for the spectra of the different elements was 15 eV of Pass Energy and 0.15 eV/step. All

the fittings Gaussian-Lorentzian functions were used (after a Shirley background correction). Analytical TLC was performed using Merck TLC Silica gel 60 F254 glass plates. Gas chromatographic (GC) analyses were performed using an Agilent Technologies 6890N chromatograph equipped with a flame ionization detector (FID) and an HB 50+ column (length = 30 m, inner diameter 320 μ m, and film thickness = 0.25 μ m). The temperature program for the GC analysis was from 70 to 200 °C at 20 °C/min, held at 200 °C for 0 min, heated from 200 to 280 °C at 10 °C/min and held at 280 °C for 1 min. The inlet and detector temperatures were set at 260 °C and 280 °C respectively. Products were identified by comparison with authentic samples. All the reactants and solvents were used as commercially available chemicals without any purification.

3.2. Preparation of Auramine-O dimeric palladacycle (ADP)

Method A: bis[4-(dimethylamino)phenyl]methaniminium chloride (Auramine-O) (67.5 mg, 0.2 mmol) was added to the solution of $Pd(OAc)_2$ (50 mg, 0.2 mmol) in toluene and the resulting mixture was refluxed for 24 hours. The resulting solution was evaporated and the green solid was recrystallized with cold 1:5 CH₂Cl₂/ *n*-hexane and cold Et₂O to give dark-green chloro-bridge dimeric complex.

Method B: bis[4-(dimethylamino)phenyl]methaniminium chloride (Auramine-O) (67.5 mg, 0.2 mmol) was added to the solution of $Pd(OAc)_2$ (50 mg, 0.2 mmol) in THF and the resulting mixture was stirred for 72 hours. The solvent was then evaporated and the solid residue treated with 1:5 CH_2Cl_2/n -hexane and cold Et₂O to give dark-green chloro-bridge dimeric complex.

Yield (62-76 %); Anal. Calc. for $C_{34}H_{24}N_6$ Cl_2Pd_2 : C, 51.03; H, 3.02; N, 10.50; Found. C, 51.87; H, 2.98; N, 10.28; IR (KBr, cm⁻¹): v (Pd-N) = 416, v (Pd-C) = 674, v (C=N) = 1606; ¹H NMR (DMSO-d_6, ppm): δ = 3.00 (d, 24H, aliphatic), 6.38 (d, 2H, aromatic), 6.81 (d, 4H, aromatic), 7.01 (d, 2H, aromatic), 7.41 (d, 4H, aromatic), 7.47 (s, 1H, aromatic), 8.94 (s, 1H, aromatic).

3.3. Preparation and characterization of the TiO₂- supported Pd catalyst

TiO₂ was activated by refluxing in concentrated hydrochloric acid (6 M) for 24 h and then washed thoroughly with the deionized water and dried before undergoing chemical surface modification. Refluxing the activated TiO₂ (10 g) with 1.5 mmol 3-aminopropyltrimethoxysilane in dry toluene for 18 h. The solid materials were filtered off and washed with hot toluene and then dried in oven at 110 $^{\circ}$ C overnight to give the surface bound amine group. The catalyst was prepared by stirring a mixture of surface bound ligand L@TiO₂ (4 g) and ADP (0.52 mmol, 0.117 g) in dry acetone (100 ml) at room temperature for 24 h. After stirring, the resulting greenish solid was filtered, washed with large volume of acetone, ethanol and ether. It was then dried in an oven at 95 $^{\circ}$ C overnight to furnish the corresponding catalyst.

3.4. General experimental procedure for Sonogashira reaction with aryl iodides

A round bottomed flask equipped with a condenser was charged with aryl iodides (1.0 mmol), phenylacetylene (1.2 mmol), K_2CO_3 (2.0 mmol) and Pd catalyst (0.005 mol% of Pd) in EtOH (4 ml). Typical procedure for Sonogashira cross-coupling reaction was placed in an oil bath and the mixture was stirred and heated at 85 °C for 30 minutes.

3.5. General experimental procedure for Sonogashira reaction with aryl bromides and chlorides

A round bottomed flask equipped with a condenser was charged with aryl aryl bromides or chlorides (1.0 mmol), phenylacetylene (1.2 mmol), K_2CO_3 (2.0 mmol) and Pd catalyst (0.02 mol% of Pd) in DMF (4 ml). Typical procedure for Sonogashira cross-coupling reaction was placed in an oil bath and the mixture was stirred and heated at 110 °C for 8h.

3.6. General procedure for recycling reactions

When the corresponding Sonogashira reaction according to the procedure described in previous sections was finished, the catalyst was washed with acetone and water. It was dried under air and reused without any pretreatment for repeating cycles.

3.7. Characterization of the products of Sonogashira cross-coupling reactions

1,2-diphenylethyne: ¹H NMR (400 MHz, CDCl₃): δ 7.59-7.62 (m, 2H), 7.47-7.50 (m, 1H), 7.40-7.45 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ 133.3, 132.5, 121.6, 129.1, 82.4.⁷⁸

1-amino-4-(phenylethynyl)benzene: ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.59-7.68 (m, 2H), 7.38-7.29 (m, 5H), 6.70 (m, 2H), 3.54 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 149.36, 133.91, 132.22, 129.22, 127.70, 122.81, 112.22, 112.91, 89.29, 87.32.⁷⁸

1-methyl-3-(phenylethynyl)benzene: ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.60-7.67 (m, 2H), 7.45-7.54 (m, 5H), 7.29 (t, 1H, *J* = 7.5 Hz), 7.17 (d, 1H, *J* = 7.3 Hz), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 138.21, 134.11, 131.36, 129.22, 128.54, 128.52, 128.37, 128.0, 123.11, 122.45, 87.63, 86.19, 22.36.⁷⁸

1-nitro-2-(phenylethynyl)benzene: ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 8.11$ (m, 1H), 7.70 (m, 1H), 7.68 (m, 2H), 7.52 (m, 1H), 7.41 (m, 1H), 7.35 (m, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): $\delta = 46.59, 133.97, 132.80, 132.11, 128.98, 128.64, 128.12, 125.44, 122.42, 119.11, 99.22, 85.21.⁷⁸$

1-nitro-3-phenylethynyl-benzene: ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 8.31$ (dd, 1H), 8.11 (m, 1H), 7.76 (ddd, 1H), 7.76 (ddd, 1H), 7.46-7.50 (m, 3H), 7.31-7.32 (m, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): $\delta = 148.2$, 137.2, 131.8, 129.4, 129.1, 128.5, 126.4, 125.2, 122.9, 122.2, 91.9, 86.9.⁷⁹

1-nitro-4-(phenylethynyl)benzene: ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.23 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.47-7.57 (m, 2H), 7.24-7.36 (m, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 144.2, 132.8, 132.3, 131.3, 128.9, 128.2, 126.4, 125.1, 93.3, 87.3.⁷⁸

4-(phenylethynyl)benzaldehyde: ¹H NMR (400 MHz, CDCl₃, ppm): δ = 9.96 (s, 1H), 7.75-7.84 (m, 2H), 7.56-7.66 (m, 2H), 7.45-7.52 (m, 2H), 7.30-7.37 (m, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 193.3, 138.2, 133.5, 132.4, 130.6, 129.4, 128.8, 127.3, 121.2, 93.3, 88.4.⁷⁸

1-(4-phenylethynyl-phenyl)-ethanone: ¹H NMR (400 MHz, DMSO, ppm): $\delta = 8.0$ (d, 2H), 7.7 (d, 2H), 7.6 (m, 2H), 7.5 (m, 3H), 2.6 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): $\delta = 197.5$, 136.3, 131.7, 131.6, 128.8, 128.5, 128.2, 122.6, 92.7, 88.6, 26.6.⁷⁹

1-methoxy-4-(phenylethynyl)benzene: ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.42 (2H, m), 7.38 (d, 2H, *J* = 8.8 Hz), 7.25 (m, 3H), 6.79 (d, 2H, *J* = 8.8 Hz), 3.73 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 159.60, 133.0, 131.4, 128.30, 127.90, 123.60, 115.40, 114.0, 89.30, 88.0, 55.30.⁷⁹

2-(phenylethynyl)pyridine: ¹H NMR (400 MHz, CDCl₃, ppm): δ = 8.55 (d, 1H, *J* = 5 Hz), 7.58-7.63 (m, 1H), 7.51- 7.55 (m, 2H), 7.46 (d, 1H, *J* = 7 Hz), 7.26-7.35 (m, 2H), 7.20 (s, 1H), 7.12-7.17 (m, 1H).⁷⁹

4. Conclusion

A general approach has been designed to synthesize a new dinuclear chloro-bridged CN-palladacycle derived from bis[4-(dimethylamino)phenyl]methaniminium chloride (Auramine-O). In the next step, we have successfully developed a new heterogeneous TiO₂-supported palladium catalyst originated from the CN-palladacycle precursor which is fully characterized with FT-IR, XRD, SEM, EDX, TEM and XPS techniques. This hybrid catalyst demonstrated high catalytic activities in the copper-, amine and phosphine-free Sonogashira coupling reactions of phenylacetylene with aryl halides (Cl, Br, I) in the presence of very low catalyst Pd- loading. This class of heterogeneous Pd catalyst allows the reaction of phenylacethylene and aryl iodides to promote with remarkable yields under environmentally green condition.

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Tables

Table 1. Optimization of the reaction condition for the Sonogashira cross-coupling reaction of iodobenzene with

phenylacetylene.

Contraction of the second seco						
Entry	[Pd](mol%)	Solvent	Base	Time	Temperature (°C)	Conversion (%) ^a
1	0.005	DMF	K ₂ CO ₃	6 h	85	60
2	0.005	CH ₃ CN	K ₂ CO ₃	6 h	85	41
3	0.005	toluene	K ₂ CO ₃	4 h	85	trace
4	0.005	THF	K ₂ CO ₃	4 h	85	trace
5	0.005	H ₂ O	K ₂ CO ₃	4 h	85	trace
6	0.005	Ethanol: H_2O	K ₂ CO ₃	4 h	85	70
7	0.005	Ethanol	K ₂ CO ₃	30 min	85	99
8	0.005	Ethanol	Na ₂ CO ₃	6 h	85	43
9	0.005	Ethanol	K ₃ PO ₄ .3H ₂ O	6h	85	90
10	0.005	Ethanol	NaOAc	4 h	85	10
11	0.005	Ethanol	K ₂ CO ₃	6h	R. T.	trace
12	0.02	Ethanol	K ₂ CO ₃	15 min	85	99

^aReactions were monitored using GC.

Table 2. Sonogashira coupling reactions of aryl iodides with phenylacetylene using TiO₂-supported catalyst^a



Entry	R	R Time Conversion (%		TON ^b	TOF(h ⁻¹) ^c
1	Н	30 min	98	5880	5880
2	p-NO ₂	20 min	99	5940	11880
3	m-NO ₂	1 h	90	5400	2700
4	p-MeO	2 h	99	5940	5940
5	<i>m</i> -MeO	3 h	99	5940	1980

^aReaction conditions: aryl halides (1.0 mmol), phenylacetylene (1.2 mmol), K₂CO₃ (2.0 mmol), EtOH

(4 ml), catalyst (0.005 mol% [Pd]), 85 °C. Reactions were monitored using GC.

^bTON =mmol of products/mmol of catalyst.

^cTOF = TON/time.

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Table 3. Optimization of the reaction condition for the Sonogashira cross-coupling reaction of bromobenzaldehyde with phenylacetylene.

	HC Br	+ =-	catalyst Base-Solve Temperature	nt -Time	O I CH
Entry	Pd catalyst (mol%)	solvent	Time (h)	Temperature (°C)	Conversion (%) ^a
1	0.005	Ethanol	8	85	20
2	0.04	Ethanol	10	85	94
3	0.02	Ethanol: H_2O	8	85	58
4	0.02	H ₂ O	8	85	trace
5	0.02	DMF:H ₂ O (1:1)	8	110	60
6	0.02	DMF	8	110	95

^aReactions were monitored using GC.

 Table 4. Sonogashira coupling reactions of aryl bromides and chlorides with phenylacetylene using TiO₂

 supported catalyst^a



^aReaction conditions: aryl halides (1.0 mmol), phenylacetylene (1.2 mmol), K₂CO₃ (2.0 mmol), DMF (4 ml), catalyst (0.02 mol% [Pd]), 110 °C. Reactions were monitored using GC and TLC.

^bTON =mmol of products/mmol of catalyst.

^cTOF = TON/time.

Table 5. Comparison with reported results for Sonogashira cross-coupling reactions using TiO₂-supported Pd catalyst

	$\begin{array}{c c} \hline \\ \hline $						
Entry	Catalyst ^a	temp.(°C)/time (h)	Medium	Yield (%)	Ref.		
1	MMT@Pd/Cu (1)	65/24	DME/H ₂ O	97	72		
2	$Pd@Fe_{3}O_{4}(0.5)$	110 /24	DMF	84	73		
3	PNP-SSS (1.2)	100/3	H_2O	95	74		
4	FDU-NHC/Pd(II) (1)	100/3	DMA	94	75		
5	CS/MMT/Pd (0.3)	110/5	DMSO	94	76		
6	Si-P4VPy-Pd (0.5)	120/0.25	NMP	90	77		
7	Pd/APTES/TiO ₂ (0.005)	85/0.5	EtOH	99	This study		

^aData in parentheses indicate mol% of Pd used.

Synthesis and characterization of functionalized titania-supported Pd catalyst deriving from orthopalladated complex of benzophenone imine: catalytic activity in the Sonogashira cross-coupling reactions at low palladium loadings

Kazem Karami,*^a Sedigheh Abedanzadeh,^a Pablo Hervés,^b

^aDepartment of Chemistry, Isfahan University of Technology, Isfahan 84156/83111, Iran. E-mail: karami@cc.iut.ac.ir ^bDepartamento de Quimica Fisica, Universidade de Vigo, 36310 Vigo, Spain. E-mail: jherves@uvigo.es



Efficient catalytic activity of TiO2-supported Pd catalyst in the copper, amine and phosphine free

Sonogashira cross-coupling reactions at low Pd-loadings