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Carbon–Carbon and Carbon–Nitrogen Coupling Reactions Catalyzed by Palladium Nanoparticles Derived from a Palladium Substituted Keggin-Type Polyoxometalate

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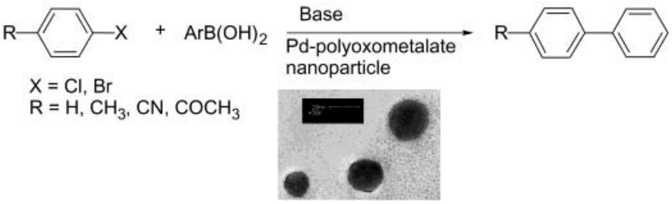
ABSTRACT



Palladium 15–20 nm particles stabilized by a Keggin-type polyoxometalate were prepared by reduction of $K_5PPdW_{11}O_{39}$ with H_2. The nanoparticles were shown to be effective catalysts for Suzuki-, Heck-, and Stille-type carbon–carbon coupling and carbon–nitrogen coupling reactions of bromoarenes in aqueous media. Chloroarenes were also reactive in reaction media without solvent.

Various carbon−carbon cross-coupling reactions such as the Suzuki, Heck, and Stille reactions and carbon−nitrogen coupling reactions are generally considered to be homogeneous reactions most commonly catalyzed by soluble Pd(II) species with a wealth of ligands.[1] Although stabilizing phosphane ligands are often used in these reactions, increasingly simple palladium salts such as $Pd(OAc)_2$ in the presence of quaternary ammonium salts (the Jeffrey system)[2] or water[3] are being used effectively in such reactions. Reetz and Westermann[4] noted the formation of colloidal Pd nanoparticles stabilized by quaternary ammonium salts in such systems[5] and claimed that a true heterogeneous catalyst was functioning. More recently, additional palladium nanoparticle systems such as palladium hollow spheres[6] and nanoparticulate palladium species involving stabilization by ionic liquids,[7] dendrimers,[8] polyvinylpyridine,[9] or fluorous ligands[10] have been described as catalysts active for carbon−carbon coupling reactions. The idea that such nanoparticulate

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palladium systems are truly heterogeneous and do not involve soluble intermediates has been disputed at least in somewhat different cases where commercially available Pd/C or Pd/Al_2O_3 catalysts are used.[11] A dissolution/reprecipitation process of palladium has been concluded to operate, although this does not necessarily limit the practical advantages of such "heterogeneous" systems.[11b]

The use of polyoxometalates as catalysts has become an important area of research over the past two decades.[12] One sub-area of this research field involves the use of noble metal clusters stabilized by polyoxometalates. Thus, Rh^0 and Ir^0 nanoparticles have be used for the hydrogenation of alkenes.[13] Recently, we have shown that palladium nanoparticles stabilized by a Keggin-type polyoxometalate showed unusual selectivity in hydrogenation reactions, for example, arene hydrogenation in the presence of a ketone.[14] In this paper, we describe the use of palladium nanoclusters stabilized by a polyoxometalate as catalysts for carbon−carbon (Suzuki, Heck, and Stille) and carbon−nitrogen coupling reactions.

The previously reported palladium-substituted Keggin-type polyoxometalate[14,15] formulated by elemental analysis as $K_5[PPd(H_2O)W_{11}O_{39}]\cdot 12H_2O$ [16−17] was used as a precursor for the preparation of palladium nanoparticles. Thus, the palladium nanoparticles, hereafter referred to as catalyst **A**, were prepared as follows. $K_5[PdPW_{11}O_{39}]\cdot 12H_2O$ (1 g) was reacted with 5 g of acetophenone at 200 °C under 30 bar H_2 for 4 h. After the slurry was cooled, the blue-black solid was filtered, washed with dichloromethane, and dissolved at 90 °C in 25 mL of water. Originally, a dark blue solution was obtained due to the presence of the reduced polyoxometalate moiety. However, after exposure of the solution to air (2−3 h) in order to reoxidize the polyoxometalate, a yellow-red solution indicative of formation of Pd clusters is formed.[4] The stabilization of nanoparticles by the polyoxometalate is thought to be due to the high anionic charge of the polyoxometalate.[13] A transmission electron microscope image, Figure 1, revealed formation of spherical 15−20 nm nanoparticles. Electron diffraction measurements were consistent with the formation of Pd(0) clusters with a closed-packed arrangement of the Pd atoms. ^{31}P NMR measurements, $\delta = -13.3$ ppm, indicate the presence of $[PW_{11}O_{39}]^{7-}$ polyoxometalate anions. Catalyst **A**, therefore, is formulated as $Pd_x - ([PW_{11}O_{39}]^{7-})_y$.

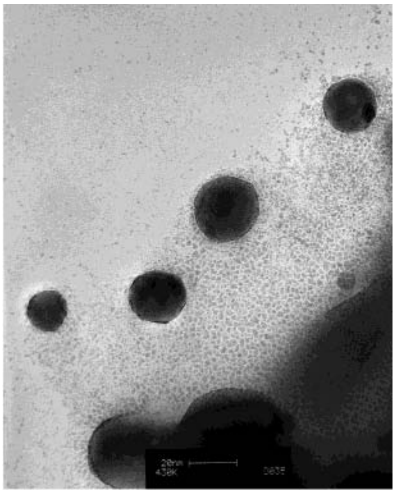

Figure 1. $Pd_x - ([PW_{11}O_{39}]^{7-})_y$ nanoparticles.

The results of Suzuki cross-coupling reactions carried out using various aryl bromide substrates and phenylboronic acid with diisopropylamine as a base is presented in Table 1. The results showed nearly a quantitative formation of the biphenyl product for a range of substrates using an environmentally preferred aqueous−alcohol reaction medium. No debromination was observed, although for aryl iodides such deiodonation was encountered (up to 20% depending on the substrate). 2-Thiophenboronic acid and 3-thiophenboronic acid yielded similar results. The Suzuki coupling reactions with phenylboronic acid on 4-bromotoluene and 1-bromo-4-chlorobenzene as representative substrates were also carried out using alternative bases instead of diisopropylamine. Under typical reaction conditions (1 mmol of substrate, 2 mmol of phenylboronic acid, 2.5 of mmol base, 1 mL (~0.01 mmol Pd) of catalyst **A** in 8 mL of water and 2 mL of EtOH, ~80−85 °C, 12 h), results similar to those reported in Table 1 were observed using potassium acetate, cesium carbonate, potassium fluoride, or triethylamine.

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(16) $K_5PPdW_{11}O_{39}\cdot 12H_2O$ was prepared by adding dropwise $PdCl_2$ (1.1 mmol, 200 mg) dissolved in 20 mL of deionized water to a solution of $Na_7PW_{11}O_{39}\cdot xH_2O$ (1.0 mmol, 3.2 g) dissolved in 20 mL of hot deionized water. After additional heating for 1 h at 90 °C, a saturated solution of KCl (20 mL) was added and the solution was cooled. The brown precipitate was collected and recrystallized from water (yield 2.9 g, 90%). ICP elemental analysis experimental (calcd) K − 5.86 (6.08), P − 1.02 (0.96), Pd − 3.12 (3.31), W − 63.15 (62.94), H_2O − 7.37 (7.29). ^{31}P NMR (85% H_3PO_4 as external standard): major peak at −15.17 ppm (95%) attributable to $[PPd(H_2O)W_{11}O_{39}]^{5-}$ and/or $[PW_{11}O_{39}Pd - O - PdPW_{11}O_{39}]$,[15b] minor peak at −13.32 ppm (5%) $[PW_{11}O_{39}]^{7-}$ impurity. IR − 1100, 1046, 950, 851, 805 cm^{-1}.

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Table 1. Suzuki Cross-Coupling Catalyzed by $Pd_x - ([PW_{11}O_{39}]^{7-})_y$ Nanoparticles in $EtOH/H_2O$[a]

substrate	product	yield[b]
1-bromo-4-nitrobenzene	4-nitro-1,1′-biphenyl	>99
4-bromobenzonitrile	4-cyano-1,1′-biphenyl	97
4-bromotoluene	4-methyl-1,1′-biphenyl	89
2-bromotoluene	2-methyl-1,1′-biphenyl	87
bromobenzene	biphenyl	94
1-bromo-4-chlorobenzene	4-chloro-1,1′-biphenyl	91
4-bromoacetophenone	4-acetyl-1,1′-biphenyl	92
4-bromobenzoic acid	4-carboxy-1,1′-biphenyl	>99

[a] Reaction conditions: 1 mmol of substrate, 2 mmol of phenylboronic acid, 2.5 mmol of diisopropylamine, 1 mL (∼0.01 mmol Pd) of catalyst **A** in 8 mL of water and 2 mL of EtOH, ∼80−85 °C, 12 h. At the completion of the reaction, the solution was extracted by dichloromethane and analyzed by GC and GC-MS. [b] Yield is in mol % as computed by GC with pentadecane as the external standard. Response factors were determined by calibration of standards.

In the H_2O−EtOH reaction medium, chloroarenes, except for 1-chloro-4-nitrobenzene, reacted sluggishly. However, chloroarenes successfully underwent Suzuki cross-coupling with phenylboronic acid in the absence of solvent using a supported catalyst system, Table 2. Supported catalyst **B** was prepared by adding 0.4 g of KF and 5.6 g of γ-Al_2O_3 (Strem, surface area 250 m^2/g) to 25 mL of catalyst solution A. Water was removed under vacuum yielding a $Pd_x - ([PW_{11}O_{39}]^{7-})_y$ − KF catalyst impregnated on alumina. The results, Table 2, show that chloroarenes can effectively be coupled with phenylboronic acid using a variety of chloroarenes substituted with either electron-withdrawing or electron-donating moieties. In one case, with 2-chlorotoluene as the substrate, some 2,4-dichlorotoluene was formed as a byproduct probably via acid-catalyzed transfer chlorination (halogen “dance” reaction) presumably due to the acidity of the polyoxometalate moiety. Previously, Suzuki coupling reactions in a solvent-free system with heterogeneous Pd catalysts showed good activity for iodoarenes but no or only marginal activity for chloroarenes.[17] This is the major advantage of this catalytic system.

Table 2. Solvent-Free System for Suzuki Cross-Coupling of Chloroarenes[a]

substrate	product	yield[b]
1-chloro-4-nitrobenzene	4-nitro-1,1′-biphenyl	>99 (98)
4-chlorobenzonitrile	4-cyano-1,1′-biphenyl	>99 (53)
4-chloroacetophenone	4-acetyl-1,1′-biphenyl	>99 (25)
2-chlorotoluene	2-methyl-1,1′-biphenyl	94 [c]
chlorobenzene	biphenyl	>99
2-chloropyridine	2-phenylpyridine	>99
3-chloropyridine	3-phenylpyridine	>99

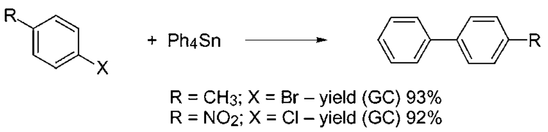
[a] Reaction conditions: 1 mmol of substrate, 2 mmol of phenylboronic acid, 280 mg of catalyst **B**, 130 °C, 16 h. Values in parentheses are results obtained for reaction under the conditions described in Table 1. At the completion of the reaction, the solution was extracted by dichloromethane and analyzed by GC and GC-MS. [b] Yield is in mol % as computed by GC with pentadecane as the external standard. Response factors were determined by calibration of standards. [c] 2,4-Dichlorotoluene (6%) was formed.

In a specific example to investigate the synthetic utility of the reaction and the recovery/recycle of the catalyst, chlorobenzene (0.3 g, 2.55 mmol) was reacted with phenylboronic acid (0.32 g, 2.62 mmol) in the presence of 400 mg of catalyst **B** at 130 °C for 18 h. Biphenyl (0.35 g, 95% yield) was recovered by extraction with hot CH_2Cl_2 (2 × 10 mL); the combined organic phase was washed with water and dried with $MgSO_4$. The catalyst was reused under the same conditions with essentially no loss in activity.

It is interesting to comment also on whether the $Pd_x - ([PW_{11}O_{39}]^{7-})_y$ − KF on alumina catalyst is a true heterogeneous catalyst. Thus, insoluble poly(4-bromostyrene) (0.1 g) was reacted with 3-formylphenylboronic acid (0.15 g, mp 110 °C) in the presence of catalyst **B** (200 mg) at 140 °C for 12 h. The polymer was recovered after the reaction. IR analysis showed no characteristic aldehyde peak at ∼1700 cm^{-1}, indicating that 3-formylphenylboronic acid had not reacted with the 4-bromopolystyrene substrate. On the other hand, 4-bromotoluene reacted quantitatively with 3-formylphenylboronic acid under the same reaction conditions. Therefore, it may be concluded that the coupling reaction is initiated by reaction of the haloarene with the Pd catalyst at the surface of the nanoparticle rather than with dissolved Pd species. It may be assumed that the oxidative addition to Pd(0) with the ArX substrate may lead to dissolution of palladium and its reprecipitation at the nanoparticle surface at the conclusion of the catalytic cycle. Alternatively, the ArPd(II)X intermediate could remain at the nanoparticle surface throughout the catalytic cycle. Since KF is essentially insoluble in the reaction mixture, we assume that the completion of the catalytic cycle occurs at the nanoparticle surface.

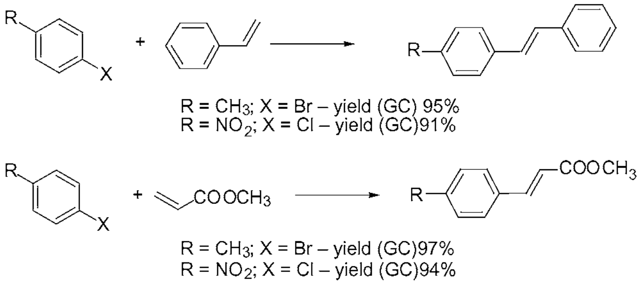
The $Pd_x - ([PW_{11}O_{39}]^{7-})_y$ catalyst was also effective for other types of coupling reactions. For example, Stille-type coupling reactions between 4-bromotoluene and 1-chloro-4-nitrobenzene with tetraphenyltin (1 mmol of substrate, 2 mmol of tetraphenyltin, 2.5 mmol of diisopropylamine, 1 mL (∼0.01 mmol Pd) of catalyst **A** in 5 mL of water and 5 mL of DMF, 110 °C, 12 h) yielded almost quantitative yields of 4-methyl-1,1′-biphenyl and 4-nitro-1,1-biphenyl, respectively, Scheme 1.

Scheme 1. Stille Coupling Catalyzed by $Pd_x - ([PW_{11}O_{39}]^{7-})_y$ Nanoparticles



Heck-type coupling with both styrene and methylacrylate as alkenes and with bromoarenes, e.g., 4-bromotoluene and activated chloroarenes, e.g., 1-chloro-4-nitrobenzene, Scheme 2, was also demonstrated. Under typical reaction conditions (1 mmol of substrate, 2.5 of mmol alkene, 3 mmol of diisopropylamine, 1 mL (∼0.01 mmol Pd) of catalyst **A** in 8 mL of water and 2 mL of EtOH, ∼80−85 °C, 16 h), nearly

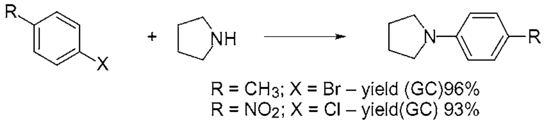
Scheme 2. Heck Coupling Catalyzed by $Pd_x - ([PW_{11}O_{39}]^{7-})_y$ Nanoparticles



quantitative yields of the respective stilbene and methyl cinnamate derivatives were obtained in all cases.

Finally, carbon−nitrogen coupling reactions, for example, with pyrrolidine and 4-bromotoluene or 1-chloro-4-nitrobenzene (1 mmol of substrate, 2 mmol of pyrrolidine, 1 mL (~0.01 mmol Pd) of catalyst **A** in 5 mL of water and 5 mL of DMF, 90 °C, 12 h), were also effectively catalyzed by the $Pd_x - ([PW_{11}O_{39}]^{7-})_y$ catalyst, Scheme 3.

Scheme 3. Carbon−Nitrogen Coupling Catalyzed by $Pd_x - ([PW_{11}O_{39}]^{7-})_y$ Nanoparticles



Palladium nanoparticles stabilized by polyoxometalates were found to be versatile catalysts for carbon−carbon and carbon−nitrogen coupling reactions of bromoarenes in aqueous media or chloroarenes in the absence of solvent.

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