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WATER-SOLUBLE PALLADIUM AND GOLD NANOPARTICLES FUNCTIONALIZED BY A NEW PHOSPHINE WITH ZWITTERIONIC LIQUID BASED ON IMIDAZOLIUM SULFONATE LINKED ETHYLENE GLYCOL MOIETY

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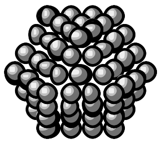
Abstract – A new phosphine with zwitterionic liquid based on imidazolium sulfonate linked ethylene glycol moiety (**1**) as a protective ligand for metal nanoparticles has been prepared. Its phosphine **1**-stabilized palladium and gold nanoparticles (**1**-Pd and **1**-Au) were found to be soluble in water, and remarkably stable in high concentration of aqueous electrolyte and ionic liquid. **1**-Pd nanoparticles behave as an efficient catalyst for the Suzuki cross-coupling reaction in an aqueous medium.

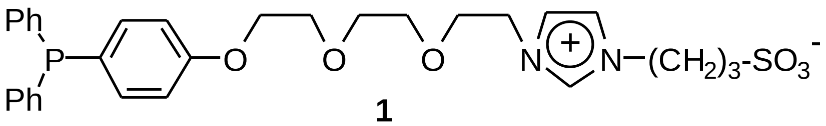
Ionic liquids represent a rapidly emerging field of great fundamental and practical interest and are receiving worldwide attention.[1,2] While most ionic liquids investigated up to now are based on 1,3-dialkylimidazolium ions the use of cations with functionalized alkyl groups has only been described in a few papers. Owing to their molecular structure, associating a cation and an anion, their physicochemical properties can be easily modulated by changing one of the ions. Ionic liquids are now widely used in organic synthesis, catalysis, chemical separations, and in preparation of nanostructured materials due to their high solvation ability and their tunable nature. Currently, many attempts have been made to explore functional ionic liquids through incorporation of additional functional groups as a part of the cation and/or anion. For example, phosphine-functionalized imidazolium salts as ligand for transition-metal complex have been prepared.[2b,3] However, such phosphine ligand functionalized by imidazolium ion moiety has not been used as protecting ligand for metal nanoparticles.

Metal nanoparticles are the focus of intense investigation because of their interesting optical, electrical, and catalytic properties.[4] Control of the surface properties and reactivities on metal nanoparticles is an important aspect of developing nanomaterial applications. The surface properties of metal nanoparticles are crucially controlled by the nature of protective ligands. A limited number of syntheses and properties of metal nanoparticles in imidazolium ionic liquids,[5] and of gold nanoparticles with imidazolium ionic liquid moieties have been reported.[6,7] More recently, we reported that gold nonoparticles stabilized by a alkylthiol with zwitterionic imidazolium sulfonate function were soluble in only aqueous electrolyte, although their gold nanoparticles were insoluble in water and organic solvents.[7,8] Although a number of functional thiol-stabilized metal nanoparticles have been reported,[4] metal nanoparticles stabilized by functional phosphines have received less attention.

Herein we report the synthesis of a new phosphine with zwitterionic liquid based on imidazolium sulfonate linked ethylene glycol moiety (**1**) as a protective ligand for metal nanoparticles and its phosphine **1**-stabilized palladium and gold nanoparticles (**1**-Pd and **1**-Au) which were soluble in water and were remarkably stable in aqueous electrolyte and ionic liquid. Generally, metal nanoparticles were unstable and aggregated in electrolyte solutions.[4] Alkanethiol-protected gold nanoparticles are usually insoluble in water; most biological applications require that the gold nanoparticles readily dissolve in aqueous media and do not aggregate non-specifically due to electrostatic interactions. The stable dispersion of metal nanoparticles in an aqueous electrolyte is important to many applications. We also provide our preliminary study on the catalytic property of **1**-Pd nanoparticles for the Suzuki cross-coupling reaction in an aqueous medium. The Suzuki coupling is one of the preeminent methods for formation of carbon-carbon bonds and has been used in numerous synthetic ventures.[9] Traditionally, the Suzuki coupling reactions are carried out in organic solvents and catalyzed by various palladium/ligand systems. Phosphine-based palladium (phosphine-palladium complex) catalysts are generally used. The use of water as a reaction medium for transition-metal-catalyzed reactions is very attractive for organic synthesis due to environmental, economical, and safety reasons. However, much less is known about the Suzuki coupling reaction catalyzed by water-soluble phosphine-stabilized palladium nanoparticles.[10]



Pd, Au



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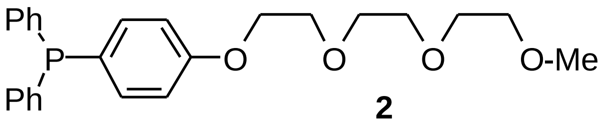
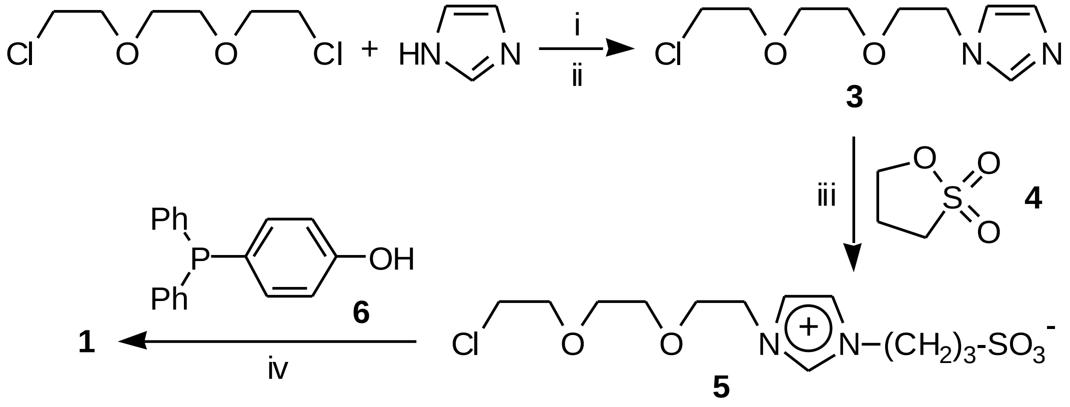


2

Synthesis

A new zwitter-oxy-phosphine (**1**)[11] was synthesized according to Scheme 1 and 4-hydroxyphenyldiphenylphosphine (**6**)[12] in Scheme 1 was obtained by the reported method. Imidazole was treated with sodium hydride in THF to form the anion which was reacted with 1,2-bis(chloroethoxy)ethane to yield the compound (**3**). The reaction of compound **3** with 1,3-propanesultone (**4**) afforded the zwitter ion bearing oligoether (**5**). Finally, treatment of the zwitter ion **5** with the hydroxyphenylphosphine **6** gave the zwitter-oxy-phosphine (**1**).



Scheme 1 *Reagents and conditions*: i. NaH, THF, room temp., 1 h; ii. 60 °C, 18 h; iii. acetone, room temp., 5 days; iv. K_2CO_3, MeCN, reflux, 18 h.

Typical procedure for the preparation of **1**-Pd and **1**-Au nanoparticles is as follows. To a vigorously stirred solution of K_2PdCl_4 (135 mg, 0.41 mmol) in 20 mL of deionized water was added a zwitter-oxy-phosphine **1** (240 mg, 0.41 mmol) in 10 mL of MeOH. $NaBH_4$ (155 mg, 4 mmol) in 10 mL of MeOH was then added. The mixture was stirred for 1 h at room temperature. After the reaction, the filtrate was evaporated *in vacuo* to yield **1**-Pd nanoparticles. Similarly, the zwitter-oxy-phosphine **1**-stabilized gold nanoparticles (**1**-Au) were prepared by the reduction of $HAuCl_4$ with $NaBH_4$ in the presence of the phosphine **1**. Purification of **1**-Pd and **1**-Au was repeated until no free phosphine remained, as detected by TLC, ^1H and ^{13}C NMR spectroscopy. **1**-Pd and **1**-Au nanoparticles are remarkably stable both in solution, as well as in the solid state.

Results and Discussion

The particle size and size distribution of **1**-Pd and **1**-Au nanoparticles were analyzed with transmission electron microscopy (TEM). The nanoparticles were redissolved in water (1 mg mL^{-1}) and a drop of the resulting dispersion was placed on a carbon coated copper grid. The TEM picture of the nanoparticles showed dispersed nanoparticles: 2.2 ± 0.3 nm for **1**-Pd (Figure 1a) and 2.4 ± 0.4 nm for **1**-Au (Figure 1b).

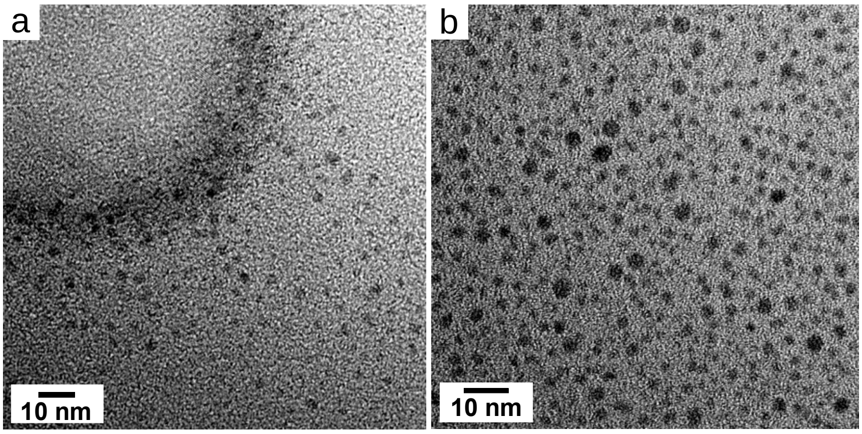


Figure 1 TEM micrographs of (a) **1**-Pd and (b) **1**-Au nanoparticles.

The metal nanoparticles (**1**-Pd and **1**-Au) were characterized by spectroscopic means. FT-IR spectra of **1**-Pd and **1**-Au showed the O=S=O stretching vibrations at 1196 and 1041 cm^{-1} and the C=C stretch vibration of the imidazolium ring at 1653 cm^{-1}. The proton signals in the ^1H NMR spectra of **1**-Pd and **1**-Au, though significantly broadened, appeared at positions that are almost identical to those of free phosphine **1**.[13] The X-ray photoelectron spectroscopy (XPS) spectrum of **1**-Au showed the Au 4f binding energies at 84.2 and 87.9 eV. While, the XPS spectrum of **1**-Pd displayed that the binding energies for the Pd 3d doublet are 336.0 and 341.3 eV. There was a feature at 285 eV due to C 1s and 132 eV due to P 2p.

We have previously reported that zwitter-alkylthiol-stabilized gold nanoparticles were found to be insoluble in water and organic solvents, although their gold nanoparticles were soluble in aqueous electrolyte.[7] Interestingly, however, **1**-Pd and **1**-Au nanoparticles were soluble in water in the absence or presence of electrolyte. Meanwhile, a phosphine (**2**: Structural Formula 1) without imidazolium zwitterionic liquid function has been synthesized and its phosphine-stabilized palladium nanoparticles (**2**-Pd) were obtained by the reduction of K_2PdCl_4 with $NaBH_4$ in the presence of a phosphine **2**. The **2**-Pd nanoparticles (2.8 ± 0.6 nm) cannot be dissolved in water. This result indicates the importance of the imidazolium zwitterionic liquid function.

The UV-vis spectrum of **1**-Au nanoparticle solution in water exhibited a small plasmon resonance at ~510 nm (Figure 2b). While, there is no obvious surface plasmon band in the UV-vis spectrum of **1**-Pd nanoparticle solution in water (Figure 2a). The absence of a plasmon band for **1**-Pd is in accord with theoretical predictions[14] and experimental observations for 2.2 nm alkanethiolate-stabilized Pd nanoparticles,[15] but not with the report of a 302 nm surface plasmon band for 2.2 nm octadecanethiolate-protected Pd nanoparticles.[16] The stability of **1**-Pd and **1**-Au nanoparticles in aqueous solutions was examined by UV-vis spectroscopy. Lyophilized particles could be readily redissolved in aqueous electrolyte to form a clear solution. After one month of storage in aqueous NaCl (6 M), no agglomeration was seen. It has been known that gold nanoparticles were aggregated in aqueous solution of electrolyte such as NaCl.[4] These results suggest that the surface property of **1**-Pd and **1**-Au does not change with the addition of the electrolyte, because the zwitterionic liquid is composed of a covalently tethered cation and anion.

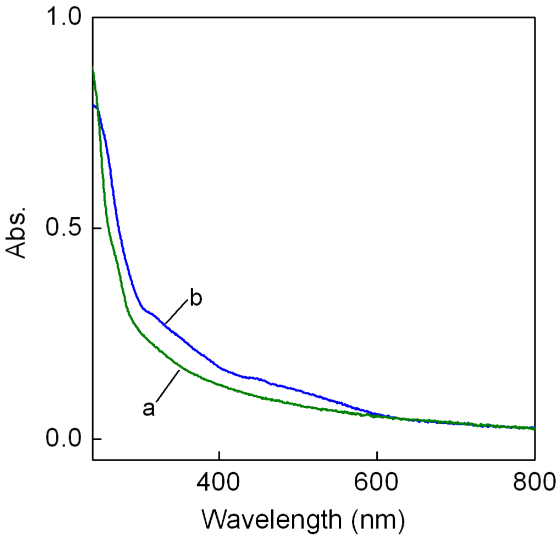
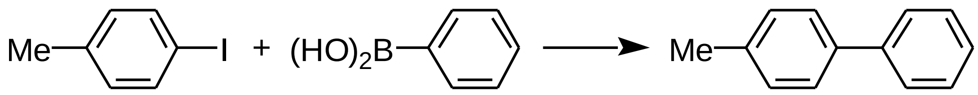


Figure 2 UV-vis spectra of (a) **1**-Pd and (b) **1**-Au nanoparticles in H_2O.

Thus, zwitter-oxy-phosphine **1**-stabilized palladium and gold nanoparticles were found to be soluble and stable in aqueous electrolyte. Although it was reported that citrate-capped gold nanoparticles were aggregated to precipitate in a 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF_6) ionic liquid,[17] very few properties of metal nanoparticles in ionic liquids are known. Accordingly, we have investigated the behavior of **1**-Pd and **1**-Au in a new type of electrolyte such as ionic liquid, *i.e.*, a water-soluble ionic liquid, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF_4). We have found that those nanoparticles were soluble and stable in the EMIM-BF_4 ionic liquid.

The catalytic property of **1**-Pd nanoparticles dispersed in aqueous electrolyte was tested in very important carbon-carbon bond-forming reaction, the Suzuki coupling reaction. It has been known that the Suzuki coupling reactions were carried out in organic solvents under reflux.[9] Interestingly, **1**-Pd nanoparticle-catalyzed Suzuki cross-coupling reaction of 4-iodotoluene (**7**) with phenylboronic acid (**8**) in aqueous medium was found to proceed smoothly at moderate temperature to give the corresponding coupling product in a good yield (Scheme 2). Typically, a mixture of **7** (220 mg, 1 mmol) and **8** (188 mg, 1.5 mmol) in the presence of **1**-Pd (10 mg) and KF (180 mg, 3 mmol) in H_2O (2 mL)-EtOH (1 mL) was stirred at 50 °C under argon for 6 h. After work-up, the crude products were purified by silica-gel column chromatograph (*n*-hexane) to give the coupling product (**9**) in 87% yield. Separation of the product from the catalyst is easy and the **1**-Pd recovered from the reaction was freely soluble in water.



7 **8** **9**

Scheme 2

In summary, we have developed a new phosphine with zwitterionic liquid based on imidazolium sulfonate linked ethylene glycol moiety (**1**) that can be used to prepare remarkably stable metal nanoparticles in aqueous electrolyte and ionic liquid. New **1**-Pd nanoparticles were easily dissolved in water, while **2**-Pd nanoparticles modified by a phosphine (**2**) without imidazolium zwitterionic liquid function were insoluble in water. The **1**-Pd nanoparticles were found to be a versatile catalyst for the Suzuki coupling reaction in aqueous medium under mild conditions. These first examples of zwitter-oxy-phosphine **1** and its phosphine-stabilized metal nanoparticles open up interesting perspectives in the fields of reaction and catalysis using water- and ionic liquid-soluble metal nanoparticles based on green chemistry. Further work is currently in progress in this and related areas involving metal complex.

ACKNOWLEDGMENTS

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11. **1**: FT-IR 1652 cm^{-1} (C=C), 1191 and 1042 cm^{-1} (SO_2); ^{1}H NMR (CD_3CN) δ 8.93 (s, 1H, NCHN), 7.45-7.17 (m, 14H, NCHCHN, ArH), 6.92-6.87 (m, 2H, ArH), 4.37-4.33 (m, 2H, NCH_2), 4.27-4.23 (m, 2H, NCH_2), 4.08-4.04 (m, 2H, OCH_2), 3.77-3.57 (m, 8H, OCH_2), 2.51 (t, 2H, CH_2SO_3), 2.15 (q, 2H, CH_2); ^{13}C NMR (CD_3CN) δ 160.5, 138.8, 138.6, 137.6, 136.4, 136.0, 134.1, 133.8, 129.4, 128.5, 128.4, 123.6, 122.9, 115.8, 115.7, 70.9, 70.8, 70.0, 69.3, 68.3, 50.3, 49.0, 47.8, 27.4; MS (FAB), *m/z* 583 (MH^+).

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