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Multifunctional Phosphine Stabilized Gold Nanoparticles: An Active Catalytic System for Three-Component Coupling Reaction

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Multifunctional phosphine based ligands, 1,1,1-tris(diphenylphosphinomethyl)ethane $[CH_3C(CH_2 PPh_2)_3][P_3]$ and 1,1,1-tris(diphenylphosphinomethyl)ethane trisulphide $[CH_3C(CH_2P(S)Ph_2)_3][P_3S_3]$ have been introduced to stabilize Au°-nanoparticles having small core diameter and narrow size distribution. The Au°-nanoparticles were synthesized by the reduction of HAuCl₄ precursor with NaBH₄ in the presence of ligand P₃ or P₃S₃ using two phases, one pot reaction at room temperature. The Au°-nanoparticles exhibit face centered cubic (fcc) lattice having different crystalline shape i.e., single crystallite stabilized by P₃ while P₃S₃ forms decahedral shapes. Surface plasmon bands at ~ 520 nm and TEM study indicate particle size below 2 and 4 nm for Au°-nanoparticles stabilized by P₃ and P₃S₃ respectively, which are attributable to the stronger interaction of Au° (Soft) with P (Soft) than Au° (Soft) with S (less Softer than P). Au°-nanoparticles stabilized by P₃S₃ shows higher thermal stability than that of P₃. The synthesized Au°-nanoparticles serve as an efficient catalyst for one-pot, three-component (A³) coupling of an aldehyde, an amine and an alkyne via C—H alkyne-activation to synthesize propargylamines (85–96%) without any additives and precaution to exclude air.

Keywords: Au^o-Nanoparticles, Decahedral, Single crystallite, Surface Plasmon, Propargylamines, C—H Activation.

1. INTRODUCTION

In the recent years, there has been increasing interest in gold for using as catalysts in organic transformations, though gold was traditionally considered to be chemically inert and regarded as a poor catalyst.¹ The development of facile synthetic methods and choice of suitable support towards the synthesis of Au°-nanoparticles having uniform size (less than 5 nm) and controllable preparation of nanocrystals with different shapes and exposed surfaces appear to be of key importance for their specific applications.^{1,2} Different types of supports like mesoporous materials, activated carbons, polymers, dendrimers, metal oxides, organic ligands, etc. have been employed to stabilize nanoparticles.³ Among the different supports, organic ligands have aroused much attention recently as supports because they provide important building blocks to construct nano-organised systems with different shape and size.⁴ The ligands are choosen by considering

their donor sites affinity towards nanoparticles and also structural suitability. The physico-chemical properties of metal nanoparticles can be tuned by variations in both the nature of the ligand and size of the metal core. Phosphine stabilized metal nanoparticles are excellent building blocks possessing well organized metallic cores. Schmid et al.⁵ reported the Ph₃P stabilized Au°-nanoparticles prepared by reduction of Ph₃PAuCl with diborane. After the development of biphasic reduction procedure,^{4a} the synthesis of phosphine stabilized Au°-nanoparticles ($d \sim$ 1.5 nm) is further improved^{4b} by reduction of HAuCl₄ precursor with NaBH₄. The biphosphine ligands having different skeletons are also reported for the synthesis of Pd°- and Au°-nanoparticles having narrow size distribution and their catalytic applications.^{4c, d} Recently, our group has introduced tripodal phosphine based ligands system for stabilization of Pd°- and Au°-nanoparticles.⁶ In case of Pd°-nanoparticles, a details study including catalytic activity in C-C bond formation coupling reactions were reported.6a but for Au°-nanoparticles, a very preliminary investigation was presented.^{6b} In this present study, we

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have reported the detail study of Au^o-nanoparticles having different sizes and shapes stabilized by tripodal phosphine based ligands and their catalytic activities for one-pot synthesis of propargylamines with excellent yields and selectivity under mild reaction conditions.

Propargylamines are versatile intermediates for the preparation of various nitrogen-containing compounds and are key components of biologically active pharmaceuticals and natural products and also for the synthesis of polyfunctional amino derivatives.⁷ Recently, considerable afford has also been devoted to the application of various metal nanoparticles such as Cu, Fe, Au, In, etc. for the synthesis of propargylamines via C-H alkyneactivation.⁸ Among the different metals, gold based catalysts are highly explored in this regards because of alkynophilicity nature of gold.^{3a, 7c, 8a} In the recent time, gold nanoparticles stabilized on various supports have been extensively used for three component coupling reactions and therefore, there is a high scope of introduction of new catalytic system.3a,7,8a Herein, we have reported a well-defined catalytic system by preparing monodispersed, tripodal phosphine based ligands capped Au°-nanoclusters having different crystalline properties and their catalytic activities for one-pot synthesis of propargylamines.

2. EXPERIMENTAL DETAILS

2.1. Syntheses

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2.1.1. Synthesis of 1,1,1-Tris(Diphenylphosphinomethyl) Ethane Trisulphide [CH₃C(CH₂P(S)Ph₂)₃]P₃S₃ Ligand

 $[CH_3C(CH_2PPh_2)_3]P_3$ (1 g, 1.6 mmol) was dissolved in 50 ml of toluene and the solution was stirred at room temperature (r.t.) under nitrogen atmosphere. Three fold excess of elemental sulphur (155 mg, 4.85 mmol) was added to the stirred solution over a period of 30 min. After the addition of sulphur was complete, the solution was stirred for another 2 h at room temperature. The solvent was evaporated under vacuum and the white product so obtained was recrystallized from dichloromethane/*n*-hexane to obtain $[CH_3C(CH_2P(S)Ph_2)_3, P_3S_3]$. The synthesized ligand is characterized by different analytical techniques.

2.1.2. Synthesis of Au°-Nanoparticles

The Au^o-nanoparticles stabilized by phosphine and its sulphur functionalized one were synthesized by following a slightly modified procedure reported by Hutchison et al.^{4b} (Scheme 1). 10 ml aqueous solution of HAuCl₄ · $3H_2O$ (100 mg, 0.254 mmol) and 15 ml of toluene solution of tetra-*n*-octylammonium bromide (TOAB) (160 mg, 0.293 mmol) were taken into a two necked round bottom flask and after vigorous stirring for about 45 min, the transfer of [AuCl₄]⁻ anion from aqueous layer to organic

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Scheme 1. Synthesis of sulfur functionalized tripodal ligand and phosphine based ligands stabilized Au^o-nanoparticles.

layer took place. The complete transfer was confirmed by the color changes that occurred in the two phases i.e., the initial light yellow color of aqueous layer became completely colorless, while the organic phase turned into deep red. The ligand P_3 or P_3S_3 (0.253 mmol) in 10 ml toluene was added to the organic phase and the resulting mixture was stirred for about 1 h (stirring was done under nitrogen atmosphere for P_3 since the ligand is air sensitive). In case of P_3 , the organic phase became white and cloudy but for P_3S_3 , no color change was observed. 10 ml aqueous solution of NaBH₄ (134 mg, 3.54 mmol) was then added slowly to the organic phase, the reaction started immediately and the organic phase turned into dark purple. The reaction mixture was stirred for another 2 h at r.t. The organic phase was separated and washed with water and the solvent was removed in vacuo to yield a black solid product. The washing of the crude solid was repeated until no free ligand or phase transfer catalyst was detected by TLC and ¹H NMR spectroscopy. The synthesized Au^onanoparticles were designated as Au^o-P₃ and Au^o-P₃S₃ respectively for P_3 and P_3S_3 ligands and they were evaluated as catalyst precursors for one-pot three-component coupling reaction.

2.1.3. General Procedure for the One-Pot Synthesis of Propargylamines

Aldehyde (1 mmol), amine (1 mmol), alkyne (1.2 mmol), 25 mg catalyst and 7 ml toluene were taken in a 25 ml round bottom flask and reaction mixture was refluxed at 110 °C for stipulated time period. The progress of the reactions was monitored by TLC. After completion of the reaction, the solvent was removed under low pressure in a rotavapour. The crude product obtained was then purified by silica gel column chromatography using ethyl acetate and hexane as eluents. The products were characterized by ¹H, ¹³C NMR and mass spectrometry.

3. RESULTS AND DISCUSSION

3.1. Characterization of Au°-Nanoparticles

During the preparation of Au°-nanoparticles, addition of ligand P₃ turns the organic layer white and cloudy because of partial reduction of Au(III) to Au(I) state by trivalent phosphorous atom of ligand P3. Au(I) forms some stable complex through phosphorus donor of triphos ligand, which on reduction with NaBH₄ generates Au°nanoparticles. The formation of Au(I) triphos complex is substantiated by ³¹P NMR data, a downfield shift in the ³¹P NMR peak of ligand by trivalent phosphorous atom of ligand P_3 from -21 ppm to 29 ppm, indicates that the ligand ligand P_3 is coordinated to Au(I)⁹ through its trivalent phosphorous atom. On the other hand, in case of the ligand P₃S₃, no color change was observed in the organic layer and the partial reduction could not be possible due to presence of pentavalent phosphorous atom (Scheme 1). Finally, reduction was carried out with NaBH₄ to generate Au°-nanoparticles.

The immediate evidence for the formation of Au°-nanoparticles was obtained by UV-Visibe spectroscopy. The pattern of surface plasmon resonance bands at around ~ 520 nm of Au°-P₃ and Au°-P₃S₃ signifies different characteristics [Fig. 1]. A broad surface plasmon band for ligand P₃S₃ reveals the formation of Au°-nanoparticles having the particles size below 4 nm (also substantiated by TEM and XRD studies) and for P₃ ligand, shows no significant plasmon resonance band at ~ 520 nm (consistent with its smaller particles size having diameter < 2 nm and narrower distribution). This is due to the lack of *quasi* delocalized electrons that are necessary for the interaction with visible light.^{4b-d}

The core size and size distribution of the stabilized Au°-nanoparticles were examined by TEM [Figs. 2(A) and (B)]. The TEM images of both the ligands stabilized Au°-nanoparticles show that the particles are uniformly distributed. The TEM images along with particles



Fig. 1. UV-Visible spectra of (A) $Au^{\circ}-P_{3}$ and (B) $Au^{\circ}-P_{3}S_{3}$ in toluene.

size histogram for ligands P_3 and P_3S_3 stabilized Au^o-nanoparticles (Au^o-P₃ and Au^o-P₃S₃) showed narrow size distribution of particles of 1.6 ± 0.4 nm and 3.0 ± 0.7 nm respectively.

The XRD pattern of Au°–P₃S₃ [Fig. 3(A)] shows broad peaks of 2θ values at 38.4, 43.5, 64.65 and 78.27° assigned to the corresponding (111), (200), (220) and (311) planes and a broad peak appears at around 2θ value at 38° for Au°–P₃ [Fig. 3(B)], which corresponding to the fcc lattice of gold. The average particle sizes of Au-1 and Au-2 were calculated by the Scherrer equation, using the FWHM of the intense (111) plane reflection and the average sizes are found to be 1.27 and 3.27 nm respectively.

The microstructure of Au[°]-nanoparticles were further characterized by HRTEM and SAED. The HRTEM pattern of Au°-P₃ shows that the lattice planes continuously extended to the whole particles without stacking faults or twins, indicating their single-crystal nature [Fig. 4(A)].¹⁰ The inset of Figure 4(A) shows the corresponding SAED pattern obtained by directing the electron beam perpendicularly to one of the particles. The hexagonal symmetry of this pattern also proved the single crystalline nature of the particles. Au^{\circ}-nanoparticles stabilized by ligand P₃S₃ $(Au^{\circ}-P_{3}S_{3})$ exhibit decahedral shape [Fig. 4(B)]. The decahedral is one of the basic multiply twinned structures, which consists of five tetrahedral crystallites with (111) surfaces and found in many fcc lattice.^{2,10a} The Figure 4(B)shows the HRTEM image of an individual decahedral nanoparticle where the five triangular facets of the gold decahedron can be clearly observed. This image also displays symmetric lattice fringe images against the twin boundary, where a few parallel layers are observed. Each triangular face represents a single crystalline nature by continuous lattice fringes.^{2, 10a} The complex SAED pattern, inset of Figure 4(B) may be interpreted by five twinned subunits with their common (110) axis along a 5-fold axis.²

The Au^o-nanoparticles were analyzed by XPS in order to determine the electronic state of the atom. The Au^o-P₃ shows Au 4f doublet $(4f_{5/2}, 88.5 \text{ ev} \text{ and } 4f_{7/2}, 84.8 \text{ ev})$ and peak-to-peak distance (3.7 ev) [Fig. 5(A)] which is in good agreement with the value due to Au^o oxidation state.¹¹ The core-level Au $4f_{7/2}$ is shifted to a value +0.8 ev, relative to the bulk value of Au (84.0 ev), and this positive shift can be attributed due to smaller cluster size of Au^o-nanoparticles.^{11a-c} In case of Au^o-P₃S₃ [Fig. 5(B)], exhibits Au 4f doublet at $4f_{5/2}$, 87.5 ev and $4f_{7/2}$, 83.8 ev with peak-to-peak distance (3.7 ev) which is also in good agreement with the value due to Au^o oxidation state.¹¹ The core-level Au $4f_{7/2}$ is shifted to a value -0.2 ev, relative to the bulk value of Au (84.0 ev), and this negative shift may be due to faceted nature of Au^o-nanoparticles.^{11c, d}

The presence of ligands on the surface of metal nanoparticles are determined by FTIR study.^{3b, 4e} The IR spectra of ligands P_3 and P_3S_3 after and before stabilization gives slightly different band assignments [Figs. 6(A) and (B)]. Some of the characteristic bands, e.g., in case of ligand P_3 ,



Fig. 2. Representative TEM images and their particles size histogram of (A) Au°-P₃ and (B) Au°-P₃S₃.

sharp peak at 1433.1 cm⁻¹, ascribed to the P–C stretching vibration mode is shifted to 1436.8 cm⁻¹ and also the most characteristic $\nu_{p=s}$ bands of ligand P₃S₃ at 624.4 and 611.0 cm⁻¹ are shifted to 624.0 and 610.6 cm⁻¹



Fig. 3. Powder XRD patterns of Au°-nanoparticles stabilized by ligands (A) P_3 and (B) P_3S_3 .



Fig. 4. Representative HRTEM images and their corresponding SAED pattern (inset) of $Au^{\circ}-P_3$ and (B) $Au^{\circ}-P_3S_3$ showing reticular planes inside the particle.



1800

1500

respectively. These observations give the evidence that the ligands are grafted on the surface of Au^o-nanoparticles through phosphorous and sulphur atom for ligands P_3 and P_3S_3 respectively.

The Thermogravimetric Analyses (TGA) data [Figs. 7(A) and 6(B)] indicate that Au°-nanoparticles stabilized by P₃ and P₃S₃ started decomposition of the ligand at lower temperature i.e., at 170 and 190 °C respectively compared to the corresponding free ligands i.e., at \sim 300 and \sim 380 °C.¹² The lower decomposition temperature of Au°-P₃ may be attributed to stronger and symmetrical interaction of ligand P₃S₃, where a weaker surface interaction is likely due to its structural characteristics.

In general, the multi-twinned particles (MTPs) including five-fold twinned decahedral shaped Au^{\circ}-nanoparticles are theoretically more stable than those of single crystalline counterparts.^{2b} However, the MTPs are chemically more reactive than single crystalline structures because of high defect density on their surfaces.^{2b} Therefore, Au^{\circ}-nanoparticles stabilized by ligand P₃S₃ should be thermally more stable than ligand P₃. This is well

Fig. 6. FTIR spectra (A) of ligand P_3 and $Au^\circ - P_3$ nanocomposite and (B) ligand P_3S_3 and $Au^\circ - P_3S_3$ nanocomposite. The upper and lower spectrums are for pure ligand and Au° -ligands nanocomposite respectively.

Wavenumber (cm⁻¹)

1200

900

600

substantiated by TGA data that ligand P_3S_3 forms thermally more stable Au^o-nanoparticles than ligand P_3 .

The ligand P_3 forms relatively smaller sized particles than P_3S_3 , which may be due to the stronger interaction of Au° (Soft) with P (Soft) of P_3 than Au° (Soft) with S (less Softer than P) of P_3S_3 . In addition, the tertiary phosphorous atom has a strong affinity towards the surface of Au°-nanoparticles and therefore, the symmetrical tripodal ligands $(P_3)^{13}$ interacts very strongly with Au°-nanoparticles and could lead to formation of ligand stabilized stable small size and orderly core structure nanoparticles. Also, such ligand-metal (atom) interaction is responsible for determining the size and shape of metal nanoparticles.¹⁴ On the other hand, in case of P_3S_3 ligand, which is bulkier than P_3 and having

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Fig. 7. TGA plots (A) of ligand P_3 and $Au^\circ - P_3$ nanocomposite and (B) ligand P_3S_3 and $Au^\circ - P_3S_3$ nanocomposite.

unsymmetrical tripodal character,¹⁵ interact with the surface of the Au^o-nanoparticles through sulphur atom only and make less stronger interaction than that of P-atom because of two factors: (i) the latter atom exhibits much stronger interaction with the metal surface and (ii) steric hindrance of bulky ligand (P_3S_3) and as a result lead to formation of bigger size nanoparticles with multi facet decahedral shape particles.

Table I. Three-component coupling of aldehyde, alkyne and amine for the synthesis of propargylamine.



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Entry	Alkyne	Aldehyde	Amine	Products	Catalyst	Yield* (%)
1		CHO	N H H	N	Auº-P ₃	89
		Сно			Au°-P ₃ S ₃	94
2		н ₃ со – Сно			Auº-P ₃	87
			N H	H ₃ CO	Au°-P ₃ S ₃	90
3		сі — Сно	N H	N	Auº-P ₃	91
				CI	Au°-P ₃ S ₃	96
4		СНО			Auº-P ₃	85
					Au°-P ₃ S ₃	88

Notes: Reaction conditions: Aldehyde (1.0 mmol), amine (1.0 mmol), alkyne (1.2 mmol), 25 mg catalyst ($Au^\circ - P_3$ or $Au^\circ - P_3S_3$) and toluene (7 ml) stirred at 110 °C for 3 h. *Isolated yields based on aldehyde after silica gel column chromatography.

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3.2. Catalytic Activity

The main theme of this three component coupling is the C-H alkyne-activation, which can be accomplished by using late transition metals in both complexes as well as nano form catalyst. These metals are well known to form π complexes with terminal alkynes and hence increase the acidity of the C-H bond. Among the transition-metal based catalysts, gold exhibits excellent alkynophilicity.^{3a,7c,8a} Therefore, it is obvious that in the present case also the surface of Au(0) only is responsible for the activation of C-H alkyne bond. The goldalkylide complex thus formed, react with iminium ions which are formed in situ from reaction between aldehyde and amine, to give corresponding desired propargylamine product. This is further substantiated by the catalytic reaction conducted only in presence of the ligands molecules, where no product was observed.

In order to determine the best reaction condition (i.e., solvent, reaction time etc.) that are required to afford excellent yields of propargylamines, a series of threecomponent reactions were carried out using benzaldehyde, piperidine and phenylacetylene as the model substrates. After screening a wide range of reactions, we have found that our catalytic system (Au°-P₃ and Au°-P₃S₃) is most efficient for the three-component coupling reaction in toluene as a solvent at refluxing temperature. The reactions required 3 h time for completion. Using optimized reaction conditions, we explored the versatility and limitations of various substrates as well as efficiency of our catalyst for the said one-pot three-component coupling to synthesise propargylamines and the results are summarized in Table I. In this study, we used phenylacetylene as alkyne, various electronically diverse aldehydes e.g., benzaldehyde, 4-methoxybenzaldehyde, 4-chlorobenzaldehyde and amines e.g., piperidine, diethylamine and all the substrates produce the expected propargylamines with very good to excellent yields and selectivity irrespective of nature of the substrates. The model reaction, i.e., coupling between benzaldehyde, phenylacetylene and piperidine gives maximum 94% isolated yield (entry 1). It is observed that the aromatic aldehyde containing electron withdrawing group (entry 3) gives slightly higher yield than that bearing electron donating group (entry 2). Again, the aliphatic amine i.e., diethylamine (entry 4) shows lower conversion than the cyclic amine i.e., piperidine (entry 1).

In all the reactions, it is observed that the catalyst $Au^{\circ}-P_3S_3$ showed higher activity than $Au^{\circ}-P_3$ although the later has smaller sized particles, which may be due to the multi-twinned particles property of $Au^{\circ}-P_3S_3$. The multiple twinned decahedral particles nature of $Au^{\circ}-P_3S_3$ imparts high defect density on the surface of nanoparticles as a consequence they exhibit high catalytic activity than $Au^{\circ}-P_3$, which has orderly oriented single crystalline surfaces.

4. CONCLUSION

The effect of donor site environment of the ligands P₃ and P₃S₃ towards the stability of Au°-nanoparticles and their bonding capabilities are demonstrated. These ligands are found to be excellent stabilizer of Au°-nanoparticles having small core diameter (less than 4 nm) and narrow size distribution and also these ligands allow the isolation of Au°-nanoparticles as solid materials that can be redispesed in appropriate solvents for further utilities. The ligand P_3 forms relatively smaller size Au°-nanoparticles than P₃S₃ ligand. The ligands P₃ and P₃S₃ form single-crystalline and decahedral shape Au°-nanoparticles respectively. The Au°nanoparticles show good to excellent catalytic activities for one-pot three-component coupling reaction for synthesis of propargylamines. The work reported here points towards a new direction in the design of new ligands for the stabilization of metal nanoparticles for an alternative catalyst for three component coupling reactions.

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