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Pd(II)-acylthiourea complex and its immobilized counterpart catalyzed condensation of phenylacetylene with aryl halides

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Abstract

New Pd(II) complex, *trans*-[PdCl₂L₂] (1) (L = *N*-carbamothioylthiophene-2-carboxamide), was prepared and characterized. Its heterogeneous counterpart, *trans*-[PdCl₂(L-SNPs)₂] (2) (L-SNPs = ligand immobilized on silica nanoparticles), was also prepared through covalent modification of the ligand using silica nanoparticles and characterized. Both 1 and 2 were exploited for their catalytic activity towards condensation of phenylacetylene with aryl halides. The complexes exhibited good activity when aryl halide bears Γ or Br⁻ group. Further, catalyst 2 can be reused for four cycles.

Keywords: Palladium complexes; Acylthiourea ligand; Silica nanoparticles; Heterogeneous catalysis; Phenylacetylene; Aryl halides

* Corresponding author. Tel.: +91 431 2503636; fax: +91 431 2500133. *E-mail address:* kar@nitt.edu (R. Karvembu). Pd-catalyzed coupling reactions are versatile in the aspect of single-step formation of C–C bond. The essential role of Pd assisted coupling in contemporary organic chemistry has been recognized with the Nobel Prize [1,2]. Sonogashira coupling is one such reaction in which a bond is formed between sp^2 and sp hybridized carbons of any halide and terminal alkyne respectively[3]. The synthesized alkyne derivatives constitute the backbone of many natural products, pharmaceutically relevant compounds, sensors etc [4-6]. Although the literature reports suggested that the coupling proceeded in the presence of catalytic amount of Cu along with Pd, self-coupling of copper acetylinide species under O_2 atmosphere was also seen [7,8]. In recent years, there have been considerable efforts to avoid the use of Cu and extend the scope of Pd to various aryl halides [9,10]. Since the discovery of Sonogashira reaction, much attention has been paid to the Pd catalysts containing NHC, phosphine, salen, etc. ligands, and ligand/Cu-free systems [11-13]. Many heterogeneous catalytic systems like Pd/SiO_2 [14,15], magnetic nanoparticles [16,17], MOFs [18], melamine network [19], Cu/Pd alloy system on reduced graphene oxide [20] etc. were also reported. The coupling reaction was also carried out in the presence of non-Pd equivalents like Au/SiO₂ along with copper ferrite nanoparticles [21].

Due to high activity and selectivity in catalytic processes, many organometallic compounds of Pd [22], Ru [23], Rh [24] and Ir [25] were used as homogeneous catalysts for a variety of organic transformations. But commercialization has happened only to a little extent due to lack of reusable property. Heterogeneous catalysts are playing a major role in many industrially relevant processes because of their easy separation and reusability. Heterogeneous catalyst can be metal nanoparticles [26,27], nanoparticles doped on inert support [28], MOFs [29-31], immobilized homogeneous catalyst [32–34] etc. Immobilization of an active complex is an interesting strategy, which enable recovery of the catalyst from the reaction medium [35-38]. Pd complexes were known for their superior catalytic and biological activities [39-41]. To the best of our knowledge, there is no immobilized Pd complex of acylthiourea ligand reported for the condensation of phenylacetylene with aryl halide. Hence, we have prepared Pd(II)-acylthiourea complex which was then immobilized on SiO_2 nanoparticles (SNPs). Catalytic efficacy of both the complexes (homogeneous and heterogeneous) has been studied in the condensation of phenylacetylene with aryl halide. SNPs were used as a support since they are inert, have high surface area and can be easily functionalized.

Synthesis and characterization of the ligand (L) were reported by us earlier [42]. Treatment of 2 equiv. of L with 1 equiv. of $PdCl_2$ in CH_3CN resulted the Pd complex (1) as orange coloured precipitate (Scheme 1) [43]. Complex is stable in air, non-hygroscopic, soluble in DMF, DMAc and DMSO, and insoluble in CHCl₃, CH_2Cl_2 and H_2O .

SNPs were activated and functionalized with L to give L-SNPs by following the reported procedure [42]. PdCl₂ (1 mmol) was added to L-SNPs (0.2 g) in dry acetone, and the reaction mixture was stirred for 8 h under N_2 atmosphere. The resulting solid was centrifuged, washed with distilled water, dry acetone and dry ethanol, and dried at 100 °C under vacuum for overnight to get **2** (Scheme 2).



Synthesis of 2

UV-visible spectrum of **1** showed two bands at 264 and 296 nm, which may be attributed to the ligand centred transitions. The FT-IR spectrum showed the presence of N–H, NH₂, C=O and C=S groups. The stretching frequencies at 3332, 3182 and 3203 cm⁻¹ corresponded to NH₂ and N–H moieties respectively. The C=O and C=S stretching occurred

at 1673 and 1251 cm⁻¹ respectively. The reduction in C=S stretching frequency and unalteration of other frequencies compared to the ligand supported the coordination of ligand to Pd *via* S atom only. In the ¹H NMR spectrum (Figure S1), signals due to N–H (11.84 ppm) and NH₂ (10.46 and 10.21 ppm) protons appeared in the deshielded region as singlets. Also, protons of the thiophene ring showed signals at 7.07-8.30 ppm. ¹³C NMR spectrum of **1** (Figure S2) showed signals due to C=O and C=S carbons at 161.69 and 177.85 ppm respectively. Similarly, aromatic carbons in the thiophene ring resonated in the region 129.28-136.57 ppm. Molecular ion peak at 476.8804 [M–2Cl–H]⁺ in the mass spectrum confirmed the complex formation. From the above observations, Pd is believed to have square planar geometry with two acylthiourea ligands (L) *trans* to each other. Our attempts to crystallize the complex have failed, and hence characterization was limited to spectroscopic techniques.

The protocol used for the immobilization of Pd(II) complex on SNPs is shown in scheme 2. EDAX results obtained for 2 is shown in Figure S4; it showed the presence of various elements along with Pd. The TEM images are shown in Figure S5. SNPs in 2 were found to be in spherical shape. The Pd(II) complex was homogeneously dispersed on the silica surface, which was seen as dark spots in the images. There was no change in the morphology of the support even after its modification. Surface area of SNPs and 2 was found to be 200 and 95 m^2/g respectively. Reduction in the surface area of 2 confirmed the immobilization of 1 on the surface of SNPs. N₂ adsorption-desorption isotherm (Figure S5) showed type IV hysteresis loop for SNPs, which is characteristic of mesoporous material. XPS analyses of 2 showed binding energies at 338.4 and 343.7 eV corresponding to Pd $3d_{5/2}$ and Pd $3d_{3/2}$ respectively (Figure 1) [44]. These values were due to divalent Pd ions, and the possibility of formation of Pd(0) on SNPs was ruled out as no binding energy was seen at 335 and 340 eV [45]. Also, 2 did not show binding energy at 336.4 eV corresponding to PdO, confirming the presence of Pd(II) complex on SNPs [46,47]. In addition, binding energies at 534, 401, 283 and 102 eV were assigned to O 1s, N 1s, C 1s and Si 2p respectively. Pd loading in 2 was 0.920 mmol/g as determined by ICP-OES analysis.



Fig. 1 XPS spectra of 2 (a) wide spectrum of 2, (b) Si 2p peak, (c) N 1s peak, (d) O 2s peak and (e) Pd 3d peak

The results obtained for the condensation of phenylacetylene with different aryl halides are summarized in Table 1. Scope of 1 (homogeneous) and 2 (heterogeneous) was extended to various aryl halides bearing I or Br, and electron releasing or electron withdrawing group, and heterocyclic halide under optimized reaction conditions (Table S1). Iodobenzene was reacted with phenylacetylene in the presence of 1 or 2 to give 1,2diphenylethyne (100%) in 3 h (3a, Table 1). Similarly, Pd-catalyzed (1 or 2) coupling of 4iodoanisole with phenylacetylene formed the desired coupled product in 100% selectivity (3b, Table 1). As expected, reactivity of aryl iodides was more than that of bromides. 5bromoindole was coupled with phenylacetylene to produce 5-(phenylethynyl)-1H-indole in 100% selectively, but the conversion (81%) was better with 2 compared to that (71%) with 1 (3c, Table 1). While using 1-bromo-4-iodobenzene along with phenylacetylene in the presence of 1, 1-bromo-4-(phenylethynyl)benzene was obtained in good selectivity (100%) (3e, Table 1). The reaction of 4-bromoacetopheneone with phenylacetylene in the presence of 1 yielded 1-(4-(phenylethynyl)phenyl)ethanone in 55% selectivity (3e, Table 1). In this case, phenylacetylene underwent self-coupling and gave 1,4-diphenylbuta-1,3-diyne as a side product. Similarly, catalytic activity of 2 was studied with 4-iodonitrobenzene and phenylacetylene; the reaction proceeded smoothly to offer 1-nitro-4-(phenylethynyl)benzene (3f, Table 1) with good conversion (99%) and selectivity (100%). Also, 1-iodonaphthalene or

1-bromonaphthalene was coupled with phenylacetylene to provide only 1-(phenylethynyl)naphthalene (3g and 3h, Table 1) in 76 or 65% conversion respectively. While extending the scope to Br substituted aldehydes (2-bromobenzaldehyde, 3bromobenzaldehyde and 4-bromobenzaldehyde), desired product was not formed, but cinromide was observed (Figures S15 and S16). Aldol reaction might have happened before coupling in the presence of the catalyst [48]. In the presence of strong base (KO^tBu), α hydrogen of N,N-dimethyl acetamide was removed to generate carbanion which might attack the carbonyl carbon of Br substituted benzaldehyde, followed by dehydration leads to α,β unsaturated compound (cinromide). The reported magnetic nanoparticles supported Pd catalyst performed the coupling using 1 mol% catalyst at 100 °C [49]. However, present conditions are comparatively milder and catalyst loading is also less.



3g, 12 h,
$$76/100\%^{\circ}$$
 (X = I) **3h**, 15 h, $65/100\%^{\circ}$ (X = Br)

Reaction conditions: Aryl halide (0.5 mmol), phenylacetylene (0.55 mmol), 1 (0.4 mol% when X = I; 0.6 mol% when X = Br), KO^tBu (0.55 mmol), DMAc (3 mL), 80 °C. ^a1 is used as a catalyst, ^b2 is used as a catalyst, Conversion/selectivity were determined by GC-MS.

Condensation was performed between iodobenzene and phenylacetylene in the presence of base without the catalyst. No coupled product (1,2-diphenylethyne) was seen, and it demonstrated the catalytic involvement of Pd(II). Catalyst **2** was used for the condensation of phenylacetylene with iodobenzene under optimum conditions. The catalyst was recovered from the reaction mixture by simple centrifugation, washed with diethyl ether and dried under vacuum. Recovered catalyst was used for the next run. Further cycles of catalysis were proceeded under identical conditions, and the results were noted.



Reaction conditions: Iodobenzene (0.5 mmol), phenylacetylene (0.55 mmol), **2** (5 μ mol) and KO^tBu (0.55 mmol), DMAc (3 mL), 80 °C, 3 h. Conversion and selectivity were determined by GC.

Homogenous and heterogeneous Pd(II) complexes of acylthiourea ligand (L) were prepared and characterized. In the heterogenous catalyst, Pd(II) complex was uniformly distributed over nano silica. Both the catalysts showed good activity in the condensation of phenylacetylene with aryl halides. Bromobenzaldehyde derivatives could not be used as substrate due to the formation of cinromide. Importantly, the heterogeneous Pd(II) catalyst can be isolated easily and used satisfactorily at least for four cycles.

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- ➤ Homogeneous Pd(II)-acylthiourea complex was prepared
- It was immobilized on nano silica
- Catalytic activity of homogeneous and heterogeneous catalysts was evaluated for condensation of phenylacetylene with aryl halides
- > Heterogeneous catalyst can be reused up to four cycles

There are no conflicts to declare.

The manuscript is original. Authors certify that this has not been submitted/published anywhere.