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Synthesis of 5-substituted 1*H*-tetrazoles from aryl halides using nanopolymer-anchored palladium(II) complex as a new heterogeneous and reusable catalyst

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Abstract This paper reports on the preparation and use of chloromethylated polystyrene-anchored palladium(II) complex, [Ps-ttet-Pd(II)], as a separable nanocatalyst for the synthesis of 5-substituted 1*H*-tetrazoles by treating aryl halides with $K_4[Fe(CN)_6]$ as non-toxic cyanide source, to generate in situ the corresponding aryl nitriles which then react through [2 + 3] cycloaddition with sodium azide. High yields of the products, simple methodology, easy work-up procedure, high catalytic activity, and superior cycling stability of the catalyst are the main advantages of this protocol. The structure of the catalyst was characterized using the powder XRD, SEM, TG-DTA, EDS, AAS, and FT-IR spectroscopy techniques. Graphical abstract



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Introduction

The substituted benzonitriles represent important materials for the preparation of different commercial compounds, pharmaceutical, herbicides, pesticides, natural products, dyes, and pigments [1–4]. Aryl nitriles valuable intermediates in organic synthesis and can be easily converted to a range of heterocycles, benzoic acids/esters, amidines, amides, imidoesters, benzamidines, amines, and aldehydes [5].

Tetrazoles are one of the important nitrogen-rich compounds with a wide range of applications in the fields of organic synthesis, pharmaceutical, coordination chemistry, material science, especially explosives and in the synthesis of N-containing heterocycles [6–10].

Classical methods for the preparation of benzonitriles involve the Rosenmund-von Braun reaction of aryl halides with stoichiometric amounts of copper(I) cyanide [11], diazotization of anilines and subsequent Sandmeyer reaction [12], and on an industrial scale the ammoxidation reaction [13]. Modifications to these methods have been made using palladium-, copper-, or nickel-catalyzed aryl cyanation approaches [14, 15]. The transition metal-catalyzed cyanation of aryl halides was performed using toxic inorganic or organic cyanide sources such as alkali metal cyanides (KCN [16], NaCN [17]), trimethylsilyl cyanide (Me_3SiCN) , [18] or Zn(CN)₂ [19, 20]. The toxicity of KCN and NaCN, the sensitivity of Me₃SiCN to moisture, the release of HCN and production of heavy metal waste, in the case of $Zn(CN)_2$, significantly restrict the applications of these reagents. These difficulties have been overcome using inexpensive and non-toxic potassium hexacyanoferrate(II), K_4 [Fe(CN)₆], as an efficient source of cyanide [21, 22].

On the other hand, the most conventional methods for the synthesis of 5-substituted 1*H*-tetrazoles is via [2 + 3]cycloaddition between corresponding nitriles and azides. Several methods for the synthesis of 5-substituted tetrazoles have been reported through the cycloaddition of nitriles using NaN₃ or TMSN₃ in the presence of homogeneous and heterogeneous catalysts such as Zn(II) [23], AlCl₃ [24], BF₃-OEt₂ [25], FeCl₃–SiO₂ [26], Zn/Al HT [27], ZnS [28], Pd(PPh₃)₄ [29], and GO/ZnO nanocomposite [30].

However, despite these advances, papers reporting the synthesis of 5-substituted 1*H*-tetrazoles from in situ formed benzonitriles have stayed sparse. The successful examples for the one-pot synthesis of 5-substituted 1*H*-tetrazoles are based on the direct transformation of primary alcohols and aldehydes into tetrazoles in aqueous media [31, 32], and the sequential one-pot synthesis of tetrazoles from aryl halides using toxic cyanide sources [33–36]. Despite the advantages of homogeneous catalysts, difficulties in recovering the catalyst from the reaction mixture severely inhibit their wide use in industry.

Development of heterogeneous catalysts for industrial applications has become important from both the environmental and economic viewpoints, and has been reviewed in the literature [37]. The use of heterogeneous catalysts such as organometallic complexes onto a solid support is often desirable from the perspective of process development due to their recycling, simple recovery, and easy handling [38]. The use of heterogeneous catalysts for coupling reactions gives rise to a reduction in waste. As such, highly active polymer-anchored transition metal complexes have gained significant interest because they could be easily recovered and reused [39]. We used chloromethylated polystyrene (CMP) cross-linked with 2 % of divinylbenzene (DVB) as a support because it is a popular polymeric material due to its ready availability, low cost, ease of functionalization, and mechanical robustness.

In continuation of our recent works on the synthesis of tetrazoles and applications of heterogeneous catalysts [40–47], we herein report a new protocol for the preparation and characterization of the nanopolystyrene-anchored Pd(II) thiotetrazole complex abbreviated as [Ps-ttet-Pd(II)] (2) and its application as a new and stable heterogeneous catalyst for the cyanation of aryl halides to the corresponding benzonitriles by the use of potassium hexacyanoferrate(II), K_4 [Fe(CN)₆], as a non-toxic cyanide source. The formed benzonitriles without isolation underwent [2 + 3] cycloaddition with sodium azide to afford high yields of the desired tetrazoles (Scheme 1).

Catalyst was readily prepared in two steps. The synthesis of the polymer-anchored Pd(II) complex is shown in Scheme 2. Treatment of chloromethylated polystyrene with phenylthiotetrazole in DMF, followed by the treatment of the resulting phenylthiotetrazole-functionalized polymer (I) with a solution of palladium(II) chloride in ethanol resulted in covalent attachment of the palladium complex to give the polymer-anchored Pd(II) complex catalyst [Ps-ttet-Pd(II)] (2).

Results and discussion

Successful synthesis of the [Ps-ttet-Pd(II)] was characterized using powder XRD, SEM, TG-DTA, EDS, AAS and FT-IR. The presence of the phenyl-1H-tetrazole-5-thiol ligand bonded CMP and the formation of [PS-ttet-Pd(II)] (2) were verified by FT-IR. The FT-IR spectrum of the chloromethylated polystyrene was compared with the thiotetrazole bonded polystyrene (1) and nanopolymer-anchored [PS-ttet-Pd(II)] (2) catalyst to confirm the coordination of the metal atom with the phenyl-1H-tetrazole-5-thiol ligand (Fig. 1). As depicted in Fig. 1a, the sharp C-Cl peak (due to CH₂Cl groups) at 1274 cm⁻¹ in the starting polymer practically decreased or was seen as a weak band after introduction of the thiotetrazole ligand on the polymer. The stretching vibrations of the N=N double bonds appear at 1449 and 1403 cm⁻¹ for polystyrene-anchored ligand (Fig. 1a) and complex (Fig. 1b), respectively. Signals ranging under 3000–2800 cm⁻¹ identify the methylene stretching bonds. The functionalized beads exhibited a band at 1652 cm^{-1} due to stretching vibrations of the C=N double bond, which was shifted to 1598 cm^{-1} in the anchored beads. This verified that a metal complex was formed on the surface of the polymer.

The presence of polystyrene and palladium was confirmed with powder XRD measurements. The powder X-ray diffraction pattern of the complex is shown in Fig. 2. Polystyrene displays a broad peak at about $2\theta = 22.7^{\circ}$ [48]. The size of the [PS-ttet-Pd(II)] catalyst can be found by applying Sherrer's equation and the average size is found to be 30 nm.

Scanning electron micrograph (SEM) was recorded to understand the morphological changes occurring on the surface of the polystyrene. Figure 3 shows SEM images of the polymer-anchored complex in different magnifications. As expected, the pure polystyrene bead had a smooth and flat surface [49], while the supported complex showed roughening of the top layer. On the other hand, after metal loading on the surface of the polymer, a change in morphology of the polymer surface is observed and the smooth and flat surface of the polymer shows a slight roughening on complexation.



Scheme 2







CI







Fig. 3 SEM images of the [PS-ttet-Pd(II)] complex

We used energy dispersive X-ray spectroscopy (EDS) to determine chemical composition of the catalyst. The presence of the Pd is verified by EDS. In the EDS spectrum of catalyst (Fig. 4), peaks related to C, S, Pd, Cl, and O were observed. The excess oxygen is due to physical absorption of oxygen from environment during sample preparation for SEM experiment. The metal loading of polymer-supported palladium complex, as determined by atomic absorption spectrometry, was 0.29 mmol/g.

TGA curve of the chloromethylated polystyrene-anchored palladium(II) complex is shown in Fig. 5. Thermal stability of polymer-anchored complex was measured using TG-DTA at a heating rate of 2 °C min⁻¹ in air over a temperature range of 30–600 °C. TGA of chloromethylated



Fig. 4 EDS spectrum of the [PS-ttet-Pd(II)] complex

[PS-ttet-Pd(II)] complex



polystyrene-anchored palladium(II) complex indicates that thermolysis of the phenylthiotetrazole ligand bound to the polymer proceeds at higher temperatures in comparison with the free ligand molecule. Thus, whereas pure phenylthiotetrazole decomposes at about 140 °C [50], being deposited on the surface of complex, it decomposes at about 220 °C. Also, we can see another degradation step, roughly 280-470 °C, could be due to the degradation of the polystyrene as reported in the literature [51].

In next step, we tested the catalytic activity of the [PSttet-Pd(II)] in tandem synthesis of 5-substituted 1H-tetrazoles from aryl halides with K₄[Fe(CN)₆] as non-toxic cyanide source. Initial studies were performed to optimize the reaction conditions between iodobenzene, potassium

hexacyanoferrate(II), and sodium azide in the presence of the [PS-ttet-Pd(II)] (Table 1). The reaction conditions were optimized and the best conditions were found to be 0.05 g of catalyst, 0.22 mmol of K₄[Fe(CN)₆] in N,N-dimethylformamide as solvent and the results are summarized in Table 1. Several bases were screened for the reaction in the presence of a catalytic amount of the [PS-ttet-Pd(II)] catalyst. As shown in Table 1, the reaction was influenced significantly by the base employed. The reaction worked very well when inorganic bases such as Na2CO3 and K2CO3 were used (entries 7 and 8), and the best result was obtained in the case of Na₂CO₃ (entry 7). Control experiments show that there is no reaction in the absence of catalyst (Table 1, entry 9). A decrease in the catalyst loading from 0.05 to 0.02 g afforded

Table 1	Optimization	of the synthesis	of 5-phenyl-1H-tetraz	ole
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Entry	[PS-ttet-Pd(II)]/g	Solvent	Base	Temp./°C	Yield/% ^b
1	0.05	DMF	Et ₃ N	120	45
2	0.05	DMF	Piperidine	120	35
3	0.05	CH ₃ CN	Na ₂ CO ₃	80	0
4	0.05	Toluene	Na ₂ CO ₃	110	Trace
5	0.05	NMP	Na ₂ CO ₃	120	50
6	0.05	DMAC	Na ₂ CO ₃	120	65
7	0.05	DMF	Na ₂ CO ₃	120	89
8	0.05	DMF	K ₂ CO ₃	120	81
9	_	DMF	Na ₂ CO ₃	120	0
10	0.02	DMF	Na ₂ CO ₃	120	70
11	0.08	DMF	Na ₂ CO ₃	120	90

^a Reaction conditions: iodobenzene (1 mmol), K₄[Fe(CN)₆] (0.22 mmol), base (1 mmol), 0.05 g [Ps-ttet-Pd(II)], sodium azide (1.5 mmol), 5 cm³ degassed DMF at 120 °C for 12 h

^b Isolated yield

the product in lower yield (Table 1, entry 10). No significant improvement on the yield was observed using higher amount of the catalyst (Table 1, entry 11).

To explore the general applicability of the [PS-ttet-Pd(II)] as a catalyst for the synthesis of 5-sustituted 1*H*-tetrazoles, different aryl halides contain both electron-releasing and electron-withdrawing groups were reacted with K_4 [Fe(CN)₆] and NaN₃ under optimal reaction conditions and the results are tabulated in Table 2. In all cases, the electron-neutral, electron-rich and electron-poor aryl halides give the corresponding products in good yields under the standard reaction conditions. Aryl bromides, in contrast to aryl iodides, require much longer periods of time for the synthesis of 5-substituted 1*H*-tetrazoles.

The reusability of the catalyst is one of the most important benefits and makes them useful for commercial applications. The reusability of the catalyst was investigated for the synthesis of 5-(4-methylphenyl)-1*H*-tetrazole under the present reaction conditions (Table 2, entry 2). After completion of the reaction, the [PS-ttet-Pd(II)] was separated from the reaction mixture by centrifuge. The catalyst was washed with water several times, dried, and employed for the next run. The activity of the catalyst in five consecutive runs (85, 85, 83, 83, and 82 %) revealed the practical recyclability of the catalyst. This reusability exhibits the high stability of the catalyst under the operating conditions. To investigate the palladium leaching in this reaction, the filtrate of the reaction after completion was analyzed by AAS technique. The amount of palladium leaching after the second recycle was determined by AAS analysis to be only 0.04 %, and after five repeated recycling was 0.24 %.

In conclusion, we have proved that the heterogeneous palladium catalyst [PS-ttet-Pd(II)] is a highly efficient and stable catalyst for the synthesis of 5-substituted 1*H*-tetrazoles by treating aryl halides with K_4 [Fe(CN)₆], to generate in situ the corresponding aryl nitriles which then react through [2 + 3] cycloaddition with NaN₃. The catalyst was characterized by FT-IR, SEM, EDS, XRD, AAS, and TG-DTA analysis. This simple synthetic method has the advantages of high yields, easy preparation, using non-toxic potassium hexacyanoferrate(II) as cyanide source, elimination of dangerous and harmful hydrazoic acid, provides simple work-up procedure, and handling of the catalyst. The [PS-ttet-Pd(II)] is an eco-friendly catalyst because it can be recovered and reused without any significant loss of activity.

Experimental All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. Chloromethylated polystyrene (4–5 % Cl and 2 % cross-linked with divinylbenzene) was

Table 2 Sequential one-pot synthesis of 5-substituted 1H-tetrazoles from aryl halides with K₄[Fe(CN)₆] as non-toxic cyanide source

Arvl halide	Product	Time/h	Yield/% ^c	M.p./°C (reported)
	0.11.77	10		
C_6H_5I	C_6H_5 let	12	89	213–214 (215–216 [23])
4-MeC ₆ H ₄ I	$4-\text{MeC}_6\text{H}_4\text{Tet}$	12	85(82) ^d	248 (248–249 [34])
4-MeOC ₆ H ₄ I	4-MeOC ₆ H ₄ Tet	12	83	232–233 (231–232 [34])
4-ClC ₆ H ₅ I	4-ClC ₆ H ₅ Tet	12	86	261–262 (262 [30])
3-ClC ₆ H ₄ I	3-ClC ₆ H ₄ Tet	12	86	137–139 (137–138 [52])
4-FC ₆ H ₄ I	4-FC ₆ H ₄ Tet	12	81	193 (193–194 [53])
3-IC ₅ H ₄ N	3-TetC ₅ H ₄ N	12	80	238-239 (239-240 [54])
4-IC ₅ H ₄ N	4-TetC ₅ H ₄ N	12	84	254–255 (253–254 [54])
$1,4-I_2C_6H_4$	1,4-(Tet) ₂ C ₆ H ₄	12	81	295 (290-291 [53])
$1,3-I_2C_6H_4$	1,3-(Tet) ₂ C ₆ H ₄	12	78	258 (260 [55])
C ₆ H ₅ Br	C ₆ H ₅ Tet	20	81	213–214 (215–216 [23])
4-MeC ₆ H ₄ Br	4-MeC ₆ H ₄ Tet	20	77	248 (248–249 [34])
3-ClC ₆ H ₄ Br	3-ClC ₆ H ₄ Tet	20	79	137–139 (137–138 [52])
3-BrC ₅ H ₄ N	3-TetC ₅ H ₄ N	20	75	238–239 (239–240 [54])
	Aryl halide C_6H_5I $4-MeC_6H_4I$ $4-MeOC_6H_4I$ $4-ClC_6H_5I$ $3-ClC_6H_4I$ $4-FC_6H_4I$ $4-FC_6H_4I$ $3-IC_5H_4N$ $4-IC_5H_4N$ $1,4-I_2C_6H_4$ $1,3-I_2C_6H_4$ C_6H_5Br $4-MeC_6H_4Br$ $3-ClC_6H_4N$ $3-FlC_5H_4N$	Aryl halideProduct C_6H_5I C_6H_5Tet $4-MeC_6H_4I$ $4-MeC_6H_4Tet$ $4-MeOC_6H_4I$ $4-MeOC_6H_4Tet$ $4-ClC_6H_5I$ $4-ClC_6H_5Tet$ $3-ClC_6H_4I$ $3-ClC_6H_4Tet$ $4+FC_6H_4I$ $4-FC_6H_4Tet$ $3-lC_5H_4N$ $3-TetC_5H_4N$ $4-IC_5H_4N$ $4-TetC_5H_4N$ $1,4-I_2C_6H_4$ $1,4-(Tet)_2C_6H_4$ $1,3-I_2C_6H_4$ $1,3-(Tet)_2C_6H_4$ $2-GH_5Br$ C_6H_5Tet $4-MeC_6H_4Br$ $4-MeC_6H_4Tet$ $3-ClC_6H_4Br$ $3-ClC_6H_4Tet$ $3-BrC_5H_4N$ $3-TetC_5H_4N$	Aryl halideProductTime/h C_6H_5I C_6H_5Tet 12 4 -MeC_6H_4I 4 -MeC_6H_4Tet12 4 -MeOC_6H_4I 4 -MeOC_6H_4Tet12 4 -ClC_6H_5I 4 -ClC_6H_5Tet12 3 -ClC_6H_4I 3 -ClC_6H_4Tet12 4 -FC_6H_4I 4 -FC_6H_4Tet12 4 -FC_6H_4I 4 -FC_6H_4Tet12 3 -ClC_6H_4I 4 -FC_6H_4Tet12 4 -FC_6H_4I 4 -FC_6H_4N12 4 -IC_5H_4N 3 -TetC_5H_4N12 1 , 4 -I_2C_6H_4 1 , 4 -(Tet)_2C_6H_412 1 , 3 -I_2C_6H_4 1 , 3 -(Tet)_2C_6H_412 1 , 3 -I_2C_6H_4 4 -MeC_6H_4Tet20 4 -MeC_6H_4Br 4 -MeC_6H_4Tet20 3 -ClC_6H_4Br 3 -TetC_5H_4N20	Aryl halideProductTime/hYield/% C_6H_5I C_6H_5Tet 1289 4 -MeC_6H_4I 4 -MeC_6H_4Tet1285(82)^d 4 -MeOC_6H_4I 4 -MeOC_6H_4Tet1283 4 -ClC_6H_5I 4 -ClC_6H_5Tet1286 3 -ClC_6H_4I 3 -ClC_6H_4Tet1286 4 -FC_6H_4I 3 -ClC_6H_4Tet1281 3 -ClC_6H_4I 4 -FC_6H_4Tet1280 4 -IC_5H_4N 3 -TetC_5H_4N1284 $1,4$ -I_2C_6H_4 $1,4$ -(Tet)_2C_6H_41281 $1,3$ -I_2C_6H_4 $1,3$ -(Tet)_2C_6H_41278 C_6H_5Br C_6H_5Tet 2081 4 -MeC_6H_4Br 4 -MeC_6H_4Tet2079 3 -BrC_5H_4N 3 -TetC_5H_4N2075

ArX + K₄[Fe(CN)₆]
$$\xrightarrow{[Ps-ttet-Pd(II)]}{NaN_3, DMF, Na_2CO_3, 120 °C} Ar \xrightarrow{N}_{H} N$$

^a Reaction conditions: aryl halide (1 mmol), $[K_4Fe(CN)_6]$ (0.22 mmol), Na_2CO_3 (1 mmol), 0.05 g [Ps-ttet-Pd(II)], sodium azide (1.5 mmol), 5 cm³ degassed DMF at 120 °C

^b Products were identified by comparison of their melting point and ¹H NMR spectral data those reported in the literature

c Yield after work-up

^d Yield after fifth cycle

purchased from Merck. Products were characterized by different spectroscopic methods (FT-IR and ¹H NMR spectra) and melting points. The NMR spectra were recorded on a Bruker Avance DRX 400 MHz instrument in DMSO- d_6 . The chemical shifts (δ) are reported in ppm relative to the TMS as internal standard. J values are given in Hz. FT-IR (KBr) spectra were recorded on a Perkin-Elmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and were uncorrected. TLC was performed on silica gel polygram SIL G/UV 254 plates. X-ray diffraction measurements were performed with a Philips powder diffractometer type PW1373 goniometer. It was equipped with a graphite monochromator crystal. The X-ray wavelength was 1.5405 Å and the diffraction patterns were recorded in the range $2\theta = 0-90^\circ$ with scanning speed of 2°/min. Morphology and particle dispersion was investigated by scanning electron microscopy (SEM) (Cam scan MV2300). The chemical composition of the prepared nanostructures was measured by EDS performed in SEM. Palladium loadings were determined by atomic absorption spectroscopy (AAS) using a VARIAN Spectra AA-20 instrument. Thermogravimetric-differential thermal analysis (TG-DTA) was performed using STA 1500 Rheometric (England). The flow rate of air was 120 cm³/min and the ramping rate of sample was 2 °C/min.

Preparation of nanopolystyrene-anchored Pd(II) thiotetrazole complex

The reaction was performed in the 250 cm³ round-bottomed flask. To a mixture of 2.0 g CMP (1.25 mmol/g of Cl) in 50 cm³ DMF, 1-phenyl-1*H*-tetrazole-5-thiol (5.0 mmol) and K₂CO₃ (5.0 mmol) were added. The mixture was stirred at 100 °C for 24 h, and then filtered, washed with DMF, and finally dried under vacuum for 12 h. The functionalized polymer (1) (1.0 g) was treated with 0.45 g PdCl₂ in 50 cm³ EtOH, and the mixture was stirred under reflux conditions for 24 h. The resulting polymer, impregnated with the metal complex, was filtered, washed with EtOH, and subsequently dried at 60 °C to give [PS-ttet-Pd(II)] (Scheme 2).

General procedure for the synthesis of 5-substituted 1H-tetrazoles

A mixture of aryl halide (1.0 mmol), $K_4[Fe(CN)_6]$ (0.22 mmol), 0.05 g [PS-ttet-Pd(II)], and sodium carbonate (1.0 mmol) was stirred in 5 cm³ DMF at 120 °C for 1 h under an argon atmosphere. To the aryl nitrile compound generated in situ was added sodium azide (1.5 mmol) and the mixture was stirred at 120 °C for appropriate time. After completion of the reaction (as indicated by TLC), the catalyst was centrifuged, washed with EtOH and the residue was diluted with 35 cm³ ethyl acetate and 20 cm³ HCl (4 N) and stirred vigorously. The resultant organic layer was separated and the aqueous layer was extracted with 25 cm³ ethyl acetate. The combined organic layer was washed with 8 cm³ water and concentrated to give a crude product. Column chromatography using silica gel gave the pure product. All products were characterized by ¹H NMR and melting point which were in agreement with literature [23, 30, 31, 35, 52–55].

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