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Introduction

Palladium catalyzed Suzuki Miyaura C–C coupling (SMC) reaction is among the very important organic transformations.¹ The biaryl derivatives prepared *via* this coupling play promising roles in the production of pharmaceutical ingredients, agrochemicals and natural products² for industrial purposes. For this coupling bulky and electron-rich phosphine–Pd³ or carbene–Pd complexes^{3b,4} are the most active catalysts. Such coupling reactions are performed in very large number of cases under an inert atmosphere because many of the known catalytic species are sensitive to oxygen or moisture.⁴ Therefore such reactions giving high yield under aerobic conditions continue to be an important challenge. Further, mixtures of water

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Palladium(II)-(E,N,E) pincer ligand (E = S/Se/Te) complex catalyzed Suzuki coupling reactions in water *via in situ* generated palladium quantum dots†

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The (E,N,E) pincer ligands (ArECH₂CH₂)₂NH (L1/L2: Ar = Ph, E = S/Se; L3: Ar = CH₃O-p-C₆H₄, E = Te) synthesized by reaction of PhS⁻/PhSe⁻/CH₃O-p-C₆H₄Te⁻ with bis(2-chloroethyl)amine react with Na_2PdCl_4 in aqueous ethanol, resulting in nearly square planar diamagnetic complexes [Pd(L)Cl]Cl (1-3), where L = L1-L3. All the ligands (L1-L3) and their complexes (1-3) have been characterised with ¹H, ¹³C(¹H), ⁷⁷Se(¹H) and ¹²⁵Te(¹H) NMR spectra and high resolution mass spectrometry. The single crystal structures (determined with X-ray diffraction) of 2 and 3 have been solved (Pd-Se: 2.4104(5)/2.4222(6) Å; Pd-Te: 2.560(2)/2.588(2) Å). The conversions for Suzuki-Miyaura coupling (SMC) of various aryl bromides with phenylboronic and 4-formyl/acetyl phenylboronic acid in water using 2-3 mol% of each of the complexes 1-3 have been found good. Complexes 1 and 2 show better catalytic activity than 3, as higher yields were observed with them in a relatively short time. The coupling reactions appear to be catalyzed with Pd(0) nanoparticles (NPs) generated in situ in the course of reaction. The NPs have been isolated and HRTEM studies on them have revealed their size as ~1–3 nm. The SEM-EDX indicates their protection with organochalcogen fragments. Addition of TBAB was essential in some cases to get good yield of cross coupled product. The isolated NPs show catalytic activity for SMC independently. The yields of cross coupled product were excellent when NPs were reused. The two phase test suggests a relatively low contribution of homogeneous Pd species in catalysis.

and organic solvent have been generally used in Pd catalyzed SMC. The pure water as a reaction medium has been used in much less number of reports. Use of water as solvent now-a-days appeals to chemists⁵ as it is green, cheapest among solvents and readily available. Although organic solvents have many attractive features, they still suffer from serious drawbacks such as inflammable nature, low heat capacity and difficulty in their quantitative recovery.⁶

The Pd(π) complexes of chalcogenated Schiff bases⁷⁻¹³ and some other S or Se containing ligands¹¹⁻¹⁸ have emerged as a family of phosphine free, air and moisture insensitive efficient catalysts. However with most of them SMC reactions have been carried out in organic solvents. The use of water as a solvent in the case of catalysis by such kind of complexes is rare.^{19–22} Among the advantages⁶ of using water as solvent in SMC reactions one may include the ease in separation of product and catalyst, high solubility of inorganic bases in water and stability of aqueous solution of phenylboronic acid. The clubbing of advantages of using Pd(π)-complexes of organochalcogen ligands in catalyzing SMC with those of using water as a solvent system is worth exploring and has been carried out in this paper. For Pd based SMC in pure water, the

[†]Electronic supplementary information (ESI) available: Spectral data of L1–L3 and 1–3; single crystal data of 2 and 3 (CCDC 945010 and 945011), SEM, EDX and TGA of NPs. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51658j

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Scheme 1 Synthesis of ligands and complexes.

catalytic species used are Pd(OAc)₂ with or without additives²³ including ligands and palladium species immobilized²⁴ on various supports. Some discrete and well characterized Pdcomplexes^{25,26} of carbenes and other ligands have also been explored for catalysis of this coupling reaction in water. The pincer ligands are considered very important for designing Pd catalysts for SMC because combination of donor groups may be easily varied to control the steric and electronic properties of palladium in their complexes.²⁷ Palladium(II)-complexes of (N,C,N), (P,N,P), (S,C,S), (S,N,S), (Se,N,Se), (P,C,P), (P,Si,P) and other unsymmetrical pincer ligands have been reported as efficient catalysts for SMC.²⁷⁻³⁰ However, only a limited number of such complexes have been reported to show catalytic activity in water.^{19-22,25} It was therefore thought worthwhile to explore the Pd-complexes of tridentate (E,N,E) pincer ligands L1-L3 (E = S, Se, Te) for this purpose in pure water (Scheme 1). These three complexes reported here efficiently catalyze SMC of various aryl bromides. The catalysis occurs via Pd NPs protected with organochalcogen fragments. To understand these NPs including their role in catalysis is among the major objectives of this work. The two phase test in the present case has revealed cocktail like catalysis,¹⁴ but mostly heterogeneous. The NPs formed in the course of reaction on isolation from reaction mixture show catalytic activity for SMC independently and they do not become inactive after a reaction as they can be reused.

Results and discussion

Syntheses and structures

The syntheses of ligands L1–L3 and their palladium complexes 1–3 are summarized in Scheme 1. The reactions of bis(2-chloroethyl)amine hydrochloride with nucleophiles PhS⁻/PhSe⁻/ CH₃O-p-C₆H₄Te⁻ in EtOH under inert atmosphere result in tridentate ligands L1-L3. Palladium complexes of these ligands are easily formed on the reaction of Na₂PdCl₄ with L1, L2 or L3, as the donor groups present in them are much stronger in comparison to Cl. The complexes were isolated by filtration. As the complexes are ionic, their substantial amount goes to filtrate. The filtrate on slow evaporation has resulted in orange crystals of complexes 2 and 3. The ligands L1-L3 were found soluble in common organic solvents. Their air stable complexes are sparingly soluble in CH₂Cl₂, CH₃CN and CHCl₃ but soluble in DMSO and DMF. The ¹H and ¹³C{¹H} NMR spectra of L1-L3 and their complexes are characteristic. On complexation ECH₂ (E = S/Se/Te) and NCH₂ signals in ¹H NMR spectra have been found to appear as multiplets and deshielded by ~0.1-0.3 and 0.1-0.6 ppm respectively with respect to those of corresponding free ligands. Further the magnitude of deshielding for ECH₂/NCH₂ protons is highest in case of 1 and lowest in case of 3. The signals of SCH_2 and NCH₂ in ${}^{13}C{}^{1}H$ NMR spectra of **1** show shielding of 3.3 and 7.4 ppm respectively with respect to those of free L1.

The signal of ECH₂ (E = Se/Te) in ${}^{13}C{}^{1}H$ NMR spectra shows deshielding of 14.0 and 4.1 ppm (with respect to that of corresponding free ligand) in case of 2 and 3 respectively. In $^{13}C{^{1}H}$ NMR spectra of L2 and L3, the signals of -NCH₂ group appear at 47.7 and 49.4 ppm respectively. On complexation these signals are deshielded by 8.2 and 4.5 ppm respectively. These observations imply the co-ordination of N and E with palladium(II) in case of at least 2 and 3. The signals in 77 Se{¹H} and ¹²⁵Te{¹H} NMR spectra of L2 and L3 appear at 284.9 and 414.1 ppm respectively (Fig. S9 and S12 in ESI[†]). However, ⁷⁷Se-{¹H} and ¹²⁵Te{¹H} NMR spectra of 2 and 3 could not be recorded due to instability of their solutions in DMSO. ¹H NMR spectra of complexes 1, 2 and 3 were recorded in D_2O . These complexes have been further treated with K₂CO₃ in D₂O at 100 °C for 0.5 h. No sign of their decomposition was noticed in case of 1 and 2 but 3 decomposed immediately. The single crystal structures of 2 and 3 have been established with X-ray diffraction. However, attempts to crystallize complex 1 were unsuccessful. The crystal data and details of structure refinement for complexes 2 and 3 are given in Table S1 of ESI.† Tables S2 and S3 in ESI⁺ contain selected bond lengths and angles for complexes 2 and 3 respectively. Fig. 1 and 2 show ORTEP diagram of 2 and 3 with few bond lengths and angles. There is a distorted square planar geometry around Pd in both the complexes. The Pd–N bond lengths, 2.046(3) and 2.07(1) Å of 2 and 3 respectively are close to each other and greater than the value, 1.985(3) Å reported for palladium complex of (Se,N, Se) pincer.¹⁷ These Pd–N bond lengths are almost similar to the value, 2.010(4) Å reported for $Pd(\pi)$ complex of a tridentate selenated Schiff base.⁷ The Pd–Se bond distances [2.4104(5) and 2.4222(6) Å] of 2 have been found to be somewhat longer than the value 2.3891(7) Å reported for palladium complex of (Se,N,Se) pincer.¹⁷ The Pd-Cl bond lengths of 2 and 3 are 2.297(1) and 2.300(4) Å respectively and consistent with the value, 2.3159(7) Å reported for the Pd(II) complex of a tridentate sulphated Schiff base.⁷ The Pd–Te bond lengths 2.560(2) and 2.588(2) Å in 3 are longer than the reported values



Fig. 1 ORTEP diagram of 2 with 40% probability ellipsoids. H, water and chloride ion have been omitted for clarity. Bond lengths (Å): Pd(1)-Se(1)/Pd(1)-Se(2) 2.4104(5)/2.422(6), Pd(1)-N(1) 2.046(3); Pd(1)-Cl(1) 2.297(1). Bond angles (°): N(1)-Pd(1)-Cl(1) 178.8(1); N(1)-Pd(1)-Se(1) 87.8(1); Cl(1)-Pd(1)-Se(2) 92.36(3); N(1)-Pd(1)-Se(2) 87.3(1); Cl(1)-Pd(1)-Se(2) 92.42(3); Se(1)-Pd(1)-Se(2) 174.04(2).



Fig. 2 ORTEP diagram of **3** with 40% probability ellipsoids. H, water and chloride ion have been omitted for clarity. Bond lengths (Å): Pd(2)–N(2D) 2.07(13); Pd(2)–Cl(2) 2.288(4); Pd(2)–Te(3)/Pd(2)–Te(4) 2.560(2)/2.588(2). Bond angles (°): N(2D)–Pd(2)–Cl(2) 178.8(4); N(2D)–Pd(2)–Te(3) 89.6(4); Cl(2)–Pd(2)–Te(3) 90.0(1); N(2D)–Pd(2)–Te(4) 87.4(4); Cl(2)–Pd(2)–Te(4) 92.96(1), Te(3)–Pd(2)–Te(4) 176.35(6).

2.526(7)/2.518(9) Å (for Pd(II) complex of *meso*-(4-MeOC₆H₄Te)₂-CH₂))^{31*a*} and 2.517(1) Å (for a palladium complex of Me-4-C₆H₄-TeCH₂CH₂C₆H₄N).^{31*b*} Both the complexes crystallise with one molecule of water in their crystal lattice. The N-H···Cl, C-H···Cl and O-H···Cl secondary interactions in the crystal of **2** result in the formation of a three dimensional structure shown in Fig. 3, where as N-H···Cl, N-H···O, O-H···O and C-H···Cl interactions shown in Fig. 4 result in the formation of three dimensional network in the case of **3**. The non-covalent interactions are more extensively shown in ESI (Fig. S2 and S3[†]).

Catalysis of Suzuki-Miyaura coupling

The complexes 1–3 have been explored for SMC. The solvent and base always have a significant role in SMC.^{5,32} Consequently different solvents have been found suitable for different complexes used as catalysts. However, water has been used as a co-solvent with many organic solvent *viz*. DMF, EtOH, dioxane, and THF.^{5,6} We have optimised with the present complexes the reaction conditions in water. There are few reports to our knowledge which have described the use of palladium complexes of organochalcogen ligands to catalyze



Fig. 3 Intermolecular N–H…Cl and O–H…Cl interactions in complex 2



Fig. 4 Intermolecular N-H····O, C-H···O and N-H····Cl interactions in complex 3.

Table 1 Suzuki–Miyaura coupling catalyzed with 1 and 2^a

$R-4-C_6H_4-X + PhB$	$(OH)_2 \rightarrow$	R-4-C ₆ H ₄ -Ph
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Entry no.	Aryl halide	Complex 1 Yield ^b	Complex 2 Yield ^c
1	4-Bromobenzaldehyde	96	~100
2^d	4-Bromobenzaldehyde	91	90
3	1-Bromo-4-nitrobenzene	84	~ 100
4	1-Bromobenzonitrile	94	~ 100
5	4-Bromoacetophenone	60	83
6^d	4-Bromobenzoic acid	93	~ 100
7	4-Bromoanisole	10	8
8 ^e	4-Bromoanisole	76	72
9	4-Bromotoluene	6	5
10^e	4-Bromotoluene	75	70
11	4-Bromopyridine	50	
12	4-Chlorobenzaldehyde	—	—

^{*a*} Reaction conditions: aryl/heteroaryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), water (3 mL), reaction time 12 h and temperature of bath 100 °C. 2 mol% of complex 1/2. ^{*b*} Isolated yield after column chromatography. ^{*c*} NMR % yield. ^{*d*} Reaction time 4 h. ^{*e*} 1 mmol of TBAB was added.

SMC in green solvent water.^{19–22} In the present study SMC of 4-bromobenzaldehyde with phenylboronic acid was used to optimize reaction conditions in water using K_2CO_3 as a base. Complex 1 (2 mol%) catalyzes the reaction at 100 °C in presence of K_2CO_3 and the yield of cross coupled product after 12 h has been found as ~96% (Table 1: entry 1). However cross

 Table 2
 Suzuki–Miyaura coupling of various arylboronic acids catalyzed with 1 and 2^a

Entry no.	Arylboronic acid	Arylbromide	Complex 1 Yield ^b	Complex 2 Yield ^c
1	4-Formylphenylboronic acid	4-Bromo benzaldehyde	95	~100
2	4-Acetylphenylboronic acid	·	82	92
3	4-Formylphenylboronic acid	1-Bromo-4-nitrobenzene	93	95
4	4-Acetylphenylboronic acid		89	~ 100
5	4-Formylphenylboronic acid	4-Bromo benzoic acid	96	94
6	4-Acetylphenylboronic acid		95	91

 $R-4-C_6H_4-X + ArB(OH)_2 \rightarrow R-4-C_6H_4-Ar$

^{*a*} Reaction conditions: aryl bromide (1.0 mmol), arylboronic acid (1.2 mmol), K₂CO₃ (2.0 mmol), water (3 mL), reaction time 12 h, temperature of bath 100 °C and 3 mol% of 1/2. ^{*b*} Isolated yield after column chromatography. ^{*c*} NMR % yield.

coupled product was obtained in 71% yield only when the reaction was carried out for 12 h at 70 °C with 1 mol% catalyst loading in the presence of K_2CO_3 . When catalyst 2 was used for the same coupling under similar reaction conditions the conversion was ~100%. Under optimum reaction conditions (see footnote of Table 1) the 3 catalyzes the coupling of 4-bromobenzoic acid efficiently (yield of product biphenyl-4carboxylic acid ~100%). However 3 does not show significant activity for other aryl bromides even at its 2 mol% loading. The Te containing complex has been found less catalytically active probably because Te is large in size and does not increase much electronic charge density on Pd. It may cause steric effect also on Pd. Earlier^{10*a*} also a complex of $Pd(\pi)$ with Teligands has been found much less efficient catalyst for C-C coupling than their S/Se analogues.^{14,16} The results of SMC given in Tables 1 and 2 indicate that the coupling of several activated aryl bromides can be successfully achieved when 1 and 2 are used as catalyst without tetrabutylammonium bromide (TBAB) additive. However for deactivated aryl bromides (4-bromotoluene and 4-bromoanisole) the coupled products were obtained in <10% yield (Table 1: entries 7 and 9). On addition of TBAB to the reaction mixture in these cases, the yields of cross coupled products were found considerably increased (Table 1: entries 8 and 10). Possibly TBAB acts as a phase transfer catalyst or stabilizes Pd(0) species generated during the coupling process. This observation indirectly supports the *in situ* generation of Pd NPs. However none of the catalysts (1-3) shows any significant activity towards ArCl (Table 1: entry 12).

The activities of complexes **1** and **2** were also studied (Table 2) towards the coupling of aryl bromides with two other arylboronic acids. Both the catalysts have been found to show (Table 2) good activity for the coupling of 4-formyl/acetyl-phenylboronic acid with activated aryl bromides at a catalyst loading of 3 mol%.

The complex 3 does not show any significant catalytic activity for the coupling of aryl bromides with these arylboronic acid derivatives even at its 3 mol% loading. The 1–3 and Pd(π) complexes of other organochalcogen ligands (of course scantly reported) are competitive in their efficiencies.^{19,21,22}

In the course of coupling reactions black particles appear. It is possible that the present complexes are not true catalysts but dispensers of real catalysts, as it has already been proposed that a palladacycle of reduced sulphated Schiff base decomposes to release $Pd_{16}S_7$ species when catalysing SMC and the $[Pd(0)-Pd(\pi)]$ cycle is involved in the catalytic process.^{14,33*a,b*} *In situ* formation of Pd NPs has also been observed in many cases during the catalytic process.^{33*c*-*f*} Thus reactions of 4-bromobenzoic acid with PhB(OH)₂ in water catalyzed with **1–3** under optimum conditions have been examined in detail to understand the nature of black particles generated *in situ* during catalytic process. This reaction is selected because each of the three complexes shows good activity for this coupling (yield of cross coupled product ~100%) with the formation of black particles. These black particles were washed to remove soluble impurities (see Experimental) and dissolved in chloroform which does not leave any residue.

The HR-TEM, SEM, SEM-EDX and powder X-ray diffraction have been used to characterize these black particles after their separation. Powder X-ray diffraction shows their amorphous nature. The HRTEM (Fig. 5) indicates that the black particles are uniform spherical shaped NPs (size of most of them ~1-2 nm) (Fig. 5 and 7). The SEM-EDX has revealed that NPs contain Pd as well as chalcogen and approximate Pd : E (E = S/Se/Te) ratios (in atom%) in NPs generated from 1-3 are ~42:58, 45:55 and 46:54 respectively. In the UV-Vis spectra of NPs obtained from complexes 1-3 in CHCl₃, a peak around 257-260 nm (Fig. 6a) was observed.^{33g} Their fluorescence spectra in CHCl₃ show a strong emission at λ = 341, 337 and 340 nm respectively (Fig. 6b) for NPs obtained from 1-3, as expected for quantum dots. The NPs obtained from 1-3 were examined for SMC reaction (Table 3) of 4-bromobenzoic acid with PhB(OH)₂ to ascertain whether the catalytic activity is associated with them or not. The reaction was smooth in presence of the NPs (Pd content ~2 mol%) obtained from either of 1-3. The reactions for 5 h at 100 °C, resulted in the cross coupled products in excellent yields for NPs obtained from 1-2 (Table 3). The recyclability of NPs was studied by reusing them. It has been noticed that the catalytic activity remains same for second reaction cycle (yield \geq 96%) in case of 1 and 2. However it diminishes significantly for second reaction cycle in case of NPs obtained from complex 3 as the coupled product was obtained in 79% yield even after 12 h of reaction time (Table 3). These results support the involvement of Pd NPs in catalysis of SMC with complexes 1-3. The time

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Fig. 5 HRTEM images for NPs obtained from complexes 1, 2 and 3 respectively (scale bar 10, 10 and 20 nm).



Fig. 6 UV-Vis and photoluminescence spectrum of NPs obtained from complex 1–3.



Fig. 7 Size distribution of NPs obtained from 1–3 from Suzuki–Miyaura coupling.

Table 3 Suzuki–Miyaura coupling catalyzed with NPs obtained from complexes 1 to 3°

$HOOC\text{-}4\text{-}C_6H_4\text{-}Br + PhB(OH)_2 \rightarrow HOOC\text{-}4\text{-}C_6H_4\text{-}Ph$							
Aryl halide	Cycle	Yield ^b					
		NPs from 1 ^c	NPs from 2 ^c	NPs from 3 ^d			
4-Bromobenzoic acid	1 2	~100 ~100	~100 96	~100 79			

^{*a*} Reaction conditions: 4-bromobenzoic acid (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), water (3 mL) and temperature of bath 100 °C. ^{*b*} NMR % yield. Amount of NPs equiv. not more than 2 mol% of palladium. ^{*c*} Reaction time 5 h. ^{*d*} Reaction time 12 h.

profile of reaction of 4-bromobenzoic acid with phenylboronic acid catalyzed with complex 1 and NPs obtained from it has been monitored with ¹H NMR spectroscopy and shown in ESI (Fig. S1[†]). The difference between the first 2 h time profile of isolated NPs and their precursor complex may be due to aggregation of NPs in the course of isolation. The in situ generated NPs are more active as their surfaces being fresh are very active. It is also possible that in the early stages of catalysis discrete Pd(0)is partially responsible for catalysis. The nucleation of these species results in Pd NPs engulfed by organochalcogen fragments. However, the role of formation of the present nanoparticles in catalysis cannot be denied. The nature of real catalyst and catalytic process was further investigated. The mercury poisoning and triphenylphosphine test³⁴ in the presence of 2 mol% of catalyst 1 were carried out on a representative coupling reaction of 4-bromobenzoic acid with phenylboronic acid as described in the Experimental section. On continuing reaction in the presence of mercury at 100 °C only 56% conversion of substrate into cross coupled product i.e. 4-phenylbenzoic acid could be reached after 12 h.

In triphenylphosphine poisoning test the biaryl product was obtained in 68% yield when reaction was carried out for optimum time and under optimized reaction conditions. These results suggest that catalytic process is partially poisoned by both Hg and PPh₃. This is on expected lines as Pd NPs appear to be protected by organochalcogen species as evident from the SEM-EDX results. The weight losses (%) in TGA up to 500 °C were ~50, 35 and 57% (Fig. S31–S33 in ESI[†]) respectively in case of NPs isolated from complexes 1, 2 and 3. The presence of organochalcogen skeletons most likely results in these weight losses. Presuming palladium to chalcogen ratio approximately 1:1.

The associated organic fragments with Pd(0) NPs obtained from 1, 2 and 3 may be speculated as $NH_2CH_2CH_2SPh$ (calculated wt loss 46%), $NH_2CH_2CH_2SePh$ (calculated wt loss 39%) and $[NH_2CH_2CH_2TeAr + NH_2CH_2CH_2Ar]$ (calculated wt loss 56%). The possibility of the proposed fragment appears to be logical in view of extrusion reactions of chalcogens. After TGA residue left appears to be PdE (E = S, Se or Te). Due to large size of tellurium and its more metallic nature the presence two fragments is not exceptional.



As these two poisoning tests could not fully affirm the nature of catalytic process and the possibility of involvement of surface atoms of nanoparticles of Pd in oxidative addition to form soluble $Pd(\pi)$ intermediate^{11,12} such as Ar-Pd-Br exists, a two phase test (Scheme 2) was performed to understand the nature of the reaction (heterogeneous vs. homogeneous) further.^{35,36} This test (called a three phase test when the catalyst is in solid phase), is considered more definitive for establishing the nature of catalytically active metal species and settling the issue of homogeneous vs. heterogeneous.³⁵ If the catalyst behaves in a heterogeneous fashion, the conversion of immobilized aryl bromide into cross-coupled product is not expected. When Pd is released (i.e., catalysis is at least partially homogeneous), the immobilized substrate is also converted to cross coupled product. The addition of a soluble aryl halide to the reaction mixture ensures the presence of a catalytic process and the active species in the reaction mixture. To carry out two phase test 4-bromobenzoic acid was immobilized as amide on silica and its stability established first. For this purpose it was treated with 0.8 M K₂CO₃ at 100 °C in 15 mL of ethanol-water mixture (2:1) for 12 h. The reaction mixture was acidified (20% v/v aq. HCl) and then extracted with ethyl acetate followed by dichloromethane. The residue obtained after evaporating off the solvent from extracts mixed together was subjected to ¹H NMR analysis. The expected 4-bromobenzoic, if there was any hydrolysis of silica phase, was not detected.

In a two phase test (Scheme 2) an immobilized 4-bromobenzoic acid and 4-bromoacetophenone were reacted with phenylboronic acid under optimum reaction conditions (see Experimental section for details). The soluble part was separated by filtration and analyzed after workup with ¹H NMR. The yield of the cross-coupled product (4-acetylbiphenyl) has been found to be 80% (0.156 g). The solid phase was hydrolysed, and resulting products after work up were analysed with ¹H NMR. The immobilized 4-bromobenzoic acid, was converted to the cross-coupled product (biphenyl-4-carboxylic acid) partially and ratio of cross coupled product : unreacted one was 22 : 78. This suggests that very low amount of catalytically active Pd leaches from the *in situ* generated Pd nanoparticles and is responsible for partial homogeneous catalysis. A major portion of catalysis occurs in a heterogeneous manner as large portion of immobilized 4-bromobenzoic acid remains unreacted. Thus, it appears that the coupling catalyzed with 1–3 is *via* Pd quantum dots and largely heterogeneous with some contribution of homogeneous pathway. Recently such a possibility has been described as "cocktail" of homogeneous and heterogeneous catalytic processes.^{14,37–39}

Experimental

Chemicals and reagents

Diphenyl diselenide, thiophenol, tellurium powder, bis(2chloroethyl)amine hydrochloride, sodium tetrachloropalladate, potassium carbonate, aryl halides, NaBH₄ and aryl boronic acids were procured from Sigma-Aldrich (USA) and used without any further purification. Bis(4-methoxyphenyl)ditelluride was prepared by the reported method.^{40,41} The progress of the catalytic reactions was monitored by ¹H NMR spectroscopy. The products obtained in SMC were authenticated by matching their NMR spectroscopic data with the literature values.

Physical measurements

The ¹H, ¹³C $\{^{1}H\}$, ⁷⁷Se $\{^{1}H\}$ and ¹²⁵Te $\{^{1}H\}$ NMR spectra have been recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47, 57.24 and 94.69 MHz respectively, and chemical shift are reported in ppm relative to the normal standards. Perkin Elmer Bio Lambda 20 spectrophotometer has been used to record UV-Vis spectra. Fluorescence spectra were recorded on Horiba Scientific Fluoromax-4 spectrofluorimeter. All reactions were carried out in oven dried round bottom flask under ambient condition. To create inert atmosphere commercially available nitrogen gas was used after passing through the traps containing solutions of alkaline anthraquinone, sodium dithionite, alkaline pyrogallol, concentrated H₂SO₄, and KOH pellets. Melting point of ligands and complexes were determined by taking the sample in a glass capillary sealed at one end, with an apparatus equipped with electric heating and reported as such. High-resolution mass spectral (HR-MS) measurements were made with a Bruker Micro TOF-Q II machine using electron spray ionisation (10 eV, 180 °C source temperature and sodium formate as calibrant) and dissolving the sample in CH₃CN. The diffraction data of single crystals of 2 and 3 were collected on a Bruker AXS SMART Apex CCD diffractometer using Mo-Ka (0.71073 Å) radiations at 195(2) and 298 (2) K respectively. SADABS⁴² software was used for absorption correction wherever needed and SHELXTL for space group, structure determination, and refinements.⁴³ Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in idealized positions, and a riding model was used for the refinement. The least-squares refinement cycles

on F^2 were performed until the model converged. Images of the crystals were drawn with Diamond program. TEM (Technai G² 20 operated at 200 kV) was used to study nature of nanoparticles. Samples for recording TEM were prepared by dispersing the powdered solid in ethanol by an ultrasonic treatment, dropping the slurry onto a porous carbon film supported on a copper grid and then drying in air. The phase morphologies of nanoparticles were observed with a Carl Zeiss EVO5O scanning electron microscope (SEM) associated with an EDX system model QuanTax 200, which is based on the SDD technology and provides an energy resolution of 127 eV at Mn-Ka. The samples for SEM were mounted on a circular metallic sample holder with a sticky carbon tape and scanned in different regions in order to minimize the error in the analysis made for evaluating the morphological parameters. Size distribution has been determined by analyzing one hundred and ten random NPs appearing in TEM image with the help of Irfan View software.

Synthesis of L1-L3⁴⁴⁻⁴⁶

Bis(2-chloroethyl)amine hydrochloride (0.704 g, 4 mmol) dissolved in ethanol (10 mL) was added dropwise to a solution of PhSNa/PhSeNa/CH₃O-p-C₆H₄TeNa (8 mmol) generated in situ by the reaction of NaOH with thiophenol or NaBH₄ reduction diphenyldiselenide/bis(4-methoxyphenyl)ditelluride of at 60 °C under nitrogen atmosphere. The reaction mixture was further heated at 60 °C for 8 h and then allowed to cool at room temperature. Solvent of the reaction mixture was reduced to 10 mL on rotary evaporator and mixed with 50 mL of water. The organic phase was extracted with chloroform (100 mL), washed three times with water (40 mL) and dried over anhydrous sodium sulphate. The solvent was evaporated off under reduced pressure on a rotary evaporator to obtain the product L1, L2 or L3. The present procedure is simpler and/or gives better yield in comparison to earlier reported ones.⁴⁴⁻⁴⁶

L1: yellow viscous oil, yield: (1.221 g, 85%). ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS); δ (ppm): 2.81 (t, *J* = 6.9 Hz, 4H, H₂), 3.03 (t, *J* = 6.3 Hz, 4H, H₁), 7.15–7.36 (m, 10H, H₄, H₅, H₆). ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 34.0 (C2), 60.6 (C1), 126.2 (C6), 128.9 (C5), 129.7 (C4), 135.4 (C3). HR-MS [M + H] (*m*/*z*) = 290.1025; calcd value for C₁₆H₂₀NS₂ = 290.1032 (error δ : 2.3 ppm).

L2: light yellow solid, yield: (1.713 g, 89%). m.p. 106 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS); δ (ppm): 3.08–3.12 (m, 4H, H₂), 3.21–3.26 (m, 4H, H₁), 7.24–7.27 (m, 6H, H₅, H₆), 7.49–7.53 (m, 4H, H₄). ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 22.0 (C2), 47.7 (C1), 127.6 (C3), 127.7 (C6), 129.9 (C5), 133.1 (C4). ⁷⁷Se{¹H} NMR (57 MHz, CDCl₃, 25 °C, Me₂Se): δ (ppm) 284.9. HR-MS [M + H] (*m*/*z*) = 385.9924; calcd value for C₁₆H₂₀NSe₂ = 385.9920 (error δ : 0.9 ppm).

L3: White solid, Yield: (2.511 g, 92%); m.p. 84 °C. ¹H NMR (300 MHz, CDCl₃, 25 °C, TMS); δ (ppm): 2.94 (s, 8H, H₁, H₂), 3.78 (s, 6H, OMe), 6.76 (d, *J* = 8.4 Hz, 2H, H₄), 7.69 (d, *J* = 8.4 Hz, 2H, H₅). ¹³C{¹H} NMR (75 MHz, CDCl₃, 25 °C, TMS): δ (ppm): 10.4 (C2), 49.4 (C1), 55.0 (OMe), 100.3 (C3), 115.0 (C4), 140.8 (C5), 159.6 (C6). ¹²⁵Te{¹H} NMR (94.69 MHz, CDCl₃,

25 °C, Me₂Te): 414.1. HR-MS [M + H] (m/z) = 545.9926; calcd value for C₁₈H₂₄NO₂Te₂ = 545.9928 (error δ : -0.3 ppm).

Synthesis of Pd-complexes 1–3

One out of ligands L1–L3 (1 mmol) was dissolved in ethanol and stirred for 30 minutes at room temperature. Aqueous solution of Na₂PdCl₄ (0.294 g, 1 mmol, in 3 mL of water) was added drop wise to the ligand solution. The reaction mixture was stirred for 6 h at room temperature. The orange yellow precipitate was filtered with a filter paper, washed with ethanol and dried in air. The yellow coloured single crystals of complexes 2 and 3 were grown by subjecting filtrate to slow evaporation.

Complex 1: yellow solid, yield: (0.435 g, 93%); m.p. 214 °C (d). ¹H NMR (300 MHz, DMSO-d₆, 25 °C, TMS); δ (ppm): 3.10–3.27 (m, 4H), 3.36–3.42 (m, 2H), 3.59–3.66 (m, 2H), 7.54–7.58 (m, 6H), 8.03–8.08 (m, 4H). ¹³C{¹H} NMR (75 MHz, DMSO-d₆, 25 °C, TMS): δ (ppm): 30.7 (C2), 53.2 (C1), 129.8 (C5), 130.1 (C3), 130.3 (C6), 131.7 (C4). HR-MS [M – Cl] (*m*/*z*) = 429.9678; calcd value for C₁₆H₁₉ClNPdS₂ = 429.9679 (error δ : 0.1 ppm).

Complex 2: yellow solid, yield: (0.495 g, 88%); m.p. 170 °C (d). ¹H NMR (300 MHz, DMSO-d₆, 25 °C, TMS); δ (ppm): 3.12–3.250 (m, 4H), 3.51–3.71 (m, 4H), 7.53–7.57 (m, 6H), 8.09–8.15 (m, 4H). ¹³C{¹H} NMR (75 MHz, DMSO-d₆, 25 °C, TMS): δ (ppm): 36.0 (C2), 55.9 (C1), 126.9 (C3), 129.4 (C6), 130.2 (C5), 132.8 (C4). HR-MS [M – Cl] (*m*/*z*) = 525.8575; calcd value for C₁₆H₁₉ClNPdSe₂ = 525.8576 (error δ : 0.1 ppm).

Complex 3: yellow solid, yield: (0.657 g, 91%); m.p. 134 °C (d). ¹H NMR (300 MHz, DMSO-d₆, 25 °C, TMS); δ (ppm): 2.84–3.32 (bs, 8H), 3.80 (s, 6H), 7.02 (d, J = 8.4 Hz, 4H), 8.04–8.07 (m, 4H). ¹³C{¹H} NMR (75 MHz, DMSO-d₆, 25 °C, TMS): δ (ppm): 16.1 (C2), 55.4 (C7), 59.3 (C1), 105.2 (C3), 116.3 (C4), 138.6 (C5), 161.3 (C6). HR-MS [M – Cl] (*m*/*z*) = 685.8670; calcd value for C₁₈H₂₃ClNO₂PdTe₂ = 685.8554 (error δ : –2.4 ppm).

General procedure for Suzuki-Miyaura coupling of aryl bromides with arylboronic acid

Aryl bromide (1 mmol), aryl boronic acid (1.5 mmol), K₂CO₃ (2 mmol), water (3 mL) and a catalyst out of 1-3 (2 mol%) was charged in a round bottom flask, which was placed on an oil bath under aerobic condition at 100 °C and stirred. The progress of reaction was monitored with ¹H NMR spectroscopy. When maximum conversion of ArBr into product occurred, the reaction mixture was cooled to room temperature. It was mixed with water (20 mL) and extracted with diethyl ether (3 \times 10 mL). For benzoic acid derivatives the reaction mixture was mixed with 20 mL of 20% HCl and extracted with ethyl acetate $(3 \times 10 \text{ mL})$. Organic phase was dried over anhydrous Na₂SO₄. Its solvent was removed on rotary evaporator and the product was subjected to ¹H and ¹³C{¹H} NMR studies. In case of impure product, further purification by column chromatography on silica gel using ethyl acetate and hexane mixture as eluent was carried out and thereafter subjected to NMR studies.

Isolation of nanoparticles formed from complex 1–3 in Suzuki–Miyaura C–C coupling

A complex out of 1–3 (2 mol%), 4-bromobenzoic acid (1 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2 mmol) and water (3 mL) were heated in a round bottom flask at 100 °C for 5 h. The solvent of the reaction mixture was decanted off while hot. The black residue present in the flask was washed with a mixture of ethyl acetate (10 mL) and water (30 mL). It was then dispersed in chloroform (20 mL). The solvent was evaporated off to get black nanoparticles.

Procedure for catalysis of SMC with recyclable NPs

The independent catalytic activity of NPs isolated from SMC was tested for the same coupling reaction separately, using procedure optimised for complexes and taking in the place of complex, NPs obtained from 1–3 (equivalent to ~2 mol% of Pd) as catalyst and heating the reaction mixture for 5 h. Thereafter the mixture was mixed with 20 mL of 20% HCl and extracted with ethyl acetate (3×10 mL). The organic phase was dried over anhydrous Na₂SO₄. Its solvent was removed on rotary evaporator to obtain products as white solid which were characterized as usual with ¹H and ¹³C{¹H} NMR. The conversion of 4-bromobenzoic acid to the product was almost quantitative (Table 3). The NPs were recovered and again tested for the same coupling reaction. They were found to catalyze the coupling reaction again with good efficiency. The lowest yield was 79% after the second catalytic reaction cycles.

Hg poisoning test

The coupling reaction of 4-bromobenzoic acid with phenylboronic acid in the presence of 2 mol% of 1 under optimal reaction condition was carried out. The progress of reaction was monitored with ¹H NMR spectroscopy. When 36% conversion (10 minutes) took place, 400 equivalents of Hg (for 1 equivalent of Pd) were added to the reaction mixture. After continuing reaction further for 12 h at 100 °C only 56% conversion could be reached.

PPh₃ poisoning test

Under optimal reaction conditions the 4-bromobenzoic acid (1.0 mmol) was reacted with phenylboronic acid (1.2 mmol) in the presence of PPh₃ (4 mol%) for 0.5 h. Thereafter catalyst **1** (2 mol%) was added and reaction monitored with ¹H NMR spectroscopy. After 12 h of the reaction, cross coupled product was obtained in 68% yield.

Two phase test

The 4-bromobenzoic acid-immobilized silica (0.20 g) prepared by reported procedure,⁴⁷ phenylboronic acid (0.36 g, 3 mmol), 4-bromoacetophenone (0.20 g, 1 mmol), K_2CO_3 (0.56 g, 4 mmol) and 2 mol% of catalyst 1 (best among the three complexes) were heated at 100 °C for 12 h in water (5 mL). The reaction mixture was cooled to room temperature and filtered through G-4 crucible. The residue was washed with 50 mL of water and then 30 mL of diethyl ether. The filtrate and washings were collected together and mixed with water (50 mL). The resulting mixture was extracted with 50 mL of diethyl ether. The solvent from the organic extract was evaporated off on a rotary evaporator and the white residue thus obtained was identified with ¹H NMR. The residue separated on G-4 crucible was hydrolysed with KOH (1.68 g dissolved in 5 mL of water + 10 mL of EtOH) at 90 °C for 3 days. Using aqueous 20% (v/v) HCl solution the hydrolysed reaction mixture was neutralised. It was extracted with dichloromethane (30 mL), followed by ethyl acetate (40 mL). The organic extracts were combined together. Its solvent was evaporated off and the resulting residue was subjected to ¹H NMR to identify the products.

Conclusions

Palladium complexes of type [Pd(L)Cl]Cl (1-3) (where pincer ligand $L = L1-L3 = (ArECH_2CH_2)_2NH$; (E = S/Se/Te)) have been synthesized and characterized by multinuclear NMR spectroscopy and mass spectrometry. The complexes 2 and 3 have been characterised with X-ray diffraction on their single crystals. These complexes crystallize with one molecule of water in their crystal lattice. The complexes 1-3 have been found to efficiently catalyze Suzuki-Miyaura C-C coupling reactions of various aryl bromides with three arylboronic acids in water. Their 2-3 mol% is sufficient to give good yield of cross coupled product. The activities of complexes 1 and 2 have been found better than that of 3. The catalysis of Suzuki-Miyaura coupling appears to occur via in situ generated Pd quantum dots (size 1-3 nm) protected with organochalcogen fragments as evident by SEM-EDX and TEM studies. These NPs have been isolated and show catalytic activity for SMC independently in each case. The results of two phase test suggest that there is a relatively higher contribution of heterogeneous pathway to the catalysis.

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