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Easily synthesizable benzothiazole based designers palladium complexes for catalysis of Suzuki coupling: Controlling the effect of aryl substituent of ligand on role and composition of insitu generated binary nanomaterial (PdS or Pd16S7)

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Easily synthesizable benzothiazole based designers palladium complexes for catalysis of Suzuki coupling: Controlling the effect of aryl substituent of ligand on role and composition of insitu generated binary nanomaterial (PdS or $Pd_{16}S_7$)

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Abstract

The present report is based on straightforward synthesis of molecular palladium complexes of benzothiazole based bulky ligands. Catalytic potential of **1**[Pd(**L1**)$_2$Cl$_2$] and **2**[Pd(**L2**)$_2$Cl$_2$] has been screened for Suzuki coupling . Due to structural difference between **1** and **2** (anthracen-9-yl in **1,** and pyren-1-yl in **2**), they behaves as designers pre-catalysts and show different catalytic behaviour and nature by dispensing the nanoparticles of different materials (PdS in **1** and $Pd_{16}S_7$ in **2**). This is an unprecedented observation as the size of the aryl substituent controls the efficiency (efficiency: **1** > **2**) through determining the composition and nature of insitu generated nanoparticles.

Keywords: Benzothiazole, Palladium, Nanoparticles, Suzuki coupling, Palladium sulfide

1. Introduction

In transition-metal catalysis, the role of ligands is very crucial [1−9]. The ligands show influence on (i) the operational properties of the catalytic reaction (the compatibility with air and/or moisture, the reaction temperature, pressure, etc), (ii) reactivity of a metal catalyst, (iii) selectivity (i.e., enantioselectivity, diastereoselectivity, regioselectivity, and chemoselectivity) of a chemical reaction, (iv) stabilization of *insitu* generated active and real catalytic species [1-9]. Therefore, these are considered to be chemists' "hands" for influencing the bond-making and -breaking processes, and improving known catalytic reactions. Effect of ligands architecture on catalytic process has been studied experimentally [1-9] as well as theoretically [10-12]. An appropriate ligand for a particular set of reactants or a particular reaction can be easily accessed by fine tuning its electronic and steric properties through modifications. Such modifications may involve variation in donor sites such as S/Se/Te/P/O/N and/or removal or incorporation of substituents of different sizes in the ligand. Many research groups have reported the effect of presence of bulky substituents in ligand on the catalysis. In context of phosphine ligands, Buchwald and other researchers have rationalized the influence of bulky substituents in terms of extent of stabilization of intermediate species [formed during oxidative addition step due to (i) cleavage of bond between organic R group and the heteroatom X, and (ii) simultaneous formation of a new bond] by bulky ligands [9,10]. In addition, the bulkiness of ligand also promotes reductive elimination step for release of coupling product [9,10]. This strategy of modifying the ligand architecture and screening the effects on catalysis can be successfully applied only if modifications can be carried out easily and readily. Hence, ease and simplicity of methodology for tailoring ligand's architecture has a high significance in making a particular class of ligands convenient to use. Probably it is also among the major reasons why Schiff bases, pincer ligands, organochalcogen ligands, heterocyclic compounds including triazoles, pyridine etc have emerged as large and distinguished families of ligands for developing transition metal catalytic systems for various chemical transformations [13-16].

Benzothiazole and its derivatives are very important scaffolds under the class of heterocyclic organic molecules. During last four decades, they have been explored extensively upto a great extent in the syntheses of molecules of medicinal use [17−19]. Despite the availability of a C=N- and a -S- donor group in its framework and first report on application of its palladium complex in catalysis in year 2000 [20], work done during last two decades on use of the benzothiazole or its derivatives in developing transition metal catalytic systems is negligible in comparison to that on Schiff bases, pincer ligands, organochalcogen ligands and phosphines. For this purpose, the exploration of these compounds is much lesser than that of other heterocyclic compounds e.g. pyridine and triazoles. Only a few palladium complexes of this ligand scaffold (benzothiazole or its derivatives) have been synthesized and used in catalysis of coupling reactions, CO_2 reduction, hydrogenation [20-27]. It is probably because, unlike aforementioned popular and commonly used ligands, their derivatization and functionalization has not been very facile and easy due to which scope of modulation in ligand's steric and electronic properties remains limited. Therefore syntheses of benzothiazoles derivatives by using easy, convenient, efficient methods always attract the attention of inorganic chemists. Though a variety of methodologies are reported [28] for syntheses of its derivatives, the most attractive and least explored in the synthesis of benzothiazole based ligands is a reaction between aminothiophenol and a carbonyl compound, as simple as a Schiff base reaction [28].

Suzuki Miyaura C-C coupling reaction is one of the most useful tool for formation of C-C bond during syntheses and large scale preparation of pharmaceuticals, agrochemicals and fine chemicals [29−32]. Though, a large number of catalysts have been developed [29,30], there is still a focus of various research groups on the development of more efficient, stable and easily synthesizable catalysts. Moreover, the palladium complexes of benzothiazole based ligands have been rarely explored for this reaction [21,24,25,26]

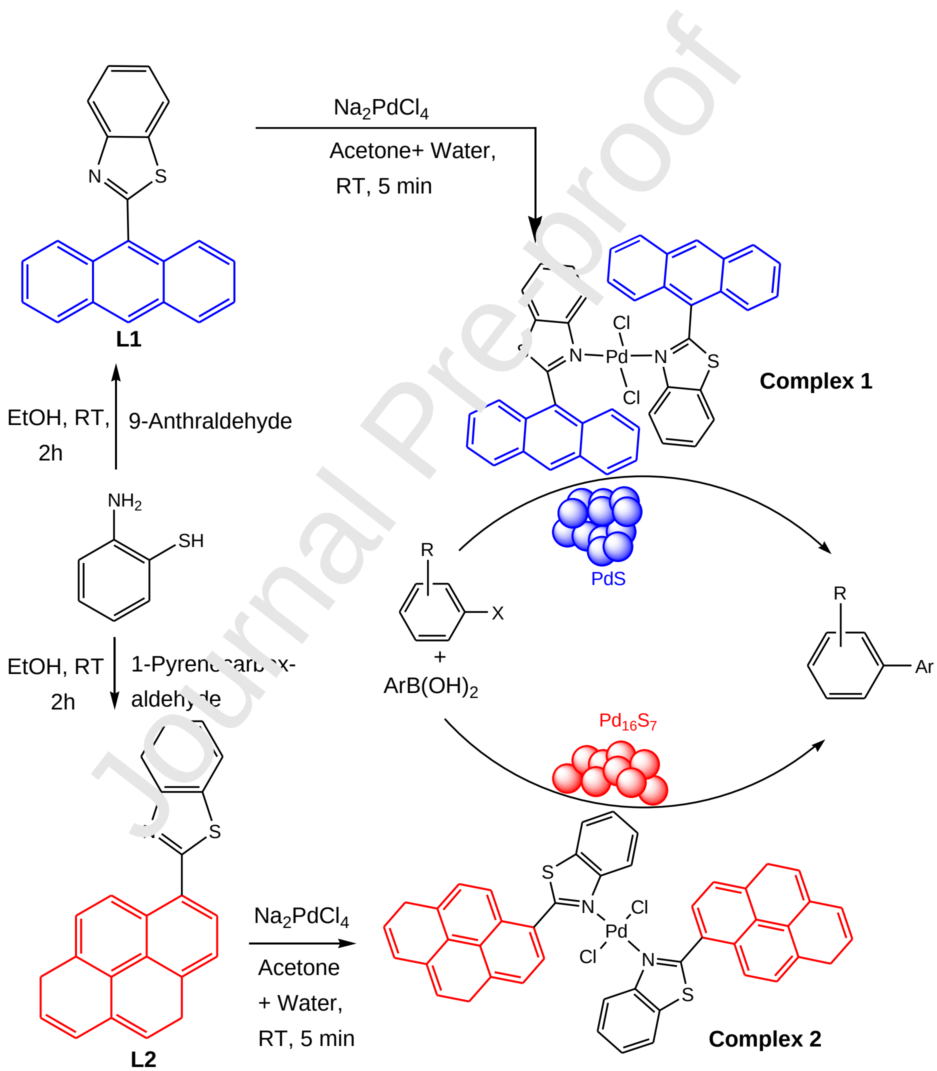
Taking into account the aforementioned status of exploration of benzothiazole based ligands in development of transition metal catalytic systems and related reasons, it was thought to be worthwhile (i) to begin the use of a green, facile, catalyst free and room temperature reaction protocol for synthesizing ligands with bulky substituents at C-2 of benzothiazole core, (ii) to synthesize their designers palladium complexes, and to screen their catalytic potential in Suzuki-Miyaura coupling with gaining insights into the role of bulky substituents in catalytic process.

In the present study, we are reporting easily synthesizable designers palladium(II) complexes **1** and **2**, designed using **L1** [33] and **L2** [34], and their applications in the catalysis of Suzuki coupling of a variety of bromo and chloroarenes. **L1** and **L2** have been prepared using one-pot and green method of syntheses. Mechanistic insights have also been gained into process of catalysis and high efficiency have been rationalized in terms of activity of insitu generated nanoparticles, the composition (i.e. PdS or $Pd_{16}S_7$) of which is controlled by the size or nature of bulky aryl group present on the ligands **L1** and **L2**.

2. Results and discussion

2.1. Syntheses and structures

Bulky ligands **L1** and **L2** have been accessed in very good yields (~80%) in short reaction time of 2 hours at room temperature using a methodology (involving a reaction between 2-aminothiophenol and an aromatic aldehyde) which is highly attractive, least explored, facile, green, one pot and catalyst-free. The **L1** and **L2** have been characterized by matching their ^{1}H NMR spectral features with reported data [33, 34]. Pd(II) complexes **1** and **2** have been synthesized by reaction of Na_2PdCl_4 with **L1**/**L2** in an extremely short reaction time of five minutes. Both **1** and **2** are stable under ambient conditions and may be stored for several months without noticeable decomposition. The **1** and **2** were characterized by ^{1}H, ^{13}C{^{1}H} NMR spectroscopy and mass spectrometry (Supplementary Material: Figs. S1−S9). These spectroscopic and spectrometric data are consistent with the molecular structures shown in Scheme 1.



Scheme 1. Syntheses of ligands (**L1** and **L2**), Pd(II) complexes (**1** and **2**) and application of **1** and **2** in catalysis of Suzuki coupling through insitu generated nanoparticles of PdS and $Pd_{16}S_7$

The molecular structures of **L1** (Fig. 1) and **1** (Fig. 1) were also authenticated by single crystal X-ray diffraction studies. The crystal data and details of structure refinement for **L1** and **1** are given in Supplementary Material. X-ray diffraction studies revealed that in the complexes, the ligand coordinates (Fig. 1) with the Pd(II) centre through nitrogen in monodentate mode in such a manner that bulky aryl substituents are oriented in opposite directions. In palladium complex **1**, the geometry around the Pd is nearly square planer. The Pd−N bond lengths are 2.023(10) Å and Pd−Cl bond lengths are found to be 2.319(2).

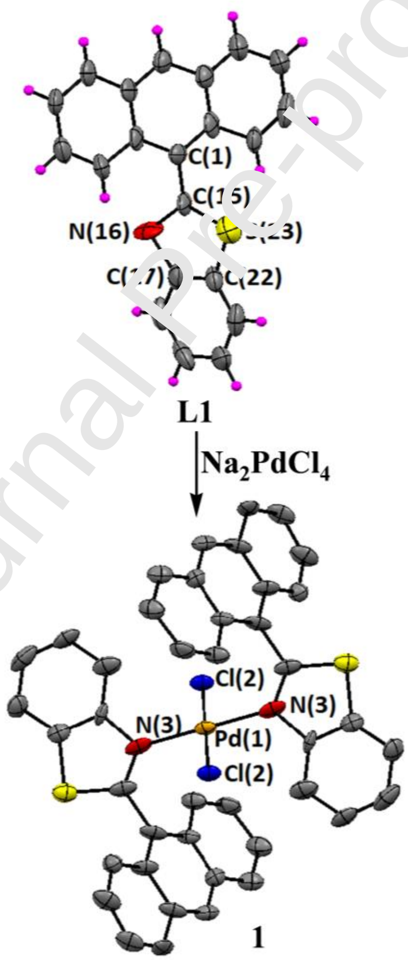


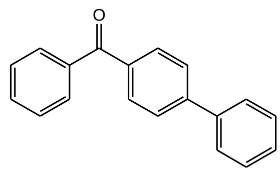
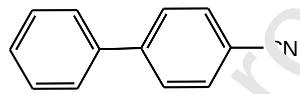
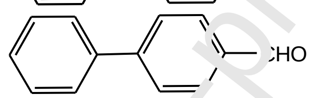
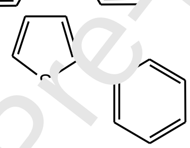
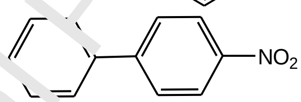
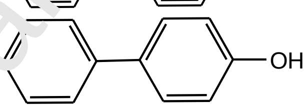
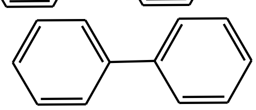
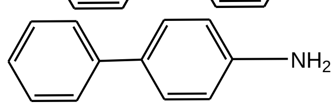
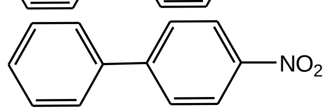
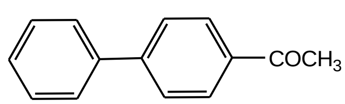
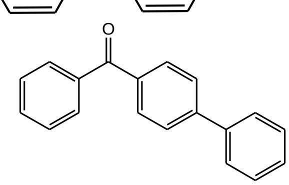
Fig. 1. Trans disposition of ligand (**L1**) molecules in square planar geometry of palladium ion in complex **1**, obtained by the reaction of **L1** and Na_2PdCl_4

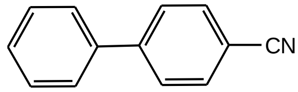
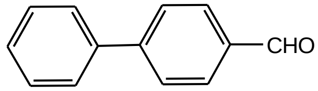
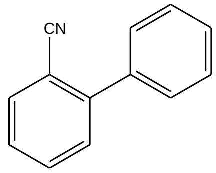
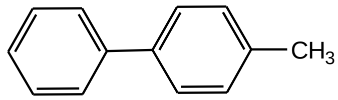
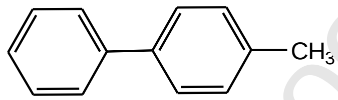
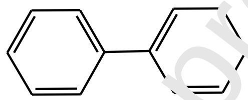
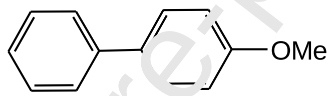
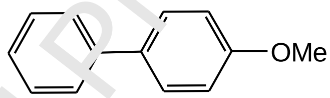
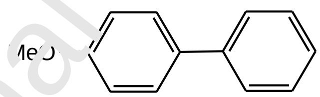
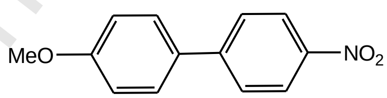
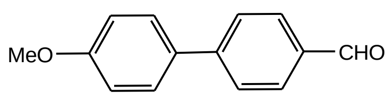
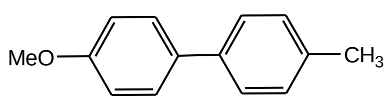
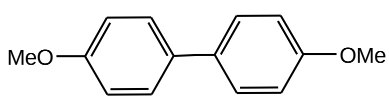
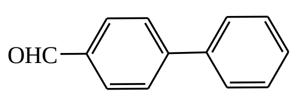
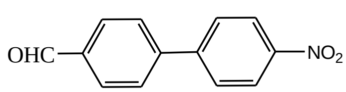
2.2. Catalysis of Suzuki coupling

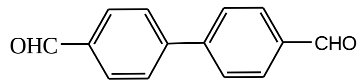
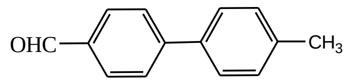
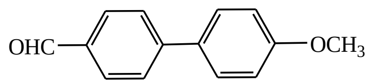
After optimizing (Table S1 in Supplementary Material) the reaction conditions, the catalytic potentials of **1** and **2** for Suzuki-Miyaura coupling reactions were screened at 90 °C using K_2CO_3 as the base for 8 hours for ArBr, and 12 hours for ArCl. It has been observed that generally the efficiency of complex **1** (in which aryl substituent at C-2 is antrcen-9-yl) is higher than that of complex **2** (in which aryl substituent i.e. pyren-1-yl group is more bulky). Among bromoarenes, maximum conversion (≥99%) was achieved (Table 1: Entry nos. 1-4) in case of 4-bromobenzophenone, 4-bromobenzaldehyde, 2-bromothiophene and 4-bromobenzonitrile when complex **1** was used as a catalyst. However, conversions of these substrates were in between 80-95% when complex **2** was used as a catalyst. Minimum conversion (< 30%) was observed (Table 1: Entry no. 6) for 4-bromophenol in presence of either of the two catalysts. 1-Bromo-4-nitrobenzene was the only substrate (Table 1: Entry no. 5) for which complex **2** was found to be slightly more efficient than complex **1**. In case of aryl bromides with electron donating substituents (such as 4-bromotoluene and 4-bromoanisole), relatively lower yields of coupled products have been obtained (Table 1: Entry no. 16 and 18).

Table 1. Results of Suzuki coupling reactions of aryl halides with phenyl boronic acid, 4-methoxyphenyl boronic acid and 4-formylphenyl boronic acid.

$$\text{Ar–X} + \text{Ar'B(OH)}_2 \longrightarrow \text{Ar–Ar'}$$

S. No.	Aryl halide (Ar-X)	Cross-coupled product	% Conversion of the aryl halide into product (value of TON)	
			Complex 1	Complex 2
1.	4-Bromobenzophenone		99% (9900)	90% (9000)
2.	4-Bromobenzonitrile		99% (9900)	90% (9000)
3.	4-Bromobenzaldehyde		99% (9900)	95% (9500)
4.	2-Bromothiophene		99% (9900)	80% (8000)
5.	1-Bromo-4-Nitrobenzene		71% (7100)	78% (7800)
6.	4-Bromophenol		29% (2900)	25% (2500)
7.	Chlorobenzene[a]		99% (9900)	78% (7800)
8.	4-Chloroaniline[a]		95% (9500)	88% (8800)
9.	1-Chloro-4-Nitrobenzene[a]		92% (9200)	85% (8500)
10.	4-Chloroacetophenone[a]		87% (8700)	80% (8000)
11.	4-Chlorobenzophenone[a]		86% (8600)	75% (7500)

12.	4-Chlorobenzonitrile[a]		76% (7600)	66% (6600)
13.	4-Chlorobenzaldehyde[a]		75% (7500)	71% (7100)
14.	2-Chlorobenzonitrile[a]		67% (6700)	63% (6300)
15.	4-Chlorotoulene[a]		53% (5300)	50% (5000)
16.	4-Bromotoulene		72% (7200)	66% (6600)
17.	Bromobenzene		83% (8300)	75% (7500)
18.	4-Bromoanisole		60% (6000)	48% (4800)
19.	4-Chloroanisole[a]		30% (3000)	26% (2600)
20.	Chlorobenzene[a,b]		91% (9100)	89% (8900)
21.	1-Chloro-4-Nitro benzene[a,b]		67% (6700)	61% (6100)
22.	4-Chlorobenzaldehyde[a,b]		10% (1000)	12% (1200)
23.	4-Chlorotoulene[a,b]		30% (3000)	30% (3000)
24.	4-Chloroanisole[a,b]		6% (600)	8% (800)
25.	Chlorobenzene[a,c]		82% (8200)	70% (7000)
26.	1-Chloro-4-Nitro benzene[a,c]		95% (9500)	84% (8400)

27.	4-Chlorobenzaldehyde[a,c]		78% (7800)	71% (7100)
28.	4-Chlorotoulene[a,c]		75% (7500)	58% (5800)
29.	4-Chloroanisole[a,c]		25% (2500)	32% (3200)

Reaction conditions: Aryl halide (1 mmol), phenyl boronic acid (1.5 mmol), [b]4-methoxyphenyl boronic acid (1.5 mmol), [c]4-formylphenyl boronic acid (1.5 mmol), [Catalyst]$_{\text{Complex } \mathbf{1/2}}$ (0.01 mol%), K_2CO_3 (2 mmol), DMF+water (5 mL), reaction time 8 h, temperature of bath, 90 °C, [a]reaction time 12 h.

For Suzuki coupling reactions, aryl chlorides are the most preferred substrates due to their low cost, wide availability and easy accessibility. However, due to high C−Cl bond strength, their reactivity is minimum and only highly active catalyst are able to convert them into coupled products. Both the complexes have also shown good catalytic potential for coupling reactions of such substrates. Chlorobenzene, 4-chloroaniline, 1-chloro-4-nitrobenzene, 4-chloroacetophenone, 4-chlorobenzaldehyde, 4-chlorobenzonitrile and 4-chlorobenzophenone were converted (Table 1: Entry nos. 7-13) successfully to desired products at same catalyst loading (0.01 mol%) as used in case of bromoarenes in 12 h at 90 °C. However, chloroarenes with electron donating substituents on benzene ring (Table 1: Entry nos. 15 and 19) gave very low yields.

To have a better understanding on the catalyst activity, other aryl boronic acids possessing electron donating and withdrawing group on benzene ring have also been investigated. When 4-methoxyphenyl boronic acid (a phenyl boronic acid with electron donating group) is used, both the complexes show suppressed activities (Table 1: Entry nos. 20−24) in comparison to those shown for $PhB(OH)_2$. However, in case of 4-formylphenyl boronic acid (a boronic acid with electron withdrawing group on benzene ring), marginally higher catalytic efficiencies (Table1: Entry nos. 25−29) are shown by both the complexes.

2.3. *Insitu generation of nanoparticles of PdS and $Pd_{16}S_7$ and their role in catalysis*

During the course of catalysis, formation of black particles was observed. Therefore, it is quite likely that palladium complexes **1** and **2** are pre-catalysts and behave as the dispensers of true catalytic species during the course of catalytic reaction. So, with a purpose to get insights into the role of such particles, a coupling reaction between 1-bromo-4-nitrobenzene and phenylboronic acid, catalyzed with complex **1** and **2** has been analyzed thoroughly and separately. The black particles, formed *insitu*, were isolated and characterized by P-XRD, SEM-EDX, HR-TEM and XPS. Powder X-ray diffraction patterns (Supplementary Material: Figs. S12 and S13) of these particles revealed that these are belonging to binary phases (PdS in case of catalysis with complex **1** and $Pd_{16}S_7$ in case of complex **2**) when matched with standard phases JCPDS # 25-1234 (for PdS) [35] and JCPDS # 43-0806 (for $Pd_{16}S_7$). The SEM-EDX studies (details in Supplementary Material) also support the presence of both the elements (i.e. Pd and S) in the nanoparticles generated from **1** and **2**. XPS studies of the nanoparticles also corroborate the presence of binary phases (PdS and $Pd_{16}S_7$) (Fig. 2 and 3). In case of PdS nanoparticles, palladium is present in +2 oxidation state. However, in case of NPs of $Pd_{16}S_7$, presence of both

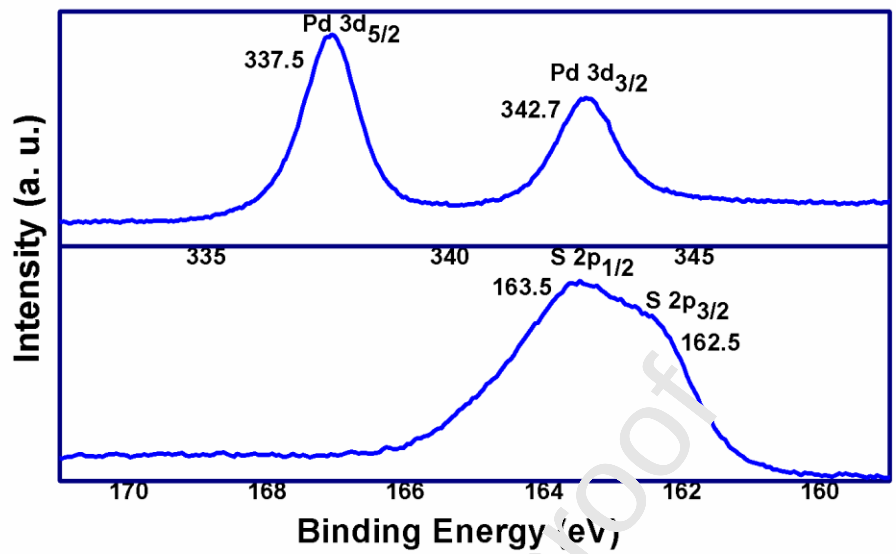


Fig. 2. XPS Spectra of **PdS** nanoparticles obtained from complex **1**

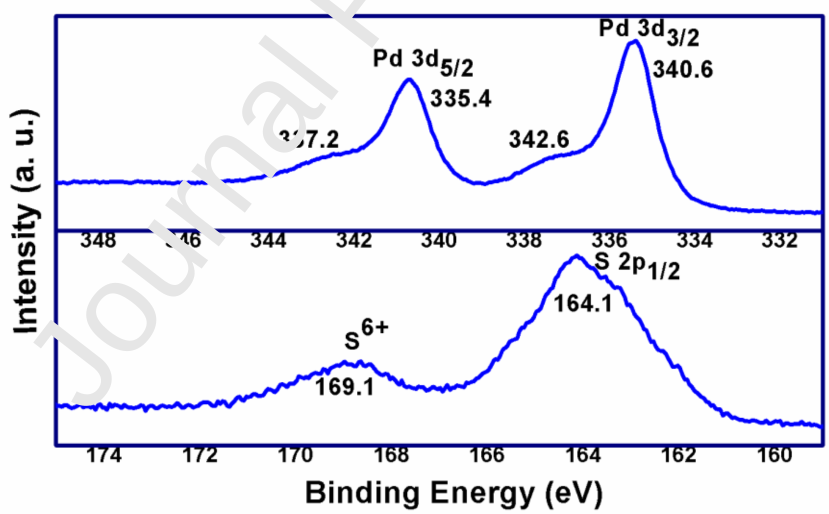


Fig. 3. XPS Spectra of $\mathbf{Pd_{16}S_7}$ nanoparticles obtained from complex **2**

Pd(0) and Pd(II) oxidation states have been observed. Presence of peaks, corresponding to sulfide ion, has also been observed in both the phases (Supplementary Material S5). On the basis of similarity in the structures of the complex and reaction conditions, it can be inferred that formation of different materials (i.e. compositions of particles) is controlled mainly by the size of the aryl group (anthracen-9-yl in case of complex **1** and pyren-1-yl in case of complex**2**) linked at C-2 of the benzothiazole framework.

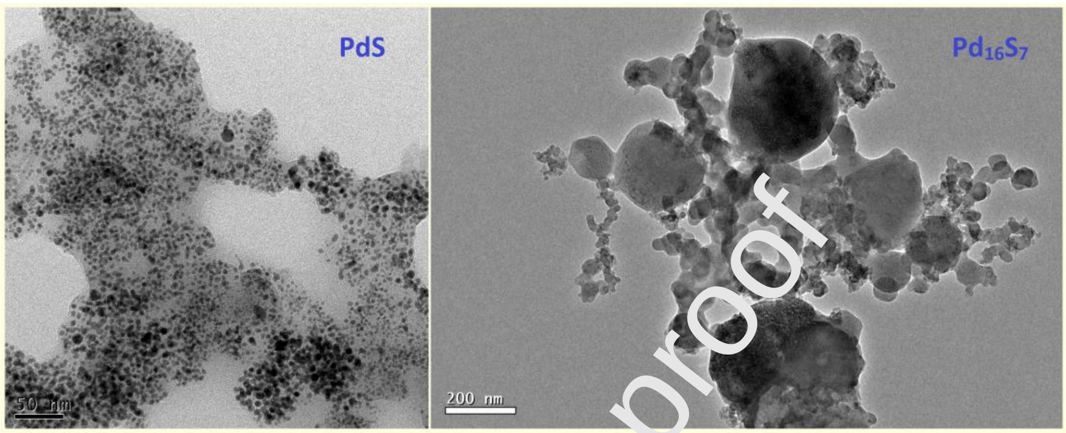


Fig 4. TEM images of nanoparticles generated in situ during catalysis

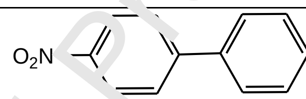
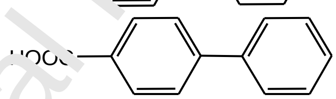
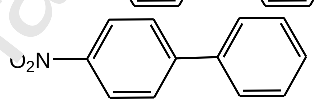
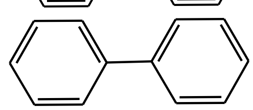
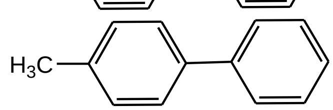
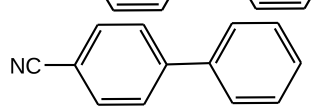
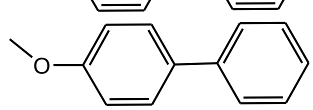
The HRTEM images (Fig. 4) revealed that the particles generated from the complexes are nanosized. Nanoparticles generated by complex **1** are ~10−12 nm in size, spherical in shape and uniformly dispersed. However, in case of isolated nanoparticles by complex **2**, there is an aggregation due to which their dispersion is not good. Hence, the difference in the catalytic activities of **1** and **2** may be attributed to two factors: (i) insitu generated nanoparticles have different compositions (i.e. PdS in case of complex **1** and $Pd_{16}S_7$ in case of complex **2**), (ii) in-situ generated PdS nanoparticles with **1** are well dispersed and small in size (Fig. 4) as compared to $Pd_{16}S_7$ nanoparticles generated with **2** in which there is an aggregation of nanoparticles (clearly visible in HRTEM image).

In order to ascertain the role of *in situ* generated nanoparticles of Pd-S materials (PdS and $Pd_{16}S_7$) in catalysis and their catalytic properties, they were isolated and obtained outside the reaction mixture. Their catalytic potential was tested separately for Suzuki coupling reactions

(Table 2) of ArBr as well as ArCl. Noticeably, a higher catalyst loading (~3.5-4.1 mol%) was required to achieve comparable conversions. It corroborates that the eventual advantages of using preformed molecular complexes **1** and **2** in catalysis is the formation of products in higher or comparable yields at very low concentration (0.01 mol%) of catalyst. The potential, shown by nanoparticles, in achieving good but different yields (Table 2) of cross-coupled products is also the basis for inferring that catalysts **1** and **2** acts as dispensers of nanoparticles PdS and $Pd_{16}S_7$ and their activity is dependent upto a significant extent on the activity of the NPs.

Table 2. Results of catalysis of Suzuki coupling reactions (between aryl halides and phenylboronic acid) catalyzed by isolated NPs of PdS and $Pd_{16}S_7$

$Ar{-}X + PhB(OH)_2 \longrightarrow Ar{-}Ph$

Entry	**Aryl halide (Ar-X)**	**Cross-coupled product**	**% Conversion of aryl halide**	
			NPs of PdS	**NPs of $Pd_{16}S_7$**
1.	1-Bromo-4-nitrobenzene		89%	86%
2.	4-Bromobenzoic acid		92%	68%
3.	1-Chloro-4-nitrobenzene[a]		29%	52%
4.	Chlorobenzene		78%	74%
5.	4-Chlorotoluene[a]		70%	66%
6.	4-Chlorobenzonitrile[a]		60%	52%
7.	4-Chloroanisole[a]		35%	28%

Reaction conditions: aryl halide (1 mmol), phenyl boronic acid (1.5 mmol), catalyst 5 mg, K_2CO_3 (2 mmol), DMF+water (5 mL), reaction time 8 h, temperature of bath 90 °C, [a]reaction time 12 h.

Mercury poisoning test and triphenyl phosphine tests were carried out in order to establish whether the nature of catalysis is homogeneous or heterogeneous. Coupling reaction between 1-bromo-4-nitrobenzene and phenyl boronic acid in presence of poison (i.e. mercury) gave 17% and 23% conversion of substrate with **1** and **2** as catalyst respectively. Similarly, a reaction between 4-bromobenzaldehyde and $PhB(OH)_2$ in presence of PPh_3 was also suppressed to a great extent and 42% and 29% conversion was obtained with **1** and **2** respectively. These results suggest that *insitu* generated palladium nanoparticles (PdS, $Pd_{16}S_7$) contribute to catalysis of Suzuki coupling upto a great extent. However, possibility of catalysis by some homogeneous low valent palladium species, stabilized by bulky substituents of ligands of both the complexes, can also not be ruled out as the reaction proceeds upto some extent even in the presence of poisoning agents such as PPh_3 and Hg. Thus, it appears that overall the catalysis in case of **1** and **2** is cocktail of homogeneous as well as heterogeneous mode [8].

3. CONCLUSION

In conclusion, the methodology used for synthesis of **L1** and **L2** opens up a field with a wider scope for the modular syntheses of a library of numerous ligands by using appropriate derivatives of either aminothiphenol or carbonyl compounds as reactants. Pd(II) complexes **1** and **2**, which are moisture- and air–insensitive and have potential to catalyze the Suzuki coupling of both ArCl and ArBr, behaves as designers catalysts and controls their activity upto a great extent through the size of aryl substituent of the ligand. This aryl substituent (anthracen-9-yl in complex **1** and pyren-1-yl in **2**), in turn, determines the nature and composition of nanosized material (i.e. PdS and $Pd_{16}S_7$) dispensed *insitu* by the complexes during reaction. Interestingly, unlike the earlier reports, it is the first time when *insitu* formation of nanoparticles of palladium chalcogenides (PdS or $Pd_{16}S_7$) has been reported from the complexes which does not contain any direct linkage (i.e. bond) between metal and chalcogen. These results imply that catalytic nature, behaviour and efficiency of the palladium complexes can be modulated simply by minor variations in the substituents at C−2 of benzothiazole based ligands.

Declaration of Competing Interest

There are no conflicts to declare.

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Declaration of interests: NONE

Easily synthesizable benzothiazole based designers palladium complexes for catalysis of Suzuki coupling: Controlling the effect of aryl substituent of ligand on role and composition of insitu generated binary nanomaterial (PdS or $Pd_{16}S_7$)

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☐The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Easily synthesizable benzothiazole based designers palladium complexes for catalysis of Suzuki coupling: controlling effect of aryl substituent of ligand on role and composition of insitu generated binary nanomaterial (PdS or $Pd_{16}S_7$)

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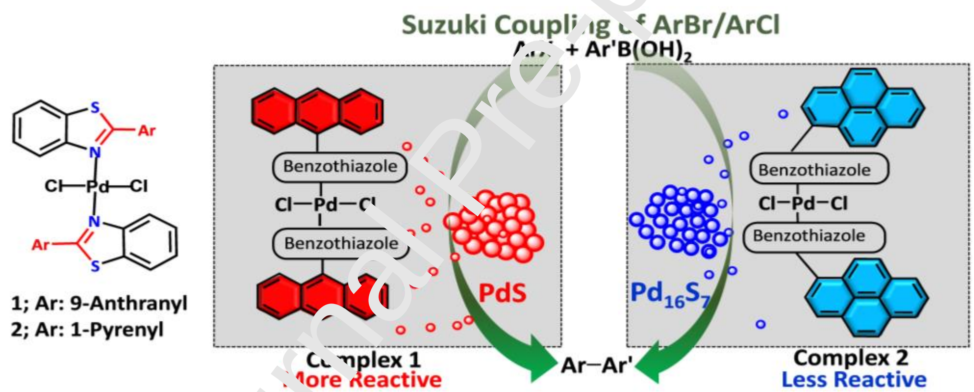

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- Straightforward synthesis of stable Pd(II)-complexes with bulky aryl groups.
- Designers catalysts with high activity for Suzuki coupling of ArBr and ArCl.
- Role of composition and nature of *insitu* generated binary materials in catalysis.
- Aryl group of ligand controls the composition (PdS or $Pd_{16}S_7$) of nanomaterials.
- Ligand synthesis protocol is green, one pot, room temperature and catalyst-free.