Received: 30 August 2019 | Revised: 25 October 2019 | Accepted: 6 November 2019

DOI: 10.1002/aoc.5405

Applied Organometallic Chemistry WILEY

FULL PAPER

Catalytic activity of Pd dithiolate complexes with large-bite-angle diphosphines in Heck coupling reactions

Pravin A. Mane[1] | **Suman Neogy**[2] | **Sandip Dey**[1,3]

[1]Chemistry Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India

[2]Mechanical Metallargy Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India

[3]Homi Bhabha National Institute, Mumbai, 400 094, India

Correspondence
Sandip Dey, Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India.
Email: dsandip@barc.gov.in

Palladium(II) complexes of aryl dithiolates and wide-bite-angle diphosphines Xantphos and dppf have been developed as efficient catalysts in Suzuki and Suzuki carbonylation reactions. The catalytic activity of these highly stable, discrete and charged complexes was investigated in Heck coupling reactions of styrene and a variety of aryl bromides. Under optimized reaction conditions these palladium complexes showed excellent activity with high turnover number (6×10^6) and high turnover frequency (4×10^5 h^{-1}). The effect of bite angle of diphosphines on the catalytic activity of the complexes $[Pd_2(P^\cap P)_2(SC_{12}H_8S)]_2(OTf)_4$ followed the trend $P^\cap P$ = Xantphos > dppf > dppe as the order of their bite angles. The catalyst could be reused, and after three cycles the formation of significant amount of Pd nanoparticles was noticed, which were characterized using powder X-ray diffraction, energy-dispersive X-ray analysis and transmission electron microscopy. The high catalytic activity has been attributed to the Pd nanoparticles.

KEYWORDS

bite angle, dithiolate, Heck reaction, macrocyclic Pd complex, Xantphos

1 | INTRODUCTION

Carbon–carbon bond forming reactions using Pd catalysts has led to a revolution in the preparation of organic compounds, biomolecules, pharmaceuticals and fine chemicals.[1,2] Multistep organic synthesis can be conveniently avoided by applying C–C bond forming reactions performed under mild reaction conditions. In particular, the Suzuki and Heck cross-coupling reactions are the most widely used arylating protocols for the preparation of biaryls and aryl-substituted olefins. A wide variety of compounds including coordination complexes, Pd on solid carriers[3] or polymers[4] and Pd nanoparticles (PdNPs)[3–5] have been reported as homogeneous and heterogeneous catalysts for C–C coupling reactions. It is well established that reactions involving soluble Pd complexes are much faster and more efficient than those involving the compounds in heterogeneous form. Phosphines[6–8] and their modified forms played a crucial role in the initial development of homogeneous Pd catalysts until the 1990s. Later Pd complexes of N-based ligands,[9] N-heterocyclic carbenes,[10] oximes,[8] imines[11] and palladacycles[3,8,11,12] have emerged as highly efficient catalysts in Suzuki and Heck C–C cross-coupling reactions.

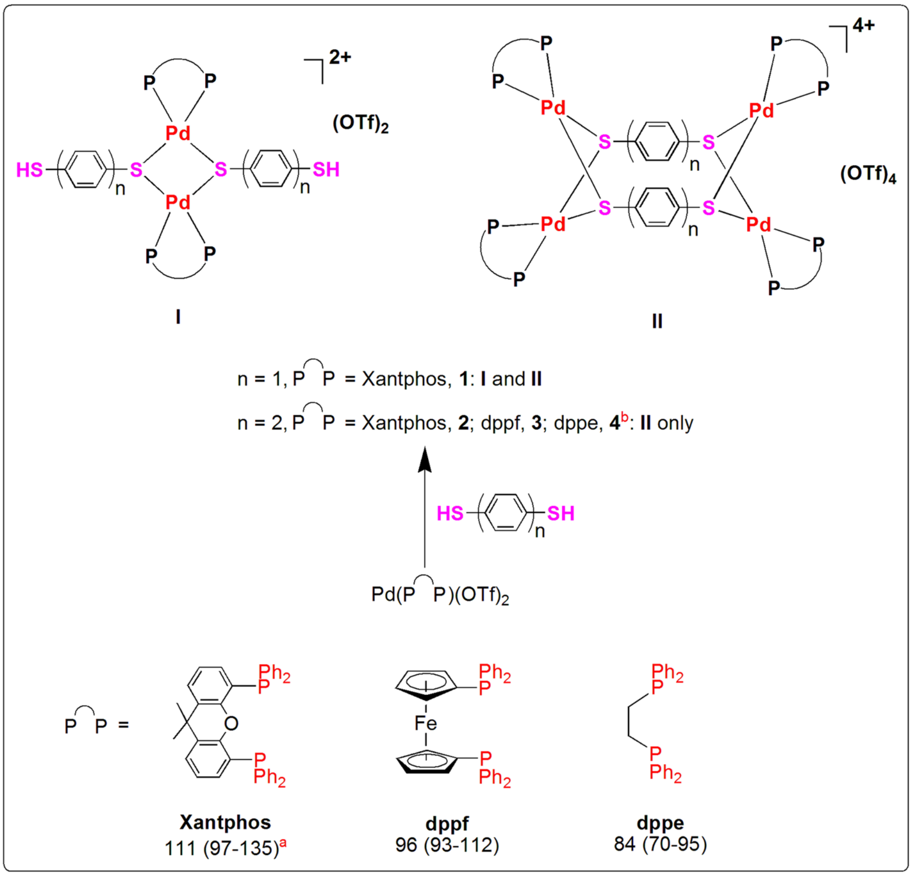
Each catalyst has its specific features and advantages. The electron-donating property of chalcogen elements has been explored in the last decade, and as a result a handful of palladium complexes with S-based[12–15] and Se-based[16–18] ligands have been recognized as phosphine-free catalysts. Sulfur ligands have now been established as catalyst promoters,[19] rather than catalyst poison[20] as an old misconception. Carbene,[13,14] cyclometalated[15] and pincer-type[12] Pd(II) complexes derived from S-based ligands are well-known highly active catalysts in C–C coupling reactions. In fact, with

https://doi.org/10.1002/aoc.5405

their features of convenient synthesis, easier handling and enhanced stability owing to the stronger Pd–S bond, the palladium thiolate complexes can be more robust catalysts than complexes derived from carbene-, amine-, thioether- and selenium-based ligands. Several Pd(II) catalysts made from carbene–thiolate[21] and hybrid thiolate (NS,[22–24] PS[25]) ligands have been successfully applied in C–C coupling reactions. Nevertheless, examples of C–C coupling reactions catalyzed by macrocycles or supramolecular coordination complexes of Pd are rare. Although a library of Pd and Pt supramolecular coordination complexes have been prepared by self-assembly processes, only a handful of examples exist in terms of molecular recognition, sensing or catalysts in Diels–Alder[26] reactions. A few self-assembled structures of the type Pd_mL_n ($m = 4$ or 6, $n = 4$ or 8; L = hydrazine[27] or oxadiazole[28] moiety) and macrocyclic Pd(II) complexes[29] have been reported as catalysts in Suzuki and C–C coupling reactions.

Moreover, complexes in macrocyclic form gain extra stability, which is an essential requirement for reactions under harsh conditions especially in Heck reactions.[29] Another reason for thiolate ligands being less explored lies in the fact that the resulting complexes are often polymeric or insoluble in nature, so they could not be applied as homogeneous catalysts. However by appropriate design of co-ligands, square planar Pd(II) complexes can be constructed as soluble discrete molecules with thiolate ligands. We have developed supramolecular palladium dithiolate complexes with capping ligand dppe, namely $[Pd_2(dppe)_2\{SX(C_6H_4)_nXS\}]_m(OTf)_{2m}$ ($n = 1, 2$; $m = 2, 4$; X = none, CH_2; dppe = 1,2-bis(diphenylphosphino)ethane), as discrete molecules. These complexes showed excellent catalytic activity in Suzuki[30] and Heck[31] C–C coupling reactions. Recently, these dithiolate complexes have been modified by replacing dppe with wide-bite-angle phosphines Xantphos (9,9-dimethyl-4,5-bis(diphenylphosphino)xanthenes) and dppf (1,1′-bis(diphenylphosphino)ferrocene)[32] (Scheme 1). The wide bite angle and flexibility range of such bisphosphines make the Pd complexes highly active catalysts in carbon–carbon[33] and carbon–heteroatom (N[34] and O[35]) bond forming reactions.

Macrocyclic Pd complexes of Xantphos exhibited excellent activity with high turnover number (TON) in Suzuki C–C coupling reactions[32] compared to the dppe analogues; moreover they also showed good activity in carbonylative Suzuki–Miyaura reactions.[36,37] Motivated by the above considerations, we decided to evaluate the catalytic activity of our Xantphos-capped Pd dithiolate complexes in Heck coupling reactions of styrene and aryl halides. We initially optimized the reaction conditions,



SCHEME 1 Diphosphine-capped palladium thiolate complexes used as catalysts in Heck reactions. [a]Bite angle and flexibility range in degrees are shown in parentheses. [b] Mane et al[32]

followed by evaluation of coupling reactions of various aryl halides and performance at low loading, and comparison of the activity with that of traditional Pd salts. The effect of bite angles of three diphosphines on the catalytic activity of $[Pd_2(P^\cap P)_2(SC_{12}H_8S)]_2(OTf)_4$ ($P^\cap P$ = dppe, Xantphos, dppf) was also assessed. Reuse of the catalysts, the formation and characterization of PdNPs and their active participation in the catalytic process are discussed here.

2 | EXPERIMENTAL

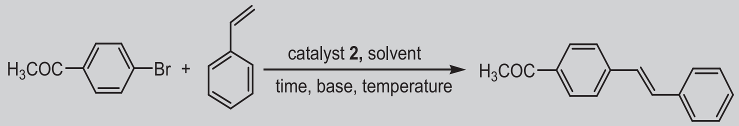
2.1 | Procedure for Heck coupling reaction

An oven-dried flask was charged with aryl halide (1.0 mmol), styrene (1.5 mmol), palladium complex **2** (0.1 mmol, equivalent to 0.4 mol% of Pd), DMA (3 ml) and NaOAc (2.0 mmol) in water (1 ml). The flask was placed in an oil bath at 120°C under a nitrogen atmosphere, and the reaction mixture was stirred until maximum conversion of aryl halide to product occurred. The reaction mixture was cooled to room temperature, diluted with water (10 ml) and neutralized by dropwise addition of dilute HCl (aq). The mixture was extracted with ethyl acetate (3 × 20 ml), washed with water (2 × 15 ml) and dried over anhydrous Na_2SO_4. The solvent of the extract was removed with a rotary evaporator, and the resulting residue was analyzed using ^1H NMR spectroscopy.

2.2 | Catalyst recycling and separation of PdNPs

Similar to the procedure described above, 4-bromoacetophenone (1.0 mmol), styrene (1.5 mmol), catalyst **2** (0.1 mmol), DMA (3 ml) and NaOAc (2.0 mmol) in water (1 ml) were used. Keeping other reaction conditions as described above, the mixture was stirred for 16 h

TABLE 1 Optimization of reaction parameters[a]



Entry	Solvent	Base	Temp. (°C)	Time (h)	Yield (%)[b]
Effect of solvent					
1	DMA	NaOAc	120	16	100
2	DMF	NaOAc	120	16	86
3	Methanol	NaOAc	120	16	No product
4	Dioxane	NaOAc	120	16	15
Effect of base					
5	DMA	NaOAc	120	16	100
6	DMA	Na_2CO_3	120	16	81
7	DMA	Et_3N	120	16	53
8	DMA	KOH	120	16	35
9	DMA	Bu_4NOH	120	16	21
Effect of temperature					
10	DMA	NaOAc	120	16	100
11	DMA	NaOAc	110	16	79
12	DMA	NaOAc	100	16	64
13	DMA	NaOAc	80	16	38
Effect of time					
14	DMA	NaOAc	120	16	100
15	DMA	NaOAc	120	12	77
16	DMA	NaOAc	120	8	51

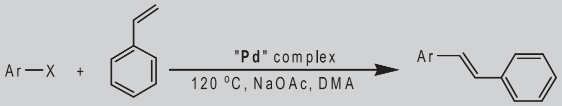
[a] Reaction conditions: aryl bromide (1.0 mmol), styrene (1.5 mmol), base (2.0 mmol) in water, DMA (3 ml), catalyst **2**, 0.4 mol% of Pd used. [b] Determined using ^1H NMR spectroscopy.

and processed analogously. After the reaction, ethyl acetate (3 × 15 ml) was added to the product mixture resulting in the formation of two layers. The upper layer of ethyl acetate, containing the product, was removed to give 99% yield. The lower aqueous layer containing the catalyst **2** was then used for another reaction, with amounts of reactants accordingly being further added. After 16 h, the first reaction cycle resulted in 92% yield; further repeating a similar process, the second and third reaction cycles yielded 75% and 62% of the product. After the third cycle, the aqueous part was centrifuged and decanted to afford a black residue. The residue was washed with water (2 × 20 ml) followed by 5 ml of each of ethanol and acetone and dried in vacuum. Powder X-ray diffraction (PXRD) analysis of the residue confirmed the formation of PdNPs.

3 | RESULTS AND DISCUSSION

The catalysts $[Pd(Xantphos)(1,4\text{-}SC_6H_4SH)]_2(OTf)_2$ (**I**) and $[Pd_2(Xantphos)_2(1,4\text{-}SC_6H_4S)]_2(OTf)_4$ (**II**) (**1**) and $[Pd_2(P^{\cap}P)_2(4,4'\text{-}SC_{12}H_8S)]_2(OTf)_4$ ($P^{\cap}P$ = Xantphos (**2**), dppf (**3**), dppe (**4**)) were prepared and characterized according to methods recently reported by us[30,32] (Scheme 1). We initially optimized the reaction conditions with respect to the parameters solvent, base, temperature and time employing the coupling reaction of 4-bromoacetophenone and styrene as a model reaction. The experiments on screening of commonly used solvents were carried out first using catalyst **2**. DMA gave quantitative yield followed by 86% yield in dimethylformamide (DMF) at 120°C within 16 h, in the presence of NaOAc as base (Table 1, entries 1 and 2). The reaction in dioxane yielded much less of the product, whereas no coupling product was found in case of methanol used as solvent. Interestingly, the same catalysts recently applied in the Suzuki–Miyaura reaction gave excellent yields of product biaryls in refluxing methanol, in fact the yields being higher than those obtained using DMA, DMF and dioxane as solvent at higher temperatures (≥95°C). So DMA was chosen as solvent for the present reaction medium and various inorganic and organic bases were investigated. The obtained results revealed that NaOAc is the

TABLE 2 Reaction between aryl halide and styrene[a]



Entry	Ar–X	Complex	"Pd" (mol%)	Time (h)	Yield (%)[b]	TON
1	$4\text{-}CH_3C_6H_4Br$	**1**[c]	0.4	16	80	200
2	$4\text{-}CH_3C_6H_4Br$	**2**[c]	0.4	16	71	178
3	$4\text{-}CH_3OC_6H_4Br$	**1**[c]	0.4	24	67	168
4	$4\text{-}H_2NC_6H_4Br$	**2**	0.4	16	88	220
5	$4\text{-}CH_3COC_6H_4Br$	**2**	0.4	16	100	250
6	$4\text{-}CH_3COOC_6H_4Br$	**1**[c]	0.4	16	99	248
7	$4\text{-}CH_3COOC_6H_4Br$	**2**[c]	0.4	16	96	240
8	$4\text{-}O_2NC_6H_4Br$	**1**	0.4	16	93	233
9	$4\text{-}O_2NC_6H_4Br$	**2**	0.4	16	87	218
10	$4\text{-}NCC_6H_4Br$	**1**	0.4	16	92	230
11	$4\text{-}NCC_6H_4Br$	**2**	0.4	16	86	215
12	$4\text{-}OHCC_6H_4Br$	**2**	0.4	16	99	248
13	$2\text{-}OHCC_6H_4Br$	**2**	0.4	16	98	245
14	$4\text{-}FC_6H_4Br$	**2**	0.4	16	72	180
15	$2\text{-}C_4H_3SBr$	**1**[c]	0.4	16	65	163
16	$2\text{-}C_4H_3SBr$	**2**[c]	0.4	16	57	143
17	$4\text{-}C_9H_6NBr$	**2**[c]	0.4	16	78	195
18	$4\text{-}CH_3COC_6H_4Cl$	**2**[d]	2	24	15	8

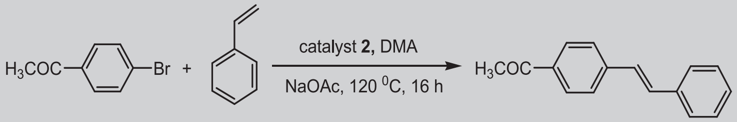
[a]Reaction conditions: aryl halide (1.0 mmol), styrene (1.5 mmol), NaOAc (2.0 mmol), DMA (3 ml), water (1 ml). [b]Determined using ^1H NMR spectroscopy. [c]TBAB (3.0 mmol) used. [d]TBAB (5.0 mmol) used.

best choice among other bases Na_2CO_3, KOH, Et_3N and Bu_4NOH (entries 5–9). Similar experiments by varying the temperature and time were carried out using DMA as solvent and NaOAc as base. The yields were improved with increasing temperature and time, which were found optimized at 120°C and 16 h, respectively (entries 10–16).

Having the optimized reaction conditions in hand, the coupling reactions of styrene with a variety of aryl bromides were investigated using 0.4 mol% of Pd of catalysts **1** and **2**. Both catalyst systems were tolerant to a wide range of functional groups, such as NH_2, OMe, COMe, COOMe, NO_2, CN and CHO. Aryl bromides containing electron-donating groups, such as methyl, methoxy and amine, at *para* position of benzene ring afforded 80%, 71%, 67% and 88% of the desired products (Table 2, entries 1–4). The presence of electron-withdrawing groups such as acetophenone, acetyl, nitro, cyano, aldehyde and fluoro groups in the aryl bromide showed improvement and gave the coupling products in excellent to quantitative yields in the range 72–100% (Table 2, entries 5, 8–14) without adding tetrabutylammonium bromide (TBAB). Furthermore, heteroaryl bromides having S or N in the aryl group also successfully reacted giving the corresponding coupling products (Table 2, entries 15–17). However, the reactions of aryl bromides with bulkier groups and aryl chlorides showed lower yields of the products.

Our next interest was to see the effect of lowering the catalyst loading on performance. The experiments with low loading of catalyst were carried out using the

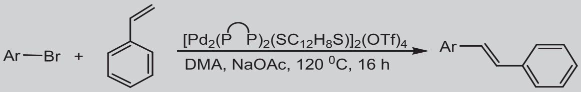
TABLE 3 Effect of catalyst loading on Heck reaction[a]



Entry	"Pd" (mol%)	Yield (%)[b]	TON	TOF (h^{-1})
1	0.4	100	250	16
2	0.01	92	9 200	575
3	0.001	80[c]	80 000	5 000
4	0.0001	69[c]	690 000	43 125
5	0.00001	58[c]	5 800 000	362 500

[a]Reaction conditions: aryl bromide (1.0 mmol), styrene (1.5 mmol), NaOAc (2.0 mmol) in water, DMA (3 ml), complex **2**. [b]Determined using ^1H NMR spectroscopy. [c]TBAB (1.0 mmol) used.

TABLE 4 Effect of bite angle of phosphine on catalysis using $[Pd_2(P^\cap P)_2(SC_{12}H_8S)]_2(OTf)_4$[a]



Entry	Ar–Br	$P^\cap P$ (complex)	Bite angle (°)	Yield (%)[b]
1	4-$CH_3C_6H_4Br$	Xantphos (**2**)	104.6[c]	71
2	4-$CH_3C_6H_4Br$	dppf (**3**)	99.6[c]	68
3	4-$CH_3C_6H_4Br$	dppe (**4**)	84.7[d]	64[e]
4	4-$CH_3COOC_6H_4Br$	Xantphos (**2**)		96
5	4-$CH_3COOC_6H_4Br$	dppf (**3**)		92
6	4-$CH_3COOC_6H_4Br$	dppe (**4**)		90[e]
7	2-C_4H_3SBr	Xantphos (**2**)		57
8	2-C_4H_3SBr	dppf (**3**)		48
9	2-C_4H_3SBr	dppe (**4**)		43[e]

[a]Reaction conditions: aryl bromide (1.0 mmol), styrene (1.5 mmol), NaOAc (2.0 mmol) in water, DMA (3 ml), TBAB (3.0 mmol) used, 0.4 mol% of Pd used. [b]Determined using ^1H NMR spectroscopy. [c]Mane *et al.* [32] [d]Vivekananda *et al.* [30] [e]Mane *et al.* [31]

coupling reaction of 4-bromoacetophenone and styrene in the presence of tetranuclear complex **2**. Upon decreasing the concentration of **2** to 0.01 mol% of Pd, an excellent yield of 92% of the product was obtained (Table 3, entry 2). On reducing the loading further to 0.0001 mol% of Pd, still a significant yield of 69% was found, and the TON is calculated as 7×10^5. The reaction using 0.00001 mol% of Pd of the catalyst showed 58% yield of the product, with the corresponding TON increased to *ca* 6×10^6 (Table 3, entry 5) turnover frequency (TOF) of *ca* 4×10^5 h^{-1}. The reusability of the catalyst was investigated using 4-bromoacetophenone and Pd complex **2** with a loading of 0.4 mol% of Pd (Table S1). After the completion of zero cycle of the reaction with styrene, the solvent ethyl acetate was added to extract the coupling product (*E*)-4-acetylstilbene in the organic phase. Then fresh reactants in required quantities were added to the aqueous phase containing the Pd catalyst for the first cycle of reaction, which yielded 92% of product. In a similar manner the second and third cycles yielded the same product in 75% and 62% yield, respectively. These results showed that the recovered catalyst still retained high catalytic activity.

A comparison of the catalytic activity of the Xantphos-capped Pd complexes revealed that complex **1** is slightly more active than complex **2**, as evident from Table 2 irrespective of aryl bromide. 4-Tolyl bromide containing electron-donating group gave 80% and 71% yield (entries 1 and 2) or the heteroaryl bromide 2-bromothiophene yielded 65% and 57% (entries 15 and 16) when catalyzed by **1** and **2**, respectively. These results agree well with the catalytic activities of the same complexes in Suzuki–Miyaura C–C coupling reactions reported by us.[30] The less stable form of **I** in comparison to **II** in **1** is mainly responsible for the difference in activity compared with **2**. Catalyst **1** consists of dinuclear complex **I** and tetranuclear complex **II** in nearly equal ratio as evidenced by ^{31}P NMR spectra in solution. Catalyst **2** exclusively exists in tetranuclear form **II** for which the stability was estimated as −872 kcal mol^{-1} using density functional theory calculation. In the case of **1**, the stability of form **II** (−870 kcal mol^{-1}) was found to be about 435 kcal mol^{-1} higher than **I** (−435 kcal mol^{-1}).[32] The less stable form **I** will generate more catalytic active species than **II**, hence **1** showed slightly higher activity. The thermogravimetric analysis of the complexes indicates that the catalysts are stable enough in the solid state, the decomposition starting after 305°C for catalyst **1**,[36] and after 320°C for catalysts **2**[36] and **3** (Figures S1–S3). Next was examined the effect of bite angle with varied flexibility range of the bisphosphines on the catalytic activity under the present optimized reaction conditions. The phosphines Xantphos, dppf and dppe were chosen, as they exclusively form tetranuclear Pd complexes with the 4,4′-biphenylenedithiolate ligand both in solid and solution states. Accordingly, complexes **2** and **3** were prepared and the catalytic activity was evaluated in the Heck coupling reactions of three different aryl bromides (Table 4) in identical reaction conditions. We have earlier investigated the same Heck coupling reactions using the analogous complex **4** with dppe ligand as catalyst.[31] The obtained results indicate that irrespective of aryl bromides, whether containing electron-donating group (entries 1–3), electron-withdrawing group (entries 4–6) or hetero atom (entries 7–9), the trend of catalytic activity of the complexes follows the order **2** > **3** > **4**. The catalytic activity of the present complexes was compared with that of commercially available Pd complexes such as $Pd(OAc)_2$, $PdCl_2(PPh_3)_2$, $PdCl_2$(Xantphos) and $PdCl_2$ (Table S2). Under the same reaction conditions, complex **1** showed higher activity than these Pd complexes. The present results for C–C coupling reactions support the literature findings that Pd complexes of wider bite angle of bisphosphine accelerate the rate of catalysis reaction. For example, in case of allylic alkylation, the rate of catalytic reaction was observed to be faster for Pd–dppf complex than the analogous Pd–dppe complex.[38]

Moreover, we investigated the state of the Pd complex after the catalysis reaction. Recently, we reported the Suzuki reaction catalyzed by the present complex **2**. After six cycles under reflux in methanol, the formation of PdNPs was noticed using PXRD. Similar intense peaks have been found at $2\theta \sim 39.9°$ in the PXRD pattern of the

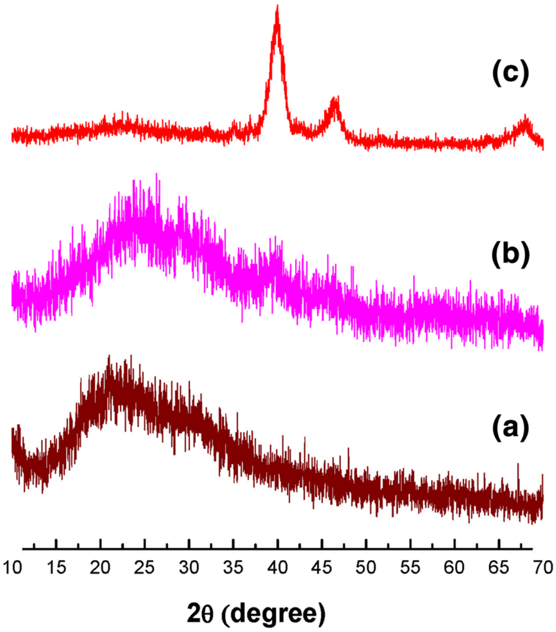


FIGURE 1 PXRD patterns of (a) complex **2** before catalysis, (b) compound after zero cycle of catalysis reaction of complex **2** and (c) compound after three cycles of catalysis reaction of complex **2**

black residue obtained after zero cycle of the present Heck reaction catalyzed by complex **2**. Similarly, the pattern of the residue obtained after three cycles showed the broad peaks become more intense at 2θ ~ 39.9°, 46.5°, 68.2°, 82.1° and 86.7° (Figure 1 and Figure S4). These reflection peaks are attributed to the (111), (200), (220), (311) and (222) planes of face-centered cubic structure of PdNPs (JCPDS file no. 46-1043). The average size of the particles was calculated as 6 nm from the Debye–Scherrer formula considering the broadening of the strongest peak, which is less than observed from transmission electron microscopy (TEM) imaging. The TEM image in Figure 2a shows the irregular shape of the PdNPs obtained after catalysis reaction. The well-defined, sharp diffraction rings in the selected area electron diffraction pattern of Figure 2b, corresponding to the planes (111), (200), (220) and (311), corroborated the nanocrystalline nature of the particles as inferred from the PXRD results. The lattice fringes with an inter-fringe distance of about 2.22 Å closely matched the inter-planar distance of (111) plane in the face-centered cubic structure of Pd (Figure 2c). The histograms of size distribution, counted from 700 particles, are shown in Figure S5. The average crystallite size of PdNPs is in the range 5–22 nm. The energy-dispersive X-ray (EDAX) spectra show the presence of Pd and S as major and minor constituent elements present in a 2.5:1 ratio of atom% (Figure S6). The S may be present as capping group of thiolate ligand; however, other elements such as P, F and Fe from the complex were absent.

The present PXRD peaks are more prominent than the peaks observed for the previously reported Suzuki reaction, due to the formation of substantial amount of PdNPs which is attributed to the harsher condition (i.e. higher temperature and longer duration) used in the Heck reaction. During the catalytic process the dithiolate complexes of Pd(II) generate PdNPs, which serve as a reservoir of catalytically active species. The thiolate ligand act as a good stabilizer of the PdNPs to inhibit their agglomeration to form inactive Pd black. The mercury poisoning test[39] (Hg:catalyst **2** = 400:1) showed complete inhibition of the catalytic activity, thus suggesting the participation of heterogeneous PdNPs in the catalytic cycle. Others have reported that thiol-capped PdNPs showed good activity in C–C coupling[40] and Heck reactions.[41] There is sufficient evidence that supports that heterogeneous Pd catalysts function as homogeneous catalysts in Heck reactions.[4,5] So, the reaction mechanism is more likely progress via Pd(0)/Pt(II) catalytic cycle[42,43] which is purely homogeneous, whatever the PdNP source or Pd atoms return to PdNPs after the catalysis.[4] The crystalline nature and reasonably narrow size distribution suggest that the nanoparticles possibly form

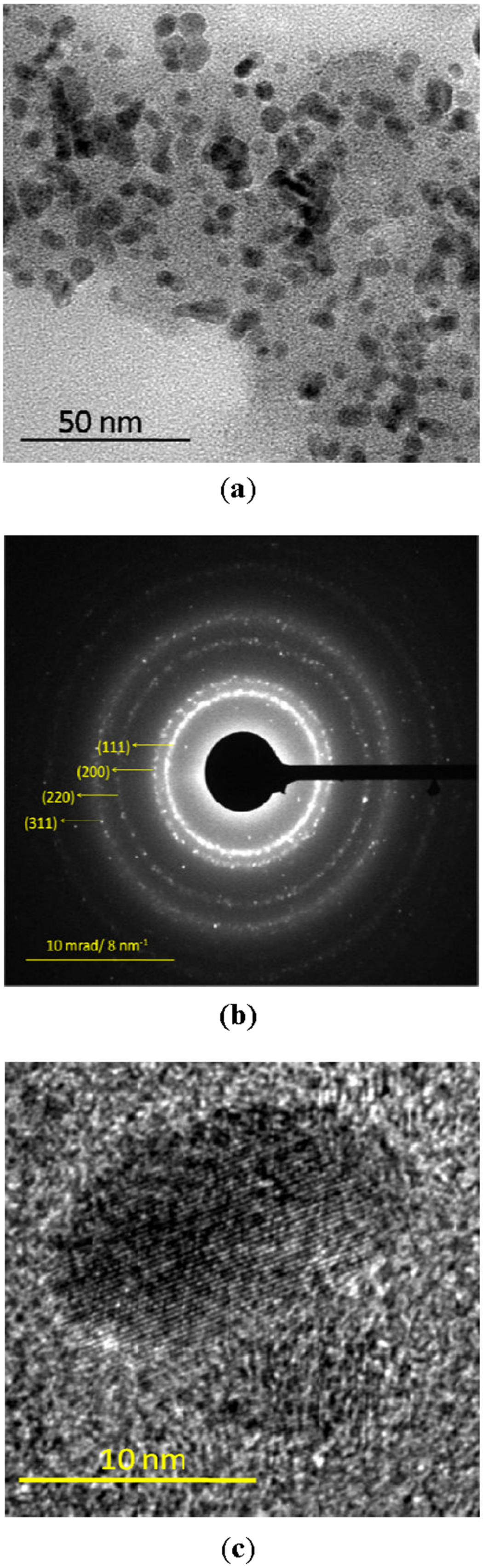


FIGURE 2 PdNPs formed after three catalysis cycles of Pd complex **2**: (a) High-magnification TEM image; (b) selected area electron diffraction pattern; (c) high-resolution TEM image

via a particular type of metal cluster during the reaction. Although the nanoparticles may contribute significantly to the activity, comparing the PXRD peaks (Figure 1) particularly after zero cycle, the cocktail of species such as molecular complex and metal clusters may also be present in the reaction mixture with the nanoparticles, as discussed by Ananikov and co-workers.[5,44] The transformation of Pd complexes to PdNPs is a well-established phenomenon.[3–5,42] However, in the case of complexes with strongly coordinated thiolate group, the formation of palladium sulfide, Pd_xS_y (x, y = rational number), was anticipated rather than Pd(0) species. In the case of Suzuki[18] reactions catalyzed by Pd(II) complexes of comparatively loosely bound thio/selenoether complexes at *ca* 100°C, the formation of Pd_xE_y (E = S,[45] Se[18]) has been encountered.

4 | CONCLUSIONS

The Xantphos-capped Pd(II) complexes with dithiolate ligands are very efficient in promoting the Heck reaction of a wide range of aryl bromides. The catalysts remain highly active at low concentration yielding high TON (6×10^6). The present Pd dithiolate complexes with wide-bite-angle diphosphines have a positive effect on the rate of the catalytic reaction and showed improved activity than our previously investigated dppe analogues. The catalyst could be conveniently reused. The formation of PdNPs has been confirmed using various techniques after the catalysis reaction of the Pd(II) dithiolate complexes. The high activity has been attributed to PdNPs, which may serve as a reservoir of catalytically active species.

Supporting information: Details of general procedures of the experiments, tables of data of reusability experiment, comparison with other catalysts, thermogravimetric curves of **1–3**, PXRD pattern of **2** after three cycles of catalysis reaction, EDAX spectrum and histograms of size distribution of particle size of PdNPs, ^{1}H NMR spectra of all the coupling products (Figures S7–S18), ^{13}C{^{1}H} NMR spectra of the coupling products (*E*)-4-acetylstilbene, (*E*)-4-stilbenecarboxylicacid methyl ester, (*E*)-4-nitrostilbene, (*E*)-4-cyanostilbene and (*E*)-2-styrylthiophene (Figures S19–S23), elemental analysis of (*E*)-4-acetylstilbene, (*E*)-4-stilbenecarboxylicacid methyl ester, (*E*)-4-nitrostilbene and (*E*)-4-styrylbenzaldehyde are provided in the supporting information.

ACKNOWLEDGMENTS

P.A.M. is grateful to BARC-Mumbai University Collaborative Scheme for providing a Senior Research Fellowship (SRF). The authors thank Mr. Asheesh Kumar of Chemistry Division for the EDAX measurements.

ORCID

Sandip Dey https://orcid.org/0000-0001-9198-8808

REFERENCES

[1] J. Tsuji, *Palladium Reagents and Catalysts: New Perspectives for the 21st Century*, Wiley, New York **2004**.
[2] C. C. J. Seechurn, M. O. Kitching, T. J. Colacot, V. Snieckus, *Angew. Chem. Int. Ed.* **2012**, *51*, 5062.
[3] J. Louie, J. F. Hartwig, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2359.
[4] D. Astruc, *Inorg. Chem.* **2007**, *46*, 1884.
[5] D. Eremin, V. P. Ananikov, *Coord. Chem. Rev.* **2017**, *346*, 2.
[6] R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461.
[7] A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **1998**, *37*, 3387.
[8] W. A. Herrmann, C. Brossmer, C-P. Reisinger, T. H. Riermeier, K. Ofele, M. Beller, *Chem. Eur. J.* **1997**, *3*, 1357.
[9] C. J. Mathews, P. J. Smith, T. Welton, *J. Mol. Catal.* **2003**, *206*, 77.
[10] E. A. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem. Int. Ed.* **2007**, *46*, 2768.
[11] C. Rocaboy, J. A. Gladysz, *Org. Lett.* **2002**, *4*, 1993.
[12] D. E. Bergbreiter, P. L. Osburn, Y. S. Liu, *J. Am. Chem. Soc.* **1999**, *121*, 9531.
[13] D. Yuan, Q. Teng, H. V. Huynh, *Organometallics* **2014**, *33*, 1794.
[14] C. Fliedel, P. Braunstein, *Organometallics* **2010**, *29*, 5614.
[15] D. Zim, A. S. Gruber, G. Ebeling, J. Dupont, A. L. Monteiro, *Org. Lett.* **2000**, *2*, 2881.
[16] K. V. Vivekananda, S. Dey, A. Wadawale, N. Bhuvanesh, V. K. Jain, *Dalton Trans.* **2013**, *42*, 14158.
[17] Q. Yao, E. P. Kinney, C. Zheng, *Org. Lett.* **2004**, *6*, 2997.
[18] G. K. Rao, A. Kumar, J. Ahmed, A. K. Singh, *Chem. Commun.* **2010**, *46*, 5954.
[19] R. Vanjari, T. Guntreddi, S. Kumar, K. N. Singh, *Chem. Commun.* **2015**, *51*, 366.
[20] J. K. Dunleavy, *Platinum Met. Rev.* **2006**, *50*, 110.
[21] D. Yuan, H. V. Huynh, *Organometallics* **2010**, *29*, 6020.
[22] D. K. Paluru, S. Dey, A. Wadawale, V. K. Jain, *J. Organometal. Chem.* **2013**, *728*, 52.
[23] D. K. Paluru, S. Dey, K. R. Chaudhari, M. V. Khedkar, B. M. Bhanage, V. K. Jain, *Tetrahedron Lett.* **2014**, *55*, 2953.
[24] H. Wang, R. Zhong, X. -Q. Guo, X. -Y. Feng, X. -F. Hou, *Eur. J. Inorg. Chem.* **2010**, 174.
[25] A. Dervisi, D. Koursarou, L.-I. Ooi, P. N. Horton, M. B. Hursthouse, *Dalton Trans.* **2006**, 5717.
[26] D. Samanta, S. Mukherjee, Y. P. Patil, P. S. Mukherjee, *Chem. Eur. J.* **2012**, *18*, 12322.
[27] S. Pradhan, R. P. John, *RSC Adv.* **2016**, *6*, 12453.
[28] C. -W. Zhao, J. -P. Ma, Q. -K. Liu, Y. Yu, P. Wang, Y. -A. Li, K. Wang, Y. -B. Dong, *Green Chem.* **2013**, *15*, 3150.
[29] C. Rohlich, K. Kohler, *Adv. Synth. Catal.* **2010**, *352*, 2263.
[30] K. V. Vivekananda, S. Dey, D. K. Maity, N. Bhuvanesh, V. K. Jain, *Inorg. Chem.* **2015**, *54*, 10153.
[31] P. A. Mane, S. Dey, K. V. Vivekananda, *Tetrahedron Lett.* **2017**, *58*, 25.
[32] P. A. Mane, S. Dey, A. K. Pathak, M. Kumar, N. Bhuvanesh, *Inorg. Chem.* **2019**, *58*, 2965.

[33] F. Liron, C. Fosse, A. Pernolet, E. Roulland, *J. Org. Chem.* **2007**, *72*, 2220.

[34] S. Wagaw, B. H. Yang, S. L. Buchwald, *J. Am. Chem. Soc.* **1999**, *121*, 10251.

[35] G. -Y. Gao, A. J. Colvin, Y. Chen, X. P. Zhang, *Org. Lett.* **2003**, *5*, 3261.

[36] V. V. Gaikwad, P. A. Mane, S. Dey and B. M. Bhanage, *Appl. Organmetal. Chem*. https://doi.org/10.1002/aoc.5255

[37] V. V. Gaikwad, P. A. Mane, S. Dey, B. M. Bhanage, *ChemistrySelect* **2019**, *4*, 8269.

[38] R. J. van Harren, K. Goubitz, J. Fraanje, G. P. F. Strijdonck, H. Oevering, B. Coussens, J. N. H. Reek, P. C. J. Kamer, P. W. N. M. Van Leeuwen, *Inorg. Chem.* **2001**, *40*, 3363.

[39] J. A. Widegren, R. G. Finke, *J. Mol. Catal.* **2003**, *198*, 317.

[40] V. P. Ananikov, N. V. Orlov, I. P. Beletskaya, V. N. Khrustalev, M. Y. Antipin, T. V. Timofeeva, *J. Am. Chem. Soc.* **2007**, *129*, 7252.

[41] C. -H. Lu, F. -C. Chang, *ACS Catal.* **2011**, *1*, 481.

[42] J. G. de Vries, *Dalton Trans.* **2006**, 421.

[43] K. Yu, W. Sommer, J. M. Richardson, M. Weck, C. W. Jones, *Adv. Synth. Catal.* **2005**, *347*, 161.

[44] V. P. Ananikov, I. P. Beletskaya, *Organometallics* **2012**, *31*, 1595.

[45] G. K. Rao, A. Kumar, S. Kumar, U. B. Dupare, A. K. Singh, *Organometallics* **2013**, *32*, 2452.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Mane PA, Neogy S, Dey S. Catalytic activity of Pd dithiolate complexes with large-bite-angle diphosphines in Heck coupling reactions. *Appl Organometal Chem*. 2019; e5405. https://doi.org/10.1002/aoc.5405