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Synthesis and structural characterization of palladium(II) thiosemicarbazone complex: application to the Buchwald–Hartwig amination reaction

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ABSTRACT

A simple route to synthesize mononuclear palladium(II) thiosemicarbazone complex has been described. Elemental analysis, spectral methods and single crystal X-ray diffraction analysis were used to confirm the composition of the complex. The new complex acts as an active homogeneous catalyst for the Buchwald–Hartwig amination reaction of a wide range of aryl and heteroaryl halides (bromides and chlorides), including activating, neutral and deactivating substrates, with various secondary amines under optimized conditions.

Derivatives of aryl- and heteroarylamines play an important role as intermediates for agrochemicals, pharmaceuticals, natural products,[1] dendrimers,[2] polymers,[3] dyes, pigments[4] as well as materials with electronic and nonlinear optical properties.[5] Buchwald and Hartwig independently developed the protocols for the palladium-mediated amination of aryl halides.[6] Several conditions have been developed since then for the Buchwald–Hartwig amination reaction and this reaction has now emerged as a highly versatile and synthetically indispensable method for the synthesis of aryl- and heteroarylamines. Compared to the other methods of carbon–nitrogen bond formation[7] such as nucleophilic aromatic substitution, Ullmann coupling and nitration followed by reduction, the Buchwald–Hartwig reaction offers a lower reaction temperature, typically between 80 and 100 °C, a wide substrate scope, a higher selectivity with respect to the amines, better functional group compatibility[8] and the reaction does not include highly reactive reactants,[9] which may cause safety problems.

There are a number of reviews highlighting the scope and versatility of the Buchwald–Hartwig amination reaction.[10] Phosphorus based ligands are known to improve the catalytic activity of this cross-coupling reaction.[11] A variety of ligands have been effectively used for this palladium-mediated coupling reaction which include chelating biaryl ligands,[12] ferrocenyl–phosphine ligands,[13] aryl–heteroaryl ligands,[14] trialkylphosphine ligands,[15] pincer-type ligands,[16] Schiff base ligands,[17] N-heterocyclic carbene ligands,[18] amino phosphine ligands[19] and cyclometallated ligands.[20] However, a major drawback of this coupling reaction is that it often requires the use of a large amount of catalyst (typically ~1–5 mol %) and longer reaction times (~15–20 h) to obtain optimal yields in these reactions.

Among the various ligands containing nitrogen and sulphur donor atoms, thiosemicarbazones are unique and multifaceted Schiff base ligands that are known for their selectivity and sensitivity towards various metal ions. These ligands and their transition metal complexes have received new impetus because of their mixed hard–soft donor character, highly interesting stereochemical, electronic and electrochemical properties as well as their potential catalytic activity and beneficial pharmacological properties.[21] They are versatile ligands which can be functionalized in many different ways and they exhibit thione–thiol tautomerism in solution owing to the presence of the –NH–C=S functional group, displaying unique coordination modes. They bind to the metal ion in neutral or anionic form, resulting in four- or five-membered chelate rings.[22]

Though palladium(II) thiosemicarbazone complexes have been employed as effective catalysts for carbon–carbon cross-coupling reactions,[23] the use of these complexes as catalysts for the Buchwald–Hartwig amination reaction has not been explored so far. We herein describe the synthesis and characterization of a structurally simple mononuclear palladium(II) complex incorporating 1-naphthaldehyde thiosemicarbazone ligand with bromide and triphenylphosphine as ancillary ligands.

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The 1-naphthaldehyde thiosemicarbazone ligand (HL, where H stands for the dissociable proton) was prepared by the condensation of 1-naphthaldehyde with thiosemicarbazide.[24] The ligand reacts with $[PdBr_2(PPh_3)_2]$ in equimolar ratio in 1:1 dichloromethane/ethanol mixture at room temperature to give the new mononuclear Pd(II) complex, $[Pd(L)Br(PPh_3)]$ (**1**) in 80% yield (Scheme 1). The oxidation state of palladium remains unchanged during the formation of the complex. The complex is air stable in both the solid and the solution states at room temperature and is non-hygroscopic. The complex is readily soluble in solvents such as chloroform, dichloromethane, acetonitrile, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO) etc., producing intense orange coloured solutions. The elemental analysis of the complex (Calcd: C, 53.23; H, 3.72; N, 6.21; S, 4.74. Found: C, 53.20; H, 3.70; N, 6.23; S, 4.72) is in good agreement with the molecular structure proposed.

The FT-IR spectrum of the complex displays $\nu_{C=N}$ stretch at 1589 cm^{-1} which is at a lower frequency than that of the free ligand (1621 cm^{-1}) indicating coordination of azomethine nitrogen to Pd(II) ion. The $\nu_{C=S}$ and ν_{N-H} of the –N–NH–C=S group at 847 and 3203 cm^{-1} respectively in the free ligand disappeared in the complex suggesting enolization and subsequent coordination through thiolate sulphur to the Pd(II) ion.[25] In the electronic spectrum of the complex, the band below 350 nm is assigned to ligand centred transitions whereas the two strong bands with absorption maxima at 397 and 419 nm and the weak broad band at 469 nm are assigned to a combination of charge transfer and d–d transitions.[26]

In the ^1H NMR spectrum of the complex, the multiplets observed in the region δ 8.3–7.4 ppm have been assigned to the aromatic protons of the coordinated PPh_3 and thiosemicarbazone ligand. The singlet due to azomethine proton (δ 8.7 ppm) in the complex is slightly downfield compared to the free ligand (δ 8.0 ppm), suggesting deshielding upon coordination to Pd(II) ion.[27] The singlet that appeared for the N–NH–C=S proton of the free ligand at δ 11.5 ppm is absent in the complex, supporting enolization and coordination of the thiolate sulphur to the Pd(II) ion. The ^{13}C NMR of the complex shows resonance in the expected regions and the complex revealed a downfield shift of the azomethine carbon relative (δ 153 ppm) to the free ligands (δ 141 ppm) indicating coordination of the azomethine nitrogen to the metal centre. Also, the signal assigned to the thioketone carbon, which moves upfield from δ 178 ppm in the free ligand to δ 168 ppm in the complex, results from the reduced C–S bond order upon coordination.[28] The ^{31}P NMR spectrum of the complex showed a singlet resonance in the region δ 26.3 ppm in agreement with the existence of one phosphorus nuclei.[29] The ^1H, ^{13}C and ^{31}P NMR spectra of the complex are given in Figures S1–S3, Supplementary data.

Single crystals of the complex **1**, were obtained by the slow evaporation of DMF–EtOH solution of the complex at room temperature. The molecular structure of the complex has been determined by single crystal X-ray diffraction to confirm the coordination mode of the ligand and geometry of the complex. The ORTEP view of complex is shown in Figure 1. The ligand coordinates to the Pd(II) ion via the azomethine nitrogen and the thiolate sulphur forming one five-membered chelate ring. One PPh_3 group (*trans* to the azomethine nitrogen) and one bromide ion (*trans* to thiolate sulphur) also coordinate to the Pd(II) ion to form a BrPNS square plane. The complex is having a distorted square planar geometry as reflected in all the bond parameters around Pd(II) ion. The crystal structure also reveals the presence of one solvent molecule (DMF) of crystallization. The bond lengths and bond angles are in good agreement with reported data on related Pd(II) thiosemicarbazone complexes.[30]

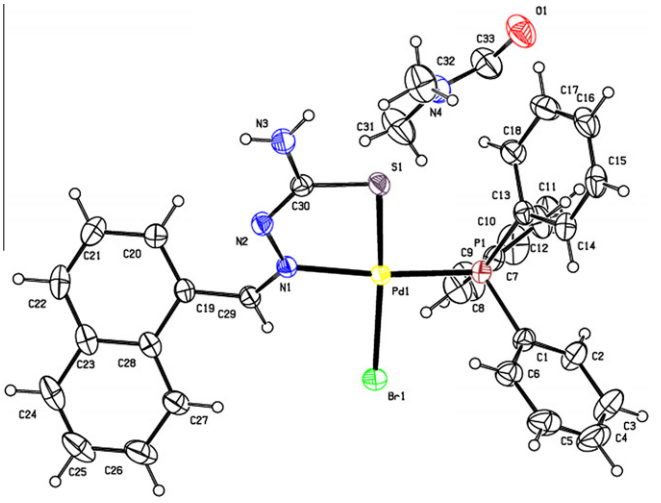
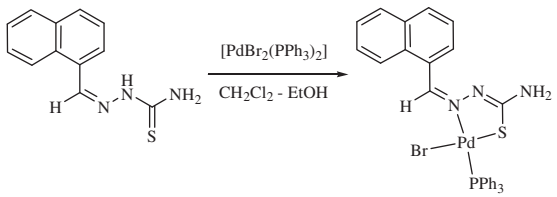


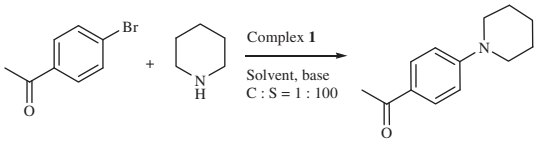
Figure 1. ORTEP diagram of **1**. DMF with 30% probability. Selected bond lengths (Å): Pd1–N1 2.0952(18), Pd1–S1 2.2680(6), Pd1–P1 2.2706(6), Pd1–Br1 2.4556(3), S1–C30 1.762(2), C30–N2 1.299(3), N1–N2 1.384(3), N1–C29 1.290(3). Selected bond angles (°): N1–Pd1–S1 82.25(5), S1–Pd1–P1 94.93(2), P1–Pd1–Br1 90.652(18), N1–Pd1–Br1 93.23(5), N1–Pd1–P1 171.56(5), S1–Pd1–Br1 170.63(2), C30–N2–N1 113.07(19), C29–N1–N2 117.33(19), N2–C30–S1 115.91(19).

Among cross-coupling reactions, the N-aryl amination has emerged as a practical and efficient method for carbon–nitrogen bond formation. A careful survey of the literature shows that there is a dramatic influence of the reaction conditions such as solvent, base and reaction temperature on the yield of the Buchwald–Hartwig amination reaction, though there is no well-defined rule that a specific solvent or a certain base can be used to attain highest efficiency. The initial tests for the efficacy of the palladium(II) thiosemicarbazone complex in the Buchwald–Hartwig amination reaction involved optimization of solvent, base



Scheme 1. Synthesis of mononuclear Pd(II) thiosemicarbazone complex.

Table 1
Optimization of reaction conditions[a]



Entry	Solvent	Base	Temp (°C)	Yield[b] (%)
1	Benzene	K_2CO_3	80	23
2	Toluene	K_2CO_3	110	32
3	1,4-Dioxane	K_2CO_3	100	43
4	2-BuOH	K_2CO_3	50	36
5	2-BuOH	K_2CO_3	100	85
6	2-BuOH	K_2CO_3	100[c]	—
7	2-BuOH	—	100	—
8	2-BuOH	Na_2CO_3	100	67
9	2-BuOH	CH_3COOK	100	25
10	2-BuOH	Et_3N	100	<10

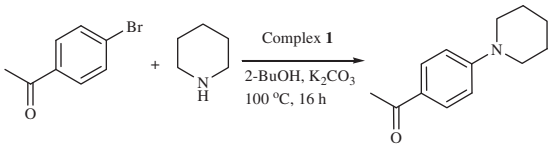
[a] Reaction conditions: 4-bromoacetophenone (5 mmol), piperidine (7.5 mmol), base (6 mmol), complex **1** (50 μmol %), solvent (5 mL) for 16 h under N_2 atmosphere.
[b] Isolated yield after column chromatography based on 4-bromoacetophenone (average of two runs).
[c] Reaction carried out in the absence of catalyst.

and reaction temperature. For this, the reaction of 4-bromoacetophenone as the aryl bromide substrate (S) with piperidine in the presence of complex **1** as catalyst (C) under various reaction conditions was initially examined (Table 1). The extent of conversion is solvent-dependent and low conversions were observed in benzene, toluene and 1,4-dioxane as solvent even under refluxing conditions. 2-Butanol was found to be the solvent of choice. It was observed in 2-BuOH, that the reaction was very slow at 50 °C but an increase in the temperature to 100 °C significantly improved the conversion. In addition, different bases were screened in 2-BuOH solvent, as the role of the base used is to neutralize and remove HBr and the reaction rates were found to be strongly dependent on the base employed. A remarkable increase in the product formation was observed in presence of bases like K_2CO_3 or Na_2CO_3 whereas in the case of bases like CH_3COOK or Et_3N, the yield of the cross-coupled product was considerably reduced. No cross-coupling product was observed in the absence of the catalyst or the base. Thus it was concluded that K_2CO_3 as base in 2-butanol solvent at 100 °C is the optimized condition for the coupling reaction.

Due to the high cost of metals and ligands used, the ability to use small amounts of catalyst and still achieve high conversions is a great concern in cross coupling reactions. In order to optimize the effect of catalyst loading, different catalyst: substrate (C/S) ratios were tested in the cross-coupling reaction of 4-bromoacetophenone with piperidine in the presence of complex **1** as catalyst and the results are summarized in Table 2. The reaction proceeds with good isolated yield of the cross-coupled product when the C/S ratio is either 1:100 or 1:500 (entries 1 and 2). When changing the C/S ratio to 1:1000 or 1:5000 (entries 3 and 4), the coupling reaction still proceeds smoothly accompanied by drop in the isolated yield. Further, even under very low catalyst loading (C/S = 1:10,000), the reaction proceeds (entry 5) with reasonably good turnover numbers (TON). Since the isolated yields are good with appreciable TON when C/S ratio is 1:500, it was concluded that this catalyst: substrate ratio is the best suitable for the coupling reaction.

The Buchwald–Hartwig amination reaction between piperidine and 4-bromoacetophenone as a function of time using complex **1** as catalyst was also used to monitor the progress of formation of 1-(4-piperidin-1-yl-phenyl)-ethanone (Fig. 2). The reaction conditions were similar as given in Table 2, where C/S = 1:500. The results indicate that the formation of the cross-coupled product increased initially with the progress of the reaction time, reached a maximum and then remained unchanged. Reasonably good isolated yield for the formation of the cross-coupled product was observed at the optimum reaction time of 24 h (~96%) was achieved.

Table 2
Effect of catalyst loading[a]



Entry	C/S	Yield[b] (%)	TON[c]
1	1:100	85	85
2	1:500	75	375
3	1:1000	42	420
4	1:5000	35	1750
5	1:10,000	22	2200

[a] Reaction conditions: 4-bromoacetophenone (5 mmol), piperidine (7.5 mmol), K_2CO_3 (6 mmol), 2-BuOH (5 mL) at 100 °C for 16 h under N_2 atmosphere.
[b] Isolated yield after column chromatography based on 4-bromoacetophenone (average of two runs).
[c] TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

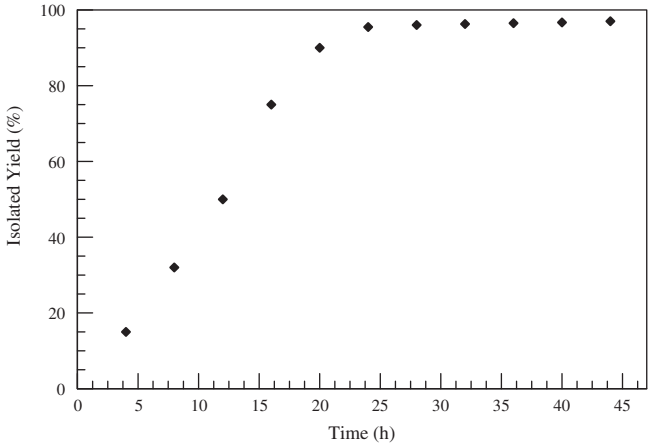
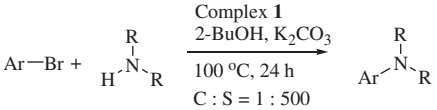
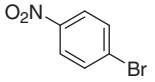
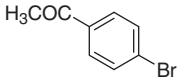
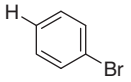
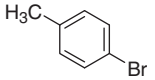
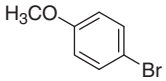
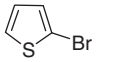
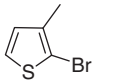
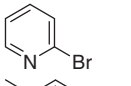
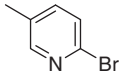


Figure 2. Influence of reaction time on isolated yield.

Using the above optimized conditions, the Buchwald–Hartwig amination reaction of aryl- and heteroaryl bromides with a variety of secondary amines (pyrrolidine, piperidine and morpholine)

Table 3
Buchwald–Hartwig reaction of aryl- and heteroaryl bromides with secondary amines[a]



Entry no.	Monobromides	Amines	Yield[b] (%)	TON[c]
1		Pyrrolidine	99.4	497
2		Piperidine	98.9	495
3		Morpholine	98.0	490
4		Pyrrolidine	96.1	481
5		Piperidine	95.5	478
6		Morpholine	94.7	474
7		Pyrrolidine	90.7	454
8		Piperidine	90.0	450
9		Morpholine	89.2	446
10		Pyrrolidine	85.5	428
11		Piperidine	84.7	424
12		Morpholine	83.7	419
13		Pyrrolidine	79.2	396
14		Piperidine	78.5	393
15		Morpholine	77.3	387
16		Pyrrolidine	87.4	437
17		Piperidine	86.6	433
18		Morpholine	85.7	429
19		Pyrrolidine	81.8	409
20		Piperidine	80.7	404
21		Morpholine	79.1	396
22		Pyrrolidine	86.8	434
23		Piperidine	85.7	429
24		Morpholine	84.3	422
25		Pyrrolidine	80.5	403
26		Piperidine	79.3	397
27		Morpholine	78.1	391

[a] Reaction conditions: aryl bromide (5 mmol), secondary amine (7.5 mmol), K_2CO_3 (6 mmol), complex **1** (10 μmol), 2-BuOH (5 mL) at 100 °C for 24 h under N_2 atmosphere.
[b] Isolated yield after column chromatography based on aryl bromide (average of two runs).
[c] TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

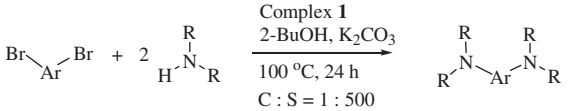
were carried out with complex **1** as catalyst using 2-BuOH/K_2CO_3 at 100 °C and the results are summarized in Table 3. In general, for a particular secondary amine, facile amination was observed when activated electron-deficient aryl bromides viz., 1-bromo-4-nitro benzene or 4-bromo acetophenone (entries 1–6), were coupled with the amine resulting in the formation of the corresponding products in excellent isolated yield after 24 h. The non-activated electron-neutral substrate viz., bromo benzene (entries 7–9) and deactivated electron-rich substrates viz., 4-bromo toluene and 4-bromo anisole (entries 10–15) gave moderate amount of products when coupling with the amines. The amination reaction is thus sensitive to the electronic changes on the aryl bromides and the electron-withdrawing substituents were more favourable for cross-coupling. In addition, for a particular aryl bromide, facile cross-coupling reaction was generally observed when pyrrolidine was used as the secondary amine and the reactivity of the amines followed the order: pyrrolidine > piperidine > morpholine. Further, the scope of complex **1** as catalyst is extended to the cross-coupling reaction of sulphur- and nitrogen-containing heteroaryl bromides with secondary amines. The reaction conditions optimized for the amination of aryl bromides were also effective for the amination of heteroaryl bromides. 2-Bromothiophene reacted smoothly with secondary amines (entries 16–18) to give the corresponding coupled products in good isolated yields. Presence of electron-donating methyl group on the thiophene ring, as in 3-methyl-2-bromothiophene, reduced the conversion slightly (entries 19–21). Similarly, nitrogen containing heteroaryl bromides such as 2-bromopyridine and 2-bromo-5-methyl-pyridine underwent smooth reaction with secondary amines (entries 22–27) to give the corresponding coupled products in moderate to good isolated yield.

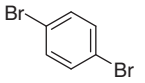
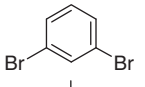
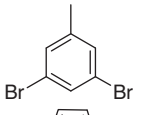
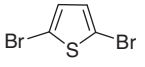
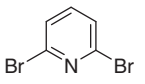
Further, this protocol was also evaluated for the double cross-coupling reaction of aryl- and heteroaryl dibromides with different secondary amines (pyrrolidine, piperidine and morpholine) using complex **1** as catalyst in 2-BuOH/K_2CO_3 at 100 °C. The double amination reactions were also quite effective as illustrated by the results in Table 4. The relative reactivity of the secondary amines was similar to that observed in the case of the corresponding monobromo derivatives. Aryl dibromo derivatives such as 1,4-dibromo benzene, 1,3-dibromo benzene and 3,5-dibromo toluene coupled with secondary amines (entries 1–9) with conversions up to ~81%. Heteroaryl dibromides such as 2,5-dibromothiophene and 2,6-dibromopyridine (entries 10–15) underwent reaction smoothly to form the corresponding coupled products in moderate yields.

Encouraged by these promising results, the Buchwald–Hartwig amination of less reactive aryl chlorides with secondary amines was also investigated with complex **1** as the catalyst using reaction conditions similar to those for the monobromides (Table 5). It was observed that complex **1** acts as an active catalyst for the amination reaction of activated aryl chlorides, 1-chloro-4-nitrobenzene and 4-chloroacetophenone, with various secondary amines (entries 1–6). The non-activated electron-neutral substrate (chlorobenzene) and heterocyclic chloride (2-chloropyridine) gave moderate amount of products when coupling with the secondary amines (entries 7–12). Also, as observed in the case of aryl bromides, for a particular aryl chloride, the reactivity of the amines followed the order: pyrrolidine > piperidine > morpholine. However, it was observed that when compared to the bromo analogue, the amination reactions of the chloro derivatives were less productive even at longer reaction times.

The Buchwald–Hartwig amination reaction between 4-bromoacetophenone and piperidine with complex **1** as catalyst using 2-BuOH/K_2CO_3 was selected to evaluate the recyclability of the catalyst and the recyclability of the complex was investigated for five cycles. The catalyst can be used two times without any detectable loss of activity (isolated yield). After that, gradual loss of activity was observed for the next three cycles with the isolated yields of ~83%, ~72% and ~65% for the third, fourth and fifth cycles respectively. The stability of the new mononuclear palladium(II) thiosemicarbazone complex and the fact that it can be synthesized conveniently from inexpensive starting materials and obtained

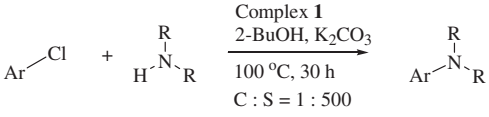
Table 4
Buchwald–Hartwig reaction of aryl- and heteroaryl dibromides with secondary amines[a]

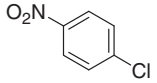
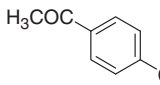
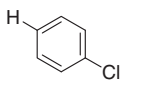
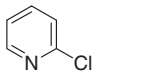


Entry no.	Dibromides	Amines	Yield[b] (%)	TON[c]
1		Pyrrolidine	81.1	406
2		Piperidine	80.0	400
3		Morpholine	78.8	394
4		Pyrrolidine	79.3	397
5		Piperidine	78.4	392
6		Morpholine	77.3	387
7		Pyrrolidine	75.8	379
8		Piperidine	74.7	374
9		Morpholine	73.2	366
10		Pyrrolidine	75.5	378
11		Piperidine	74.6	373
12		Morpholine	73.2	366
13		Pyrrolidine	74.3	372
14		Piperidine	73.2	366
15		Morpholine	72.0	360

[a] Reaction conditions: aryl bromide (5 mmol), secondary amine (15 mmol), K_2CO_3 (12 mmol), complex **1** (10 μmol), 2-BuOH (5 mL) at 100 °C for 24 h under N_2 atmosphere.
[b] Isolated yield after column chromatography based on aryl bromide (average of two runs).
[c] TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

Table 5
Buchwald–Hartwig reaction of aryl- and heteroaryl chlorides with secondary amines[a]



Entry no.	Monochlorides	Amines	Yield[b] (%)	TON[c]
1		Pyrrolidine	84.5	423
2		Piperidine	83.6	418
3		Morpholine	82.8	414
4		Pyrrolidine	81.1	406
5		Piperidine	80.3	402
6		Morpholine	79.1	396
7		Pyrrolidine	75.3	377
8		Piperidine	74.2	371
9		Morpholine	73.1	366
10		Pyrrolidine	70.5	353
11		Piperidine	69.8	349
12		Morpholine	68.2	341

[a] Reaction conditions: aryl chloride (5 mmol), secondary amine (7.5 mmol), K_2CO_3 (6 mmol), complex **1** (20 μmol), 2-BuOH (5 mL) at 100 °C for 24 h under N_2 atmosphere.
[b] Isolated yield after column chromatography based on aryl bromide (average of two runs).
[c] TON = Turnover number = ratio of moles of product formed to moles of catalyst used.

with satisfactory yields make them very promising catalyst. Further, a key advantage of this ligand and complex over some others is that the reactions can typically be performed in standard laboratory glassware without dry-box technique. Though a variety of palladium complexes have been employed as efficient catalysts for the Buchwald–Hartwig amination reaction, the use of palladium(II) thiosemicarbazone complex as catalysts for this reaction has not been explored earlier.

In conclusion, mononuclear palladium(II) thiosemicarbazone complex has been synthesized and characterized by analytical and spectral methods. X-ray diffraction study of the complex confirms the N and S coordination mode of the ligand and reveals the presence of a distorted square planar geometry around the Pd(II) ion. The utility of the new complex as excellent pre-catalysts for the Buchwald–Hartwig amination reaction has been highlighted by the coupling reaction of activating, neutral and deactivating aryl- and heteroaryl bromides or dibromides with secondary amines. The complex also acts as efficient catalyst for the Buchwald–Hartwig amination reaction of difficult substrates such as aryl- or heteroaryl chlorides with secondary amines.

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Supplementary data

Crystallographic data for the structural analysis have been deposited with Cambridge crystallographic center, CCDC No. 882239. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union roads, Cambridge CB2 1EZ, UK (email: deposit@ccdc.cam.ac.uk). The summary of the data collection and refinement parameters for the complex; Experimental procedures; ^{1}H, ^{13}C and ^{31}P NMR spectra of the complex; ^{1}H NMR data for all the Buchwald–Hartwig coupling products.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.12.070.

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