

Mixed-ligand benzaldehyde thiosemicarbazone complexes of palladium containing triphenylphosphine as ancillary ligand : Synthesis, structure and catalytic application in C-N coupling reactions

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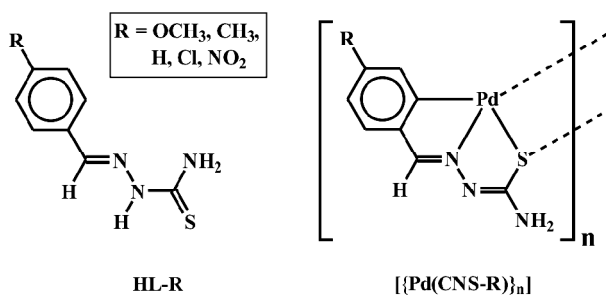
Abstract : From reaction of $\text{Na}_2[\text{PdCl}_4]$ with 4-R-benzaldehyde thiosemicarbazone (HL-R, R = OCH_3 , CH_3 , H, Cl and NO_2) and 2-picolinic acid in 1 : 1 : 1 mole ratio in refluxing ethanol a group of complexes of type $[\{\text{Pd}(\text{NS-R})\text{Cl}\}_n]$ is formed as minor product, along with another group of complexes of type $[\{\text{Pd}(\text{CNS-R})\}_n]$ as the major product (where NS-R and CNS-R denote the NS- and CNS-coordinated thiosemicarbazone respectively). Reaction of triphenylphosphine with the oligomeric $[\{\text{Pd}(\text{NS-R})\text{Cl}\}_n]$ species affords mononuclear complexes of type $[\text{Pd}(\text{NS-R})(\text{PPh}_3)\text{Cl}]$ via splitting of the sulfur-bridge. Crystal structures of $[\text{Pd}(\text{NS-CH}_3)(\text{PPh}_3)\text{Cl}]$ and $[\text{Pd}(\text{NS-NO}_2)(\text{PPh}_3)\text{Cl}]$ complexes have been determined. In these $[\text{Pd}(\text{NS-R})(\text{PPh}_3)\text{Cl}]$ complexes, the thiosemicarbazones are coordinated to the metal center, via dissociation of the acidic proton, as monoanionic bidentate NS-donors forming five-membered chelate rings and, the triphenylphosphine is *trans* to the imine-nitrogen and the chloride is *trans* to the coordinated sulfur. The $[\text{Pd}(\text{NS-R})(\text{PPh}_3)\text{Cl}]$ complexes have shown notable efficiency in catalyzing Buchwald type C-N coupling reactions.

Keywords : 4-R-Benzaldehyde thiosemicarbazone, palladium, mixed-ligand complexes, crystal structures, C-N coupling reactions.

Introduction

The chemistry of transition metal complexes of the thiosemicarbazone ligands has been receiving considerable current attention¹, largely because of their bioinorganic relevance. Many of the thiosemicarbazone complexes have found wide medicinal applications due to their potentially beneficial biological (viz. antibacterial, antimalarial, antiviral and antitumor) activities². Studies on the coordination chemistry of thiosemicarbazone ligands of different types are therefore of considerable importance. However, we have been exploring the chemistry

of thiosemicarbazone complexes of selected transition metal ions, with particular reference to variable binding mode of thiosemicarbazone ligands displayed in these complexes³, and the present work has originated from our continued interest in this area. For the present study we have selected a group of five 4-R-benzaldehyde thiosemicarbazones as the ligand and palladium as the metal center. The chosen ligands are abbreviated in general as HL-R, where H stands for the potentially dissociable acidic proton and R (R = OCH_3 , CH_3 , H, Cl and NO_2) for the *para*-substituent in the phenyl ring. Reaction of the selected thiosemicarbazones (HL-R) with $\text{Na}_2[\text{PdCl}_4]$, taken as the palladium starting material, has recently been observed to afford, under appropriate experimental condition, a group of oligomeric organopalladium complexes of type $[\{\text{Pd}(\text{CNS-R})\}_n]$ (where CNS-R denote the CNS-coordinated thiosemicarbazone)^{3a}. The sulfur bridge in these $[\{\text{Pd}(\text{CNS-R})\}_n]$ complexes is observed to undergo facile cleavage upon reaction with triphenylphosphine to yield monomeric complexes of type $[\text{Pd}(\text{CNS-R})(\text{PPh}_3)]$ ^{3a}.



While purifying these $[\text{Pd}(\text{CNS-R})(\text{PPh}_3)]$ complexes by thin layer chromatography using 1 : 7 acetonitrile-benzene as the eluant, it was observed that before the major yellow band containing the $[\text{Pd}(\text{CNS-R})(\text{PPh}_3)]$ complex, a minor orange band separated. Extraction of this minor orange band has afforded another group of mixed-ligand thiosemicarbazone complexes containing triphenylphosphine as ancillary ligand. Herein we report the chemistry of these second group of palladium thiosemicarbazone complexes, with special reference to their formation, structure and, catalytic application in C-N coupling reactions.

Experimental

Materials :

Palladium chloride was obtained from Arora Matthey, Kolkata, India. $\text{Na}_2[\text{PdCl}_4]$ was prepared by following a reported procedure⁴. The *para*-substituted benzaldehydes and thiosemicarbazide were procured from E. Merck India Pvt. Ltd. Triphenylphosphine was purchased from Spectrochem, Mumbai, India. The 4-R-benzaldehyde thiosemicarbazones were prepared by reacting equimolar amounts of thiosemicarbazide and the respective *para*-substituted benzaldehyde in a hot 1 : 1 ethanol-water mixture under stirring condition. The oligomeric $[\{\text{Pd}(\text{CNS-R})\}_n]$ complexes were prepared by following the reported method^{3a}. All other chemicals and solvents were reagent grade commercial materials and were used as received.

Syntheses of complexes :

$[\text{Pd}(\text{NS-R})(\text{PPh}_3)\text{Cl}]$ complexes : The $[\text{Pd}(\text{NS-R})(\text{PPh}_3)\text{Cl}]$ (R = OCH_3 , CH_3 , H, Cl, NO_2) complexes were prepared by following a general procedure. Specific details are given below for a particular complex.

$[\text{Pd}(\text{NS-H})(\text{PPh}_3)\text{Cl}]$: The oligomeric $[\{\text{Pd}(\text{CNS-H})\}_n]$ species (100 mg, 0.35 mmol) and triphenylphosphine (95 mg, 0.36 mmol) were taken together in hot ethanol (20 mL) and the solution was refluxed for 6 h to yield a clear yellow solution. The solvent was evaporated and the solid mass, thus obtained, was subjected to purification by thin-layer chromatography on a silica plate. With 1 : 7 acetonitrile-benzene as the eluant, a thin orange band separated first, followed by a major yellow band. Extraction of the major yellow band with acetonitrile, followed by evaporation of the extract, yielded an organopalladium complex that was reported earlier^{3a}. The minor orange band was also extracted with acetonitrile, and evaporation of the acetonitrile extract gave the $[\text{Pd}(\text{NS-H})(\text{PPh}_3)\text{Cl}]$ complex as a crystalline orange solid. Yield : 8%; Anal. Calcd. for $\text{C}_{26}\text{H}_{23}\text{N}_3\text{SClPPd}$: C, 53.62; H, 3.95; N,

7.22. Found : C, 53.83; H, 3.97; N, 7.21%; ^1H NMR⁵ : 4.83 (s, NH_2), 7.36-7.82 ($\text{PPh}_3 + 3\text{H}$)*, 8.14 (2H)*, 8.58 (1H, d, J 4.2).

$[\text{Pd}(\text{NS-OCH}_3)(\text{PPh}_3)\text{Cl}]$: Yield : 6%; Anal. Calcd. for $\text{C}_{27}\text{H}_{25}\text{N}_3\text{OSCIPd}$: C, 52.95; H, 4.08; N, 6.86. Found : C, 52.63; H, 4.17; N, 6.71%; ^1H NMR : 3.88 (s, OCH_3), 5.60 (s, NH_2), 6.86 (2H, d, J 8.9), 7.36-7.84 (PPh_3)*, 8.12 (2H, d, J 9.0), 8.59 (1H, d, J 4.2).

$[\text{Pd}(\text{NS-CH}_3)(\text{PPh}_3)\text{Cl}]$: Yield : 9%; Anal. Calcd. for $\text{C}_{27}\text{H}_{25}\text{N}_3\text{SCIPd}$: C, 54.37; H, 4.20; N, 7.05. Found : C, 54.43; H, 4.19; N, 7.11%; ^1H NMR : 2.38 (s, CH_3), 4.81 (s, NH_2), 7.22 (2H, d, J 8.2), 7.40-7.79 (PPh_3)*, 8.11 (2H, d, J 8.4), 8.57 (1H, d, J 4.2).

$[\text{Pd}(\text{NS-Cl})(\text{PPh}_3)\text{Cl}]$: Yield : 7%; Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_3\text{SCl}_2\text{PPd}$: C, 50.62; H, 3.57; N, 6.81. Found : C, 50.79; H, 3.43; N, 6.87%; ^1H NMR : 4.88 (s, NH_2), 7.39 (2H, d, J 8.3), 7.38-7.82 (PPh_3)*, 8.17 (2H, d, J 8.4), 8.59 (1H, d, J 4.2).

$[\text{Pd}(\text{NS-NO}_2)(\text{PPh}_3)\text{Cl}]$: Yield : 8%; Anal. Calcd. for $\text{C}_{26}\text{H}_{22}\text{N}_4\text{O}_2\text{SCIPd}$: C, 49.77; H, 3.51; N, 8.93. Found : C, 49.84; H, 3.47; N, 8.89%; ^1H NMR : 5.01 (s, NH_2), 7.40-7.80 (PPh_3)*, 8.23 (2H, d, J 8.9), 8.32 (2H, d, J 8.9), 8.65 (1H, d, J 4.2).

Physical measurements :

Microanalyses (C, H and N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. ^1H NMR spectra were recorded in CDCl_3 solution on a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard.

X-Ray crystallography :

Single crystals of $[\text{Pd}(\text{NS-CH}_3)(\text{PPh}_3)\text{Cl}]$ and $[\text{Pd}(\text{NS-NO}_2)(\text{PPh}_3)\text{Cl}]$ were obtained by slow evaporation of solvent from solutions of the complexes in acetonitrile. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Bruker SMART CCD diffractometer using graphite monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). X-Ray data reduction, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs⁶. The structures were solved by the direct methods.

General procedure for C-N coupling reactions :

In a typical run, an oven-dried 10 mL round bottom flask was charged with a known mole percent of catalyst, NaO^tBu (1.7 mmol), XPhos (0.1 mmol), amine (1.0 mmol) and aryl halide (1.0 mmol) with the solvent (4 mL). The flask was placed in a preheated oil bath at required tem-

Table 1. Crystallographic data for the [Pd(NS-CH₃)(PPh₃)Cl] and [Pd(NS-NO₂)(PPh₃)Cl] complexes

Complex	[Pd(NS-CH ₃)(PPh ₃)Cl]	[Pd(NS-NO ₂)(PPh ₃)Cl]
Empirical formula	C ₂₇ H ₂₅ N ₃ OPSClPd	C ₂₆ H ₂₂ N ₄ O ₂ PSClPd
Formula mass	612.41	627.39
Crystal system	Orthorhombic	Monoclinic
Space group	Pbcn	P2 ₁ /n
<i>a</i> (Å)	16.2496(4)	9.2002(2)
<i>b</i> (Å)	17.2780(4)	18.5339(4)
<i>c</i> (Å)	18.8321(4)	15.6689(3)
α (deg)	90	90
β (deg)	90	93.076(1)
γ (deg)	90	90
<i>V</i> (Å ³)	5287.3(2)	2667.94(10)
<i>Z</i>	8	4
<i>D</i> _{calcd} (mg m ⁻³)	1.539	1.562
<i>F</i> (000)	2480	1264
Crystal size (mm)	0.25 × 0.25 × 0.26	0.18 × 0.18 × 0.19
<i>T</i> (K)	296	296
μ (mm ⁻¹)	0.968	0.965
<i>R</i> ₁ ^a	0.0393	0.0303
<i>wR</i> ₂ ^b	0.1157	0.0832
GOF ^c	0.96	0.92

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$$

$$^c GOF = [\sum [w(F_o^2 - F_c^2)^2] / (M - N)]^{1/2}, \text{ where } M \text{ is the number of reflections and } N \text{ is the number of parameters refined.}$$

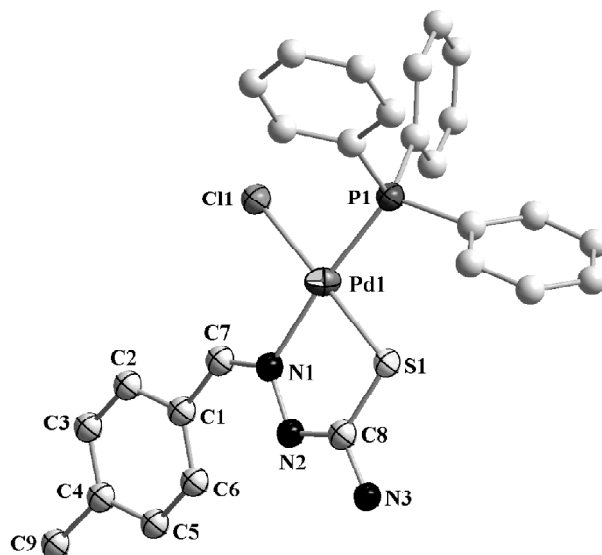
perature. After the specified time the flask was removed from the oil bath, water (20 mL) was added, and extraction with ether (4 × 10 mL) was done. The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous Na₂SO₄, and filtered. Solvent was removed under vacuum. The residue was dissolved in acetonitrile and analyzed by GCMS using a Perkin-Elmer CLARUS 680 instrument.

Results and discussion

Synthesis and structure :

As delineated in the introduction, reaction of Na₂[PdCl₄] with the five selected 4-R-benzaldehyde thiosemicarbazones (HL-R) affords, under a set of experimental conditions, palladium complexes of type [{Pd(CNS-R)}_n]^{3a}. Further reaction of each of these [{Pd(CNS-R)}_n] complexes with triphenylphosphine is observed to yield an yellow complex of type [Pd(CNS-R)(PPh₃)] as the major product^{3a}, along with an orange

product in much lower yield. The present work has originated from our curiosity to find out the identity of this minor orange species. Each synthetic reaction has been repeated several times in order to accumulate reasonable quantity of the orange product, necessary for its characterization. Microanalytical and ¹H NMR data on these orange species indicate the presence of a thiosemicarbazone

**Fig. 1.** Structure of the [Pd(NS-CH₃)(PPh₃)Cl] complex. Hydrogen atoms are omitted for clarity.

and a triphenylphosphine in them. In order to authenticate the composition of these complexes, as well as to find out the binding mode of the thiosemicarbazone ligand in them, structure of a selected member of this family, viz. the orange species obtained from the reaction of [{Pd(CNS-CH₃)}_n] with triphenylphosphine, has been determined by X-ray crystallography. The structure is shown in Fig. 1 and some relevant bond parameters are listed in Table 2. The structure shows that the thiosemicarbazone is coordinated to palladium, via dissociation of the acidic proton, as a bidentate NS-donor forming a five-membered chelate ring (as in **I** with R = CH₃).

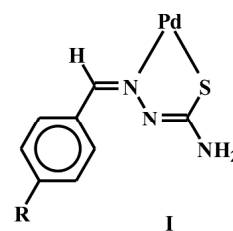


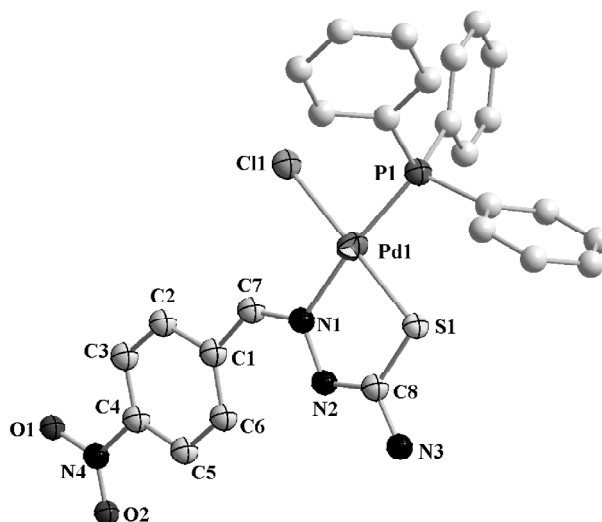
Table 2. Selected bond distances and bond angles for the [Pd(NS-CH₃)(PPh₃)Cl] and [Pd(NS-NO₂)(PPh₃)Cl] complexes

[Pd(NS-CH ₃)(PPh ₃)Cl]			
Bond distances (Å)			
Pd(1)-Cl(1)	2.3360(10)	C(7)-N(1)	1.287(4)
Pd(1)-P(1)	2.2675(8)	N(1)-N(2)	1.387(4)
Pd(1)-N(1)	2.106(3)	N(2)-C(8)	1.285(4)
Pd(1)-S(1)	2.2212(10)	C(8)-S(1)	1.751(3)
		C(8)-N(3)	1.350(5)
Bond angles (deg)			
N(1)-Pd(1)-P(1)	173.98(7)	N(1)-Pd(1)-S(1)	82.89(7)
S(1)-Pd(1)-Cl(1)	176.64(4)		
[Pd(NS-NO ₂)(PPh ₃)Cl]			
Bond distances (Å)			
Pd(1)-Cl(1)	2.3395(7)	C(7)-N(1)	1.286(3)
Pd(1)-P(1)	2.2496(7)	N(1)-N(2)	1.383(3)
Pd(1)-N(1)	2.0970(19)	N(2)-C(8)	1.293(3)
Pd(1)-S(1)	2.2423(7)	C(8)-S(1)	1.744(3)
		C(8)-N(3)	1.347(3)
Bond angles (deg)			
N(1)-Pd(1)-P(1)	172.38(6)	N(1)-Pd(1)-S(1)	83.20(5)
S(1)-Pd(1)-Cl(1)	178.36(3)		

A triphenylphosphine and a chloride are also coordinated to the metal center. The chloride is *trans* to the sulfur and the triphenylphosphine is *trans* to the imine-nitrogen. Palladium is thus nested in a NSPCl coordination sphere, which is distorted significantly from ideal square-planar geometry, as reflected in the bond parameters around the metal center. Comparison of the geometry of the palladium-coordinated thiosemicarbazone in this structurally characterized complex with that of the uncoordinated thiosemicarbazone ligand (which is similar as shown in HL-R^{3e}) reveals that a change in geometry around the pre-existing imine-bond has occurred during the complexation. Such change in geometry of benzaldehyde thiosemicarbazones, upon their coordination to palladium, has been observed before^{3b,e}. Based on the crystal structure, this particular complex is abbreviated as [Pd(NS-CH₃)(PPh₃)Cl], where NS-CH₃ refers to the NS-coordinated thiosemicarbazone ligand (as in **I** with R = CH₃).

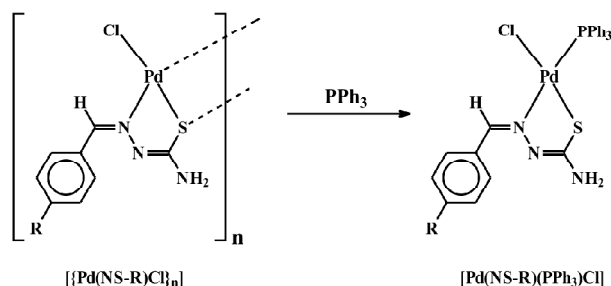
In order to ensure that the other four complexes of this family have the same composition and structure as [Pd(NS-CH₃)(PPh₃)Cl], structure of a second complex from this group, viz. the orange complex obtained from the reaction of [{Pd(CNS-NO₂)}]_n with triphenyl-phos-

phine, has also been determined by X-ray crystallography. This structure (Fig. 2) also shows that the thiosemicarbazone is coordinated to palladium in the same NS-fashion (as in **I** with R = NO₂) and, a triphenylphosphine and a chloride are bound to palladium as before. This particular complex is abbreviated, based on its crystal structure, as [Pd(NS-NO₂)(PPh₃)Cl]. In this [Pd(NS-NO₂)(PPh₃)Cl] complex the bond parameters around the metal center, as well as within the coordinated thiosemicarbazone, are found to be comparable to those observed in the [Pd(NS-CH₃)(PPh₃)Cl] complex (Table 2). As all the five complexes of this family have been synthesized similarly, and they show similar properties (*vide infra*), the other three complexes of this group are assumed to have similar structure as the [Pd(NS-CH₃)(PPh₃)Cl] or [Pd(NS-NO₂)(PPh₃)Cl] complex. All five complexes of this series are henceforth abbreviated in general as [Pd(NS-R)(PPh₃)Cl].

**Fig. 2.** Structure of the [Pd(NS-NO₂)(PPh₃)Cl] complex. Hydrogen atoms are omitted for clarity.

The presence of a chloride in each of these [Pd(NS-R)(PPh₃)Cl] complexes has been rather surprising, particularly as there was no visible source of chloride present either in the starting oligomeric [{Pd(CNS-R)]_n species, or in anything else needed for the synthesis or purification of these complexes. This clearly indicates that the starting oligomeric species, which was believed to be pure [{Pd(CNS-R)]_n, is actually not so and contains another species of type [{Pd(NS-R)Cl}]_n as minor impurity. Splitting of the sulfur-bridge in these [{Pd(NS-R)Cl}]_n com-

plexes by their interaction with triphenylphosphine has led to formation of the mononuclear $[\text{Pd}(\text{NS-R})(\text{PPh}_3)\text{Cl}]$ complexes (Scheme 1). Presence of these $[\{\text{Pd}(\text{NS-R})\text{Cl}\}_n]$ complexes as minor impurity in the $[\{\text{Pd}(\text{CNS-R})\}_n]$ complexes also accounts for the observed low yields of the derived $[\text{Pd}(\text{NS-R})(\text{PPh}_3)\text{Cl}]$ complexes. It may be mentioned in this context that preparation of the same $[\text{Pd}(\text{NS-R})(\text{PPh}_3)\text{Cl}]$ complexes in good yield can be achieved by direct reaction of the thiosemicarbazones (HL-R) with $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]^{3e}$.



Scheme 1









Catalysis :

The fact, that palladium complexes are known to efficiently catalyze Buchwald type C-N coupling reactions⁷, has encouraged us to explore similar property in the present group of $[\text{Pd}(\text{NS-R})(\text{PPh}_3)\text{Cl}]$ complexes. At first C-N coupling between iodobenzene and aniline was attempted using $[\text{Pd}(\text{NS-H})(\text{PPh}_3)\text{Cl}]$ as the catalyst. After extensive optimization, we found that 0.01 mol% catalyst, 1.0 mmol iodobenzene, 1.0 mmol aniline, 1.7 mmol $\text{NaO}^t\text{-Bu}$ as base, 0.1 mmol XPhos as additive, polyethyleneglycol as solvent, 145 °C reaction temperature, and 20 h reaction time, furnish an excellent (100%) yield of the desired C-N coupled product (entry 1 in Table 3). All the five $[\text{Pd}(\text{NS-R})(\text{PPh}_3)\text{Cl}]$ complexes were tried as catalysts, and as each of them has displayed similar catalytic efficiency, only the results obtained with $[\text{Pd}(\text{NS-H})(\text{PPh}_3)\text{Cl}]$ as the catalyst are presented in Table 3. Coupling of iodobenzene with five other primary aromatic amines, bearing different functional groups and substituents, were also attempted and each of these reactions proceed smoothly under similar reaction conditions to afford the expected products in 58–100% yields (entries 2–6). Coupling of iodobenzene with two chosen secondary amines, viz. piperidine and morpholine, was also

Table 3. C-N cross-coupling reaction of aryl halides with amines^a

Entry	X	Amine	Amt. of cat. (mol %)	Time (h)	Yield ^b (%)	TON
1	I		0.01	20	100	10000
2	I		0.01	20	100	10000
3	I		0.01	20	98	9800
4	I		0.01	20	58	5800
5	I		0.01	20	92	9200
6	I		0.01	20	85	8500
7	I		0.01	20	100	10000
8	I		0.01	20	100	10000
9	Br		0.1	20	100	1000
10	Br		0.1	20	74	740
11	Br		0.1	20	100	1000
12	Br		0.1	20	30	300
13	Br		0.1	20	50	500
14	Br		0.1	20	26	260
15	Br		0.1	20	100	1000
16	Br		0.1	20	100	1000

Table-3 (contd.)

17	Cl		1.0	20	97	97
18	Cl		1.0	20	26	26
19	Cl		1.0	20	100	100
20	Cl		1.0	20	42	42
21	Cl		1.0	20	66	66
22	Cl		1.0	20	29	29
23	Cl		1.0	20	89	89
24	Cl		1.0	20	94	94

^aReaction conditions : aryl halide (1.0 mmol), amine (1.0 mmol), NaO^t-Bu (1.7 mmol), XPhos (0.1 mmol), catalyst [Pd(NS-H)(PPh₃)Cl], polyethyleneglycol (4 mL).

^bDetermined by GCMS.

found to proceed smoothly to produce the targeted products in excellent yields (entries 7 and 8). Use of bromobenzene, instead of iodobenzene, was found to turn the C-N coupling slightly difficult, as manifested in ten times more catalyst loading needed to achieve similar yield (entries 9–16). Encouraged by the observed efficiency of [Pd(NS-H)(PPh₃)Cl] in activating C-I and C-Br bonds, and thereby induce C-N coupling with both primary and secondary amines, we have also attempted similar coupling reaction via rather difficult C-Cl bond activation of chlorobenzene. The attempted reactions did take place, but with much higher (1 mol%) catalyst loading, and the yield varied between 26–97% (entries 17–24). The turnover numbers are found to reduce significantly from iodobenzene to bromobenzene to chlorobenzene. The [Pd(NS-R)(PPh₃)Cl] complexes are thus found to be good catalysts for Buchwald type C-N coupling reactions. The observed catalytic efficiency of the present group of complexes in C-N coupling reactions is comparable to that of several other palladium complexes under similar experimental conditions⁸.

Conclusions

The present study shows that an oligomeric species of type [$\{Pd(NS-R)Cl\}_n$] is generated as a minor product, along with the major [$\{Pd(CNS-R)\}_n$] species, from the reaction of the 4-R-benzaldehyde thiosemicarbazones (HL-R) with Na₂[PdCl₄] under certain experimental conditions^{3a}. The oligomeric [$\{Pd(NS-R)Cl\}_n$] species undergo facile splitting of the sulfur-bridge upon reaction with triphenylphosphine to afford discrete mononuclear complexes of type [Pd(NS-R)(PPh₃)Cl]. This study also demonstrates that the [Pd(NS-R)(PPh₃)Cl] complexes can efficiently catalyze Buchwald type C-N coupling reactions.

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Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC numbers 941387 and 941388.

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