Syntheses, structures and efficient catalysis for C–C coupling of some benzaldehyde thiosemicarbazone complexes of palladium

Piyali Paul[a], Sayanti Datta[a], Sarmistha Halder[a], Rama Acharyya[a], Falguni Basuli[a], Ray J. Butcher[b], Shie-Ming Peng[c], Gene-Hsiang Lee[c], Alfonso Castineiras[d], Michael G.B. Drew[e], Samaresh Bhattacharya[a],*

[a] *Department of Chemistry, Inorganic Chemistry Section, Jadavpur University, 188 Raja S C Mullick Road, Kolkata 700 032, India*
[b] *Department of Chemistry, Howard University, Washington, DC 20059, USA*
[c] *Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC*
[d] *Departamento de Quimica Inorganica, Universidade de Santiago de Compostela, E-15706 Santiago de Compostela, Spain*
[e] *Department of Chemistry, University of Reading. Whiteknights, Reading RG6 6AD, UK*

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ABSTRACT

Reaction of the 4-R-benzaldehyde thiosemicarbazones (denoted in general as **L-R**; R = OCH$_3$, CH$_3$, H, Cl and NO$_2$) with *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] afforded a group of mixed-ligand complexes (denoted in general as **1-R**) incorporating a N,S-coordinated thiosemicarbazone, a triphenylphosphine and a chloride. Similar reaction with Na$_2$[PdCl$_4$] afforded a family of bis-thiosemicarbazone complexes (denoted in general as **2-R**), where each ligand is N,S-coordinated. Crystal structures of **1-CH$_3$**, **1-NO$_2$**, **2-OCH$_3$**, **2-NO$_2$** and **L-NO$_2$** have been determined. In all the complexes the thiosemicarbazones are coordinated to the metal center, via dissociation of the acidic proton, as bidentate N,S-donors forming five-membered chelate rings. With reference to the structure of the uncoordinated thiosemicarbazone, this coordination mode is associated with a conformational change around the C=N bond. All the **1-R** and **2-R** complexes display intense absorptions in the visible region. Catalytic activity of the **1-R** and **2-R** complexes towards some C–C coupling reactions (*e.g.* Suzuki, Heck and Sonogashira) has been examined and while both are found to be efficient catalysts, **1-R** is much better catalyst than **2-R**.

1. Introduction

The chemistry of thiosemicarbazone complexes of the transition metal ions has been receiving significant current attention, largely because of the bioinorganic relevance of these complexes [1]. However, we have been exploring the chemistry of platinum metal complexes of the thiosemicarbazones [2], mainly because of the variable binding mode displayed by these ligands in their complexes and also to gain a chemical control over the mode of binding, and the present work has emerged out of this exploration. The primary objective of the present study has been to scrutinize the mode of binding of a group of 4-R-benzaldehyde thiosemicarbazones (denoted in general as **L-R**, R = OCH$_3$, CH$_3$, H, Cl and NO$_2$) to palladium. This particular metal center has been chosen with an aim to explore the catalytic activity, if any, of the resulting complexes. Palladium complexes are well known to bring about C–C cross coupling of different types (such as Suzuki, Heck, Sonogashira, etc.) [3]. There are several advantages of using palladium com-

plexes as catalysts over other species, and it is due to this unique nature of palladium that we are witnessing the remarkable success in catalytic C–C cross-coupling reactions [4]. Though complexes with phosphine type ligands (such as [Pd(PPh$_3$)$_4$]) are always a favorite choice as pre-catalyst for such reactions [5], complexes with ligands other types are also gaining popularity with time [6], and hence we decided to synthesize mixed-ligand (containing PPh$_3$ as the ancillary ligand) complexes as well as homoleptic complexes of palladium with the selected thiosemicarbazones (**L-R**) and test their catalytic efficiency towards C–C cross coupling reactions. It may be relevant to mention here that though the chemistry of palladium complexes of several thiosemicarbazones has received considerable attention [2i,7], the binding of palladium to the chosen ligands (**L-R**) has remained unexplored. In our earlier studies we have observed that the 4-R-benzaldehyde thiosemi-carbazones (**L-R**) usually bind to a metal center, via dissociation of the acidic proton, as monoanionic bidentate N,S-donors forming a rather unexpected four-membered chelate ring (**I**) [2b,2c]. Our investigations have revealed that for these ligands (**L-R**), formation of the four-membered chelate ring (**I**) is most favorable and that of the five-membered chelate ring (**II**), which appears to be very likely for the thiosemicarbazones in general, is not possible

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* Corresponding author. Tel.: +91 33 2414 6223; fax: +91 33 2414 6223.
E-mail address: samaresh_b@hotmail.com (S. Bhattacharya).

because of the inevitable steric hindrance that develops between the phenyl ring of the benzaldehyde thiosemicarbazone and the metal center. It is worth noting here that we have not been able to find a single example of a structurally characterized complex of the 4-R-benzaldehyde thiosemicarbazones (**L-R**), where the thiosemicarbazone is coordinated as in **II**. Though five-membered chelate ring (**II**) formation by the 4-R-benzaldehyde thiosemicarbazones (**L-R**) has been found to be impossible, closeness of the phenyl ring to the metal center in **II** points to the possibility of its orthometallation (**III**) via C–H bond activation, which has indeed been realized recently [2f]. A five-membered chelate ring (**IV**) formation by the 4-R-bezaldehyde thiosemicarbazones (**L-R**) seems possible only via a conformational change across the C=N bond, and this has indeed been observed in the present study. Two different palladium compounds, *viz.* *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] and Na$_2$[PdCl$_4$], have been utilized in this study as the source of palladium. Reactions of the 4-R-benzaldehyde thiosemicarbazones (**L-R**) with these palladium compounds have afforded two families of complexes, in both of which the thiosemicarbazones have been found to coordinate palladium as bidentate N,S-donors forming five-membered chelate rings (**IV**). This paper deals with the chemistry of these two groups of palladium thiosemicarbazone complexes, with special reference to their formation, structure and catalytic efficiency towards C–C coupling reactions.
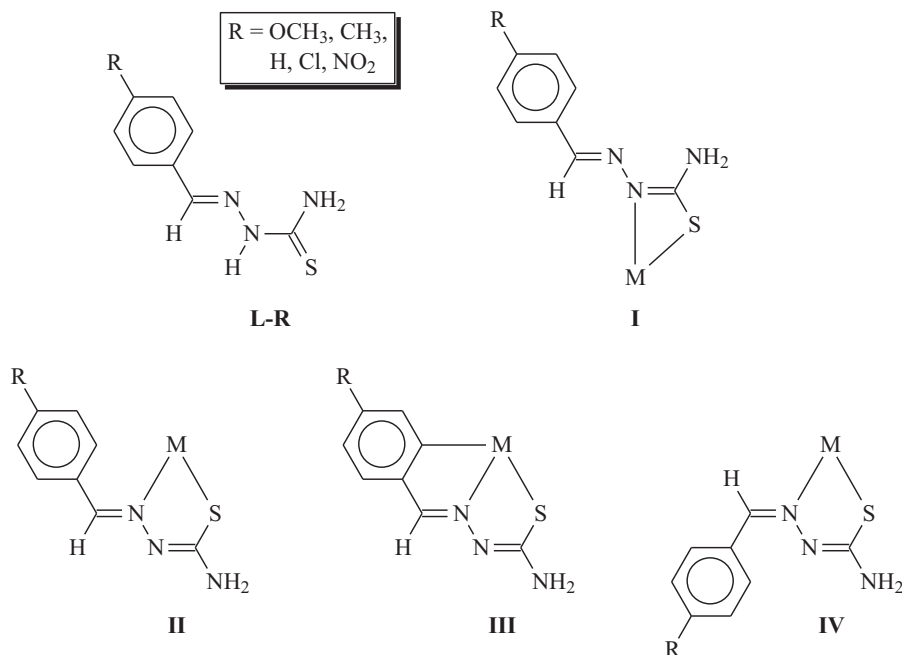
2. Experimental

2.1. Materials

Palladium chloride was obtained from Arora Matthey, Kolkata, India. The *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] and Na$_2$[PdCl$_4$] complexes were prepared by following reported procedures [8]. The 4-R-benzaldehyde thiosemicarbazones **1** were prepared by reacting equimolar amounts of thiosemicarbazide and the respective *para*-substituted benzaldehyde in 1:1 ethanol–water mixture. All other chemicals and solvents were reagent grade commercial materials and were used as received.

2.2. Syntheses

2.2.1. **1-R** complexes

The **1-R** (R = OCH$_3$, CH$_3$, H, Cl and NO$_2$) complexes were prepared by following a general procedure. Specific details are given below for a particular complex.

1-OCH$_3$: To a solution of 4-methoxybenzaldehyde thiosemicarbazone (30 mg, 0.14 mmol) in hot ethanol (30 mL) triethylamine (14 mg, 0.14 mmol) was added followed by *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] (100 mg, 0.14 mmol). The mixture was heated at reflux for 5 h to yield an orange solution. Evaporation of this solution gave an orangish-yellow solid, which was subjected to purification by thin layer chromatography on a silica plate. With benzene as the eluant, a yellow band separated, which was extracted with acetonitrile. Upon evaporation of the acetonitrile extract **1-OCH$_3$** was obtained as a crystalline yellow solid. Yield: 60%. ^{1}H NMR [9]: 3.85 (s, OCH$_3$, 3H), 6.05 (s, NH$_2$, 2H), 6.97 (d, J = 8.8 Hz, 2H), 7.43–7.78 (PPh$_3$), 8.08 (d, J = 8.8 Hz, 2H), 8.56 (d, J = 4.0 Hz, azomethine 1H). Anal. Calc. for C$_{27}$H$_{25}$N$_3$OSClPPd: C, 52.98; H, 4.08; N, 6.86. Found: C, 52.45; H, 4.25; N, 6.64%.

1-CH$_3$: Yield: 62%. ^{1}H NMR: 2.37 (s, CH$_3$, 3H), 4.79 (s, NH$_2$, 2H), 7.2 (d, J = 8.1 Hz, 2H), 7.40–7.79 (PPh$_3$), 8.05 (d, J = 8.2 Hz, 2H), 8.53 (d, J = 4.3 Hz, azomethine 1H). Anal. Calc. for C$_{27}$H$_{25}$N$_3$SClPPd: C, 54.37; H, 4.20; N, 7.05. Found: C, 54.07; H, 4.41; N, 6.82%.

1-H: Yield: 65%. ^{1}H NMR: 5.67 (s, NH$_2$, 2H), 7.34–7.78 (PPh$_3$+2H)*, 8.05–8.08 (3H), 8.64 (d, J = 4.0 Hz, azomethine 1H). Anal. Calc. for C$_{26}$H$_{23}$N$_3$SClPPd: C, 53.62; H, 3.95; N, 7.22. Found: C, 53.49; H, 4.15; N, 7.48%.

1-Cl: Yield: 67%. ^{1}H NMR: 4.87 (s, NH$_2$, 2H), 7.36 (d, J = 8.6 Hz, 2H), 7.41–7.78 (PPh$_3$), 8.11 (d, J = 8.6 Hz, 2H), 8.53 (d, J = 4.2 Hz, azomethine 1H). Anal. Calc. for C$_{26}$H$_{22}$N$_3$SCl$_2$PPd: C, 50.61; H, 3.57; N, 6.81. Found: C, 50.83; H. 3.34; N, 7.01%.

1-NO$_2$: Yield: 63%. ^{1}H NMR: 4.96 (s, NH$_2$, 2H), 7.35–7.72 (PPh$_3$), 8.16 (d, J = 9.0 Hz, 2H), 8.25 (d, J = 8.94 Hz, 2H), 8.58 (d, J = 4.3 Hz, azomethine 1H). Anal. Calc. for C$_{26}$H$_{22}$N$_4$O$_2$SClPPd: C, 49.77. H, 3.51; N, 8.93. Found: C, 49.91; H, 3.72; N, 8.66%.
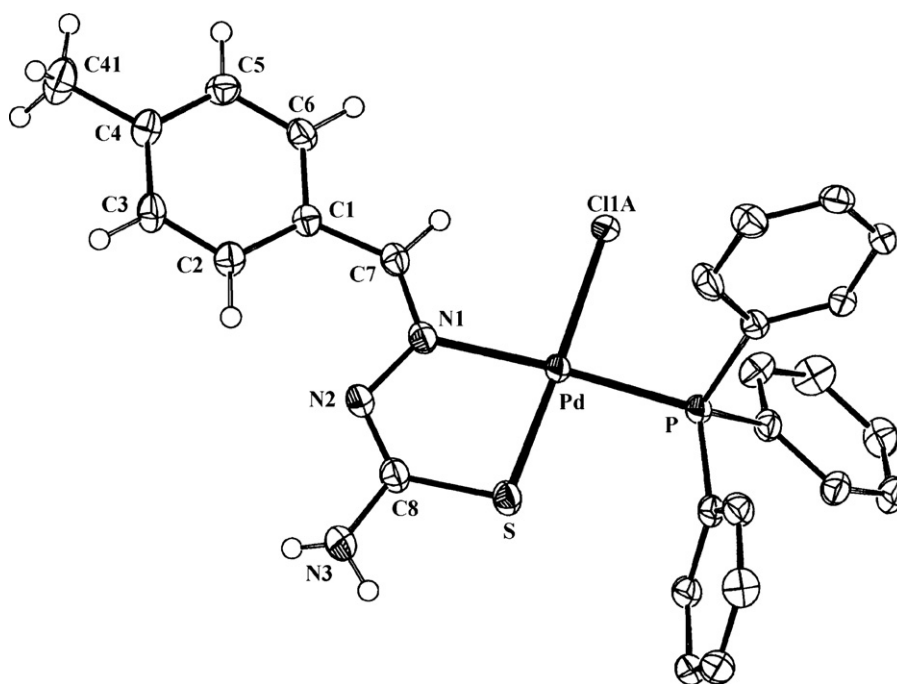
Fig. 1. Structure of **1-CH₃**.

2.2.2. *2-R complexes*

The **2-R** (R = OCH₃, CH₃, H, Cl and NO₂) complexes were prepared by following a general procedure. Specific details are given below for a particular complex.

2-OCH₃: To a solution of 4-methoxybenzaldehyde thiosemicarbazone (150 mg, 0.71 mmol) in hot ethanol (30 mL) triethylamine (80 mg, 0.79 mmol) was added followed by a solution of Na₂[PdCl₄] (100 mg, 0.34 mmol) in ethanol (10 mL). The solution was then heated at reflux for 6 h. **2-OCH₃** precipitated as a yellow crystalline solid, which was collected by filtration, washed thoroughly with water, followed by ethanol and then dried in air. Yield: 79%. ¹H NMR: 3.82 (s, OCH₃, 3H), 6.96 (d, *J* = 8.6 Hz, 2H), 7.09 (s, NH₂, 2H), 7.22 (s, azomethine 1H), 8.18 (d, *J* = 8.6 Hz, 2H). Anal. Calc. for C₁₈H₂₀N₆S₂O₂Pd: C, 44.04; H, 4.08; N, 17.13. Found: C, 44.39; H, 4.27; N, 17.01%.

2-CH₃: Yield: 77%. ¹H NMR: 2.36 (s, CH₃, 3H), 7.22 (d, *J* = 11.3 Hz, 2H), 7.26 (s, NH₂, 2H), 8.02 (d, *J* = 8.0 Hz, 2H). Anal. Calc. for C₁₈H₂₀N₆S₂Pd: C, 44.04; H, 4.08; N, 17.13. Found: C, 44.31; H, 4.34; N, 17.44%.

2-H: Yield: 81%. ¹H NMR: 7.28 (s, NH₂, 2H), 7.31 (s, 1H), 7.44–7.51 (3H), 8.12 (d, *J* = 7.6 Hz, 2H). Anal. Calc. for C₁₆H₁₆N₆S₂Pd: C, 41.52; H, 3.46; N, 18.17. Found: C, 41.74; H, 3.23; N, 18.53%.

2-Cl: Yield: 76%. ¹H NMR: 7.28 (s, 1H), 7.36 (s, NH₂, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 8.17 (d, *J* = 8.7 Hz, 2H). Anal. Calc. for C₁₆H₁₄N₆S₂Cl₂Pd: C, 36.13; H, 2.63; N, 15.81. Found: C, 36.38; H, 2.84; N, 15.67%.

2-NO₂: Yield: 75%. ¹H NMR: 7.40 (s, 1H), 7.66 (s, NH₂, 2H), 8.20 (d, *J* = 8.8 Hz, 2H), 8.39 (d, *J* = 8.7 Hz, 2H). Anal. Calc. for C₁₆H₁₄N₈O₄S₂Pd: C, 34.76; H, 2.53; N, 20.27. Found: C, 34.65; H, 2.79; N, 20.42%.

2.2.3. *Physical measurements*

Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were obtained on a Shimadzu FTIR-8300 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer fitted with a Walker scientific L75FBAL magnet. ¹H NMR spectra were recorded in CDCl₃ and DMSO-d₆ solutions on a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. Molecular orbital calculations were carried out by density functional theory (DFT) method using the Gaussian 03 (B3LYP/SDD-6-31G) package [10].

2.3. *Application as catalysts*

2.3.1. *General procedure for the Suzuki coupling reactions*

In a typical run, an oven-dried 10 mL round bottom flask was charged with a known mole percent of catalyst, NaOH (1.7 mmol), phenylboronic acid (1.2 mmol) and aryl halide (1 mmol) with the appropriate solvents (4 mL). The flask was placed in a preheated oil bath at required temp. After the specified time the flask was removed from the oil bath and water (20 mL) added, followed by extraction with ether (4 × 10 mL). 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 CDCl₃ and analyzed by ¹H NMR. Percent conversions were determined against the remaining aryl halide [11].

2.3.2. *General procedure for the Heck coupling reactions*

In a typical run, an oven-dried 10 mL round bottom flask was charged with a known mole percent of catalyst, Cs₂CO₃ (1.7 mmol), *n*-butyl acrylate (1.2 mmol) and aryl halide (1 mmol) with polyethylene glycol (4 mL). The flask was placed in a preheated oil bath at 150 °C. After the specified time the flask was removed from the oil bath and water (20 mL) added, followed by extraction with ether (4 × 10 mL). 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 CDCl₃ and analyzed by ¹H NMR. Percent conversions were determined against the remaining aryl halide [11].

2.3.3. *General procedure for Sonogashira coupling reactions*

To slurry of aryl halide (1 mmol), cuprous iodide (10 mol%) and palladium catalyst (a known mol%) in an appropriate solvent (4 mL), phenylacetylene (1.2 mmol) and NaOH (1.7 mmol) was added and

heated at required temp. After completion of the reaction (monitored by TLC), the flask was removed from the oil bath and water (20 mL) added, followed by extraction with ether (4 × 10 mL). The combined organic layers were washed with water (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered. Solvent was removed under vacuum. The residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR. Percent conversions were determined against the remaining aryl halide [11].

2.4. X-ray structure analysis

Single crystals of **1-CH₃**, **1-NO₂** and **L-NO₂** were grown by slow evaporation of solvent from acetonitrile solutions of the respective compounds. Single crystals of **2-OCH₃** were obtained by slow evaporation of solvents from a solution of the complex in acetonitrile–ethanol (3:1) mixture and those of **2-NO₂** were obtained by slow evaporation of solvent from an N,N-dimethylformamide solution of the complex. Selected crystal data and data collection parameters are given in Table 1. Data on the crystals of **1-CH₃** and **2-OCH₃** were collected on a Bruker SMART CCD diffractometer and those on the crystal of **1-NO₂** were collected on a Marresearch Image Plate system. Data on the crystal of **2-NO₂** were collected on a Nonius Kappa CCD diffractometer. Data on the crystal of **L-NO₂** were collected on an Enraf Nonius MACH3 automatic diffractometer. X-ray data reduction, structure solution and refinement were done using the SHELXS-97 and SHELXL-97 packages [12]. The structures were solved by the direct methods. The chloride of **1-CH₃** was found to be disordered between two locations, *viz.* Cl1A (59% occupancy) and Cl1B (41% occupancy). However, all the reported crystallographic parameters of this particular complex include only Cl1A.

3. Results and discussion

3.1. Syntheses and characterization

Five 4-R-benzaldehyde thiosemicarbazones (**L-R**), differing in the substituent at the *para* position of the phenyl ring, have been used in the present study. Reaction of these thiosemicarbazones with *trans*-[Pd(PPh₃)₂Cl₂] proceeds smoothly in refluxing ethanol in the presence of triethylamine to afford a group of mixed-ligand complexes (denoted in general as **1-R**) in decent yields. Preliminary characterizations (microanalysis, NMR, IR, etc.) on these **1-R** complexes (*vide infra*) indicate the presence of a thiosemicarbazone, a triphenylphosphine and a chloride in the coordination sphere. In order to find out the stereochemistry of these complexes as well as coordination mode of the thiosemicarbazones in them, structure of one representative member of this family, *viz.* **1-CH₃**, has been determined by X-ray crystallography. A selected view of the complex molecule 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 as a bidentate N,S-donor forming a five-membered chelate ring (**IV**) with a bite angle of 82.94(6)°. A triphenylphosphine and a chloride are also coordinated to the metal center. The triphenylphosphine is *trans* to the nitrogen and the chloride is *trans* to the sulfur. Palladium is thus nested in an NSPCl core, which is slightly distorted from ideal square planar geometry, as manifested in the bond parameters around the metal center. The Pd–N, Pd–P, Pd–S and Pd–Cl distances are normal, as observed in structurally characterized complexes of palladium containing these bonds [7]. In the crystal lattice of **1-CH₃**, there is one molecule of water per complex molecule. In order to find out the link between this water molecule and the complex molecule, packing pattern in the lattice has been scrutinized, which shows (Fig. 2) that a layer of water molecules lie in

between two layers of complex molecules. A closer inspection into the network reveals that each water molecule is simultaneously linked to three different **1-CH₃** molecules through hydrogen-bonding. These extended hydrogen-bonding interactions seem to be responsible for holding the crystal together. It may be relevant to note here that such non-covalent interactions are of significant importance in molecular recognition processes as well as in crystal engineering [13].
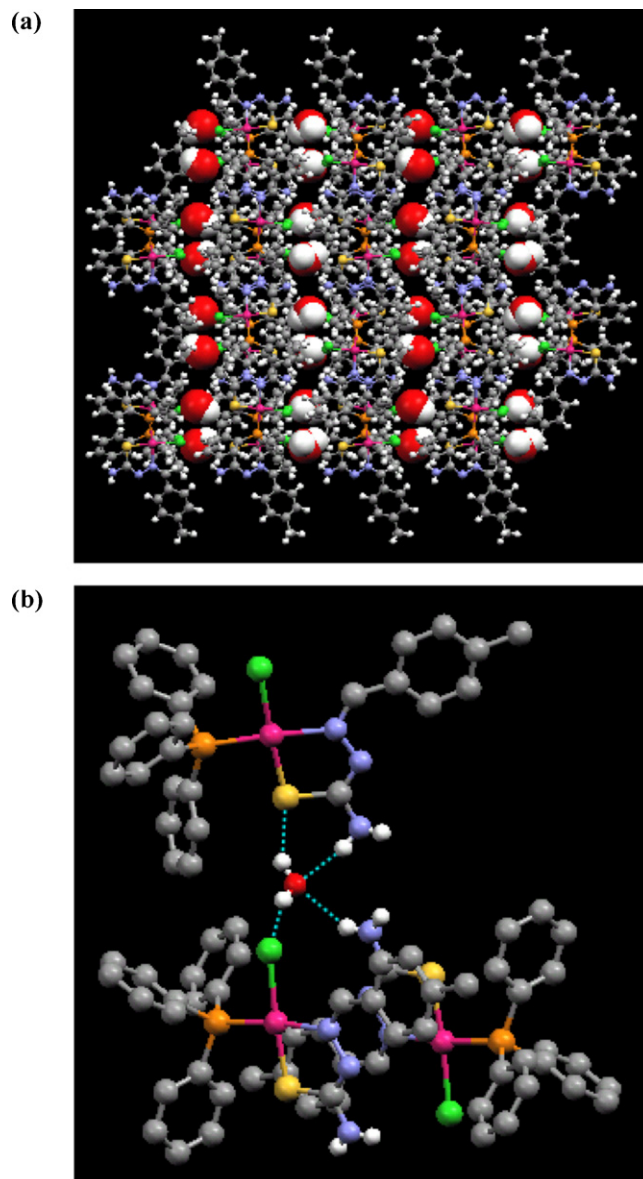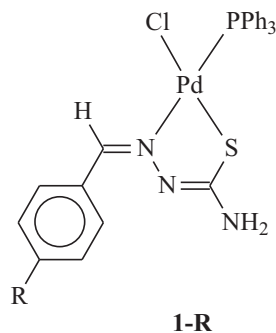

1-R

(a)

(b)

Fig. 2. (a) Packing diagram of the lattice of **1-CH₃**·H₂O viewed down the *b* axis and (b) the intermolecular hydrogen bonding.

Table 1
Crystallographic data for **1-CH$_3$**, **1-NO$_2$**, **L-NO$_2$**, **2-OCH$_3$** and **2-NO$_2$**.

	1-CH$_3$·H$_2$O	1-NO$_2$·CH$_3$CN·H$_2$O	L-NO$_2$	2-OCH$_3$	2-NO$_2$·2DMF
Empirical formula	C$_{27}$H$_{27}$N$_3$OPSClPd	C$_{26}$H$_{22}$N$_4$O$_2$PSClPd	C$_8$H$_8$N$_4$O$_2$S	C$_{18}$H$_{20}$N$_6$O$_2$S$_2$Pd	C$_{22}$H$_{28}$N$_{10}$O$_6$S$_2$Pd
M$_r$	614.43	684.44	224.24	522.92	699.06
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbcn*	*P2$_1$/n*	*P2$_1$/c*	*P2$_1$/c*	*P2$_1$/n*
a/Å	16.1294(8)	9.4107(5)	4.5686(15)	12.748(7)	13.1237(3)
b/Å	17.1073(8)	35.6481(14)	24.885(3)	5.561(3)	6.1481(2)
c/Å	18.6207(9)	9.7287(6)	8.9668(18)	14.563(8)	17.7804(5)
α/°	90	90	90	90	90
β/°	90	114.541(7)	98.557(17)	102.659(13)	100.2035(10)
γ/°	90	90	90	90	90
V/Å^3	5138.0(4)	2968.9(3)	1008.1(4)	1007.3(10)	1411.94(7)
Z	8	4	4	2	2
D$_{calcd}$/mg m^{-3}	1.589	1.531	1.478	1.724	1.644
F(0 0 0)	2496	1384	464	528	712
λ	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal size/mm^3	0.35 × 0.50 × 0.60	0.03 × 0.22 × 0.22	0.28 × 0.12 × 0.08	0.13 × 0.14 × 0.16	0.35 × 0.20 × 0.02
Temp./K	93(2)	150	293(2)	293	150(1)
μ/mm^{-1}	0.996	0.878	0.306	1.157	0.862
Independent reflections	6341	8415	1370	1301	3227
R$_{int}$	0.0336	0.064	0.1171	0.066	0.0429
Collected reflections	38,569	15,617	1461	6875	9705
R1[a]	0.0348	0.0757	0.0489	0.1187	0.0382
wR2[b]	0.0891	0.1749	0.0774	0.3546	0.0896
GOF[c]	1.13	1.05	0.915	1.61	1.167

[a] R1 = $||F_o| - |F_c||/\Sigma|F_o|$.

[b] Xxxxxxxxxxxxxx wR2 = $\left(\dfrac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right)^{1/2}$.

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

For an assessment of any changes in the structural features in the thiosemicarbazone that might have occurred upon its coordination to the metal, structure of an uncoordinated thiosemicarbazone, *viz.* 4-nitrobenzaldehyde thiosemicarbazone (**L-NO$_2$**), has also been determined by X-ray crystallography. The structure (Fig. 3) shows that the free ligand has the same symmetry as shown in the drawing of **L-R**. Comparison of the bond lengths (Table 2) shows that upon complexation the C–S bond gets elongated while the adjacent C–N bond, which forms part of the chelate ring, gets contracted. These changes in bond lengths are

Fig. 3. Structure of **L-NO$_2$**.

attributable to delocalization of the negative charge, developed upon dissociation of the acidic proton, over this N–C–S fragment, which stabilizes the imino-thiolate form of the thiosemicarbazone. Comparison of the geometry of the coordinated thiosemicarbazone with that of the uncoordinated ligand reveals another significant difference. In the free thiosemicarbazone, disposition of the aryl ring and the N(H)C(S)NH$_2$ fragment is *trans* with respect to the imine (C=N) bond. In **1-CH$_3$**, however, disposition of the aryl ring and the NC(S)NH$_2$ fragment across the imine (C=N) bond is *cis*. This indicates that coordination of the benzaldehyde thiosemicarbazone to palladium has taken place associated with an interesting conformational change around the imine (C=N) bond. It may be noted in this context that this particular binding mode (**IV**) of the 4-R-benzaldehyde thiosemicarbazones is relatively less common [14].

In the structure of **1-CH$_3$**, interesting conformational change around the C=N bond, with respect to uncoordinated **L-R** ligand, leading to formation of rather unusual five-membered ring has been observed. In order to verify that the same structural features also exist in the other **1-R** complexes, crystal structure of another complex of this group, *viz.* **1-NO$_2$**, has been determined. Besides small differences in the bond parameters, this structure (Fig. 4, Table 2) is found to be similar to that of **1-CH$_3$** (Fig. 1), with particular respect to binding mode of the thiosemicarbazone ligand. Therefore, in view of the similarity in the method of synthesis of the **1-R** complexes, as well as similarity in their properties (*vide infra*), the remaining three **1-R** (R = OCH$_3$, H and Cl) complexes are assumed to have similar structures as **1-CH$_3$** or **1-NO$_2$**.

The observed conformational change of the thiosemicarbazone upon binding to palladium was quite intriguing. Though the exact driving force behind this phenomenon is unclear, steric bulk of the triphenylphosphine seems to be one of the possibilities. To check this, reaction of the selected 4-R-benzaldehyde thiosemicarbazones has also been carried out similarly as before with another palladium starting material, *viz.* Na$_2$[PdCl$_4$], which does
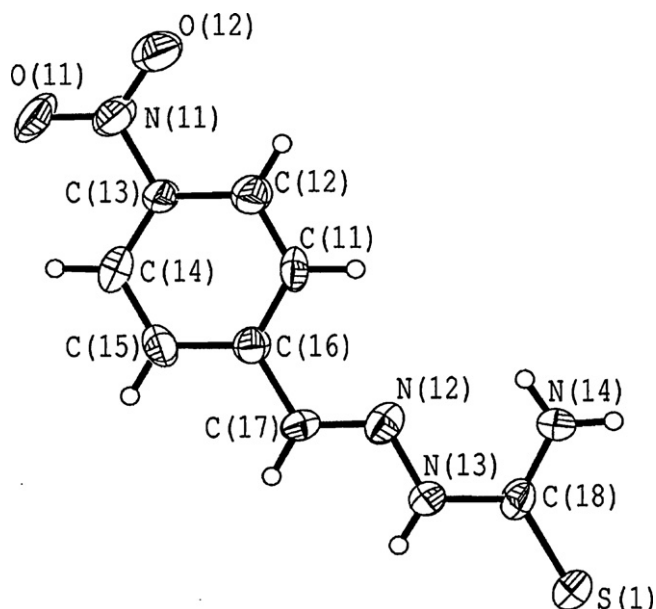
Table 2
Selected bond lengths (Å) and angles (°) for **1-CH₃**, **1-NO₂**, **L-NO₂**, **2-OCH₃** and **2-NO₂**.

1-CH₃

Bond lengths (Å)

Pd–N(1)	2.111(2)	C(7)–N(1)	1.292(3)
Pd–P	2.2707(7)	C(8)–N(2)	1.300(3)
Pd–S	2.2303(8)	N(1)–N(2)	1.392(3)
Pd–Cl1A	2.412(6)	C(8)–S	1.753(3)

Bond angles (°)

N(1)–Pd–P	174.15 (15)	S–Pd–Cl1A	175.6(2)
N(1)–Pd–S	82.94(6)		

L-NO₂

Bond lengths (Å)

C(16)–C(17)	1.473(8)	C(18)–N(14)	1.321(8)
N(12)–C(17)	1.280(7)	C(18)–S(1)	1.670(7)
C(18)–N(13)	1.370(8)	N(12)–N(13)	1.358(6)

Bond angles (°)

N(14)–C(18)–S(1)	124.1(7)	N(14)–C(18)–N(13)	116.1(7)
N(12)–N(13)–C(18)	118.8(6)	C(17)–N(12)–N(13)	117.0(6)
N(12)–C(17)–C(16)	118.8(7)		

1-NO₂

Bond lengths (Å)

Pd1–N14	2.113(5)	C15–N14	1.291(8)
Pd1–P1	2.2703(16)	C12–N13	1.309(9)
Pd1–S11	2.2441(17)	N13–N14	1.382(8)
Pd1–Cl1	2.3606(17)	C12–S11	1.749(7)

Bond angles (°)

N14–Pd1–P1	176.58(5)	S11–Pd1–Cl1	176.34(7)
N14–Pd1–S11	83.72(15)		

2-OCH₃

Bond lengths (Å)

Pd1–N1	2.020(13)	C2–N1	1.290(2)
Pd1–S1	2.299(5)	C1–S1	1.741(17)
C1–N3	1.35(2)	N1–N2	1.410(2)
C1–N2	1.31(2)		

Bond angles (°)

N1–Pd1–N1a	180.00	S1–Pd1–S1a	180.00
N1–Pd1–S1	82.80(4)		

2-NO₂

Bond lengths (Å)

Pd–N(3)	2.044(3)	C(2)–N(3)	1.298(4)
Pd–S(1)	2.2880(9)	C(1)–S(1)	1.743(3)
C(1)–N(1)	1.327(4)	N(2)–N(3)	1.377(4)

Bond angles (°)

N(3)–Pd–N(3A)	180.0(1)	S(1)–Pd–S(1A)	180.0(1)
N(3)–Pd–S(1)	82.61(8)		

not have any bulky ligand. These reactions have afforded a group of homoleptic bis-complexes (denoted as **2-R** in general) in excellent yields. Structure of a selected member of this family, *viz.* **2-NO₂**, has been determined by X-ray crystallography to ascertain the binding mode of the thiosemicarbazone. The structure (Fig. 5) shows that the thiosemicarbazones are coordinated to palladium as before, forming five-membered chelate rings (**IV**). The two coordinated nitrogens are *trans* and so are the two sulfurs. Formation of the five-membered chelate ring (**IV**) by the 4-R-benzaldehyde thiosemicarbazones, even upon their reaction with Na₂[PdCl₄], clearly indicates that the steric bulk of the PPh₃ ligands in the palladium starting material, *viz. trans*-[Pd(PPh₃)₂Cl₂], had nothing to do with the observed mode of coordination of the thiosemicarbazones in the **1-R** complexes. The observed bond parameters (Table 2) in **2-NO₂** compare well with those found in the Pd(N–S) fragment of **1-NO₂**. In the crystal lattice of **2-NO₂** there are two molecules of N,N-dimethylformamide per molecule of **2-NO₂**, and the packing pattern in the lattice (Fig. S1, Supplementary material) shows that these solvent molecules have occupied strategic locations for effective hydrogen-bonding with the complex molecules. It is revealed on zooming into the network that each N,N-dimethylformamide molecule is hydrogen-bonded to two complex molecules, and these

intermolecular hydrogen-bonding interactions contribute to the stability of the lattice.

2-R
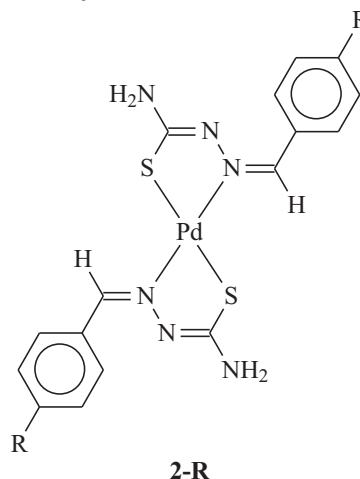
Again, to ensure that in all the **2-R** complexes the thiosemicarbazones are truly coordinated to palladium in the same fashion
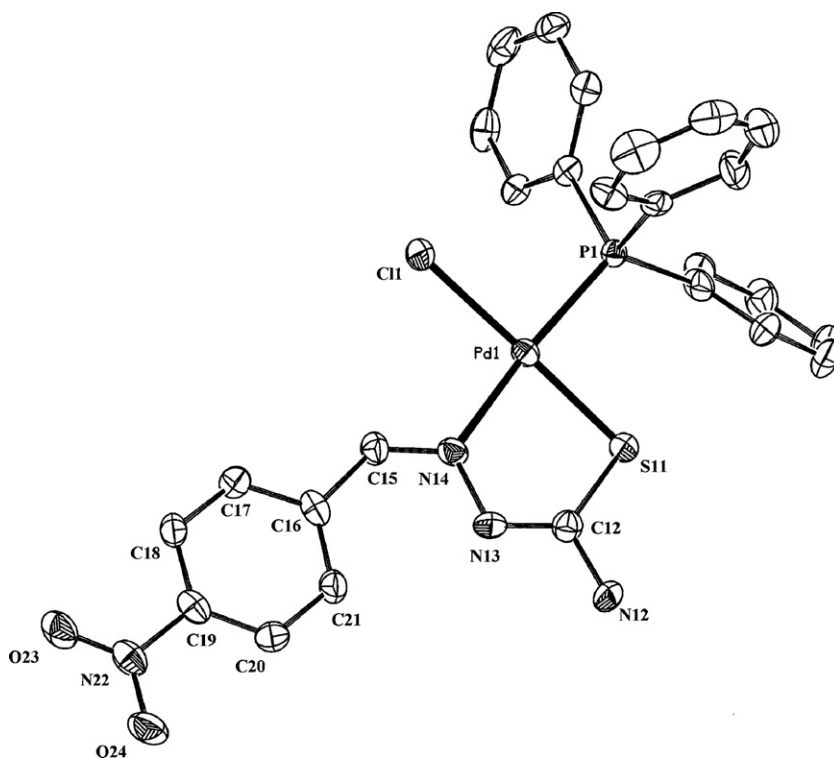
Fig. 4. Structure of **1-NO$_2$**.

(**IV**), structure of another complex of this family, *viz.* **2-OCH$_3$**, has been determined by X-ray crystallography. All the structural features of this complex (Fig. 6, Table 2) are found to be similar to those of **2-NO$_2$**, as expected. As all the **2-R** complexes were obtained similarly and they show similar properties (*vide infra*), the other three **2-R** (R = CH$_3$, H and Cl) complexes are assumed to have the same structure as their R = NO$_2$ or OCH$_3$ analogue.
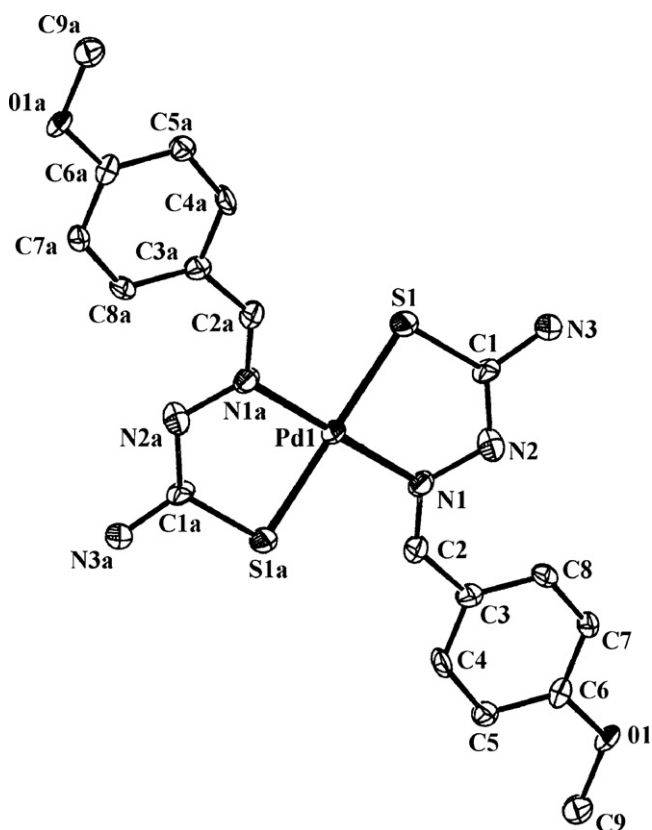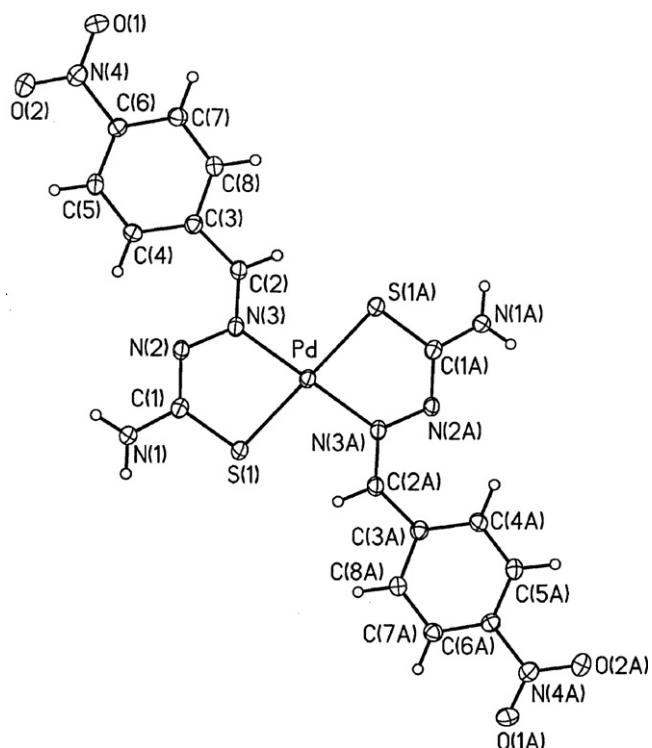

Fig. 5. Structure of **2-OCH$_3$**.

Fig. 6. Structure of **2-NO$_2$**.

Table 3
Electronic spectral data of the complexes.

Complex	λ_{max}, nm (ε, dm^3 mol^{-1} cm^{-1})
1-OCH$_3$[a]	350(17,000), 306(14,400)
1-CH$_3$[a]	347(14,400), 300(16,600)
1-H[a]	347(15,400), 297(19,300)
1-Cl[a]	353(15,400), 302(19,100)
1-NO$_2$[a]	395(12,600), 338(11,300)
2-OCH$_3$[b]	390(32,500), 330(35,700)
2-CH$_3$[b]	392(33,200), 320(42,800)
2-H[b]	394(30,100), 316(43,800)
2-Cl[b]	400(32,800), 326(42,300)
2-NO$_2$[b]	428(23,700), 390(25,200)

[a] In dichloromethane solution.
[b] In N,N-dimethylformamide solution.

3.2. Spectral properties

^{1}H NMR spectra of the **1-R** complexes, recorded in CDCl$_3$ solutions, show all the expected signals. The phenyl protons of the PPh$_3$ ligands show broad signals within 7.3–7.8 ppm. From the coordinated thiosemicarbazone, the azomethine proton signal is observed as a doublet, due to coupling with the proton at the *ortho* position of the phenyl ring, within 8.5–8.7 ppm and the NH$_2$ proton signal is observed within 4.7–6.1 ppm. Most of the expected signals from the phenyl ring of the coordinated thiosemicarbazone are clearly observed in the aromatic region, while few could not be detected due to their overlap with other signals. Signals for the OCH$_3$ and CH$_3$ substituents are observed respectively at 3.85 and 2.37 ppm. ^{1}H NMR spectra of the **2-R** complexes, recorded in DMSO-d$_6$ solutions, show the azomethine proton signal within 8.2–8.6 ppm, the NH$_2$ proton signal within 7.2–7.7 ppm and most of the expected aromatic proton signals are observed in the 6.9–8.6 ppm region. Signals for the OCH$_3$ and CH$_3$ substituents are observed at 3.83 ppm and 2.36 ppm respectively. In the infrared spectra of the **1-R** complexes, three strong bands near 520, 695 and 745 cm^{-1} are observed due to the coordinated PPh$_3$ ligands. In these spectra several new bands (in comparison with the spectrum of the *trans*-[Pd(PPh$_3$)$_2$Cl$_2$] complex) could be identified within 800–1600 cm^{-1}, which are attributable to the coordinated thiosemicarbazone ligands. Except absence of the three bands due to the PPh$_3$ ligands and small shifts in the positions of the remaining bands, infrared spectra of the **2-R** complexes have been found to be similar to those of the respective **1-R** complexes. The ^{1}H NMR and infrared spectral data of the **1-R** and **2-R** complexes are therefore in well accordance with their compositions.

The **1-R** complexes are soluble in common organic solvents like methanol, ethanol, acetone, acetonitrile, dichloromethane, chloroform, etc., producing intense yellow solutions [15]. Electronic spectra of these complexes have been recorded in dichloromethane solutions. Spectral data are presented in Table 3. Each complex shows two intense absorptions within 400–250 nm. In comparison with the spectra of the uncoordinated thiosemicarbazones **L-R**, which show an intense absorption near 300 nm, the higher energy absorption is attributable to a transition within the thiosemicarbazone orbitals. To have an understanding of the origin of the lower-energy absorption (near 350 nm), DFT calculations have been performed on the two structurally characterized **1-R** complexes, *viz.* **1-CH$_3$** and **1-NO$_2$** [10]. Compositions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are given in Table 4. Contour plots of these molecular orbitals for **1-CH$_3$** are shown in Fig. 7 and the same for **1-NO$_2$** are shown in Fig. S2 (Supplementary material). In both **1-CH$_3$** and **1-NO$_2$**, the HOMO and LUMO have major contribution from the thiosemicarbazone and minor contribution from palladium. The lower energy absorption is hence assignable to a transition from a filled thiosemicar-
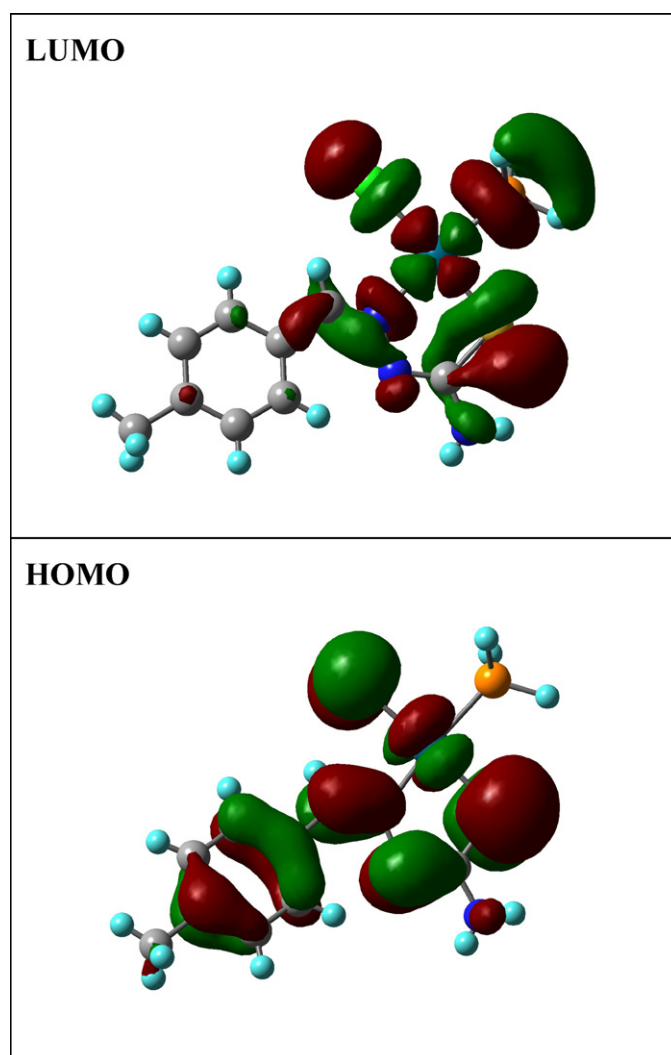
Table 4
Composition of selected molecular orbitals of the complexes.

Complex	Contributing fragments	%Contribution of fragments to	
		HOMO	LUMO
1-CH$_3$	Pd	5.44	23.59
	PPh$_3$	0	7.29
	Cl	3.18	2.06
	tsc-CH$_3$[a]	91.38	67.06
1-NO$_2$	Pd	12.99	0.34
	PPh$_3$	0	0
	Cl	7.07	0
	tsc-NO$_2$[a]	79.94	99.66
2-OCH$_3$	Pd	27.45	0.77
	tsc-OCH$_3$[a]	72.55	99.23
2-NO$_2$	Pd	17.35	0
	tsc-NO$_2$[a]	82.65	100.00

[a] tsc-R = coordinated thiosemicarbazone.

bazone orbital (HOMO) to a vacant orbital on the same ligand (LUMO).

The **2-R** complexes are found to be insoluble in most of the common organic solvents but readily soluble in N,N-dimethylformamide and dimethylsulfoxide, producing intense orange solutions [16]. Electronic spectra of these complexes in N,N-dimethylformamide solutions show two intense absorptions

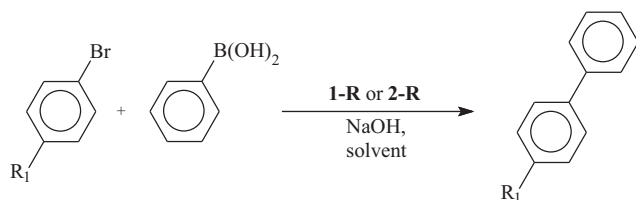**Fig. 7.** Contour plots of HOMO and LUMO of **1-CH$_3$**.

within 500–250 nm (Table 3). The higher energy absorption in these **2-R** complexes near 320 nm is attributable, as before, to a transition within the thiosemicarbazone orbitals. DFT calculations on the two structurally characterized **2-R** complexes, *viz.* **2-OCH₃** and **2-NO₂** [10], show (Figs. S3 and S4 (Supplementary material), Table 4) that the HOMO has >70% contribution from the two coordinated thiosemicarbazones, while the LUMO is almost entirely delocalized over the same two ligands. Hence the observed lower-energy absorption near 400 nm is attributable to a transition within the filled and vacant orbitals of the thiosemicarbazone ligands.

3.3. Catalysis

The fact that palladium complexes are well known to serve as efficient catalysts in bringing about C–C cross coupling reactions of different types [3] has led us to explore such catalytic properties in the present series of **1-R** and **2-R** complexes. The catalytic activity of all the five complexes of the two series **1-R** and **2-R** has been examined for C–C bond formation reactions of three types, *viz.* Suzuki, Heck and Sonogashira reactions.

Initially all the **1-R** complexes were tested as catalysts in the Suzuki coupling of phenylboronic acid and *p*-bromoacetophenone to yield the biphenyl product. All these complexes showed remarkable, as well as comparable, catalytic efficiency. For example, using **1-OCH₃** as catalyst the Suzuki coupling was achieved, under relatively mild experimental condition, in high yield as well as remarkably high turnover number (entry 1 in Table 5). The same coupling reaction, when carried out using **1-NO₂** as the catalyst, showed slightly lower yield and turnover number (entry 2 in Table 5). The results of catalysis using **1-OCH₃** and **1-NO₂** are highlighted here as representative cases, because among the five substituents (R = OCH₃, CH₃, H, Cl and NO₂) used, OCH₃ has maximum electron donating power while NO₂ has maximum electron withdrawing power. Though there are definite differences in catalytic efficiency among the individual **1-R** complexes, the magnitude of difference is relatively small. In general, higher reaction time and lower yield are observed with increase in electron withdrawing character of R. For Suzuki coupling of phenylboronic acid with the other two aryl bromides, *viz.* *p*-bromobenzaldehyde and *p*-bromobenzonitrile, using **1-OCH₃** as catalyst longer times were required (entries 3 and 4 in Table 5) to achieve similar yield (as in entry 1 in Table 5).

The observed ease of these catalytic coupling reactions, with particular reference to low catalyst loading and relatively low reaction temperature, prompted us to examine whether the same coupling reaction of phenylboronic acid with *p*-bromoacetophenone, using **1-OCH₃** as the catalyst, can be carried out at room temperature. The attempted reaction indeed proceeded smoothly at 25 °C showing high yield and turnover number as before (entry 5 and Table 5). However, the time required for the complete conversion was significantly higher (20 h). It is relevant to mention here that reports of such Suzuki coupling at room temperature are scarce in the literature [17]. Encouraged by this room temperature Suzuki coupling, we got curious to see whether such coupling can be brought about using water as a solvent. The coupling did take place in aqueous medium, however the observed catalytic efficiency was much less (entry 6 in Table 5). Though according to the modern trend, use of water as solvent is very much welcome, with particular reference to green chemistry, Suzuki coupling in water has been rarely observed [18].

While **2-OCH₃** is used as a catalyst in the Suzuki coupling of phenylboronic acid and *p*-bromoacetophenone, the observed turnover number was quite lower (entry 7 in Table 5) than that of the reaction where **1-OCH₃** is used as a catalyst (entry 1 in Table 5). Using **2-NO₂** for the same Suzuki coupling reaction almost similar (compared to **2-OCH₃**) turnover number and yield were obtained (entry 8 in Table 5). For Suzuki coupling of phenylboronic acid with the other two aryl bromides using **2-OCH₃** as the catalyst slightly longer reaction time was needed for optimum yield of the product (entries 9 and 10 in Table 5).

Encouraged by the facile Suzuki coupling reactions catalyzed by the **1-R** and **2-R** complexes, we have further investigated the catalytic activity of the same palladium complexes in Heck reaction of different aryl bromides with butyl acrylate. All the members from each family showed comparable reactivity, and the optimized results for two representative complexes, *viz.* **1-OCH₃** and **2-OCH₃**, are shown in Table 6. A fairly good yield of 72% was obtained when employing *p*-bromoacetophenone in the presence of 0.5 mol% of **1-OCH₃** (entry 1). A decrease in activity was observed in the cases of *p*-bromobenzaldehyde (yield = 65%) and *p*-bromobenzonitrile (yield = 57%) (entries 2 and 3). Whereas, for **2-OCH₃** to obtain fairly good yield higher catalyst loading (1 mol%) and higher temperature but shorter time were required (entries 4–6).

Finally we have scrutinized the catalytic efficiency of the **1-R** and **2-R** complexes in Sonogashira coupling reaction between aryl

Table 5
Suzuki cross coupling of aryl halides with phenylboronic acid.[a]

Entry	R₁	Catalyst	Solvent	Temp, °C	Time, h	Amt of cat., mol%	Conversion[b], %	TON[c]
1	COCH₃	**1-OCH₃**	Ethanol–toluene (1:1)	95	9	0.001	>99	100,000
2	COCH₃	**1-NO₂**	Ethanol–toluene (1:1)	95	12	0.001	88	88,000
3	CHO	**1-OCH₃**	Ethanol–toluene (1:1)	95	12	0.001	>99	100,000
4	CN	**1-OCH₃**	Ethanol–toluene (1:1)	95	12	0.001	>99	100,000
5	COCH₃	**1-OCH₃**	Ethanol–toluene (1:1)	25	20	0.001	>99	100,000
6	COCH₃	**1-OCH₃**	Water	100	12	1	>99	100
7	COCH₃	**2-OCH₃**	Polyethylene glycol	110	12	0.01	88	8800
8	COCH₃	**2-NO₂**	Polyethylene glycol	110	12	0.01	85	8500
9	CHO	**2-OCH₃**	Polyethylene glycol	110	13	0.01	81	8100
10	CN	**2-OCH₃**	Polyethylene glycol	110	15	0.01	80	8000

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), NaOH (1.7 mmol), Pd catalyst, solvent (4 mL).

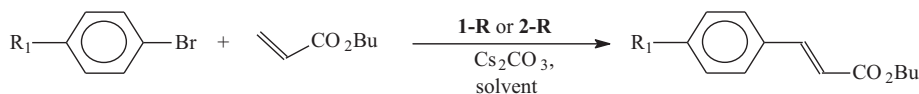[b] Determined by ¹H NMR on the basis of residual aryl halide [11].

[c] TON = turnover number ((mol of product)/(mol of catalyst)).

Table 6
Heck cross coupling of aryl halides with butyl acrylate.[a]

R_1—〈◯〉—Br + ╲╲CO_2Bu →(**1-R** or **2-R**, Cs_2CO_3, solvent)→ R_1—〈◯〉—╲╲—CO_2Bu .

Entry	R_1	Catalyst	Solvent	Temp, °C	Time, h	Amt of cat., mol%	Conversion[b], %	TON[c]
1	COCH$_3$	**1-OCH$_3$**	Ethanol–toluene (1:1)	110	24	0.5	72	144
2	CHO	**1-OCH$_3$**	Ethanol–toluene (1:1)	110	48	0.5	65	130
3	CN	**1-OCH$_3$**	Ethanol–toluene (1:1)	110	48	0.5	57	114
4	COCH$_3$	**2-OCH$_3$**	Polyethylene glycol	150	12	1	80	80
5	CHO	**2-OCH$_3$**	Polyethylene glycol	150	12	1	78	78
6	CN	**2-OCH$_3$**	Polyethylene glycol	150	14	1	62	62

[a] Reaction conditions: aryl halide (1.0 mmol), butyl acrylate (1.2 mmol), Cs_2CO_3 (1.7 mmol), Pd catalyst, solvent (4 mL), 150 °C.
[b] Determined by ^{1}H NMR on the basis of residual aryl halide [11].
[c] TON = turnover number ((mol of product)/(mol of catalyst)).

Table 7
Sonogashira cross coupling of aryl halides with phenylacetylene.[a]
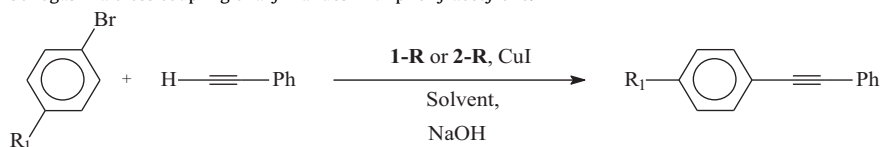
〈◯〉(Br, R_1) + H━━━Ph →(**1-R** or **2-R**, CuI, Solvent, NaOH)→ R_1—〈◯〉—━━━Ph .

Entry	R_1	Catalyst	Solvent	Temp, °C	Time, h	Amt of cat., mol%	Conversion[b], %	TON[c]
1	COCH$_3$	**1-OCH$_3$**	Ethanol–toluene (1:1)	75	10	0.5	>99	200
2	CHO	**1-OCH$_3$**	Ethanol–toluene (1:1)	75	12	0.5	76	152
3	CN	**1-OCH$_3$**	Ethanol–toluene (1:1)	75	12	0.5	74	148
4	COCH$_3$	**2-OCH$_3$**	Polyethylene glycol	110	12	0.5	>99	200
5	CHO	**2-OCH$_3$**	Polyethylene glycol	110	14	0.5	71	142
6	CN	**2-OCH$_3$**	Polyethylene glycol	110	15	0.5	68	136

[a] Reaction conditions: aryl halide (1.0 mmol), phenylacetylene (1.2 mmol), NaOH (1.7 mmol), Pd catalyst, CuI (10 mol%), solvent (4 mL).
[b] Determined by ^{1}H NMR on the basis of residual aryl halide [11].
[c] TON = turnover number ((mol of product)/(mol of catalyst)).

bromides and phenylacetylene. As before, all the members from each family showed comparable reactivity, and the results of **1-OCH$_3$** and **2-OCH$_3$** are presented in Table 7 as representatives of the two families. Fairly good yields were obtained using **1-OCH$_3$** as catalyst (0.5 mol%) at 75 °C (entries 1–3), whereas for **2-OCH$_3$** (0.5 mol%) a little higher temperature (110 °C) was required (entries 4–6).

The present studies thus demonstrate that palladium thiosemicarbazone complexes of both types **1-R** and **2-R** are efficient catalysts for C–C coupling reactions. However, the **1-R** complexes are, in general, found to be much better catalysts for these coupling reactions, especially for the Suzuki coupling. For example, the high turnover numbers ($\sim$10^5) exhibited by **1-OCH$_3$** for the coupling of aryl bromides with phenylboronic acid are substantially greater than different reported palladium pre-catalysts [19]. Another noticeable aspect of the observed catalysis by these palladium complexes **1-R** and **2-R** is that no additional ligands were necessary for the cross-coupling reactions, and such ligand-free catalysis is relatively less common [20]. **1-R** not only exhibited Suzuki coupling of very high turnover number even at room temperature, but also exhibited Suzuki coupling in water with almost 100% yield. As in these cross-coupling reactions water can be used as a solvent (or co-solvent) these cross-coupling reactions have gained prominence in recent years at an industrial level, mainly in the synthesis of pharmaceuticals and fine chemicals. The better catalytic activity of the **1-R** complexes, compared to their respective **2-R** analogues, may be attributed to the presence of PPh$_3$ ligand in the former complexes, which probably have supported the palladium(0) state, generated *in situ*. The electronic nature of

the substituents in the thiosemicarbazone ligand seemed to have no predictable influence on the catalytic activities of the complexes.

4. Conclusions

The present study shows that the 4-R-benzaldehyde thiosemicarbazones (**L-R**) can readily bind to palladium and display a rather uncommon coordination mode (**IV**) involving a restricted rotation around the imine bond. The **1-R** and **2-R** complexes are also found to be efficient catalyst for C–C coupling (*viz.* Suzuki, Heck and Sonogashira) reactions. In particular, the **1-R** complexes have turned out to be tremendously powerful catalysts towards Suzuki coupling reaction.

Appendix A. Supplementary data

CCDC 280187, 280188, 280189, 781792 and 781793 contain the supplementary crystallographic data for this paper. Packing diagram in the lattice of **2-NO₂**·2DMF (Fig. S1), contour plots of HOMO and LUMO of **1-NO₂**, **2-OCH₃** and **2-NO₂** (Figs. S2–S4) have been deposited.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.05.003.

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