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Palladium complexes of 2-formylpyridine thiosemicarbazone and two related ligands: Synthesis, structure and, spectral and catalytic properties

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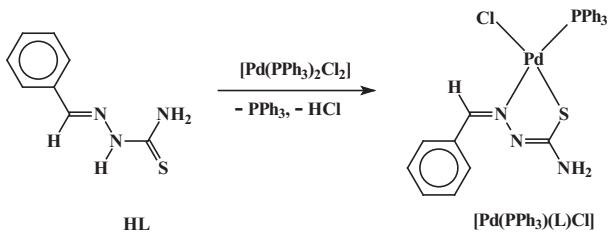
ABSTRACT

Thiosemicarbazones of 2-formylpyridine, 2-aceylpyridine and 2-benzoylpyridine, abbreviated in general as **HL-R** (where H depicts the acidic hydrogen and R the fragment (R = H, Me and Ph) linked to the imine-carbon) react with $[Pd(PPh_3)_2Cl_2]$ in refluxing ethanol in the presence of triethylamine to afford complexes of the type $[Pd(L\text{-}R)(PPh_3)]Cl$ (**1**, R = H; **2**, R = Me, **3**, R = Ph). Structures of the complexes **1** and **3** have been determined by X-ray crystallography, and the structure of complex **2** has been optimized by DFT. In all three the thiosemicarbazone ligand binds to the metal center as a monoanionic tridentate NNS-donor forming two adjacent five-membered chelate rings, the triphenylphosphine occupies the fourth coordination site on palladium. Complexes **1**–**3** display intense absorptions in the visible and ultraviolet regions, which have been analyzed by TDDFT calculations. All the complexes are found to efficiently catalyze Suzuki, Heck and Sonogashira type C–C cross-coupling, and C–N coupling reactions of aryl halides with primary and secondary amines. All the catalytic reactions are found to proceed under ligand-free condition.

1. Introduction

Thiosemicarbazone complexes of the transition metals have received considerable attention, largely because of their bioinorganic relevance [1]. However, we have been exploring the chemistry of transition metal complexes of the thiosemicarbazones, primarily because of the variable binding mode displayed by these ligands in their complexes, and the present work has emerged out of this exploration [2]. In a recent study we have observed that benzaldehyde thiosemicarbazone (**HL**), and four similar ligands, react with $[Pd(PPh_3)_2Cl_2]$ to yield a group of mixed-ligand complexes of type $[Pd(PPh_3)(L)Cl]$ (Scheme 1), in which the thiosemicarbazones display a NS-mode of coordination [2a,b]. In view of the structure of the uncoordinated thiosemicarbazone, which is similar to that shown for **HL** [2b], this NS-mode of coordination is a bit uncommon as it involves a change in geometry around the pre-existing C=N bond. In order to examine whether substitution of the phenyl ring in **HL** by a pyridyl ring, with the pyridine-nitrogen at the *ortho* position with respect to the imine group, can prevent this change in geometry via coordination of the pyridine-nitrogen to the metal center, we have selected the thiosemicarbazone of 2-formylpyridine, and two related ligands, *viz.* thiosemicarbazones of 2-aceylpyridine and 2-benzoylpyridine, for the present study. The chosen thiosemicarbazones are abbreviated in general as **HL-R**, where H depicts the acidic hydrogen and R the fragment (R = H, Me and Ph) linked to the imine-carbon. The main aim of the present work has been to study the interaction of the selected thiosemicarbazones (**HL-R**) with $[Pd(PPh_3)_2Cl_2]$ and see whether they bind to palladium in an NNS-mode (**I**) without any rotation around the pre-existing imine bond. The other, and equally important, objective has been to



Scheme 1.

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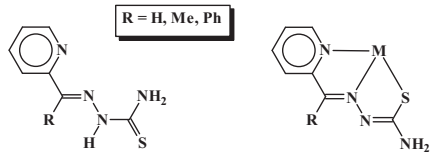
explore catalytic activity of the resulting complexes towards coupling reactions of various types. It may be worth mentioning here



that palladium complexes are extensively utilized as catalyst for the synthesis of industrially useful organic molecules, particularly via C–C and C–N coupling reactions [3,4]. Reactions of the chosen thiosemicarbazones with $[Pd(PPh_3)_2Cl_2]$ have been found to afford a group of mixed-ligand complexes, and the chemistry of these complexes is reported in this paper, with particular reference to their formation, structure and, catalytic efficiency towards C–C and C–N coupling reactions.

2. Experimental

2.1. Materials

Palladium chloride was obtained from Arora Matthey, Kolkata, India. The $[Pd(PPh_3)_2Cl_2]$ complex was prepared by following a reported procedure [5]. 2-Formylpyridine, 2-acetylpyridine and 2-benzoylpyridine were obtained from Merck (India), Spectrochem (India) and Sigma–Aldrich, respectively. The thiosemicarbazone ligands (**HL-R**; R = H, Me and Ph) were prepared by reacting equimolar amounts of thiosemicarbazide and the respective pyridine-derivative in warm ethanol [6]. All other chemicals and solvents were reagent grade commercial materials and were used as received.

2.2. Preparation of the complexes

The [Pd(L-R)(PPh_3)]Cl complexes (**1**, R = H; **2**, R = Me; **3**, R = Ph) were prepared by following a general procedure. Specific details are given below for a particular complex.

2.2.1. Complex *1*

2-Formylpyridine thiosemicarbazone (26 mg, 0.14 mmol) was dissolved in warm ethanol (30 mL) and triethylamine (14 mg, 0.14 mmol) was added to it, followed by $[Pd(PPh_3)_2Cl_2]$ (100 mg, 0.14 mmol). The mixture was then refluxed for 5 h to yield a yellowish–brown solution. The solvent was evaporated and the solid mass, thus obtained, was subjected to purification by thin layer chromatography on a silica plate. With 1:3 acetonitrile-benzene as the eluant, an orangish–yellow band separated, which was extracted with acetonitrile. Evaporation of the acetonitrile extract gave complex **1** as an orangish–yellow crystalline solid. Yield: 68%. *Anal.* Calc. for $C_{25}H_{22}N_4PSClPd$: C, 51.47; H, 3.77; N, 9.61. Found: C, 51.53; H, 3.72; N, 9.65%. Mass spectral data (ESI, positive mode, CH_3CN): *m/z* 547 for $[1\text{-Cl}]^+$. Λ_M: 145 $^{-1}$ cm^2 M^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$)[1]: 5.73 (s, NH_2), 7.19 (t, 1H, *J* = 9.0), 7.38 (s, 1H), 7.58–7.72 (PPh_3), 7.87 (d, 1H, *J* = 8.0), 8.06 (t, 1H, *J* = 8.5), 8.16 (d, 1H, *J* = 9.0). ^{31}P NMR (300 MHz, $CDCl_3$): 43.04 ppm. IR (cm^{-1}): 1646, 1602, 1562, 1480, 1458, 1434, 1375, 1318, 1255, 1179, 1098, 1020, 997, 752, 722, 697, 532, 508.

[1] Chemical shifts are given in ppm and multiplicity of the signals along with the associated coupling constants (*J* in Hz) are given in parentheses. Overlapping signals are marked with an asterisk.

2.2.2. Complex *2*

Yield: 62%. *Anal.* Calc. for $C_{26}H_{24}N_4PSClPd$: C, 52.27; H, 4.02; N, 9.38. Found: C, 52.23; H, 4.07; N, 9.36%. Mass spectral data (ESI, positive mode, CH_3CN): *m/z* 561 for $[2\text{-Cl}]^+$. Λ_M: 148 $^{-1}$ cm^2 M^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): 2.42 (s, CH_3), 5.69 (s, NH_2), 7.16 (t, 1H, *J* = 9.0), 7.59–7.68 (PPh_3), 7.80 (d, 1H, *J* = 8.0), 7.94 (t, 1H, *J* = 8.5), 8.10 (d, 1H, *J* = 9.0). ^{31}P NMR (300 MHz, DMSO-d_6): 43.03 ppm. IR (cm^{-1}): 1639, 1599, 1563, 1480, 1456, 1432, 1380, 1315, 1257, 1146, 1098, 1020, 998, 747, 721, 694, 531, 506.

2.2.3. Complex *3*

Yield: 71%. *Anal.* Calc. for $C_{31}H_{26}N_4PSClPd$: C, 56.46; H, 3.95; N, 8.50. Found: C, 56.51; H, 3.97; N, 8.46%. Mass spectral data (ESI, positive mode, CH_3CN): *m/z* 623 for $[3\text{-Cl}]^+$. Λ_M: 144 $^{-1}$ cm^2 M^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): 5.29 (s, NH_2), 7.07 (d, 1H, *J* = 9.0), 7.37–7.69 (PPh_3 + 2H*), 7.78 (t, 1H, *J* = 8.5), 7.93 (t, 1H, *J* = 8.2), 8.07 (t, 1H, *J* = 9.0), 8.73 (d, 2H, *J* = 9.0), 8.87 (d, 1H, *J* = 9.0). ^{31}P NMR (300 MHz, $CDCl_3$): 43.10 ppm. IR (cm^{-1}): 1616, 1596, 1545, 1482, 1454, 1437, 1384, 1320, 1263, 1181, 1097, 1027, 998, 745, 722, 695, 533, 510.

2.3. Physical measurements

Microanalyses (C, H and N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. Mass spectra were recorded with a Micromass LCT electrospray (Qtof Micro YA263) mass spectrometer. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution on a Bruker Avance DPX 300 NMR spectrometer. IR spectra were obtained on a Perkin Elmer Spectrum Two IR spectrometer with samples prepared as KBr pellets. Solution electrical conductivities were measured in acetonitrile solution using a Philips PR 8499 bridge with a solute concentration of 10^{-3} M. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Geometry optimization by density functional theory (DFT) method and electronic spectral analysis by TDDFT calculation were performed using the GAUSSIAN 03 (B3LYP/SDD-6–31G) package [7]. GC–MS analyses were performed using a Perkin Elmer CLARUS 680 instrument.

2.4. X-ray crystallography

Single crystals of complex **1** were obtained by slow evaporation of solvents from a solution of the complex in 1:1 methanol–acetonitrile. Single crystals of complex **3** were obtained by slow evaporation of solvent from a solution of the complex 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 Kα radiation (λ = 0.71073 Å). X-ray data reduction, structure solution and refinement were done using SHELXS-97 and SHELXL-97 programs [8]. The structures were solved by the direct methods. In the structure of complex **3**, there was severely disordered solvent present on crystallographic symmetry elements which could not be modeled. This was removed using the SQUEEZE routine from PLATON.

2.5. Application as catalysts

2.5.1. 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, Na_2CO_3 (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 Na_2SO_4, and filtered. Solvent was removed under