

## Organometallic derivatives of palladium (o) with 1-substituted tetrazoline-5- thione

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(Received: February 12, 2008; Accepted: April 08, 2008)

### ABSTRACT

Organometallic derivatives of palladium (o) have been isolated from the displacement reaction of  $\text{Pd}(\text{P}\Phi_3)_4$  with 1-substituted tetrazoline-5-thione with phenyl, orthotolyl, paratolyl, parachlorophenyl and benzoyl substitution in benzene medium. Most probable tetrahedral structure is assigned on the basis of elemental analysis, electronic, infrared, far infrared and  $^1\text{H}$  NMR spectral studies.

**Key words:** Organometallic derivatives, Palladium.

### INTRODUCTION

Organometallic derivatives of palladium(o) are well established in literature and reported to be versatile homogeneous catalyst<sup>1</sup>. They have unique and special insights into structure, bonding and reactivity of the molecules which may display reactions involving either coordinative dissociation or coordinative addition which depends on electronic factors<sup>2-4</sup>. Moreover, Pd(o) Complexes have not been investigated as extensively as those of Pt(o). In continuation of our earlier work<sup>5-8</sup>, we report here the preparation and structural investigation of some new organometallic compounds with 1- substituted tetrazoline-5 thione and triphenyl Phosphine.

### MATERIAL AND METHODS

All the chemicals used were either AnalaR or chemically pure grade. 1-substituted tetrazoline -5-thiones were prepared by the method of Lieber and Ramchandran<sup>9</sup>.  $\text{Pd}(\text{P}\Phi_3)_4$  was prepared by method described in literature<sup>10</sup>.

**Bis (Triphenyl phosphine) – bis (1 –substituted tetrazoline–5– thione) palladium(o) Complexes were prepared by the following general procedure**

$\text{Pd}(\text{P}\Phi_3)_4$  (1m. mol) was dissolved in dry

benzene (20 ml) and a solution of 1-substituted tetrazoline -5-thione (2m mol.) in dry benzene (20 ml) was added to it . The mixture was warmed on water bath at 60–80° C to final volume of about 15 ml. The resulting solution was cooled at room temperature (27°C) and treated with ether (20 ml) when a yellow precipitate of the complex  $[\text{Pd}(\text{P}\Phi_3)_2(\text{ligand})_2]$  was obtained. The complex were washed with ethanol and dried under Vacuum over  $\text{CaCl}_2$ . The analytical and physical data of complexes have been given in Tabel 1.

IR spectra of ligands and complexes were recorded with Perkin Elmer model 577 spectrophotometer in the range of 4000–200  $\text{cm}^{-1}$  as KBr pellets. The electronic spectra were recorded with Zeiss (Jena) model of automatic recording system in dioxane. Molar conductance of complexes were measured in DMF using. Wiss-Werkstatter weithein obb type LBR conductivity meter. The  $^1\text{H}$  NMR spectra of ligands and Pd(o) compounds were recoded with 90 M HZ NMR spectrometer in  $\text{CDCl}_3$  solution using TMS as the internal indicator in the range of 0 to 10 PPM.

The molecular weight of compounds were measured cryoscopically using highly purified benzene as solvent. Magnetic measurements were made on a Gouy balance using  $\text{Hg}[\text{CO}(\text{SCN})_4]$  as

calibrant. Determination of oxidation state of palladium in organometallic complexes were determined by iodometric and acidimetric titration following literature<sup>11</sup>.

### RESULTS AND DISCUSSION

All the phenyl (1Pt5TH), Paratolyl (1Ptt5TH), ortho tolyl (10tt5TH), parachloro phenyl (1PCIPt5TH) and benzoyl (1Bt5TH) derivatives of

1- substituted tetrazoline-5- thione interact with  $\text{Pd}(\text{P}\phi_3)_4$  in benzene solution. Simple replacement of two  $\text{P}\phi_3$  groups occur resulting yellow solid  $[\text{Pd}(\text{P}\phi_3)_2(\text{ligand})_2]$  by two molecules of 1-substituted tetrazoline-5-thione. All isolated products were diamagnetic as expected for  $d^{10}$  complexes and non-electrolyte in DMF. When a suspension of these complexes in  $\text{CCl}_4$  were treated with iodine solution in  $\text{CCl}_4$ , the violet colour of iodine got discharged suggesting zerovalent palladium. Moreover,

**Table 1: Analytical and physical data of complexes**

S. no	Compd./ (Colour)	Observed mol. wt	Analysis % Found/ (Calcd)			
			C	H	N	Pd
1.	$[\text{Pd}(\text{P}\phi_3)_2(1\text{Pt5TH})_2]$ (Redish yellow)	980	61.0(60.8)	4.3(4.2)	11.5(11.3)	11.1(10.8)
2.	$[\text{Pd}(\text{P}\phi_3)_2(1\text{Ptt5TH})_2]$ (deep yellow)	1010	61.6(61.5)	4.5(4.4)	11.1(11.0)	10.5(10.4)
3.	$[\text{Pd}(\text{P}\phi_3)_2(10\text{tt5TH})_2]$ (bright yellow)	1005	61.6(61.5)	4.5(4.4)	11.2(11.0)	10.5(10.4)
4.	$[\text{Pd}(\text{P}\phi_3)_2(1\text{PCIPt5TH})_2]$ (yellow)	1010	57.4(56.8)	3.8(3.7)	10.5(10.6)	9.9(9.8)
5.	$[\text{Pd}(\text{P}\phi_3)_2(1\text{Bt5TH})_2]$ (yellow)	1020	60.1(59.9)	4.5(4.5)	11.2(11.0)	5.1(4.4)

**Table 2: Shift of thioamide bands in the ligands on coordination: Ligands/ Pd(o)- (Complex) in  $\text{cm}^{-1}$**

S. no.	Ligands	Thioamide Bands*			
		I	II	III	IV
1.	1- Phenyl tetrazoline-5-thione (1Pt5TH)	1512 (S) (1510 m)	1280 (S) (1230 m)	1058 (S) (1020 m)	785 (m) (750 m)
2.	1- Paratolyl tetrazoline-5-thione (1Ptt5TH)	1504 (S) (1500 m)	1286 (m) (1256 m)	1050 (m) (1020 m)	790 (m) (740 m)
3.	1- Ortho tolyl tetrazoline-5-thione (10 tt5TH)	1520 (m) (1525 m)	1310 (m) (1270 m)	1055 (m) (1020 m)	780 (m) (730 m)
4.	1- Para Chloro phenyl tetrazoline-5-thione (1PCIPt5TH)	1500 (S) (1505 m)	1280 (m) (1230 m)	1055 (m) (1030 m)	810 (m) (780 m)
5.	1- benzoyl tetrazoline-5-thione (1Bt5TH)	1500 (S) (1500 S) (1490 m)	1300 (m) (1240 m)	1050 (m) (1020 m)	820 (m) (780 m)

Mixed Bands, Band I ( $\delta\text{NH} + \delta\text{CH} + \nu\text{C} = \text{N}$ ); Band II ( $\nu\text{C} \frac{3}{4} \text{N} + \delta\text{NH} + \nu\text{C} = \text{S}$ ); Band III ( $\nu\text{C} \dots \text{N} + \nu\text{C} \dots \text{S}$ ); Band IV ( $\nu\text{C} \text{ S}$ )

oxidation state of metal in these complexes were determined<sup>11</sup>. It was found that 1g.mol. of  $[Pd(P\phi_3)_2(\text{ligand})_2]$  reacts with 2g-equivalent of iodine and the liberated 2g. mol. of ligand consume 2g. equivalent of NaOH indicating zero oxidation state of palladium in complexes. Thus, the known preferential tetrahedral structure of all new Pd(o) complexes was tentatively assumed<sup>12-14</sup>.

Electronic spectra of all the complexes display very strong based of considerable high intensity at 350 nm due to charge transfer. The other ligand field bands are obscured by charge transfer band. This is but expected for a  $d^{10}$ - Pd(o) complexes and appears high degree of d-p mixing. Thus, no positive contribution is obtained is assigning structure from uv/vis spectral data.

#### Infrared spectra

IR spectrum of 1- substituted tetrazoline-5- thione display two distinct board absorption bands in the range  $3080\text{-}3020\text{cm}^{-1}$  are assigned to mixed  $\nu$  CH and  $\nu$  NH vibrations. Rao and venkataraghavan<sup>15</sup> on examining the spectra of tetrazoles (pka = 4.89) in very dilute solution, found the  $\nu$  N-H frequency  $\sim 3145\text{ cm}^{-1}$  which is considerably lower than other organic amines. Josien and Lebas<sup>16</sup> have discussed bands in the range  $3200\text{-}3000\text{ cm}^{-1}$  in P- substituted benzenes. Wiberley et al<sup>17</sup> have also recorded band in this region in several ortho, meta and para substituted benzenes. Thus, the bands  $\sim 3050$  and  $3220\text{-}3180\text{ cm}^{-1}$  in 1- substituted tetra zoline-5- thione have reasonably been assigned to superimposed bands of  $\nu$  N-H and  $\nu$  C-H vibrations. The  $\nu$  N-H bands of the ligands splits after coordination to Pd(o) and observed at higher frequency. Most probably N-H group in these complexes is in different environment and their shifting suggest the absence of bonding through iminonitrogen. Thus N-H group of ligands in intact in solid complexes.

The broad weak bands in the range  $1680\text{-}1600\text{ cm}^{-1}$  in 1- substituted tetra zoline-5- thione remains almost unchanged and are assigned to tetrazole ring skeletal vibrations<sup>18</sup>. The band at  $\sim 1510\text{-}1500\text{ cm}^{-1}$  in the spectrum of ligands is assigned to thioamide band 1 having mixed contributions from  $\delta$ NH,  $\nu$ C=N and  $\nu$ C=C. This band remains almost unchanged on coordination to

Pd(o), Agrawala and Rao<sup>19</sup> on the basis of normal coordinate analysis of ethylene thiourea which contains thioamide moiety, suggested that thioamide band I has contribution of 60-80%  $\delta$ NH and 12-20%  $\nu$ CN. The unchanged position of this band on coordination suggests the absence of bonding through iminonitrogen atom of ligands. Absence of bonding through imino nitrogen is also supported by blue-shifting of N-H band of ligands in few cases (Table 2) The  $\nu$  S-H bond of 1- substituted - tetra zoline - 5 - thione appears at  $2550\text{cm}^{-1}$  is not observed in the spectra of complexes indicating the presence of thione from of the ligands and Pd-S bond may be tentatively assumed. The formation of metal-sulphur bond is also supported by the systematic change in position of all the four thioamide bands of the ligand. The thioamide band II under goes red shift by  $30\text{-}35\text{cm}^{-1}$  band III by  $30\text{-}40\text{ cm}^{-1}$  and band IV by  $30\text{-}50\text{ cm}^{-1}$  due to increase in CN bond order and decrease in CS bond order resulting bonding through sulphur<sup>20-22</sup>.

Two new bands around  $480(\text{m})$  and  $420(\text{m})$  in all Pd(o) complexes are assigned to  $\nu$  Pd-P modes and new bands around  $320(\text{w})$  is tentatively assigned to  $\nu$ Pd-S mode.

#### <sup>1</sup>H NMR SPECTRA

<sup>1</sup>H NMR spectra of ligands and their Pd(o) complexes were recorded in  $\text{CDCl}_3/\text{TMS}$  to substantiate further bonding of ligands with Pd(o). The spectrum of  $[Pd(P\phi_3)_2(1\text{PT5TH})_2]$  display multipletes in the region of  $\delta = 7.3\text{-}7.5$  PPM. due to two phenyl groups of two coordinated 1-phenyl tetrazoline-5- thione molecules<sup>23</sup>. The broadening of this peak may be caused either (I) by the presence of four nitrogen atoms which may cause large quadrupole resonance broadening effect or (II) to a ligand exchange reaction occurring the solution<sup>24</sup>. Similar broadening effect of the phenyl proton bands has been observed by greaves et al<sup>23</sup>. The phenyl proton signal of the triphenyl phosphine in the complexes appears in the range of  $\delta = 7.11\text{-}6.6$  PPM in Pd(o) complexes.

<sup>1</sup>H NMR spectra of 1-0- tolyl-tetrazoline-5- thione complex display absorption at  $\delta = 1.5$  PPM due to methyl protons of the tolyl group. This signal is broad and might be due to the close proximity of

the CH<sub>3</sub> group to the tetra zoline ring with its four nitrogen atoms.

The imino proton of ligand display weak and broad signal around  $\delta = 8-6$ PPM. This is the same region as the protons of the ligands are absorbing. So, it appears that N-H Signal is masked by the strong and the broad Signal due to phenyl protons. This also indicated by the relative area of the phenyl proton peak which is greater by two units

than required for phenyl protons. Thus the <sup>1</sup>H NMR spectra are also compatible with bounding through the thiocarbonyl sulphar and no deprotonation of the N-H group.

Thus, on the basis of the IR, Visible and NMR spectral data and the diamagnetism, a tetrahedral structures is suggested for all Pd(o) complexes.

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