

## Some Low-Valent Organometallic Complexes of Pt-group Metals, Part-1: Complexes of Pd(0) and Pt (0)

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$[M(P\phi_3)_4]$  ( $M = Pd$  or  $Pt$ ) readily undergoes substitution reaction in dry benzene. Heterocyclic thioamides, 1-substituted tetrazoline-5-thione, ethylene thiourea, 2-mercapto-3-substituted-quinazoline-4-one and substituted triazoles easily displaces two molecules of  $P\phi_3$  in dry benzene from  $[M(P\phi_3)_4]$ . However, all  $P\phi_3$  molecules could not be displaced. The same reaction is also carried out using isonicotinic acid hydrazide both four and six coordinated organometallic compounds were resulted.

### INTRODUCTION

The existence of a number of Pd(0) and Pt(0) complexes has been definitely established<sup>1-7</sup>. They are versatile homogeneous catalyst and subject of increasingly vigorous activity having unique and interesting insights into structure and bonding. Many of them undergo reactions involving either coordinative dissociation or coordinative addition<sup>8</sup>.  $M(P\phi_3)_4$  ( $M = Pd$  or  $Pt$ ) readily dissociate in benzene to give planar species  $Pd(P\phi_3)_3$  and  $Pt(P\phi_3)_3$ . However, cryoscopic<sup>10</sup> and NMR data<sup>11</sup> indicate that the reaction of  $Pt(P\phi_3)_4$  in solution are somewhat complicated. Ugo *et. al.*<sup>12-14</sup> have suggested metal cluster compounds like  $Pt_3(P\phi_3)_5 \cdot C_6H_6$  and  $Pt_3(P\phi_3)_4 \cdot C_6H_6$  in benzene. However, these compounds undergo substitution reactions in benzene by 1-substituted tetrazoline-5-thione<sup>15</sup>, ethylene thiourea<sup>16</sup>, substituted triazoles<sup>17</sup>, thioquinazoles<sup>18</sup> and isonicotinic acid hydrazide<sup>19</sup>. Two coordinated  $P\phi_3$  groups are easily replaced by two molecules of these ligands. But, we have not been able to displace all the coordinated triphenyl phosphine from  $Pd(P\phi_3)_4$  or  $Pt(P\phi_3)_4$ . Some octahedral complexes are formed with ethylene thiourea and isonicotinic acid hydrazide if reaction is carried out using large excess of ligands and increasing time of reaction. Abstraction of CS group also occurs if  $CS_2$  is mixed with benzene.

### EXPERIMENTAL

All Pd(0) and Pt(0) complexes were prepared in benzene starting from  $M(P\phi_3)_4$  ( $M = Pd$  or  $Pt$ ) as reported earlier<sup>16,17</sup>. Ethylene thiourea (ETU)<sup>20</sup>, 2-mer-

capto-3-phenyl-quinazoline-4-one (PQTH)<sup>21</sup>, 2-mercapto-3-metatoyl-quinazoline-4-one (mQTH)<sup>21</sup>, 3-(4-pyridyl)-4-phenyl-1,2,4-triazole-5-thione (PPyTH)<sup>22</sup>, 4-amino-5-mercapto-3-methyl-s-triazole<sup>23</sup> (AmMTH), 1,2,4-triazole-3(5)-thiol-(tTH)<sup>24</sup>, 4-amino-3-hydrazino-1,2,4-triazole-5-thione<sup>25</sup> (AHtTH) were prepared following literature. Some novel Pd(0) and Pt(0) compounds are given in Table-1.

TABLE 1  
SOME MIXED LIGAND ORGANOMETALLIC COMPLEXES  
OF Pd(0) AND Pt(0)

Compound	M. pt. (°C)	Colour
[Pd(Pφ <sub>3</sub> ) <sub>3</sub> (PQTH)]	135	Light yellow
[Pd(Pφ <sub>3</sub> ) <sub>2</sub> (PQTH) <sub>2</sub> ]	182	Mimossa
[Pt(Pφ <sub>3</sub> ) <sub>3</sub> (PQTH)]	187	Marine grey.
[Pt(Pφ <sub>3</sub> ) <sub>2</sub> (CS)(PQTH)]	126	Light brown.
[Pt(Pφ <sub>3</sub> )(mQTH) <sub>3</sub> ]	210	Yellow.
[Pd(Pφ <sub>3</sub> ) <sub>3</sub> (AHtTH)]	205-206	Golden yellow.
[Pt(Pφ <sub>3</sub> )(AHtTH) <sub>3</sub> ]	137	Light yellow.
[Pd(Pφ <sub>3</sub> )(PPyTH) <sub>3</sub> ]	224-225	Yellow.
Pt(Pφ <sub>3</sub> ) <sub>3</sub> (PPyTH)	85	Light yellow.
[Pt(Pφ <sub>3</sub> ) <sub>2</sub> (PPyTH)]	125	Pale Cream.
[Pt(Pφ <sub>3</sub> )(PPyTH) <sub>3</sub> ]	139	Light yellow
[Pd(Pφ <sub>3</sub> )(tTH) <sub>3</sub> ]	225	Deep yellow.
[Pd(Pφ <sub>3</sub> ) <sub>2</sub> (tTH) <sub>2</sub> ]	126*	Light grey.
[Pt(Pφ <sub>3</sub> )(tTH) <sub>3</sub> ]	131*	Yellow.
[Pt(Pφ <sub>3</sub> ) <sub>2</sub> (AmMTH)(Py)]	200	Light yellow.
[Pd(Pφ <sub>3</sub> )(CS)(INAH) <sub>2</sub> ]	160-161	Golden yellow
[Pd <sub>2</sub> (Pφ <sub>3</sub> )(CS)(INAH) <sub>5</sub> ]	100-105	Deep orange.
[Pt(Pφ <sub>3</sub> ) <sub>3</sub> (INAH)]	160-162	Yellow.
[Pt(Pφ <sub>3</sub> )(INAH) <sub>5</sub> ]	116	Deep yellow.

\*With decomposition.

## RESULTS AND DISCUSSION

Pd(Pφ<sub>3</sub>)<sub>4</sub> and Pt(Pφ<sub>3</sub>)<sub>4</sub> readily undergo substitution reactions in benzene to yield the compounds having following formula:

- (i) [M(Pφ<sub>3</sub>)<sub>3</sub>(LH)] (M = Pd, Pt; LH = PQTH, AHtTH, tTH, PPyTH)
- (ii) [M(Pφ<sub>3</sub>)<sub>2</sub>(LH)<sub>2</sub>] (M = Pd, Pt; LH = PPyTH, PQTH)
- (iii) [M(Pφ<sub>3</sub>)(LH)<sub>3</sub>] (M = Pd, Pt; LH = tTH, PPyTH, AHtTH, INAH, ETU, PQTH, mQTH)

However, if reaction is carried out in the mixture of benzene and CS<sub>2</sub> (1 : 1)

abstraction of CS group occurs and compounds like  $[\text{Pt}(\text{P}\Phi_3)_2(\text{CS})(\text{PQTH})]$ ,  $[\text{Pd}(\text{P}\Phi_3)(\text{CS})(\text{INAH})_2]$  and  $[\text{Pd}_2(\text{P}\Phi_3)(\text{CS})(\text{INAH})_5]$  are isolated. Some monomeric octahedral complexes of Pt(0) are also formed with ETU<sup>16</sup> having formula  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})(\text{H}_2\text{O})_4]$  and  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})_5]$ . All the products obtained after carrying out substitution reactions are diamagnetic as expected for  $d^{10}$  complexes of Pd(0) and Pt(0) are non-conducting in DMF. The violet colour solution of iodine in  $\text{CCl}_4$  are discharged by all suggesting Pd(0) and Pt(0) compounds. However, oxidation state of metals in the compounds are determined iodometrically<sup>15</sup>.

Electronic spectra of all Pd(0) and Pt(0) complexes display very strong bands in the region of 28,800–30,300 and 30,000–29,425  $\text{cm}^{-1}$  respectively due to metal ligand charge transfer. The intensity of charge transfer band of Pt(0) complexes are higher than those of isostructural Pd(0) which attributes greater degree of d-p mixing in Pt(0) compounds.

### Thioamide Bands and Nature of Bonding

All tTH, PPytTH, AHtTH, AmMTH, PQTH, mQTH and ETU contain a thioamide group (H—N—C=S) and give rise to four characteristics thioamide



bands in their infrared spectra<sup>26-28</sup>. The change in position and intensity of four thioamide bands of these ligands on coordination to Pd(0) and Pt(0) clearly indicate the metal-ligand bonding.

Thioamide band I is mixed band having contributions from  $\delta\text{NH} + \nu\text{C}=\text{N} + \delta\text{CH}$  undergoes blue shift/or unchange in position on coordination. The band II ( $\nu_{\text{C}=\text{N}} + \delta_{\text{NH}} + \nu_{\text{C}=\text{S}} + \delta_{\text{CH}}$ ) undergoes red shift (15–20  $\text{cm}^{-1}$ ), band III ( $\nu_{\text{C}=\text{N}} + \nu_{\text{C}=\text{S}}$ ) undergoes red shift of 15–20  $\text{cm}^{-1}$  and band IV ( $\nu_{\text{C}=\text{S}}$ ) undergoes red shift in the order of 20–25  $\text{cm}^{-1}$  on coordination to Pd(0) or Pt(0). This systematic shift of four thioamide bands of ligands clearly indicate increase in CN bond order and decrease in CS bond order having bonding through thione sulphur<sup>29-35</sup>.

Some new bands are present probably due to different octahedral and tetrahedral symmetry in Pt(0) complexes of ethylene thiourea and isonicotinic acid hydrazide. Two medium bands are observed at 1128 and 1102  $\text{cm}^{-1}$  in the spectra both octahedral  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})_5]$  and  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})(\text{H}_2\text{O})_4]$  complexes. However, these two bands are almost of negligible intensity in the spectrum of tetrahedral  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})_3]$ . These bands, therefore may be due to the octahedral symmetry of  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})_5]$  and  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})(\text{H}_2\text{O})_4]$  which are almost absent from the tetrahedral complex  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})_3]$ .

Similarly, medium bands are observed at 750 and 728  $\text{cm}^{-1}$  in the IR spectra of both complexes,  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})_5]$  and  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})(\text{H}_2\text{O})_4]$  but these are

almost absent in the spectrum of  $[\text{Pt}(\text{P}\Phi_3)(\text{ETU})_3]$ . This difference may also be due to octahedral symmetry of the former two complexes and tetrahedral symmetry of the latter.

Two medium bands at  $1110$  and  $1080\text{ cm}^{-1}$  are also observed in octahedral  $[\text{Pt}(\text{P}\Phi_3)(\text{INAH})_5]$  but these bands are absent from the tetrahedral  $[\text{Pt}(\text{P}\Phi_3)_3(\text{INAH})]$  complex.

### Metal Ligand Vibrations

In the far infrared spectra two  $\nu(\text{Pd} - \text{P})(430 \pm 5$  and  $410 \pm 5\text{ cm}^{-1})$  and one  $\nu(\text{Pd} - \text{S})(360 \pm 5\text{ cm}^{-1})$  in  $[\text{Pd}(\text{P}\Phi_3)_3\text{LH}]$  ( $\text{LH} = \text{AH}\ddot{\text{T}}\text{H}$ ,  $\text{PQTH}$ ); two  $\nu(\text{Pt} - \text{S})(340 \pm 10$  and  $320 \pm 5\text{ cm}^{-1})$  and one  $\nu(\text{Pt} - \text{P})(420 \pm 5\text{ cm}^{-1})$  in  $[\text{Pt}(\text{P}\Phi_3)(\text{LH})_3]$  ( $\text{LH} = \text{AH}\ddot{\text{T}}\text{H}$ ,  $\text{PPy}\ddot{\text{T}}\text{H}$ ,  $\text{mQTH}$  and  $\text{ETU}$ ) suggest  $\text{C}_{3v}$  point group in tetrahedral structure. But lower symmetry in tetrahedral structure of  $[\text{M}(\text{P}\Phi_3)_2(\text{LH})_2]$  ( $\text{M} = \text{Pt}$  or  $\text{Pd}$ ;  $\text{LH} = \text{tTH}$ ,  $\text{PPy}\ddot{\text{T}}\text{H}$  and  $\text{PQTH}$ ) are observed as two  $\nu(\text{Pt} - \text{P})(410 \pm 5$  and  $380 \pm 10\text{ cm}^{-1})$ ,  $\nu(\text{Pd} - \text{P})(430 \pm 5$  and  $422 \pm 5\text{ cm}^{-1})$  and two  $\nu(\text{Pt} - \text{S})(340 \pm 5$  and  $325 \pm 7\text{ cm}^{-1})$ ,  $\nu(\text{Pd} - \text{S})(350$  and  $325\text{ cm}^{-1})$  are observed. Moreover,  $\text{P}\Phi_3$  molecule exhibit several bands in the far infrared spectral region<sup>36</sup>. So, mixing of  $\text{P}\Phi_3$  vibrations may not be ruled out.

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