

# LABILITY OF ORGANIC GROUPS IN THE REACTION OF 2-(2-PYRIDYL)PHENYL(P-ETHOXYPHENYL)TELLURIUM(II) WITH PALLADIUM (II) AND PLATINUM (II) CHLORIDES.

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## ABSTRACT

Reaction between 2-(2-pyridyl)phenyl(p-ethoxyphenyl)tellurium(II),  $RR'Te$ , and  $PdCl_2$  or  $PtCl_2$  are complex. The organic groups  $R$  and  $R'$  are labile, trans-metallation to form  $RM$ -groups ( $M=Pd, Pt$ ) occurs. The solid phases isolated have well defined stoichiometries, eg  $R'TePdCl$ ,  $R_2R'TePtCl_3$  and these are discussed together with IR,  $^1H$  and  $^{195}Pt$  NMR data.

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## INTRODUCTION

Mercury telluride is an important semi conductor with application in infra-red detection (Charlon 1982, Mullin & Irrine 1985). Photolysis of mixture of the organometallic compounds  $RHgTeR$  and  $RCdTeR$  can produce mercury cadmium telluride. Haris and Nissan (1987) prepared (t-butyl) $HgTe$ (t-butyl) and demonstrated that it produces a film of mercury telluride upon photolysis in the gas phase. The synthesis and crystal structure of 2-(2-pyridyl)phenyl (p-ethoxyphenyl)tellurium(II) have been

reported (Al – Salim *et al* 1988). Subsequently two papers describing the interactions of the telluride with  $HgCl_2$  and with copper salts were published (Mbogo and McWhinnie 1990, Mbogo and Lobana 1991)

Both papers established lability of organic groups from tellurium on reaction with metal compounds. In the case of  $HgCl$  (Mbogo & Mcwhinnie 1991) the reaction was clean:



(A)

(where  $R=2-(2-pyridyl)phenyl$  and  $R'=p-ethoxyphenyl$ )

An  $X$ -ray crystallographic investigation of (A) reveals six molecules in the unit cell  $2x(2RTeCl \cdot R'HgCl)$  but no significant intermolecular interactions are present (Mbogo *et al* 1992). With copper halides the reactions were much less clean but clear evidence for lability of organic groups was found (Mbogo and lobana 1991). Since (Pathirina & Mcwhirnie 1988) Kemnitz *et al* 1992) have also observed labilisation of tellurium bonded organic group when tellurides co-ordinate platinum(II) and considering the significance of the observed phenomenon in relation to Metal-Organic Chemical Vapour Deposition (MOCVD), it

was decided to extend studies of  $RR'Te$  co-ordination behavior to palladium(II) and platinum(II). The results of these investigations are briefly presented :

## MATERIALS AND METHODS

2-(2-pyridyl)phenyl(p-ethoxyphenyl)telluride,  $RR'Te$  and 2-(2-pyridyl) phenyltellurium (II) bromide,  $RTeBr$ , were prepared following the literature (Charlton 1982)

**Synthesis of palladium complexes.****Complex 1**

Palladium dichloride (0.09g, 0.5mmol) in acetonitrile (10cm<sup>3</sup>) was heated to reflux under nitrogen. RR'Te (0.2g, 0.5mmol) in acetonitrile (10cm<sup>3</sup>) was added. The mixture was cooled to room temperature and the contents of the flask were stirred for 15min. A dark brown compound separated out. The product was filtered, washed with acetonitrile and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to give compound (1) in 48 % yield, m.p 197-199 °C (dec)

**Complex 2**

2-(2-pyridyl)phenyltellurium(II)bromide, RTeBr (0.18g, 0.5mmol) in acetonitrile (10cm<sup>3</sup>) was added to a refluxing solution of palladium dichloride (0.09g, 0.5mmol) in acetonitrile (10cm<sup>3</sup>) under nitrogen. The reaction mixture was refluxed for 1hr. A brown precipitate formed which was separated, washed with acetonitrile and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to give compound (2) in 52% yield, m.p 245 – 247 ° C (dec)

**Synthesis of platinum complexes****Complex 3**

RR'Te (0.20g,0.5mmol) in acetonitrile (10cm<sup>3</sup>) was added to a refluxing solution of platinum dichloride (0.13g, 0.5mmol) in acetonitrile (10cm<sup>3</sup>) under nitrogen. The colour changed immediately to red. The mixture was stirred at room temperature for 30 min and filtered. Ethanol was added to the filtrate and a red precipitate formed which was filtered, washed with acetonitrile

and dried *in vacuo* to give compound (3) in 58% yield, m.p 210 – 211°C

**Complex 4**

RTeBr (0.18g, 0.5mmol) in acetonitrile (10cm<sup>3</sup>) was added under nitrogen, to refluxing platinum dichloride (0.13g, 0.5mmol) in acetonitrile (10cm<sup>3</sup>). The mixture was refluxed for 1h. The yellow precipitate was filtered and dried *in vacuo* over P<sub>4</sub>O<sub>10</sub> to give compound (4) in 52% yield, m.p 260 -261°C

**Physical measurements**

<sup>1</sup>H and <sup>125</sup>Te NMR spectra were determined with a bruker AC 300 MHZ spectrometer at 300 and 94.7MHZ, respectively. Tetramethyl silane was used as the reference for <sup>1</sup>H, for <sup>125</sup>Te the reference was bis – (p-ethoxyphenyl)ditelluride (external) in CDCl<sub>3</sub> which has δ =456 ppm w.r.t Me<sub>2</sub>Te, with respect to which all tellurium shifts are cited. <sup>195</sup>Pt NMR measurements were at 64.52 MHZ, the reference was aqueous Na<sub>2</sub>(PtCl)<sub>6</sub> (external).

Routine IR studies were on KBr discs with a Perkin Elmer 1710 FT-IR instrument. Melting points were determined with a Gallen Kamp electrically heated apparatus.

**RESULTS AND DISCUSSION**

The reaction of the ligand RR'Te (R = 2-(2-pyridyl)phenyl, R' = p-ethoxyphenyl) With palladium(II) and platinum(II) halides gave compounds with stoichiometrie's as shown in Table 1.

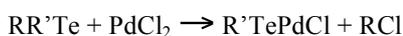
**Table 1:** Empirical formulae of complexes, analytical data and melting points

Complex	Empirical formula	Colour	Melting point °C	Found %			Calculated %		
				C	H	N	C	H	N
1	R'ClPdTe	Dark brown	197-199 (dec)	24.6	2.19	0.00	24.6	2.30	0.00
2	PdCl <sub>2</sub> (RTeBr) <sub>2</sub> MeCN	brown	245-247(dec)	28.9	1.95	3.65	28.4	1.89	3.79
3	R'TeCl.(RPtCl <sub>2</sub> ) <sub>2</sub>	red	210-211	32.0	2.7	2.42	32.0	2.23	2.49

4	PtCl <sub>2</sub> (R'TeBr) <sub>2</sub>	yellow	260-263	26.8	1.55	2.9	26.1	1.6	2.82
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### Palladium complexes

For the reaction of palladium dichloride with RR'Te, a coordination compound (1) is formed with complete loss of the (R = 2-(2-pyridyl)phenyl) group for tellurium as represented by the equation below:



This formulation is supported by IR, NMR and elemental analysis.

The infrared spectrum showed a single  $\gamma$  (Pd-Cl) at 339 cm<sup>-1</sup> comparative to that observed for [PdCl.RTe(CH<sub>2</sub>)<sub>8</sub>TeR](Pathirina & McWhinnie 1988).

The elemental analysis shows the % N to be "nil" hence formulation R'TePdCl, with no R groups. The HNMR spectrum in dime thyl sulphoxide (DMSO) reveals one environment for R' groups consistent with the formulation. The <sup>125</sup>Te NMR spectrum (DMSO) shows a single resonance at  $\delta = 1057.9$  ppm (cf. free ligand. (RR'Te), 649.1 ppm). This chemical shift is well outside the range reported in telluride (Irgolic *et al* 1983) In the compound (R'HgCl)(R'TeCl)<sub>2</sub> prepared by (Mbogo & McWhinnie) 1991), it was found that <sup>125</sup>Te NMR spectrum showed a single resonance at  $\delta = 1323.9$  ppm, a figure supporting the presence of R'TeCl species.

Interestingly, the <sup>125</sup>Te NMR spectrum of complex (2), a product formed from the reaction of RTeBr (R = 2-(2-pyridyl)phenyl) with PdCl<sub>2</sub> gave two resonances a major at  $\delta = 1315.7$  ppm typical of tellurenyl halide (Ahmed *et al* 1986), but a minor resonance  $\delta = 1297.7$  ppm is also noted. The two peaks are believed to be due to co-ordination by DMSO. It would thus appear that both R and R' are very labile in the presence of palladium(II) chloride.

### Platinum complexes

A similar pattern emerges as for palladium. Complex (3) is worth of specific comment since the C:N ration ( 15:4:1) is identical to that of the well defined reported material (R'TeCl)<sub>2</sub>( R'HgCl) (Mbogo & McWhinnie 1991).

The complex was sparingly soluble in CDCl<sub>3</sub>, a <sup>1</sup>H NMR spectrum was obtained (but not <sup>125</sup>Te or <sup>195</sup>Pt spectra due to limited solubility). The <sup>1</sup>HNMR spectrum of the complex in CHCl<sub>3</sub> shows broadening of the peaks in the aromatic region whereas the peaks in the alphatic region are well resolved and sharp. A triplet signal centered at  $\delta = 1.40$  ppm is assigned to -CH<sub>3</sub> protons and a quartet centered at  $\delta = 3.88$  ppm is assigned to - CH<sub>2</sub> protons.

In particular, two distinct resonances arising from the protons ortho to the pyridyl - nitrogen atoms were seen at  $\delta = 9.51$  and 9.98 ppm.

In summary, it appears that these very complex system created from the reaction of RR'Te with MCl<sub>2</sub> (M = Pd, Pt) involve labile organic groups (R'R) and trans-metallation to form RM-groups.

This observation highlights the potential usefulness of tellurides with particularly labile organic groups as precursors for the Metal Organic Chemical Vapour Deposition ( MOCVD) of both main group and transitional metal chalcogenides.

### ACKNOWLEDGMENTS

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