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The 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

Reactions 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, transmetallation to form RM- groups (M=Pd, Pt) occurs and the intermediacy of radical and/or M(III) species is likely. Some solid phases isolated have well defined stoicheiometries, e.g. R′TePdCl, $R_2R'TePt_2Cl_5$, $(RTeCl)_2MCL_2$, and these are discussed together with ^{1}H, ^{125}Te and ^{195}Pt NMR data. The use of forcing conditions produces phases with higher inorganic content suggesting that the solids isolated are intermediates in the passage to an ultimate phase, '$M_{3x}Te_{2x}Cl_{2x}$' (M=Pd, Pt).

Introduction

The synthesis and crystal structure of 2-(2′-pyridyl)phenyl(*p*-ethoxyphenyl)tellurium(II) have been reported [1]. Subsequently two papers describing the interaction of the telluride with $HgCl_2$ [2] and with copper salts [3] were published. Both papers established lability of organic groups from tellurium on reaction with the metal compounds. In the case of $HgCl_2$ [2] the reaction was clean:

$$2RR'Te + 2HgCl_2 \longrightarrow \underset{\mathbf{A}}{(RTeCl)_2 \cdot R'HgCl} + R'HgCl \qquad (1)$$

R = 2-(2′-pyridyl)phenyl–; R′ = *p*-ethoxyphenyl–

An X-ray crystallographic investigation of **A** reveals six molecules in the unit cell 2×(2 RTeCl, R′HgCl) but no significant intermolecular interactions are present [4].

With copper halides the reactions were much less clean but clear evidence for the lability of organic groups was found [3]. Since we [5] and others [6] have observed labilisation of tellurium bonded organic groups when tellurides coordinate platinum(II), it was decided to extend studies of RR′Te coordination behaviour to palladium(II) and platinum(II). The results of these investigations are briefly presented.

Experimental

2-(2′-Pyridyl)phenyl(*p*-ethoxyphenyl)telluride, RR′Te, 2-(2′-pyridyl)phenyltellurium(II) bromide, RTeBr, were prepared following the literature [1].

Palladium complexes (see Table 1 for numbering scheme)

Complexes 1 and 2

Palladium dichloride (0.09 g, 0.5 mmol) was treated with a mixture of ethanol (10 cm^3) and conc. hydrochloric acid (1 cm^3) and heated to reflux under dinitrogen. RR′Te (0.2 g, 0.5 mmol) in ethanol (10 cm^3) was added. A dark precipitate formed and the reaction mixture was refluxed for 15 min. Complex **1** was separated, washed with ethanol and dried *in vacuo*; m.p. 180 °C (dec.). An identical experiment with the second reflux period increased to 1.5 h afforded complex **2**; m.p. 254 °C (dec.).

Complexes 3–5

Palladium dichloride (0.09 g, 0.5 mmol) in acetonitrile (10 cm^3) was heated to reflux under dinitrogen. RR′Te (0.2 g, 0.5 mmol) in acetonitrile (10 cm^3) was added. The reaction mixture was subjected to one of three treatments, after which the solid was filtered, washed with ethanol and dried *in vacuo*:

(a) cooled to room temperature and stirred for 15 min, complex **3**, m.p. 197 °C (dec.)

(b) refluxed for 1 h, complex **4**, m.p. 285 °C (dec.)

(c) refluxed for 6 h, complex **5**, m.p. >300 °C. In this case the filtrate was evaporated to dryness to give a greenish yellow solid, m.p. 245 °C (dec.) for which

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C, 44.3; H, 2.82; N, 4.16%. This corresponds to palladated 2-phenylpyridine, i.e. $C_{11}H_8ClNPd$ requires: C, 44.6; H, 2.71; N, 4.72%.

*Complex **6***

2-(2′-Pyridyl)phenyltellurium(II) bromide, RTeBr (0.18 g, 0.5 mmol) in acetonitrile (10 cm^3) was added to a refluxing solution of palladium dichloride (0.09 g, 0.5 mmol) in acetonitrile under dinitrogen. The reaction mixture was refluxed for 1 h, the brown precipitate was then separated, washed with acetonitrile and dried *in vacuo*, m.p. 210 °C (dec.).

Platinum complexes (see Table 1 for numbering scheme)

Complexes 7 and 8

RR′Te (0.20 g, 0.5 mmol) in acetonitrile (10 cm^3) was added to a refluxing solution of platinum dichloride (0.13 g, 0.5 mmol) in acetonitrile under dinitrogen. The colour changed immediately to red. The mixture was stirred at room temperature for 30 min and filtered. Ethanol was added to the filtrate to precipitate a red powder, complex **7**, m.p. 210 °C (dec.). Refluxing the same reaction mixture for 3 h gave a brown solid which was separated, washed with ethanol and dried *in vacuo* — complex **8**, m.p. 265 °C.

Complex 9

RR′Te (0.20 g, 0.5 mmol) in ethanol (10 cm^3) was added to a refluxing solution of platinum dichloride (0.13 g, 0.5 mmol) in ethanol (10 cm^3) and conc. hydrochloric acid (1.6 cm^3) under dinitrogen. The mixture was refluxed for 1.5 h to give a red precipitate which was separated, washed with ethanol and dried *in vacuo*, m.p. 212 °C (dec.).

Complex 10

RTeBr (0.18 g, 0.5 mmol) in acetonitrile (10 cm^3) was added, under dinitrogen, to refluxing platinum dichloride (0.13 g, 0.5 mmol) in acetonitrile (10 cm^3). The mixture was refluxed for an additional hour to give a yellow material which was filtered, washed with acetonitrile and dried *in vacuo*, m.p. 260 °C (dec.).

Physical measurements

^1H and ^{125}Te NMR spectra were determined with a Bruker AC 300 MHz spectrometer at 300 and 94.7 MHz, respectively. Tetramethylsilane was used as the reference for ^1H. For ^{125}Te the reference was bis(*p*-ethoxyphenyl)ditelluride (external) in $CDCl_3$ which has $\delta = 456$ ppm with respect to Me_2Te with respect to which all tellurium shifts are cited. ^{195}Pt NMR measurements were at 64.52 MHz, the reference was aqueous $Na_2[PtCl_6]$ (external).

Routine IR studies were on KBr discs with a Perkin-Elmer 1710 FTIR instrument. Melting points (uncorrected) were determined with a Gallenkamp electrically heated apparatus.

Results and discussion

Analytical data for the materials described in this paper are gathered into Table 1. The empirical formulae cited represent a 'best fit' to the data and, with the exception of complexes **3**, **6**, **7** and **10** do not imply single phases.

Palladium complexes

Trends noted in the preparative work were as follows. When relatively mild preparative conditions were used to react RR′Te and $PdCl_2$, e.g. complex **3**, a single phase, R′TePdCl, precipitated from acetonitrile. From a different solvent medium, aqueous acid, even a 15 min reflux gives a product essentially the same as **3** but contaminated with a phase containing R, complex **1**. A longer reflux period in aqueous acid gives a product, complex **2**, with a greater proportion of R but which is also 'inorganic rich'. Similar trends are noted in acetonitrile but longer reflux periods produce solid phases which contain even greater proportions of R, e.g. complex **4**. A 6 h reflux produces an 'inorganic rich' material, complex **5**, which could be re-written (R′TePdCl) (RPdCl)($Pd_2Te_3Cl_2$). That RPdCl, i.e. *ortho*-palladated 2-phenylpyridine [7], may be implicated is supported by the isolation of this material from the filtrate of complex **5**.

The lability of the organic groups of the telluride, RR′Te, is again illustrated. Under mild conditions a relatively clean product is obtained (as was the case with $HgCl_2$ [2]) but prolonged reaction times produce complex products (cf. reactions with copper salts [3]) with the ratio of inorganic materials increasing with reaction time. If the driving force for the reaction in the case of $HgCl_2$ was provided in part by the stronger $Te \leftarrow N$ interaction in RTeCl than in RR′Te or the alternative product RHgCl, in the present case the stability of the *ortho*-palladated 2-phenylpyridine, RPdCl, may provide some of the thermodynamic incentive for the lability of the organic groups.

Of the complexes **1–5**, only complex **3** is monophasic. Examination of the ^1H NMR spectrum in dimethyl sulfoxide (dmso) solution reveals *two* environments for the R′ groups (one major, one minor; ratio approximately 6:1). Shielding differences between the two environments are slight. The ^{125}Te NMR spectrum of **3** in dmso shows a major resonance at $\delta = 1329.9$ ppm relative to Me_2Te, a poorly resolved shoulder is seen a few ppm to higher field. It is probable that R′TePdCl is polymeric in the solid state with a structure based on square planar palladium and bridging Cl and R′Te groups. Solubility in dmso is doubtless achieved by

TABLE 1. Empirical formulae[a] of complexes, and analytical data

Empirical formulae	No.	Anal. Found (calc.) (%)			Colour
		C	H	N	
$R'R_{0.016}ClPdTe$	**1**	25.5 (25.0)	2.19 (2.32)	0.06 (0.06)	dark brown
$R'R_{0.08}Cl_{1.33}Pd_{1.33}Te_{1.33}$	**2**	22.1 (21.7)	1.93 (1.96)	0.26 (0.24)	dark brown
$R'ClPdTe$	**3**	24.6 (24.6)	2.19 (2.30)	0.00 (0.00)	dark brown
$R'R_{0.57}ClPdTe$	**4**	35.3 (35.8)	2.68 (2.83)	1.65 (1.67)	dark brown
$R'_{0.5}RCl_{3.5}Pd_{3.5}Te_{3.5}$	**5**	14.3 (14.5)	0.95 (0.94)	1.32 (1.34)	black
$PdCl_2 \cdot (RTeBr)_2 \frac{1}{2}MeCN$	**6**	28.9 (29.4)	1.95 (1.89)	3.68 (3.79)	brown
$R'TeCl_3(RPtCl)_2$ $R'TeCl \cdot (RPtCl_2)_2$	**7**	32.0 (32.0)	2.70 (2.23)	2.42 (2.49)	red
$R'_7R_4Cl_9Pt_9Te_9$	**8**	26.3 (25.6)	1.68 (2.02)	1.23 (1.20)	brown
$R'_{28}R_{25}Cl_{35}Pt_{35}Te_{35}$	**9**	30.6 (30.3)	2.17 (2.28)	1.79 (1.77)	red–brown
$PtCl_2 \cdot (RTeBr)_2$	**10**	26.8 (26.7)	1.55 (1.60)	2.90 (2.82)	yellow

[a] R′ = *p*-ethoxyphenyl–, C_8H_9O; R = 2-(2′-pyridyl)phenyl–, $C_{11}H_8N$.

breaking of bridge bonds and coordination of dmso. The observation of two sets of NMR resonances is not consistent with a monomeric formulation e.g. [(R′Te)ClPd(dmso)$_2$] since *cis–trans* isomeric pairs would be expected to produce larger differences in ^{125}Te chemical shifts than those observed [8]. Clearly, the two R′Te environments must be very similar; the presence of oligomers terminating as shown in Fig. 1 provides a possible explanation. The environment of Te 2 is similar to that of 1 (given the similar electronegativies, O and Cl may have similar *trans*-influences), thus major differences in ^{125}Te and ^{1}H shielding would not be expected, however the R′Te groups are chemically and magnetically distinct. Alternative explanations can be based on the concept of 'invertomers', i.e. the relative configurations of the R′ groups in adjacent three-coordinate tellurium atoms [9]. Further speculation is not merited.

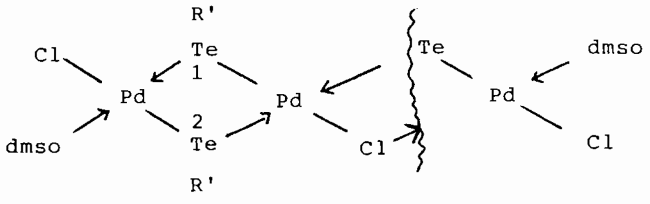

Fig. 1. Speculative structure for **3**.

The reaction of RR′Te with HgCl$_2$ gave an inclusion compound, (RTeCl)$_2$R′HgCl [2]. The ^{125}Te NMR chemical shift of **3** is not consistent with the presence of RTeCl but, to check, a reaction was carried out between PdCl$_2$ and the related RTeBr to give compound **6**: (PdCl)$_2$(RTeBr)$_2$·1MeCN. IR data support the presence of MeCN. The ^{125}Te NMR spectrum of the material in dmso shows a major resonance at $\delta = 1315.7$ ppm, typical of a tellurenyl halide [9], but a minor resonance $\delta = 1297.7$ ppm (versus Me$_2$Te) is also noted. Similar behaviour was noted for the tellurium(IV) compound chloro-*p*-ethoxyphenyl-2-(2′-pyridyl)phenyl tellurium(IV) trichloromercurate(II) [10] which, in dmso solution, gave two resonances at $\delta = 1056.4$ (major) and 1059.1 (minor) ppm although in this case the minor resonance was to lower field. It is possible that a similar explanation may serve in both cases, i.e. some displacement of Te N by Te dmso. The different directions of shifts for Te(II) and Te(IV) may repay further investigation, it is not clear for example if the same donor atom need be involved in the two cases. It is also interesting that the ability of RTeX(R = 2-(2′-pyridyl)phenyl) to form inclusion compounds appears general.

Although it is believed that compounds **2**, **4** and **5** are multiphases, examination of the ^{1}H NMR spectrum of **5** did reveal considerable broadening of the lines attributable to 2-(2′-pyridyl)phenyl- suggesting that a small concentration of paramagnetic species was present; this in turn may imply that the loss of organic groups from RR′Te could involve homolytic fission of C–Te bonds and the involvement of intermediate oxidation states of palladium.

Platinum complexes

A similar pattern emerges as for palladium. More forcing conditions afford multiphase systems although the 2-(2′-pyridyl)phenyl- group is now a more resistant component of the solid phase. Only complex **7** is worthy of specific comment since the C:N ratio (15.4:1) is identical to that of the well defined material $(RTeCl)_2(R'HgCl)$ [4] suggesting a stoicheiometry of $R_2R'TePt_2Cl_5$. The complex was sparingly soluble in $CDCl_3$, a ^1H NMR spectrum was obtained (but not ^{125}Te or ^{195}Pt spectra due to the limited solubility). Clean, sharp, signals arose from the *p*-ethoxyphenyl-group, but those attributable to the 2-(2′-pyridyl)phenyl-group were broad as noted for complex **5** above. The complex was more soluble in dmso, broadening of 2-(2′-pyridyl)phenyl- proton signals was again observed as was a considerable complication of the spectrum. In particular, two distinct resonances arising from the proton *ortho* to the pyridyl-nitrogen atom were seen at $\delta = 9.51$ and 9.98 ppm (versus TMS), also the *p*-ethoxyphenyl- resonances were double. It was possible to obtain ^{195}Pt NMR data for the dmso solutions of **7** both 3 and 24 h after dissolution of the complex. Data are given in Table 2. The simultaneous presence of four platinum species supports the ^1H NMR observations that several species co-exist. After 24 h, as many as six platinum containing species are seen.

The ^{195}Pt chemical shift range is large [11]; Pt(IV) may resonate at both higher and lower fields than the reference, aqueous $Na_2[PtCl_6]$. Of the six platinum environments present after 24 h, only one ($\delta = 2798$ ppm) is unambiguously associated with tellurium. The satellite peak main peak area ratios suggest the coupling is to a single Te atom. Pt(IV) coupling constants are usually about 0.67 of the corresponding Pt(II) value [12]; Pt(II) Te coupling constants in related systems have been noted around 1014 Hz [5], hence the value of 748 Hz in Table 2 is compatible with a Pt(IV) species. The other resonances may be from both Pt(IV) and Pt(II). Given the possible intermediacy of paramagnetic species (^1H NMR data), e.g. Pt(III), following Waltz and co-workers [13] it is speculated that such species disproportionate to Pt(II) and Pt(IV) compounds.

TABLE 2. ^{195}Pt NMR data for dmso solution of complex **7** after 3 and 24 h

(ppm) vs. $Na_2[PtCl_6]$ (all shifts upfield)	
dmso/3 h	dmso/24 h
2612	2611
	2597w
	2650w
2798	2798(J(Pt–Te) = 748 Hz)
2954(m)	2954(s)
2957(s)	2957(m)

In summary, it appears that these very complex systems created from the reaction of RR′Te with MCl_2 (M = Pd, Pt) involve labile organic groups (R, R′), transmetallation to form RM– groups, and the possible intermediacy of radicals (R centred) and/or M(III). Under these circumstances it is not surprising that the solid phases are, in general, neither single, nor representative of an equilibrium situation. The materials isolated in Table 1 can in a sense be seen as intermediates towards the synthesis of inorganic phase '$M_{3x}Te_{2x}Cl_{2x}$'. In this context a recent observation of Steigerwald and co-workers is of interest [14]. Organometallic intermediates were used to produce NiTe but intermediates (well defined) $Ni_{20}Te_{18}(PEty)_{12}$ and $Ni_9Te_6(PEty)_8$ were isolated.

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