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Platinum(II) Complexes with Aryl Tellurols and Diaryl Ditellurides: Syntheses and Spectral Investigations

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Abstract

Aryltellurol complexes $[PtCl(TeAr)(PPh_3)_2]$ (I) and $[Pt(TeAr)_2(PPh_3)_2]$ (II) are readily obtained from *cis*-$[PtCl_2(PPh_3)_2]$ and NaTeAr (Ar = C_6H_5, 4-$CH_3OC_6H_4$ and 4-$CH_3CH_2OC_6H_4$) in ethanol–benzene at room temperature. ^{31}P NMR spectra of I and II indicate their *trans* configuration in solution. Metathetical reactions between I (Ar = 4-CH_3-OC_6H_4) and NaX (X = I, Br, SCN) occur in methanol to give $[Pt(X)(TeC_6H_4OCH_3\text{-}4)(PPh_3)_2]$. ^{1}H NMR shows that equimolar proportions of NaTe-C_6H_5, $NaTeC_6H_4OCH_2CH_3$-4 and *cis*-$[PtCl_2(PPh_3)_2]$ give a mixture of three complexes: II, Ar = C_6H_5; II, Ar = 4-$CH_3CH_2OC_6H_4$; and $[Pt(TeC_6H_5)(TeC_6H_4\text{-}OCH_2CH_3\text{-}4)(PPh_3)_2]$. Polymeric complexes $[PtCl(TeAr)]_n$ (III) and $[Pt(TeAr)_2]_n$ (IV) result from reaction between $K_2[PtCl_4]$ and NaTeAr in aqueous ethanol. They react with excess of PPh_3 in $CDCl_3$ to yield monomeric complexes I and II respectively which were characterised *in situ* by ^{1}H and ^{31}P NMR of the reaction mixtures. IR spectra indicate the presence of bridging chloride ligands in III. An alternating chloride and tellurol bridged chain structure for III and a tellurol bridged one for IV have been proposed. Reaction between equimolar amounts of III and PPh_3 in dichloromethane yielded a tellurol bridged dimeric complex $[PtCl(\mu\text{-}TeAr)(PPh_3)]_2$ (V) with terminal chloride ligand as suggested by IR study. Ethanolic solutions of diarylditellurides also react readily with an aqueous solution of $K_2[PtCl_4]$ at 10 °C to give complexes for which the structure *trans*-$[PtCl_2(ArTeTeAr)_2]$ (VI) is suggested from their elemental analyses, IR, Raman (in one case only), ^{1}H, ^{125}Te (in one case only), and ^{195}Pt NMR spectra and reactions with triphenylphosphine which liberated free ditellurides. At 40 °C or above the same ditellurides form polymeric complexes III with $K_2[PtCl_4]$ in aqueous ethanol.

Introduction

The coordination chemistry of ArS^- (Ar = aryl) or RS^- (R = alkyl) has been extensively explored [1, 2]. The incorporation of these species in the coordination sphere of transition metal ions in conjunction with several donors has resulted in novel structures in which the thiol groups are present as terminal or bridging ligands. Some of such complex species also have interesting catalytic properties. The ligation of tellurium analogues of thiols, called tellurols, has received little attention so far and this has stemmed our interest in them. The tellurols are generally obtained *in situ* by reductive cleavage of the Te–Te bond of the ditellurides and therefore it was also thought worthwhile to study the complexation of their precursor ditellurides as it may assist in planning the synthetic strategies for the tellurol–metal complexes. In the present paper the results of our investigations on the complexation of aryltellurols and their precursor diaryl ditellurides with platinum(II) are reported.

Experimental

$K_2[PtCl_4]$ (Aldrich Chemicals) and *cis*-$[PtCl_2(PPh_3)_2]$ (Strem Chemicals) were commercially available. The diaryl ditellurides, Te_2Ar_2 (Ar = C_6H_5, 4-$CH_3OC_6H_4$ and 4-$CH_3CH_2OC_6H_4$) were prepared by published methods [3–5]. Their purities were checked by melting points (m.p.), elemental analyses and ^{1}H NMR.

Melting points were recorded in open capillary tubes and are uncorrected. IR and Raman spectra were recorded either in the solid state as CsI pellets or in Nujol mull between CsI plates. ^{1}N NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solutions on a JEOL FX 100 FT instrument with TMS as an internal standard. ^{125}Te and ^{195}Pt NMR spectra were recorded in DMSO on a JEOL FX 90Q FT instrument with diphenyltelluride and potassium hexachloroplatinate respectively as external references. ^{31}P NMR spectra were recorded in $CDCl_3$ solution on a JEOL 500 MHz FT instrument, H_3PO_4 being used as an external reference. Conductance was measured in acetonitrile or DMF solution using

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a high sensitive PYE Conductance Bridge (Model No. 11700).

Solvents were dried and distilled before use. All reactions were carried out under an atmosphere of dry oxygen–free nitrogen.

Preparation of $[Pt(TeAr)_2(PPh_3)_2]$ *and* $[PtCl(TeAr)(PPh_3)_2]$ *(Ar =* C_6H_5*,* $4\text{-}CH_3OC_6H_4$ *and* $4\text{-}CH_3CH_2OC_6H_4$*)*

The appropriate ditelluride, Te_2Ar_2 (0.50 mmol) was dissolved in ethanol at room temperature and a solution of $NaBH_4$ in ethanol was added dropwise to it under stirring. The red colour of the ditelluride quickly faded due to the formation of NaTeAr. Borohydride addition was stopped when the reduction was complete which was indicated by the pale yellow (completely free from any tinge of red) colour of the solution. A suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.50 mmol) in benzene (30 ml) was added to the tellurolate solution all at one go. Stirring was continued for 6 h during which the *cis*-$[PtCl_2(PPh_3)_2]$ dissolved to give a clear brown solution. It was filtered (celite) to remove the NaCl formed and any unreacted platinum complex. The clear filtrate, thus obtained, was evaporated to dryness under reduced pressure to give a brown solid. It was dissolved in the minimum amount of chloroform and poured into 200 ml of a mixture of petroleum ether and ether (1:1, *v/v*) under rapid stirring. The product separated in the form of microscopic crystals. It was dried *in vacuo*.

The complexes $[PtCl(TeAr)(PPh_3)_2]$ were similarly prepared using 1:1 molar ratios of NaTeAr with *cis*-$[PtCl_2(PPh_3)_2]$.

Preparation of $[Pt(X)(TeC_6H_4OCH_3\text{-}4)(PPh_3)_2]$ *(X = I, Br and SCN)*

A suspension of $[PtCl(TeC_6H_4OCH_3\text{-}4)(PPh_3)_2]$ (0.2 g) in methanol (100 ml) was treated with an excess of NaX (0.2 g) and the mixture stirred at room temperature for 24 h. The solid obtained after removal of the solvent was treated with dichloromethane (30 ml) and a little charcoal. It was filtered (celite) and the filtrate concentrated under low pressure. Addition of n-pentane precipitated the product, which was dried *in vacuo.*

Attempted preparation of $[Pt(TeC_6H_5)(TeC_6H_4OCH_2CH_3\text{-}4)(PPh_3)_2]$

A benzene suspension of *cis*-$[PtCl_2(PPh_3)_2]$ (0.40 mmol) was added to a mixture of $NaTeC_6H_5$ (0.20 mmol) and $NaTeC_6H_4OCH_2CH_3\text{-}4$ (0.20 mmol) in ethanol and stirred for 6 h at room temperature. The product was isolated as in the case of the bis(tellurol) complexes. TLC using ethanol/benzene showed it to be a mixture of three complexes.

Preparation of $[PtCl(TeAr)]_n$ *(Ar =* C_6H_5*,* $4\text{-}CH_3OC_6H_4$ *and* $4\text{-}CH_3CH_2OC_6H_4$*)*

An aqueous solution of $K_2[PtCl_4]$ (2 mmol) was mixed with an ethanolic solution of NaTeAr (2 mmol), prepared in the same way as described for the preparation of $[Pt(TeAr)_2(PPh_3)_2]$ complexes, and the mixture stirred at room temperature for 4 h. A dark brown solid was obtained. It was separated by filtration, washed with water, ethanol and ether and dried in air.

Preparation of $[Pt(TeAr)_2]_n$ *(Ar =* C_6H_5*,* $4\text{-}CH_3OC_6H_4$ *and* $4\text{-}CH_3CH_2OC_6H_4$*)*

These were prepared in the same way as $[PtCl(TeAr)]_n$ except that $K_2[PtCl_4]$ and NaTeAr were taken in 1:2 molar ratios.

Reactions between $[PtCl(TeC_6H_4OCH_3\text{-}4)]_n$ *and* PPh_3

A mixture of $[PtCl(TeC_6H_4OCH_3\text{-}4)]_n$ (0.1 g) and an excess of PPh_3 (0.15 g) was shaken with $CDCl_3$ (2 ml) for 6 h. Most of the solid dissolved to give a red solution which was used to record a ^{31}P NMR spectrum. The presence of a single platinum complex (^{31}P NMR parameters: δ 13.01 ppm, $^1J(Pt-P)$ 3030 Hz) together with free PPh_3 ($-\delta$ 7.03 ppm) was indicated by the spectrum. The complex was identified as *trans*-$[PtCl(TeC_6H_4OCH_3\text{-}4)(PPh_3)_2]$ from a comparison of its ^{31}P NMR parameters with those of an authentic sample of the pure complex.

A mixture of $[PtCl(TeC_6H_4OCH_3\text{-}4)]_n$ (0.1 g) and PPh_3 (0.056 g) in stoichiometric amount (1:1 ratio) in dichloromethane (25 ml) was vigorously stirred for 6 h at room temperature. The clear solution thus obtained was treated with a large volume of ether–petroleum ether (1:1) mixture when a solid separated out. It was washed with the same mixture, dried *in vacuo* and characterised as $[PtCl(\mu\text{-}TeC_6H_4OCH_3\text{-}4)(PPh_3)]_2$.

Reaction between $[Pt(TeC_6H_4OCH_2CH_3\text{-}4)_2]_n$ *and* PPh_3

$[Pt(TeC_6H_4OCH_2CH_3\text{-}4)_2]_n$ (0.03 g) and PPh_3 (0.03 g) were shaken in 2 ml of $CDCl_3$ for 6 h and a ^1H NMR spectrum of the resulting solution was recorded. The spectrum showed sharp signals for the $-OCH_2CH_3$ group [δ 3.99 (q, $J = 7$ Hz, 2H, CH_2), 1.40 (t, $J = 7$ Hz, 3H, CH_3)] which indicated the formation of $[Pt(TeC_6H_4OCH_2CH_3\text{-}4)_2(PPh_3)_2]$ from a comparison of its ^1H NMR parameters (see Table II).

Preparation of $[PtCl_2(ArTeTeAr)_2]$ *(Ar =* C_6H_5*,* $4\text{-}CH_3OC_6H_4$ *and* $4\text{-}CH_3CH_2OC_6H_4$*)*

The appropriate ditelluride (2 mmol) was dissolved in ethanol at 10 °C and the solution was slowly added to an aqueous solution of $K_2[PtCl_4]$ (1 mmol) at the same temperature. A red–brown solid formed almost immediately after mixing the reactants. The mixture was stirred at 10 °C for 2 h and the solid was separated. It was washed with ice-cold water, cold alcohol and cold ether and dried *in vacuo*.

The same reactants at 40 °C or above gave mostly the polymeric complexes $[PtCl(TeAr)]_n$ which were isolated pure after successive washing with water, alcohol and chloroform.

Reaction between $[PtCl_2(ArTeTeAr)_2]$ *and* PPh_3

$[PtCl_2(ArTeTeAr)_2]$ (Ar = 4-$CH_3OC_6H_4$ or 4-$CH_3CH_2OC_6H_4$) (0.1 g) was stirred with an excess of PPh_3 (0.1 g) in diethylether (50 ml) for 1 h at room temperature. The ether solution had turned red by this time. It was filtered and the clear filtrate thus obtained was evaporated to dryness to give a red solid. ^1H NMR of this solid in $CDCl_3$ showed it to be a mixture of Te_2Ar_2 and PPh_3. Ditelluride was also detected *in situ* from a reaction mixture of the two reactants in $CDCl_3$ by ^1H NMR.

Results and Discussion

The yields, colour, decomposition temperature and analytical data of all the isolated complexes have been tabulated in Table I. Complexes **I** and **II**

TABLE I. Characterisation Data of Platinum(II) Complexes

Complex	Yield (%)	Colour	Decomposition temperature (°C)	Analysis (%)[a]		
				C	H	Te
$[PtCl(TeC_6H_5)(PPh_3)_2]$	55	yellow	158	52.3 (52.5)	3.6 (3.6)	12.8 (13.3)
$[PtCl(TeC_6H_4OCH_3\text{-}4)(PPh_3)_2]$	52	yellow	160	51.8 (52.2)	3.6 (3.6)	12.6 (12.9)
$[PtCl(TeC_6H_4OCH_2CH_3\text{-}4)(PPh_3)_2]$	47	yellow	145	52.2 (52.6)	3.7 (3.8)	11.9 (12.7)
$[Pt(TeC_6H_5)_2(PPh_3)_2]$	57	brown	132	50.8 (51.0)	3.5 (3.5)	21.7 (22.6)
$[Pt(TeC_6H_4OCH_3\text{-}4)_2(PPh_3)_2]$	48	brown	137	50.2 (50.5)	3.6 (3.7)	21.0 (21.5)
$[Pt(TeC_6H_4OCH_2CH_3\text{-}4)_2(PPh_3)_2]$	52	brown	130	51.4 (51.3)	3.8 (3.9)	20.4 (21.0)
$[PtBr(TeC_6H_4OCH_3\text{-}4)(PPh_3)_2]$	40	yellow–brown	188	49.5 (49.7)	3.6 (3.5)	[b]
$[PtI(TeC_6H_4OCH_3\text{-}4)(PPh_3)_2]$	45	brown	175	47.6 (47.7)	3.3 (3.4)	[b]
$[Pt(SCN)(TeC_6H_4OCH_3\text{-}4)(PPh_3)_2]$[c]	47	yellow–brown	164	51.7 (52.1)	3.5 (3.7)	[b]
$[PtCl(TeC_6H_5)]_n$	60	dark brown	230	17.0 (16.6)	1.2 (1.2)	[b]
$[PtCl(TeC_6H_4OCH_3\text{-}4)]_n$	53	dark brown	210	18.1 (18.1)	1.5 (1.5)	[b]
$[PtCl(TeC_6H_4OCH_2CH_3\text{-}4)]_n$	65	dark brown	225	20.1 (20.0)	2.0 (1.9)	[b]
$[Pt(TeC_6H_5)_2]_n$	59	dark brown	220	23.6 (23.8)	1.5 (1.6)	[b]
$[Pt(TeC_6H_4OCH_3\text{-}4)_2]_n$	62	dark brown	225	24.9 (25.3)	1.9 (2.1)	[b]
$[Pt(TeC_6H_4OCH_2CH_3\text{-}4)_2]_n$	68	dark brown	218	26.6 (27.3)	2.3 (2.6)	[b]
$[PtCl(TeC_6H_4OCH_3\text{-}4)(PPh_3]_2$	51	brownish orange	197	40.4 (41.2)	2.9 (3.0)	[b]
$[PtCl_2(Te_2(C_6H_5)_2)_2]$	68	red–brown	168	26.7 (26.6)	1.8 (1.8)	46.2 (47.0)
$[PtCl_2(Te_2(C_6H_4OCH_3\text{-}4)_2)_2]$	52	red–brown	200	27.8 (27.9)	2.3 (2.3)	41.2 (42.4)
$[PtCl_2(Te_2(C_6H_4OCH_2CH_3\text{-}4)_2)_2]$	63	red–brown	220	29.3 (30.4)	2.7 (2.8)	39.1 (40.5)

[a] Calculated values are given in parentheses. [b] Tellurium was not estimated. [c] Found N: 1.3%, calc. N: 1.4%.

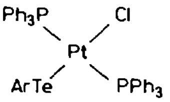
TABLE II. ^1H NMR Spectra[a] of Complexes $[PtCl(TeAr)(PPh_3)_2]$ (I) and $[Pt(TeAr)_2(PPh_3)_2]$ (II)

Complex	δ(aromatic H) (ppm)	δ(CH_2) (ppm)	δ(CH_3) (ppm)
I Ar = C_6H_5	6.30–7.74(m)		
I Ar = $4\text{-}CH_3OC_6H_4$	6.37–7.64(m)		3.75(s)
I Ar = $4\text{-}CH_3CH_2OC_6H_4$	6.52–7.70(m)	4.03(q, J = 7Hz)	1.37(t, J = 7Hz)
II Ar = C_6H_5	6.32–7.72(m)		
II Ar = $4\text{-}CH_3OC_6H_4$	6.47–7.27(m)		3.85(s)
II Ar = $4\text{-}CH_3CH_2OC_6H_4$	6.55–7.71(m)	3.99(q, J = 7Hz)	1.40(t, J = 7Hz)

[a] Recorded in $CDCl_3$, s = singlet, t = triplet, q = quartet, m = multiplet.

are soluble in common organic solvents except petroleum ether and diethylether. They are stable for several months at room temperature in the solid state. Conductance measurements in acetonitrile showed their non-electrolyte nature. Elemental analyses agree well with their formulations.

IR spectra (Nujol mull) showed one ν(Pt–Cl) band in I (Ar = C_6H_5, 295 cm^{-1}; Ar = $4\text{-}CH_3OC_6H_4$, 293 cm^{-1}; Ar = $4\text{-}CH_3CH_2OC_6H_4$, 293 cm^{-1}) and none in II. ^1H NMR spectra of these complexes (Table II) showed all the expected peaks in the proper intensity ratio. Thus the complex II, Ar = $4\text{-}CH_3OC_6H_4$ showed only a single methoxy resonance with intensity ratio 3:19 to the aromatic protons. This established the equivalence of all aryl groups in the complex and its molecular stoichiometry and excluded the possibility occurring of both terminal and bridged tellurol ligands simultaneously as expected for the dimeric formulation $Pt_2(TeC_6H_4\text{-}OCH_3\text{-}4)_4(PPh_3)_2$. $^{31}P\{^1H\}$ NMR spectra (in $CDCl_3$ solution, H_3PO_4 as external reference) of both I, Ar = $4\text{-}CH_3OC_6H_4$, (δ 13.07 ppm, ^1J(Pt–P) 3030 Hz) and II, Ar = C_6H_5, (δ 9.63 ppm, ^1J(Pt–P) 3161 Hz) showed a single ^{31}P resonance associated with platinum satellites (approximately 1:4:1 triplet structure). This indicated the equivalence of the two phosphorus atoms in the complexes. The coupling constant ^1J(Pt–P) is of the order of 3000 Hz characteristic of a *trans*-$Ph_3P\text{–}Pt\text{–}PPh_3$ system [6–8]. This suggested the *trans* configuration of these complexes.



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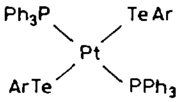
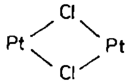


II

Metathetical reactions between I, Ar = $4\text{-}CH_3\text{-}OC_6H_4$, and anionic ligands X^- (X = I, Br, SCN) occurred in MeOH to give complexes $[Pt(X)(TeAr)\text{-}(PPh_3)_2]$. IR spectra (Nujol mull) of these complexes showed the absence of the ν(Pt–Cl) band, but a strong ν(C–N) band at 2096 cm^{-1} and a medium intensity ν(C–S) band at 822 cm^{-1} appeared for the thiocyanate derivative indicating the presence of the Pt–NCS link [9] in this complex. Elemental analyses (Table I) were satisfactory for all the three derivatives.

In an attempt to prepare the mixed tellurol complex $[Pt(TeC_6H_5)(TeC_6H_4OCH_2CH_3\text{-}4)(PPh_3)_2]$ the reaction was carried out using the reactants $NaTeC_6H_5$, $NaTeC_6H_4OCH_2CH_3\text{-}4$ and *cis*-$[PtCl_2(PPh_3)_2]$ in 1:1:1 molar proportions. After the usual work up (see 'Experimental') a brown solid was isolated which was indicated by TLC (C_6H_6/EtOH) to be a mixture of three compounds. The IR spectrum of the solid (Nujol) showed the absence of ν(Pt–Cl) bands indicating the displacement of both the chloride ligands by tellurol groups. ^1H NMR in $CDCl_3$ showed two sets of OCH_2CH_3 resonances one of which was identified for the complex II, Ar = $4\text{-}CH_3\text{-}CH_2OC_6H_4$. The other may be most reasonably assumed to originate from the mixed tellurol complex $[Pt(TeC_6H_5)(TeC_6H_4OCH_2CH_3\text{-}4)(PPh_3)_2]$. Since the total concentration of the two tellurolate ligands was double that of the *cis*-$[PtCl_2(PPh_3)_2]$, it is inferred that the complex II, Ar = C_6H_5, was also formed in the reaction.

Polymeric tellurol complexes III and IV were prepared from reactions between $K_2[PtCl_4]$ and NaTeAr (Ar = C_6H_5, $4\text{-}CH_3OC_6H_4$ and $4\text{-}CH_3CH_2\text{-}OC_6H_4$). These are insoluble in all common organic solvents including DMF and DMSO. Far IR spectra of complexes III in the solid state as CsI pellets (Table III) showed ν(Pt–Cl) bands in the region 300–249 cm^{-1} characteristic for bridging chloride ligands [10] while complexes IV displayed no ν(Pt–Cl) bands. A polymeric chain structure having alternate chloride and aryltellurol bridges (Fig. 1) is tentatively suggested for III. The large difference between the sizes of the chloride and aryltellurol ligands favours the alternating chloride and tellurol bridges. (The complex $[PdCl(SC_6H_5)]_n$ also has alternating chloride and thiol bridges [11].) The occurrence of more than two ν(Pt–Cl) bands in the complexes may be due to either Cl^{37} isotope effect or non planarity of



units.

TABLE III. ν(Pt–Cl) Bands for Complexes $[PtCl(TeAr)]_n$ (III)

Complex	(Pt–Cl) (cm^{-1})[a]
III Ar = C_6H_5	290(sh), 283(ms), 249(m)
III Ar = 4-$CH_3OC_6H_4$	298(m), 282(m), 270(ms), 259(w), 251(w)
III Ar = 4-$CH_3CH_2OC_6H_4$	300(m), 290(m), 281(ms), 272(w), 249(ms)

[a] Recorded in the solid state as CsI pellets.

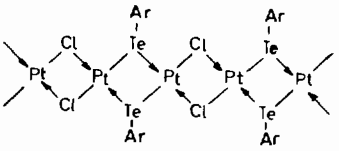


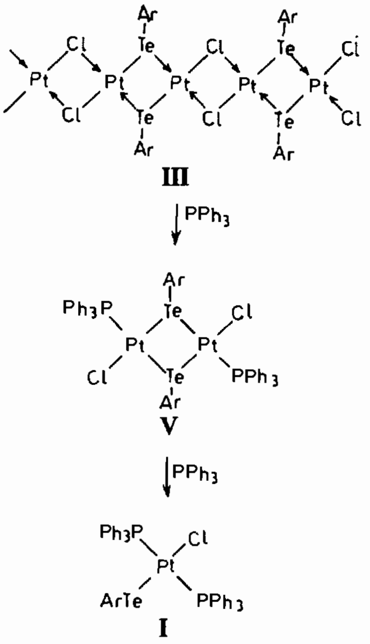
Fig. 1. Suggested structure of complex III.

Reaction between III, Ar = 4-$CH_3OC_6H_4$, and an excess of triphenylphosphine in $CDCl_3$ yielded the soluble monomeric complex *trans*-$[PtCl(TeC_6H_4OCH_3\text{-}4)(PPh_3)_2]$ which was characterised *in situ* by ^{31}P NMR of the reaction mixture from a comparison of the ^{31}P NMR parameters of the resulting complex (δ 13.01 ppm, ^1J(Pt–P) 3030 Hz) with those of complex I, Ar = 4-$CH_3OC_6H_4$, described earlier. However, the complex III, Ar = 4-$CH_3OC_6H_4$, with PPh_3 in 1:1 molar ratio yielded the product V which showed a ν(Pt–Cl) vibration (at 319 cm^{-1}) suggestive of the presence of terminal chloride ligands rather than the bridging ones.

Hence the formation of *trans*-$[PtCl(TeC_6H_4OCH_3\text{-}4)(PPh_3)_2]$ from the reaction between III, Ar = 4-$CH_3OC_6H_4$, and an excess of PPh_3 may be explained by Scheme 1 in which it is evident that PPh_3 first splits the chloride bridges to give an aryltellurol-bridged dimer which then with more PPh_3 yields the monomeric complex by cleavage of the tellurol bridges.

Complexes IV similarly react with excess of PPh_3 to give monomeric complexes II. Formation of II, Ar = 4-$CH_3CH_2OC_6H_4$, from IV, Ar = 4-$CH_3CH_2OC_6H_4$, and an excess of PPh_3 was demonstrated by ^1H NMR (see 'Experimental'). A polymeric chain structure with aryl tellurol bridges may be most reasonably assumed for these complexes.

The diarylditellurides, Te_2Ar_2 (Ar = C_6H_5, 4-$CH_3OC_6H_4$ and 4-$CH_3CH_2OC_6H_4$) reacted with $K_2[PtCl_4]$ in aqueous ethanol at 10 °C to give red–brown solids whose elemental analyses showed the molecular stoichiometry $PtCl_2\cdot(Te_2Ar_2)_2$ (VI). The red–brown colour of the complexes strongly suggests that the tellurium–tellurium bond has survived the complex forming reaction. The presence of the



Scheme 1. Suggested mechanism for the formation of I from reaction between III and PPh_3 (excess).

diarylditelluride ligands in these complexes was confirmed by their reaction with triphenylphosphine in diethylether which liberated the free ditellurides.

Far IR spectra of complexes VI in Nujol mull showed a strong ν(Pt–Cl) band in the region 338–350 cm^{-1} (Ar = C_6H_5, 338 cm^{-1}; Ar = 4-$CH_3OC_6H_4$, 338 cm^{-1}; Ar = 4-$CH_3CH_2OC_6H_4$, 350 cm^{-1}). The occurrence of only one ν(Pt–Cl) band is characteristic for the *trans* configuration of the complexes and the observed values are in the range expected for two terminal chlorine atoms *trans* to each other in platinum(II) complexes [12]. The diphenyl ditelluride complex showed a strong band at 260 cm^{-1} which has been assigned following the literature report to ν(Te–C_6H_5) and a weak band at 175 cm^{-1} for ν(Te–Te) [13]. In the Raman spectrum of the complex ν(Te–Te) appeared as a strong band at 170 cm^{-1}. Complexes VI with Ar = 4-$CH_3OC_6H_4$ and 4-$CH_3CH_2OC_6H_4$ also showed ν(Te–Te) absorption bands at 190 and 185 cm^{-1} respectively in their far IR spectra but the samples decomposed on exposure to laser radiation and hence their Raman spectra could not be recorded.

^1H NMR spectra (DMSO-d_6, 25 °C) of complexes VI (Ar = 4-$CH_3OC_6H_4$ and 4-$CH_3CH_2OC_6H_4$) showed the presence of two different types of aryl groups in them [Ar = 4-$CH_3OC_6H_4$, δ 6.77–7.92 (m, 8H, aromatic H), 3.75 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3); Ar = 4-$CH_3CH_2OC_6H_4$, δ 6.76–7.93 (m, 8H, aromatic H), 3.99 (q, J = 7 Hz, 2H, OCH_2), 4.01 (q, J = 7 Hz, 2H, OCH_2), 1.30 (t, J = 7 Hz, 3H, CH_3),

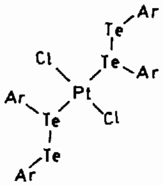


Fig. 2. Proposed structure for complexes **VI**.

1.34 (t, $J = 7$ Hz, 3H, CH_3)]. Thus the complex **VI**, Ar = 4-$CH_3OC_6H_4$, showed two sharp signals of equal intensity for OCH_3 and the complex **VI**, Ar = 4-$CH_3CH_2OC_6H_4$, showed two sets of equal intense signals for OCH_2CH_3 group. ^{125}Te NMR (DMSO, 25 °C) of the complex **VI**, Ar = C_6H_5, also showed two signals ($-\delta$ 0.60 and 57.97 ppm w.r.t. diphenyl telluride) indicating the non-equivalence of the two tellurium atoms in the complex (the platinum satellites, however, were not resolved due to the weak nature of the spectrum). That the samples were not really a mixture of two platinum complexes was verified by recording their ^{195}Pt NMR in DMSO (K_2PtCl_6 in D_2O as standard) which gave only a single ^{195}Pt resonance for each of the complexes (Ar = C_6H_5, $-\delta$ 3548.9; Ar = 4-$CH_3OC_6H_4$, $-\delta$ 3805.8; Ar = 4-$CH_3CH_2OC_6H_4$, $-\delta$ 3776.8 ppm).

The low solubility of the complexes in suitable organic solvents precluded their molecular weight determination but analytical and spectral evidences strongly suggest that they have the structure shown in Fig. 2. The non-electrolyte nature (DMF) of the complexes eliminated the possibility of any ionic structure. These complexes add more examples for the monodentate behaviour of ditelluride ligands in their coordination complexes with transition metals previously reported [14]. It is worth mentioning that we failed to isolate the dimeric complexes using even 1:1 molar ratio of $K_2[PtCl_4]$ with Te_2Ar_2. The diaryl ditellurides, however, reacted with $K_2[PtCl_4]$ in aqueous ethanol at 40 °C or higher temperatures to give polymeric complexes **III** in good yields. This reaction seems to be analogous to the reaction of $Na_2[PdCl_4]$ with $S_2(C_6H_5)_2$ in methanol which yielded the polymeric complex $[PdCl(SC_6H_5)]_n$ [11].

^{31}P{^{1}H} NMR spectra of complex **I** (Ar = C_6H_5 and 4-$CH_3CH_2OC_6H_4$) recorded later indicated that in both cases ^{31}P chemical shifts were split by both platinum and tellurium and are in the correct order of intensity. The parameters are: **I**, Ar = C_6H_5, (δ 15.27 ppm, ^1J(Pt–P) 3066 Hz, ^2J(Te–P) 2992 Hz) and Ar = 4-$CH_3CH_2OC_6H_4$, (δ 15.03 ppm, ^1J(Pt–P) 3057 Hz, ^2J(Te–P) 2983 Hz). The ^2J(Te–P) values are reported here for the first time.

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