

Synthesis and Characterization of Palladium(II) Complexes with Aryl Tellurols and Diaryl Ditellurides

BISHAN L. KHANDELWAL*, KALIPADA KUNDU and SUSHIL K. GUPTA

Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India

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Abstract

Polymeric complexes of formula $[\text{PdCl}(\text{TeAr})]_n$ (I) and $[\text{Pd}(\text{TeAr})_2]_n$ (II) are readily obtained by the reaction between $\text{Na}_2[\text{PdCl}_4]$ and NaTeAr ($\text{Ar} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{OCH}_3$ -4 and $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4) in ethanol at room temperature. Chemical and far infrared spectral evidences support alternating chloride and tellurol bridges in I and tellurol bridges in II. While the reaction of I ($\text{Ar} = \text{C}_6\text{H}_4\text{OCH}_3$ -4) with PPh_3 in stoichiometric amount results in splitting of chloride bridges and formation of a tellurol bridged dimeric complex $[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_3\text{-4})(\text{PPh}_3)]_2$ (III), with excess of PPh_3 , cleavage of both chloride and tellurol bridges leads to the formation of a monomeric compound $[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_3\text{-4})(\text{PPh}_3)_2]$ (IV). Furthermore, the reaction of I ($\text{Ar} = \text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4) with 1,2-bis(diphenyl phosphino)ethane in equimolar ratio also resulted in a monomeric compound $[(\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{-4})(\text{di-phos}))]$ (V). The complex III ($\text{Ar} = \text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4) is also prepared by the reaction between $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Ph}_3\text{Sn}-\text{TeC}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4 in 1:1 molar ratio or between $\text{Pd}_2\text{Cl}_4(\text{PPh}_3)_2$ and $\text{Ph}_3\text{Sn}-\text{TeC}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4 in 1:2 molar ratio in benzene at room temperature. Sodium tetrachloropalladate reacts readily with diarylditellurides in ethanol at 0 °C to form dimeric complexes $[\text{PdCl}_2(\text{ArTeTeAr})]_2$ (VI). However, at 40 °C or above the same ditellurides form polymeric complexes I with $\text{Na}_2[\text{PdCl}_4]$ in ethanol. The complex VI is also obtained by the reaction of $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ with Te_2Ar_2 in benzene at room temperature. The complexes were characterized by elemental analysis, IR, Raman and ^1H NMR spectra and, where possible, by conductivity measurements and molecular weight determinations.

Introduction

Pt(II) complexes with aryl tellurols and diaryl ditellurides have been recently reported by us [1].

* Author to whom correspondence should be addressed.

Dimeric complexes of palladium(II) containing both bridging and terminal tellurol ligands have been reported by Chia and McWhinnie [2] and polymeric complexes(II) with only tellurol bridges by Gardner *et al.* [3, 4]. The present work reports the synthesis and bridge-splitting reactions of new polymeric complexes of palladium(II) containing alternating chloride and tellurol bridges (I) and an alternate method for the preparation of II. We also report here some new palladium(II) complexes which add to the few known examples where ditelluride coordinates with transition metals keeping the Te–Te bond intact [5–11].

Experimental

$\text{Na}_2[\text{PdCl}_4]$, $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ (Aldrich Chemicals) and 1,2-bis(diphenylphosphino)ethane (Fluka Chemicals) were commercially available. The diaryl ditellurides, Te_2Ar_2 ($\text{Ar} = \text{C}_6\text{H}_5$, $\text{C}_6\text{H}_4\text{OCH}_3$ -4 and $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4), were prepared by published methods [12–14]. Their purity was checked by melting points, elemental analyses and ^1H NMR. Organotriphenylstannyl tellurium(II) ($\text{Ar} = \text{C}_6\text{H}_4\text{-OCH}_2\text{CH}_3$ -4) was prepared and purified by the literature method [3].

Melting points were recorded in open capillary tubes and are uncorrected. IR spectra were recorded on a Nicolet 5DX FT instrument either in the solid state as CsI pellets or in Nujol mull between CsI plates. Far IR ($450\text{--}50\text{ cm}^{-1}$) and Raman spectra ($40\text{--}1040\text{ cm}^{-1}$) using argon ion laser at 5145 Å with 100 MW power were obtained from RSIC, I.I.T., Madras. ^1H NMR spectra were recorded in CDCl_3 or DMSO-d_6 solutions on a Jeol FX100 FT instrument with TMS as an internal standard. Conductance was measured in acetonitrile and DMF solutions using a high sensitive PYE conductance bridge (Model No. 11700) and molecular weights were determined in chloroform using a Knauer vapour pressure Osmometer (Model No. 11.00). Elemental analyses were done on Perkin-Elmer 240C rapid analyser.

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

Preparation of [PdCl(TeAr)]_n (I) (Ar = C₆H₅, C₆H₄OCH₃-4 and C₆H₄OCH₂CH₃-4)

The appropriate Te₂Ar₂ (0.50 mmol) was dissolved in ethanol at room temperature and a solution of NaBH₄ in ethanol was added dropwise to it under stirring. The red colour of the ditelluride quickly faded due to the formation of NaTeAr. Sodium borohydride addition was stopped when the reduction was complete as indicated by the pale yellow (completely free from any tinge of red) colour of the solution. A clear solution of Na₂[PdCl₄] (1 mmol) in ethanol was added to the telluroate solution all at once and the mixture stirred for 4 h. A dark brown solid was obtained. It was separated by filtration, washed with water, ethanol and ether, and dried *in vacuo*.

Preparation of [Pd(TeAr)₂]_n (II) (Ar = C₆H₅, C₆H₄OCH₃-4 and C₆H₄OCH₂CH₃-4)

These were prepared in the same way as [PdCl(TeAr)]_n (I) except that Na₂[PdCl₄] and NaTeAr were taken in 1:2 molar ratio.

Preparation of [PdCl(TeAr)(PPh₃)]₂ (III) (Ar = C₆H₄OCH₃-4 and C₆H₄OCH₂CH₃-4)

Method a

A 300 mg sample of [PdCl(TeC₆H₄OCH₃-4)]_n suspended in 40 ml of dichloromethane was treated with the stoichiometric amount of PPh₃ (1:1 ratio) and the mixture was kept under vigorous stirring 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 and dried *in vacuo*.

Method b

To a benzene solution of Ph₃Sn—TeC₆H₄OCH₂CH₃-4 (1 mmol) was added solid Pd(PPh₃)₂Cl₂ (1 mmol) and the clear solution obtained after mixing for some time was stirred overnight. A brownish yellow suspension thus obtained was centrifuged. It was washed with benzene and diethyl ether and its purity was checked by TLC.

Method c

Solid Ph₃Sn—TeC₆H₄OCH₂CH₃-4 (2 mmol) was added to a benzene solution of Pd₂Cl₄(PPh₃)₂ (1 mmol) and stirred until a clear solution was obtained. It was then left overnight when a solid separated out. It was centrifuged, washed with benzene and diethyl ether and its purity was checked by TLC.

Preparation of [PdCl(TeC₆H₄OCH₃-4)(PPh₃)₂] (IV)

A 250 mg sample of [PdCl(TeC₆H₄OCH₃-4)]_n was treated with an excess of PPh₃ in dichloromethane (40 ml) and the solution was stirred vigorously for 6 h. The clear solution thus obtained was concentrated and then treated with petroleum ether (40–60 °C) when a solid separated out. It was washed successively with petroleum ether and diethyl ether and dried *in vacuo*.

Preparation of [PdCl(TeC₆H₄OCH₂CH₃-4)(dipho)] (V)

A 200 mg sample of [PdCl(TeC₆H₄OCH₂CH₃-4)]_n suspended in 40 ml of dichloromethane was treated with the stoichiometric amount of 1,2-bis(diphenylphosphino) ethane (1:1 ratio) and the mixture was stirred for 4 h. To the clear solution thus obtained was added a large volume of diethyl ether and a greenish yellow product was isolated. It was washed thoroughly with ether and dried *in vacuo*.

Preparation of [PdCl₂(ArTeTeAr)]₂ (VI) (Ar = C₆H₅, C₆H₄OCH₃-4 and C₆H₄OCH₂CH₃-4)

Method a

A clear solution of Te₂Ar₂ (1 mmol) in ethanol was slowly added to another clear solution of Na₂—[PdCl₄] (1 mmol) in the same solvent at 0 °C and the mixture was stirred for 2 h at the same temperature. The material separated on keeping 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 [PdCl(TeAr)]_n (I) which were isolated pure after successive washings with water, alcohol and chloroform.

The same product VI was obtained on mixing the ligand to metal ions in a 2:1 molar ratio.

Method b

Solid Te₂Ar₂ (1 mmol) was added to a clear solution of Pd(PhCN)₂Cl₂ (1 mmol) in benzene at room temperature. The brown suspension which appeared immediately after addition was stirred for 6 h. The red—brown solid was filtered, washed with benzene and diethyl ether and dried *in vacuo*.

The reactants with higher ditelluride concentration also yielded the same product.

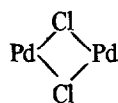
Reaction between [PdCl₂(ArTeTeAr)]₂ and PPh₃

An excess of PPh₃ in diethyl ether (50 ml) was added to [PdCl₂(ArTeTeAr)]₂ (Ar = C₆H₄OCH₃-4 or C₆H₄OCH₂CH₃-4) (0.1 g) and the suspension stirred for 1 h at room temperature. The ether solution 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 in CDCl₃ showed it to be a mixture of Te₂Ar₂ and

PPh_3 . Ditetelluride was also detected *in situ* from a reaction mixture of the two reactants in CDCl_3 by ^1H NMR.

Results and Discussion

The yields, colours, decomposition temperatures and analytical data of all the isolated complexes are given in Table I. The complexes I obtained from reaction between $\text{Na}_2[\text{PdCl}_4]$ and NaTeAr are insoluble in most common organic solvents. Their elemental analyses correspond to the empirical formula $[\text{PdCl}(\text{TeAr})]$. IR spectra in the solid state as CsI pellets (Table II) exhibit bands in the range $300\text{--}245\text{ cm}^{-1}$ which are typical of Pd–Cl bridging stretching frequencies [15]. The occurrence of more than two $\nu(\text{Pd}\text{--}\text{Cl})$ bands in the complexes may be due to either Cl^{37} isotope effect or non-planarity of



units. A polymeric chain structure having alternate chloride and aryl tellurol bridges (Fig. 1) is tentatively suggested for I. The large difference between the sizes of the chloride and aryl tellurol ligands favours the alternating chloride and tellurol bridges. (The complex $[\text{PdCl}(\text{SC}_6\text{H}_5)]_n$ also has alternating chloride and thiol bridges [16].) In order to characterize the complexes, bridge-splitting reactions with mono and bidentate neutral ligands were carried out. The reaction of I ($\text{Ar} = \text{C}_6\text{H}_4\text{OCH}_3\text{--}4$) with PPh_3 in 1:1 molar ratio afforded the complex of formula $[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_3\text{--}4)(\text{PPh}_3)]_2$ (III), consistent with its molecular weight measurement. Complex III ($\text{Ar} = \text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{--}4$) has also been synthesized by the reaction between $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Ph}_3\text{Sn}\text{--}\text{TeC}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{--}4$ (1:1) or between $\text{Pd}_2\text{Cl}_4(\text{PPh}_3)_2$ and $\text{Ph}_3\text{Sn}\text{--}\text{TeC}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{--}4$ (1:2) in benzene.

TABLE I. Characterization Data of Palladium(II) Complexes

Complex	Yield (%)	Colour	Decomposition temperature (°C)	Analysis ^a (%)				Molecular weight ^c
				C	H	Cl	Te	
$[\text{PdCl}(\text{TeC}_6\text{H}_5)]_n$	66	dark brown	130	21.1 (20.7)	1.4 (1.4)	10.7 (10.2)	^b	
$[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_3\text{--}4)]_n$	56	dark brown	138	22.0 (22.3)	1.8 (1.8)	9.8 (9.4)	^b	
$[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{--}4)]_n$	69	dark brown	134	24.4 (24.5)	2.2 (2.3)	8.4 (9.0)	^b	
$[\text{Pd}(\text{TeC}_6\text{H}_5)_2]_n$	59	dark brown	146	27.7 (27.9)	1.8 (1.9)		^b	
$[\text{Pd}(\text{TeC}_6\text{H}_4\text{OCH}_3\text{--}4)_2]_n$	62	dark brown	135	29.0 (29.1)	2.4 (2.4)		^b	
$[\text{Pd}(\text{TeC}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{--}4)_2]_n$	68	dark brown	140	31.7 (31.8)	2.8 (2.9)		^b	
$[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_3\text{--}4)(\text{PPh}_3)]_2$	50	brownish orange	169	46.6 (46.9)	3.6 (3.4)	5.0 (5.5)	19.4 (19.9)	1310 (1277)
$[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{--}4)(\text{PPh}_3)]_2$	65	yellow	160	47.6 (47.8)	3.6 (3.6)	5.0 (5.4)	19.1 (19.5)	1285 (1305)
$[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_3\text{--}4)(\text{PPh}_3)_2]$	58	yellow	178	57.5 (57.3)	4.3 (4.1)	3.6 (3.9)	14.4 (14.1)	
$[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{--}4)(\text{diphos})]$	61	greenish yellow	128	51.4 (51.7)	3.9 (4.1)	4.0 (4.4)	15.7 (16.1)	820 (789)
$[\text{PdCl}_2(\text{Te}_2(\text{C}_6\text{H}_5)_2)]_2$	60	red–brown	170	24.3 (24.5)	1.6 (1.7)	11.6 (12.1)	42.6 (43.5)	1199 (1173)
$[\text{PdCl}_2(\text{Te}_2(\text{C}_6\text{H}_4\text{OCH}_3\text{--}4)_2)]_2$	54	brown	162	26.3 (25.9)	2.1 (2.1)	10.2 (10.9)	38.6 (39.4)	1340 (1293)
$[\text{PdCl}_2(\text{Te}_2(\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{--}4)_2)]_2$	48	brown	140	28.7 (28.4)	2.6 (2.6)	10.0 (10.5)	37.1 (37.8)	1410 (1349)

^aCalculated values are given in parentheses. ^bTellurium was not estimated. ^cMolecular weights were determined in CHCl_3 .

TABLE II. $\nu(\text{Pd}-\text{Cl})$ Bands for Complexes $[\text{PdCl}(\text{TeAr})]_n$ (I)

Complex	$\nu(\text{Pd}-\text{Cl})^a$ (cm^{-1})
I (Ar = C_6H_5)	290(w), 281(s), 266(sh), 246(sh)
I (Ar = $4\text{-CH}_3\text{OC}_6\text{H}_4$)	292(w), 285(w), 268(m), 255(s), 247(sh)
I (Ar = $4\text{-CH}_3\text{CH}_2\text{OC}_6\text{H}_4$)	300(w), 292(w), 280(m), 267(w), 247(ms)

^aRecorded in the solid state as CsI pellets; s = strong, sh = shoulder, m = medium, w = weak.

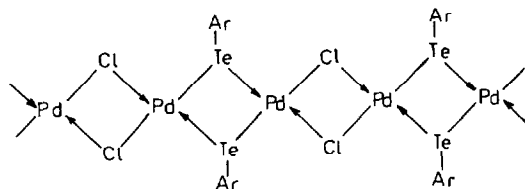
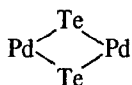
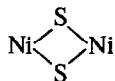


Fig. 1. Suggested structure for complexes I.

IR spectra showed $\nu(\text{Pd}-\text{Cl})$ vibrations (III, Ar = $\text{C}_6\text{H}_4\text{OCH}_2\text{-4}$, 306 cm^{-1} ; Ar = $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{-4}$; 304 cm^{-1}) suggestive of the presence of terminal chloride ligands rather than bridging ones. A dimeric structure with tellurol bridging and PPh_3 in the *trans* position was assumed as the most probable one, at least in the solid state, on the basis of the $\nu(\text{Pd}-\text{Cl})$ vibration and the structures of complexes of type $\text{Pd}_2\text{L}_2\text{X}_4$ (with L neutral ligand, X = Cl, Br) for which X-ray investigations have shown the *trans* configuration [17]. This also suggests that like thiol bridges, the tellurol bridges between two Pd atoms are quite resistant to cleavage. The occurrence of a bent

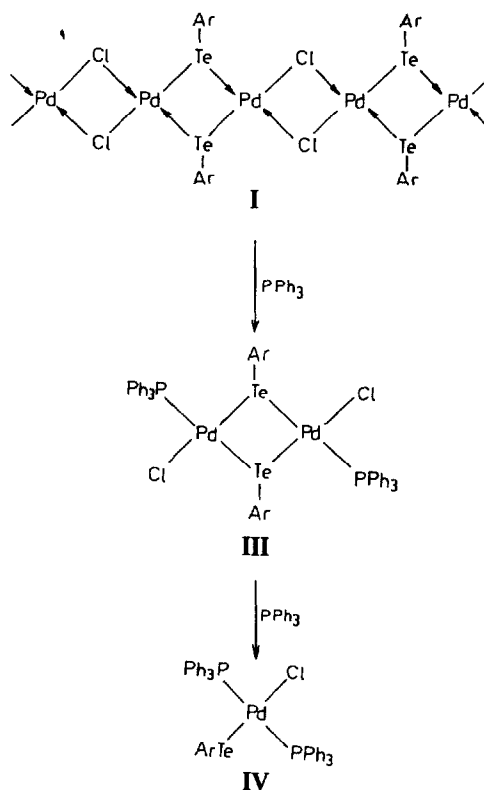


unit is not surprising since an X-ray structure of a Ni^{II} complex with thiolato bridges [18] confirms the presence of bent



units.

The reaction of I (Ar = $\text{C}_6\text{H}_4\text{OCH}_3\text{-4}$) with excess of PPh_3 gives *trans*- $[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_3\text{-4})(\text{PPh}_3)_2]$ (IV) which has been characterized by elemental analysis, an IR spectrum ($\nu(\text{Pd}-\text{Cl}) = 302\text{ cm}^{-1}$) typical for Cl *trans* to Te ligands [19] and ^1H NMR (CDCl_3 , 25°C , $\delta 6.26\text{--}7.68$ (m, aromatic H), 3.76 (s, 3H, CH_3)). Conductance measurements in acetonitrile showed its non-electrolytic nature.

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

Hence the formation of *trans*- $[\text{PdCl}(\text{TeAr})(\text{PPh}_3)_2]$ (IV, Ar = $\text{C}_6\text{H}_4\text{OCH}_3\text{-4}$) from the reaction between I (Ar = $\text{C}_6\text{H}_4\text{OCH}_3\text{-4}$) 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 the tellurol bridged dimer III which then with more PPh_3 yields the monomeric complex IV by cleavage of the tellurol bridges.

Further evidence for the cleavage of the chloride and tellurol bridges has been observed when I (Ar = $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{-4}$) reacted with diphos in a 1:1 molar ratio to yield a chelated complex $[\text{PdCl}(\text{TeC}_6\text{H}_4\text{OCH}_2\text{CH}_3\text{-4})(\text{diphos})]$ (V) (Fig. 2). The infrared spectrum of V exhibits $\nu(\text{Pd}-\text{Cl})$ at 296 cm^{-1} consistent with a Cl *trans* to phosphine [20]. The complex is soluble in chloroform and dichloromethane and its molecular weight is consistent with the above formulation.

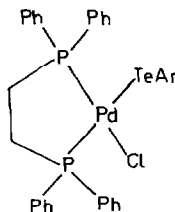


Fig. 2. Proposed structure for V.

TABLE III. ^1H NMR^a Spectra of Complexes $[\text{PdCl}_2(\text{ArTeTeAr})]_2$ (VI)

Complex	$\delta(\text{aromatic H})$ (ppm)	$\delta(\text{CH}_2)$ (ppm)	$\delta(\text{CH}_3)$ (ppm)
VI (Ar = C_6H_5)	7.30–7.67(m)		
VI (Ar = $4\text{-CH}_3\text{OC}_6\text{H}_4$) ^c	6.68–7.84(m) ($J = 8.5$ Hz)		3.71(s)
VI (Ar = $4\text{-CH}_3\text{CH}_2\text{OC}_6\text{H}_4$)	6.95–7.45(m) ($J = 8.8$ Hz)	4.03(q) ($J = 7$ Hz)	1.31(t) ($J = 7$ Hz)

^aRecorded in CDCl_3 except in c where it is DMSO-d_6 ; s = singlet, t = triplet, q = quartet, m = multiplet.

The reaction of $[\text{Pd}(\text{TeAr})_2]_n$ with PPh_3 is very slow and resulted in a dimeric species of the type $[\text{Pd}(\text{TeAr})_2(\text{PPh}_3)]_2$ (Ar = $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4), as reported by earlier workers [2]. This dimer was found to be inactive on further treatment with PPh_3 and no monomeric species could be formed.

The diarylditelluride Te_2Ar_2 reacted with $\text{Na}_2[\text{PdCl}_4]$ in ethanol at 0°C to yield red-brown or brown complexes VI. Although earlier workers [2] failed, the same product could be obtained by reaction between Te_2Ar_2 and $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ in benzene at room temperature. Their elemental analyses corresponded to the empirical formula $[\text{PdCl}_2(\text{ArTeTeAr})]$. The possibility of any ionic structure is eliminated by their conductance measurements in DMF which showed their non-electrolytic nature. Molecular weight measurements in chloroform suggested a dimeric species in solution (Fig. 3). The red to brown colour of the products strongly suggests that the tellurium-tellurium bond has survived the complex forming reactions. The presence of the ditelluride ligands in the complexes was confirmed by their reaction with PPh_3 in diethyl ether which gave the free ditelluride. IR spectra indicated two $\nu(\text{Pd}-\text{Cl})$ bands (Ar = C_6H_5 : 292, 277 cm^{-1} ; Ar = $\text{C}_6\text{H}_4\text{OCH}_3$ -4: 301, 285 cm^{-1} ; Ar = $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4: 296, 283 cm^{-1}) which favour the *cis*-configuration of the complexes. The observed $\nu(\text{Pd}-\text{Cl})$ values are also typical for Cl *trans* to Te ligands [19]. Complexes VI (Ar = C_6H_5 and $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4), for which far IR were recorded up to 50 cm^{-1} , also showed $\nu(\text{Te}-\text{Te})$ (170 and 175 cm^{-1} respectively) and $\nu_{\text{as}}(\text{Te}-\text{C}_6\text{H}_5)$ (261 cm^{-1}) bands. (For $\text{Te}_2(\text{C}_6\text{H}_5)_2$, $\nu(\text{Te}-\text{Te})$ and $\nu_{\text{as}}(\text{Te}-\text{C}_6\text{H}_5)$ are at 167 and 255 cm^{-1} respectively

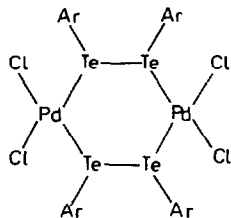


Fig. 3. Proposed structure for complexes VI.

[21].) In the Raman spectrum of the complex VI (Ar = C_6H_5) $\nu(\text{Te}-\text{Te})$ (168s cm^{-1}), $\nu_s(\text{Te}-\text{C}_6\text{H}_5)$ (196m cm^{-1}) and $\nu_{\text{as}}(\text{Te}-\text{C}_6\text{H}_5)$ (256w cm^{-1}) bands were observed. Complexes VI (Ar = $\text{C}_6\text{H}_4\text{OCH}_3$ -4 and $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4) decompose on exposure to laser radiation and hence their Raman spectra could not be recorded. All complexes showed the absence of $\nu(\text{Ph}-\text{CN})$ bands which favours the facile replacement of benzonitrile in the initial palladium complex. ^1H NMR spectra of complexes VI (Ar = $\text{C}_6\text{H}_4\text{OCH}_3$ -4 and $\text{C}_6\text{H}_4\text{OCH}_2\text{CH}_3$ -4) (Table III) showed the equivalence of all aryl groups in the complex. Thus a dimeric structure with two PdCl_2 moieties bridged by two molecules of ditelluride is reasonably proposed for complexes VI. (The complex, $[\text{PdCl}_2(\text{S}_2\text{Ph}_2)]_2$ has also a dimeric structure with disulphide bridges [16].)

It may be noted that the addition of Te_2Ar_2 to $\text{Na}_2[\text{PdCl}_4]$ in ethanol at 40°C or above gives polymeric complexes I in good yields. This reaction seems to be analogous to the reaction of $\text{Na}_2[\text{PdCl}_4]$ with $\text{S}_2(\text{C}_6\text{H}_5)_2$ in methanol which yielded the polymeric complex $[\text{PdCl}(\text{SC}_6\text{H}_5)]_n$ [16].

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