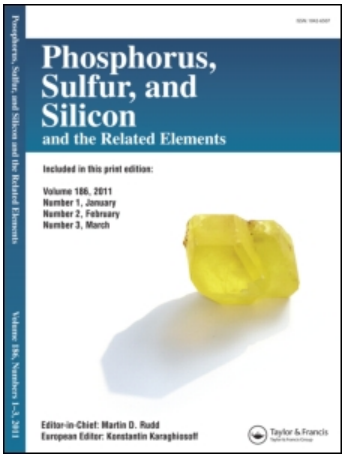

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A NOVEL DITELLUROETHER LIGAND $ArTeCH_2CH(OH)CH_2TeAr$ (Ar = 4-$CH_3OC_6H_4$) AND ITS COMPLEXATION BEHAVIOR

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A NOVEL DITELLUROETHER LIGAND $ArTeCH_2CH(OH)CH_2TeAr$ (Ar = 4-$CH_3OC_6H_4$) AND ITS COMPLEXATION BEHAVIOR

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$ArTe^-$ generated *in situ* by borohydride reduction of Ar_2Te_2 (Ar = 4-$CH_3OC_6H_4$) reacts readily with $ClCH_2CH(OH)CH_2Cl$ resulting in the formulation of $ArTeCH_2CH(OH)CH_2TeAr$(**1**) which forms complexes of stoichiometry MCl_2.**1** (where M = Hg(II), Pd(II) and Pt(II)). The presence of the OH signal and the deshielding of aryl and CH_2 protons in ^1H NMR spectra of these complexes suggest that only two tellurium atoms coordinate with the metal atoms. **1** partially dissociates out from Hg(II) complex as evidenced by complicated aryl signals of the ligand in its ^1H NMR. $^{125}Te\{^1H\}$ NMR spectra of Pd(II) and Pt(II) complexes have two signals. This in conjunction with the splitting of aryl doublets in their ^1H NMR spectra suggest that *dl* and *meso* invertomers of both these complexes coexist in solution. The red shift (~10 cm^-) in ν(Te—CH_2) and ν[Te—C(aryl)] further supports the ligation of **1** through tellurium atoms. Attempts to synthesize $[Pd(\mathbf{1})_2](ClO_4)_2$, $[Pd(\mathbf{1})(ArTeCH_2COO)]ClO_4$ and $[Pd(\mathbf{1})(Ph_2PCH_2CH_2PPh_2)](ClO_4)_2$ by reacting $[PdCl_2.\mathbf{1}]$ with an appropriate second ligand in presence of $AgClO_4$ did not succeed, but resulted in elemental tellurium, Ar—Ar and $CH_2{=}CH{-}CH_2OH$.

Key words: Ditelluroether; palladium(II); platinum(II); complexation.

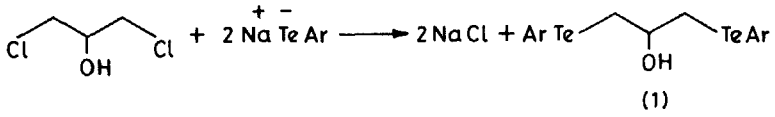
INTRODUCTION

The coordination chemistry of tellurium ligands has been little investigated in comparison with their sulphur and selenium analogues.[1–3] There currently exists a greater interest in organotellurium chemistry and its applications in organic synthesis,[4] nuclear medicine,[5] photography[6] and new conducting materials.[7] Multidentate organotellurium ligands including those which contain other donor atoms along with tellurium are less studied[3] than the monodentate ones. The rich ligand chemistry of $R_2P(CH_2)_nPR_2$ (R = alkyl or aryl) where $n \geq 1$ and diverse applications of their metal-complexes have aroused interest in the chemistry of their tellurium analogues, *viz*, $RTe(CH_2)_nTeR$ ($r \geq 1$). Such derivatives can be easily synthesized[8] by the reaction between the dihalide $X(CH_2)_nX$ and RTe^-Na^+, when n = 1, 5, 6, 7, 8 or 9. For n = 2, 3 or 4 either olefin R_2Te_2 or telluronium salts were obtained in such a reaction. We have observed that a ligand having two tellurium atoms separated by three carbons, $ArTeCH_2CHOHCH_2TeAr$(**1**) (where Ar = 4-$MeOC_6H_4$) may be synthesized by reacting $ClCH_2CHOHCH_2Cl$ with $ArTe^-Na^+$. Compound **1** ligates through two tellurium atoms and OH remains inactive. The results of these investigations are reported in the present paper.

RESULTS AND DISCUSSION

1,3-Dichloro-2-propanol reacts with $ArTe^-$ (Ar = 4-$MeOC_6H_4$) generated *in situ* by borohydride reduction of Ar_2Te_2 according to Equation (1). However, yield of

1 was only <20%.

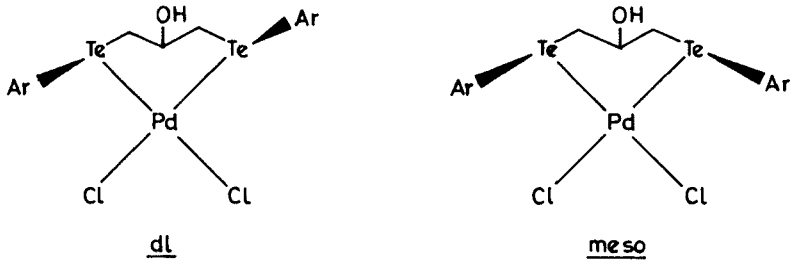


(1)

(1)

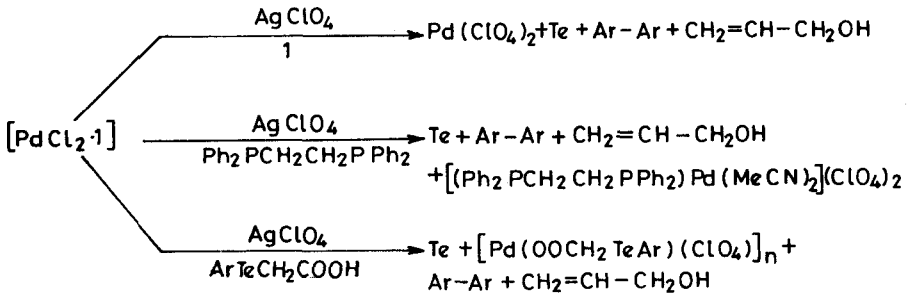
Attempts to raise it by increasing the time of reflux up to ~15 h and changing the ratio of reactants did not succeed. The presence of chloroform in solid **1** was supported by its TGA which has four overlapping steps. The first is slowest and starts at 135°C (heating rate 10°C/min). The total weight loss observed is ~65% at 500°C and does not differ from the value 61% (residual elemental Te) expected if 1 mole of chloroform is presumed to be present with 1 mole of **1**. Compound **1** does not give crystals suitable for x-ray work, therefore further confirmation of the amount of $CHCl_3$ could not be made. In ^1H NMR spectra of **1** the OH, CH and CH_2 signals appear shielded (~1.3, 0.2 and 0.7, respectively) with respect to those of the precursor dichloride. Tellurium is much less electronegative than chlorine and has been shown to shield the carbon linked to it. Therefore the present shielding effect on CH_2 signals when chlorine atoms are substituted by ArTe groups is not unreasonable. The hydrogen of OH is probably engaged in an intra molecular hydrogen bond in the precursor dichloride of **1** which breaks down on the formation of **1** resulting in a shielded OH signal. The presence of ν(Te—CH_2) and ν(Te—C(aryl)) at 325 and 280, 288 cm^{-1}, respectively in the IR spectra[12] of **1** further gives evidence for its formation. The synthesis of an analogue of **1** in which Ar = 4-$EtOC_6H_4$ was carried out to see whether yield increases with the change in Ar group. However, the improvement was found to be marginal (5–8%). In ^1H NMR of **1** CH signal merges with that of OCH_3 but the spectra of its ethoxy analogue clearly depicts CH signal at δ 3.6–3.7 ppm (multiplet) and CH_2 at δ 3.0 ppm (doublet), whereas other signals in the spectra are at δ, 1.4 (t, 3H, CH_3 of Et), 4.0 (q, 2H, OCH_2), 6.8–6.9 (d, 2H, ArH *ortho* to Te) and 7.6–7.7 (d, 2H, ArH *meta* to Te). These observations further authenticate the synthesis of **1** ^{13}C NMR spectrum[13] of **1** also supports its formation in the reaction 1.

Compound **1** readily forms complexes of the type MCl_2.**1** (where M = Hg(II), Pd(II) or Pt(II)) which were found to be air stable and moisture insensitive. The mercury complex exhibits good solubility in DMSO only, whereas Pd(II) and Pt(II) complexes are reasonably soluble in CH_3CN and acetone. These complexes in the solid state may be stored for 2–3 months but in their solutions the elemental tellurium begins to deposit after one week. In acetonitrile all these complexes behave as non-electrolytes. ^1H NMR data in conjunction with the results of elemental analyses support the stoichiometries of these complexes. The TGA of palladium complex does not exhibit separately the loss of chloroform but 55% weight loss giving $PdCl_2$ + Te finally cannot be accounted without considering its presence. After taking into account the solvent effects, the deshielding of CH_2 (except for Hg) and phenyl signals (~0.2, 0.4–0.6 ppm, respectively for Hg and Pd/Pt complexes) in the ^1H NMR spectra of these complexes with respect to those of ligand **1** is not negligible. The OH signal has been observed in ^1H NMR of all these complexes. These observations suggest that probably the two tellurium atoms of **1** ligate with the metal ions. In ^1H NMR spectra of palladium and platinum com-



plexes each signal of the two phenyl doublets is also a doublet, suggesting the presence of both *dl* and *meso* invertomers in solution. The phenyl signals in ^1H NMR spectra of mercury complex appear as multiplet which may be considered as composed of four doublets. The positions of two of them are very close to those of free ligand **1** and the other two appear deshielded with respect to the aryl signals of **1**. This observation suggests that the complex decomposes in solution. In the $^{125}Te\{^1H\}$ NMR spectra of palladium and platinum complexes recorded in acetonitrile and acetone, respectively, weak signals appear probably due to their low solubility. However, the presence of two signals at 525 and 560 ppm in the spectrum of palladium complex supports the presence of *dl* and *meso* invertomers in the solution, respectively. The $^{125}Te\{^1H\}$ NMR spectrum of $PtCl_2.\mathbf{1}$ also has two signals at 505 and 545 ppm due to the presence of *dl* and *meso* invertomers, respectively. In the IR spectra of these complexes ν(Te—C(aryl)) and ν(Te—CH_2) appear with a red shift of the order 10 cm^{-1}. The ν(Pt—Cl) appears as a doublet at 390 cm^{-1} as expected for two *cis* chlorines. The ν(Pd—Cl) appears at 360 cm^{-1}. However ν(Hg—Cl) could not be unequivocally assigned. All these observations suggest that **1** ligates through two tellurium atoms only and OH remains intact. Probably palladium(II) and platinum(II) adopt the usual square planar geometry and mercury tetrahedral. Electronic spectrum of the platinum complex recorded in acetone exhibits a band at 326 nm which indicates square planar geometry of Pt(II) and appears to originate from $^1A_{1g} \rightarrow {}^1B_{1g}$ transition. Such an electronic band was not observed for the palladium complex dissolved in acetonitrile probably because a charge transfer band occurring at 250 nm masked it. Single crystals suitable for x-ray work could not be grown for either of these complexes.

Attempts were made to synthesize the complex $[Pd(\mathbf{1})_2](ClO_4)_2$ and mixed ones $[Pd(\mathbf{1})(L)](ClO_4)_n$ ($n = 1$, L = 4-$MeOC_6H_4TeCH_2COO$; $n = 2$, L = $Ph_2PCH_2CH_2PPH_2$) by reacting $PdCl_2.\mathbf{1}$ with **1** or L in the presence of $AgClO_4$



but instead of desired derivatives following reactions occurred mainly. These proposals are based on the analyses and ^1H NMR spectra of the reaction products. Since in the course of all these reactions AgCl could be separated quantitatively before perceptible dissociation, it is reasonable to presume that the expected complexes are formed at the first instance but decompose readily in the solution.

EXPERIMENTAL

Published methods were used to synthesize bis(4-methoxyphenyl)ditelluride,[9] bis(4-ethoxyphenyl)ditelluride,[9] 4-methoxyphenyltelluroacetic acid[10] and bis(diphenylphosphino)palladium(II)-chloride.[12] The $ClCH_2CHOHCH_2Cl$ was used as received from Lancaster Synthesis(U.K.). Carbon and hydrogen analyses were carried out on a Perkin-Elmer elemental analyzer 240°C. Molecular weights were determined with a Knauer vapour pressure osmometer and conductivity measurements were made on 0.1–1.0 mM solutions with Metrohm Conductometer 660. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX-100 FT-NMR spectrometer at 99.55 and 25 MHz, respectively. IR spectra in the range 4000–200 cm^{-1} (of Nujol mulls between CsI windows or KBr/CsI discs) were recorded on a Nicolet 5DX FT-IR spectrometer. $^{125}Te\{^1H\}$ NMR were recorded on a Bruker AM360 instrument at 113.6 MHz using neat Me_2Te as an external reference. Electronic spectra were recorded on a Hitachi UV-visible spectrophotometer model 330.

Synthesis of **1**. Bis(2-methoxyphenyl)ditelluride (2 mmol) was refluxed in 30 cm^3 ethanol under a N_2 atmosphere. Sodium borohydride (0.2 g dissolved in 2 cm^3 ethanol) was added to this solution dropwise until it became colorless. The solution was cooled to 35°C, mixed with 1,3-dichloropropan-2-ol (2 mmol in 5 cm^3 ethanol) and refluxed with stirring for 4–5 h. The pale yellow reaction mixture was cooled to room temperature and poured into 200 cm^3 of water. Compound **1** and regenerated ditelluride was extracted into 150 cm^3 chloroform. The extract was washed with water, dried over anhydrous Na_2SO_4, reduced in volume to 15–20 cm^3 (under reduced pressure) and mixed with petroleum ether 40–60°C (10 cm^3). The precipitated **1** was washed several times with petroleum ether to remove regenerated precursor ditelluride and dried *in vacuo*. Yield 15–20%. M.P. 100°C. The results of elemental analyses, ^1H and ^{13}C NMR spectral data are given below.

Analyses: Found C, 32.34; H, 3.34%; calc. for $(C_{17}H_{20}Te_2O_3).CHCl_3$: C, 33.40; H, 3.24%. NMR (^1H, $CDCl_3$, 25°C) δ 1.72 (b, OH), 3.01–3.08 (m, 4H, CH_2), 3.50–3.97 (m, 7H, CH + CH_3), 6.68, 6.77 (d, 2H, ArH *ortho* to Te), 7.60, 7.69 (d, 2H, ArH *meta* to Te); ($^{13}C\{^1H\}$, $CDCl_3$, 25°C): δ 43.7 (CH_2), 55.3 (CH), 115.3 (phenyl carbon *meta* to Te), 134.3 (phenyl carbon *ortho* to Te), 161.5 (phenyl carbon *para* to Te. Signal of carbon linked to tellurium however could not be observed.

Synthesis of $[PdCl_2.\mathbf{1}].2CHCl_3$. Palladium(II) chloride (0.1 mmol) was refluxed in CH_3CN (10 cm^3) for 5 h. After cooling to room temperature this solution was mixed with the solution of **1** (0.1 mmol) made in chloroform (15 cm^3) and the mixture was stirred for 2 h. Petroleum ether was added to the mixture and the resulting precipitate of palladium complex was filtered, washed with petroleum ether, recrystallized from a chloroform-hexane (3:1) mixture and dried in *vacuo*. Yield 80%. M.P. 110°C(d). The results of elemental analyses and ^1H NMR spectral data are given below.

Analyses: Found C, 21.50; H, 1.86%; calc for $(C_{17}H_{20}Te_2O_3PdCl_2).2CHCl_3$: C, 22.89; H, 2.33%. NMR (^1H, CD_3CN, 25°C): δ 2.21 (b, OH), 3.2 (m, 4H, CH_2), 3.85 (m, 7H, CH + CH_3), 7.13, 7.15 (d, 2H, ArH *ortho* to Te), 7.97, 8.06 (d, 2H, ArH *meta* to Te).

Synthesis of $[PtCl_2.\mathbf{1}]$. The ligand **1** (0.1 mmol) dissolved in 15 cm^3 chloroform-acetone mixture (1:1) was added to an aqueous solution (10 cm^3) of K_2PtCl_4 (0.1 mmol) and the mixture was stirred for 5–6 h at room temperature. The resulting yellow precipitate was filtered, washed several times with water and dried *in vacuo*. Yield 50%. M.P. 180°C (d). The results of elemental analyses and ^1H NMR spectral data are given below.

Analyses: Found: C, 25.81; H, 2.72%; calc. for $C_{17}H_{20}Te_2O_3PtCl_2$: C, 25.72; H, 2.52%. NMR (^1H, $(CD_3)_2CO$, 25°C): δ, 2.68 (b, OH) 3.2 (m(broad), 4H, CH_2) 3.85 (m, 7H, CH + CH_3), 6.96–7.00 (d, 2H, ArH *ortho* to Te), 7.48, 7.57 (d, 2H, ArH *meta* to Te).

Synthesis of $[HgCl_2.\mathbf{1}]$. The solution of $HgCl_2$ (0.3 mmol) in 5 cm^3 of acetone was stirred with **1** (0.3 mmol) dissolved in 5 cm^3 of $CHCl_3$ at room temperature for 1 h. Hexane was added to the mixture

and resulting yellow precipitate was filtered, washed with acetone and dried *in vacuo*. Yield 60%. M.P. 145°C(d). The results of elemental analyses and ^1H NMR spectral data are given below.

Analyses: Found: C, 24.15; H, 2.45%; calc. for $C_{17}H_{20}Te_2O_3HgCl_3$: C, 25.15; H, 2.50%. NMR (^1H, DMSO-d_6, 25°C): δ, 2.50 (b, OH), 2.9 (m, CH_2), 3.63–3.87 (m, 7H, CH + CH_3), 7.32–7.94 (m, 2H, ArH).

Attempted synthesis of $[Pd(\mathbf{1})_2](ClO_4)_2$. $[PdCl_2.1].2CHCl_3$ (0.1 mmol) dissolved in CH_3CN (10 cm^3) was stirred with the solution of **1** (0.1 mmol) in $CHCl_3$ (10 cm^3) in the presence of $AgClO_4$ (0.2 mmol) at room temperature for 2–3 h. White precipitates of AgCl was filtered off, the volume of filtrate reduced to 5 cm^3 under reduced pressure and the solution kept for crystallization at 10–15°C. Mixture of elemental tellurium and palladium(II) perchlorate settled.

Attempted synthesis of mixed ligand complexes:

(i) $[Pd(Ph_2PCH_2CH_2PPh_2)(\mathbf{1})](ClO_4)_2$. The suspension of $PdCl_2(Ph_2PCH_2CH_2PPh_2)Cl_2$ (0.1 mmol) in 10 cm^3 of $CHCl_3$ was mixed with the solution of $AgClO_4$ (0.2 mmol) in CH_3CN (5 cm^3) and **1** (0.1 mmol) dissolved in 5 cm^3 of $CHCl_3$. Mixture was stirred for 2–3 h and the precipitate of AgCl was filtered off. The volumes of filtrate was reduced to 5 cm^3 under reduced pressure and it was kept for crystallization at 10–15°C elemental tellurium settled.

(ii) $[Pd(4\text{-}MeOC_6H_4TeCH_2COO)(\mathbf{1})]ClO_4$. On using a procedure similar to that described above for $[Pd(\mathbf{1})_2](ClO_4)_2$ a mixture of elemental tellurium and probably a polymeric compound $[Pd(4\text{-}MeOC_6H_4TeCH_2COO)ClO_4]_n$ resulted.

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