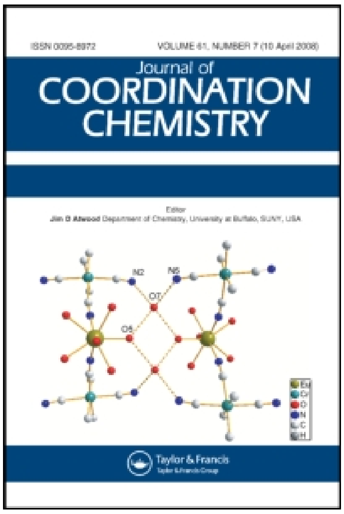

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A NOVEL (Te, S) DONOR, 2-(ARYLTELLURO)BENZYLMERCAPTAN. SYNTHESIS AND REACTIONS WITH MERCURY(II) AND PALLADIUM(II)

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(Received 7 July 1998)

PhTeLi/ArTeNa ($Ar = 4\text{-}Me/EtOC_6H_5$) generated *in situ* by reaction of 2-chlorobenzylmercaptan gives 2-(aryltelluro)benzylmercaptan (**1**), the first example of a hybrid (Te, S) ligand having a mercaptan group. On reaction with $HgCl_2$, **1** gives ArTeHgCl species. The reaction of $[(Ph_3P)_2Pd(ClO_4)_2]$ with **1** result in species of the type $[(Ph_3P)_2Pd(\mathbf{1})](ClO_4)_2$. ^1H NMR and IR spectra suggest that **1** ligates through Te and S (without loss of proton, a rare observation in platinum metal chemistry). On keeping these complexes in chloroform for more than 48 h dimerization occurs as evidenced by deshielding of the CH_2 signal, shielding of the SH proton (~ 0.2 ppm) and mass spectra. Reaction of **1** with $(PhCN)_2PdCl_2$ gives species of unusual stoichiometry $[(PdCl_2)_2 \cdot \mathbf{1}]$. These are the first examples where reactions of telluroether ligands with palladium(II) have given bimetallic species. ^1H and $^{13}C\{^1H\}$ NMR and IR spectra of these complexes authenticate them and support the bidentate mode of coordination for **1** (through S and Te). The two Pd atoms in these bimetallic species are bridged *via* chlorine as $\nu(Pd\text{–}Cl\text{–}Pd)$ has been noticed around 260 cm^{-1}.

Keywords: 2-(aryltelluro)benzylmercaptan; mercury; palladium; synthesis; complexation

INTRODUCTION

The synthesis and ligation of organotellurium ligands are the subject of considerable current interest, as highlighted in two recent reviews.[1,2] Symmetrical bidentate as well as a variety of hybrid polydentate organotellurium ligands have been studied.[1–4] We have recently reported synthesis and complexation behaviour of some novel hybrid ligands that contain both

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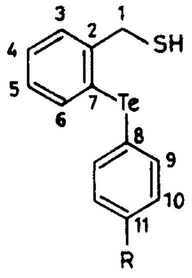
hard (N or O) and soft (Te) donor atoms.[5–8] The tellurium analogue of *bis*-(diphenylphosphino)methane has also been shown to form four membered chelate ring with palladium.[9] The main reason for the current interest is probably the possible applications of metal–tellurium compounds in chemical vapour deposition processes[10] for thin film fabrication of new electronic materials. Despite all these developments in the ligand chemistry of tellurium, only one (Te, S) ligand, 2-(aryltelluro)ethylmethyl sulphide, is known so far.[11] Pt–Cl bond lengths in the crystal structure of $[PtCl_2L]$,[12] the first example of a species containing Pt–Te and Pt–S bonds in the same molecule, indicate that the *trans* influence of Te is somewhat greater than that of sulphur. It was therefore thought worthwhile to design (Te, S) ligands containing a mercaptan group (**1**) as no such system is yet known and to study their complexation reactions. In the present paper results of these investigations are reported.



R = H (a)
MeO (b)
EtO (c)

1

EXPERIMENTAL

Bis(4-methoxyphenyl)ditelluride and *bis*(4-ethoxyphenyl)ditelluride were prepared by published methods.[13] 2-Chlorobenzylmercaptan (Aldrich, USA) was used as received. C, H and N analyses were carried out with a Perkin Elmer 240C instrument. Estimations of chlorine[14(a)] and tellurium[14(b)] were made volumetrically. ^1H NMR spectra were recorded on a JEOL JNR FX-100 FT NMR spectrometer at 99.55 MHz. $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Spectrospin DPX 300 NMR spectrometer at 75.47 MHz. IR spectra were recorded in the range 200–4000 cm^{-1} on a Nicolet 5 DX FT-IR spectrophotometer using CsI pellets. Far IR spectra were recorded (up to 50 cm^{-1}) in polyethylene discs on a Perkin Elmer 1700X FT Far-IR spectrophotometer. FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer using argon (6 kV, 10 mA) as the FAB gas. For conductance measurements, an Orion conductivity meter (model 162) was used. Molecular weight measurements were made on a Knauer vapour pressure osmometer (model A028).

Synthesis of 2-(phenyltelluro)benzylmercaptan (1a)

Bromobenzene (1.57 g, 10 mmol) was dissolved in THF (50 cm^3) and lithium metal (0.14 g, 20 mmol) added to the solution. The mixture was stirred until the lithium metal dissolved, giving a purple solution. Tellurium powder (1.27 g, 10 mmol) was added to this solution and the mixture stirred until the tellurium dissolved. The resulting solution was cooled to 0°C and 2-chlorobenzylmercaptan (1.58 g, 10 mmol) dissolved in 10 cm^3 of THF was added to it dropwise with stirring. The mixture was further stirred for 12 h. The yellowish-red solution was slowly added to ice cold water. The complex **1a** was extracted into 150 cm^3 of chloroform. The solvent was removed under reduced pressure resulting in a viscous liquid. Yield ~80%. Mol. wt. found (calc.): 315.58 (328). *Analyses*: found (calc.): C, 47.36 (47.56); H, 3.55 (3.65); Te, 38.52 (39.02)%. NMR (^{1}H, CDCl$_3$, 25°C): δ, 1.92 (t, 1H, SH), 3.78 (d, 2H, CH$_2$), 7.35 (m, 9H, ArH); (^{13}C{^{1}H}, CDCl$_3$, 25°C): δ, 49.3 (C$_1$), 99.3 (C$_8$), 115.5 (C$_{10}$, C$_3$), 126.5 (C$_6$), 127.7 (C$_4$), 128.6 (C$_5$), 133.1 (C$_7$), 137.5 (C$_9$), 138.7 (C$_2$), 163.1 (C$_{11}$), FAB mass spectrum: m/z 331 ($M+H^+$), 284 ($M\text{-}CH_2SH+H^+$), 207 ($M\text{-}PhCH_2SH+H^+$), 130 (Te).

Synthesis of 2-(4-methoxy/ethoxyphenyltelluro)benzylmercaptan (1b/1c)

A solution of *bis*(4-methoxyphenyl)ditelluride (0.95 g, 2 mmol) or *bis*(4-ethoxyphenyl)ditelluride (1.0 g, 2 mmol) in ethanol (30 cm^3) was refluxed under dinitrogen atmosphere and sodium borohydride (0.2 g dissolved in 2 cm^3 of 1 M NaOH) was added dropwise until the refluxing solution became colourless. The solution was cooled to room temperature and thereafter 2-chlorobenzylmercaptan (0.65 g, 4 mmol) dissolved in 10 cm^3 of ethanol was added dropwise with stirring. The resulting yellowish red solution was refluxed for 1 h, cooled to room temperature and poured into 200 cm^3 of water. The ligands **(1b/1c)** were extracted into CHCl$_3$ (150 cm^3) from the aqueous mixture. The extract was washed with water, dried over anhydrous sodium sulphate and concentrated under reduced pressure, resulting in a viscous liquid. Yield ~70–75%.

1b: Mol. wt. found (calc.): 354.2 (358). *Analyses*: found (calc.): C, 46.63 (46.92); H, 3.39 (3.91); Te, 34.90 (35.75)%. NMR (^{1}H CDCl$_3$, 25°C): δ, 1.94 (t, 1H, SH), 3.81 (d, 2H, CH$_2$), 4.15 (S, 3H, OMe), 6.72 (d, 2H, ArH *m* to Te) 7.68 (d, 2H, *o* to Te), 7.23 (m, 4H, ArH); (^{13}C{^{1}H}, CDCl$_3$, 25°C): δ, 49.2 (C_1), 55.1 (OCH_3), 97.8 (C_8), 115.1 (C_{10}, C_3), 126.6 (C_6), 127.2 (C_4), 128.4 (C_5), 133.2 (C_7), 138.8 (C_9), 140.2 (C_2) 160.2 (C_{11}).

1c: Mol. wt. found (calc.): 371.1 (372). *Analyses*: found (calc.): C, 48.23 (48.28); H, 3.86 (4.30); Te, 34.01 (34.40)%. NMR (^1H, $CDCl_3$, 25°C): δ, 1.40 (t, 3H, CH_3 of OEt), 1.96 (t, 1H, SH), 3.82 (d, 2H, CH_2), 3.97 (q, 2H, OCH_2), 6.72 (d, 2H, ArH *m* to Te), 7.24 (m, 4H, ArH), 7.67 (d, 2H, ArH *o* to Te); ($^{13}C\{^1H\}$, $CDCl_3$, 25°C): δ, 20.32 (CH_3 of OEt), 52.5 (C_1), 64 (OCH_2), 99.3 (C_8), 119 (C_{10}, C_3) 131 (C_6), 134 (C_4), 135 (C_5), 136.7 (C_7), 140.2 (C_9), 146.1 (C_2), 168.2 (C_{11}).

Reaction of Mercury(II) chloride with 1

Mercury(II) chloride (0.28 g, 1 mmol) dissolved in 20 cm^3 of acetone was added to a solution **1**(**a**, **b** or **c**) (1 mmol) in acetone (10 cm^3) and the mixture stirred for 2 h. The resulting yellow precipitate was filtered, washed with acetone thoroughly and dried *in vacuo*. Yield ~60%. $C_6H_5TeHgCl$: m.p. 105°C. *Analyses*: found (calc.): C, 16.44 (16.30); H, 1.27 (1.13); Cl, 8.20 (8.08)%. NMR (^1H, DMSO-d_6, 25°C): δ, 7.23 (d, 2H, ArH *m* to Te), 7.87 (t, 3H, ArH *o* and *p* to Te). 4-$MeOC_6H_4TeHgCl$: m.p. 159°C. *Analyses*: found (calc.): C, 17.25 (17.83); H, 1.53 (1.48)%. NMR (^1H, DMSO-d_6, 25°C): δ, 3.82 (bs, 3H, OMe) 6.82 (d, 2H, ArH *m* to Te), 7.68 (d, 2H, ArH *o* to Te). 4-$EtOC_6H_4TeHgCl$: m.p. 132–135°C. *Analyses*: found (calc.): C, 19.21 (19.79); H, 2.09 (1.85)%. NMR (^1H, DMSO-d_6, 25°C): δ, 1.30 (t, 3H, CH_3 of OEt), 3.87 (q, 2H, OCH_2), 6.67 (d, 2H, ArH *m* to Te), 7.66 (t, 2H, ArH *o* to Te).

Reactions of [$(PhCN)_2PdCl_2$] with 1

To a solution of [$(C_6H_5CN)_2PdCl_2$] (0.18 g, 0.5 mmol) in chloroform (25 cm^3) was added the ligand **1a**, **b** or **c** (0.5 mmol) dissolved in $CHCl_3$ (10 cm^3) dropwise with continuous stirring. Thereafter, the resulting mixture was stirred further for 2 h and hexane or petroleum ether (40–60°C) was added. The resulting precipitate was filtered, washed with hexane and dried *in vacuo*. Yield ~65%. [$(PdCl_2)_2 \cdot$ **1a**]: m.p. 150°C. *Analyses*: found (calc.): C, 24.07 (23.84); H, 2.04 (1.76)%. NMR (^1H, DMSO-d_6, 25°C): δ, 3.61 (bs, 2H, CH_2), 7.69 (m, 9H, ArH). [$(PdCl_2)_2 \cdot$ **1b**]: m.p. 170°C. *Analyses*: found (calc.): C, 24.03 (23.56); H, 2.28 (1.96)%. NMR (^1H, DMSO-d_6, 25°C): δ, 3.69 (bs, 2H, CH_2), 3.90 (s, 3H, OMe), 7.08 (d, 2H, ArH *m* to Te), 7.47 (m, 4H, ArH), 7.86 (d, 2H, ArH *o* to Te); ($^{13}C\{^1H\}$, DMSO-d_6, 25°C): δ, 49.3, 49.6, 49.9 (C_1), 55.4, 55.5, 55.8 (OCH_3), 94.6, 100.0, 101.6 (C_8), 115.5 (C_{10}, C_3), 127.5 (C_6), 129.8 (C_4), 134.2 (C_5), 134.0 (C_7), 136.4 (C_9), 140.1 (C_2), 160.3, 160.6, 161.4 (C_{11}). [$(PdCl_2)_2 \cdot$ **1c**]: m.p. 230°C. *Analyses*: found (calc.): C, 24.88 (24.76); H; 2.31 (2.20)%. NMR (^1H, DMSO-d_6, 25°C): δ, 1.34 (t, 3H, CH_3 of OEt), 3.65 (bs, 2H, CH_2), 4.01 (q, 2H, OCH_2) 7.10 (d, 2H, ArH *m* to Te), 7.36 (m, 4H, ArH), 7.86 (d, 2H, ArH *o* to Te).

Synthesis of $[(Ph_3P)_2Pd \cdot \mathbf{1}](ClO_4)_2$

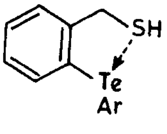
A solution of *bis*(triphenylphosphine)palladium(II) chloride (0.18 g, 0.25 mmol) in CH_3CN (20 cm^3) was mixed with $AgClO_4$ (0.10 g, 0.5 mmol) dissolved in CH_3CN (10 cm^3). The mixture was stirred for 30 min, and the resulting AgCl was filtered off. A solution of **1a**/**1b** (0.25 mmol) in CH_3CN (10 cm^3) was added to the filtrate and the mixture stirred for 3 h. Thereafter, the volume of mixture was reduced to 10 cm^3 and the concentrate mixed with hexane. The resulting precipitate of $[(Ph_3P)_2Pd \cdot \mathbf{1}](ClO_4)_2$ was filtered, washed thoroughly 3 or 4 times with hexane–chloroform mixture (1 : 1) and dried *in vacuo*. Yield ~80%. $[(PPh_3)_2Pd \cdot \mathbf{1a}](ClO_4)_2$: Mol. wt. found (calc.): 1089.79 (1157.8), m.p. 152–155°C (d.). *Analyses*: found (calc.): C, 50.43 (50.82); H.3.43 (3.63)%. NMR (^1H, $CDCl_3$, 25°C): δ 2.06 (bs, 1H, SH), 3.79 (d, 2H, CH_2), 7.58 (m, 39H, ArH). $[(PPh_3)_2Pd \cdot \mathbf{1b}](ClO_4)_2$: Mol. wt. found (calc.): 1088.64 (1187.8), m.p. > 230°C (d.). *Analyses*: found (calc.): C, 49.24 (49.55); H, 3.80 (3.73)%. NMR (^1H. $CDCl_3$, 25°C): δ, 2.09 (bs, 1H, SH), 3.78 (d, 2H, CH_2), 4.20 (s, 3H, OMe) 7.48 (m, 38H, ArH).

RESULTS AND DISCUSSION

The ligand **1a** has been synthesized by the sequence of reactions given in

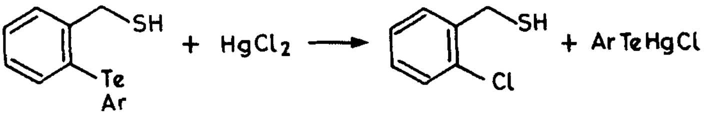
(1)

equation (1) whereas **1b** and **1c** have been obtained by reacting 2-chlorobenzylmercaptan with $ArTe^-Na^+$ generated *in situ* by borohydride reduction of Ar_2Te_2 ($Ar = 4\text{-}MeOC_6H_4$ or $4\text{-}EtO\text{-}C_4H_4$). Compounds **1a**–**c** are soluble in common organic solvents but do not ionize significantly as evidenced by molecular weight measurements. All ligands have been authenticated by elemental analyses, ^1H and $^{13}C\{^1H\}$ NMR and mass spectra. The substitution of Cl in 2-chlorobenzylmercaptan with a tellurium moiety having a much lower electronegativity is expected to have a shielding effect of CH_2 and SH protons. However, this is not found, probably because of intramolecular coordination of Te with sulfur as shown below. The Te–C(Ar) vibrations in IR spectra of **1** have been observed[15] at 294–303 and 250 cm^{-1} whereas ν(S–H) appears[16] around 2500 cm^{-1}.



1

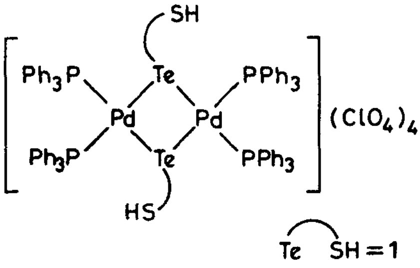
The reaction of **1a** to **c** with $HgCl_2$ gives a precipitate of stoichiometry ArTeHgCl. The mother liquor was an intricate mixture and could not be separated and characterized further. The ^1H NMR of these precipitates could be recorded in DMSO-d_6 only due to solubility problems. These spectra do not have signals of aryl protons of the ring containing CH_2SH as observed for palladium(II) complexes [$(PdCl_2)_2 \cdot$ **1**] and therefore support the formation of ArTeHgCl. It seems to form through some intriguing path as we could not isolate 2-chlorobenzylmercaptan (in good yield) expected to be formed if cleavage of **1** takes place by the



(2)

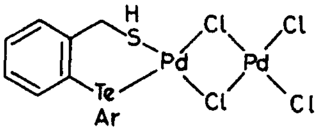
reaction given in equation (2). ArTeHgCI in the solid state seems to be polymeric, involving bridging chlorine and ArTe groups (making tetrahedral coordination around each mercury) as in their IR spectra only ν(Cl–Hg–Cl)[17] was observed around 206 cm^{-1} and no band due to terminal HgCl was noticed. The ν(Te–C(Ar)) bands appear red shifted by 10 cm^{-1}, with respect to those of the free ligand in the IR spectra of ArTeHgCl. On dissolving in DMSO, the bridges are probably cleaved and tetrahedral coordination of Hg is attained *via* coordination with two DMSO molecules. In non-coordinating solvents these polymeric materials are therefore insoluble. The attempts to grow suitable crystals of ArTeHgCl for X-ray diffraction were not successful.

Reaction of $(Ph_3P)_2Pd(ClO_4)_2$ with **1a**/**1b** resulted in species of composition [$(Ph_3P)_2Pd \cdot$ **1**]$(ClO_4)_2$ which have been authenticated by ^1H NMR, mass and IR spectra in conjunction with elemental analyses. The SH proton on complexation is not lost but appears deshielded by 0.1 ppm, supporting coordination of Pd through sulfur of ligands **1a** and **b** as deshielding due to any intramolecular hydrogen bonding is not possible in **1**. This coordination of SH without deprotonation is a rare event in platinum metal chemistry. The aryl protons also appear deshielded (> 0.17 ppm) in the ^1H NMR of these complexes with respect to those of free **1a**/**1b**. This observation in conjunction with a red shift (10–15 cm^{-1}) in ν(Te–C(Ar)) suggests that, in these complexes, **1** ligates through tellurium also. ClO_4 does not seem to be in the coordination sphere[17] as its vibrations appear around 1100 and 650 cm^{-1}. The ν(Pd–S)[7(b)] and ν(S–H) modes appear around 275–280 and 2495 cm^{-1}, respectively, in the spectra of these species. The band around 360 nm in the electronic spectrum of $[(PPH_3)_2Pd \cdot$ **1a**/**1b**$](ClO_4)_2$ concurs with the square planar geometry of donor atoms around palladium.[18] On keeping a chloroform solution of $[(PPh_3)_2Pd \cdot$ **1a**$](ClO_4)_2$ for 48 h or more, significant changes occur in its ^1H NMR spectrum. The SH triplet shifts to high field and appears around 1.7 ppm. The CH_2 signal is deshielded (~0.4 ppm) relative to the monomeric complex as well as free **1**, whereas minor shielding of CH_2 on chelation with Pd(II) has been noticed in the ^1H NMR of the monomer. The aromatic multiplet also shifts downfield (~0.1 ppm). The compound isolated from this solution shows a molecular ion peak in the FAB mass spectrum at *m/z* 2318 along with peaks at 631 ($(PPh_3)_2Pd$), 331 (**1a**) and 99 (ClO_4). These observations suggest that a dimer **2** is formed. To further authenticate these observations attempts were made to grow single crystals of **2** and its precursor suitable for X-ray diffraction, but these did not succeed.



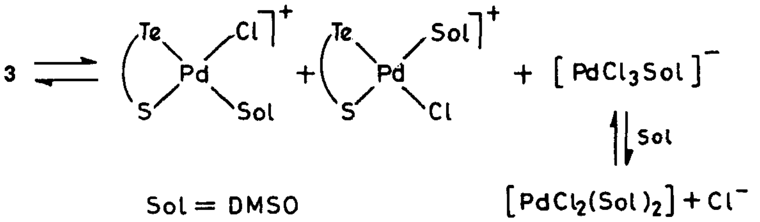
2

Reactions of **1a–c** with $(PhCN)_2PdCl_2$ give compounds of stoichiometry $[(PdCl_2)_2 \cdot$ **1**$]$. These species are microcrystalline materials and do not give crystals suitable for X-ray diffraction. Therefore only spectroscopic investigations were possible on them. Their ^1H NMR could be recorded in DMSO-d_6 only. In these spectra the SH signal, probably due to deshielding and solvent effects, merges with the solvent signal, whereas the CH_2 signal appears nearly as shielded as in the case of $[(PPh_3)_2Pd \cdot$ **1**$](ClO_4)_2$ if we take into account the effect of solvent. The aryl protons are deshielded even after considering the solvent effect. Thus the ligation mode of **1** in the species [$(PdCl_2)_2 \cdot$ **1**] appears to be similar to that in [$(PPh_3)_2Pd \cdot$ **1**]$(ClO_4)_2$. This is supported by a red shift ($\sim 15\,cm^{-1}$) in ν(Te–C(Ar)) in comparison to that of the corresponding ligand and the occurrence of ν(Pd–S) between 275–282 cm^{-1}.[7(b)] The two bands around 320 and 300 cm^{-1} suggest the presence of two *cis* Pd–Cl bonds.[17] Bands around 260 cm^{-1} in the Far IR spectra of complexes of the type [$(PdCl_2)_2 \cdot$ **1**] probably originate from Pd–Cl–Pd bridges.[17]



3

These observations concur with the structure **3** for these species. The $^{13}C\{^1H\}$ NMR spectrum of [$(PdCl_2)_2 \cdot$ **1b**] shows three signals for OCH_3, CH_2 and C_8, each. This probably occurs due to the existence of the following equilibria when it is dissolved in DMSO. The molar conductance, Λ_M of [$(PdCl_2)_2 \cdot$ **1**] in DMSO is $\sim 80\,ohms^{-1}\,cm^2\,mol^{-1}$, very close to that of a 1 : 2 electrolyte.



Thus the above structure **3** seems to be most plausible for [$(PdCl_2)_2 \cdot$ **1**] on the basis of both ^{13}C NMR and conductance data. Electronic spectra of these complexes, recorded in DMSO, exhibit a band around 280 nm which suggests that the complexes are not simple square planar monomeric species.[18] The structure **3** is further supported by a molecular ion peak observed in the FAB mass spectrum of [$(PdCl_2)_2 \cdot$ **1a**] at m/z 686 ($M + H^+$) along with peaks due to $PdCl_2 \cdot$ **1a** (m/z 508), **1a** (m/z 331) and $PdCl_2$ (m/z 177).

Acknowledgements

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