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NOVEL 2-(ARYLTELURO)ETHYLMETHYL-SULFIDES SYNTHESIS AND LIGATION WITH PALLADIUM(II) AND PLATINUM(II)

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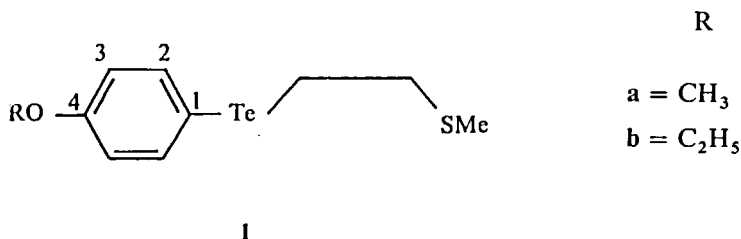
(Received November 7, 1989)

2-(Aryltelluro)ethylmethylsulfide (**1**), where aryl = 4-MeOC₆H₄ (a) and 4-EtOC₆H₄ (b), has been synthesized by reacting sodium aryltelluroolate with ClCH₂CH₂SCH₃. ¹H and ¹³C NMR spectra indicate the existence of intramolecular Te←S secondary interactions in **1**. IR spectra suggest that both the *trans* and *gauche* conformations of two CH₂ groups coexist, at least in the solid state. (C₆H₅CN)₂PdCl₂ and K₄PtCl₄ react with **1** to give diamagnetic complexes of the type Pd/PtCl₂. **1**. IR, ¹H and ¹³C NMR data in conjunction with molecular weight and conductivity measurements suggest that **1** in the complexes acts as a bidentate ligand and two Cl (*cis* to each other), S and Te atoms constitute the square planar geometry around Pd/Pt, as supported by electronic spectra.

Keywords: 2-(aryltelluro)ethylmethylsulfide, platinum(II), palladium(II), complexes, synthesis

INTRODUCTION

The first stable hybrid organotellurium ligand, 1-(diphenylphosphino)-2-(phenyltelluro)benzene, was reported by Gysling and Luss.¹ Since then, some research groups,²⁻⁴ including ours have been actively engaged in synthesizing such ligands and exploring their chemistry. Recently we reported the synthesis and ligation of some (N,Te),⁵⁻⁷ (N,Te₂),⁸ (N,Te₃)⁹ and (O,Te)¹⁰ donors. In continuation of these studies of the development of hybrid organotellurium donors, we have synthesized a novel (Te,S) donor **1** by reacting sodium aryltelluroolate with 2-chloroethyl methyl sulfide. Its synthesis and complexation with palladium(II) and platinum(II) are reported in the present paper. The selenium analogue of **1** is known¹¹ and was found to possess interesting properties as a ligand.



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EXPERIMENTAL

Published methods¹² were used to synthesize bis(4-methoxyphenyl)- and bis(4-ethoxyphenyl)ditellurides. The C and H analyses were carried out on a Perkin-Elmer 240C elemental analyzer. Tellurium was estimated volumetrically.¹³ ¹H and ¹³C NMR spectra were recorded on a JEOL JNM FX-100 FT-NMR spectrometer at 99.55 and 25 MHz respectively. IR spectra (KBr discs or Nujol mulls sandwiched between CsI windows) in the range 4000–200 cm⁻¹ were recorded on a Nicolet 5DX FT-IR spectrometer. Electronic spectra in chloroform were recorded on a Hitachi 300 spectrometer. The conductivity measurements were made (*ca* 1 mM solution) in acetonitrile/nitrobenzene with a Metrohm 660 conductometer. Molecular weights were determined in chloroform (~1 millimolar) on a Knauer vapour pressure osmometer.

Synthesis of 2-(aryltelluro)ethylmethylsulfide, (1)

Bis(2-methoxyphenyl)- or bis(2-ethoxyphenyl)ditelluride (~2 mmol) was refluxed in ethanol (30 cm³) under a nitrogen atmosphere (oxygen free). Sodium borohydride (~0.2 g dissolved in 2 cm³ of 1 M NaOH) was added to the refluxing solution dropwise until it became colourless. The solution was cooled to ~35°C and thereafter 2-chloroethylmethylsulfide (~4 mmol) in 5 cm³ of ethanol was added dropwise with stirring. The resulting pale yellow solution was refluxed for ~30 min, cooled to room temperature and poured into 200 cm³ of water. The ligand **1** was extracted into hexane (~150 cm³). The organic extract was washed with water and dried over anhydrous sodium sulphate. Hexane was evaporated off under reduced pressure, resulting in a pale yellow oil. Yield, results of elemental analyses and ¹H and ¹³C{¹H} NMR spectral data are given below.

1a: Yield, 85%. Analysis: Found: C, 39.64; H, 4.67; Te, 40.16%. Calc. for C₁₀H₁₄OSTe: C, 38.84; H, 4.52; Te, 41.21%. Mol. wt.: found 325; calc. 309.6. NMR (¹H, CDCl₃, 25°C): δ, 2.06 (s, 3H, SMe), 2.70–3.10 (m, 4H, CH₂), 3.77 (s, 3H, OMe), 6.70–6.79 (d, 2H, phenyl protons *m* to Te), 7.67–7.73 (d, 2H, phenyl protons *o* to Te); (¹³C{¹H}, CDCl₃, 25°C): δ, 7.0 (CH₂Te), 14.4 (SMe), 35.7 (CH₂S), 54.5 (OMe), 99.9 (C₁), 114.6 (C₃), 140.5 (C₂), 159.2 (C₄).

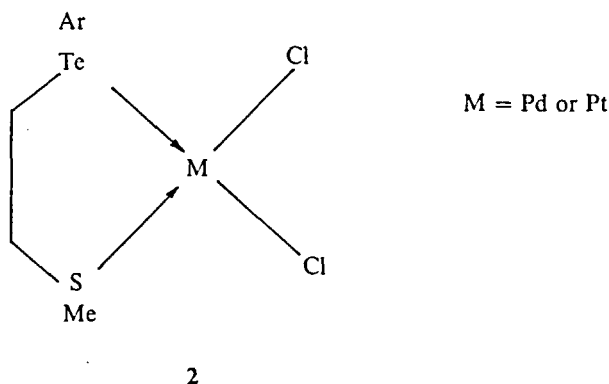
1b: Yield, 90%. Analysis: Found: C, 41.61; H, 4.84; Te, 38.13%. Calc. for C₁₁H₁₆OSTe: C, 40.79; H, 4.94; Te, 39.43%. Mol. wt.: found 342; calc. 323.6. NMR (¹H, CDCl₃, 25°C): δ, 1.32–1.46 (t, 3H, CH₃ of OEt), 2.06 (s, 3H, SMe), 2.72–3.15 (m, 4H, CH₂), 3.89–4.10 (q, 2H, OCH₂), 6.69–6.78 (d, 2H, phenyl protons *m* to Te), 7.62–7.71 (d, 2H, phenyl protons *o* to Te); (¹³C{¹H}, CDCl₃, 25°C): δ, 7.1 (CH₂Te), 14.5 (SMe), 14.8 (CH₃ of OEt), 36.1 (CH₂S), 63.1 (OCH₂), 100 (C₁), 115.6 (C₃), 140.8 (C₂), 158.9 (C₄).

Synthesis of palladium(II) complexes of 1a and 1b

A solution of **1a** or **1b** (0.5 mmol) in chloroform (10 cm³) was added dropwise to (C₅H₅CN)₂PdCl₂ (0.5 mmol) dissolved in chloroform (20 cm³) with stirring. Thereafter, the resulting mixture was stirred for a further 2 h and hexane or 40–60 petroleum ether was added. The resulting precipitate was filtered, washed with hexane and recrystallized from a 1:4 mixture of hexane and chloroform. Elemental analysis, yield, m.p. and NMR (¹H and ¹³C{¹H}) spectral data for the complexes are given below.

Te-C(alkyl) and S-CH₃ vibrations at 290, 325 and 1325 cm⁻¹. The regions in the IR spectrum generally assigned to CH₂ rocking modes¹⁵ have bands around 740, 860 and 950 cm⁻¹ which suggest that **1a** and **1b** probably exist in both *trans* and *gauche* forms, at least in the solid state.

The palladium(II) and platinum(II) complexes of **1a** and **1b** have been found to be non-ionic, diamagnetic and monomeric in nature. Their electronic spectra have two bands. One, around 25 kK, seems to arise from the ¹A_{1g} → ¹B_{1g} transition,¹⁶ and the other around 31.2 kK probably originates from some intraligand transition. These observations suggest that the two complexes adopt square planar geometry. On complexation a red shift (~15–25 cm⁻¹) has been observed in Te-C(alkyl), Te-C(aryl) and S-CH₃ vibrations in their IR spectra. This suggests that **1a/1b** coordinates with Pd(II)/Pt(II) through Te and S as a bidentate ligand. In the ¹H NMR spectra of the complexes the phenyl protons appear downfield (0.2–0.3 ppm) relative to **1a** and **1b**, supporting the suggestion of the formation of a metal-tellurium bond. SMe protons are deshielded on complexation and overlap somewhat with the CH₂ multiplet, resulting in a very broad signal (integration 7H). This broadness seems to arise partly from the fluxionality of the MeS-Pd/Pt and/or ArTe-Pd/Pt bond (the possibility of the first is much higher). The ¹³C{¹H} NMR spectrum of PdCl₂.**1b** is as expected. The deshielding of the C₁ (~7 ppm), SCH₂ (~8 ppm) and SMe (~7 ppm) signals on complexation supports the involvement of both Te and S in coordination with the metal. In the ¹³C{¹H} NMR spectrum of PtCl₂.**1b**, the deshielded signals (~4–11 ppm) of SMe, SCH₂, TeCH₂ and C₁ were found to appear as doublets. Since other carbons, viz CH₃, OCH₂, C₄, C₃ and C₂, appear as singlets, the origin of these doublets does not seem to be the fluxionality of the metal-ligand bonds but lies in the coupling between ¹³C and ¹⁹⁵Pt. The ²J value is found to be 22–26 Hz, a value lower than the ¹J value reported in the literature.¹⁷ On the basis of the above the structure **2** seems to be the most plausible for Pd/PtCl₂.**1a/1b**. The two ν(Pd-Cl) modes around 350 and 390 cm⁻¹ in the IR spectrum of PdCl₂.**1a/1b** support the presence of two chlorides *cis* to each other.¹⁵ Similarly, IR spectra of PtCl₂.**1a/1b** have two ν(Pt-Cl) bands around 320 and 300 cm⁻¹.



The occurrence of CH₂ rocking vibrations¹⁵ around 960, 860 and 760 cm⁻¹ in the IR spectra of PtCl₂.**1a/1b** indicates that the two CH₂ groups in these complexes are in both *gauche* and *trans* conformations,¹⁵ at least in the solid state. In the IR spectrum of PdCl₂.**1a**, no band around 950 and 850 cm⁻¹ is present, but there is a

band at 750 cm^{-1} which indicates that the two CH_2 groups in this complex are probably in a *trans* conformation. The band around 750 cm^{-1} is absent in the IR spectrum of $\text{PdCl}_2\cdot\mathbf{1b}$, but the other two are observed. This suggests that the two CH_2 groups in this complex are probably in a *gauche* conformation.

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