

N-[2-(4-Methoxyphenyltelluro)ethyl]phthalimide: synthesis and complexation with palladium(II)

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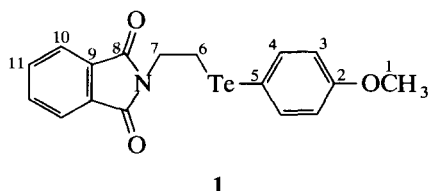
Abstract

The first example of a (Te, O, N) type of hybrid organotellurium ligand *N*-[2-(4-methoxyphenyltelluro)ethyl]phthalimide (**1**) has been made by reaction of *N*-(2-bromoethyl)phthalimide with the nucleophile 4-MeOC₆H₄Te⁻ generated in situ by borohydride reduction of bis(4-methoxyphenyl)ditelluride under a nitrogen atmosphere. Palladium(II) complexes of **1**, namely [PdCl₂.**1**], [PdCl.**1**ClO₄] (**2**), [(Ph₃P)₂Pd.**1**](ClO₄)₂ (**3**) and [(DPPE)Pd.**1**](ClO₄)₂ (**4**), where DPPE ≡ Ph₂PCH₂CH₂PPh₂ have been synthesized. In all the complexes except **2** the ligand **1** is coordinated through N and Te, as indicated by deshielding (0.1–0.7 ppm) of the CH₂Te and CH₂N signals in their ¹H NMR spectra with respect to those for free **1**, and a red shift (10–25 cm⁻¹) in ν(Te–C) alkyl–aryl. Complex **2** was found to be a 1:1 electrolyte and the ligand **1** in this complex is coordinated through oxygen as well as the through N and Te, as indicated by a red shift (30 cm⁻¹) in the ν(C=O) band of **1** on complexation. Complexes **3** and **4** were found to be 1:2 electrolytes. The presence of CHCl₃ in [PdCl₂.**1**], **3** and **4** was revealed by weight losses in thermogravimetric analysis at 65–70°C. The UV-visible spectra of all the complexes suggest a square planar geometry of the ligands around palladium.

Keywords: Tellurium; Palladium; Imide

1. Introduction

There is some current interest in the chemistry [1–6] of polydentate organotellurium ligands including hybrid ligands. However, all the hybrid organotellurium ligands synthesized so far are of the type (Te_a, X_b), where X = N, P, O, S or Se, *a* = 1–4 and *b* = 1 or 2. There is no report of a (Te_a, X_b, Y_c) type of ligand, and we therefore thought it of interest to synthesize **1**:



It is potentially a (Te, N, O₂) type of ligand, but it is more likely to behave as a (Te, N, O) donor in its

mononuclear metal complexes. In the present paper the synthesis and spectral characteristics of **1** and its palladium(II) complexes are reported.

2. Experimental details

Bis(4-methoxyphenyl)ditelluride was made by a published method [7]. *N*-(2-bromoethyl)phthalimide was used as received from Lancaster Synthesis (UK). The [(Ph₃P)₂PdCl₂] was obtained from Aldrich (USA) and [(DPPE)PdCl₂] (DPPE ≡ Ph₂PCH₂CH₂PPh₂) from Strem (USA). The C, H and N analyses were carried out with a Perkin–Elmer elemental analyser 240C. The ¹H and ¹³C {¹H} NMR spectra were recorded on a JEOL JNM FX-100 FT NMR spectrometer at 99.55 MHz and 25 MHz respectively. The conductivity measurements were made on an approximately 1 mM solution in CH₃CN with a Metrohm 660 conductometer. Far-IR spectra were recorded on a Perkin–Elmer

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Fourier transform (FT)far-IR spectrometer 1700X, using polyethylene discs. The IR spectra in the range 200–4000 cm^{-1} were recorded in CsI on a Nicolet 5DX FT IR spectrometer. Electronic spectra were recorded on a Hitachi UV-visible spectrometer model 330. A Stanton Redcroft thermal analyser STA-780 was used for the thermogravimetric analysis (TGA) studies.

2.1. Synthesis of *N*-[2-(4-methoxyphenyltelluro)ethyl]-phthalimide (**1**)

A solution of bis(4-methoxyphenyl)ditelluride (2.13 mmol) in ethanol (30 cm^3) was refluxed under dinitrogen, and sodium borohydride (0.2 g in 2 cm^3 of 1 M NaOH) was added dropwise until the refluxing solution became colourless. A solution of *N*-(2-bromoethyl)-phthalimide (4.26 mmol) in tetrahydrofuran (5 cm^3) was then added dropwise to the refluxing solution with constant stirring. The mixture was refluxed for a further 0.5 h, cooled to 25°C and poured into 100 cm^3 of water. The ligand **1** was extracted into CHCl_3 (100 cm^3) from the aqueous mixture. The extract was washed with water, dried over anhydrous sodium sulphate and concentrated to a volume of 15 cm^3 . Hexane (7 cm^3) was added to this concentrate and the precipitated ligand **1** was washed three to four times with hexane and recrystallized from a chloroform–hexane (1:1) mixture (yield, 75–80%; melting point (m.p.) 118–120°C). The results of elemental analyses and the ^1H and ^{13}C { ^1H } NMR spectral data are as follows:

Anal. Found: C, 49.20; H, 3.78; N, 3.51. $\text{C}_{17}\text{H}_{15}\text{NO}_3\text{Te}$ Calc.: C, 49.90; H, 3.67; N, 3.42%. ^1H NMR (CDCl_3 , 25°C): δ 3.0–3.1 (t, 2H, CH_2Te), 3.86 (m, 5H, $\text{CH}_2\text{N} + \text{OCH}_3$), 6.64–6.72 (d, 2H, ArH *ortho* to Te), 7.56–7.76 (m, 6H, ArH *meta* to Te + phthalimide ring protons). ^{13}C { ^1H } NMR (CDCl_3 , 25°C) [8]: δ 6.5 (C_6), 38.3 (C_7), 56.0 (C_1), 100.0 (C_5), 115.6 (C_3), 123.0 (C_{10}), 129.0 (C_9), 132.0 (C_{11}), 141.0 (C_4), 160.0 (C_2), 162.2 (C_8).

2.2. Reaction of **1** with PdCl_2

A mixture of palladium(II) chloride (0.1 g, 0.56 mmol) and CH_3CN (10 cm^3) was heated under reflux for 2–3 h. When the solution became clear and yellow, it was cooled to 25°C and mixed with a solution of **1** (0.232 g, 0.57 mmol) in chloroform (15 cm^3). The mixture was stirred for 2–3 h at 25°C, concentrated to 7–8 cm^3 and mixed with hexane (5 cm^3). The precipitated brown $[\text{PdCl}_2.1]$ was thoroughly washed with a hexane–chloroform mixture (1:1) and dried in vacuo (yield, 90%; m.p., 144°C (decomposition)). The results of elemental analyses and ^1H NMR spectral data are as follows:

Anal. Found; C, 31.46; H, 2.62; N, 2.34. $\text{C}_{17}\text{H}_{15}\text{NO}_3\text{TePdCl}_2.\text{CHCl}_3$ Calc.: C, 30.60; H, 2.27; N, 2.0%. ^1H NMR (CDCl_3 , 25°C): δ 3.86 (t, 5H, $\text{OCH}_3 + \text{CH}_2\text{Te}$), 4.58 (t, 2H, CH_2N), 6.90–7.0 (d, 2H, ArH *ortho* to Te), 7.58–7.80 (m, 6H, ArH *meta* to Te + phthalimide ring protons).

2.3. Synthesis of $[\text{PdCl}_2.1]\text{ClO}_4$ (**2**)

A solution of $[\text{PdCl}_2.1]$ (0.2 g, 0.28 mmol) in refluxing CHCl_3 (25 cm^3) was mixed with a solution of AgClO_4 (0.078 g, 0.34 mmol) in 15 cm^3 of methanol. The mixture was stirred for 2 h at 25°C. The white precipitate of AgCl was filtered off, and the filtrate was concentrated to 10 cm^3 and mixed with 5 cm^3 of hexane. The resulting precipitate of **2** was filtered off, washed three to four times with hexane–chloroform (1:1) mixture and dried in vacuo (yield, 88%; m.p., 150–152°C). The elemental analyses and ^1H NMR spectral data are as follows:

Anal. Found: C, 32.01; H, 2.56; N, 2.75. $\text{C}_{17}\text{H}_{15}\text{NO}_7\text{TePdCl}_2$ Calc.: C, 31.38; H, 2.30; N, 2.15%. ^1H NMR (CDCl_3 , 25°C): δ 3.76 (t, 5H, $\text{OCH}_3 + \text{CH}_2\text{Te}$), 4.61 (t, 2H, CH_2N), 6.80–6.90 (d, 2H, ArH *ortho* to Te), 7.56–7.82 (m, 6H, ArH *meta* to Te + phthalimide ring protons).

2.4. Reaction of **1** with $[(\text{Ph}_3\text{P})_2\text{PdCl}_2]$

Bis(triphenylphosphine)palladium(II) chloride (0.1 g, 0.23 mmol) was dissolved in CHCl_3 (15 cm^3) under dinitrogen. The solution was then mixed with a solution of AgClO_4 (0.12 g) and the mixture was stirred for 10–20 min in 10–15 cm^3 of methanol. A solution of **1** (0.1 g, 0.25 mmol) in CHCl_3 was then added and the mixture stirred for 3 h. The AgCl was filtered off. The filtrate was concentrated to 10 cm^3 and mixed with hexane (7 cm^3). The resulting precipitate of $[(\text{Ph}_3\text{P})_2\text{Pd}.1](\text{ClO}_4)_2$ (**3**) was filtered off, washed thoroughly three to four times with hexane–chloroform mixture (1:1), and dried in vacuo (yield, 85%; m.p., 88–90°C). The elemental analyses and the ^1H NMR spectral data are as follows:

Anal. Found: C, 46.92; H, 3.30; N, 1.51. $\text{C}_{53}\text{H}_{45}\text{NP}_2\text{O}_{11}\text{Cl}_2\text{TePd}.\text{CHCl}_3$ Calc.: C, 47.71; H, 3.37; N, 1.03%. ^1H NMR (CDCl_3 , 25°C): δ 3.32–3.52 (t, 2H, CH_2Te), 3.74 (s, 3H, OCH_3), 4.10 (t, 2H, CH_2N), 6.56–6.76 (d, 2H, ArH *ortho* to Te), 7.56–7.92 (m, 36H, ArH *meta* to Te + phthalimide ring protons + ArH of PPh_3).

2.5. Reaction of **1** with $[(\text{DPPE})\text{PdCl}_2]$

A solution of bis(diphenylphosphinoethane)palladium(II) chloride (0.1 g, 0.18 mmol) made in CHCl_3

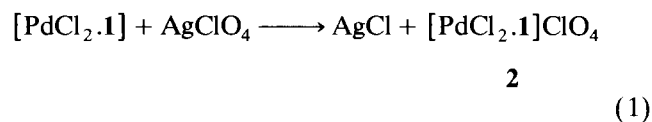
(15 cm³) was mixed with a solution AgClO₄ (0.1 g, 0.48 mmol) in methanol (10 cm³) and the mixture was stirred for 0.5 h. A solution of **1** (0.08 g, 0.20 mmol) in chloroform (10 cm³) was added and stirred for 3 h. The white precipitate of AgCl was filtered off. The filtrate was concentrated to 10 cm³ and mixed with hexane. The resulting precipitate of [(DPPE)Pd.1](ClO₄)₂ (**4**) was washed with hexane–chloroform mixture (1:1) three to four times and dried in vacuo (yield, 85%; m.p., 152–154°C. The results of elemental analysis and the ¹H NMR spectral data are as follows.

Anal. Found: C, 42.20; H, 3.56; N, 1.34. C₄₃H₃₉NP₂O₁₁Cl₂TePd·CHCl₃. Calc.: C, 42.86; H, 3.25; N, 1.14%. ¹H NMR (CDCl₃, 25°C): δ 3.1–3.2 (t, 2H, CH₂Te), 2.26 (bd, 4H, CH₂ of DPPE), 3.62 (s, 3H, OCH₃), 3.92–4.00 (t, 2H, CH₂N), 6.49–6.57 (d, 2H, ArH *ortho* to Te), 7.05–7.76 (m, 36H, ArH *meta* to Te + ArH of PPh₂ + phthalimide ring protons).

3. Results and discussion

Compound **1**, the first example of a ligand which can coordinate as a (Te, N, O) donor was synthesized by reaction of the nucleophile ArTe⁻ with *N*-(2-bromoethyl)phthalimide. This approach has been used to make several polydentate tellurium ligands [1,2,6]. The synthesis of **1** with a good yield further establishes the general applicability of the method. Complex **1** gives characteristic NMR spectra (¹H and ¹³C). However, relative to those for the precursor bromide, the –CH₂CH₂– protons are shielded (0.25 ppm CH₂N and 0.5 ppm CH₂Te). The lower electronegativity of tellurium than of Br seems to be responsible for this shielding.

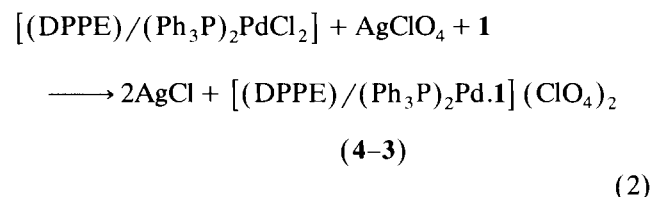
Compound **1** readily reacts with PdCl₂ to give the adduct [PdCl₂.1]·CHCl₃. A TGA study of this adduct exhibits a weight loss of 16.4% between 70 and 75°C, confirming the presence of chloroform. The ligand **1** in this adduct is coordinated through N and Te, since the protons of both CH₂ groups are deshielded with respect to those in free **1** (about 0.7 ppm). The phenyl protons of ArTe also show a small deshielding (about 0.2 ppm) on ligation of **1** with palladium, in keeping with the above observation. The reaction of AgClO₄ with [PdCl₂.1] occurs according to Eq. (1)



The ¹H NMR spectrum of **2** also exhibits deshielded CH₂ signals (about 0.7 ppm) with respect to those of

free **1**. The Δ_M of **2** in CH₃CN (about 1 mM) was found to be 148 Ω⁻¹ cm⁻¹ mol⁻¹, confirms that the ClO₄⁻ ion was outside the coordination sphere. The IR spectra of **2** were compared with those of **1**. The bands due to uncoordinated ClO₄ group at 940 and 1120 cm⁻¹ were observed in the spectra of **1**. The ν(C=O) band in the IR spectrum of **2** was observed at 1670 cm⁻¹, red shifted (30 cm⁻¹) with respect to that of free **1**. These observations in conjunction with the diamagnetic nature of **2** and appearance of bands at 270 and 335 nm in the UV–visible spectrum of **2** recorded in CHCl₃ suggest that **2** is a square planar complex in which **1** acts as a tridentate (N, O, Te) ligand. Unfortunately crystals of **2** suitable for X-ray diffraction could not be obtained, and we had to rely on spectral data.

The reaction of **1** with (Ph₃P)₂PdCl₂ and (DPPE)PdCl₃ takes place as follows:



The weight losses upon TGA of **3** and **4** were found to be 10% at 65–70°C, confirming the presence of a CHCl₃. The Δ_M of [(Ph₃P)₂Pd.1](ClO₄)₂ (**3**) and [(DPPE)Pd.1](ClO₄)₂ (**4**) were found to be 240 and 230 Ω⁻¹ cm⁻¹ mol⁻¹ respectively, indicating their 1:2 electrolytic nature. The CH₂N and CH₂Te signals in the ¹H NMR spectra of **3** and **4** were found to be deshielded (0.1–0.3 ppm) with respect to those of **1**. The deshielding is smaller than that for [PdCl₂.1] or **2** but sufficient to indicate the ligation of **1** in **3** and **4** through both Te and N. The strong *trans* influence of phosphorus may be responsible for this smaller deshielding. In the IR spectra of **3** and **4**, bands due to uncoordinated ClO₄ [9] were observed at 930 and 1100 cm⁻¹, and ν(C=O) was found at 1700 cm⁻¹, unshifted with respect to that of **1**. This suggests that in **3** and **4** the ligand **1** is coordinated through N and Te only. Complexes **3** and **4** were also found to be diamagnetic, and to give bands at 280 and 325 nm in the UV–visible spectra recorded in CHCl₃. These observations confirm the square planar geometry around palladium in **3** and **4** that is implied by the ¹H and IR spectra.

The IR spectra of all the four complexes exhibit bands at 500–510 and 220–230 cm⁻¹ which may be assigned [10] to ν(Te–CH₂) and ν(Te–C(Ar)) respectively. Both are red shifted, by 15–25 and 10–20 cm⁻¹ respectively with respect to the corresponding bands of **1**. The ν(Pd–Cl) bands in the IR spectra of [PdCl₂.1] and **2** were observed at 320 and 330 cm⁻¹, respectively.

The $\nu(\text{Pd-N})$ band was observed in the IR spectra of **4** at 490 cm^{-1} . For other complexes this band could not be unequivocally assigned. The $\nu(\text{Pd-O})$ and $\nu(\text{Pd-Te})$ vibrations appear to merge and could not be assigned unequivocally. Complexes **3** and **4** did not give crystals suitable for X-ray diffraction, and so we could not, as we had wished, use the Pd-Te bond length to assess the *trans* influence of Ph_3P and DPPE. However, results show that **1** can act as a (Te, N, O) ligand. So far no example of a hybrid organotellurium ligand in which two other different atoms are present has been reported.

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