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], [PdCl₂(CIO₄)₂] (2), [(Ph₃P)₂Pd.₁](CIO₄)₂ (3) and [(DPPE)Pd.₁](CIO₄)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 (Teₐ, Xₐ, Yₐ) where X = N, P, O, S or Se, a = 1-4 and b = 1 or 2. There is no report of a (Teₐ, Xₐ, Yₐ) 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 CH₂CN with a Metrohm 660 conductometer. Far-IR spectra were recorded on a Perkin–Elmer
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 CH\(_2\)Cl\(_2\) (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 \(^1\)H and \(^13\)C \({\{^1\}H}\) NMR spectral data are as follows:

Anal. Found: C, 49.20; H, 3.78; N, 3.51. C\(_{17}\)H\(_{15}\)NO\(_3\)Te Calc.: C, 49.90; H, 3.67; N, 3.42%. \(^1\)H NMR (CDCl\(_3\), 25°C): \(\delta\) 3.0–3.1 (t, 2H, CH\(_2\)Te), 3.86 (m, 5H, CH\(_2\)N + OCH\(_3\)), 6.64–6.72 (d, 2H, ArH \text{ortho} to Te), 7.56–7.76 (m, 6H, ArH \text{meta} to Te + phthalimide ring protons). \(^{13}\)C\({\{^1\}H}\) NMR (CDCl\(_3\), 25°C) [\(\delta\): 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\(_2\)CN (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 [PdCl\(_2\)I 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 \(^1\)H NMR spectral data are as follows:

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

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

A solution of [PdCl\(_2\)I] (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 \(^1\)H NMR spectral data are as follows:

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

2.4. Reaction of 1 with [(Ph\(_3\)P)\(_2\)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 [(Ph\(_3\)P)\(_2\)Pd.I](ClO\(_4\)) \(_2\) (3) was filtered off, washed thoroughly three to four times with hexane–chloroform mixture (1:1), dried in vacuo, (yield, 85%; m.p., 88–90°C). The elemental analyses and the \(^1\)H NMR spectral data are as follows:

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

2.5. Reaction of 1 with [(DPPE)PdCl\(_2\)]

A solution of bis(diphenylphosphinoethane)palladium(II) chloride (0.1 g, 0.18 mmol) made in CHCl\(_3\)
(15 cm$^3$) was mixed with a solution AgClO$_4$ (0.1 g, 0.48 mmol) in methanol (10 cm$^3$) and the mixture was stirred for 0.5 h. A solution of I (0.08 g, 0.20 mmol) in chloroform (10 cm$^3$) was added and stirred for 3 h. The white precipitate of AgCl was filtered off. The filtrate was concentrated to 10 cm$^3$ and mixed with hexane. The resulting precipitate of [(DPPE)Pd.I](ClO$_4$)$_2$ (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 $^1$H NMR spectral data are as follows.

Anal. Found: C, 42.20; H, 3.56; N, 1.34.
C$_{43}$H$_{39}$NP$_2$O$_{11}$Cl$_2$TePd.CHCl$_3$ Calc.: C, 42.86; H, 3.25; N, 1.14%. $^1$H NMR (CDCl$_3$, 25°C): $\delta$ 3.1–3.2 (t, 2H, CH$_2$Te), 2.26 (bd, 4H, CH$_2$ of DPPE), 3.62 (s, 3H, OCH$_3$) , 3.92–4.00 (t, 2H, CH$_2$N) , 6.49–6.57 (d, 2H, ArH ortho to Te), 7.05–7.76 (m, 36H, ArH meta to Te + ArH of PPh$_2$ + 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 ($^1$H and $^{13}$C). However, relative to those for the precursor bromide, the $-CH_2CH_2-$ protons are shielded (0.25 ppm CH$_2$N and 0.5 ppm CH$_2$Te). The lower electronegativity of tellurium than of Br seems to be responsible for this shielding.

Compound 1 readily reacts with PdCl$_2$ to give the adduct [PdCl$_2$.I]·CHCl$_3$. 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 I in this adduct is coordinated through N and Te, since the protons of both CH$_2$ groups are deshielded with respect to those in free I (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 AgClO$_4$ with [PdCl$_2$.I] occurs according to Eq. (1)

$$[\text{PdCl}_2.\text{I}] + \text{AgClO}_4 \rightarrow \text{AgCl} + [\text{PdCl}_2.\text{I}]\text{ClO}_4$$

(1)

The $^1$H NMR spectrum of 2 also exhibits deshielded CH$_2$ signals (about 0.7 ppm) with respect to those of free I. The $\Delta_m$ of 2 in CH$_3$CN (about 1 mM) was found to be 148 $\Omega^{-1}$ cm$^{-1}$ mol$^{-1}$, confirms that the ClO$_4^-$ ion was outside the coordination sphere. The IR spectra of 2 were compared with those of I. The bands due to uncoordinated ClO$_4^-$ group at 940 and 1120 cm$^{-1}$ were observed in the spectra of 1. The $\nu$(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 I. 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 CHCl$_3$ suggest that 2 is a square planar complex in which I 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 (Ph$_3$P)$_2$PdCl$_2$ and (DPPE)PdCl$_3$ takes place as follows:

$$[\text{(DPPE)}/\text{(Ph}_3\text{P})_2\text{PdCl}_2] + \text{AgClO}_4 + \text{I}$$

$$\rightarrow 2\text{AgCl} + [(\text{DPPE})/\text{(Ph}_3\text{P})_3\text{Pd.I}] \text{(ClO}_4)_2$$

(4–3)

The weight losses upon TGA of 3 and 4 were found to be 10% at 65–70°C, confirming the presence of a CHCl$_3$. The $\Delta_m$ of [(Ph$_3$P)$_2$Pd.I](ClO$_4$)$_2$ (3) and [(DPPE)Pd.I](ClO$_4$)$_2$ (4) were found to be 240 and 230 $\Omega^{-1}$ cm$^{-1}$ mol$^{-1}$ respectively, indicating their 1:2 electrolytic nature. The CH$_2$N and CH$_2$Te signals in the $^1$H NMR spectra of 3 and 4 were found to be deshielded (0.1–0.3 ppm) with respect to those of I. The deshielding is smaller than that for [PdCl$_2$.I] or 2 but sufficient to indicate the ligation of I 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 ClO$_4^-$ [9] were observed at 930 and 1100 cm$^{-1}$, and $\nu$(C=O) was found at 1700 cm$^{-1}$, unshifted with respect to that of I. This suggests that in 3 and 4 the ligand I 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 CHCl$_3$. These observations confirm the square planar geometry around palladium in 3 and 4 that is implied by the $^1$H 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 $\nu$(Te–CH$_2$) and $\nu$(Te–C(Ar)) respectively. Both are red shifted, by 15–25 and 10–20 cm$^{-1}$ respectively with respect to the corresponding bands of I. The $\nu$(Pd–Cl) bands in the IR spectra of [PdCl$_2$.I] 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 \textit{trans} influence of Ph\(_3\)P 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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\section*{References}