

Ternary complexes of palladium(II) containing (Te,S) and (Te,N) hybrid organotellurium ligands: synthesis, spectra and cis–trans isomeric conversion

Raman Batheja, S.K. Dhingra, Ajai K. Singh *

Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

Received 19 December 1994

Abstract

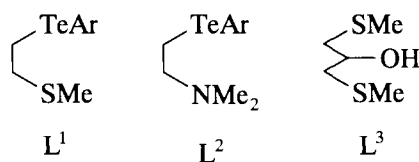
Five ternary complexes of palladium(II) namely $[\text{Pd}(\text{L}^1)_2](\text{ClO}_4)_2$ (**1**), $[\text{Pd}(\text{L}^1)(\text{L}^2)](\text{ClO}_4)_2$ (**2**), $[(\text{PPh}_3)_2\text{Pd}(\text{L}^1)](\text{ClO}_4)_2$ (**3**), $[(\text{DPPE})\text{Pd}(\text{L}^2)](\text{ClO}_4)_2$ (**4**) and $[\text{Pd}(\text{L}^1)(\text{L}^3)](\text{ClO}_4)_2$ (**5**) where $\text{L}^1 = \text{MeSCH}_2\text{CH}_2\text{TeAr}$, $\text{L}^2 = \text{Me}_2\text{NCH}_2\text{CH}_2\text{TeAr}$ ($\text{Ar} = 4\text{-MeOC}_6\text{H}_4$) and $\text{L}^3 = \text{MeSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{SMe}$ were synthesized by treating $[\text{PdCl}_2 \cdot (\text{L}^1)]$ or $[(\text{PPh}_3)_2/(\text{DPPE})\text{PdCl}_2]$ with AgClO_4 and the appropriate ligand. The ligands L^1 , L^2 and L^3 in these complexes are judged to be coordinated in bidentate mode on the basis of ^1H NMR and IR spectral data. All the complexes behave as 1:2 electrolytes in CH_3CN . The $^{125}\text{Te}\{^1\text{H}\}$ NMR spectra of **1** and **2** indicate that the ligands L^1 and L^2 in them are in a *cis* disposition in freshly prepared dimethylsulphoxide- d_6 - CD_3CN solutions, implying a similar configuration in the solid state but within a few hours there is partial conversion into the *trans* isomer.

Keywords: Palladium; Tellurium; Sulfur

1. Introduction

Knowledge of the behaviour of tellurium ligands [1–5] is still limited in comparison with those of sulphur and selenium donors. This is because only a few complexes containing tellurium donors (including hybrid donors) and ligands other than halides and P donors have been studied [4,5]. The limited commercial availability of suitable tellurium donors has also contributed to the present situation. Structural studies on the complexes of hybrid organotellurium ligands may thus be very rewarding; for example, an X-ray diffraction study [6] of *cis*- $[\text{PtCl}_2(\text{MeSCH}_2\text{CH}_2\text{TeC}_6\text{H}_4\text{-4-OEt})]$ revealed that Pt–Cl *trans* to Te is longer than Pt–Cl *trans* to S (2.336(3) and 2.324(4) Å respectively). Investigations of ternary complexes (containing ligands other than halides), particularly structural studies, would increase knowledge of the relative donor behaviour of tellurium and other ligands, but few reports of such mixed complexes have appeared up to now [1,4,5], we therefore decided to make the ternary complexes of

palladium(II) containing the ligands L^1 , L^2 and L^3 , triphenylphosphine and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$:



Unfortunately no single crystals of these ternary complexes could be grown, but the syntheses and spectra are described below.

2. Experimental details

Published methods were used to synthesize 2-(4-methoxyphenyltelluro) ethyl methyl sulphide (L^1) [7] and 2-(4-methoxyphenyltelluro)ethyl dimethylamine (L^2) [8]. Dichloro(triphenylphosphine)palladium(II) and dichloro[1,2-bis(diphenylphosphino)ethane]palladium(II) were obtained from Aldrich (USA) and 1,3-bis(methylthio)propan-2-ol from Lancaster Synthesis (UK), and all three were used as received. Conductivity measurements were made on 0.1–1.0 mM solutions of

* Corresponding author.

the complexes with a Metrohm conductometer 660. The ^1H NMR spectra were recorded on a JEOL FX-100 Fourier transform NMR spectrometer at 99.55 MHz, and $^{125}\text{Te}\{^1\text{H}\}$ NMR spectra on a Bruker AMX 360 instrument at 113.6 MHz with neat Me_2Te as an external reference. The UV–visible spectra (300–700 nm) of the complexes in solution were recorded on a Hitachi 330 UV–visible spectrometer and IR spectra, in the range 4000–200 cm^{-1} (CsI pellets) on a Nicolet-5DX Fourier transform IR spectrometer.

2.1. Synthesis of $[\text{Pd}(\text{L}^1)_2](\text{ClO}_4)_2$ (1)

A solution of $[\text{PdCl}_2(\text{L}^1)]$ (0.5 mmol) [7] in CHCl_3 (25 cm^3) was mixed under N_2 with a solution of AgClO_4 (1.0 mmol) in 25 cm^3 of methanol. The mixture was stirred for 30 min and solution of ligand L^1 (0.45 mmol) in CHCl_3 (15 cm^3) was then added. The mixture was refluxed for 2 h, the AgCl then filtered off, and the filtrate concentrated to 10–15 cm^3 under reduced pressure and diluted with hexane (10 cm^3). The resulting precipitate was filtered off, washed with hexane recrystallized from chloroform: hexane (5:1) and dried in vacuo (yield, 75%; melting point (m.p.), 141–143°C (decomposition)). Anal. Found: C, 25.39; H, 3.39. $\text{C}_{20}\text{H}_{28}\text{S}_2\text{Te}_2\text{O}_{10}\text{Cl}_2\text{Pd}$ Calc.: C, 25.89; H, 3.02%. ^1H NMR (dimethylsulfoxide- d_6 (DMSO- d_6), 25°C): δ , 2.8 (s, 3H, SMe), 3.4 (m, 4H, CH_2), 3.8 (s, 3H, OMe), 6.8–6.9 (d, 2H, ArH *o* to Te), 7.8–7.9 (d, 2H, ArH *m* to Te) ppm.

2.2. Synthesis of $[\text{Pd}(\text{L}^1)(2)](\text{ClO}_4)_2$ (2)

A solution of $[\text{PdCl}_2(\text{L}^2)]$ (0.23 mmol) in CHCl_3 (15 cm^3) was mixed under N_2 with a solution of AgClO_4 (0.5 mmol) in CH_3OH (20 cm^3). The mixture was stirred for 30 min and a solution of ligand L^2 (0.25 mmol) in CHCl_3 was added. The resulting mixture was refluxed for 4h, the AgCl was filtered off, and the filtrate concentrated to 15 cm^3 under reduced pressure and diluted with 15 cm^3 of hexane. The precipitate was filtered off, washed with hexane, recrystallized from CHCl_3 : hexane (5:1) and dried in vacuo (yield, 60%, m.p., 126°C (decomposition)). Anal. Found: C, 28.05; H, 3.61; N, 1.81. $\text{C}_{21}\text{H}_{31}\text{O}_{10}\text{NSCl}_2\text{PdTe}_2$. Calc.: C, 27.34; H, 3.36; N, 1.51%. ^1H NMR (CD_3CN , 25°C): δ ,

2.6 (s, 6H, NMe_2), 2.7 (s, 3H, SMe), 2.9–3.0 (m, 4H, CH_2Te), 3.2–8.4 (m, 4H, $\text{CH}_2\text{N}/\text{CH}_2\text{O}$), 3.8 (s, 3H, OMe), 6.8–7.1 (m, 4H, ArH *o* to Te), 7.8–8.0 (m, 4H, ArH *m* to Te) ppm.

2.3. Synthesis of $[(\text{Ph}_3\text{P})_2\text{Pd}(\text{L}^1)](\text{ClO}_4)_2$ (3)

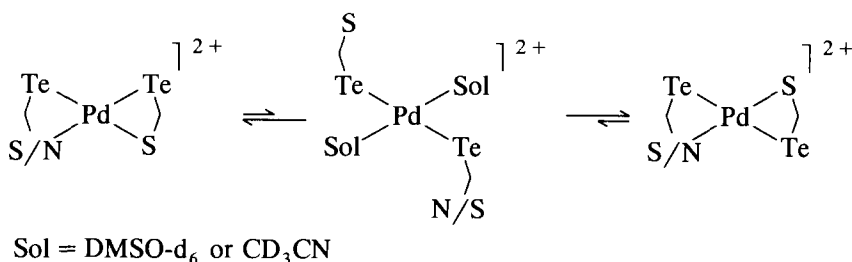
A solution of bis(triphenylphosphine) palladium(II) chloride (0.23 mmol) in CHCl_3 (15 cm^3) under a dinitrogen atmosphere was treated with a solution of AgClO_4 (0.5 mmol) in CH_3OH (15 cm^3) and the mixture was stirred for 30 min. A solution of L^1 (0.25 mmol) in CHCl_3 (5 cm^3) was added, and the mixture stirred for 3 h. The AgCl was filtered off, and the filtrate concentrated to 10 cm^3 under reduced pressure and diluted with 7 cm^3 of hexane. The precipitate was washed three to four times thoroughly with hexane: chloroform (1:1) and dried in vacuo (yield, 80%; m.p., 109°C (decomposition)). Anal. Found: C, 49.15; H, 3.60. $\text{C}_{46}\text{H}_{44}\text{O}_9\text{P}_2\text{SCl}_2\text{TePd}$: Calc.: C, 49.95; H, 3.98%. ^1H NMR (CDCl_3 , 25°C): δ , 2.7 (s, 3H, SMe), 2.9–8.1 (m, 4H, CH_2), 3.8 (s, 3H, OMe), 6.7–6.9 (d, 2H, ArH, *o* to Te), 7.1–7.7 (m, 17H, ArH *m* to Te + PPh_3) ppm.

2.4. Synthesis of $[(\text{DPPE})\text{Pd}(\text{L}^1)](\text{ClO}_4)_2$ (4)

A slurry of $[(\text{DPPE})\text{PdCl}_2]$ (0.25 mmol) in CH_3CN (20 cm^3) was mixed with a solution of AgClO_4 (0.5 mmol) in CH_3OH (20 cm^3). The mixture was stirred for 30 min, and a solution of L^1 (0.28 mmol) in chloroform (20 cm^3) was added. The mixture was stirred for a further 2 h and the AgCl then filtered off. The filtrate was concentrated to 10–15 cm^3 and 10 cm^3 of hexane was added. The resulting precipitate was filtered off, washed with hexane, recrystallized from CHCl_3 : hexane (1:1) and dried in vacuo (yield, 68%; m.p., 133–135°C (decomposition)). Anal. Found: C, 43.21; H, 4.01. $\text{C}_{36}\text{H}_{38}\text{O}_9\text{SCl}_2\text{P}_2\text{PdTe}$ Calc.: C, 42.60; H, 3.75%. ^1H NMR (CDCl_3 , 25°C): δ , 2.3 (bd, 4H, CH_2 of DPPE), 2.6 (s, 3H, SMe), 2.8–3.0 (m, 4H, CH_2 of L^1), 3.81 (s, 3H, OMe), 7.3–7.8 (m, 24H, ArH of L^1 + DPPE) ppm.

2.5. Synthesis of $[\text{Pd}(\text{L}^1)(\text{L}^3)](\text{ClO}_4)_2$ (5)

A solution of $[\text{Pd}(\text{L}^1)\text{Cl}_2]$ (0.23 mmol) in CHCl_3 (20 cm^3) was mixed with a solution of AgClO_4 (0.5 mmol)

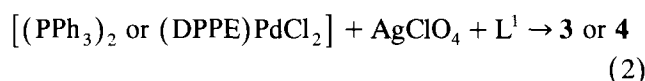
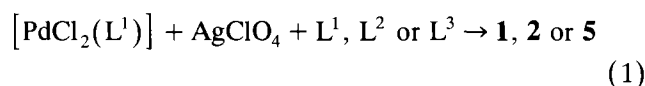


Scheme 1.

in CH₃OH. The mixture was stirred for 30 min, and a solution of L³ (0.25 mmol) in CHCl₃ (20 cm³) was then added. The mixture was stirred for 3 h, the AgCl then filtered off, the filtrate concentrated under reduced pressure to 10–15 cm³, and hexane (10 cm³) was added. The precipitate was filtered off, washed with hexane, recrystallized from CHCl₃: hexane (1:1) and dried in vacuo (yield, 60%; m.p., 155°C (decomposition)). Anal. Found: C, 24.18; H, 3.51. C₁₅H₂₆O₁₀S₃Cl₂PdTe Calc.: C, 23.46; H, 3.38%. ¹H NMR (CDCl₃, 25°C); δ 2.5–2.6 (m, 9H, SMe), 2.9–3.4 (m, very broad, 10H, CH₂ + CH + OH), 3.8 (s, 3H, OMe), 6.9–7.1 (d, 2H, ArH, *o* to Te). 7.7–7.9 (d, 2H, ArH *m* to Te). ppm.

3. Results and discussion

The reactions used to produce the palladium complexes **1–5** are



The A_M values of **1–5** in CH₃CN were found to be in the range 230–250 Ω⁻¹ cm⁻¹, showing them to be 1:2 electrolytes. ¹H NMR spectra of **1–5** were compared with those of the free ligands L¹, L² and L³ [7,8]. In the spectra of all these complexes the signals from the SMe protons are deshielded (by 0.4–0.7 ppm) with respect to those from the corresponding ligands L¹ and L³. The NMe₂ signal in the ¹H NMR spectrum of **2** was found to be deshielded by 0.3 ppm with respect to the corresponding signal for L². The signals of the TeAr protons were also found to be deshielded (by 0.1–0.3 ppm) on complexation, except in the case of **4** for which they merged with PPh₂ signals. These observations suggest that, in all the palladium complexes, L¹, L² and L³ act as bidentate ligands. In the IR spectra of **1–5** the presence of bands due to the uncoordinated ClO₄⁻ anion at 950 and 1125 cm⁻¹ confirms the nature of the complexes. The ν_4 band for uncoordinated ClO₄ seems to appear at 625 cm⁻¹, but owing to overlap with a band from ligands L¹ and L² at 630 cm⁻¹ could not be assigned unequivocally in either case. A band at 950 cm⁻¹ seems to come from the IR-inactive ν_1 frequency of uncoordinated ClO₄ allowed by the too low site symmetry. The $\nu(\text{Te}-\text{CH}_2)$ and $\nu(\text{Te}-\text{C}(\text{Ar}))$ bands [9] in the IR spectra of **1–5** were found in the regions 510–520 and 220–230 cm⁻¹ respectively. Their red shift (10–15 cm⁻¹) with respect to those for L¹ and L² confirms that tellurium is coordinated to palladium in all the complexes. The $\nu(\text{Pd}-\text{S})$ band was observed between 280 and 300 cm⁻¹. In the IR spectrum of **1** this

band is split by 15 cm⁻¹, indicating that **1** is present in the *cis* isomer. The diamagnetic complexes **1–5** exhibited bands between 280 and 320 nm in their UV–visible spectra in CHCl₃. These observations support the square planar geometry around palladium in **1–5** as implied by ¹H NMR and IR spectra.

The ¹²⁵Te(¹H) NMR spectrum of a fresh solution of **1** in DMSO-*d*₆ showed a signal at 589 ppm deshielded by about 86 ppm with respect to that of L¹, consistent with the ligation of L¹ through tellurium. After 1.5 h a new signal appeared in the ¹²⁵Te NMR spectrum at 668 ppm; its intensity reached a maximum and constant value (one quarter of the original signal) after 3 h. The *trans* form of **1** would be expected to exhibit a downfield signal [10] in the ¹²⁵Te NMR spectrum relative to that for the *cis* form. Thus **1** appears to be a *cis* isomer but slowly changes into the *trans* form as shown in Scheme 1. Similarly the ¹²⁵Te NMR spectrum of a fresh solution of **2** in CD₃CN exhibits two signals at 569 and 610 ppm, and after 1 h a new signal at 686 ppm appears. Its intensity (one quarter of that of the original signal) also reaches a constant maximum after 2 h, with the appearance of a relatively weak signal at 720 ppm. This observation indicates that, in **2**, two tellurium atoms are again *cis* to each other, but in CD₃CN solution there is partial conversion to the *trans* form as indicated in Scheme 1. The solvated intermediate does not generate a new signal, probably owing to its very fast conversion to the *cis* or *trans* form. In the ¹H NMR spectra of **1** and **2** the positions of the signals due to NMe₂ and SMe showed no change during the 4 h after preparation of the solutions, but some unresolved splitting occurred. This is consistent with the observations mentioned above and with Scheme 1. These dissociations of **1** and **2** are very significant for exploring the use of complexes containing Te ligands in catalysis. In view of the strong *trans* effect [6] of tellurium the formation of solvated species such as those shown in Scheme 1 appears logical. The crystal structures of **1–5** would have been of much interest, but in no case could suitable crystals be obtained.

Acknowledgement

We thank the Department of Atomic Energy (India) for financial support.

References

- [1] H.J. Gysling, *Coord. Chem. Rev.*, 42 (1982) 133.
- [2] H.J. Gysling, in S. Patai and Z. Rapport (eds.), *The Chemistry of Organic Selenium and Tellurium Compounds*, Vol. 1, Wiley, New York, 1986, Chapter 18, p. 815.
- [3] F.J. Berry, in G. Wilkinson, R.D. Gillard and J.A. McCleverty

- (eds.), *Comprehensive Coordination Chemistry*, Pergamon, Oxford, 1987, Chapter 17, p. 668.
- [4] A.K. Singh and V. Srivastava, *J. Coord. Chem.*, 27 (1992) 237.
- [5] E.G. Hope and W. Leavason, *Coord. Chem. Rev.*, 122 (1993) 109.
- [6] A.K. Singh, V. Srivastava, S.K. Dhingra, J.E. Drake and J.H.E. Bailey, *Acta Crystallogr., Sect. C*, 48 (1992) 655.
- [7] A.K. Singh and V. Srivastava, *J. Coord. Chem.*, 21 (1990) 269.
- [8] V. Srivastava, R. Batheja and A.K. Singh, *J. Organomet. Chem.*, 484 (1994) 93.
- [9] K.J. Irgolic, *The Organic Chemistry of Tellurium*, Gordon and Breach, New York, 1974, p 325.
- [10] H.J. Gysling, N. Zumbulyadis and J.A. Robertson, *J. Organomet. Chem.*, 209 (1981) C41.