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 [Pd(L1)2][ClO4]2 (1), [Pd(L1)(L2)][ClO4]2 (2), [(PPh3)2Pd(L1)][ClO4]2 (3), [(DPPE)Pd(L3)][ClO4]2 (4) and [Pd(L1)(L2)][ClO4]2 (5) where L1 = MeSCH2CH2TeAr, L2 = Me2NCH2CH2TeAr (Ar = 4-MeOC6H4) and L3 = MeSCH2CH(OH)CH2SMe were synthesized by treating [PdCl2 • (El)] or [(PPh3)2/PDPE]PdCl2 with AgClO4 and the appropriate ligand. The ligands L1, L2 and L3 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 CH3CN. The 125Te{1H} NMR spectra of 1 and 2 indicate that the ligands L1 and L2 in them are in a cis disposition in freshly prepared dimethylsulphoxide-d6–CD3CN 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-[PtCl2(MeSCH2CH2TeC6H4−4-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 L1, L2 and L3, triphenylphosphine and Ph2PCH2CH2PPh2:

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TeAr  TeAr  SMe
SMe  NMe2  OH  SMe
L1    L2    L3
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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-methoxyphenyletelluro)ethyl methyl sulphide (L1) [7] and 2-(4-methoxyphenyletelluro)ethyl dimethylamine (L2) [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
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 Te{1H} NMR spectra on a Bruker AMX 360
instrument at 113.6 MHz with neat Me2Te as an exter-
nal 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 [Pd(Z1)2](ClO4)2 (1)

A solution of [PdCl2(L 1)] (0.5 mmol) [7] in CHCl3
(25 cm³) was mixed under N2 with a solution of
AgClO4 (1.0 mmol) in 25 cm³ of methanol. The mix-
ture was stirred for 30 min and solution of ligand. L I
(0.45 mmol) in CHCl3 (15 cm³) was then added. The
mixture was refluxed for 2 h, the AgCl then filtered off,
and the filtrate concentrated to 10–15 cm³ under re-
duced pressure and diluted with hexane (10 cm³). The
resulting precipitate was filtered off, washed with hex-
ane recrystallized from choloform: 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. C20H19Cl2O10PdS2Te2: Calc.: C, 25.89; H, 3.02%.
1H NMR (dimethylsulfoxide-d 6 (DMSO-d6), 25°C): δ,
2.8 (S, 3H, SMe), 3.4 (m, 4H, CH₂), 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 [Pd(L1)(2)](ClO4)2 (2)

A solution of [PdCl2(L2)] (0.23 mmol) in CHCl3
(15 cm³) was mixed under N2 with a solution of
AgClO4 (0.5 mmol) in CH3OH (20 cm³). The mixture
was stirred for 30 min, and a solution of ligand L 2 (0.25
mmol) in CHCl3 was added. The resulting mixture was
refluxed for 4 h, the AgCl then filtered off, and the
filtrate concentrated to 10 cm³ under reduced pressure
diluted with 7 cm³ of hexane. The precipitate was
washed three to four times thoroughly with hexane:
chloroform (1:1) and dried in vacuo (yield, 60%; m.p.,
109°C (decomposition)). Anal. Found: C, 49.15; H,
3.60. C46H38O9P2S2Cl2TePd: Calc.: C, 49.95; H, 3.98%.
1H NMR (CDCl3, 25°C): δ, 2.7 (S, 3H, SMe), 2.9–8.1
(m, 4H, CH₂ of L1), 3.2–8.4 (m, 4H, CH₂N/CH₂O), 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 [(Ph3P)2 Pd(L1)](ClO4)2 (3)

A solution of bis(triphenylphosphine) palladium(II)
chloride (0.23 mmol) in CHCl3 (15 cm³) under a
dinitrogen atmosphere was treated with a solution of
AgClO4 (0.5 mmol) in CH3OH (15 cm³) and the
mixture was stirred for 30 min. A solution of L 1 (0.25
mmol) in CHCl3 (5 cm³) was added, and the mixture
stirred for 3 h. The AgCl was filtered off, and the
filtrate concentrated to 10 cm³ under reduced pressure
and diluted with 7 cm³ 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. C46H38O9P2S2Cl2TePd: Calc.: C, 49.95; H, 3.98%.
1H NMR (CDCl3, 25°C): δ, 2.7 (S, 3H, SMe), 2.9–8.1
(m, 4H, CH₂ of L1), 3.2–8.4 (m, 4H, CH₂N/CH₂O), 3.8 (S,
3H, OMe), 6.8–7.1 (m, 4H, ArH o to Te), 7.1–7.7 (m, 17H, ArH m to Te + Ph₃P) ppm.

2.4. Synthesis of [(DPPE)Pd(L1)](ClO4)2 (4)

A slurry of [(DPPE)PdCl₂] (0.25 mmol) in CH₂CN
(20 cm³) was mixed with a solution of AgClO4 (0.5
mmol) in CH₃OH (20 cm³). The mixture was stirred for
30 min, and a solution of L 1 (0.28 mmol) in chloroform
(20 cm³) was added. The mixture was stirred for a
further 2 h and the AgCl then filtered off. The filtrate
was concentrated to 10–15 cm³ and 10 cm³ of hexane
was added. The resulting precipitate was filtered off,
ashed with hexane, recrystallized from CHCl₃: hexane
(1:1) and dried in vacuo (yield, 68%; m.p., 133–135°C
(decomposition)). Anal. Found: C, 43.21; H, 4.01.
C₃₆H₄₃O₁₄P₂Cl₂PdTe: Calc.: C, 42.60; H, 3.75%. 1H
NMR (CDCl₃, 25°C): δ, 2.3 (bd, 4H, CH₂ of DPPE),
2.6 (S, 3H, SMe), 2.8–3.0 (m, 4H, CH₂ of L₁), 3.81(S,
3H, OMe), 7.3–7.8 (m, 24H, ArH of L₁ + DPPE) ppm.

2.5. Synthesis of [Pd(L1)(2)](ClO4)2 (5)

A solution of [Pd(L1)Cl₂] (0.23 mmol) in CHCl₃ (20
cm³) was mixed with a solution of AgClO₄ (0.5 mmol)
3. Results and discussion

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

$$\text{[PdCl}_2(L')\text{]} + \text{AgClO}_4 + \text{L}^1, \text{L}^2 \text{ or } \text{L}^3 \rightarrow \text{1, 2 or 5}$$  \hspace{1cm} (1)

$$\text{[(PPh}_3)_2 \text{ or (DPPE)}\text{PdCl}_2\text{]} + \text{AgClO}_4 + \text{L}^1 \rightarrow \text{3 or 4}$$  \hspace{1cm} (2)

The \(\Lambda_M\) values of 1–5 in CH\(_3\)CN were found to be in the range 230–250 \(\Omega \text{ cm}^{-1}\), showing them to be 1:2 electrolytes. \(^1\)H NMR spectra of 1–5 were compared with those of the free ligands \(\text{L}^1\), \(\text{L}^2\) and \(\text{L}^3\) \(^7,8\). 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 \(\text{L}^1\) and \(\text{L}^2\). The NMe\(_2\) signal in the \(^1\)H NMR spectrum of 2 was found to be deshielded by 0.3 ppm with respect to the corresponding signal for \(\text{L}^1\). 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 PPh\(_3\) signals. These observations suggest that, in all the palladium complexes, \(\text{L}^1\), \(\text{L}^2\) and \(\text{L}^3\) act as bidentate ligands. In the IR spectra of 1–5 the presence of bands due to the uncoordinated \text{ClO}_4\(^-\) anion at 950 and 1125 cm\(^{-1}\) confirms the nature of the complexes. The \(\nu_4\) band for uncoordinated \text{ClO}_4\(^-\) seems to appear at 625 cm\(^{-1}\), but owing to overlap with a band form ligands \(\text{L}^1\) and \(\text{L}^2\) 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 \(\nu_3\) frequency of uncoordinated \text{ClO}_4\(^-\) allowed by the low site symmetry. The \(\nu(\text{Te}-\text{CH}_2\text{)}\) and \(\nu(\text{Te}-\text{C(At)}\text{)}\) 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 \(\text{L}^1\) and \(\text{L}^2\) confirms that tellurium is coordinated to palladium in all the complexes. The \(\nu(\text{Pd-S})\) 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 \textit{cis} isomer. The diamagnetic complexes 1–5 exhibited bands between 280 and 320 nm in their UV–visible spectra in CHCl\(_3\). These observations support the square planar geometry around palladium in 1–5 as implied by \(^1\)H NMR and IR spectra.

The \(^{125}\text{Te}(^1\text{H})\) 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 \(\text{L}^1\), consistent with the ligation of \(\text{L}^1\) through tellurium. After 1.5 h a new signal appeared in the \(^{125}\text{Te}\) NMR spectrum at 668 ppm; its intensity reached a maximum and constant value (one quarter of the original signal) after 3 h. The \textit{trans} form of 1 would be expected to exhibit a downfield signal \(^10\) in the \(^{125}\text{Te}\) NMR spectrum relative to that for the \textit{cis} form. Thus 1 appears to be a \textit{cis} isomer but slowly changes into the \textit{trans} form as shown in Scheme 1. Similarly the \(^{125}\text{Te}\) NMR spectrum of a fresh solution of 2 in CD\(_3\)CN 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 \textit{cis} to each other, but in CD\(_3\)CN solution there is partial conversion to the \textit{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 \textit{cis} or \textit{trans} form. In the \(^1\)H NMR spectra of 1 and 2 the positions of the signals due to NMe\(_2\) 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 \textit{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


