3-(4-METHOXYPHENYLTELLEURO)PROPANE-1,2-DIOL—SYNTHESIS AND REACTIONS WITH MERCURY(II), PALLADIUM(II) AND PLATINUM(II) HALIDES

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Abstract—The reaction of \(\text{ArTe}^+\text{Na}^+\) (\(\text{Ar} = 4\text{-MeOC}_6\text{H}_4\)) generated in situ by borohydride reduction of \(\text{Ar}_2\text{Te}_2\) under a nitrogen atmosphere, with \(\text{CH}_3\text{OH} \cdot \text{CHOH} \cdot \text{CH}_2\text{Cl}\) gave 3-(4-methoxyphenyltelluro)propane-1,2 diol (I). The reactions of I with \(\text{HgCl}_2\), \(\text{HgBr}_2\), \([\text{PdCl}_2\) (\(\text{MeCN})_2\)], \(\text{K}_2\text{[PtCl}_4]\), \(\text{cis}-\{\text{PPPh}_3\text{PdCl}_2\}\) and \(\text{cis}-\{\text{PPPh}_3\text{PtCl}_2\}\) have been investigated. Complexes of the types \([\text{MX}_2\) \(\text{I})_2\], \([\text{MX}_2(\text{I})_2]\), \([\text{PPh}_3\text{P}]\text{Cl}(\text{I})\text{ClO}_4\) and \([\text{PPh}_3\text{P}]_2\text{M(II)}\) \([\text{ClO}_4]_2\) \((\text{M} = \text{Hg, Pd or Pt})\) were synthesized. In the \(1^H\) NMR spectra of the first three types of complexes, \(\text{CH}_3\) —Te and aryl signals of I undergo a downfield shift of 0.3 to 0.7 ppm. This observation, in conjunction with no change in the position of v(OH) and a red shift in \(\nu\text{[Te—C(aryl/alkyl)]}\) bands in their IR spectra, suggests that I coordinates through tellurium only. The \(\nu\text{[Pd—Cl]}\) band for \([\text{PdCl}_2(\text{I})]\) suggests a cis-configuration. The last two species behave as 1 : 1 and 1 : 2 electrolytes, respectively. In \([\text{PPh}_3\text{P}]_2\text{M(II)}\) \([\text{ClO}_4]_2\) coordination of the ligand I through Te and one OH group is possible, as indicated by the \(1^H\) NMR and IR/sr IR spectra. The \(3^P\{^1H\}\) spectra of \([\text{PPh}_3\text{P}]_2\text{Pd(II)}\text{Cl}\text{ClO}_4\) and \([\text{PPh}_3\text{P}]_2\text{Pd(II)}\) \([\text{ClO}_4]_2\) suggest that the two \text{PPh}_3 groups of these species are cis to each other. \(3^J(\text{P(III)—Pd—P})\) was 22–26 Hz. Attempts to stabilize metal diolates of palladium through chelation with tellurium did not succeed as the reaction between the disodium salt of I with \([\text{CH}_3\text{CN}_2\text{PdCl}_2]\) instantaneously gave elemental tellurium. The UV–vis spectra of palladium and platinum complexes support a square planar geometry of ligands.

There is a current interest in the chemistry of organotellurium ligands as they are much less studied than their sulphur and selenium analogues. The ligation of hybrid organotellurium donors is even less explored, particularly of the type with oxygen as the donor atom along with tellurium. No attempt has been made to study the complexation of any \((\text{Te}_2\text{O}_2)\) ligand. It was, therefore, thought worthwhile to synthesize 3-(4-methoxyphenyltelluro)propane-1,2-diol (I), which is potentially of this type, and study its ligational behaviour with mercury(II), palladium(II) and platinum(II).

\[
\text{CH}_3\text{OH} \quad \text{Te} \quad \text{OH} \quad \text{OH}
\]

Since coordination with tellurium stabilizes the alkoxydes of platinum metals, which are otherwise prone to \(\beta\)-hydrogen elimination, it was thought worthwhile to examine whether such stabilization may be achieved for the metal diolates. The results of these investigations are reported in the present paper.
EXPERIMENTAL

Published methods were used to synthesize bis(4-
methoxyphenyl)ditelluride. 3-Chloropropane-1,2-
diol was procured from Lancaster Synthesis, U.K.
Dichlorobis(triphenylphosphine)palladium(II) and
dichlorobis(triphenylphosphine)platinum(II) were
used as received from Aldrich, U.S.A. Carbon and
hydrogen analyses were performed on a Perkin-
Elmer 240C elemental analyser. Conductance
measurements were obtained using a Metrohm 660
conductometer and a Toshniwal conductivity
bridge. IR spectra in the range 400–4000 cm\(^{-1}\) (KBr
pellets) were recorded on a Nicolet-5DX FT-IR
spectrometer. Far-IR spectra (700–50 cm\(^{-1}\)) were
recorded in polyethylene on a Perkin-Elmer 1700-
X FT-IR spectrometer. UV-vis spectra (300–700
nm) of the complexes in solution and reflectance
spectra were recorded on a Hitachi-330 UV-vis
spectrometer. \(^1\)H NMR spectra were recorded at 90
MHz on a Perkin-Elmer 32 FT-NMR spectrometer
and at 99.55 MHz on a JEOL FX-100 FT-NMR
spectrometer. \(^31\)P[\(^1\)H] NMR spectra were recorded
on a Bruker AMX 400 spectrometer at 162 MHz
using H\(_2\)PO\(_4\) as an external reference.

Synthesis of 3-(4-methoxyphenyl)ditelluride (I)

Bis(4-methoxyphenyl)ditelluride (2 mmol) was
refluxed in ethanol (30 cm\(^3\)) under an oxygen-free
dinitrogen atmosphere. Sodium borohydride (0.2 g
dissolved in 5 cm\(^3\) of 1 M NaOH) was added drop-
wise to the refluxing solution until it became colour-
less. The solution was cooled to 35°C and 3-chlo-
ropropane-1,2-diol (4 mmol) dissolved in ethanol
(5 cm\(^3\)) was added dropwise with stirring. The
resulting pale yellow mixture was refluxed for 30–
60 min, cooled to room temperature and poured
into water (200 cm\(^3\)). Compound I was extracted
into CH\(_2\)Cl\(_2\) or CHCl\(_3\) (150 cm\(^3\)) and the extract
was washed with water, dried over anhydrous
Na\(_2\)SO\(_4\) and reduced in volume to 15–20 cm\(^3\) under
reduced pressure. Petroleum ether (40–60°C) or
hexane (10 cm\(^3\)) was then added to the concentrated
extract. The resulting white precipitate was washed
3–4 times with petroleum ether or hexane to remove
the precursor ditelluride, recrystallized from a hex-
ane-chloroform (30:70) mixture and dried in vacuo.

Synthesis of [HgX\(_2\)·1] and [HgX\(_2\)·(I)] (X = Cl or
Br)

Mercury(II) chloride or bromide (1 mmol) dis-
solved in acetone (5 cm\(^3\)) was added to a solution
of 1 (1 mmol) in CHCl\(_3\) (10 cm\(^3\)) and the mixture
was stirred for 30 min. The complex [HgX\(_2\)·1] was
precipitated as an off-white solid and was washed
5–6 times successively with methanol and hexane
and dried in vacuo.

For the synthesis of [HgX\(_2\)·(I)] mercury(II)
chloride or bromide (1 mmol) was reacted with 1
(2 mmol) in an analogous manner except that the
reaction mixture was refluxed for 30 min and hex-
ane (10 cm\(^3\)) was added to the mixture to precipitate
the white complex.

Synthesis of [PdCl\(_2\)·I] and [PdCl\(_2\)·(I)]

[(CH\(_3\)CN)\(_2\)PdCl\(_2\)] (0.1 mmol) was dissolved in
CHCl\(_3\) (10 cm\(^3\)) and mixed with a solution of I (0.1
mmol) in chloroform (15 cm\(^3\)). The mixture was
stirred for 2 h and mixed with petroleum ether (10
cm\(^3\)) (40–60°C). The brown [PdCl\(_2\)·I] complex
which precipitated was filtered, washed with pet-
roleum ether, recrystallized from a chloroform-
hexane (3:1) mixture and dried in vacuo.

To synthesize [PdCl\(_2\)·(I)], I (1 mmol) was reacted
with [(CH\(_3\)CN)\(_2\)PdCl\(_2\)] (0.5 mmol) as described
above for [PdCl\(_2\)·I], except that hexane or
petroleum ether (15 cm\(^3\)) (40–60°C) was added
after stirring and the resulting reddish-brown pre-
cipitate was washed 4–5 times with hexane and
recrystallized from acetonitrile.

Synthesis of [PtCl\(_2\)·I]

A slurry of 1 (0.3 mmol) in ethanol (5 cm\(^3\)) was
added to an aqueous solution (10 cm\(^3\)) of K\(_2\)PtCl\(_4\)
(0.1 mmol). The mixture was then stirred for 5–6 h
at room temperature. The complex was extracted
in chloroform (50 cm\(^3\)). The extract was washed
with water, dried over anhydrous Na\(_2\)SO\(_4\), reduced
in volume to 5–6 cm\(^3\) under reduced pressure and
mixed with petroleum ether (10 cm\(^3\)) (40–60°C).
The complex which precipitated was washed with
petroleum ether 5–6 times and dried in vacuo.

Synthesis of [(Ph\(_3\)P)\(_2\)MCI(M)]ClO\(_4\) and [(Ph\(_3\)P)\(_2\)M(M)]
(ClO\(_4\))\(_2\) (M = Pd or Pt)

Dichlorobis(triphenylphosphine)palladium(II) or
dichlorobis(triphenylphosphine)platinum(II) (0.1
mmol) dissolved in CHCl\(_3\) (10 cm\(^3\)) was stirred
with a solution of I (0.1 mmol) in CHCl\(_3\) in the
presence of AgClO\(_4\) (0.1 mmol) at room tem-
perature for 2–3 h. The white precipitate of AgCl
was then filtered off. The volume of filtrate was
reduced to 5 cm\(^3\) under reduced pressure and pet-
roleum ether (10 cm\(^3\)) (40–60°C) was added to this
concentrated filtrate. The resulting precipitate of
3-(4-Methoxyphenyltelluro)propane-1,2-diol

Table 1. Physical properties and analytical data of 1 and its metal complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>M.p. (°C)</th>
<th>Analyses: Found (Calc.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
<td>39.2</td>
<td>43 (4.5)</td>
</tr>
<tr>
<td>[HgCl₂·I₂] (2)</td>
<td>75</td>
<td>54-56</td>
<td>20.2 (26.8)</td>
</tr>
<tr>
<td>[HgBr₂·I₂] (3)</td>
<td>78</td>
<td>59-61</td>
<td>18.3 (17.9)</td>
</tr>
<tr>
<td>[HgCl₂(I₃)] (4)</td>
<td>71</td>
<td>66-68</td>
<td>27.0 (26.9)</td>
</tr>
<tr>
<td>[HgBr₂(I₃)] (5)</td>
<td>73</td>
<td>76-78</td>
<td>24.7 (24.5)</td>
</tr>
<tr>
<td>[PtCl₆·I₂] (6)</td>
<td>85</td>
<td>110(d)</td>
<td>24.5 (24.6)</td>
</tr>
<tr>
<td>[PtCl₆·I₂] (7)</td>
<td>62</td>
<td>140(d)</td>
<td>21.6 (20.8)</td>
</tr>
<tr>
<td>[PdCl₆·I₂] (8)</td>
<td>85</td>
<td>62-64</td>
<td>30.5 (30.1)</td>
</tr>
<tr>
<td>[(P₆)P₂PdCl₄·(1)]ClO₄ (9)</td>
<td>82</td>
<td>140(d)</td>
<td>52.0 (51.3)</td>
</tr>
<tr>
<td>[(P₆)P₂PtCl₄·(1)]ClO₄ (10)</td>
<td>80</td>
<td>140(d)</td>
<td>49.1 (48.5)</td>
</tr>
<tr>
<td>[(P₆)P₂PtCl₄·(1)]ClO₄ (11)</td>
<td>82</td>
<td>130(d)</td>
<td>48.0 (47.4)</td>
</tr>
<tr>
<td>[(P₆)P₂PtCl₄·(1)]ClO₄ (12)</td>
<td>85</td>
<td>120(d)</td>
<td>45.6 (44.9)</td>
</tr>
</tbody>
</table>

~d₈ = decomposes.

([(P₆)P₂PdCl₄·(1)]ClO₄ (yellow) or [(P₆)P₂PtCl₄·(1)]ClO₄ (light yellow) was filtered, washed with petroleum ether, recrystallized from CH₂Cl₂ and dried in vacuo.

For the synthesis of [(P₆)P₂PdCl₄·(1)]ClO₄ or [(P₆)P₂PtCl₄·(1)]ClO₄, dichlorobis(triphenylphosphine)palladium(II) or dichlorobis(triphenylphosphine)platinum(II) (0.1 mmol) was reacted with 1 (0.1 mmol) in the presence of AgClO₄ (0.2 mmol) in an analogous manner as described for [(P₆)P₂MCl₆·I₂]ClO₄ except that the dark yellow precipitate of the palladium complex and the yellow precipitate of the platinum complex were recrystallized from chloroform.

Elemental analyses, m.p., ¹H NMR data and important IR bands of 1 and its complexes are recorded in Table 1 and 2.

Attempted synthesis of palladium(II) diolates

Compound 1 (0.5 mmol) was dissolved in dry THF and stirred with excess sodium metal for 2 h at 50°C. The excess sodium was filtered off and the filtrate was mixed with (CH₂CN)₄PdCl₂ and stirred for 30 min. The orange solution quickly turned black, precipitating elemental tellurium.

RESULTS AND DISCUSSION

The potential (Te₂O₄)₃⁻ type ligand 3-(4-methoxyphenyltelluro)propane-1,2-diol (1) has been synthesized by the reaction in eq. (1).

\[
\text{1/2Ar₂Te₂} + \text{NaBH₄} \rightarrow \text{ArTe}^- \text{Na}^+ + \text{Cl(CH₂)CHOHCHO} \rightarrow 1 \quad (1)
\]

The asymmetric telluride 1 was found to be soluble in CHCl₃, CH₂Cl₂ and other common organic solvents. It behaves as a non-electrolyte (Δm, 27.8 Ω⁻¹ cm² mol⁻¹) in dimethylformamide. The ¹H NMR signals of 1 and their assignments are given in Table 2. The ¹H NMR spectrum of the precursor 1-chloro-propane-1,2-diol in CDCl₃ exhibits two signals, one at δ 2.75 ppm (due to OH) and the other at 3.5–3.8 ppm (multiplet due to overlap of CH and CH₂ signals). On substitution of Cl with a much less electronegative tellurium, one of these CH₂ signals shifts upfield and the composite signal of the OH groups splits into two. The important IR bands of 1 along with their assignments are also given in Table 2 and support its formation in the reaction of eq. (1). The UV–vis spectrum of 1 in CHCl₃ exhibits a shoulder at 380 nm. None of the complexes of 1 produce single crystals suitable for X-ray diffraction. The solubilities of these complexes were also inadequate for ¹²⁵Te NMR. Thus, ¹H NMR and IR spectra could only be used to study their structural features.

Table 2 indicates that the aryl protons in the ¹H NMR spectra of [MCl₂·I₂] and [MCl₆·I₂] type complexes appear deshielded (0.5–0.7 ppm) with respect to those of 1. The deshielding is significant even after applying corrections for the solvent effect. In the ¹H NMR spectra of [(P₆)P₂MCl₄·(1)]ClO₄ and [(P₆)P₂MCl₄·(1)]ClO₄ type species aryl signals of ArTc and Ph₂P groups are merged together and therefore could not be used for any diagnostic purpose. The CH₂—Te signal was deshielded (0.3 to 0.5 ppm) in the spectra of 6–12, but could not be observed in the ¹H NMR spectra of 4 and 5 as it merged with OH, CH and OCH₂ signals. These observations suggest that 1
Table 2. $^1$H NMR data and important IR bands of 1 and its metal complexes

| Compound | Solvent | 1H NMR data at 25°C Chemical shift (δ, ppm) | Important IR bands (cm$^{-1}$) | ν(M—X) | ν(M—X—M) | ν(OH) | ν(Te—C) ary/alkyl
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CDCl$_3$</td>
<td>1.92(b,OH,linked to CH$_2$), 2.48(b,OH,linked to CH$_3$), 2.72(d,2H,CH$_2$Te), 3.10-3.75(m,6H,CH + CH$_2$ + OCH$_3$), 6.12-6.21(d,2H,ArH o to Te), 6.91-7.12(d,2H,m to Te)</td>
<td>—</td>
<td>—</td>
<td>3280-3340b</td>
<td>240,318/522</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Solubility inadequate for NMR</td>
<td>234</td>
<td>178</td>
<td>3275-3345b</td>
<td>220,290/510</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>Solubility inadequate for NMR</td>
<td>180</td>
<td>143</td>
<td>3280-3335b</td>
<td>218,245/510</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>DMSO-d$_6$</td>
<td>2.78-3.50(vb,OH + CH + CH$_2$ + OCH$_3$), 6.62-6.73(d,2H,ArH o to Te), 7.43-7.62(d,2H,ArH m to Te)</td>
<td>237</td>
<td>—</td>
<td>3278-3345b</td>
<td>225,292/512</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>DMSO-d$_6$</td>
<td>2.79-3.52(vb,OH + CH + CH$_2$ + OCH$_3$), 6.63-6.70(d,2H,ArH o to Te), 7.42-7.61(d,2H,ArH m to Te)</td>
<td>181</td>
<td>—</td>
<td>3280-3345b</td>
<td>225,292/512</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>DMSO-d$_6$</td>
<td>2.97(d,2H,CH$_2$Te), 3.45-3.85(vb,OH + CH + CH$_2$ + OCH$_3$), 6.82-6.92(d,2H,ArH o to Te), 7.52-7.72(d,2H,ArH m to Te)</td>
<td>325</td>
<td>268</td>
<td>3272-3340b</td>
<td>220,288/507</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>DMSO-d$_6$</td>
<td>3.0(d,2H,CH$_2$Te), 3.25-3.72(vb,OH + CH + CH$_2$ + OCH$_3$), 6.79-6.91(d,2H,ArH o to Te), 7.61-7.71(d,2H,ArH m to Te)</td>
<td>320</td>
<td>257</td>
<td>3278-3345b</td>
<td>220,288/507</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>DMSO-d$_6$</td>
<td>2.02(b,OH), 3.0(d,2H,CH$_2$Te), 3.65-3.85(b,6H,CH + CH$_2$ + OCH$_3$), 6.75-6.84(d,2H,ArH o to Te), 7.65-7.75(d,2H,ArH m to Te)</td>
<td>283</td>
<td>—</td>
<td>3275-3340b</td>
<td>220,283/512</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>CD$_3$CN</td>
<td>2.50(b,OH), 3.10(d,2H,CH$_2$Te), 3.35-3.85(m,6H,CH + CH$_2$ + OCH$_3$), 6.40-7.95(m,34H,ArH of PPh$_3$ and Ar group linked to Te)</td>
<td>275</td>
<td>—</td>
<td>3275-3340b</td>
<td>215,293/507</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>CD$_3$CN</td>
<td>2.88(b,OH), 3.16(d,2H,CH$_2$Te), 3.30-3.87(m,6H,CH + CH$_2$ + OCH$_3$), 6.45-8.05(m,34H,ArH of PPh$_3$ and Ar group linked to Te)</td>
<td>—</td>
<td>—</td>
<td>3230-3380b</td>
<td>215,294/512</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>CD$_3$CN</td>
<td>2.61(b,OH), 3.21(d,2H,CH$_2$Te), 3.41-3.89(m,6H,CH + CH$_2$ + OCH$_3$), 6.50-8.04(m,34H,ArH of PPh$_3$ and Ar group linked to Te)</td>
<td>300</td>
<td>—</td>
<td>3278-3340b</td>
<td>215,293/507</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>CD$_3$CN</td>
<td>2.82(b,OH), 3.12(d,2H,CH$_2$Te), 3.24-3.78(m,6H,CH + CH$_2$ + OCH$_3$), 6.51-8.01(m,34H,ArH of PPh$_3$ and Ar group linked to Te)</td>
<td>—</td>
<td>—</td>
<td>3220-3290b</td>
<td>215,293/512</td>
<td></td>
</tr>
</tbody>
</table>

X = Cl or Br; o, ortho; m, meta; b, broad; vb, very broad.
ligates in 4–12 through tellurium. The IR spectra of all complexes 2–12 exhibit, with respect to the IR spectrum of 1, a red shift (Table 2) of the order 10–15 cm⁻¹ in ν(Te—C(alkyl))² and 15–35 cm⁻¹ in ν(Te—C(aryl))². This observation further supports the ligation of I through tellurium in all the complexes. The dimeric species [MX₂·(I)]₂ appear to be formed by chloro/bromo bridges between the two metallic centres, as evidenced by ν(X—M—X) bands in their IR spectra (Table 2). Since not all bridging vibrations exhibit any splitting, the bridges appear centrosymmetric. The OH signals in the ¹H NMR spectra of [Pd/PtCl₃·I]₂ (6 and 7) species do not appear separately. However, in the IR spectra of all four species of the type [MX₂·I]₂ ν(OH) appears at a position similar to that in I. These observations suggest that I in these bimetallic species behaves as a monodentate ligand coordinating only through tellurium. They were all found to exhibit non-electrolyte behaviour (ΔM 30–33 Ω⁻¹ cm² mol⁻¹) in DMF, which commensurates with the tentative structures for 2/3 and 6/7 given below, presuming tetrahedral geometry around mercury and square planar around palladium/platinum.

\[
\text{\[MX_2 \cdot I\]_2, X = Cl or Br}
\]

In the UV–vis spectra of palladium and platinum complexes recorded in DMSO (concentration of complexes 10 mM), a band appears at 330 and 340 nm, respectively, which supports a square planar geometry. The reflectance spectra of these complexes exhibited bands at 345 and 350 nm, respectively. Thus, it appears that the species in DMSO solution are not different from those present in the solid state, except in dilute solutions (0.1 mM) which exhibit shoulders at 300 and 400 nm for both the metals.

The [MX₂·(I)]₂-type species also behave as non-electrolytes in DMF (ΔM 29–35 Ω⁻¹ cm² mol⁻¹). In their IR spectra ν(OH) was observed at a position similar to that of I and only terminal ν(Hg—Cl), ν(Hg—Br) and ν(Pd—Cl) bands were observed (Table 2). The OH signals are not observed separately in any of the ¹H spectra of the [MX₂·(I)]₂-type species, but the broad peak in which the OH signals appear to be merged cannot be explained without such an assumption. On the basis of these observations it appears that 1 ligates in a monodentate manner in these species, coordinating only through tellurium. The position of ν(Pd—Cl) suggests that the two Cl atoms are cis to each other. Thus, the following tetrahedral and square-planar structures may be proposed for the mercury (4/5) and palladium complexes (8), respectively. The UV–vis spectrum of [PdCl₃(I)]₂ in DMF exhibits two bands at 330 and 405 nm, which further support the square planar geometry around palladium.

\[
\text{\[PdCl₃(I)\]_2, X = Cl or Br}
\]

The complex species [PPh₃]₂MCl₃(I)ClO₄ (9 and 11) (where M = Pd/Pt) were found to behave as 1:1 electrolytes in CH₃CN (ΔM 134–140 Ω⁻¹ cm² mol⁻¹). [PPh₃]₂MCl₃(I)ClO₄ (10 and 12) behave as 1:2 electrolytes (ΔM 222–235 Ω⁻¹ cm² mol⁻¹) in the same solvent. ν(OH) in the IR spectra of 9 and 11 was unaffected (Table 2). This observation suggests that I behaves as a monodentate ligand coordinating through tellurium in 9 and 11 also. The ¹H NMR spectrum of [PPh₃]₂PdCl₃(I)ClO₄ (9) in DMSO-d₆ exhibits two doublets of almost equal intensities at δ 20.6 and 23.7 ppm [²J(P—Pd—P) 24–26 Hz], which suggest that the two PPh₃ groups are cis to each other. The square-planar geometry of the metal in 9 and 11 is supported by the UV–vis spectra as the palladium derivative exhibits bands at 275 and 340 nm (in CH₃CN) whereas the platinum complex exhibits a band at 310 nm in CH₃CN. In the reflectance spectra of 9 and 11 the bands were found to be 15 nm red-shifted with respect to those observed in solution. In the IR spectra of 10 and 12 a red shift of 50–60 cm⁻¹ was observed in ν(OH). An OH signal was observed separately in the ¹H NMR spectra of 10 and 12, which was 0.4 ppm downfield with respect to the low-field OH signal of free I. For the OH group this value of deshielding, after considering the solvent correction, does not conclusively suggest that in 10 and 12 ligand I is coordinating in a bidentate mode through one oxygen and one tellurium. However, this possibility has not been dismissed. In the ¹H NMR spectrum of [PPh₃]₂PdCl₃(I)ClO₄ (10) two signals were observed at 19.1 and 24.2 ppm [²J(P—Pd—P) 22–24 Hz], which suggest that the two PPh₃ groups are cis to each other. Since PPh₃ groups in 9–12 appear to be cis it is possible that OH coordinates through oxygen in 10/12. The UV–vis spectra in CH₃CN (complex concentration 10 mM) exhibit bands at 330 and 350 nm for 10 and 12, respectively, sug-
gesting a square-planar geometry around the metal. This is supported by the reflectance spectra of 10/12, which exhibit bands at 340 and 365, respectively, for the metals.

\[
\text{Ph}_3\text{P} - \text{M} - \text{Cl} \\
\text{Ph}_3\text{P} - \text{Te} \\
\text{M} = \text{Pd or Pt}
\]

It is possible that in 10/12 one \(\text{ClO}_4\) is in the coordination sphere and due to its substitution by a solvent molecule, on dissolving in \(\text{CH}_3\text{CN}\) the complex exhibits \(\Delta m\) corresponding to a 1:2 electrolyte. However, no clear picture regarding this emerges on comparing the solution and reflectance spectra of 10 and 12 as the solution spectra on dilution to 0.1 mmol become different from the reflectance spectra exhibiting shoulders at 310 and 390 nm for both the species. Moreover, IR bands indicating coordinated \(\text{ClO}_4\) groups could not be observed. As stated earlier, since 9–12 do not give crystals suitable for X-ray work, further support for the speculated geometrical configurations and coordination of OH could not be obtained.

Since chelation through tellurium stabilizes the alkoxides of palladium it was thought worthwhile to attempt the stabilization of palladium(II) diolates through the support of the Pd–Te bond. However, the reaction of the disodium salt of 1 with \((\text{CH}_3\text{CN})_2\text{PdCl}_2\) resulted in an orange solution which quickly decomposed to give elemental tellurium and an intricate mixture which defied all attempts of separation and identification.

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REFERENCES