Pergamon

PII: S0277–5387(96)00525–6

Polyhedron Vol. 16, No. 14, pp. 2509–2516, 1997

0277–5387/97 $17.00+0.00

Hybrid (Te,O) ligands 2-(phenyltelluromethyl)tetrahydro-2*H*-pyran (L^1) and 2-(2-{4-methoxyphenyl}telluorethyl)-1,3-dioxane (L^2), and their palladium(II) and platinum(II) complexes

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(Received 3 April 1996; accepted 25 October 1996)

Abstract—The nucleophilic reaction of *in situ* generated [$ArTe^-$] with appropriate organic halides has been used to synthesize 2-(phenyltelluromethyl)-tetrahydro-2*H*-pyran (L^1) and 2-(2-{4-methoxyphenyl}telluorethyl-1,3-dioxane (L^2). Their complexes with stoichiometries [$MCl_2(L)_2$],[$M(L)_2$](ClO_4)$_2$, [M(DPPE)$(L)_2$](ClO_4)$_2$, [$M(PPh_3)_2(L)_2$](ClO_4)$_2$ and [M(phen)$(L)_2$](ClO_4)$_2$ [where M = Pd^{II} or Pt^{II}; L = L^1 or L^2, DPPE = 1,2-bis(diphenylphosphino)ethane], have been synthesized. Molecular weight, conductance measurements, IR, UV–visible, ^1H, ^{125}Te-{^1H} and ^{31}P-{^1H} NMR spectra have been used to characterize L^1, L^2 and their complexes. Ligation of the two (Te,O) ligands, in all the complexes, except [$M(L)_2$](ClO_4)$_2$, is in the monodentate mode through tellurium only. [$PtCl_2(L)_2$]-type complexes exist in solution as a mixture of *cis* and *trans* isomers, the latter being present in very high abundance. The complexes [$PdCl_2(L)_2$] exhibit only one ν(Pd—Cl) between 340 and 350 cm^{-1}, consistent with a *trans* structure. The ^1J(Pt—Te) values (658–704 Hz) in the ^{125}Te NMR spectra of [$Pt(L)_2$](ClO_4)$_2$ and [$Pt(PPh_3)_2(L)_2$](ClO_4)$_2$ correspond to *trans* structures, which are supported in the second type of complexes by ^1J(Pt—P) (*ca* 3000 Hz). The ^{31}P NMR spectral data indicate that the mixed ligand complexes of Pd^{II} and Pt^{II} containing PPh_3 and DPPE are isostructural. The chelate shifts in the ^{125}Te NMR spectra have been found to be large and positive (113–127 ppm) when five-membered chelate rings are formed, but for six-membered chelation the shift is small and negative (−15 to 19 ppm). The quenching of $^1O_2$ by [Pd(phen)$(L)_2$](ClO_4)$_2$ has been observed. © 1997 Elsevier Science Ltd

Keywords: 2-(phenantelluromethyl)tetrahydro-2H-pyran; palladium 2-(2-{4-methoxyphenyl}telluroethyl)-1,3-dioxane; platinum complex; hybrid; ligand.

The complexation of substrates by organotransition metal compounds represents an important step in the course of catalytically operating processes [1,2]. This generally occurs by elimination of solvent molecules, which are usually ethers or ketones. On using (P,O) ligands for designing the catalytically active species [3], the role of solvent is replaced by weak coordination with oxygen. The pendant arm of the ligand containing oxygen protects the metal until substrates reach it. The metal–oxygen bond is cleaved reversibly and, owing to an opening and closing mechanism [4], empty coordination sites are made available when needed in the course of the catalytic cycles without separation of the oxygen donors from the complex fragment. Thus, the hemilabile (P,O) ligands find applications [3] in important types of catalytic processes, namely oligomerization of olefins, carbonylation of methanol and hydrogenations. Despite the current interest in hybrid telluroether ligands [5–10] only one (Te,O) ligand [9a], which can mimic the ligation behaviour of (P,O) ligands, has been designed. However, it is unstable and so further investigations on it have been restricted. It was therefore thought worthwhile to design (Te,O) ligands L^1 and L^2, which are reasonably stable, and investigate their ligation behaviour. The synthesis of L^1, L^2 and their palladium(II) and platinum(II) complexes, spectro-

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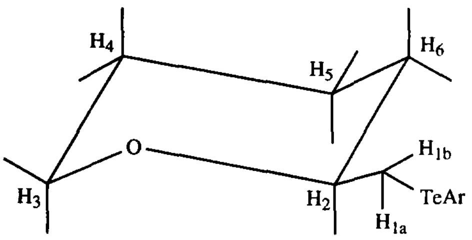
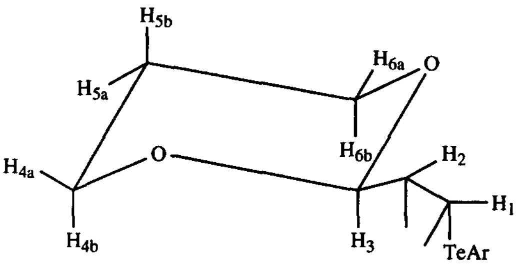


L^1



L^2

scopic properties of the ligand and complexes are the subject of the present paper.

EXPERIMENTAL

Published methods were used to synthesize bis(4-methoxyphenyl)ditelluride [11] and diphenyl ditelluride [12]. 2-(Bromomethyl)tetrahydro-2*H*-pyran and 2-(2-bromoethyl)-1,3-dioxane were obtained from Aldrich, U.S.A. and used as received. Bis(triphenylphosphine)platinum(II) chloride and bis(triphenylphosphine)palladium(II) chloride were used as received from Strem, U.S.A. Dichloro{1,2-bis (diphenylphosphino)ethane}palladium(II) and dichloro{1,2 - bis(diphenylphosphino)ethane}platinum (II) were synthesized by the literature method [13]. Dichloro(1,10-phenanthroline)palladium(II) and dichloro(1,10-phenanthroline)platinum(II) were also prepared by a published method [14].

Carbon and hydrogen analyses were carried out on a Perkin–Elmer 240C rapid elemental analyzer. Tellurium was estimated titrimetrically [15]. Melting points were determined in an open capillary and reported as such. Molecular weights were determined by Knauer vapour pressure osmometer, and conductance measurements were carried out on a Metrohm 660 conductometer with *ca* 1 mM solutions. IR spectra in the range 4000–200 cm^{-1} were recorded on a Nicolet 5DX FT-IR spectrometer in KBr/CsI pellets or in Nujol mull between CsI windows. The far-IR spectra (700–30 cm^{-1}) were recorded in polyethylene on a Perkin–Elmer 1700X FT-IR spectrometer. A Hitachi 330 UV–vis spectrometer was used for recording UV–vis spectra in the range 200–750 nm. The ^{1}H NMR spectra were recorded at 500 MHz (Bruker AMX 500) and 400 MHz (Bruker AMX 400) using TMS as an internal reference. The ^{31}P-{^{1}H} and ^{125}Te-{^{1}H} NMR spectra were recorded at 162 and 126 MHz using H_3PO_4 and $(CH_3)_2Te$ as external references. A photoirradiator equipped with a 150 W xenon arc lamp was used for generating singlet oxygen. The $NaNO_2$ solution (7%) was used to cut off [16] the light of wavelength less than 400 nm.

Synthesis of L^1 *and* L^2

Diphenylditelluride or bis(4-methoxyphenyl)ditelluride (2 mmol) was dissolved in ethanol (30 cm^3) and set to reflux under dinitrogen. A 5% solution of $NaBH_4$ made in 5% NaOH was added dropwise under dinitrogen to the refluxing solution of ditelluride until it became colourless, resulting in [ArTe$^-$Na$^+$]. 2-(Bromomethyl)tetrahydro-2*H*-pyran or 2-(2-bromoethyl)-1,3-dioxane (4 mmol) were dissolved in ethanol (15 cm^3) and added to the solution of [ArTe$^-$Na$^+$]. The mixture was refluxed for 2–3 h, cooled to 25°C and poured into 200 cm^3 of water. The volume of organic extract containing L^1 or L^2 was reduced to 10 cm^3 under reduced pressure and hexane (10 cm^3) was added to the concentrated extracts. The resulting off-white precipitate was washed 3–4 times with hexane to remove impurity of the precursor ditelluride, recrystallized from hexane/chloroform (30 : 70) and dried *in vacuo*.

Synthesis of [$PtCl_2(L)_2$] (L = L^1 *or* L^2)

The solution of K_2PtCl_4 (0.08 g, 0.2 mmol) in water (15 cm^3) was treated with L^1 (0.12 g, 0.4 mmol) or L^2 (0.14 g, 0.4 mmol) dissolved in acetone (10 cm^3). The resulting mixture was stirred for 3 h at room temperature and poured into water (100 cm^3). The complex was extracted into 100 cm^3 of chloroform from this aqueous mixture. The organic extract was dried over anhydrous sodium sulfate, concentrated to *ca* 10 cm^3 and mixed with hexane. The precipitate was filtered, washed with hexane and recrystallized from chloroform/benzene (3 : 1) and dried *in vacuo.*

Synthesis of [$PdCl_2(L)_2$] (L = L^1 *or* L^2)

To a solution of bis(acetonitrile)palladium(II) chloride (0.05 g, 0.2 mmol) in chloroform (15 cm^3) was added L^1 or L^2 (0.12/0.14 g, 0.4 mmol) dissolved in chloroform (10 cm^3) and the mixture was stirred for 2 h at room temperature. It was concentrated to 7–8 cm^3 and mixed with hexane (5 cm^3). The resulting precipitate was filtered, washed with hexane, recrystallized from chloroform/benzene (3 : 1) and dried *in vacuo*.

Synthesis of $[M(L)_2](ClO_4)_2$ ($L = L^1$ *or* L^2)

A solution of $[PtCl_2(L)_2]$ (0.20 g, 0.2 mmol) or $[PdCl_2(L)_2]$ (0.16, 0.2 mmol) in chloroform (15 cm^3) was mixed with a solution of $AgClO_4$ (0.08 g, 0.4 mmol) in methanol (15 cm^3) and the mixture stirred for 2 h. The white precipitate of AgCl was filtered off. The filtrate was concentrated to *ca* 10 cm^3 and mixed with hexane (5 cm^3). The resulting precipitate was filtered and washed 3–4 times with hexane/chloroform (5 : 1). The platinum complexes were recrystallized from chloroform/benzene (3 : 1) and dried *in vacuo*. The complexes of palladium with L^1 and L^2 were recrystallized from $CHCl_3$-C_6H_6 and $CHCl_3$-$(C_2H_5)_2O$ respectively and also dried *in vacuo*.

Synthesis of $[M(DPPE)(L)_2)](ClO_4)_2$ ($L = L^1$ *or* L^2)

The suspension of dichloro{1,2-bis(diphenylphosphino)ethane}platinum(II) (0.13 g, 0.2 mmol) or dichloro{1,2 - bis(diphenylphosphino)ethane}palladium(II) (0.12 g, 0.2 mmol) in chloroform (10 cm^3) was mixed with a solution of $AgClO_4$ (0.08 g, 0.4 mmol) in methanol (10 cm^3), under dinitrogen. The resulting mixture was stirred for 30 min, mixed with the solution of L^1 or L^2 (0.12/0.14 g, 0.4 mmol) in chloroform (10 cm^3) and further stirred for 2 h. The white precipitate of AgCl was filtered off. The filtrate was concentrated to 10 cm^3 and mixed with hexane (10 cm^3). The resulting precipitate was filtered and washed with hexane. The $[PtCl_2(L^1)_2](ClO_4)_2$ was recrystallized from chloroform/diethylether (4 : 1). The two palladium complexes and $[PtCl_2(L^2)_2](ClO_4)_2$ were recrystallized from chloroform/benzene (2 : 1). All the complexes were dried *in vacuo*.

Synthesis of $[M(PPh_3)_2(L)_2)](ClO_4)_2$ ($L = L^1$ *or* L^2)

Dichlorobis(triphenylphosphine)platinum(II) (0.16 g, 0.2 mmol) or dichlorobis(triphenylphosphine)palladium(II) (0.14 g, 0.2 mmol) was dissolved in $CHCl_3$ (15–20 cm^3) and mixed under dinitrogen with the solution of $AgClO_4$ (0.08 g, 0.4 mmol) in methanol (10 cm^3). The mixture was stirred for 30 min and a solution of L^1 or L^2 (0.12/0.14 g, 0.4 mmol) in chloroform (10 cm^3) was added to the reaction mixture, which was further stirred for 2 h. The AgCl was filtered off. The filtrate was concentrated to 10 cm^3 and mixed with hexane (10 cm^3). The resulting precipitate was filtered and washed with hexane/chloroform (5 : 1). The platinum complex of L^1 was recrystallized from chloroform/benzene (1 : 1) mixture. The complex of L_2 with platinum and two palladium complexes were recrystallized from chloroform/diethylether (3 : 1) mixture. All the complexes were dried *in vacuo*.

Synthesis of $[M(phen)(L)_2](ClO_4)_2$ ($L = L^1$ *or* L^2)

The suspension of $[Pt(phen)Cl_2]$ (0.09 g, 0.2 mmol) or $[Pd(phen)Cl_2]$ (0.07 g, 0.2 mmol) in chloroform (15 cm^3) was mixed with a solution of $AgClO_4$ (0.08 g, 0.4 mmol) in methanol (10 cm^3). The resulting mixture was stirred for 30 min, mixed with the solution of L^1 or L^2 (0.12/0.14 g, 0.4 mmol) in chloroform and the reaction mixture stirred for a further 2 h. The AgCl was filtered off. The filtrate was concentrated to 7 cm^3 and hexane (10 cm^3) was added. The resulting precipitate was filtered, washed with hexane/chloroform (5 : 1), recrystallized from acetonitrile and dried *in vacuo*.

RESULTS AND DISCUSSION

The nucleophilic attack of $ArTe^-$ on the organic halides leads to the formation of the two hemilabile (Te,O) ligands. The physical properties of L^1 and L^2 and their complexes are given in Table 1. Analytical data are given in Table 2 and confirm the stoichiometries of the various species. All the complexes, as well as the ligands, have reasonable solubility in common organic solvents except **5**, **10**, **15** and **20** which are soluble in solvents like DMF and DMSO only. The molecular weight and molar conductance values of L^1 and L^2 (Table 1) do not indicate dissociation or association equilibria in solution. In the ^1H NMR spectrum of L^1 (Table 3) the two H_1 protons are not magnetically equivalent. The H_{1a}, H_{1b} and H_2 protons constitute an AA′B type spin system [17]. Thus the H_{1a} and H_{1b} protons appear as four lines of equal intensity at δ 2.96–3.03 [$J(AA') = 6$ Hz, $J(AB) = 14$ Hz] and δ 3.12–3.19 [$J(AA') = 6$ Hz, $J(AB) = 14$ Hz]. The H_2 and H_3 protons are deshielded in comparison to H_1 because their carbon atoms are linked to oxygen. In the ^1H NMR spectrum of L^2, H_{4a} and H_{6a} (equitorial proton) appear more deshielded than axial protons, as reported earlier [18].

The complexes having compositions $[MCl_2L]$, $[M(PPh_3)_2L](ClO_4)_2[M(DPPE)L](ClO_4)_2$, $[M(phen)L](ClO_4)_2$ ($M = Pd/Pt$; $L = L^1/L^2$) in which the ligand L coordinates as a bidentate moiety through Te as well as oxygen, could not be isolated. None of the complexes **1**–**20** could be crystallized in a single-crystal form suitable for X-ray diffraction.

The molar conductance values (*ca* 1 mM solutions) in acetonitrile and nitromethane of $[MCl_2L_2]$-type complexes (Table 1) are much lower than the values expected for a 1 : 1 electrolyte [19]. Their molecular weights (Table 1) also support their non-ionic nature. The Λ_M values of all other complexes and their molecular weights (Table 1) indicate that they behave as 1 : 2 electrolytes in solution.

In the electronic spectra of all the platinum complexes (recorded in $CHCl_3$ or DMSO), a band around 390 nm may be assigned to the $^1A_{1g} \rightarrow {}^1E_{1g}$ transition of platinum in a square-planar ligand field [20] and the

Table 1. Physical properties of L^1, L^2 and their Pd^{II} and Pt^{II} complexes

Ligand/complex	Colour	Yield %	M.p. °C	m.w. Found (Calc.)	Molar conductance (Λ_M) (ohm^{-1} cm^2 mol^{-1})
L^1	off-white	80	71	320 (304)	$14.5^a/20.8^b$
L^2	off-white	78	81	359 (340)	$19.2^a/24.9^b$
$[Pt(L^1)_2Cl_2]$ (**1**)	yellow	74	78	895 (873)	42^a 29^b
$[Pt(L^1)_2](ClO_4)_2$ (**2**)	mustard	68	84	345 (1001)	268^a 172^b
$[Pt(L^1)_2(DPPE)](ClO_4)_2$ (**3**)	pale yellow	77	92	475 (1399)	250^a 169^b
$[Pt(L^1)_2(PPh_3)_2](ClO_4)_2$ (**4**)	yellow	78	120	520 (1528)	240^a 159^b
$[Pt(L^1)_2(phen)](ClO_4)_2$ (**5**)	orange	67	122	—	166^c
$[Pt(L^2)_2Cl_2]$ (**6**)	yellow	78	94	979 (965)	42^a 31^b
$[Pt(L^2)_2](ClO_4)_2$ (**7**)	mustard	67	86	356 (1043)	279^a 156^b
$[Pt(L^2)_2(DPPE)](ClO_4)_2$ (**8**)	pale yellow	76	102	504 (1491)	267^a 156^b
$[Pt(L^2)_2(PPh_3)_2](ClO_4)_2$ (**9**)	yellow	79	104	547 (1617)	253^a 159^b
$[Pt(L^2)_2(phen)](ClO_4)_2$ (**10**)	orange	71	90	—	171^c
$[Pd(L^1)_2Cl_2]$ (**11**)	reddish brown	84	64 —	807 (785)	45^a 22^b
$[Pd(L^1)_2](ClO_4)_2$ (**12**)	dark brown	71	76	313 (913)	27^a 176^b
$[Pd(L^1)_2(DPPE)](ClO_4)_2$ (**13**)	yellow	73	86	447 (1311)	254^a 167^b
$[Pd(L^1)_2(PPh_3)_2](ClO_4)_2$ (**14**)	orange	79	96	490 (1437)	249^a 157^b
$[Pd(L^1)_2(phen)](ClO_4)_2$ (**15**)	reddish brown	70	76	—	152^c
$[Pd(L^2)_2Cl_2]$ (**16**)	reddish brown	81	88	895 (877)	45^a 33^b
$[Pd(L^2)_2](ClO_4)_2$ (**17**)	brown	72	84	343 (1005)	247^a 156^b
$[Pd(L^2)_2(DPPE)](ClO_4)_2$ (**18**)	yellow	74	96	476 (1403)	257^a 172^b
$[Pd(L^2)_2(PPh_3)_2](ClO_4)_2$ (**19**)	orange	70	114	409 (1209)	283^a 169^b
$[Pd(L^2)_2(phen)](ClO_4)_2$ (**20**)	reddish brown	68	102	—	163^c

[a] CH_3CN.
[b] CH_3NO_2.
[c] DMF.

band at 320 nm appears to be a result of intraligand transitions of L^1/L^2. The palladium complexes, except **15** and **20**, exhibit bands around 420, 385 and 320 nm. The first two may be assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ transitions of a square-planar palladium [20], and the last to an intraligand transition as in the case of platinum. The electronic spectra of $[Pd(phen)(L^1/L^2)_2](ClO_4)_2$ have more bands compared with other palladium complexes [21]. The band around 385 nm in this case is probably a composite one, contributed by charge transfer from palladium *d*-orbitals to the π-antibonding orbital of 1,10-phenanthroline and the spin forbidden $^1A_{1g} \rightarrow {}^1E_{1g}$ transition of the square-planar palladium. The bands around 360 and 320 nm are a result of the internal transition of phen and L^1/L^2, respectively. The additional strong band in the visible region (between 440 and 455 nm) is most likely to be owing to charge

Table 2. Analytical data

Ligand/complex	Analysis (%) Found (Calc.) C	H	N	Te
L^1	47.0 (47.4)	5.0 (5.3)	—	41.4 (42.0)
L^2	44.0 (44.6)	4.8 (5.1)	—	34.4 (35.5)
1	32.5 (33.0)	3.3 (3.7)	—	—
2	28.1 (28.7)	3.4 (3.2)	—	—
3	42.5 (42.9)	3.7 (4.0)	—	—
4	47.6 (47.2)	4.3 (4.1)	—	—
5	37.5 (37.8)	3.0 (3.3)	2.0 (2.3)	—
6	31.9 (32.3)	3.5 (3.7)	—	—
7	28.0 (28.5)	3.0 (3.3)	—	—
8	41.5 (41.8)	4.2 (4.6)	—	—
9	45.7 (46.0)	4.4 (4.1)	—	—
10	36.5 (37.0)	3.0 (3.3)	2.4 (2.1)	—
11	36.2 (36.7)	3.9 (4.1)	—	—
12	31.1 (31.5)	3.3 (3.5)	—	—
13	45.2 (45.8)	4.1 (4.3)	—	—
14	49.6 (50.1)	4.5 (4.3)	—	—
15	40.2 (40.8)	3.3 (3.6)	2.2 (2.5)	—
16	35.0 (35.6)	3.9 (4.1)	—	—
17	30.6 (31.0)	3.2 (3.6)	—	—
18	44.4 (44.6)	4.0 (4.3)	—	—
19	48.1 (48.7)	4.6 (4.3)	—	—
20	39.3 (39.7)	3.3 (3.6)	2.1 (2.3)	—

transfer from the HOMO of tellurium ligand to the LUMO of phen [22–24].

The weak/medium intensity ν[Te—(aryl)] bands in the IR spectrum of L^1 appear [25,26] at 288 and 242 cm^{-1}, and those of L^2 at 303 and 254 cm^{-1}. In all complexes these bands undergo a red shift of *ca* 10–15 cm^{-1}, suggesting the ligation of L^1 and L^2 *via* tellurium. The ν[Te—(alkyl)] band, expected to appear [25, 26] around 460–510 cm^{-1}, could not be unequivocally assigned. However, a band appearing in the spectra of L^1 and L^2 around 330–340 cm^{-1} exhibits a red shift (10–15 cm^{-1}) on complexation with Pd or Pt. It appears that ν[Te—(alkyl)] vibrations probably contribute to this band. One ν(Pt—Cl) band observed in the IR spectra of **1** and **6**, at 311 and 314 cm^{-1}, respectively, suggests that the two Pt—Cl bonds in these complexes are *trans* to each other. Similarly, one ν(Pd—Cl) band in the spectra of **11** and **16**, at 342 and 351 cm^{-1}, respectively, also suggests the *trans* arrangement of two Cl atoms. All the complexes containing the perchlorate group exhibit bands in their IR spectra around 620 and 1100 cm^{-1}, which suggest that the ClO_4 group is not coordinated [27] to metal in these moieties.

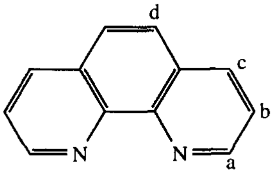
^1H NMR spectra of complexes

The H_{1a} and H_{1b} protons of L^1 invariably appear deshielded (0.2–0.3 ppm) relative to free L^1 upon ligation with Pt^{II} or Pd^{II} (Table 3). The H_{1a} signal merged with that of DMSO in the spectra of **5** and **15**, and deshielding of H_{1b} alone could be observed. The aromatic protons in the spectra of **1**, **2**, **11** and **12** also appear deshielded (up to *ca* 0.4 ppm) with respect to the aromatic protons of free L^1. The aromatic protons in the spectra of other complexes of L^1 merge with aromatic protons of DPPE, PPh_3 or phen, fully or partially. However, in the case of complexes **5** and **15**, the deshielding (Table 3) of aromatic protons of L^1 is apparent in spite of their merging, but difficult to quantify.

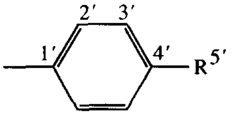
In the ^1H NMR spectra of complexes of L^2 not containing phen, the H_1 protons have been found to be deshielded (up to 0.6 ppm) relative to those of free L^2, but in the spectra of **10** and **20** H_1 was found to be merged with the DMSO signal. The aromatic protons of L^2 in the spectra of **6**, **7**, **16** and **17** were found to be deshielded (*ca* 0.2 ppm) with respect to those of uncoordinated L^2 (Table 3), but they merged with the aromatic protons of phosphines in the case of **8**, **9**, **18** and **19**. In the ^1H NMR spectra of **5**, **10**, **15** and **20** the aromatic protons *meta* to Te appear to be deshielded (*ca* 0.2 ppm), but other aromatic protons merge with the signals of the phen protons. All these deshielding effects suggest that in **1**–**20** the (Te,O) ligands coordinate through tellurium. In the ^1H NMR spectra of **2** and **12**, the H_2 and H_3 protons have been found to be deshielded (*ca* 0.2 ppm) with respect to those of **1** and **11**, respectively. Similarly, H_3 and H_{4a}, protons in the spectra of **7** and **17** are deshielded (*ca* 0.2 ppm) with respect to those of **6** and **16**. These deshielding effects can be explained by invoking lig-

Table 3. ^1H NMR data for L^1, L^2 and their Pd^{II} and Pt^{II} complexes

Complex	Chemical shift, δ (ppm)*
L^1	1.55 (m, 6H, $H_4+H_5+H_6$), 3.0 (dd, J 6, 14 Hz, 1H, H_{1a}), 3.16 (dd, J 6, 14 Hz, 1H, H_{1b}), 3.65 (m, 2H, H_3), 3.99 (d, 1H, H_2), 7.21 (m, 3H, ArH, *m*+*p* to Te), 7.74 (m, 2H, ArH, *o* to Te)
L^2	1.31 (m, 1H, H_{5b}), 2.05 (m, 3H, H_2+H_{5a}), 2.84 (t, 2H, H_1), 3.76 (m, 5H, $H_{4b}+H_{6b}+H_5$), 4.05 (m, 2H, $H_{4a}+H_{6a}$), 4.60 (t, 1H, H_3), 6.71 (d, 2H, ArH, *m* to Te), 7.68 (d, 2H, ArH, *o* to Te)
1/11	1.55 (m, 12H, $H_4+H_5+H_6$), 3.24 (m, 2H, H_{1a}), 3.45 (m, 2H, H_{1b}), 3.69 (m, 4H, H_3), 3.95 (m, 2H, H_2), 7.31 (m, 6H, ArH, *m*+*p* to Te), 8.11 (m, 4H, ArH, *o* to Te)
2/12	1.58 (m, 12H, $H_4+H_5+H_6$), 3.25 (m, 2H, H_{1a}), 3.46 (m, 2H, H_{1b}), 3.91 (m, 4H, H_3), 4.05 (m, 2H, H_2). 7.32 (m, 6H, ArH, *m*+*p* to Te), 8.11 (m, 4H, ArH, *o* to Te)
3/13	1.52 (12H, $H_4+H_5+H_6$), 2.57 (d, 4H, CH_2 of DPPE), 3.17 (m, 2H, H_{1a}), 3.43 (m, 2H, H_{1b}), 3.71 (m, 4H, H_3), 3.90 (m, 2H, H_2), 7.50 (m, 30H, ArTe+ArH of DPPE)
4/14	1.53 (12H, $H_4+H_5+H_6$), 3.20 (m, 2H, H_{1a}), 3.44 (m, 2H, H_{1b}), 3.61 (m, 4H, H_3), 3.97 (m, 2H, H_2), 7.50 (m, 40H, ArTe+ArH of PPh_3)
5/15	1.55 (m, 12H, $H_4+H_5+H_6$), 3.46 (m, 2H, H_{1b}), 3.69 (m, 4H, H_3), 3.95 (m, 2H, H_2), 7.37 (m, 6H, ArH, *m*+*p* to Te), 7.96 (m, 8H, ArH, *o* to Te+H_b+H_d of phen), 8.92 (m, 2H, H_c of phen), 9.53 (m, 2H, H_a of phen)
6/16	1.24 (m, 2H, H_{5b}), 2.08 (m, 6H, H_2+H_{5a}), 3.45 (t, 4H, H_1), 3.71 (m, 10H, $H_{4b}+H_{6b}+H_{5'}$), 4.04 (m, 4H, $H_{4a}+H_{6a}$), 4.62 (ut, 2H, H_3), 6.82 (d, 4H, ArH, *m* to Te), 7.82 (d, 4H, ArH, *o* to Te)
7/17	1.23 (m, 2H, H_{5b}), 2.08 (m, 6H, H_2+H_{5a}), 3.41 (t, 4H, H_1), 3.79 (m, 10H, $H_{4b}+H_{6b}+H_{5'}$), 4.03 (m, 2H, H_{6a}), 4.23 (m, 2H, H_{4a}), 4.85 (ut, 2H, H_3), 6.84 (d, 4H, ArH, *m* to Te), 7.84 (d, 4H, ArH, *o* to Te)
8/18	1.25 (m, 2H, H_{5b}), 2.04 (m, 6H, H_2+H_{5a}), 2.60 (d, 4H, CH_2 of DPPE), 3.40 (t, 4H, H_1), 3.71 (m, 10H, $H_{4b}+H_{6b}+H_{5'}$), 4.05 (m, 4H, $H_{4a}+H_{6a}$), 4.58 (t, 2H, H_3), 7.48 (m, 38H, ArTe+ArH of DPPE)
9/19	1.22 (m, 2H, H_{5b}), 2.08 (m, 6H, H_2+H_{5a}), 3.40 (ut, 4H, H_1), 3.72 (m, 10H, $H_{4b}+H_{6b}+H_{5'}$), 4.01 (m, 4H, $H_{4a}+H_{6a}$), 4.60 (t, 2H, H_3), 7.48 (m, 38H, ArTe+ArH of PPh_3)
10/20	1.23 (m, 2H, H_{5b}), 2.06 (m, 6H, H_2+H_{5a}), 3.70 (m, 10H, $H_{4b}+H_{6b}+H_{5'}$), 4.05 (m, 4H, $H_{4a}+H_{6a}$), 4.63 (t, 2H, H_3), 6.86 (d, 4H, ArH, *m* to Te), 7.86 (m, 8H, ArH, *o* to Te+H_b+H_b+H_d of phen) 8.88 (m, 2H, H_c of phen), 9.52 (m, 2H, H_a of phen)



Phen



Ar

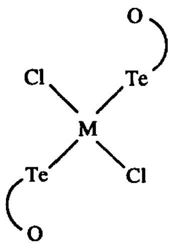
L^1 R = H
L^2 R = OCH_3

ation of L^1 and L^2 through oxygen in complexes **2**, **7**, **12** and **17** as well.

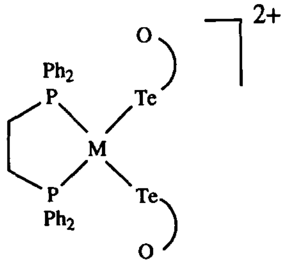
^{125}Te-{^1H} *and* ^{31}P-{^1H} *NMR spectra*

The ligands L^1 and L^2 show a sharp signal in their ^{125}Te-{^1H} NMR spectra at δ 488.9 and 466.7, respectively, which is in accord with the chemical shift values reported in the literature [28] for asymmetric alkyl/aryl tellurides. In the ^{125}Te-{^1H} NMR spectra of **1** and **6**, two signals (intensity ratio 1 : 5) have been observed at 600.8, 619.2 [^1J(Pt—Te), 658 Hz] and 601.5, 617.9 [^1J(Pt—Te), 662 Hz] respectively. Both of them are downfield (122–150 ppm) in comparison with those of L^1 and L^2, respectively. Thus, in **1** and **6** ligands are coordinated through tellurium only and probably in solution they exist as a *cis–trans* isomeric mixture. The signal at low field is very strong and is due to the *trans* isomer [29] and the other weak signal is due to the *cis* isomer. The ^1J(Pt—Te) value is also consistent with the coupling constants reported earlier [29] for *trans* systems. The *trans* isomer predominates, and, owing to low intensity, the satellite peaks of the *cis* form could not be observed. The signals in the ^{125}Te NMR spectra of **2** and **12** {at δ 732 [^1J(Pt—Te), 694 Hz] and 768.4, respectively} have been observed *ca* 113–127 ppm downfield with respect to those of **1** and **11**, respectively. On the other hand, signals in the NMR spectra of **7** and **17** are at δ 602 [^1J(Pt—Te), 704] and 607, respectively, which are 15–19 ppm upfield with respect to those of **6** and **16**, respectively. This variation may be explained on the basis of the chelate ring size effect as mentioned for ^{31}P NMR chemical shifts [30] of diphosphine complexes; according to which a chelate parameter ΔR may be defined as ΔR = coordination shift of chelate − coordination shift of equivalent monodentate complex.

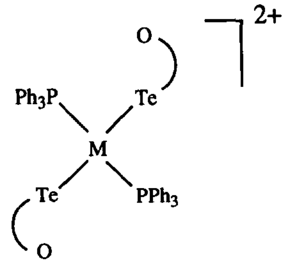
The parameter ΔR is large and positive for a five-membered chelate ring and small and positive or nega-



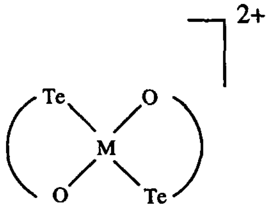
1,6,11,16



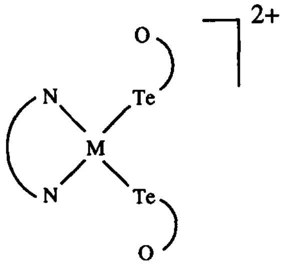
3,8,13,18



4,9,14,19



2,7,12,17



5,10,15,20

M = Pd or Pt (II) Te O = L^1 or L^2 N N = phen

tive for four- or six (or larger)-membered rings. A similar correlation exists between the ^{125}Te chemical shifts and chelate ring size. The present examples are the first in which ΔR is calculated on the basis of structurally identical monodentate and chelating ligands. The ^1J(Pt—Te) values in **2** and **7** are close to those reported for a *trans* Te—Pt—Te system [29]. Thus they appear to have the *trans* structure.

The $\delta_P[^1J(\text{Pt—P})]$ values are 40.3 (2850), 17.0 (3025), 41 (2873) and 17 (3001) respectively for **3**, **4**, **8** and **9**. For **13**, **14**, **18** and **19** δ_P values are 43.2, 20.2, 44.4 and 20.9, respectively. The ^1J(Pt—P) values of **3** and **8** are characteristic of a *cis* structure [31] and of **4** and **9** of a *trans* structure [32]. It has been observed that the chemical shift [30] values in the ^{31}P NMR of isostructural complexes of palladium(II) and platinum(II) with identical phosphine ligands differ in a large number of cases by 2–3 ppm only, palladium complexes showing a signal at a higher frequency than those of platinum. The same kind of relationship between the ^{31}P-{^{1}H} NMR chemical shift of **4** and **14** and of **9** and **19** indicates that these pairs are isostructural. Thus, the following structures seem to be most plausible for **1**—**20**.

The complexes **11** and **16** do not show any feature in their ^{125}Te-{H} NMR spectra indicating isomerism. The single ν(Pd—Cl) band observed in the IR spectra of both these species suggests that their structure is *trans*. The presumption about the *trans* structure of **12** and **17** appears to be logical in view of the structure of their precursors.

Singlet oxygen quenching by $[Pd(phen)(L)_2](ClO_4)$

Molecular oxygen-saturated solutions of **15** and **20** (5×10^{-4} M) in DMF were photolyzed, in the presence of sensitizers methylene blue, rose bengal or eosin (5×10^{-5} M) using a beam of light of wavelength 400–800 nm (UV light was cut off with a 7.5% $NaNO_2$ solution filter) for different intervals of time. The photolysis was monitored by following the decrease in absorbance at 452 and 450 nm for **15** and **20**, respectively. The 5 minutes irradiation decreased the absorbance significantly. However, decay of both the complexes was negligible in the dark, in the presence of pure nitrogen or in the absence of sensitizers. Addition of NaN_3 stops the photolysis. These observations indicate that **15** and **20** act as chemical quenchers of $^1O_2$. The plots of log[complex] *vs* time were found to be linear [33]. The relative efficiencies of sensitizers are in the order methylene blue > rose bengal > eosin. The reaction product of the photolysis could not be isolated; however, the disappearance of the LLCT band during photolysis indicates that the tellurium atom in $[Pd(phen)(L_2)](ClO_4)_2$ is oxidized. Similar observations [34] have been made for the sulfur atom of

[Pd(phen)(DMT)] (DMT = dimercaptotoluene) in the presence of hematoporphyrinIX as a sensitizer.

Acknowledgement—The authors thank DST (India) for financial assistance.

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