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2-(Phenyltelluromethyl)tetrahydrofuran (L^1) and 2-(2-{4-methoxyphenyl}telluroethyl)-1,3-dioxolane (L^2) and their palladium(II) and platinum(II) complexes

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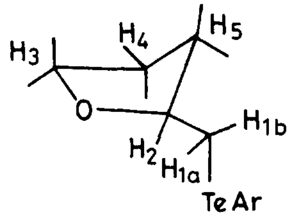
Abstract—The nucleophile [ArTe$^-$] generated *in situ* borohydride solution of Ar_2Te_2, reacts with 2-(chloromethyl)tetrahydrofuran and 2-(2-bromoethyl)-1,3-dioxolane resulting in L^1 and L^2, respectively. The complexes of palladium(II) and platinum(II) with L^1/L^2 having stoichiometries $[MCl_2 \cdot L_2]$, $[ML_2](ClO_4)_2$, $[(DPPE)ML_2](ClO_4)_2$, $[(PPh_3)_2ML_2](ClO_4)_2$ and $[(phen)ML_2](ClO_4)_2$ (where $L = L^1/L^2$ DPPE = $Ph_2PCH_2CH_2PPh_2$, phen = 1,10-phenanthroline and M = Pd/Pt) have been synthesized. IR, ^1H, $^{125}Te\{^1H\}$ and $^{31}P\{^1H\}$ NMR and UV–vis spectral data of these species in conjunction with their molar conductance and molecular weight data have been used to authenticate the new species. In all complexes (**1**–**20**) the ligands L^1 and L^2 are coordinated through tellurium and in the complexes of formula $[ML_2](ClO_4)_2$ (M = Pd, Pt) the ligand is bidentate with the oxygen atom used in complexation. In solution, complexes $PtCl_2L_2$ exist as a mixture of *cis* and *trans* isomers whereas only the *trans* isomer was observed for the palladium analogues. The $[(phen)PdL_2](ClO_4)_2$(Q) quenches $^1O_2$ readily. The plot of log [Q] *vs* time is linear. Mechanism compatible with the experimental observations is proposed. © 1997 Elsevier Science Ltd

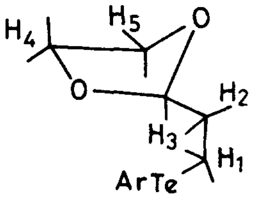
Keywords: tellurium; ligand; palladium; platinum; 2-(phenyltelluromethyl)tetrahydrofuran; 2-(2-{4-methoxyphenyl}telluroethyl)-1,3-dioxolane.

The hemilabile ligands are interesting as one of their ligating groups, may protect temporarily the coordination site of metal ion, before it is replaced by a substrate in the course of a catalytic reaction at the metal centre. The functionalized phosphines, particularly (P, O) type hybrid donors are most interesting hemilabile ligands [1]. However, such ligands containing tellurium moieties are little explored [2–3]. It was therefore thought worthwhile to design the ligands L^1 and L^2 and investigate their complexation behaviour.

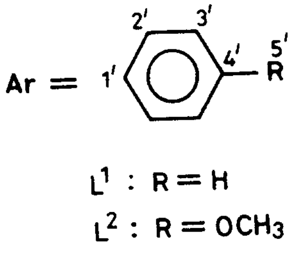
In the present paper the synthesis of L^1, L^2 and their platinum(II) and palladium(II) complexes and their characterization by IR, ^1H, $^{125}Te\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra in conjunction with molecular weight



L^1



L^2



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and conductance measurements are reported. The complexes of composition $[Pd(phen)(L)_2](ClO_4)_2$ quench the singlet oxygen quickly. The mechanism and kinetics of such reactions are also reported.

EXPERIMENTAL

Diphenylditelluride [4], bis(4-methoxyphenyl) ditelluride [5], dichloro(1,10-phenanthroline) palladium(II) [6], dichloro(1,10-phenanthroline) platinum(II) [6], dichloro{1,2-bis(diphenylphosphino) ethane} palladium(II) [7] and dichloro{1,2-bis(diphenylphosphino)ethane}platinum(II) [7] were prepared by published methods. Tetrahydrofurfuryl chloride, 2-(2-bromoethyl)-1,3-dioxolane, potassium tetrachlorplatinate(II), potassium tetrachloropalladate(II), bis(acetonitrile) dichloropalladium(II), dichlorobis (triphenylphosphine) palladium(II) and dichlorobis (triphenylphosphine) platinum(II) were used as received from Aldrich (U.S.A.).

The carbon, hydrogen and nitrogen analyses were carried out on a Perkin–Elmer 240C elemental analyzer. Tellurium was estimated volumetrically [8]. Melting points determined in open capillary, are reported as such. The molecular weights were determined with a Knauer vapour pressure osmometer and conductance measurements were carried out on a Metrohm 660 conductometer. 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. ^1H NMR spectra were recorded on a JEOL JNM FX-100 FT-NMR spectrometer at 99.55 MHz, and also at 500 and 400 MHz on Bruker AMX 500 and AMX 400 FT NMR spectrometer. The $^{31}P\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectra were recorded on a Bruker AMX 400 FT-NMR at 162 and 126 MHz, respectively, using H_3PO_4 and $(CH_3)_2Te$ as external references. For $^1O_2$ quenching experiments, a photoirradiator (Applied Photophysics, U.K.) equipped with 150 W xenon arc lamp was used. A solution filter (7% $NaNO_2$) was employed to cut off the light of wavelength less than 400 nm [9]. UV–vis spectra were recorded on a Hitachi 330 UV–vis spectrometer.

Synthesis of L^1

Diphenylditelluride (1 mmol) was dissolved in 30 cm^3 of ethanol and set to reflux under dinitrogen atmosphere. The solution of $NaBH_4$ (5%) made in 5% NaOH was added to it until it became colourless due to the formation of $PhTe^- Na^+$. The solution of tetrahydrofurfuryl chloride (2 mmol) made in 5 cm^2 of ethanol was added to the solution of sodium phenyltellurolate with constant stirring and the reaction mixture was further refluxed for 2–3 h, cooled to 25°C and poured into 200 cm^3 of water. The L^1 from aqueous layer was extracted into 200 ml of CH_2Cl_2. The extract was concentrated at 15 cm^3 under reduced pressure and hexane (10 ml) was added to the concentrate. The resulting off-white precipitate was filtered, washed 3–4 times with hexane and recrystallized from hexane–chloroform (30 : 70) mixture and dried *in vacuo*. Yield 70% ; m.p. 77°C.

Synthesis of L^2

Bis(4-methoxyphenyl)ditelluride (1 mmol) dissolved in 25 ml of ethanol was set to reflux under dinitrogen atmosphere and treated with $NaBH_4$ as given in the synthesis of L^1. The resulting $ArTe^-Na^+$ was reacted with 2-(2-bromoethyl)-1,3-dioxolane (2 mmol) by a method similar to the one used for preparing L^1. The yield of off-white L^2 was 76% and m.p. 67°C.

Synthesis of $[PtCl_2(L^1)_2]$ **(1)** *and* $[PtCl_2(L^2)_2]$ **(6)**

The K_2PtCl_4 (0.08 g, 0.2 mmol) was dissolved in 15 cm^3 of water. The solution of L^1 or L^2 (0.4 mmol) made in 10 cm^3 of acetone was added to it and the resulting mixture was stirred for 3 h at room temperature and poured into 100 cm^3 of water. The complex **1** or **6** was extracted from aqueous layer into 100 cm^3 of chloroform. The extract was dried over anhydrous sodium sulfate and concentrated to 10 cm^3. The concentrate was mixed with 15 cm^3 of hexane and the resulting yellow precipitate of **1**/**6** was filtered. **1** was recrystallized from a chloroform–benzene (2 : 1) mixture and **6** from a chloroform–hexane (3 : 1) mixture. The two yellow complexes were dried *in vacuo*. Yield (%) and m.p.: 79 and 60°C for **1** and 74 and 86°C for **6**.

Synthesis of $[Pt(L^1)_2](ClO_4)_2$ **(2)** *and* $[Pt(L^2)_2](ClO_4)_2$ **(7)**

A solution of $[PtCl_2(L^1)_2]$ or $[PtCl_2(L^2)_2]$ (0.2 mmol) made in 15 cm^3 of $CHCl_3$ was mixed with a solution of $AgClO_4$ (0.08 g, 0.4 mmol) made in 15 cm^3 of methanol and the mixture was stirred for 2 h. The white precipitate of AgCl was filtered off. The filtrate was concentrated to 10 cm^3 and mixed with 5 cm^3 of hexane. The resulting precipitate of **2**/**7** was filtered and washed 3 to 4 times with a hexane–chloroform (5 : 1) mixture. The recrystallization of **2** was made from a chloroform–benzene (3 : 1) mixture and of **7** with chloroform–benzene (2 : 1) mixture. Both mustard coloured complexes were dried *in vacuo*. Yield (%) and m.p. 76 and 92°C for **2** and 68 and 80°C for **7**.

Synthesis of $[(DPPE)Pt(L^1)_2](ClO_4)_2$ **(3)** *and* $[(DPPE)Pt(L^2)_2](ClO_4)_2$ **(8)**

The suspension of $[(DPPE)PtCl_2]$ (0.13 g, 0.2 mmol), where DPPE = 1,2-bis(diphenylphosphino) ethane, in chloroform (10 cm^3), was mixed with a solution of $AgClO_4$ (0.08 g, 0.4 mmol) made in 10 cm^3 of methanol under dinitrogen atmosphere. The mixture was stirred for 30 min. A solution of L^1 or L^2 (0.4 mmol) made in 10 cm^3 of chloroform was added to the mixture and it was stirred further 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 pale-yellow precipitate of **3**/**8** was filtered, washed with hexane, recrystallized from a chloroform–hexane (4 : 1)/(3 : 1) mixture and dried *in vacuo*. Yield (%) and m.p.: 82 and 86°C for **3** and 78 and 106°C for **8**.

Synthesis of $[(PPh_3)_2Pt(L^1)_2](ClO_4)_2$ **(4)** *and* $[(PPh_3)_2Pt(L^2)_2](ClO_4)_2$ **(9)**

Dichlorobis(triphenylphosphine)platinum(II) (0.14 g, 0.2 mmol) was dissolved in 15 cm^3 of $CHCl_3$ (under dinitrogen atmosphere) and mixed with a solution of $AgClO_4$ (0.08, 0.4 mmol) made in 10 cm^3 methanol. The mixture was stirred for 30 min. A solution of L^1 or L^2 (0.4 mmol) made in 10 cm^3 of chloroform was added to the mixture which was stirred further for 2 h. The white precipitate of AgCl was filtered off. The filtrate was concentrated to 10 ml and mixed with hexane (10 cm^2). The resulting precipitate of **4** or **9** was filtered and washed with a hexane–chloroform (5 : 1) mixture. Dichloromethane–benzene (1 : 1) mixture was used to recrystallize **4** and chloroform–benzene (2 : 1) mixture for **9**. Both the yellow complexes were dried *in vacuo*. Yield (%) and m.p. 84 and 88°C for **4** and 70 and 120°C for **9**.

Synthesis of $[(phen)Pt(L^1)_2](ClO_4)_2$ **(5)** *and* $[(phen)Pt(L^2)_2](ClO_4)_2$ **(10)**

The suspension of $[(phen)PtCl_2]$ (0.09 g, 0.2 mmol) made in 15 cm^3 of chloroform was mixed with a solution of $AgClO_4$ (0.08 g, 0.4 mmol) made in 10 cm^3 of methanol. The resulting mixture was stirred for 30 min and mixed with the solution of L^1 or L^2 (0.4 mmol) made in 10 cm^3 of $CHCl_3$. It was further stirred for 2 h. The white precipitate of AgCl was filtered off. The filtrate was concentrated to 7 cm^3, and 10 cm^3 of hexane was added to it. The resulting precipitate of complex **5** and **10** was filtered and washed with hexane–chloroform (5 : 1) mixture. After recrystallization from acetonitrile, both the complexes were dried *in vacuo*. Yield (%) and m.p.: 74 and 84°C and 66 and 108°C for **5** and **10**, respectively.

Synthesis of $[PdCl_2(L^1)_2]$ **(11)** *and* $[PdCl_2(L^2)_2]$ **(16)**

To a solution of dichlorobis(acetonitrile)palladium(II) (0.05 g, 0.2 mmol) made in $CHCl_3$ (15 cm^3) was added L^1 or L^2 (0.4 mmol) dissolved in 10 cm^3 of chloroform. The resulting mixture was stirred for 2 h at room temperature, concentrated to 7–8 cm^3 and mixed with 5 cm^3 of hexane. The resulting precipitate of **11**/**16** (orange/reddish brown) was filtered, washed with hexane, recrystallized from chloroform–benzene (3 : 1) mixture and dried *in vacuo*. Yield (%) and m.p.: 84 and 62°C and 82 and 80°C for **11** and **16**, respectively.

Synthesis of $[Pd(L^1)_2](ClO_4)_2$ **(12)** *and* $[Pd(L^2)_2](ClO_4)_2$ **(17)**

A solution of $[PdCl_2(L^1)_2]$ or $[PdCl_2(L^2)_2]$ (0.2 mmol) made in 15 cm^3 of chloroform was mixed with a solution of $AgClO_4$ (0.08 g, 0.4 mmol) made in 15 cm^3 of methanol and the mixture stirred for 2 h. The white precipitate of AgCl was filtered off. The filtrate was concentrated to 10 cm^3, and mixed with 5 cm^3 of hexane. The resulting brown precipitate of **12**/**17** was filtered and washed 3 to 4 times with hexane–chloroform (5 : 1) mixture. The recrystallization of **12** was made with chloroform–benzene (1 : 1) mixture and **14** with chloroform–diethyl ether (2 : 1) mixture. Yield (%) and m.p.: 76 and 84°C and 71 and 76°C for **12** and **17**, respectively.

Synthesis of $[(DPPE)Pd(L^1)_2](ClO_4)_2$ **(13)** *and* $[(DPPE)Pd(L^2)_2](ClO_4)_2$ **(18)**

The suspension of $[(DPPE)PdCl_2]$ (0.12 g, 0.2 mmol) in 10 cm^3 of chloroform was treated with $AgClO_4$ (0.08, 0.4 mmol) and L^1/L^2 (under dinitrogen atmosphere) as described for the corresponding platinum complexes **3** and **8**. The resulting two yellow complexes **13** and **18** were recrystallized from chloroform–benzene (2 : 1) mixture and dried *in vacuo*. Yield (%) and m.p.: 78 and 98°C for **13** and 76 and 92°C for **18**.

Synthesis of $[(PPh_3)_2Pd(L^1)_2](ClO_4)_2$ **(14)** *and* $[(PPh_3)_2Pd(L^2)_2](ClO_4)_2$ **(19)**

The solution of $[(PPh_3)_2PdCl_2]$ (0.14 g, 0.2 mmol) in chloroform (15 cm^3) was mixed with a solution of $AgClO_4$ (0.08 g, 0.4 mmol) made in 15 cm^3 of methanol (under dinitrogen atmosphere). The mixture was treated with L^1/L^2 as described for **4** and **9**. The resulting orange coloured **14** and **19** recrystallized from chloroform–benzene mixture (2 : 1 and 1 : 1 respectively) were dried *in vacuo*. Yield (%) and m.p.: 82 and 82°C and 73 and 88°C for **14** and **19**, respectively.

Synthesis of $[(phen)Pd(L^1)_2](ClO_4)_2$ **(15)** *and* $[(phen)Pd(L^2)_2(ClO_4)_2$ **(20)**

The slurry of $[(phen)PdCl_2]$ (0.07 g, 0.2 mmol) made in $CHCl_3$ (10 cm^3) was treated with $AgClO_4$ and L^1/L^2 as described for **5** and **10**. The resulting complexes **15** (orange) and **20** (reddish brown) were also recrystallized in a similar manner and dried *in vacuo*. Yield (%) and m.p.: 72 and 78°C for **15** and 69 and 104°C for **20**.

Elemental analyses, molecular weight and molar conductivity data for L^1, L^2 and complexes **1–20** are given in Table 1. Their ^1H NMR data are given in Table 2 and selected ^{31}P and ^{125}Te NMR data in Table 3.

RESULTS AND DISCUSSION

The reasonably good yield of ligands L^1 and L^2 obtained by the reaction of nucleophile $ArTe^-$ with an appropriate organic halide, further establishes the wide applicability of this synthetic procedure [10–12] exploited in the recent past by several workers [2–3] to design novel tellurium ligands. The non-electrolyte

Table 1. Physical properties and analytical data of L^1, L^2 and **1–20**

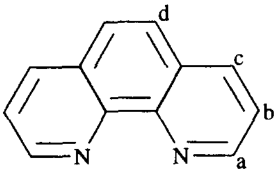
Ligand/ complex	Elemental analyses (%): found (calc.)				Mol. wt found (Calc.)	Molar conductance ohm^{-1} cm^2 mol^{-1} CH_3CN/CH_3NO_2
	C	H	N	Te		
L^1	45.01	4.32	—	43.23	301	20.6/23.6
	(45.58)	(4.80)		(44.06)	(289.6)	
L^2	42.43	4.23	—	37.11	354	17.6/21.2
	(42.90)	(4.76)		(38.02)	(335.6)	
1	30.84	3.02	—	—	860	41/32
	(31.23)	(3.07)			(845.28)	
2	26.84	2.59	—	—	332	252/156
	(27.12)	(2.87)			(975.28)	
3	42.52	4.03	—	—	466	278/172
	(42.00)	(3.79)			(1371.28)	
4	46.03	3.59	—	—	506	242/166
	(46.48)	(3.87)			(1497.28)	
5	36.12	2.85	2.01	—	—	168[b]
	(36.69)	(3.05)	(2.37)			
6	30.39	3.12	—	—	962	42/29
	(30.72)	(3.41)			(937.28)	
7	26.69	2.73	—	—	361	269/164
	(27.03)	(3.00)			(1065.28)	
8	40.68	3.57	—	—	486	237/159
	(41.00)	(3.82)			(1436.28)	
9	45.30	3.59	—	—	539	245/168
	(44.87)	(3.90)			(1589.28)	
10	35.48	2.92	2.43	—	—	166[a]
	(35.92)	(3.15)	(2.20)			
11	34.23	3.52	—	—	778	41/27
	(34.89)	(3.70)			(756.62)	
12	29.48	2.98	—	—	302	278/170
	(29.84)	(3.16)			(884.62)	
13	44.38	3.86	—	—	436	261/168
	(44.90)	(4.05)			(1282.62)	
14	48.92	3.88	—	—	476	240/158
	(49.41)	(4.11)			(1408.62)	
15	39.02	3.05	2.29	—	—	158[a]
	(39.68)	(3.33)	(2.58)			
16	33.42	3.99	—	—	872	46/29
	(33.93)	(3.77)			(848.62)	
17	28.94	3.51	—	—	332	246/159
	(29.48)	(3.27)			(972.62)	
18	43.07	3.91	—	—	467	269/163
	(43.64)	(4.07)			(1374.62)	
19	47.41	3.91	—	—	507	281/172
	(47.98)	(4.13)			(1500.62)	
20	38.06	3.63	2.59	—	—	156[b]
	(38.62)	(3.38)	(2.37)			

[a] In DMF.

Table 2. ^{1}H NMR data of L^1, L^2 and **1–20**

Ligand/complex	Chemical shift (δ ppm)
L^1	1.91 (m, $4H_1$, H_4+H_5), 3.10 (dd $J(AA') = 6$ Hz, $J(AB) = 14$ Hz, 1H, H_{1a}), 3.51 $J(AA') = 6$ Hz, $J(AB) = 14$ Hz, 1H, H_{1b}), 3.84 (m, 2H, H_3), 4.14 (m, 1H, H_2), 7.23 (m, 3H, ArH, *m*+*p* to Te), 7.74 (m, 2H, ArH, *o* to Te)
L^2	2.12 (m, 2H, H_2), 2.78 (t, 2H, H_1), 3.70 (m, 7H, $H_4+H_5+H_{5'}$), 4.76 (t, 1H, H_3), 6.69 (d, 2H, ArH, *m* to Te), 7.67 (d, 2H, ArH, *o* to Te)
1/11	1.77 (m, 8H, H_4+H_5), 3.47 (m, 2H, H_{1a}), 3.71 (m, 6H, $H_{1b}+H_3$), 4.10 (m, 2H, H_2), 7.39 (m, 6H, ArH, *m*+*p* to Te), 7.98 (d, 4H, ArH, *o* to Te)
2/12	1.77 (m, 8H, H_4+H_5), 3.43 (m, 2H, H_{1a}), 3.70 (m, 2H, H_{1b}), 4.16 (m, 4H, H_3), 4.43 (m, 2H, H_2), 7.27 (m, 6H, ArH, *m*+*p* to Te), 7.97 (d, 4H, ArH, *o* to Te)
3/13	1.77 (m, 8H, H_4+H_5), 2.56 (d, 4H, CH_2 of DPPE), 3.50 (m, 2H, H_{1a}), 3.71 (m, 6H, $H_{1b}+H_3$), 4.10 (m, 2H, H_2), 7.47 (m, 30H, ArTe+ArH of DPPE)
4/14	1.78 (m, 8H, H_4+H_5), 3.47 (m, 2H, H_{1a}), 3.71 (m, 6H, $H_{1b}+H_3$), 4.13 (m, 2H, H_2), 7.43 (m, 40H, ArTe+ArH of PPh_3)
5/15	1.76 (m, 8H, H_4+H_5), 3.68 (m, 6H, $H_{1b}+H_3$), 4.09 (m, 2H, H_2), 7.36 (m, 6H, ArH, *m*+*p* to Te), 7.95 (m, 8H, *o* to Te+H_b+H_d of phen), 8.91 (m, 2H, H_c of phen), 9.55 (m, 2H, H_a of phen)
6/16	2.08 (m, 4H, H_2), 3.17 (ut, 4H, H_1), 3.75 (m, 14H, $H_4+H_5+H_{5'}$), 4.79 (t, 2H, H_3), 6.93 (d, 4H, ArH, *m* to Te), 7.95 (d, 4H, ArH, *o* to Te)
7/17	2.08 (m, 4H, H_2), 3.17 (ut, 4H, H_1), 3.73 (m, 10H, $H_5+H_{5'}$), 4.06 (m, 4H, H_4), 5.01 (t, 2H, H_3), 6.91 (d, 4H, ArH *m* to Te), 7.96 (d, 4H, ArH *o* to Te)
8/18	2.00 (m, 4H, H_2), 2.60 (d, 4H, CH_2 of DPPE), 3.20 (ut, 4H, H_1), 3.77 (m, 14H, $H_4+H_5+H_{5'}$), 4.82 (t, 2H, H_3), 7.44 (m, 28H, ArTe+ArH of DPPEE)
9/19	2.08 (m, 4H, H_2), 3.13 (ut, 4H, H_1), 3.84 (m, 14H, $H_4+H_5+H_{5'}$), 4.82 (t, 2H, H_3), 7.42 (m, 38H, ArTe+ArH of PPh_3)
10/20	1.99 (m, 4H, H_2), 3.71 (m, 14H, $H_4+H_5+H_{5'}$), 4.80 (t, 2H, H_3), 6.87 (d, 4H, ArH, *m*+*p* to Te), 7.88 (m, 8H, ArH *o* to Te+H_b+H_d of phen), 8.90 (m, 2H, H_c of phen), 9.53 (m, 2H, H_a of phen)

^{a}Solvent : $CDCl_3$: DMSO-d_6 for **5, 10, 15** and **20**.



phen

Table 3. $^{31}P\{^1H\}$ and $^{125}Te\{^1H\}$ NMR data (solvent : $CHCl_3$)

Complex/ligand	δ (P) ppm [^1J(Pt—P)]	δ (Te) ppm [^1J(Pt—Te)]
L^1	—	470.6
L^2	—	485.6
1	—	628.0 (667), 610.3
2	—	741.1 (696)
3	40.0 (2885)	—
4	16.91 (2990)	—
6	—	611.1 (634), 597.2
7	—	598.1 (668)
8	40.8 (2868)	—
9	17.3 (3006)	—
11	—	653.3
12	—	783.6
13	42.2	—
14	20.4	—
16	—	629.2
17	—	617.2
18	42.7	—
19	21.0	—

behaviour and monomeric nature of L^1 and L^2 in solution as revealed by conductance and molecular weight measurements (Table 1), respectively, are as expected. The ^{1}H NMR spectral data (Table 2) in conjunction with elemental analyses (Table 1) authenticate the synthesis of L^1 and L^2. The two H_1 protons in L^1 are not magnetically equivalent and therefore in its ^{1}H NMR spectrum H_{1a} and H_{1b} protons appear as four lines of equal intensity at δ, 3.06–3.13 and 3.48–3.55 ppm as expected for an AA′B type system [13] constituted by H_{1a}, H_{1b} and H_2 protons ($J(AA') = 6$ Hz, $J(AB) = 14$ Hz). The H_2 protons appear at relatively low field (δ 4.10–4.18 ppm). In ^{1}H NMR spectrum of L^2 the signal due to H_2 appears at a high field relative to those of H_3, H_4 and H_5. The ν[Te—C (alkyl)] vibrations expected to occur around 460–510 cm^{-1} in the IR spectra of L^1 and L^2 could not be unequivocally assigned due to overlap with deformation vibrations of phenyl group. On the other hand ν [Te—C(aryl)] seems to contribute to the bands appearing at 299 and 243 cm^{-1} in the IR spectrum of L^1 and at 294 and 238 cm^{-1} in that of L^2, as reported earlier [14].

The complexation of L^1 and L^2 with $(CH_3CN)_2PdCl_2$, K_2PtCl_4, $(PPh_3)_2PdCl_2$, $(PPh_3)_2PtCl_2$, $(DPPE)PdCl_2$, $(DPPE)PtCl_2$, $(phen)PdCl_2$ and $(phen)PtCl_2$ has been explored. Attempts to synthesize complexes of the type $[MCl_2L]$, $[MClL_2]ClO_4$, $[M(DPPE)L](ClO_4)_2$, $[M(PPh_3)_2L](ClO_4)_2$ and $[M(phen)L](ClO_4)_2$ (where M = Pd or Pt (II) ; L = L^1 or L^2) have not been successful. The synthesis of **2–5, 7–10, 12–15,** and **17–20** without activation of the precursor complex with $AgClO_4$ was not possible. All complexes are soluble in common organic solvents such as chloroform, CH_3CN, CH_3NO_2, DMSO and DMF except **5, 10, 15** and **20** which exhibit good solubility in DMSO and DMF only. The stoichiometries of all the complexes have been authenticated by elemental analyses (Table 1). Their molar conductance and molecular weight data are given in Table 1. These data indicate that **1, 6, 11** and **16** behave as a non-electrolyte and are monomeric in solution. All other complexes are ionic (1 : 2 electrolyte) in nature, suggesting that the perchlorate groups are non-coordinating. The ClO_4 vibrations appearing around 620 and 1100 cm^{-1} in IR spectra of **2–5, 7–10, 12–15** and **17–20** further support the non-coordinating nature of this group in these complexes. The ν[Te—C(aryl)] bands of L^1 and L^2 [25], on formation of complexes **1–20,** exhibit a red shift ($\sim$ 10–15 cm^{-1}). The medium intensity bands appearing in IR spectra of L^1 and L^2 at 338 and 343 cm^{-1} undergo a red shift ($\sim$ 10–15 cm^{-1}) on the formation of complexes **1–20**. This suggests that these bands too have some contribution from Te—C(alkyl) vibrations. In IR spectra of **1** and **6** appearance of one ν(Pt—Cl) band at 310 and 302 cm^{-1}, respectively is a characteristic of two *trans* Pt—Cl [26] bonds of a square planar complex of platinum. Similarly the occurrence of one ν(Pd—Cl) at 344 and 348 cm^{-1} [26] in the spectra of **11** and **16,** respectively indicates that two Cl atoms are also *trans* to each other in these palladium complexes.

The electronic spectra (recorded in $CHCl_3$ and DMSO for **5** and **10**) of all platinum complexes (**1–10**) exhibit two bands. The band appearing around 390 nm may be assigned to $^1A_{1g} \rightarrow {}^1E_{1g}$ transition of a square planar platinum complex [27]. The other band at 320 nm is probably due to intraligand transition. All palladium complexes which do not have phen as a co-ligand, exhibit bands in their UV–vis spectra (recorded in $CHCl_3$) around 420, 385 and 320 nm. The first two most probably originate from $^1A_{1g} \rightarrow {}^1B_{1g}$ and $^1A_{1g} \rightarrow {}^1E_{1g}$ transitions, respectively of a palladium complex having a square planar geometry [27]. The third band in these spectra is also due to intraligand transition. The phen containing palladium complexes (**15** and **20**) exhibit in their UV–vis spectra a band around 385 nm which is probably a composite one, resulting from overlap of a band due to charge transfer from d orbital of palladium to π^* orbital of phen and $^1A_{1g} \rightarrow {}^1E_{1g}$ transition (spin forbidden) of a square planar palladium [27]. The bands around 360 and 320 nm in their spectra are due to intraligand transitions of phen and tellurium ligand (L^1 or L^2) respectively. The bands at 440 and 455 nm are most likely due to charge transfer from HOMO of tellurium ligand to LUMO of phen [15–17].

^{12}Te{^{1}H} *and* ^{31}P{^{1}H} *NMR spectra*

The ^{125}Te NMR spectra of L^1 and L^2 exhibit sharp singlets in the range δ 470–485 ppm, which are in concordance with the value of δ(Te) known for asymmetric alkyl/aryltellurides [18]. ^{125}Te NMR spectra (Table 3) of **1** and **6** have two signals (intensity ratio 1 : 5) but both of them are down field (120–158 ppm) in comparison to those of free L^1/L^2. This indicates that the platinum complexes exist in *cis–trans* isomeric forms. The *trans* form predominates, exhibits satellites and gives signal at a higher frequency relative to that of *cis* form [20]. The *cis* isomer on the other hand does not exhibit satellite peaks due to relatively lower concentration and consequently poor intensity. In case of palladium analogues of **1** and **6** (**11** and **16**) the deshielding (183–198 ppm) is greater in comparison to the corresponding platinum species but no evidence for the existence of isomeric mixture has been observed. The signals in ^{125}Te NMR spectra of **2** and **12** appear at further higher frequency ($\sim$ 113/130 ppm) in comparison to those of **1** and **11,** respectively. On contrary signals in ^{125}Te NMR spectra of **7** and **17** appear shielded with respect to those of **6** and **16** (12–13 ppm). This may be explained on the basis of chelate effect and the concept of chelate parameter, ΔR = coordination shift of chelate − coordination shift of equivalent monodentate ligand complex, as applied to diphosphines [19] on ^{31}P NMR chemical shifts. When the ring size is five membered as in the case of **1, 2, 11** and **12,** the ΔR is large and positive and for higher or lower membered chelate rings ΔR is small positive or negative as in the case of **6, 7, 16** and **17**. The ^1J(Pt—Te) values observed for complexes **2** and **7** are close to those reported for *trans*-Te—Pt—Te system [20].

The ^{31}P {^{1}H} NMR spectra of platinum complexes containing DPPE as a ligand exhibit signals around 40 ppm with ^1J(Pt—P) $\sim$ 2868/2885 Hz which are characteristic of a *trans* Te—Pt—P system [21]. The palladium complexes containing DPPE as a co-ligand exhibit signals in their ^{31}P NMR spectra at δ 42.2/42.7 ppm. The palladium complexes of phosphines have been found to be isostructural to their platinum analogues when the signal in ^{31}P NMR spectra of palladium moieties appears 2–3 ppm downfield relative to that of analogous platinum species [19]. The ^1J(Pt—P) values observed in ^{31}P NMR spectra (Table 3) of complexes having PPh_3 as a co-ligand are characteristic of *trans*-Ph_3P—Pt—PPh_3 system [22]. The palladium complexes containing PPh_3 as a co-ligand also exhibit in their ^{31}P NMR spectra, signals which are 2–3 ppm down field with respect to those of corresponding platinum complexes. Thus the present palladium and platinum complexes containing PPh_3 appear to be isostructural.

^{1}H NMR *spectra of complexes* **1–20**

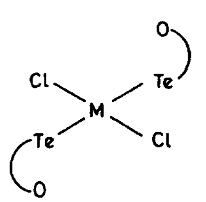
On comparing ^{1}H NMR spectrum of L^1 with those of its complexes (except **5** and **15**), it appears that the H_{1a} proton signal is deshielded (0.30 to 0.40 ppm) on complexation (Table 2). The ^{1}H NMR spectra of phen containing complexes were recorded in DMSO-d_6 due to solubility problem and therefore H_{1a} signal was found merged with that of the solvent. The signal due to H_{1b} has been found deshielded (0.2 ppm) on complexation but merged with the signal of H_3, except in the spectra of **2** and **12**. The aromatic protons in the spectra of **1, 2, 11** and **12** appear deshielded with respect to those of L^1. In the complexes containing DPPE and PPh_3 as a co-ligand, ArTe protons appear merged with the phenyl protons of phosphorus ligands and therefore they are of no diagnostic use. In ^{1}H NMR spectra of **5** and **15** ArTe protons *ortho* to Te merge with H_b and H_d protons of phen but may be certainly considered as deshielded with respect to those of L^1 (even after considering solvent effect). However, deshielding can not be quantified. These observations suggest that in all the complexes of L^1, the hemilabile tellurium ligand is coordinated through tellurium. In ^{1}H NMR spectra of **2** and **12** H_2 and H_3 protons also undergo deshielding (~ 0.3 and 0.5 ppm, respectively) as compared to those of free L^1. This suggests that in these complexes oxygen of furan or dioxolane ring also coordinates with Pd/Pt along with tellurium attached to the side chain.

On comparing ^{1}H NMR spectra of complexes of L^2 with that of free ligand it appears that H_1 protons of this (Te, O) donor undergo deshielding (0.35–0.50 ppm) on ligation with palladium/platinum. In the complexes containing phen as a co-ligand these protons merge in the DMSO signal and therefore deshielding could not be quantified. The ArTe protons could be assigned separately in ^{1}H NMR spectra of **6, 7, 16** and **17** only. These appear deshielded (0.30/0.34 ppm) with respect to those of free L^2. In the spectra of other complexes ArTe signals merge with the aromatic signals of phosphorous co-ligands or phen. In ^{1}H NMR spectra of **10** and **20** ArTe protons *ortho* to tellurium appear to merge with H_a and H_c protons of phen. However, they can be considered deshielded with respect to those of L^2 even after taking into account the effect of solvent. In ^{1}H NMR spectra of **7** and **17** the H_3 protons appear deshielded with respect to similar protons of their precursor complexes **6** and **16**, respectively. The multiplet assigned to H_4, H_5 and OCH_3 protons (merged together) in ^{1}H NMR spectra of **6** and **16** is splitted into two multiplets (Table 2) in the spectra of **7** and **17**, which probably occurs due to deshielding of H_4 (~ 0.30 ppm). On the basis of these observations it can be inferred that in all the complexes of L^2, the (Te, O) donor ligates through tellurium and in **7** and **17** through oxygen as well.

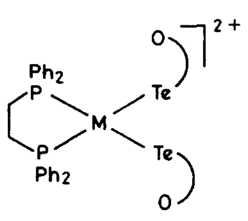
None of the complexes **1–20** gave single crystals suitable for X-ray diffraction and, therefore on the basis of spectral and other data following structures appear to be most plausible for **1–20**.

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

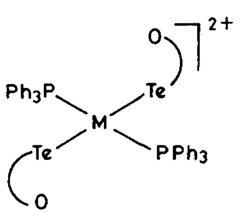
Molecular oxygen saturated solution of **15** and **20** (5×10^{-4} M) in DMF were photolyzed, in presence of sensitizers methylene blue, rose bengal or eosin (5×10^{-5} M) using a beam of light of wavelength 400–800 nm (UV light was cut off with a 7.5% $NaNO_2$ solution filter) for different intervals of time. The pho-



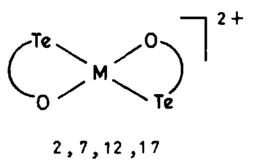
1,6,11,16



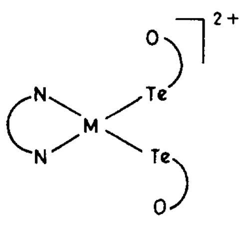
3,8,13,18



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 tolysis was monitored by following the decrease in absorbance at 440 and 455 nm for **15** and **20**, respectively. The irradiation of 5 min decreased the absorbance significantly. However decay of both the complexes was negligible in dark, in the presence of pure nitrogen, or in the absence of sensitizers. This indicates the decay as a combined action of sensitizer and O_2. The NaN_3 stops the photolysis indicating the involvement of $^1O_2$ in the decay. The following mechanism [24] seems to be most plausible for the decay of these palladium complexes.

$$S \xrightarrow{h\nu} {}^1S$$

$${}^1S \xrightarrow{ISC} {}^3S$$

$${}^3S + {}^3O_2 \xrightarrow{ET} S + {}^1O_2$$

$${}^1O_2 \xrightarrow{k_d} {}^3O_2$$

$${}^1O_2 + Q \xrightarrow{k_q} {}^3O_2 + Q^* \rightarrow {}^3O_2 + Q$$

$$Q + {}^1Q_2 \xrightarrow{k_r} QO_2$$

where S = methylene blue, rose bengal or eosin and Q = **15** or **20**. Based on the mechanism the production of $^1O_2$ is given by eq. 1

$$\frac{d[{}^1O_2]}{dt} = I_{ab}\Phi_{{}^1O_2} - (k_r[Q] + k_q[Q] + k_d) \qquad (1)$$

Where $\Phi{}^1O_2$ is the quantum yield of $^1O_2$ production and I_{ab} is the intensity of absorbed light. Under steady state condition

$$\frac{d[{}^1O_2]}{dt} = 0$$

and

$$I_{ab}\Phi_{{}^1O_2} = [{}^1O_2](k_r[Q] + k_q[Q] + k_d)$$

$$[{}^1O_2] = \frac{I_{ab}\Phi_{{}^1O_2}}{k_r[Q] + k_q[Q] + k_d} \qquad (2)$$

The rate of decay of **15** or **20** is given by eq. 3

$$\frac{-d[Q]}{dt} = k_r[{}^1O_2][Q] = I_{ab}\Phi_{{}^1O_2}\frac{k_r[Q]}{k_r[Q] + k_q[Q] + k_d} \qquad (3)$$

When $k_d \gg (k_q + k_r)[Q]$

$$\frac{-d[Q]}{dt} = I_{ab}\Phi_{{}^1O_2}\frac{k_r}{k_d}[Q] \qquad (4)$$

$$\log[Q] = -Kt + C \qquad (5)$$

where

$$K = I_{ab}\Phi_{{}^1O_2}\frac{k_r}{k_d}$$

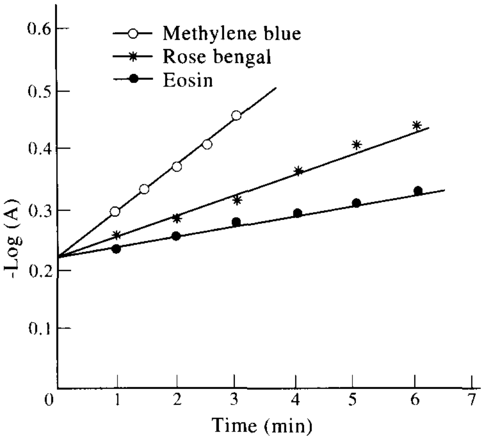


Fig. 1. Plot of $-\log A$ *vs* time for **15**.

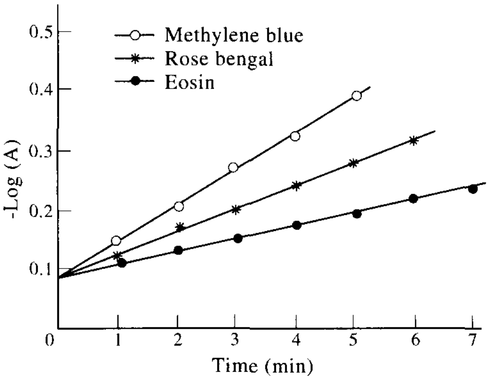


Fig. 2. Plot of $-\log A$ *vs* time for **20**.

The plot of log [Q] *vs* time, where [Q] is a quencher **15** or **20**, has been experimentally found to be straight line (Figs 1–2). The relative efficiencies of sensitizers are in the order methylene blue > rose bengal > eoson. The slope of these linear curves are proportional to rate constant (0.14–0.76 min^{-1} for **15** and 0.26–0.62 min^{-1} for **20**). The reaction product of the photolysis could not be isolated, however, the disappearance of LLCT band during photolysis indicates that tellurium atom in $[Pd(phen)(L_2)](ClO_4)_2$ is oxidized. Similar observations [23] have been made for the sulfur atom of [Pd(phen)(DMT)] (DMT = dimercaptoluene) in the presence of hematoporphyrin IX as a sensitizer.

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