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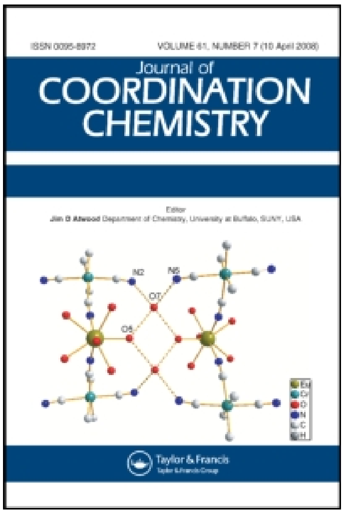

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SYNTHESIS, REACTIVITY AND MULTINUCLEAR N.M.R. STUDIES OF 2-(2-ARYLTELLUROETHYL)PYRIDINES AND THEIR PALLADIUM(II) AND PLATINUM(II) COMPLEXES: CRYSTAL STRUCTURES OF 4-MeO-$C_6H_4TeCH_2CH_2$-2-(C_5H_4N)MCl_2 (M = Pd,Pt)

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SYNTHESIS, REACTIVITY AND MULTINUCLEAR N.M.R. STUDIES OF 2-(2-ARYLTELLUROETHYL)PYRIDINES AND THEIR PALLADIUM(II) AND PLATINUM(II) COMPLEXES: CRYSTAL STRUCTURES OF 4-MeO-$C_6H_4TeCH_2CH_2$-2-(C_5H_4N)MCl_2 (M = Pd,Pt)

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New organotellurium ligands (L), 2-(2-aryltelluro-ethyl)pyridines (**a–d**), (aryl = ph (**a**), 4-Me-C_6H_4 (**b**), 4-MeO-C_6H_4 (**c**) and 4-EtO-C_6H_4 (**d**)), and their complexes with palladium(II) and platinum(II) of the type $MLCl_2$ [**Ia–d**(Pd); **IIa–d** (Pt)] have been synthesized. Addition of methanolic $AgClO_4$ to **Ic**/**IIc** in chloroform and subsequently an excess of (**c**) after removal of the precipitated AgCl results in the formation of [M(c)$_2$] $(ClO_4)_2$ (**III**/**IV**). The bimetallic complexes [(c)Pd(μ-EPh)$_2$M(dppe)]$^{2+}$ (M = Pd/Pt, E = Se/Te, dppe = 1,2-bis (dephenylphosphino) ethane) (**V–VIII**) have been obtained by reaction of Pd(c)(MeOH)$_2^{2+}$ with the metallo-ligands, (EPh)$_2$M(dppe). Elemental analyses, conductance and molecular weight measurements of these complexes, together with IR, electronic and NMR (^{1}H, ^{125}Te{^{1}H}, ^{195}Pt{^{1}H} and ^{31}P{^{1}H}) data suggest coordination of ligands (**a–d**) through tellurium and nitrogen. The structures of **Ic** and **IIc** have been determined by X-ray methods. Crystals belong to the triclinic crystal system, space group $P\bar{1}$, with a - 9.061(1), b - 10.058(2), c - 13.044(1)Å, α - 96.38(1), β - 95.22(2), γ - 91.54(1)° and Z - 2 for **Ic**, and a - 9.030(1), b - 10.576(2), c - 13.074(2)Å, α - 96.18(1), β - 94.88(1), γ - 90.64(2)° and Z - 2 for **IIc**. The coordination about the metal atom is square planar; the two Cl atoms are *cis* to each other and the ligand forms a six-membered non-planar chelate ring around the metal atom with the tellurium atom as a centre of chirality. The Pd-Te distance is observed to be longer than that of the Pt-Te distance by some 0.04 Å. The M-Cl bond opposite to tellurium is longer than the other, a manifestation of the *trans* influence of the Te-C (methoxyphenyl) bond.

KEYWORDS: 2(2-Aryltelluroethyl) pyridines, palladium and platinum complexes, structure, reactivity, synthesis

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INTRODUCTION

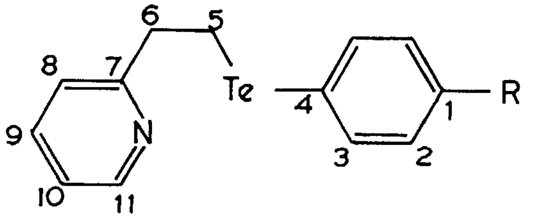
The synthesis and coordination chemistry of hybrid organotellurium ligands has been the subject of active research over the past few years.[1–16] Such ligands, having in addition to tellurium a harder donor atom, *e.g.*, oxygen or nitrogen, are not only capable of forming complexes with transition metals of novel structures and unique reactivities but are also suitable for synthesis of heterobimetallics. Interest in developing methodologies for synthesis of heterobimetallics is growing mainly because of their implication in catalytic processes. Attention is being focused on the synthesis of complexes containing widely divergent metal centres[17,18] since they can exhibit unique features and can give rise to a rich chemistry that can be regarded as a model for homogeneous as well as heterogeneous catalysis.[19,20] A few reports on the use of thiolates,[21–23] selenolates and tellurolates[24,25] for the synthesis of heterobimetallics have recently appeared in the literature.

In pursuit of our studies on the coordination chemistry of hybrid organotellurium ligands, we report herein the synthesis and properties of 2-(2-aryltelluroethyl) pyridines (**a–d**; Fig. 1), their complexes with palladium(II) and platinum(II) and some bimetallic (Pd,Pd) and heterobimetallic (Pd,Pt) complexes with an arylchalogen bridge. ^{1}H,^{31}P{^{1}H}, ^{125}Te{^{1}H} and ^{195}Pt{^{1}H} NMR spectra of these complexes and X-ray crystal structures of **Ic** and **IIc** are discussed.

EXPERIMENTAL

Published methods were used to synthesize diaryl ditellurides, Ph_2Te_2, $(4\text{-}Me\text{-}C_6H_4)_2Te_2$,$(4\text{-}MeO\text{-}C_6H_4)_2Te_2$,$(4\text{-}EtO\text{-}C_6H_4)_2Te_2$,[26,27] 2-chloroethylpyridine[28] and $(dppe)M(EPh)_2$[24] (M = Pd/Pt, E = Se/Te).

IR spectra in the range 4000-200 cm^{-1} were recorded on a Nicolet 5DX FT spectrophotometer in KBr/CsI pellets and far IR spectra in the range 700-30 cm^{-1} were recorded in polyethylene on a Perkin- Elmer 1700X FT instrument. Electronic spectra in acetonitrile were obtained on a Hitachi 330 spectrophotometer. ^{1}H and ^{13}C{^{1}H} NMR spectra were obtained on Jeol FX 100 FT instrument at 99.5 and 25 MHz, respectively, using Me_4Si as internal standard. The ^{31}P, ^{125}Te and ^{195}Pt NMR spectra were recorded at 162, 126 and 86 MHz on a Bruker AMX 400 FT spectrometer using H_3PO_4, $(CH_3)_2Te$ and H_2PtCl_6 as external references, respectively. Conductance measurements were made on 1 mM solutions in acetonitrile or nitromethane using a Metrohm 660 conductometer and molecular weights were determined in chloroform or acetonitrile using a Knauer vapour pressure osmo-



R = H (a)
= Me (b)
= OMe (c)
= OEt (d)

Figure 1 Ligand formulations.

meter. Elemental analyses were performed on a Perkin-Elmer 240C analyser. Solvents were dried using appropriate drying agents and distilled before use.

*2-(2-aryltelluroethyl)pyridines(**a-d**)*

To an ethanolic solution of diaryl ditelluride (2 mmol in 20 cm^3 ethanol), a solution of $NaBH_4$ (in 0.1 M NaOH) was added dropwise with vigorous stirring in oxygen-free dinitrogen atmosphere until it became colourless. To this, a solution of 2-(2-chloroethyl)pyridine (4 mmol in 5 cm^3 ethanol) was added dropwise and the resultant solution was refluxed for 1 h. The ligand thus formed was extracted with chloroform, washed with water and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the remaining pale yellow liquid was further purified on a column packed with silica gel using chloroform-hexane (5:95, 10:90).

*$PdCl_2.L$ (**Ia-d**) and $PtCl_2.L$(**IIa-d**)*

To a solution of K_2PdCl_4(147 mg, 0.5 mmol) or K_2PtCl_4 (208 mg, 0.5 mmol) in 5 cm^3 of water, a solution of 0.5 mmol of the ligand (**a–d**) in 5 cm^3 of methanol was added dropwise with stirring at room temperature. The mixture was further stirred for 1 h. The resulting orange (palladium) or pale yellow (platinum) precipitate was filtered and washed with water, recrystallized from chloroform and dried *in vacuo.*

$[Pd(c)_2](ClO_4)_2$ (III) and $[Pt(c)_2](ClO_4)_2$ (IV)

A solution of silver perchlorate (33 mg, 0.16 mmol) in 5 cm^3 of methanol was added dropwise to a solution of **Ic** or **IIc** (0.08 mmol) in 5 cm^3 chloroform protected from light in dry oxygen-free dinitrogen atmosphere. The mixture was stirred for 30 min and centrifuged. To the clear solution, ligand **c** (38 mg, 0.08 mmol) in chloroform (5 cm^3) was added with constant stirring at room temperature. It was further stirred for 1 h, filtered through celite and evaporated to dryness *in vacuo.* The product was washed with hexane to remove unreacted ligand and dried *in vacuo.*

*$[(dppe)M(\mu\text{-}EPh)_2Pd(c)](ClO_4)_2$, (M,E = Pd, Se(**V**); Pd,Te(**VI**); Pt,Se(**VII**); Pt,Te(**VIII**))*

A solution of silver perchlorate (208 mg, 1 mmol) in methanol (10 cm^3) was added dropwise to **Ic** (259 mg, 0.5 mmol) in chloroform (10 cm^3) protected from light in dry oxygen-free dinitrogen atmosphere with constant stirring at room temperature. The mixture was stirred for 30 min and filtered through celite. A solution of $[M(dppe)(EPh)_2]$ (0.5 mmol) in chloroform (7 cm^3) was added dropwise with rapid stirring. The mixture was stirred for another 2 h at 35°C and then evaporated to dryness. The crude product was purified on a column packed with neutral active alumina using methanol-chloroform (10:90).

X-Ray Data and Structure Solution

Single crystals of **Ic** (orange needles) and **IIc** (yellow needles) were grown from chloroform solution. X-ray diffraction data were collected on an Enraf-Nonius

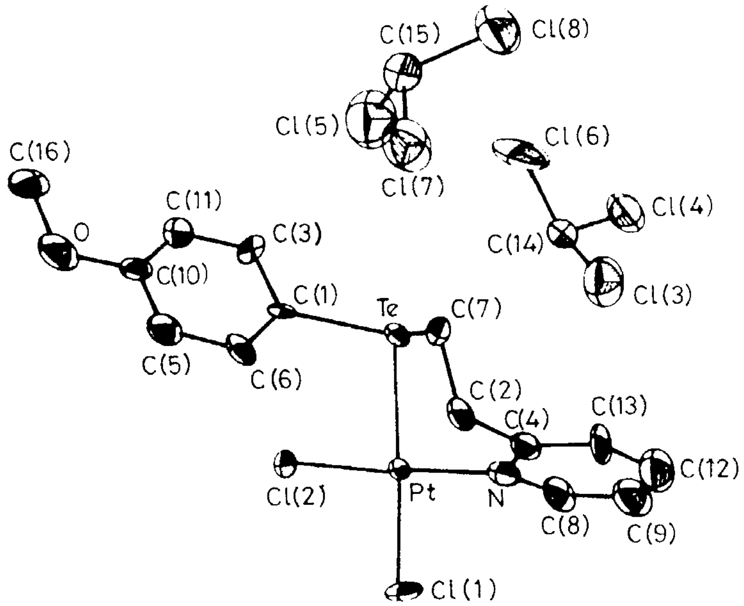


Figure 2 ORTEP drawing of the complex **IIc** (ellipsoids at 50% probability levels).

CAD-4 four circle diffractometer using nickel-filtered CuK_α radiation (λ = 1.5418 Å). Intensities were measured at the azimuth position corresponding to minimum absorption using an imaginary crystal with infinite but small thickness having an infinitely large surface area (flat psi mode). The $\omega - 2\theta$ scan mode was used and $2\theta_{max}$ = 130° (h = -8-> + 8, k = -13-> + 13, l = -17-> + 17) for a total of 9624 independent reflections, of which 4107 reflections were observed ($I \geq 3\sigma(I)$) for **Ic**, and $2\theta_{max}$ = 140°(h = 0-> 11, k = -13-> + 13, l = -16-> + 16) for a total of 5055 independent reflections of which 3985 reflections were observed ($I \geq 3\sigma(I)$) for **IIc**. The intensities were corrected for Lorentz and polarization effects and semi-empirical absorption corrections were also applied.

Initial coordinates of Pd, Pt and Te were determined using SHELXS 86.[29] The remaining atoms were located from successive difference Fourier maps. Refinement was carried out by full-matrix least-squares procedures using SHELX 76[30] for positional parameters, initially isotropic and finally anisotropic temperature factors for all the non-hydrogen atoms. Constant weights were applied. The atomic scattering factors used in the calculations for non-hydrogen atoms were taken from refs. 31 and 32. The crystal data, data collection parameters, structure refinement details, final atomic coordinates and selected bond distances and angles are listed in Tables 4, 5, 6 and 7, respectively. Supplementary material* comprises of full table of bond lengths and bond angles, thermal parameters and structure factors. A perspective view of the complex **IIc** is illustrated in Fig. 2. All computations were carried out on a Microwax II computer at AIIMS, New Delhi.

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*Available from B.L.K. upon request.

RESULTS AND DISCUSSION

2-(2-Aryltelluroethyl)pyridines (**a–d**), belonging to the asymmetric class of ligands have been synthesized by reactions of aryltellurolates on 2-(2-chloroethyl)pyridine. Physical and analytical data are given in Table 1.

These compounds, like other tellurides, are fairly soluble in non-polar solvents and behave as non-electrolytes in solution. However, they are not very stable and their chloroform solutions, on keeping for a week or so, change colour from pale yellow to dark red and result in decomposition to a white solid of unknown composition. ^{1}H NMR spectra of **a–d** (Table 2) are as expected except that each shows a multiplet at 3.2 ppm rather than two triplets for H_5 and H_6 protons as observed in the precursor, 2-(2-chloroethyl)pyridine (which exhibits two triplets centred at 3.9 and 3.2 ppm). In fact, it is the substitution of chlorine by less electronegative tellurium in **a–d** that results in shielding of the H_5 proton and

Table 1 Physical and analytical data.

Compound	Yield (%)	Colour	B.p. (°C; dec)	Analysis (calcd.) %			MW (calcd.)
				C	H	N	
Ligand							
a	87	Pale Yellow	175				306(311)
b	83	Yellow	181				300(325)
c	90	Orange Yellow	180				350(341)
d	91	Pale Yellow	182				360(355)
Complex			M.P. (°C; dec)				
Ia	83	Orange	120	31.5 (31.5)	2.3 (2.3)	28 (2.8)	470(488)
Ib	72	Orange	118	33.5 (33.5)	3.0 (3.0)	28 (2.8)	510(502)
Ic	80	Orange	123	28.2 (32.4)	2.4 (2.9)	2.4 (2.7)	510(518)
Id	78	Orange	122	34.0 (33.8)	3.2 (3.2)	2.6 (2.6)	516(532)
IIa	72	Yellow	132	26.9 (27.0)	2.3 (2.2)	2.4 (2.4)	581(575)
IIb	70	Yellow	137	28.6 (28.4)	2.5 (2.5)	2.0 (2.0)	573(591)
IIc	75	Yellow	133	27.9 (27.7)	2.5 (2.5)	2.2 (2.3)	590(607)
IId	73	Yellow	135	29.1 (29.0)	2.7 (2.7)	2.2 (2.2)	600(621)
III	90	Red		33.9 (34.0)	3.1 (3.0)	2.6 (2.6)	951(956)
IV	85	Orange		32.1 (31.1)	2.9 (2.8)	2.5 (2.6)	1050(1076)
V	65	Red		42.5 (42.7)	3.3 (3.3)	0.9 (0 .9)	1484(1462)
VI	69	Red		39.9 (40.2)	3.1 (3.1)	0.9 (0.9)	1490(1560)
VII	70	Red		37.1 (37.6)	3.0 (3.0)	1.8 (1.8)	1559(1551)
VIII	70	Red		39.0 (40.1)	3.1 (3.1)	0.9 (0.9)	1640(1648)

Table 2 ^1H and $^{125}Tc\{^1H\}$ NMR data for the ligands and their palladium and platinum complexes (ppm).

Compound	$(^1H)^a$				$^{125}Te\{^1H\}^b$
	H_{11} (d)	Aryl protons except H_{11} (m)	H_5, H_6 (m or bm)	H(R)	$^1J(^{125}Te\text{-}^{195}Pt)$ (Hz)
a	8.56	7.00–7.60	3.2		
b	8.55	6.95–7.70	3.2	2.38s	
c	8.50	6.70–7.70	3.2	3.75s	481
d	8.56	6.70–7.70	3.2	3.97q 1.40t	
Ia	8.88	6.78–7.88	2.5–4.2		
Ib	9.00	6.94–7.78	2.3–4.2	2.28s	
Ic	9.00	6.78–7.88	2.5–4.5	3.75s	670
Id	9.00	6.76–7.88	2.4–4.1	4.00q 1.32t	
IIa	9.00	7.22–7.93	3.1–4.0		
IIb	9.27	6.96–7.76	3.2–4.1	2.28s	
IIc	9.13	6.76–7.96	2.5–4.0	3.74s	656 (1224)
IId	9.12	6.76–7.96	2.4–4.0	4.00q 1.32t	
III	8.76	6.01–8.32	3.2–4.1	3.77s	
IV	8.50	6.71–7.72	2.9–3.9	3.78a	535 (915) 536 (505)
VIII	8.87	6.54–7.36	3.5–3.8	3.66s	

[a] Proton NMR spectra of all 1:1 palladium and platinum complexes recorded in acetonitrile; others in $CDCl_3$. [b] Ligands in $CDCl_3$ and complexes in d_6-dmso due to poor solubility in $CDCl_3$.

consequently the appearance of a multiplet due to H_5 and H_6. The $^{13}C\{^1H\}$ NMR of **a–d** (Table 3) show the C_5 resonances between 3.2 to 6.8 ppm, consistent with earlier reported values[33] and indicate shielding of the carbon attached to tellurium; C_6 in all cases appears around 40 ppm.

*Complexes of **a–d** with palladium(II) and platinum(II)*

Tetrachloropalladate or platinate reacts with telluroethylpyridines (**a–d**) to form complexes of the type $[MLCl_2]$. The complex stoichiometry is unaltered by the change of metal: ligand ratio or of complex precursor (*e.g.*, $[MCl_4]^{2-}$ or $MCl_2(PhCN)_2$, M = Pd,Pt).

The resulting palladium and platinum complexes, in contrast to the air-sensitivity of the free ligands, are air stable in the solid state as well as in solution. The presence of two bands in their far IR spectra around 290 and 330 cm^{-1} assignable to M-Cl vibrations suggests that the two M-Cl bonds in the complexes are in a *cis* conformation of a square planar arrangement of the ligands around the metal atom.[34] The electronic spectra of these complexes are also consistent with square planar geometry.

In the ^1H NMR spectra of these complexes (Table 2) the pyridine ring protons *ortho* to nitrogen (H_{11}) are deshielded (by 0.3–0.5 ppm in Pd complexes and 0.5–0.7 ppm in Pt complexes) with respect to the free ligands, indicating coordination of the pyridine N with Pd and Pt. The protons of the two CH_2 groups, which appear as a broad multiplet in the ligand, are partly resolved, exhibit

Table 3 $^{13}C\{^{1}H\}$ NMR chemical shifts (ppm) for ligands [**a–d**] in $CDCl_3$ at 25°C.

Ligand	C_5 & C_6	Aryl carbons	C(R)
a	6.5 40.0	127.3(C_1), 129.0(C_2), 138.3(C_3), 112.6(C_4), 137.8(C_7), 121.4(C_8), 136.2(C_9), 122.7(C_{10}), 149.5(C_{11})	
b	3.2 40.1	*-(C_1), 126.5(C_2), 132.5(C_3), 105.6(C_4), 134.0(C_7), 117.7(C_8), 135.0(C_9), 119.0(C_{10}), 141.5(C_{11})	17.6
c	6.8 40.3	160.1(C_1), 115.1(C_2), 141.0(C_3), 101.2(C_4), 140.0(C_7), 121.3(C_8), 136.3(C_9), 122.7(C_{10}), 149.5(C_{11})	55.1
d	6.8 40.2	159.3(C_1), 115.8(C_2), 141.1(C_3) 101.2(C_4), 140.0(C_7), 121.4(C_8), 136.4(C_9), 122.2(C_{10}), 149.5(C_{11})	63.5(CH_2) 14.9(CH_3)

* not observed.

anAA'BB' pattern and are significantly deshielded, suggesting coordination of Te to the metal atom. $^{13}C\{^{1}H\}$ NMR spectra (recorded only for **Ic** and **IIc**) exhibit downfield shifts for C_{11} and C_5 by 3.5 and 11 ppm in the palladium complexes and 4.5 and 9 ppm in the platinum complexes, supporting the coordination of both nitrogen and tellurium with the metal. $^{125}Te\{^{1}H\}$ NMR spectra of **Ic** and **IIc** (Table 2) exhibit a single resonance (associated with platinum satellites in the Pt complex) in each case appearing 189 and 175.5 ppm downfield in comparison to the ligand. This is an anticipated consequence of coordination of tellurium with Pd or Pt. Further, the $^{1}J(^{195}Pt\text{-}^{125}Te)$ coupling of 1224 Hz unambiguously suggests the *cis* configuration of the complex.[35,36] The $^{195}Pt\{^{1}H\}$ NMR spectrum of **IIc** in dmso shows a resonance at −3878 ppm as a broad, unresolved triplet; the broadness may be due to the quadrupole moment of ^{14}N (I = 1).[37]

Structures of $[M\{(NC_5H_4\text{-}2\text{-}(CH_2)_2\text{-}Te\text{-}C_6H_4\text{-}4\text{-}OMe\}Cl_2]$ *(M = Pd,Pt)*

The structure of **IIc** in the solid state consists of discrete molecules and is shown in Figure 2 together with the atom numbering system. Crystallographic parameters are listed in Table 4. Platinum has the expected square planar geometry. The ligand forms a six-membered, non-planar chelate ring. This ring adopts an *endo*-puckered conformation with respect to C_2 and Pt in which C_2 deviates by −0.88(2)Å and C_7 by − 0.77(2)Å whereas the Pt atom deviates by −0.0024(8)Å. The torsion angle across C(7)–C(2) *i.e.*, C(7)–C(2)–C(4)–N, is −81(2)°. The aromatic ring makes an angle of 116.8° with respect to the square plane while the pyridine ring is inclined to it by 56.6°. A literature survey shows only a few examples of crystal structure data on chelating (Te,Te),[36,38] (Te,S),[39] (Te,P)[1] and (Te,N)[16,40] ligands with Pd and Pt. The Pt–Te distance of 2.512(1)Å observed in this case is considerably shorter than the sum of the covalent radii (2.688Å) and also is slightly shorter than that of the other reported value in a six-membered ring system.[36] In fact, it is also shorter than those reported for five-membered chelate ring systems[1,16,38] as well, except for $(Pt\{1\text{-}NMe_2\text{–}2\text{–}TeAr\text{–}4\text{–}Me\text{–}C_6H_3\}Cl_2)$[40] where the aniline ring assists tellurium to form a stronger bond with Pt. Shortening of the Pt–Te bond length may be attributed to a $d_{\pi} - d_{\pi}$ interaction. The Pt–N bond distance, although slightly longer than that observed in the five-membered ring system,[16] is comparable with earlier observations.[40] The two M–Cl bond

Table 4 Crystallographic parameters.

	Ic	**IIc**
Formula	$C_{14}H_{15}NOTePdCl_2.2CHCl_3$	$C_{14}H_{15}NOTePtCl_2.2CHCl_3$
a, Å	9.061(1)	9.030(1)
b, Å	10.058(2)	10.576(2)
c, Å	13.044(1)	13.074(2)
α, deg	96.38(2)	96.18(1)
β, deg	95.22(1)	94.88(1)
γ, deg	91.54(1)	90.64(2)
Cryst. system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
V, $Å^3$	1236.5(3)	1236.6(3)
D_c, g cm^{-3}	2.033	2.271
Z	2	2
F(000)	720	788
Crystal size, mm	0.7x0.2x0.2	0.7x0.2x0.2
Temp., °C	20	20
$R(I \geq 3\sigma(I))$	0.100 (4049)	0.081 (3908)
R_w	0.108	0.081
S	4.452	6.207

Table 5 Fractional atomic coordinates ($x10^4$) for **Ic**.

Atom	*x/a*	*y/b*	*z/c*
Pd	2147(1)	9723(1)	5220(1)
Te	1608(1)	9559(1)	3281(1)
Cl(1)	1594(4)	11825(3)	5293(2)
Cl(2)	2577(4)	9817(4)	7021(2)
N	2545(11)	7796(9)	5062(7)
C(1)	2389(13)	11313(10)	2840(9)
C(2)	4429(15)	8130(12)	3855(11)
C(3)	3808(16)	11773(13)	3127(10)
C(4)	3514(14)	7266(11)	4447(9)
C(5)	1965(16)	13042(13)	1838(11)
C(6)	1444(16)	11914(11)	2184(10)
C(7)	3555(15)	8504(12)	2910(11)
C(8)	1716(15)	7068(15)	5614(11)
C(9)	1849(17)	5756(14)	5494(13)
C(10)	3402(17)	13503(13)	2138(9)
C(11)	4352(17)	12871(15)	2786(11)
C(12)	2790(20)	5199(16)	4851(14)
C(13)	3654(17)	5967(14)	4322(12)
C(14)	-1379(17)	7053(14)	2196(10)
C(15)	3159(18)	8484(14)	-0632(12)
C(16)	3249(21)	15113(16)	0974(13)
O	4013(14)	14570(10)	1829(8)
Cl(3)	0092(5)	6187(5)	2636(4)
Cl(4)	-3078(5)	6127(4)	2101(3)
Cl(5)	1984(7)	9367(6)	0144(5)
Cl(6)	-1119(7)	7557(6)	0987(3)
Cl(7)	2343(6)	7034(5)	-1144(4)
Cl(8)	4843(5)	8258(5)	0107(4)

Table 6 Fractional atomic coordinates (x10^4) for **IIc.**

Atom	x/a	y/b	z/c
Pt	2160(1)	9769(1)	5228(1)
Te	1571(1)	9593(1)	3305(1)
Cl(1)	1689(6)	11904(4)	5345(3)
Cl(2)	2654(7)	9874(5)	7031(3)
N	2472(19)	7888(15)	5142(11)
C(1)	2402(20)	11317(15)	2846(12)
C(2)	4380(21)	8085(18)	3860(17)
C(3)	3797(23)	11779(18)	3193(16)
C(4)	3475(21)	7286(16)	4471(14)
C(5)	1922(29)	13049(18)	1837(16)
C(6)	1438(22)	11926(16)	2161(15)
C(7)	3509(23)	8455(17)	2875(15)
C(8)	1719(21)	7123(18)	5599(15)
C(9)	1773(26)	5852(21)	5555(20)
C(10)	3333(25)	13501(17)	2157(15)
C(11)	4295(26)	12870(20)	2849(17)
C(12)	2743(32)	5236(20)	4900(20)
C(13)	3598(28)	5973(18)	4349(19)
C(14)	-1405(30)	7050(20)	2169(16)
C(15)	3244(29)	8521(22)	-687(18)
C(16)	3246(37)	15111(21)	993(19)
O	3973(20)	14586(14)	1859(12)
Cl(3)	125(9)	6172(7)	2646(6)
Cl(4)	-3018(8)	6100(6)	2080(5)
Cl(5)	2007(11)	9383(9)	136(8)
Cl(6)	-1068(13)	7524(9)	971(5)
Cl(7)	2392(11)	7060(7)	-1142(7)
Cl(8)	4871(9)	8266(7)	113(6)

Table 7 Selected bond angles (deg.) and lengths (Å) with estimated standard deviations.

	Ic	**IIc**		**Ic**	**IIc**
Cl(1)-M-Te	88.4(1)	90.4(1)	Te-M	2.518(1)	2.512(1)
Cl(2)-M-Te	177.9(1)	178.0(1)	Cl(1)-M	2.286(3)	2.293(4)
Cl(2)-M-Cl(1)	92.7(1)	90.9(2)	Cl(2)-M	2.338(3)	2.351(4)
N-M-Te	88.1(3)	89.9(4)	N-M	2.070(9)	2.005(17)
N-M-Cl(1)	176.0(3)	177.2(5)	C(1)-Te	2.124(10)	2.127(15)
N-M-Cl(2)	90.7(3)	88.8(4)	C(7)-Te	2.175(12)	2.211(19)
C(7)-Te-M	96.4(3)	97.4(5)	C(4)-N	1.335(15)	1.424(24)
C(7)-Te-C(1)	95.7(5)	95.0(7)	C(8)-N	1.367(15)	1.277(24)
C(1)-Te-M	105.9(3)	105.2(4)	C(2)-C(4)	1.533(17)	1.503(28)
C(4)-N-M	123.5(8)	121.2(12)	C(1)-C(3)	1.367(18)	1.371(25)
C(8)-N-M	115.7(9)	124.1(15)	C(1)-C(6)	1.374(16)	1.408(24)
C(3)-C(1)-Te	121.6(8)	121.4(13)	C(2)- C(7)	1.501(18)	1.540(28)
C(6)-C(1)-Te	117.0(9)	115.8(12)			
C(7)-C(2)-C(4)	112.2(11)	113.1(16)			
C(8)-N-C(4)	120.8(11)	114.5(17)			
C(6)-C(1)-C(3)	121.2(10)	122.8(15)			
C(2)-C(7)-Te	112.6(9)	109.5(13)			
C(2)-C(4)-N	118.6(10)	119.4(15)			

distances in the Pt complex molecule differ by 0.058Å; that *trans* to the tellurium is longer than the other. This clearly illustrates the *trans* influence of the Te—C covalent bond.

The structure of **Ic** is similar to that of **IIc**. However, the chelate ring of the palladium complex is more puckered than that of the platinum complex; C_2 deviates by −1.00(1)Å, C_7 by 0.83(1)Å and Pd by 0.0063(1)Å. The torsion angle C(7)—C(2)—C(4)—N is −79(1)°; the aromatic ring makes an angle of 111.5° with respect to the square plane while the pyridine ring is inclined to it by 55.7°. The Pd—Te bond (2.518(1)Å is slightly longer than that of the Pt—Te bond (2.512Å) and Pt—N is shorter than Pd—N by 0.065Å. The difference between the two Pd—Cl bond distances (0.052Å) is a consequence of the *trans* influence of the Te—C bond.

Crystals of both complexes are associated with two chloroform (solvent) molecules per molecule of complex. There is no apparent interaction between the chloroform molecules and the complex; they do appear to stabilize the crystals by filling voids in them.

Complexation of (**c**) *with palladium(II) and platinum(II) at 2:1 molar ratio*

Having realised that the addition of excess ligand to [$LMCl_2$] does not results in $[(L)_2M]^{2+}$, a methodology involving the action of $AgClO_4$ on **Ic**/**IIc** subsequently followed by the addition of excess (**c**) has been successfully used for synthesizing **III** and **IV**. In attempting these reactions the instability of the species $[(c)M(MeOH)_2]^{2+}$ or $[(c)M(ClO_4)_2]$ was realised and no effort was therefore made to isolate them. Instead, one mol of the ligand (**c**) was added to obtain the complexes **III** and **IV**.

The complexes are highly air and moisture sensitive. Elemental analyses agree well with their formulation. Molar condutance values in acetonitrile (236 and 243 $ohm^{-1}\ cm^2\ mol^{-1}$ for **III** and **IV**, respectively) suggest them to be 1:2 electrolytes. This is supported by molecular weight measurements in acetonitrile which are 1/3 of the expected values. IR spectra of the complexes show no M-Cl vibration. The presence of characteristic bands (around 1090 and 621 cm^{-1}) of perchlorate ions is consistent with conductance and molecular weight data.

^1H NMR spectra of the complexes **III** and **IV** show all the expected peaks in the proper intensity ratio and suggest the coordination of both N and Te to the metal atom. The pyridine ring proton (H_{11}) *ortho* to N is shielded by 0.24 and 0.63 ppm as compared with **Ic** and **IIC** respectively. The lower deshielding of pyridine ring protons *ortho* to N is a consequence of the presence of the less electronegative nitrogen and tellurium atoms in place of the highly electronegative chlorine atom. Appearance of two ^{125}Te signals (535 and 536 ppm) with ^{195}Pt satellites in **IV** suggests the existence of two isomers in an approximately 1:1 ratio in chloroform solution.

Bimetallic and heterobimetallic complexes with arylchalcogen bridging

We have recently described the preparation of some homo-[41,42] and hetero-[24,25] bimetallic complexes. Addition of KCl to **Ic** or **III** did not yeild the N-uncoordinated product because of much stronger interaction of pyridine N with Pd and Pt as revealed by ^1H NMR. However, reactions of $[(dppe)M(EPh)_2]$ with

$Pd(c)(MeOH)_2)^{2+}$ in solution resulted in the formation of **V–VIII**. These complexes are fairly stable in air and are unaffected by moisture. Elemental analyses (Table 1) agree well with their formulation. They behave as 1:2 electrolytes in solvents such as acetonitrile and nitromethane.

^1H NMR spectra of all of these complexes show the expected peaks in the proper intensity ratio. The pyridine ring protons of these complexes are found to be shielded by 0.13 ppm in comparison to **Ic**, a fact which may be attributed to the presence of EPh as a bridging group; EPh is a stronger *trans* directing group than Cl. The $P(CH_2)$ protons appear as doublet at 2.3 ppm with $^2J(P\text{-}H)$ coupling of 18.5 Hz. $^{31}P\{^1H\}$ NMR spectra recorded for heterobimetallic complexes in $CDCl_3$ display a single ^{31}P resonance (40.8 ppm (**VII**); 42.3 ppm (**VIII**)) associated with platinum satellites (approximately 1:4:1, triplet structure). This clearly indicates the equivalence of the two phosphorus atoms and their linkage with Pt. The observed $^1J(Pt\text{-}P)$ values (3625 Hz (**VII**); 3630 Hz (**VIII**)) are higher than those expected for P *trans* to Se or Te. This is most probably because of the bridging nature of EPh which makes the interaction between Pt and E relatively weak and as a consequence the Pt-P bonds become strong. $^{195}Pt\{^1H\}$ NMR spectra of the two complexes also show a single ^{195}Pt resonance [-4570 ppm (**VII**); -4572 ppm (**VIII**)] associated with selenium/tellurium satellites.

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