Available online at www.sciencedirect.com

ScienceDirect

Inorganica Chimica Acta 361 (2008) 1426–1436

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Synthesis and single crystal structures of first examples of tridentate ligands of (Te, N, S) type and their complexes with palladium(II), platinum(II) and ruthenium(II)

P. Raghavendra Kumar, Shailesh Upreti, Ajai K. Singh *

Department of Chemistry, Indian Institute of Technology, New Delhi 110 016, India

Received 6 June 2007; received in revised form 31 August 2007; accepted 11 September 2007
Available online 15 September 2007

Abstract

The First examples of (Te, N, S) type ligands, 2-$CH_3SC_6H_4CH{=}NCH_2CH_2TeC_6H_4$-4-$OCH_3$ (**L**^{1}) and 2- $CH_3SC_6H_4$-$CHNHCH_2CH_2TeC_6H_4$-4-OCH_3 (**L**^{2}), and their metal complexes, $[PdCl(\mathbf{L}^1)]PF_6 \cdot CHCl_3 \cdot 0.5H_2O$ (**4**), $[PtCl(\mathbf{L}^1)]PF_6$ (**5**), $[PdCl(\mathbf{L}^2)]ClO_4.CHCl_3$ (**6**), $[PtCl(\mathbf{L}^2)]ClO_4$ (**7**), and $[Ru(p\text{-cymene})(\mathbf{L}^2)](PF_6)_2 \cdot CHCl_3$ (**8**), have been synthesized and characterized. The single crystal structures of **4**, **6** and **8** have revealed that both the ligands coordinate in them in a tridentate (Te, N, S) mode. The geometry around Pd in both the complexes has been found to be square planar, whereas for Ru in a half sandwich complex **8**, it is found to be octahedral. Between two molecules of **4** there are intra and inter molecular weak Te···Cl [3.334(3) and 3.500(3) Å, respectively] interactions along with weak intermolecular Pd···Te [3.621(2) Å] interactions. The Pd–Te bond lengths are between 2.517(6) and 2.541(25) Å and the Ru–Te bond length is 2.630(6) Å. The crystal structure of $[PdCl_2(4\text{-MeO–}C_6H_4\text{– }TeCH_2CH_2NH_2)]$ (**9**) is also determined. It is formed when KPF_6 is not added in the synthesis of **4** and Pd-complex of **L**^{1} is recrystallized. Apart from Te···Cl secondary interactions, C–H···π interactions also exist in the crystal of **9**.

Keywords: Tellurated Schiff bases; (Te, N, S) ligands; Platinum; Palladium; Ruthenium; Metal complex; Synthesis; Single crystal structure; X-ray diffraction

---

1. Introduction

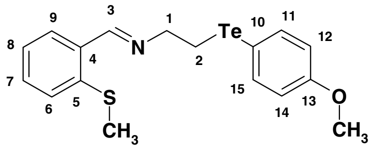
Hybrid organotellurium ligands, which have tri or higher dentate character, are not known in large number [1–8]. 1,6-Bis-2-butyltellurophenyl-2,5-diazahexa-1,5-diene [9] bis[(2-arytelluro)ethyl]amine/methylamine [10], bis(2-aminoethyl) ditelluride, bis(2-dimethylaminoethyl) ditelluride, bis(2-aryltelluroethyl) ether, 1,2-bis(2-aryltelluroethoxy) ethane, *N,N,N′,N′*-tetrakis(2-aryltelluroethyl) ethane-1,2-diamine, (where aryl = 4-MeO–C_6H_4) [11], 2-(2-pyridoethyltelluro)-ethylpyridine [12], bis(1-methylthiopropyl/ethyl)/(1-aminopropyl) telluride [13,14], bis[(8-(dimethylamino)-1-naphthyl] ditelluride [15], bis{(2-[(dimethylamino)methyl]-phenyl} telluride [16], macrocyclic Schiff bases [17] bis{2-(*N*-morpholino)ethyl}telluride [18] and tritelluroethers [19], are the important hybrid organotellurium ligands belonging to this category. Tellurated Schiff bases which also belong to this category are scantly known [20,21]. Schiff bases like ‘Salen’ and related derivatives form complexes with transition metals which are suitable catalysts for epoxidation reactions [22–26] and a variety of others like dehydrogenation plus intramolecular Diels–Alder cycloaddition [27], enantioselective conjugate addition [28], and ring opening polymerization [29]. The catalytic properties of such complexes may favourably change if Te is introduced into ligand skeleton. The lability of M–Te bond and steric influence of large size Te can, respectively, make

---

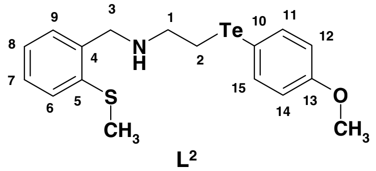
* Corresponding author. Tel.: +91 011 26591379; fax: +91 011 26581102.
E-mail addresses: ajai57@hotmail.com, aksingh@chemistry.iitd.ac.in (A.K. Singh).

0020-1693/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2007.09.012

the metal centre easily accessible to substrate and catalytic reaction more selective. It was therefore thought worthwhile to design ligands **L**^{1} and **L**^{2}, which are of (Te, N, S) type and understand their ligation with Pd(II), Pt(II) and Ru(II) first so that further investigation on catalytic activities of metal complexes of such ligands may be carried out. The results of these investigations are reported in this paper. **L**^{1} and **L**^{2} both have been found to coordinate in (Te, N, S) mode with Pd(II) and Ru(II) as shown by single crystal structures of their complexes.



L^1



L^2

2. Experimental

2.1. Physical measurement

The C and H analyses were carried out with a Perkin–Elmer elemental analyzer 240 °C. Tellurium was estimated by atomic absorption spectrometry. The ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13 and 75 MHz, respectively. IR spectra in the range 4000–250 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. The melting points determined in open capillary are reported as such. The conductivity measurements were carried out in CH_3CN (Concentration ca 1 mM) using ORION conductivity meter model 162.

2.2. Chemicals

2-(4-Methoxyphenyltelluro)ethylamine [30] and bis(4-methoxyphenyl) ditelluride [31] were synthesized by reported methods. 2-Ethanolamine and 2-methylthiobenzaldehyde were procured from Merck (India) and Aldrich (USA), respectively, and used as received. The [Ru(*p*-cymene)$_2$Cl$_2$]$_2$ was prepared by the method reported in literature the [32].

2.3. X-ray diffraction analysis

Single crystal X-ray diffraction studies were carried out on a Bruker SMART CCD diffractometer with MoKα (0.71073 Å) radiations at 25 °C. Table 1 lists the crystal data and structural refinement parameters for **4**, **6**, **8** and **9**. The software SADABS was used for absorption corrections and SHELXTL for space group, structure determination and refinements [33,34]. All non-hydrogen atoms were located from difference Fourier map using geometrical constraints and were refined anisotropically. The least-squares refinement cycles on F^2 were performed until the model converged. Selected bond lengths and angles are given in Table 2. The structure of **8** can be solved efficiently in space groups *I*2/*b* and *I*2/*a*.

The precursors of **L**^{2} viz. **1**, **2** and **3** (See Scheme 1) were synthesized by the following methods:

2.4. Synthesis of **1**

2-Ethanolamine (0.48 ml, 8 mmol) dissolved in 10 ml of dry ethanol was added to 2-methylthiobenzaldehyde (1 ml, 8 mmol) dissolved in 10 ml of dry ethanol along with 0.5 g of 4 Å molecular sieves. The mixture was stirred under reflux for 4 h and then cooled to room temperature. The molecular sieves were separated by filtration and the solvent was evaporated on a rotary evaporator, which resulted in **1** as yellow viscous oil. Yield 90%; $\Lambda_M = 3.0$ cm^2 mol^{-1} ohm^{-1}. NMR: ^{1}H (CDCl$_3$, 25 °C): δ (vs TMS): 2.29 (bs, 1H, OH), 2.46 (s, 3H, SCH$_3$), 3.79 (t, $J = 5.1$ Hz, 2H, H$_2$), 3.91 (t, $J = 4.8$ Hz, 2H, H$_1$), 7.18–7.37 (m, 1H, H$_8$), 7.30–7.40 (m, 2H, H$_{7,9}$), 7.79–7.82 (d, $J = 7.66$ Hz, 1H, H$_6$), 8.76 (s, 1H, H$_3$); ^{13}C{^{1}H} (CDCl$_3$, 25 °C): δ (vs TMS): 16.04 (SCH$_3$), 61.27 (C$_2$), 62.96 (C$_1$), 124.71 (C$_8$), 125.84 (C$_9$), 126.92 (C$_6$), 127.77 (C$_7$),133.18 (C$_4$), 138.72 (C$_5$), 160.46 (C$_3$). IR (KBr, cm^{-1}): 3556 (O–H), 1590 (C=N), 705 (C–S).

2.5. Synthesis of **2**

1 (0.20 g, ~1 mmol) was dissolved in 20 ml of dry ethanol and the solution was cooled in an ice bath. Solid NaBH$_4$ (0.38 g, 10 mmol) was added to this cooled reaction mixture slowly with stirring in a period of 15 min. The contents were refluxed for 4 h, cooled and the solvent was evaporated completely on a rotary evaporator. The residue was extracted with 100 ml of dry dichloromethane and the solution was filtered and dried with anhydrous sodium sulfate. The solvent was again removed on a rotary evaporator completely. Compound **2** was obtained as a highly viscous colorless oil. Yield, 80%; $\Lambda_M = 4.5$ cm^2 mol^{-1} ohm^{-1}. NMR: ^{1}H (CDCl$_3$, 25 °C): δ (vs TMS): 2.38 (bs, 2H, OH & NH), 2.47 (s, 3H, SCH$_3$), 2.79 (t, $J = 4.43$ Hz, 2H, H$_1$),

Table 1
Crystal data and refinement parameters of **4**, **6**, **8** and **9**

Empirical formula	$C_{36}H_{40}Cl_8F_{12}N_2O_{32}Pd_2S_2Te_2$ (**4**)	$C_{18}H_{22}Cl_5NO_5PdSTe$ (**6**)	$C_{28}H_{36}Cl_3F_{12}NOP_2$ Ru STe (**8**)	$C_9H_{13}ONCl_2PdTe$ (**9**)
Formula weight	1654.42	775.68	1059.60	456.113
Temperature (K)	298.0(2)	298(2)	298(2)	273(2)
Wavelength (Å)	0.71073	0.71069	0.71069	0.71073
Crystal system	orthorhombic	triclinic	monoclinic	monoclinic
Space group	*Pbcm*	$P\bar{1}$	*I2/a* or *I2/b*	*C2/c*
Unit cell dimensions				
a (Å)	18.258(3)	14.0935(8)	8.578(2)	19.423(5)
b (Å)	14.5105(8)	10.369(3)	14.282(4)	13.6145(19)
c (Å)	26.1305(14)	14.526(4)	27.882(11)	21.232(3)
α (°)	90	87.678(4)	90	90
β (°)	90	81.314(4)	90	91.129(2)
γ (°)	90	84.639(4)	103.294(8)	90
Volume (Å^3)	5343.8(5)	1271.2(6)	7527(4)	5276.8(14)
Z	4	2	8	16
D_{calc} (g/cm^3)	2.056	2.027	1.87	2.296
Absorption coefficient (mm^{-1})	2.361	2.493	1.615	3.945
$F(000)$	3184	752	4160	3424
Crystal size (mm)	0.372 × 0.108 × 0.058	0.373 × 0.17 × 0.109	0.251 × 0.186 × 0.037	0.215 × 0.192 × 0.135
θ Range (°)	1.44–25.50	1.42–25.12	1.50–25.5	1.87–25.50
Index ranges	$-17 \leqslant h \leqslant 17$, $-17 \leqslant k \leqslant 17$, $-31 \leqslant l \leqslant 31$	$-10 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 12$, $-17 \leqslant l \leqslant 17$	$-23 \leqslant h \leqslant 23$, $-17 \leqslant k \leqslant 17$, $-33 \leqslant l \leqslant 33$	$-22 \leqslant h \leqslant 22$, $-16 \leqslant k \leqslant 16$, $-25 \leqslant l \leqslant 25$
Reflections collected	38548	11831	36695	16699
Independent reflections	4803 [$R_{int} = 0.0545$]	3901 [$R_{int} = 0.0332$]	5168 [$R_{int} = 0.0635$]	3695 [$R_{int} = 0.1426$]
Maximum and minimum transmission	0.742 and 0.874	0.605 and 0.764	0.702 and 0.944	0.442 and 0.588
Data/restraints/parameters	5096/0/344	4443/0/318	7007/0/461	4078/0/273
Goodness-of-fit on F^2	1.266	1.228	1.090	1.083
Final R indices [$F^2 > 4\sigma(F^2)$]	$R_1 = 0.0885$, $wR_2 = 0.1749$	$R_1 = 0.0646$, $wR_2 = 0.1586$	$R_1 = 0.0584$, $wR_2 = 0.1756$	$R_1 = 0.0392$, $wR_2 = 0.1108$
R indices (all data)	$R_1 = 0.0934$, $wR_2 = 0.1773$	$R_1 = 0.0761$, $wR_2 = 0.1694$	$R_1 = 0.0814$, $wR_2 = 0.1954$	$R_1 = 0.0425$, $wR_2 = 0.1132$
Extinction coefficient	none	none	none	0.00069(13)
Largest difference peak and hole, e. (Å^{-3})	2.118 and −1.697	1.299 and −1.290	1.581 and −0.950	1.580 and −0.936

3.64 (t, $J = 4.74$ Hz, 2H, H_2), 3.86 (s, 2H, H_3), 7.12 (m, 1H, H_8), 7.17–7.33 (m, 3H, H_6, H_7 and H_9); $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ (vs TMS): 16.09 (SCH_3), 48.20 (C_3), 48.80 (C_1), 56.74 (C_2), 125.86 (C_7), 127.27 (C_6), 128.84 (C_4), 129.92 (C_9), 130.61 (C_8), 138.35 (C_5). IR (KBr, cm^{-1}): 3578, 1423 (O–H), 3444,1650 (N–H), 1045 (C–N), 733 (C–S).

2.6. Synthesis of **3**

2 (2 g, 10 mmol) was dissolved in 10 ml of dry chloroform and cooled in an ice bath. Freshly distilled $SOCl_2$ (5 g, 40 mmol) dissolved in 10 ml of dry chloroform was added to it dropwise in a period of 15 min. When the addition was complete the temperature of reaction mixture was increased slowly and it was stirred under reflux for 6 h. Thereafter, reaction mixture was cooled and concentrated to 10 ml on a rotary evaporator to give a light brown solid. The solid was dissolved in 10 ml of methanol, boiled with a pinch of activated charcoal and filtered. The filtrate was treated with 20 ml of diethyl ether. It gave a white crystalline product (Eye and skin irritant), which was filtered, washed with diethyl ether (10 ml × 4) and dried between the folds of filter papers. Yield, 70%. m.p. 140 °C. *Anal.* Calc. for $C_{10}H_{15}NSCl_2$: C, 51.38; H, 6.90; N, 5.99. Found: C, 57.87; H, 6.68; N, 5.95%. NMR: ^1H($CDCl_3$, 25 °C): δ (vs TMS): 2.55 (s, 3H, SCH_3), 3.25 (t, $J = 6.09$ Hz, 2H, H_1), 3.90 (t, $J = 6,6$ Hz, 2H, H_2), 4.94 (s, 2H, H_3), 7.26–7.28 (m, 1H, H_8), 7.34–7.46 (m, 2H, $H_{6,7}$), 7.72–7.74 (d, $J = 7.5$ Hz, 1H, H_9), 10.03 (bs, 2H, $NH_2{}^+$; $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ (vs TMS): 16.85 (SCH_3), 48.17 (C_2), 49.27 (C_1), 57.12 (C_3), 126.26 (C_6), 127.89 (C_7), 128.87 (C_4), 130.25 (C_8), 131.50 (C_9), 138.95 (C_5). IR (KBr, cm^{-1}): 3415,1569 (N–H), 847 (C–Cl), 763 (C–S).

2.7. Synthesis of $\mathbf{L^1}$

2-Methylthiobenzaldehyde (0.5 ml, 4 mmol) dissolved in 10 ml of dry ethanol was stirred for 15 min and 2-(4-methoxyphenyl)telluroethylamine (1.12 g, 4 mmol) dissolved in 10 ml of dry ethanol was added to it. The mixture was

Table 2
Selected bond lengths (Å) and bond angles (°) of **4**, **6**, **8** and **9**

[PdCl(2-MeS–C_6H_4–CH=NCH_2CH_2Te–C_6H_4-4-OMe)] $PF_6 \cdot CHCl_3 \cdot 0.5H_2O$ (**4**)

Pd(1)–N(1)	2.020(9)	Pd(1)–Cl(1)	2.293(3)
Pd(1)–S(1)	2.341(3)	Pd(1)–Te(1)	2.534(2)
Pd(1)–Te(1D)	2.541(25)	Pd(1D)–N(1)	1.984(18)
Pd(1D)–Cl(1)	2.326(16)	Pd(1D)–S(1)	2.391(17)
Pd(1D)–Te(1)	2.483(17)	Te(1)–C(10)	2.113(12)
Te(1)–C(9)	2.131(11)	Te(1D)–C(10)	2.030(28)
S(1)–C(1)	1.79(1)	S(1)–C(17)	1.794(13)
N(1)–C(8)	1.471(14)		
N(1)–Pd(1)–Cl(1)	174.07(26)	N(1)Pd(1)–S(1)	90.26(25)
Cl(1)–Pd(1)–S(1)	95.31(11)	N(1)–Pd(1)–Te(1)	87.22(25)
Cl(1)–Pd(1)–Te(1)	87.23(9)	S(1)–Pd(1)–Te(1)	177.44(10)
N(1)–Pd(1)–Te(1D)	87.11(56)	Cl(1)–Pd(1)–Te(1D)	87.42(52)
S(1)–Pd(1)–Te(1D)	176.42(58)	N(1)–Pd(1D)–Cl(1)	175.60(89)
N(1)–Pd(1D)–S(1)	89.70(66)	Cl(1)–Pd(1D)–S(1)	93.11(58)
N(1)–Pd(1D)–Te(1)	89.44(65)	Cl(1)–Pd(1D)–Te(1)	87.72(54)
S(1)–Pd(1D)–Te(1)	178.87(78)	C(10)–Te(1)–C(9)	97.72(42)
C(10)–Te(1)–Pd(1D)	100.04(49)	C(9)–Te(1)–Pd(1D)	89.72(48)
C(10)–Te(1)–Pd(1)	100.40(31)	C(9)–Te(1)–Pd(1)	90.58(31)
C(10)–Te(1D)–Pd(1)	102.54(106)	C(1)–S(1)–C(17)	100.93(54)
C(1)–S(1)–Pd(1)	100.30(34)	C(17)–S(1)–Pd(1)	104.87(46)
C(17)-S(1)–Pd(1D)	103.88(59)	C(7)–N(1)–Pd(1D)	127.70(88)
C(8)–N(1)–Pd(1D)	113.61(79)	C(7)–N(1)–Pd(1)	126.15(73)
C(8)–N(1)–Pd(1)	115.19(63)		

Symmetry codes: (i) x, $0.5 - y$, $1 - z$; (ii) x, y, $1.5 - z$; (iii) x, y, $0.5 - z$.

[PdCl(MeS–C_6H_4– $CH_2NH_2CH_2CH_2$Te–C_6H_4-4-OMe)] $ClO_4.CHCl_3$ (**6**)

Pd(1)–N(1)	2.076(8)	Pd(1)–Cl(1)	2.283(5)
Pd(1)–S(1)	2.348(6)	Pd(1)–Te(1)	2.517(6)
Te(1)–C(9)	2.113(10)	Te(1)–C(10)	2.117(10)
S(1)–C(7)	1.772(9)	S(1)–C(17)	1.810(12)
N(1)–C(1)	1.485(12)	N(1)–C(8)	1.490(12)
N(1)–Pd(1)–Cl(1)	173.20(21)	N(1)–Pd(1)–S(1)	91.55(21)
Cl(1)–Pd(1)–S(1)	95.04(9)	N(1)–Pd(1)–Te(1)	86.21(20)
Cl(1)–Pd(1)–Te(1)	87.35(7)	S(1)–Pd(1)–Te(1)	174.99(7)
C(9)–Te(1)–C(10)	98.56(32)	C(9)–Te(1)–Pd(1)	91.70(24)
C(10)–Te(1)–Pd(1)	99.41(20)	C(7)-S(1)–C(17)	103.23(47)
C(7)–S(1)–Pd(1)	101.55(29)	C(17)–S(1)–Pd(1)	110.51(35)
C(1)—N(1)—Pd(1)	115.29(55)	C(8)—N(1)—Pd(1)	112.41(52)

[Ru(p-cymene)(2-MeS–C_6H_4–CH_2– NHCH_2CH_2Te-4-C_6H_4–OMe)] $(PF_6)_2$ (**8**)

Ru(1)–N(1)	2.163(10)	Ru(1)–C(19)	2.184(6)
Ru(1)–C(22)	2.213(9)	Ru(1)–C(23)	2.218(8)
Ru(1)–C(20)	2.221(7)	Ru(1)–C(21)	2.248(7)
Ru(1)–C(18)	2.251(7)	Ru(1)–S(1)	2.376(2)
Ru(1)–Te(1)	2.630(6)	Te(1)–C(10)	2.126(7)
Te(1)–C(9)	2.134(12)	S(1)–C(1)	1.767(9)
S(1)–C(27)	1.773(10)	N(1)–C(8)	1.491(11)
N(1)–C(7)	1.495(10)		
N(1)–Ru(1)–C(19)	88.15(22)	N(1)–Ru(1)–C(22)	161.07(22)
C(19)–Ru(1)–C(22)	78.68(24)	N(1)–Ru(1)–C(23)	124.35(25)
C(19)–Ru(1)–C(23)	66.07(25)	N(1)–Ru(1)–C(20)	110.05(22)
C(19)–Ru(1)–C(20)	36.85(24)	C(22)–Ru(1)–C(20)	66.50(24)
C(23)–Ru(1)–C(20)	78.31(25)	N(1)–Ru(1)–C(21)	146.68(21)
C(19)–Ru(1)–C(21)	67.05(23)	C(22)–Ru(1)–C(21)	36.66(23)
C(23)–Ru(1)–C(21)	66.73(25)	C(20)–Ru(1)–C(21)	37.44(24)
N(1)–Ru(1)–C(18)	93.91(22)	C(19)–Ru(1)–C(18)	37.00(22)
C(22)–Ru(1)–C(18)	67.41(25)	C(23)–Ru(1)–C(18)	36.93(26)
C(20)–Ru(1)–C(18)	66.89(25)	C(21)–Ru(1)–C(18)	79.71(24)
N(1)–Ru(1)–S(1)	85.56(16)	C(19)–Ru(1)–S(1)	147.93(17)

Table 2 (*continued*)

[Ru(p-cymene)(2-MeS–C_6H_4–CH_2– NHCH_2CH_2Te-4-C_6H_4–OMe)] $(PF_6)_2$ (**8**)

C(22)–Ru(1)–S(1)	98.37(18)	C(23)–Ru(1)–S(1)	92.04(20)
C(20)–Ru(1)–S(1)	164.34(18)	C(21)–Ru(1)–S(1)	127.25(18)
C(18)–Ru(1)–S(1)	112.16(19)	N(1)–Ru(1)–Te(1)	83.82(15)
C(19)–Ru(1)–Te(1)	120.54(15)	C(22)–Ru(1)–Te(1)	114.55(16)
C(23)–Ru(1)–Te(1)	151.83(20)	C(20)–Ru(1)–Te(1)	92.83(16)
C(21)–Ru(1)–Te(1)	89.93(15)	C(18)-Ru(1)–Te(1)	157.54(17)
S(1)–Ru(1)–Te(1)	90.00(5)	C(10)–Te(1)–C(9)	99.30(31)
C(10)–Te(1)–Ru(1)	106.05(21)	C(9)–Te(1)–Ru(1)	92.55(22)
C(1)–S(1)–C(27)	104.87(38)	C(1)–S(1)–Ru(1)	99.52(25)
C(27)–S(1)–Ru(1)	113.34(30)	C(8)–N(1)–Ru(1)	114.24(45)
C(7)–N(1)–Ru(1)	118.96(43)		

Symmetry codes: (i) $1.5-x$, y, $1-z$; (ii) $1.5-x$, $1.5-y$, $1.5-z$.

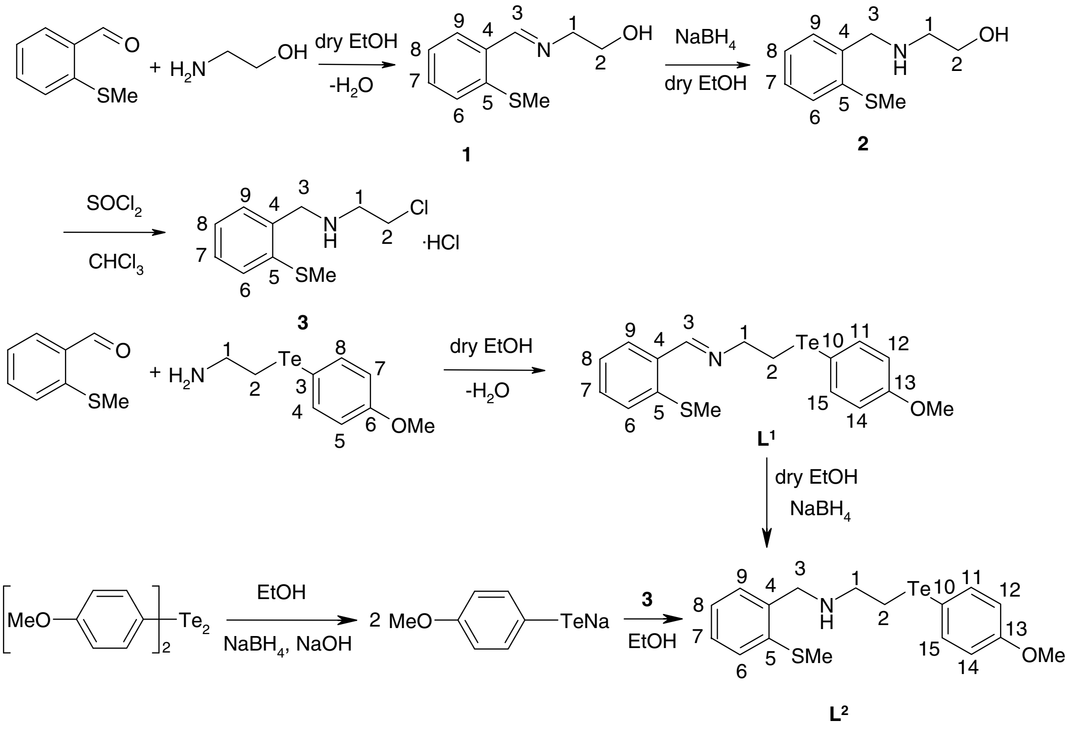
[$PdCl_2$(4-MeO–C_6H_4– Te$CH_2CH_2NH_2$)] (**9**)

Pd(1)–N(1)	2.059(5)	Pd(1)–Cl(2)	2.2981(15)
Pd(1)–Cl(1)	2.3798(15)	Pd(1)–Te(1)	2.5101(6)
Pd(2)–N(2)	2.056(5)	Pd(2)–Cl(3)	2.3060(16)
Pd(2)–Cl(4)	2.3744(16)	Pd(2)–Te(2)	2.5007(6)
Te(1)–C(3)	2.104(5)	Te(1)–C(2)	2.172(6)
Te(2)–C1(2)	2.118(6)	Te(2)–C1(1)	2.144(6)
N(1)–C(1)	1.474(7)		
N(1)–Pd(1)–Cl(2)	176.43(15)	N(1)–Pd(1)–Cl(1)	89.26(15)
Cl(2)–Pd(1)–Cl(1)	94.30(6)	N(1)–Pd(1)–Te(1)	87.64(14)
Cl(2)–Pd(1)–Te(1)	88.79(4)	Cl(1)–Pd(1)–Te(1)	176.55(4)
N(2)–Pd(2)–Cl(3)	175.88(14)	N(2)–Pd(2)–Cl(4)	90.58(14)
Cl(3)–Pd(2)–Cl(4)	93.24(6)	N(2)–Pd(2)–Te(2)	87.43(14)
Cl(3)–Pd(2)–Te(2)	88.75(5)	Cl(4)-Pd(2)–Te(2)	178.00(5)
C(3)–Te(1)–C(2)	93.3(2)	C(3)–Te(1)–Pd(1)	101.01(16)
C(2)–Te(1)–Pd(1)	90.16(17)	C(12)–Te(2)–C(11)	95.8(2)
C(12)–Te(2)–Pd(2)	98.32(16)	C(11)–Te(2)–Pd(2)	90.03(18)
C(6)–O(1)–C(9)	119.2(5)	C(15)–O(2)–C(18)	116.9(5)
C(1)–N(1)–Pd(1)	117.6(4)	C(10)-N(2)–Pd(2)	118.2(4)
N(1)–C(1)–C(2) 110.7(5)			

further stirred overnight and then refluxed for 3 h. After cooling to room temperature, the solvent was evaporated on a rotary evaporator to obtain $\mathbf{L}^1$ as red viscous oil. Yield 88%; $\Lambda_M = 0.5\ cm^2\ mol^{-1}\ ohm^{-1}$. *Anal.* Calc. for $C_{17}H_{19}NOSTe$: Te, 30.90. Found: Te, 30.58%. NMR: ^1H ($CDCl_3$, 25 °C): δ (vs TMS): 2.46 (s, 3H, SCH_3), 3.15 (t, $J = 7.19$ Hz, 2H, H_2), 3.78 (s, 3H, OCH_3), 4.04 (t, $J = 6.97$ Hz, 2H, H_1), 6.73–6.76 (d, $J = 8.23$ Hz, 2H, $H_{12,14}$), 7.19–7.23 (m, 2H, H_8), 7.25–7.39 (m, 1H, $H_{6,7}$), 7.70–7.73 (d, $J = 8.27$ Hz, 1H, $H_{11,15}$), 7.78–7.80 (d, $J = 7.49$ Hz, 1H, H_9), 8.70 (s, 1H, H_3); $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ (vs TMS): 10.07 (C_2), 16.59 (SCH_3), 54.90 (OCH_3), 62.53 (C_1), 100.49 (C_{10}), 114.92 ($C_{12,14}$), 125.16 (C_6), 126.87 (C_8), 128.16 (C_9), 130.54 (C_7), 133.71 (C_4), 139.10 (C_5), 140.77 ($C_{11,15}$), 159.23 ($C_{3,13}$). IR (KBr, cm^{-1}): 1633, 1585 (C=N), 1243 (C–N), 1283(C–O), 753(C–S), 473, 515(C–Te(alkyl)), 295 (C–Te(aryl)).

2.8. Synthesis of $\mathbf{L}^2$

Method I: Bis(4-methoxyphenyl)ditelluride (0.50 g, 1.0 mmol) was dissolved in 50 ml of dry ethanol and the



Scheme 1.

solution was refluxed for 1 h under dry nitrogen atmosphere. A solution of sodium borohydride made in NaOH (5%) was added dropwise to the refluxing solution slowly under nitrogen atmosphere until it became colourless due to the formation of $ArTe^{-}Na^{+}$. (2-Chloroethyl)[2-(methylsulfanyl)benzyl]ammonium chloride (**3**) (0.253 g, 1 mmol) dissolved in 10 ml of ethanol was added to this colourless solution with constant stirring. The resulting reaction mixture was refluxed further for 2 h. It was cooled to room temperature and poured into 100 ml of ice-cold distilled water. The aqueous solution was neutralized with 1–2 M NaOH solution. The ligand $\mathbf{L}^2$ was extracted into 100 ml of chloroform from this aqueous mixture. The chloroform extract was washed with water (50 ml × 4) and dried over anhydrous sodium sulfate. On removing chloroform with a rotary evaporator, $\mathbf{L}^2$ was obtained as red viscous oil. Yield: 75%.

Method II: $\mathbf{L}^1$ (0.4127 g, 1 mmol) was dissolved in 20 ml of dry ethanol and the solution cooled in an ice bath. Solid $NaBH_4$ (0.38 g, 10 mmol) was added with stirring in small lots within 15 min. The reaction mixture was refluxed for 4 h and cooled to room temperature. Using a rotary evaporator, solvent was removed giving a semisolid, which was leached with dry dichloromethane (25 ml × 4). The resulting dichloromethane extract was washed with distilled water (50 ml × 3) and dried with anhydrous sodium sulfate. The $\mathbf{L}^2$ was obtained as red viscous oil, when dichloromethane from this dried extract was removed on a rotary evaporator. Yield 90%; $\Lambda_M = 0.8\ cm^2\ mol^{-1}ohm^{-1}$. *Anal.* Calc. for $C_{17}H_{21}NOSTe$: Te, 30.75. Found: Te, 30.55%. NMR: ^1H ($CDCl_3$, 25 °C): δ (vs TMS): 1.89 (s, 1H, NH), 2.47 (s, 3H, SCH_3), 2.96–3.02 (m, 4H, $H_{1,2}$), 3.78 (s,3H, OCH_3), 3.85 (s, 2H, H_3), 6.71–6.74 (d, $J = 8.4$ Hz, 2H, $H_{12,14}$), 7.11–715 (m, 1H, H_8), 7.23–7.26 (m, 3H, $H_{6,7,9}$), 7.66–7.66 (d, $J = 8.41$ Hz, 2H, $H_{11,15}$); $^{13}C\{^1H\}$ ($CDCl_3$, 25 °C): δ (vs TMS): 10.06 (C_2), 15.33 (SCH_3), 49.19 (C_1), 54.69 (OCH_3), 50.45 (C_3), 100.07 (C_{10}), 114.92 ($C_{12,14}$), 124.42 (C_9), 125.14 (C_6), 128.51 (C_4), 129.26 (C_7), 131.71 (C_8), 140.56 ($C_{11,15}$), 140.99 (C_5), 159.26 (C_{13}) IR (KBr, cm^{-1}) 3302, 1586, 821 (N–H) 1287, 1247 (C–N), 1177 (C–O), 749, 676 (C–S), 473, 515 (C–Te(alkyl)), 290 (C–Te(aryl)).

2.9. Synthesis of $[PdCl(L^1)]PF_6 \cdot CHCl_3 \cdot 0.5\ H_2O$ (4)

$Na_2[PdCl_4]$ (0.294 g, 1 mmol) was dissolved in 2 ml of distilled water. The solution of $\mathbf{L}^1$ (0.413 g, 1 mmol) made in 20 ml of acetone was added to it with vigorous stirring. The solution was stirred further for 1/2 h at room temperature and poured into 50 ml of distilled water. The complex was extracted into 50 ml of chloroform. The chloroform extract was dried with anhydrous sodium sulfate and solvent was evaporated on a rotary evaporator to yield an orange solid. The solid was dissolved in a 1:1 mixture of chloroform and methanol and mixed with a solution of potassium hexafluorophosphate (0.187 g, 1 mmol) dissolved in 10 ml of acetone. The mixture was stirred for 3 h and filtered. The solvent was evaporated off on a rotary evaporator, resulting in a yellow solid. The single crystals of **4** were grown by slow evaporation of its solution in methanol and chloroform mixture (1:1). Yield 61%; m.p. 125(d) °C. $\Lambda_M = 155\ cm^2\ mol^{-1}\ ohm^{-1}$. *Anal.* (Powder form) Calc. for $C_{17}H_{19}ClF_6NOPPdSTe$: C, 29.18; H, 2.74; N, 2.00; Te, 18.23. Found: C, 28.55; H, 2.48; N, 2.20; Te, 18.68%. NMR: ^1H (DMSO-d_6, 25 °C): δ (vs TMS): 2.65 (bs, 1H, H_2), 2.81 (bs, 1H, H_2), 3.06 (s, 3H, SCH_3), 3.78 (s,3H, OCH_3), 4.56 (bs, 1H, H_1), 5.53 (bs, 1H, H_1), 7.02–7.05 (d, $J = 6.82$ Hz, 2H, $H_{12,14}$), 7.80–7.83 (m,, 2H, H_8), 7.94–7.99 (m, 1H, $H_{6,7,9}$), 8.11–8.14 (d, $J = 7.49$ Hz, 1H, $H_{11,15}$), 9.02 (s, 1H, H_3); $^{13}C\{^1H\}$ (DMSO-d_6, 25 °C): δ (vs TMS): 16.34 (C_2), 23.84 (SCH_3), 55.37 (OCH_3), 74.35 (C_1), 105.73 (C_{10}), 115.79 ($C_{12,14}$), 130.66 (C_6), 131.40 (C_8), 135.41 (C_9), 137.27 (C_7), 124.53 (C_4), 133.70 (C_5), 138.09 ($C_{11,15}$), 161.09 (C_{13}), 164.73 (C_3). IR (KBr, cm^{-1}) 1628, 1581 (C=N), 848 (P–F), 780 (C–S), 518 (C–Te(alkyl)) 291(C–Te (aryl)).

*2.10. Synthesis of [PtCl(L¹)]PF₆ (**5**)*

The solution of $K_2[PtCl_4]$ (0.105 g, 0.25 mmol) made in 2 ml of distilled water was treated with a solution of $\mathbf{L}^1$ (0.104 g, 0.25 mmol) made in 10 ml of acetone as described for **4**. Using the workup similar to that of **4**, an orange solid **5** was obtained. It was dissolved in 10 ml of methanol and mixed with a solution of potassium hexafluorophosphate (0.187 g, 1 mmol) dissolved in 10 ml of acetone. The mixture was stirred for 3 h and filtered. The solvent was evaporated off on a rotary evaporator to yield a yellow solid. The crystals of **5** were grown by slow evaporation of its solution in a mixture of DMSO and chloroform (1:9). Yield 61%; m.p. 181 °C (d). $\Lambda_M = 145.5\ cm^2\ mol^{-1}\ ohm^{-1}$. *Anal.* Calc. for $C_{17}H_{19}NOTeSClPtPF_6$: C, 25.90; H, 2.42; N, 1.78; Te, 16.18. Found: C, 26.10; H, 2.53; N, 1.84; Te, 17.01%. NMR: ^1H (DMSO-d_6, 25 °C): δ (vs TMS): 2.64 (bs, 1H, H_2), 2.79 (bs, 1H, H_2), 3.01 (s, 3H, SCH_3), 3.78 (s, 3H, OCH_3), 4.53 (bs, 1H, H_1), 5.55 (bs, 1H, H_1), 7.02–7.05 (d, $J = 6.82$ Hz, 2H, $H_{12,14}$), 7.80–7.83 (m, 1H, H_8), 7.94–8.00 (m, 1H, $H_{6,7,9}$), 8.11–8.16 (d, $J = 7.49$ Hz, 1H, $H_{11,15}$), 9.00 (s, 1H, H_3); $^{13}C\{^1H\}$ (DMSO-d_6, 25 °C): δ (vs TMS): 16.34 (C_2), 23.84 (SCH_3), 55.37 (OCH_3), 74.35 (C_1), 105.73 (C_{10}), 115.79 ($C_{12,14}$), 130.66 (C_6), 131.40 (C_8), 135.41 (C_9), 137.27 (C_7), 124.53 (C_4), 133.70 (C_5), 138.09 ($C_{11,15}$), 161.09 (C_{13}), 164.73 (C_3). IR (KBr, cm^{-1}): 1582 (C=N), 842 (P–F), 710 (C–S), 512 (C–Te((alkyl)), 280 (C–Te(aryl)).

*2.11. Synthesis of [PdCl(L²)]ClO₄ · CHCl₃ (**6**)*

$Na_2[PdCl_4]$ (0.294 g, 1 mmol) was dissolved in 5 ml of dry methanol and mixed with a solution of $\mathbf{L}^2$ (0.415 g, 1 mmol) made in 10 ml of methanol with vigorous stirring. The mixture was stirred further for 1/2 h at room temperature and silver perchlorate (0.208 g, 1 mmol) dissolved in 10 ml of dry methanol was added. It was again stirred for 1 h and the resulting precipitate was filtered through Celite. The solvent from the filtrate was removed on a rotary evaporator to yield an orange solid. The single crystals of **6** were obtained from a mixture (2:1) of chloroform and hexane. Yield 60%; m.p 110 °C (d). $\Lambda_M = 134.8\ cm^2\ mol^{-1}\ ohm^{-1}$. *Anal.* (Powder form) Calc. for $C_{17}H_{21}Cl_2NO_5PdSTe$: C, 31.11; H, 3.22; N, 2.13; Te, 19.44. Found: C, 31.53; H, 3.37; N, 2.23; Te, 20.10%. NMR: ^1H ($CDCl_3$, 25 °C): δ (vs TMS): 2.17 (bs, 1H, NH), 2.92 (s, 3H, SCH_3), 3.38–3.50 (m, 2H, H_2), 3.97–4.02(m, 2H, H_1), 3.77 (s, 3H, OCH_3), 5.53–5.56 (d, 2H, H_3), 6.93–6.96 (d, $J = 8.66$ Hz, 2H, $H_{12,14}$), 7.46–7.48 (m, 1H, H_8), 7.47–7.60 (m, 3H, $H_{6,7,9}$), 7.82–7.85 (d, $J = 8.51$ Hz, 2H, $H_{11,15}$); $^{13}C\{^1H\}$ ($CDCl_3$ + DMSO-d_6 (20%), 25 °C): δ (vs TMS): 17.39 (C_2), 16.70 (SCH_3), 55.92 (C_1), 55.31 (OCH_3), 64.45 (C_3), 104.83 (C_{10}), 115.76 ($C_{12,14}$), 124.47 (C_9), 126.26 (C_6), 129.28 (C_4), 131.02 (C_7), 133.85 (C_8), 137.82 ($C_{11,15}$), 138.56 (C_5), 161.45 (C_{13}). IR (KBr, cm^{-1}) 3437(b), 1590 (N–H) 3028 (ArC–H), 1258 (C–N), 1111, 1048, 555 (ClO_4), 708 (C–S), 513 (C–Te(alkyl)), 280 (C–Te(aryl)).

*2.12. Synthesis of [PtCl(L²)]ClO₄ (**7**)*

$K_2[PtCl_4]$ (0.294 g, 1 mmol) dissolved in 5 ml of dry methanol was treated with the solution of $\mathbf{L}^2$ (0.415 g, 1 mmol) made in 10 ml of methanol as described for **6**. Further reaction with silver perchlorate (0.208 g, 1 mmol) dissolved in 10 ml of dry methanol and a workup as mentioned in the case of **6** gave an orange-red solid **7**. Its crystals were grown from a 1:1 mixture of chloroform and hexane by slow evaporation of the solvent at room temperature. Yield 67%; m.p. 126 °C (d). $\Lambda_M = 144.5\ cm^2\ mol^{-1}\ ohm^{-1}$. *Anal.* Calc. for $C_{17}H_{21}Cl_2NO_5PtSTe$: C, 27.41; H, 2.84; N, 1.88; Te, 17.13. Found: C, 28.51; H, 2.97; N, 1.96; Te, 16.54%. ^1H ($CDCl_3$, 25 °C): δ (vs TMS): 2.50 (s, 1H, NH), 2.95 (s, 3H, SCH_3), 3.40–3.48 (m, 2H, H_2), 3.94–4.03(m, 2H, H_1), 3.80 (s, 3H, OCH_3), 5.55–5.57 (d,, 2H, H_3), 6.93–6.97 (d, $J = 8.46$ Hz, 2H, $H_{12,14}$), 7.51 (t, $J = 5.52$ Hz, 1H, H_8), 7.56–7.68 (m, 3H, $H_{6,7,9}$), 7.93–8.18 (d, $J = 8.51$ Hz, 2H, $H_{11,15}$). IR (KBr cm^{-1}): 3437(b), 1580 (N–H), 3028 (ArC–H), 1101, 1046, 555 (ClO_4), 730 (C–S), 507 (C–Te(alkyl)), 290 (C–Te(aryl)).

*2.13. Synthesis of [Ru(p-cymene)(L²)](PF₆)₂ · CHCl₃ (**8**)*

$[RuCl_2(p\text{-cymene})]_2$ (0.061 g, 0.1 mmol) was dissolved in 5 ml of dry dichloromethane. The solution of $\mathbf{L}^2$ (0.083 g, 0.2 mmol) also made in 10 ml of dichloromethane was added to it with vigorous stirring. The reaction mixture was stirred further for 1/2 h at room temperature and KPF_6 (0.035 g, 0.2 mmol) dissolved in 10 ml of acetone was added. The mixture was stirred further for 2 h and filtered through Celite. The solvent of filtrate was evaporated on a rotary evaporator to obtain **8**. Yellow coloured flaky crystals of **8** were obtained by slow evaporation of its solution made in a 1:2 mixture of chloroform and hexane. Yield 63%; m.p. 145 °C (d). $\Lambda_M = 244.6\ cm^2\ mol^{-1}\ ohm^{-1}$; *Anal.* (Powder form) Calc. for $C_{27}H_{35}F_{12}NOP_2RuSTe$: C, 34.25; H, 3.59; N, 1.45; Te, 13.27. Found: C, 34.49; H, 3.75; N, 1.49; Te, 13.57%. NMR: ^1H ($CDCl_3$, 25 °C): δ (vs TMS): 1.41 (d, $J = 6.6$ Hz, 6H, CH_3 of *i*-pr), 1.91 (s, 3H, CH_3 *p* to *i*-pr), 2.45 (sp, 1H, CH of *i*-pr), 2.85 (s, 3H, SCH_3), 3.30 (bs, 2H, H_2), 3.51 (m, 2H, H_1), 3.83 (s, 3H, OCH_3), 4.2 (bs, 2H, H_3), 5.85–6.10 (m, 4H, Ar–H of *p*-cymene), 6.75 (m, 3H, $H_{7,12,14}$), 6.94 (d, $J = 8.7$ Hz, 1H, H_9), 7.10–7.32 (m, 1H, H_8), 7.45–7.61 (m, 2H, $H_{6,11,15}$), 8.14 (bs, 1H, NH). IR (KBr, cm^{-1}): 3424(b) 1578 (N–H), 3028 (ArC–H), 750(C–S), 844(P–F), 511(C–Te(alkyl)), 285 (C–Te(aryl)).

2.14. *Synthesis of [$PdCl_2(NH_2CH_2CH_2Te–C_6H_4$-4- OMe)] (**9**)*

The $Na_2[PdCl_4]$ (0.294 g, 1 mmol) was dissolved in 5 ml of distilled water. The solution of 2-(4-methoxyphenyltelluro)ethylamine (0.279 g, 1 mmol) made in 10 ml of acetone was added to it with vigorous stirring. The stirring was continued further for 2 h, which gave an orange coloured precipitate of **4**. It was filtered and dried. Its recrystallization from a mixture of chloroform (5 ml) and DMF (1 ml) gave red crystals of **4**. Yield 68%; m.p. 145 °C (d), *Anal.* Calc. for $C_9H_{13}NOPdTeCl_2$: C, 23.70; H, 2.87; N, 3.07; Te 27.98. Found: C, 23.87; H, 2.66; N, 3.45; Te, 27.78%. NMR: ^1H (DMSO-d_6 25 °C): δ (vs TMS), 3.30 (bs 1H, H_1) 3.80 (s, 3H, OCH_3), 4.11 (bs, 1H, H_1), 4.80 (bs, 1H, H_2), 5.01(bs, 1H, H_2), 7.04–7.07 (d, $J = 8.52$ Hz, 2 H, $H_{5,7}$), 8.04–8.06 (d, $J = 8.40$ Hz, 2H, $H_{4,8}$), 8.50 (NH_2); ^{13}C (DMSO-d_6, 25 °C): δ (vs TMS): δ 19.62 (C_2), 50.25 (C_1), 55.33 (OCH_3), 106.13, (C_3), 115.64 ($C_{5,7}$), 138.04 ($C_{4,8}$), 160.73 (C_6).

3. Results and discussion

The reactions involved in the synthesis of ligands $\mathbf{L}^1$ and $\mathbf{L}^2$ are shown in Scheme 1. Both ligands are stable viscous liquids under ambient conditions and soluble in common organic solvents except hexane.

The complexes of $\mathbf{L}^1$ with Pd(II) and Pt(II) and of $\mathbf{L}^2$ with Pd(II), Pt(II) and Ru(II) are also stable under ambient conditions and soluble in DMSO. In other common organic solvents, the Pd(II) and Pt(II) complexes of $\mathbf{L}^1$ show limited solubility, but those of $\mathbf{L}^2$ are more soluble than those of $\mathbf{L}^1$. In methanol and chloroform the solubility of complexes of $\mathbf{L}^1$ is moderate. However, Ru(II) complex of $\mathbf{L}^2$ is soluble in common organic solvents except hexane and diethyl ether. All complexes of $\mathbf{L}^1$ and $\mathbf{L}^2$are electrolytes (1:1 in the case of Pd/Pt; 1:2 for Ru). The IR bands resulting from ClO_4^- indicate that the anion is uncoordinated [35]. The Te–C(alkyl) bands appear at higher frequencies than those of Te–C(aryl) bands. The $\nu_{(C=N)}$ of $\mathbf{L}^1$ undergoes a small red shift ~5 cm^{-1} on complex formation. The product of the reaction of $PdCl_2(C_6H_5CN)_2$ (in chloroform) or Na_2PdCl_4 (in water) with $\mathbf{L}^1$(in acetone) if not treated with $NaPF_6$ and left for crystallization in a mixture of chloroform and DMF (5:1), results in red crystals of [$PdCl_2$(4-MeO–C_6H_4–$TeCH_2CH_2NH_2$)] (**9**) due to hydrolysis of Schiff base. **9** may also be synthesized by vigorously stirring (for 2 h) $Na_2[PdCl_4]$ with 2-(4-methoxyphenyltelluro)ethylamine (see Section 2.14). It is authenticated by NMR and X-ray diffraction on its single crystal.

3.1. *^1H and ^{13}C {^1H} NMR spectra*

The $\mathbf{L}^1$ and $\mathbf{L}^2$ give characteristic ^1H and ^{13}C {^1H} NMR spectra [36]. In ^1H NMR spectra of complexes **4–8** the signal of SCH_3 protons is deshielded (with respect to those of free ligand) by ~0.5 ppm, indicating the coordination of metal by sulfur. In the ^1H NMR spectra of **4** and **5** the protons of N/$TeCH_2$ become chemically non-equivalent to give four signals. The signals due to NCH_2 protons were found deshielded (0.5–1.5 ppm) whereas those of $TeCH_2$ appeared shielded (0.2–0.4 ppm). However, the formation of metal–tellurium bond in **4** is established by its single crystal structure unequivocally. Carbon-13 NMR spectra of both **4** and **5** indicate the formation of metal – Te bond in the two complexes as carbon atoms attached to Te show signals deshielded upto 6.3 ppm with respect to those of the free ligand. The formation of metal–nitrogen bond in **4** and **5** is also supported by deshielding (with respect to that of free ligand) of –HC=N– signal in their proton (upto 0.3 ppm) and carbon-13 (5 ppm) NMR spectra. In ^1H NMR spectra of **6** and **7** the signals of H_3 protons become a doublet because the two protons become chemically nonequivalent due to the rigidity imposed by chelation of the ligand. On comparing proton NMR spectra of complexes **6–8** with that of free $\mathbf{L}^2$, it has been found that the N/$TeCH_2$ signals are deshielded (1.0/0.4 ppm) with respect to those of the free ligand. Moreover, deshielding in the signals of ArH (*o* to Te), NH and $ArCH_2$ has been found to be of the order 0.2, 0.9 and 1.6 ppm, respectively. These observations have been further corroborated by carbon-13 NMR spectrum, as $ArCH_2$, NCH_2 and $TeCH_2$ signals in the spectrum of **6** appear deshielded by 11.0, 7.0 and 7.3 ppm, respectively, with respect to those of the free ligand. The $^{13}C\{^1H\}$ NMR of **7** and **8** could not be recorded due to their inadequate solubility. The deshielding of aryl proton signals of tellurated ethyl amine when it coordinates with Pd giving **9** has been found to be 0.3–0.4 ppm. This is corroborated by $^{13}C\{^1H\}$ NMR spectrum of **9**. The signals of carbon atoms attached to N or Te are deshielded up to ~7 ppm with respect to those of the free ligand [30].

3.2. *Crystal structures*

Single crystals of **4**, **6**, **8** and **9** were found good for X-ray diffraction and their single crystal structures were solved. The twinning in the crystals of complex **5** restricted us from proceeding further in solving its structure.

The molecular structure of **4** is shown in the Fig. 1. The selected bond lengths and bond angles are given in the Table 2. This is among the first two structurally characterized Pd(II) complexes of a (Te, N, S) ligand (other one is **6** described below) There is one molecule of $CHCl_3$ and 0.5 molecule of H_2O per molecule of **4** in the lattice. The

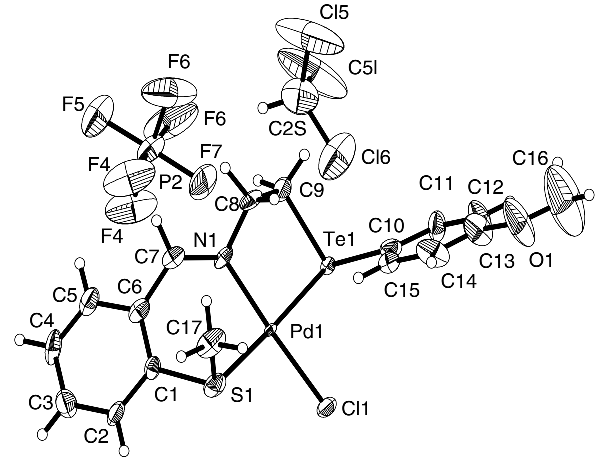


Fig. 1. ORTEP diagram of [PdCl(2-MeS–C_6H_4–CH=NCH_2CH_2Te–C_6H_4-4-OMe)]$PF_6 \cdot CHCl_3 \cdot 0.5H_2O$ (**4**) with 50% thermal ellipsoids; water molecule has not been shown for clarity.

Pd–Te, Pd–Cl and Pd–N bond lengths (2.534(2), 2.293(3) and 2.020(9) Å, respectively) are consistent with the values reported' for [PdCl{4-$MeOC_6H_4TeCH_2CH_2N$=C(CH_3)–C_6H_4-2-O^-}] [20] viz. 2.504(1), 2.290(4) and 2.01(1) Å, respectively. For Pd(II) complex of *N*-{2-(4-methoxyphenyltelluro)ethyl}pyrrolidine [37] Pd–Te, Pd–Cl and Pd–N bond lengths have been reported as 2.478(3), 2.3160(7)–2.3915(7) and 2.086(2) Å, respectively. On comparing these values with those of **4** the difference appears larger in case of Pd–Cl. It probably accrues due to *trans* influence of Te. For *cis*-[Pd{C_6H_5CH=NCH_2–CH_2–SEt}Cl_2] [38] Pd–S, Pd–N and Pd–Cl bond distances are reported as 2.255(1)–2.421(2), 1.992(4)–2.038(2) and 2.296(1)–2.312(1) Å, respectively, and appear to be consistent with those of **4**. The Pd–Te bond length, 2.534(2) Å in **4** is shorter than the sum of covalent radii 2.65 Å, indicating a strong coordination of Te with Pd. The Pd–Cl, Pd–N, and Pd–S bond lengths (Table 2) are closer to the corresponding sum of covalent radii (2.27, 1.98 and 2.32 Å), respectively. There are two asymmetric Pd and Te atoms in the lattice of crystal **4**. Between the two molecules of **4** there are intra [3.334(3) Å] and inter molecular [3.500(3) Å] Te···Cl secondary interactions. Also there are intermolecular Pd···Te [3.621(2) Å] secondary interactions (Fig. 2), which we have observed for the first time. The geometry of Pd(II) is square planar. The hypervalent nature of tellurium makes the Pd···Te as well as the Te···Cl secondary interaction possible.

The ORTEP diagram of **6** is shown in Fig. 3. The selected bond lengths and bond angles are given in Table 2. The crystal contains a molecule of $CHCl_3$ per molecule of **6**. With **4** it makes the first two structurally characterized Pd(II) complexes of (Te, N, S) type hybrid organotellurium ligands. The Pd–S, Pd–Te, Pd–N and Pd–Cl bond lengths are 2.348(6), 2.517(6), 2.076(8) and 2.283(5) Å, respectively, and consistent with earlier reported values [20,37,38] discussed above. However, Pd–Te bond length 2.517(6) Å is shorter than the value observed for **4** as well as the sum of covalent radii 2.65 Å. Probably the reduction of >C=N– makes the skeleton of $\mathbf{L}^2$ more flexible than that of $\mathbf{L}^1$ and consequently large size Te atom makes a stronger bond with Pd. The Pd–S, Pd–N and Pd–Cl bond lengths (Table 2) are also closer to the sum of covalent radii mentioned above. In complex **6** also there is a square planar geometry around Pd(II). In both **4** and **6**, Te is *trans* to S but Pd–S bond distance is not significantly influenced by the *trans* influence of Te.

The molecular structure of **8** is shown in Fig. 4. The selected bond lengths and bond angles are given in Table 2. **8** is the first structurally characterized complex, in which coordination sphere of Ru(II) is completed by *p*-cymene ring and a tridentate hybrid organotellurium ligand of (Te, N, S) type. The crystal contains a molecule of $CHCl_3$ and there are two PF_6^- ions per molecule of **8**. Ru has an octahedral geometry. The Ru–Te, and Ru–N bond lengths (2.630(6) and 2.163(10) Å, respectively) are consistent with the reported values 2.4983(8)–2.6371(4) and 2.041(6)–

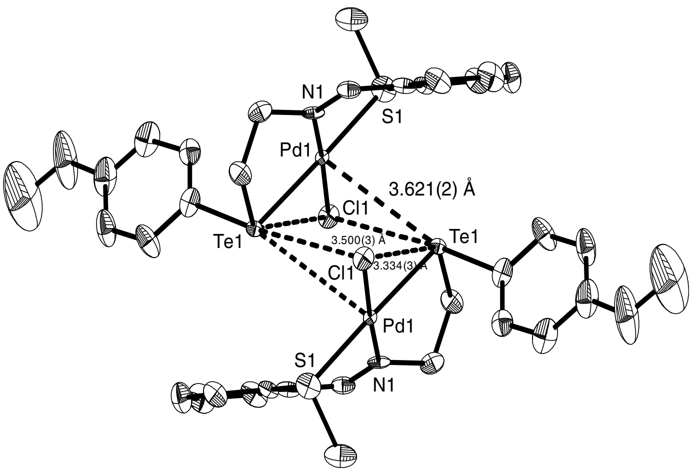


Fig. 2. Intra intermolecular Te···Cl and inter molecular Pd···Te secondary interactions in [PdCl(2-MeS–C_6H_4-CH=NCH_2CH_2Te–C_6H_4-4-OMe)]PF_6 (**4**) PF_6^- ion $CHCl_3$, H_2O molecules and H atoms have been omitted for clarity).

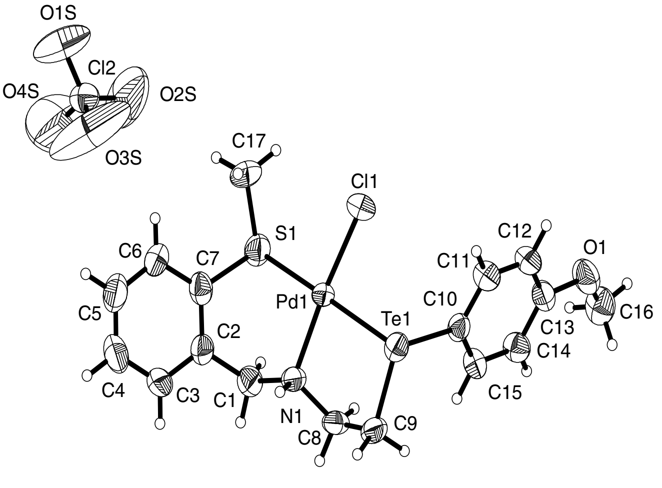


Fig. 3. ORTEP diagram of [PdCl(MeS–C_6H_4–$CH_2NH_2CH_2CH_2$Te–C_6H_4-4-OMe)]$ClO_4 \cdot CHCl_3$ (**6**) with 50% probability ellipsoids ($CHCl_3$ molecule has been omitted for clarity).

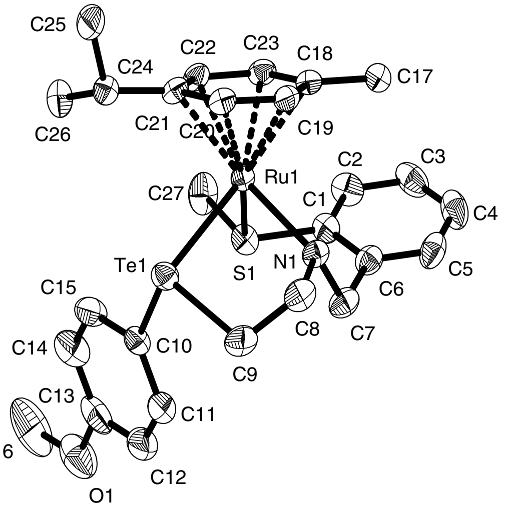


Fig. 4. ORTEP diagram of [Ru(*p*-cymene)(2-MeS–C_6H_4–CH_2NHCH_2-CH_2Te-4-C_6H_4OMe)] $(PF_6)_2 \cdot CHCl_3$ (**8**) with 30% probability ellipsoids (the PF_6^- anions, $CHCl_3$ molecule and H atoms have been omitted for clarity).

2.142(3) Å, respectively, for [(Ru(*p*-cymene)Cl(H_2NCH_2-$CH_2TeC_6H_4$-4-OCH_3)] and [Ru($^-$O-2- C_6H_4C(Me)NH-$CH_2CH_2TeC_6H_4$-4-OMe)$_2$] [21] For complexes [Ru(PPh_3)-(CH_3CN)Cl(2-(Ph_2P)C_6H_4CH=N(CH_2)$_2$OH)]Cl, [$RuCl_2$-(2-(Ph_2P)C_6H_4CH=N– CH(Me)CH(Ph)OH)(PPh_3)] and Ru(CH_3CN)$_2$(2-(Ph_2P)C_6H_4CH=NCH(Et)CH_2OH) PPh_3)]-$(BF_4)_2$ [39] Ru–N bond distance is reported between 2.00(1)–2.127(9) Å, some what shorter than that of **8**. Probably the steric influence of Te in complex **8** makes this difference. In the case of complexes [$RuCl_2$**L**] (**L** = *N,N′*-bis(2-*tert*-butylthiobenzilidene)-1,3-propanediamine) and [RuCl(CH_3CN)(**L**)] (*N,N′*-bis(2-*tert*-butylthiobenzilidene)-1,2-ethylenediamine) the Ru–S and Ru–N distances [40] are reported between 2.3436(7)–2.3737(8) and 2.032(3)–2.053(2) Å, respectively. The Ru–S bond distance of complex **8**, 2.376(2) Å, is consistent with this report, however, its Ru–N bond length is longer. The ligand in **8** is not a Schiff base but its reduced product. This may be one of the possible reasons for the difference. Moreover, the M–L bond lengths (Ru–S, Ru–Te and Ru–N) of **8** are somewhat longer (Table 2) than the sum of the corresponding covalent radii 2.24, 2.61 and 1.94 Å, respectively. The bond lengths and angles of *p*-cymene group have been found normal. The Ru–C bond lengths (Table 2) are almost similar and consistent with the earlier reports [36]. In all complexes, **4**, **6**, and **8**, the bond angles and bond lengths of benzene ring and the organic skeleton of the ligands have been found to be normal. The molecular structure of **9** is shown in Fig. 5. There are two asymmetric molecules in the crystal. Pd has square planar geometry. The methyl group attached to sulfur and 4-methoxy group attached to Te are *cis* to each other. The Pd–Cl bond *trans* to Te is somewhat longer than the other Pd–Cl bond length (Table 2) due to the strong *trans* influence of Te. The Pd–N and Pd–Te bond lengths are consistent with the recently reported values [2.086(2)–2.01(1), 2.4781(3)–2.504(1) Å, respectively] for chelates of Pd(II) formed with (Te, N) and (Te, N, O) ligands [20,37]. Between the neighbouring molecules of **9** there are Te···Cl secondary interactions (Fig. 6). This is probably due to hypervalent nature of tellurium. The Pd–Pd distance is 3.37(6) Å, which is greater than the sum of van der Waal's radii of Pd, 3.26 Å. There exist C–H···π interactions (Fig. 3) also in the crystal of **9**. On comparing Pd–N and Pd–Te bond distances of **9** with those of a palladium complex, [$PdCl_2$**L**] (**L** = (4-ethoxyphenyl) [2-amino-5-methyl)phenyl]telluride [41] in which skeleton containing Te and N donor sites is aromatic (Pd–Te = 2.4698(5) Pd–N = 2.045(5), Pd–Cl = 2.301(2)/2.371(1) Å), it appears that Pd–Te distance of **9** (2.5101(6) Å) is somewhat longer but Pd–N and Pd–Cl bond lengths (Table 2) are consistent. This is surprising because aromatic system is expected to reduce the donor character of nitrogen.

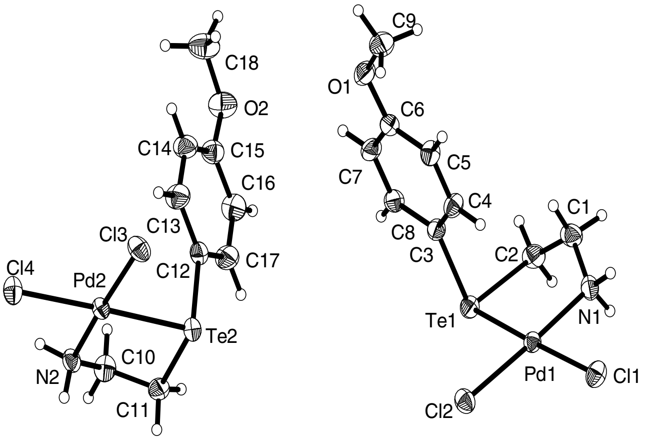


Fig. 5. ORTEP diagram showing two asymmetric molecules of complex [$PdCl_2$(2-MeO–C_6H_4–$TeCH_2CH_2NH_2$)] (**9**) with 30% thermal ellipsoids.

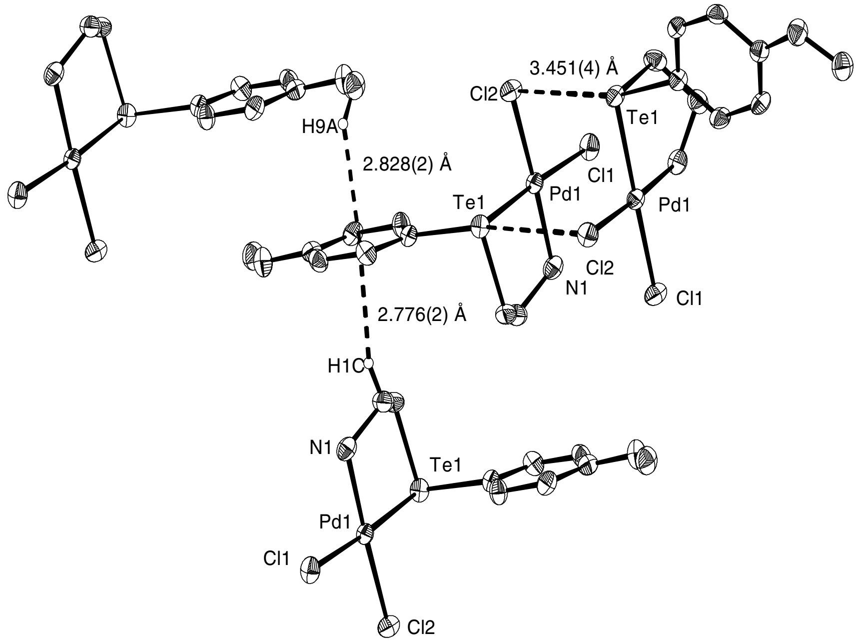


Fig. 6. Te···Cl and CH···π secondary interactions in [PdCl$_2$(2-MeO–C$_6$H$_4$–TeCH$_2$CH$_2$NH$_2$)] (**9**) (Some of the H atoms have been omitted for clarity).

4. Conclusions

The first examples of (Te, N, S) ligands, 2-CH$_3$S-C$_6$H$_4$CH=NCH$_2$CH$_2$TeC$_6$H$_4$-4-OCH$_3$ (**L**^{1}) and 2-CH$_3$-SC$_6$H$_4$CHNHCH$_2$CH$_2$TeC$_6$H$_4$-4-OCH$_3$ (**L**^{2}), and their complexes with Pd(II), Pt(II) and Ru(II) have been synthesized. The mode of bonding of **L**^{1} and **L**^{2} with Pd(II) and Ru(II) has been shown to be (Te, N, S) by single crystal structure determination. The tendency of Te to exhibit hypervalence results in Te···Cl and Pd···Te secondary interactions, which are not much investigated so far. [PdCl$_2$-(4-MeO–C$_6$H$_4$– TeCH$_2$CH$_2$NH$_2$)] (**9**) has been formed due the hydrolysis of Schiff base, when attempts were made to grow crystals of a Pd-complex of **L**^{1}. **9** has also been synthesized by the reaction of an appropriate tellurated amine and PdCl$_2$ and characterized by X-ray diffraction on its single crystal.

Acknowledgements

A.K.S. thanks the Department of Science and Technology (India) for research Project SR/S1/IC-23/06. The authors also thank the Department of Science and Technology (India) for partial financial assistance given to establish single crystal X-ray diffraction facility under its FIST programme. R.K.P. thanks University Grants Commission (India) for Senior Research Fellowship.

Appendix A. Supplementary material

CCDC 299503, 299504 299499 and 299501 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.09.012.

References

[1] A.K. Singh, V. Srivastava, J. Coord. Chem. 27 (1992) 237.
[2] A.K. Singh, S. Sharma, Coord. Chem. Rev. 209 (2000) 49.
[3] A.K. Singh, Proc. Indian Acad. Sci. (Chem. Sci.) 114 (2002) 357.
[4] A.K. Singh, in: M.A. Cato (Ed.), Focus on Organometallic Chemistry, Nova Science Publishers, USA, 2005, Chapter 3, pp. 79–109.
[5] A.K. Singh, Phosphorus Sulfur Silicon 180 (2005) 903.
[6] E.G. Hope, W. Levason, Coord. Chem. Rev. 122 (1993) 109.
[7] W. Levason, D. Orchard, G. Reid, Coord. Chem. Rev. 225 (2002) 59.
[8] J.A. Barton, A.R.J. Genge, N.J. Hill, W. Levason, S.D. Orchard, B. Patel, G. Reid, A.J. Ward, Heteroatom Chem. 13 (2002) 550.
[9] N. Al-Salim, T.A. Hamor, W.R. McWhinnie, J. Chem. Soc., Chem. Commun. (1986) 453.
[10] A.K. Singh, V. Srivastava, B.L. Khandelwal, Polyhedron 9 (1990) 851.
[11] V. Srivastava, R. Batheja, A.K. Singh, J. Organomet. Chem. 484 (1994) 93.
[12] A. Khalid, A.K. Singh, Polyhedron 16 (1997) 33.
[13] M. Hesford, W. Levason, S.D. Orchard, G. Reid, J. Organomet. Chem. 649 (2002) 214.
[14] M. Mishra, A.K. Singh, Phosphorus Sulfur Silicon 134–135 (1998) 537.
[15] S. C Menon, H.B. Singh, J.M. Jasinski, J.P. Jasinski, R.J. Butcher, Organometallics 15 (1996) 1707.
[16] R. Kaur, H.B. Singh, R.J. Butcher, Organometallics 14 (1995) 4755.
[17] S. C Menon, H.B. Singh, R.P. Patel, S.K. Kulashreshta, J. Chem. Soc., Dalton Trans. (1996) 203.
[18] A.K. Singh, J. Sooriyakumar, S. Husebye, K.W. Tornroos, J. Organomet. Chem. 612 (2000) 46.
[19] A.J. Barton, W. Levason, G. Reid, A.J. Ward, Organometallics 20 (2001) 3644.

[20] P.R. Kumar, A.K. Singh, P. Sharma, J.E. Drake, M.B. Hursthouse, M.E. Light, Inorg. Chem. Commun. 7 (2004) 502.

[21] P.R. Kumar, A.K. Singh, R.J. Butcher, P. Sharma, R.A. Toscano, Eur. J. Inorg. Chem. (2004) 1107.

[22] E.M. McGarrigle, D.G. Gilheany, Chem. Rev. 105 (2005) 1563.

[23] D. Wang, M. Wang, X. Wang, Y. Chen, A. Gao, L. Sun, J. Catal. 237 (2006) 248.

[24] R. Ferreira, H. Garcia, B. de Castro, C. Freire, Eur. J. Inorg. Chem. (2005) 4272.

[25] A. Martinez, C. Hemmert, C. Loup, G. Barre, B. Meunier, J. Org. Chem. 71 (2006) 1449.

[26] H. Zhang, S. Xiang, C. Li, Chem. Commun. (2005) 1209.

[27] C.P. Chow, K.J. Shea, J. Am. Chem. Soc. 127 (2005) 3678.

[28] M.S. Taylor, D.N. Zalatan, A.M. Lerchner, E.N. Jacobsen, J. Am. Chem. Soc. 127 (2005) 1313.

[29] D.J. Darensbourg, P. Ganguly, D. Billodeaux, Macromolecules 39 (2006) 2722.

[30] A.K. Singh, V. Srivastava, Phosphorus Sulfur and Silicon 47 (1990) 471.

[31] K.J. Irgolic, R.A. Zingaro, Reactions of Organotellurium Compounds, in: E. Becker, M. Tsutsui (Eds.), Organometallic Synthesis, Vol. 2, John Wiley and Sons, Inc., 1971.

[32] M.A. Bennet, T.N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74.

[33] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

[34] G.M. Sheldrick, SHELXTL-NT2000, Version 6.12, Reference Manual, University of Göttingen, Germany, 2001.

[35] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compound, third ed., John Wiley and Sons, Inc, 1978.

[36] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, fifth ed., John Wiley & Sons, Inc., 1991, p. 165, 227.

[37] G. Singh, A.K. Singh, P. Sharma, J.E. Drake, M.B. Hursthouse, M.E. Light, J. Organomet. Chem. 688 (2003) 20.

[38] X. Riera, A. Caubet, C. Lopez, V. Moreno, E.Freisinger.M. Willermann, M. Willermann, B. Lippert, J. Organomet. Chem. 629 (2001) 97.

[39] K. Nakajima, S. Ishibashi, M. Inamo, M. Kojima, Inorg. Chim. Acta 325 (2001) 36.

[40] K. Nakajima, Y. Ando, H. Mano, M. Kojima, Inorg. Chim. Acta 274 (1998) 184.

[41] B. Ji, K. Ding, Inorg. Chem. Commun. 2 (1999) 347.