Organotellurium(IV) Derivatives of Tetraphenyldichalcogenoimidodiphosphinates − The Crystal and Molecular Structure of [C_4H_8TeI{Ph_2(Se)PNP(Se)Ph_2}], [C_4H_8TeI{Ph_2(S)PNP(S)Ph_2}], [C_4H_8Te{Ph_2(S)PNP(S)Ph_2}$_2$], [C_8H_8TeI{Ph_2(S)PNP(S)Ph_2}], and [O(TeC_4H_8)$_2${Ph_2(O)PNP(O)Ph_2}]$_2$[I, I_3] Representing a Novel Type of Ring Systems

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The synthesis of the following organotellurium(IV) compounds [C_4H_8TeI{Ph_2(Se)PNP(Se)Ph_2}] (**2**), [C_4H_8TeI{Ph_2(S)PNP(S)Ph_2}] (**3**), [C_8H_8TeI{Ph_2(S)PNP(S)Ph_2}] (**4**), [C_4H_8Te{Ph_2(S)PNP(S)Ph_2}$_2$] (**5**), and [O(TeC_4H_8)$_2${Ph_2(O)PNP(O)Ph_2}]$_2$[I, I_3] (**6**) was achieved. These compounds have been characterized by microanalysis, multielement NMR and IR spectroscopy, positive ion FAB mass spectrometry and single-crystal X-ray diffraction analysis. The solid-state structures show that the coordination geometry at the tellurium center in every derivative can be described as a distorted pseudo-trigonal bipyramid, in which the lone-pair of electrons is supposed to occupy an equatorial position. The selenium and sulfur ligands exhibit an aniso-bidentate chelating coordination mode on interaction with the tellurium center. When the aniso-bonded donor atoms are included in the coordination sphere, the environment about Te becomes distorted square-pyramidal for the monochelate derivatives **2**–**4** and distorted octahedral for the bis(chelate) compound **5**. In compound **6**, two oxygen ligands act as bridges between two C_4H_8Te–O–TeC_4H_8 units, forming a 16-membered cationic ring. The anions, I^- and I_3^-, are located above and below the twisted ring with Te···I interactions ranging from 3.532(2) to 3.902(3) Å.

Introduction

We became interested in the chemistry of organotellurium(IV) in conjunction with our studies on the coordination chemistry of heavy main group elements with tetraphenyldichalcogenoimidodiphosphinate ligands. It became apparent that the [Ph_2(Q)PNP(Q′)Ph_2]$^-$ [Q/Q′ = O/O (**1a**), S/S (**1b**), Se/Se (**1c**), O/S (**1d**), S/Se(**1e**)] ligands are ideal for studying the influence of distinct donor-atom sets and the stereochemical influence of the electron lone-pair on the geometry of main group metal complexes.[1−5] This is because they offer the opportunity to vary both the donor atoms and because of the large degree of conformational freedom observed in the variable M−Q−P angle and P−N−P conjugated systems. Some interesting and unusual examples of compounds containing these ligands are certain lanthanide complexes,[1] the quasi-ideal *trans*-octahedral organotin compounds,[2] the true square-planar [Sn{Ph_2(Se)PNP(Se)Ph_2}$_2$],[3] [Te{Ph_2(Q)PNP(Q)Ph_2}$_2$] (Q= S[6] and Se[7]), [Se{Ph_2(Q)PNP(Q)Ph_2}$_2$] (Q= S[8] and Se[9]) complexes, and the tellurium-containing 12-membered ring, [4-MeOC_6H_4Te{Ph_2(S)PNP(S)Ph_2}]$_2$.[7]

We decided to synthesize new 2,2-dihydrobenzotellurophene and 1,1-tetrahydrotellurophene derivatives employing the symmetrical imidodichalcogenidephosphinates **1a**−**c** in order to study the effect of the donor atom strength on the tellurium geometry and the comparison with analogous organotellurium(IV) derivatives containing oxygen- sulfur- and selenium-based ligands such as dithio-[10−12] and monothiocarbamates,[13] dithiophosphinates,[12] dithiophosphates,[14] carboxylates,[15] R_2(Q)PNP(Q′)R_2,[6,7,16,17] and R_2(S)P$(CH_2)_2$P(S)R_2,[17] etc.

Here we report five new organotellurium(IV) compounds, [C_4H_8TeI{Ph_2(Se)PNP(Se)Ph_2}] (**2**), [C_4H_8TeI{Ph_2(S)PNP(S)Ph_2}] (**3**), [C_8H_8TeI{Ph_2(S)PNP(S)Ph_2}] (**4**), [C_4H_8Te{Ph_2(S)PNP(S)Ph_2}$_2$] (**5**), and the ionic ring [O(TeC_4H_8)$_2${Ph_2(O)PNP(O)Ph_2}]$_2$[I, I_3] (**6**). They have been characterized by microanalysis, multielement NMR and IR spectroscopy, positive ion FAB mass spectrometry and single-crystal X-ray diffraction analysis.

Results and Discussion

The reported compounds were obtained by the reaction of $C_4H_8TeI_2$ or $C_8H_8TeI_2$ with the appropriate sodium or potassium salt of the ligands in either a twofold excess or in equimolecular amounts. The mono- or disubstituted derivatives were isolated from the selenium and sulfur ligands [RTeIL] [R = C_4H_8, C_8H_8 (**2**−**4**)] and [$C_4H_8TeL_2$] (**5**).

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As byproducts the known Te^{II} bis(chelates), $[Te\{Ph_2(Q)PNP(Q)Ph_2\}_2]$ (Q= S[6] and Se[7]), were also obtained. By using the oxygen ligand, only the unexpected 16-membered ionic ring $[O(TeC_4H_8)_2\{Ph_2(O)PNP(O)Ph_2\}]_2^{2+}$ (**6**) was isolated. This compound is probably formed from a 1,1-oxydiiodine ditellurium compound ($[C_4H_8TeI]_2O$) in the reaction mixture as the analogous 1,1-oxydibromide[18] was isolated previously from aqueous alkali solution. The formation of **6** may be explained by the fact that the $C_4H_8TeI_2$ was added to the non-anhydrous alkali solution in which the ligand salt was synthesized. Two of the oxygen ligands could then react with the $[C_4H_8TeI]_2O$ to form the ring system. All the compounds are soluble in common organic solvents (CH_2Cl_2, $CHCl_3$, C_6H_6). However, in solution they undergo rapid exchange and reductive elimination, such as has been observed previously in many chalcogen-bonded organotellurium(IV) derivatives.[12−14,16b,16c,17] Due to the difficulty of relying on the characterization in solution, every effort was made to obtain X-ray quality crystals of each compound.

The NMR spectroscopic data presented in the Exp. Sect. were assigned based on the spectra recorded immediately after dissolution in $CDCl_3$ solution. The ^1H and ^{13}C NMR spectra show the expected methylene (and also aromatic for **4**) protons and carbon atoms from the organoyltellurium moiety, as well as the phenyl resonance from the ligands. The signal of the CH_2 group attached to the tellurium center experiences a small upfield shift relative to that of the starting materials $C_4H_8TeI_2$ and $C_8H_8TeI_2$. The peaks of the 16-membered ring are the most upfield-shifted. The peaks in the phenyl region of the spectra are similar to those found for other derivatives containing imidophosphinates, but are poorly resolved so that the phosphorus-carbon coupling was ill-defined in some cases and the *ipso*-carbon resonances are not observed in others. In all cases the spectra recorded after one day, in the case of the selenium compound after a few hours, show more signals than those of the initially dissolved compound. According to the observed chemical shifts, some of these peaks may be attributable to the $[Te\{Ph_2(Q)PNP(Q)Ph_2\}_2]$ (Q= S[6] and Se[7]) species and the free acid ligands. The ^{31}P resonances are upfield-shifted by about 15 ppm relative to the corresponding free-acid ligand for all the compounds. The signals are closer to the chemical shift of the corresponding deprotonated ligands. The ^{125}Te resonance of C_4H_8TeIL and $C_4H_8TeL_2$ are shifted downfield compared to that of $C_4H_8TeI_2$ ($\delta = 782$ ppm). This is in contrast to the upfield shift observed for the related $C_4H_8TeI(S_2PR_2)$ (R = Me, Et)[12] and some R_2TeL_2 and R_2TeXL (L = $SOCNR_2$,[10b][10e] S_2CNR_2 [13]) species. Some other analogous derivatives also exhibit deshielded ^{125}Te resonances relative to R_2TeI_2, such as R_2TeIL (R = Me and L = S_2COR,[10c] S_2POGO[10a] with G = alkylene moieties) and R_2TeL_2 (R = *p*-$MeOC_6H_4$ and L = dimethyl- and diethyldithiocarbamates).[10d] The ^{125}Te resonance of the 16-membered ionic compound is shifted upfield compared to that of $C_4H_8TeI_2$.

The positive ion FAB mass spectra recorded immediately after dissolving the compounds in CH_2Cl_2 show low-intensity signals for the corresponding molecular ions, but rather intense peaks of fragments containing tellurium, i.e. m/z = 186 $[C_4H_8Te]^+$, 313 $[C_4H_8TeI]^+$, $[C_4H_8Te\ L]^+$ with L = **1a** (m/z = 416), **1b** (m/z = 448), and **1c** (m/z = 544). All of the observed signals exhibit the expected isotopic distribution patterns.

The infrared spectra of **2** to **6** exhibit strong absorption bands in the range of 1259 to 1219 cm^{-1} for the $\nu(P_2N)$ vibrations and two characteristic bands for phosphorus−donor atom stretching vibrations {1122 and 1095 cm^{-1} [ν(PO)] for **6**, two ν(PS) bands in the range 554−517 for **3**−**5**, and 437 [ν(PSe)] for **2**}.

Structural Description

Figure 1 shows the molecular structures and atomic labeling scheme for derivative **2**, while those of **3** and **4** are illustrated in Figure 2. The molecular structure of **5** is given in Figure 3, and that of $[O(TeC_4H_8)_2\{Ph_2(O)PNP(O)Ph_2\}]_2[I, I_3]$ (**6**) is shown in Figure 4. Selected bond lengths and angles are summarized in Table 1.

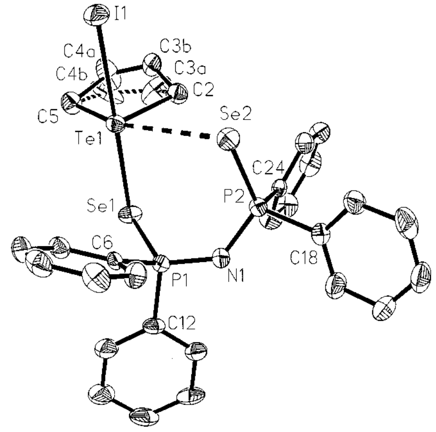
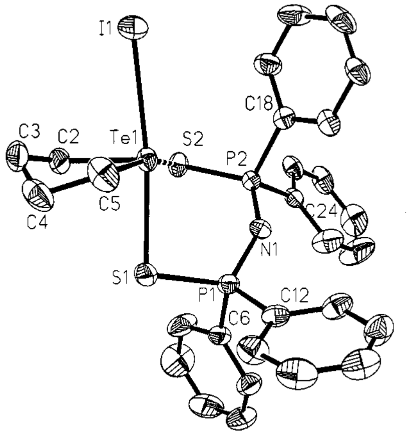


Figure 1. Molecular structure of $[C_4H_8TeI\{Ph_2(Se)PNP(Se)Ph_2\}]$ (**2**); the ellipsoids enclose a 30% probability

The coordination geometry at the tellurium center in every compound can be described as the sawhorse structure typical of tellurium(IV) compounds in which the lone-pair of electrons is supposed to occupy an equatorial position in a distorted trigonal bipyramid.[10−16c] The carbon atoms occupy the remaining equatorial positions with an average C−Te−C angle of 84.8°. The average Te−C bond length (2.135 Å) is within the range of the values observed in related organotellurium(IV) derivatives with chalcogen-containing ligands.[10−18]

In compounds containing sulfur and selenium donor atoms (**2**−**5**), the ligands display an asymmetrical chelating coordination mode on interaction with the tellurium center. This results in two sets of Te−donor atom bond lengths. The short Te−S bond lengths cover the range 2.61−2.67 Å, comparable with the values reported for related R_2TeXL structures containing analogous $R_2(Q)PNP(Q')R_2$,[6,7,16,17]



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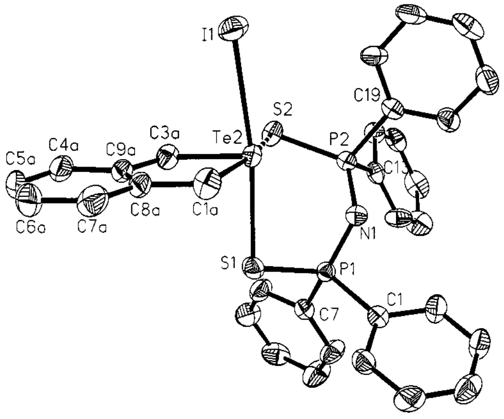

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Figure 2. Molecular structures of $[C_4H_8TeI\{Ph_2(S)PNP(S)Ph_2\}]$ (**3**) and $[C_8H_8TeI\{Ph_2(S)PNP(S)Ph_2\}]$ (**4**); the ellipsoids enclose a 30% probability

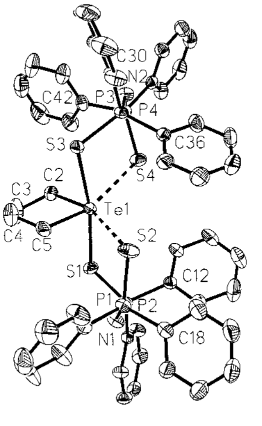

Figure 3. Molecular structures of the bis(chelate) compound $[C_4H_8Te\{Ph_2(S)PNP(S)Ph_2\}_2]$ (**5**); the ellipsoids enclose a 30% probability

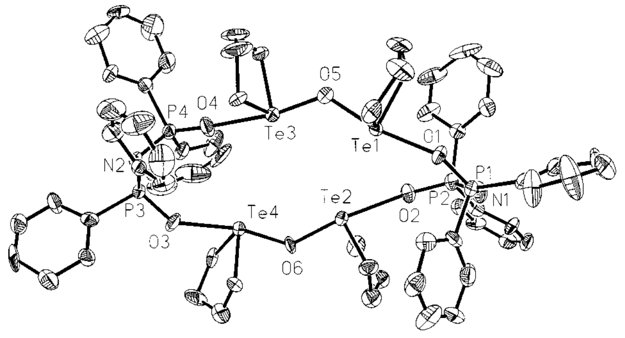

Figure 4. Molecular structure of the cation $[O(TeC_4H_8)_2\{Ph_2(O)PNP(O)Ph_2\}]_2^{2+}$; the ellipsoids enclose a 30% probability

and $R_2(S)P(CH_2)_2P(S)R_2$ [17] ligands. The short Te−Se bond length [2.721(1) Å] is slightly shorter than the values observed in $[Te\{R_2(Se)PNP(Se)R_2\}_2]$ [R = Ph (av. 2.797 Å)[6] and R = *i*Pr (av. 2.804 Å)[16d]]. The weakly bonded donor atoms are attached to the tellurium atom at larger Te···S distances ranging from 3.282(2) to 3.451(2) Å and at a Te···Se length of 3.4650(12) Å. The normalized Pauling partial bond orders[16c] of these longer Te···S/Se bonds are within the range of 0.16 to 0.27, that of Te···Se being 0.19. Thus, they are still compatible with their being part of the coordination sphere, and hence aniso-bonded. The S−Te−S bite angles in complexes **3**−**5** are similar to those found in the analogous $[Me_2Te\{Ph_2(S)PNP(S)Ph_2\}_2]$ and $[Me_2TeI\{Ph_2(S)PNP(S)Ph_2\}]$.[16c]

In the bis(chelate) derivative **5**, the two strongly bonded sulfur atoms occupy the axial positions, while in the mono-substituted compounds the axial sites are occupied by the iodine atom and the strongly bonded donor atom. The I−Te−Se axial angle [177.51(3)°] is considerably larger than the I−Te−S angle [171.8(1)°], while the S−Te−S axial angle is smaller [170.59(5)°]. When the aniso-bonded donor atoms are included in the coordination sphere, the environment about Te becomes distorted square-pyramidal in the mono derivatives **2**−**4** and distorted octahedral in the bis(chelate) compound **5**.

The Te−I bond lengths of RTeIL (**2** and **4**) are similar to those in $C_4H_8TeI_2$,[12] $C_8H_8TeI_2$ [19] and related R_2TeI_x species.[20] This and the generally longer Te−S bond in compounds containing imidodiphosphinates suggest a lower *trans* influence than in analogous halodithiocarbamates, -monothiocarbamates and dithiocarbonates.[10−13,15] However, the most remarkable difference with these 1,1-dithiolate compounds is that the imidophosphinate compounds do not exhibit any intermolecular interactions.

The TeS_2P_2N chelate rings of **3** and **4** are arranged in a distorted boat conformation with the tellurium and nitrogen atoms at the apices.[21] However, the $TeSe_2P_2N$ and TeS_2P_2N rings of the remaining chelate compounds **2** and **5** exhibit a folded geometry with one phosphorus atom lying essentially within the coordination plane and with the P−N−P−Se/S plane folded by 120.2° out of the coordination plane Te1−Se1−Se2−P2 for **2**, and by 40.7° and 129.9° out of the planes Te1−S1−S2−P1 and Te1−S3−S4−P4 for **5**. The ring bond lengths are consistent with some localization of the bonding, i.e. the short

Table 1. Selected bond lengths [Å] and angles [°] for compounds **2**−**6**

	2 (Q = Se)	**3** (Q = S)	**4** (Q = S)	**5** (Q = S)		**6**
Te−Q1	2.721(1)	2.616(3)	2.622(2)	2.670(2)	Te1−O1	2.27(2)
Te···Q2	3.465(2)	3.435(3)	3.282(2)	3.300(2)	Te2−O2	2.42(2)
Te−Q3				2.643(2)	Te4−O3	2.33(2)
Te···Q4				3.451(2)	Te3−O4	2.45(2)
Te−I1	2.967(1)	2.946(1)	2.922(1)		Te1−O5	1.99(2)
Te−C2	2.149(9)	2.144(9)	2.165(8)[a]	2.152(7)	Te3−O5	1.96(2)
Te−C5	2.162(9)	2.141(1)	2.136(8)[a]	2.153(6)	Te2−O6	1.97(2)
P1−Q1	2.226(2)	2.058(3)	2.058(3)	2.060(2)	Te4−O6	2.01(2)
P2−Q2	2.121(2)	1.973(3)	1.986(3)	1.966(2)	P1−O1	1.55(2)
P3−Q3				2.056(2)	P2−O2	1.52(2)
P4−Q4				1.970(2)	P3−O3	1.51(2)
P1−N1	1.572(7)	1.571(8)	1.570(6)	1.581(5)	P4−O4	1.479(2)
P2−N1	1.614(7)	1.604(8)	1.607(6)	1.614(5)	P1−N1	1.56(2)
P3−N2				1.574(5)	P2−N1	1.61(2)
P4−N2				1.611(5)	P3−N2	1.57(2)
C2−Te−C5	84.3(4)	83.5(5)	85.9(3)[a]	84.8(3)	P4−N2	1.61(2)
C2−Te−Q1	89.9(3)	86.8(3)	84.5(2)[a]	83.7(2)	av. Te−C	2.121
C5−Te−Q1	87.4(3)	87.2(4)	86.1(2)[a]	89.3(2)	av. Te···I	3.682
C2−Te−Q3				89.7(2)	Te1−O5−Te3	127.9(9)
C5−Te−Q3				83.4(2)	Te2−O6−Te4	124.9(9)
Q1−Te···Q2	93.6(3)	81.9(3)	88.7	91.2(5)	O1−Te1−O5	166.5(7)
Q1−Te−Q3				170.59(5)	O2−Te2−O6	170.1(8)
Q3−Te···Q4				87.6(5)	O4−Te3−O5	170.7(8)
Q1−Te−I1	177.51(3)	172.73(7)	171.8(1)		O3−Te4−O6	168.3(7)
Q2···Te−I1	88.7(3)	97.3(7)	95.9		Te1−P1−O1	139.1(10)
P1−Q1−Te	99.55(7)	99.3(2)	101.6(1)	106.52(9)	Te2−P2−O2	169.8(14)
P2−Q2···Te	97.7(7)		86.30	110.40(9)	Te4−P3−O3	140.7(13)
P3−Q3−Te				108.64(7)	Te3−P4−O4	176.9(13)
P4−Q4···Te				103.80(7)	N1−P1−O1	120.5(13)
N1−P1−Q1	118.7(3)	117.4(3)	117.3(3)	117.2(2)	N1−P2−O2	120.4(12)
N1−P2−Q2	119.3(3)	119.3(3)	118.4(2)	118.3(2)	N2−P3−O3	120.5(12)
N2−P3−Q3				119.2(2)	N2−P4−O4	117.2(11)
N2−P4−Q4				119.4(2)	P1−N1−P2	131.4(17)
P1−N1−P2	132.1(5)	138.9(5)	140.1(4)	129.9(3)	P3−N1−P4	129.2(13)
P3−N1−P4				132.5(3)	I2−I3−I4	177.5(16)

[a] In molecule **4**, the C2 and C5 labels correspond to the C1a and C3a atoms, respectively.

and long bonds alternate through the six-membered ring (see Table 1).

The molecular structure of $[O(TeC_4H_8)_2\{Ph_2(O)PNP(O)Ph_2\}]_2[I, I_3]$ (**6**) is shown in Figure 4. In the 16-membered cationic ring two oxygen ligands behave as bridges between two $C_4H_8Te-O-TeC_4H_8$ units. The Te−O(ligand) bond lengths cover the range 2.273(17) to 2.453(17) Å. These bonds are slightly longer than the sum of the covalent radii,[22] and are also longer than the corresponding distances found in chelates like $[Me_2TeCl\{Ph_2(O)PNP(S)Ph_2\}]$,[16c] $[Ph_2Te(O_2CR)_2]$ (R = CH_3, CCl_3),[15b,15c] and $[C_4H_8Te(O_2CPh)_2]$.[15a] The average Te−O bond length in the $C_4H_8Te-O-TeC_4H_8$ moiety is 1.988 Å. The Te−O−P angles (av. 154.5°) are notably larger than the observed Te−S−P angles (av. 104.84°) in the complexes containing the sulfur-bridge ligand, i.e. $[4\text{-}MeOC_6H_4Te\{Ph_2(S)PNP(S)Ph_2\}]_2$ [7] and $[(4\text{-}MeOC_6H_4TeCl_3)_2\{\mu\text{-}Ph_2(S)PCH_2CH_2P(S)Ph_2\}]$.[17] The average of the axial O−Te−O angles is 168.9°, comparable with the values observed in related tellurium(IV) sawhorse structures.[10−18] The 16-membered ring adopts a twisted conformation. The two anions I^- and I_3^- are located above and below the 16-membered ring $[O(TeC_4H_8)_2\{Ph_2(O)PNP(O)Ph_2\}]_2^{2+}$ with Te···I1 and Te···I2 distances ranging from 3.532(2) to 3.902(3) Å, within the sum of the van der Waals radii (4.35 Å).[23]

Conclusion

The isolation and spectroscopic characterization of mono- and disubstituted tetrahydro- and benzodihydrotelluropheno-containing symmetric $[Ph_2(Q)PNP(Q)Ph_2]^-$ ligands was achieved despite the propensity for such species to undergo disproportionation and reductive elimination in solution. The selenium and sulfur ligands act as anisobidentate chelate ligands such as was observed previously in related organotellurium derivatives containing 1,1-dithio- or monothio ligands, carboxylates, and asymmetric $R_2(Q)PNP(Q')R_2$.[10−16] The bite angles and Te−Q bond lengths are larger than those in compounds with 1,1-ligands, so that the angles about Te are less distorted. No intermolecular interactions involving iodine or donor atoms were observed. The employment of the oxygen ligand leads to the formation of a novel 16-membered cationic ring $[O(TeC_4H_8)_2\{Ph_2(O)PNP(O)Ph_2\}]_2^{2+}$ (**6**) in which the ligand acts as a bridge. This compound may be formed from the two ligands and the $[C_4H_8TeI]_2O$ formed in the reaction mixture.

Experimental Section

General Remarks: Chemicals of commercial grade were purchased from Aldrich and were used as supplied. The compounds $C_4H_8TeI_2$ and $C_8H_8TeI_2$ were prepared according to the methods described by Al-Rubaie et al.[24] and by Ziolo et al.[19b] The ligand salts were prepared by treatment of the free ligands with potassium ethoxide or sodium hydroxide. The FAB mass spectra were measured using a 3-nitrobenzyl alcohol support in the positive ion mode with a Jeol JMS-SX102A instrument. The ^1H (300 MHz), ^{13}C (75 MHz), ^{31}P (121 MHz), ^{77}Se (57 MHz) and ^{125}Te (94 MHz) NMR spectra were recorded in $CDCl_3$ with a Jeol Eclipse+ 300 spectrometer at room temperature using as external references TMS, 85% H_3PO_4, $TeCl_4$, and Ph_2Se_2. The IR spectra (KBr discs) were recorded with a Nicolet FT-IR Magna 750 spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

$[C_4H_8TeI\{Ph_2(Se)PNP(Se)Ph_2\}]$ (2): A solution of $C_4H_8TeI_2$ (0.25 g, 0.57 mmol) in dichloromethane was added to freshly prepared $K[Ph_2(Se)PNP(Se)Ph_2]$ (0.33 g, 0.57 mmol). The mixture was stirred and elemental Te precipitated almost immediately from the solution. The mixture was filtered after 10 min of stirring and the filtrate was concentrated by pumping off the solvent. A layer of *n*-hexane was allowed to diffuse slowly into the concentrated solution leading to yellow crystals of $[C_4H_8TeI\{Ph_2(Se)PNP(Se)Ph_2\}]$ (**2**) and orange-yellow crystals of $[Te\{Ph_2(Se)PNP(Se)Ph_2\}_2]$[7] [m.p. 266 °C, ref.[7] 275 °C; ^{31}P NMR ($CDCl_3$): $\delta = 23.6$ (s) (ref.[7] $\delta = 24.4$)]. − **2**: Yield: 0.31 g (64.6%); m.p. (dec.) 153−154 °C. −IR (KBr): $\tilde{\nu} = 1220\ cm^{-1}$ s [ν(PN)], 437 m [ν(PSe)]. − MS (FAB^+, $CHCl_3$): *m*/*z* = 186 $[C_4H_8{}^{130}Te^+]$, 313 $[C_4H_8{}^{130}TeI^+]$, 544 $[(^{80}SePPh_2)_2N^+]$, 672 $[^{130}Te(^{80}SePPh_2)_2N^+]$, 728 $[C_4H_8{}^{130}Te(^{80}SePPh_2)_2N^+]$, 854 $[C_4H_8{}^{130}TeI(^{80}SePPh_2)_2N^+]$. − ^1H NMR ($CDCl_3$): $\delta = 2.16-3.0$ (m, 4 H, $TeCH_2CH_2$), 3.3−3.8 (m, 4 H, $TeCH_2$) 7.37 (m, 12 H, Ph-H_{m+p}), 7.9 (m, 8 H, Ph-H_o). − ^{13}C NMR ($CDCl_3$): $\delta = 33.9$ ($TeCH_2CH_2$), 45.34 ($TeCH_2$), 128.3 (Ph-C_m), 130.68 (Ph-C_p), 131.4−131.1 (Ph-C_o). − ^{31}P NMR ($CDCl_3$): $\delta = 35.5$ (br. s). − ^{77}Se NMR ($CDCl_3$): $\delta = -146.64$ (d). − ^{125}Te NMR ($CDCl_3$): $\delta = 797$ (t). − $C_{28}H_{28}INP_2Se_2Te$ (852.9): calcd. C 39.43, H 3.31; found C39.17, H 3.19. − A similar procedure was attempted starting from $C_8H_8TeI_2$ and the ligand, however only the tellurium(II) derivative $[Te\{Ph_2(Se)PNP(Se)Ph_2\}_2]$,[7] was isolated.

$[C_4H_8TeI\{Ph_2(S)PNP(S)Ph_2\}]$ (3): This compound was synthesized by placing $C_4H_8TeI_2$ (0.5 g, 1.14 mmol), $K[Ph_2(S)PNP(S)Ph_2]$ (0.55 g, 1.14 mmol), and approximately 25 mL of dichloromethane in a flask, and stirring this mixture was stirred at room temperature for 30 min. It was then filtered and the filtrate was concentrated by pumping off all the solvent. The compounds were crystallized by allowing a layer of *n*-hexane to diffuse slowly into a concentrated solution of the remaining solid in CH_2Cl_2. Yield: 0.72 g (82.9%); m.p. (dec.) 146−147 °C. − IR (KBr): $\tilde{\nu} = 1216\ cm^{-1}$ vs [ν(PN)], 544 s, 517 m [ν(PS)]. − MS (FAB^+, $CHCl_3$): *m*/*z* = 186 $[C_4H_8{}^{130}Te^+]$, 448 $[(SPPh_2)_2N^+]$, 578 $[^{130}Te(SPPh_2)_2N^+]$, 634 $[C_4H_8{}^{130}Te(SPPh_2)_2N^+]$. −$^1H$ NMR ($CDCl_3$): $\delta = 2.56-2.78$ (m, 4 H, $TeCH_2CH_2$), 3.3−3.6 (m, 4 H, $TeCH_2$) 7.36 (m, 12 H, Ph-$CH_{m,p}$), 7.88 (m, 8 H, Ph-CH_o). − ^{13}C NMR ($CDCl_3$): $\delta = 33.6$ ($TeCH_2CH_2$), 46.06 ($TeCH_2$), 128.08 (Ph-C_m), 130.4 (Ph-C_p), 131.0 (Ph-C_o). − ^{31}P NMR ($CDCl_3$): $\delta = 45$ (br. s). −^{125}Te NMR ($CDCl_3$): $\delta = 834.2$ (t). − $C_{28}H_{28}INP_2S_2Te$ (759.11): calcd. C 44.30, H 3.72; found C43.99, H 3.60.

$[C_8H_8TeI\{Ph_2(S)PNP(S)Ph_2\}]$ (4): This compound was obtained according to the procedure described for **3** from $C_8H_8TeI_2$ (0.5 g, 1.03 mmol) and $K[Ph_2(S)PNP(S)Ph_2]$ (0.49 g, 1.03 mmol). Yield: 0.51 g (61.3%); m.p. (dec.) 127−129 °C. − IR (KBr): $\tilde{\nu} = 1226\ cm^{-1}$ s [ν(PN)], 546 m, 525 s [ν(PS)]. − MS (FAB^+, $CHCl_3$): *m*/*z* = 234 $[C_8H_8{}^{130}Te^+]$, 361$[C_8H_8{}^{130}TeI^+]$, 448 $[(SPPh_2)_2N^+]$, 682 $[C_8H_8{}^{130}Te(SPPh_2)_2N^+]$. − ^1H NMR ($CDCl_3$): $\delta = 4.99$ (m, 4 H, $TeCH_2$), 7.14 (m, 4 H, C_6H_4), 7.35 (m, 12 H, Ph-$CH_{m,p}$), 7.9 (m, 8 H, Ph-CH_o). −^{13}C NMR ($CDCl_3$): $\delta = 49.92$ ($TeCH_2$), 127.7 ($C_{4,7}$) 128.27 (Ph-C_m), 129.8 ($C_{5,6}$), 130.9 (Ph-C_p), 131.2 (Ph-C_o), 139.2 ($C_{3a,7a}$). −^{31}P NMR ($CDCl_3$): $\delta = 42.3$ (br. s). − ^{125}Te NMR ($CDCl_3$): $\delta = 760$ (m). − $C_{38}H_{28}INP_2S_2Te$ (807.16): calcd. C 47.62, H 3.50; found C47.36, H 3.37

$[C_4H_8Te\{Ph_2(S)PNP(S)Ph_2\}_2]$ (5): This compound was prepared as described for **3** from $C_4H_8TeI_2$ (0.5 g, 1.14 mmol) and $K[Ph_2(S)PNP(S)Ph_2]$ (1.10 g, 2.28 mmol). Yield: 0.86 g (69.6%); m.p. (dec.) 135−137 °C. − IR (KBr): $\tilde{\nu} = 1219\ cm^{-1}$ s [ν(PN)], 554 s, 508 m [ν(PS)]. −MS (FAB^+, $CHCl_3$): *m*/*z* = 186 $[C_4H_8Te^+]$, 448 $[(SPPh_2)_2N^+]$, 578 $[^{130}Te(SPPh_2)_2N^+]$, 634 $[C_4H_8{}^{130}Te(SPPh_2)_2N^+]$. − ^1H NMR ($CDCl_3$): $\delta = 2.30$ (br. s, 4 H, $TeCH_2CH_2$), 3.18 (br. s, 4 H, $TeCH_2$), 7.27 (m, 12 H, P-$CH_{m,p}$), 7.88 (m, 8 H, P-CH_o). −^{13}C NMR ($CDCl_3$): $\delta = 33.21$ ($TeCH_2CH_2$), 47.46 ($TeCH_2$), 128.2 (Ph-C_m), 130.12 (Ph-C_p), 131.3 (Ph-C_o). − ^{31}P NMR ($CDCl_3$): $\delta = 44.2$ (br. s). − ^{125}Te NMR ($CDCl_3$): $\delta = 856$ (m). − $C_{52}H_{48}N_2P_4S_4Te$ (1080.71): calcd. C 57.79, H 4.8; found C57.51, H 4.71

$[O(TeC_4H_8)_2\{Ph_2(O)PNP(O)Ph_2\}]_2[I, I_3]$ (6): This compound was prepared as described for **3** from $C_4H_8TeI_2$ (0.8 g, 1.83 mmol), freshly prepared $Na[Ph_2(O)PNP(O)Ph_2]$ (0.8 g, 1.83 mmol), and approximately 25 mL of ethanol. $[O(TeC_4H_8)_2\{Ph_2(O)PNP(SO)Ph_2\}]_2$ (**6**) was isolated as dark brown crystals from the bottom of the crystallization flask. Yield 0.79 g (20.5%); m.p. (dec.) 137 °C. − IR (KBr): $\tilde{\nu} = 1259\ cm^{-1}$s [ν(PN)], 1122 vs, 1095 s [ν(PO)]. − MS (FAB^+, $CHCl_3$): *m*/*z* = 416 $[(OPPh_2)_2N^+]$, 602 $[C_4H_8{}^{130}Te(OPPh_2)_2N^+]$, 760 $[^{130}Te_4O_6P_4N_2{}^+]$. − ^1H NMR ($CDCl_3$): $\delta = 2.21$ (m, 4 H, $TeCH_2CH_2$), 2.97 (m, 4 H,$TeCH_2$), 7.26 (m, 12 H, P-$CH_{m,p}$), 7.73 (m, 8 H, P-CH_o). − ^{13}C NMR ($CDCl_3$): $\delta = 29.8$ ($TeCH_2CH_2$), 31.27 ($TeCH_2$), 127.96 (Ph-C_m), 130.33 (Ph-C_p), 131.39 (Ph-C_o). − ^{31}P NMR ($CDCl_3$): $\delta = 14.3$ (s). − ^{125}Te NMR ($CDCl_3$): $\delta = 777.2$ (br. s). − $C_{64}H_{72}I_4N_2O_6P_4Te_4$ (2107.18): calcd. C 36.48, H 3.44; found C36.11, H 3.25.

X-ray Crystallographic Study: Suitable crystals were mounted on glass fibers and sealed with epoxy glue. Data were collected at room temperature on a Siemens P4/PC diffractometer with graphite-monochromated Mo-K_α radiation ($\lambda = 0.71073$). Details of the data collections and refinements are summarized in Table 2. Data were collected using the ω-scan mode ($3° \leq 2\theta \leq 50°$). The intensity data (except those for **5**) were corrected for absorption (Ψ-scan). The structures were solved by direct methods using SHELXS-97[25] (for **2**, **5** and **6**) and SIR-97[26] (for **3** and **4**). They were all refined by full-matrix least-squares calculations using the program system SHELXL-97.[27] Non-hydrogen atoms were refined anisotropically. In the case of **2**, there was disorder involving atoms

Table 2. Crystallographic data for compounds **2**−**6**

	2	**3**	**4**	**5**	**6**
Empirical formula	$C_{28}H_{28}INP_2Se_2Te$	$C_{28}H_{28}INP_2S_2Te$	$C_{32}H_{28}INP_2S_2Te$	$C_{52}H_{48}N_2P_4S_4Te$	$C_{64}H_{72}I_4N_2O_6P_4Te_4$
Color; habit	yellow; prism	yellow; prism	yellow; prism	yellow; prism	purple; prism
Molecular mass	852.87	759.07	807.1	1080.64	2107.12
Crystal size [mm]	0.64 × 0.40 × 0.24	0.30 × 0.16 × 0.16	0.38 × 0.10 × 0.06	0.28 × 0.22 × 0.08	0.40 × 0.24 × 0.24
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$ (no. 14)	Cc (no. 9)	$P2_1/c$ (no.14)	$P2_1/c$ (no.14)	$P2_12_12_1$ (no.19)
a [Å]	14.450(3)	10.738(5)	16.331(2)	14.890(3)	14.026(2)
b [Å]	10.126(1)	14.479(5)	8.493(2)	10.748(3)	20.924(4)
c [Å]	20.615(3)	19.604(5)	23.312(4)	32.311(7)	25.114(2)
α [°]	90	90	90	90	90
β [°]	94.74(1)	90.860(5)	91.45(2)	91.08(1)	90
γ [°]	90	90	90	90	90
Z	4	4	4	4	4
V [Å^3]	3006.1(8)	3047.6(2)	3232.4(2)	5170(2)	7376.8(2)
μ [mm^{-1}]	4.563	2.249	2.126	0.897	3.74
Transmission, max/min	0.140/0.079	0.7149/0.5579	0.8830/0.4988		0.372/0.225
Reflections collected	5499	2841	5874	9487	7117
Independent reflections	5275 (R_{int} = 0.0411)	2841 (R_{int} = 0.0)	5661 (R_{int} = 0.088)	9110 (R_{int} = 0.1084)	7117 (R_{int} = 0.0)
Number of parameters	336	317	353	568	756
$R(F_o)$[a]	0.0479	0.0328	0.0397	0.0483	0.0651
$Rw(F_o)$[b]	0.0967	0.0703	0.0736	0.0984	0.1464
Goodness-of-fit	1.026	0.930	0.831	0.847	1.062

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. − [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

C3 and C4 from the C_4H_8Te moiety. The best solution was obtained with occupancies of 0.53 for C4A and C3B and 0.47 for C3A and C4B. The hydrogen atoms were calculated as a riding model with fixed isotropic U. The calculated absolute structure parameter for **3** was η = 0.0033 (0.0311).[28]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-153533 (**2**), -153534 (**3**), -153535 (**4**), -153536 (**5**), -153537 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] I. Rodríguez, C. Alvarez, J. Gómez-Lara, R. Cea-Olivares, *Lanthanide Actinide Res.* **1985− 1986**, *1*, 253−256.

[2] See, for example: C. Silvestru, I. Haiduc, R. Cea-Olivares, A. Zimbron, *Polyhedron* **1994**, *13*, 3159−3165.

[3] [3a] R. Cea-Olivares, V. García-Montalvo, J. Novosad, J. D. Woollins, A. M. Z. Slawin, G. Espinosa-Pérez, P. García y García, *Chem. Commun.* **1996**, 519−520. − [3b] V. García-Montalvo, R. Cea-Olivares, J. Novosad, J. D. Woollins, A. M. Z. Slawin, G. Espinosa-Pérez, P. García y García, *J. Chem. Soc., Dalton Trans.* **1997**, 1025−1029.

[4] V. García-Montalvo, R. Cea-Olivares, D. J. Williams, G. Espinosa-Pérez, *Inorg. Chem.* **1996**, 3948−3953.

[5] V. García-Montalvo, R. Cea-Olivares, J. Novosad, J. D. Woollins, R. A. Toscano, G. Espinosa-Pérez, *Chem. Ber.* **1996**, *129*, 919−923.

[6] S. Bjørnevåg, S. Husebye, K. Maartmann-Moe, *Acta Chem. Scand., Ser. A* **1982**, *36*, 195−202.

[7] J. Novosad, S. V. Lindeman, J. Marek, J. D. Woollins. S. Husebye, *Heteroatom Chem.* **1998**, *9*, 615−621.

[8] S. Husebye, K. Maartmann-Moe, *Acta Chem. Scand., Ser. A* **1983**, *37*, 219−225.

[9] R. Cea-Olivares, G. Canseco-Melchor, V. García-Montalvo, S. Hernández-Ortega, J. Novosad, *Eur. J. Inorg. Chem.* **1998**, 1573−1576.

[10] See, for example: [10a] J. E. Drake, L. N. Khasrou, A. G. Mislankar, R. Ratnani, *Inorg. Chem.* **1999**, *38*, 3994−4004. − [10b] J. E. Drake, J. Yang, *Inorg. Chem.* **1997**, *36*, 1890−1903. − [10c] J. E. Drake, R. J. Drake, L. N. Khasrou, R. Ratnani, *Inorg. Chem.* **1996**, *35*, 2831−2840. − [10d] J. H. E. Bailey, J. E. Drake, *Can. J. Chem.* **1993**, *71*, 42−50. − [10e] J. H. E. Bailey, J. E. Drake, *Can. J. Chem.* **1991**, *69*, 1948−1956. − [10f] S. Husebye, K. Maartmann-Moe, W. Steffenson, *Acta Chem. Scand.* **1990**, *44*, 139.

[11] [11a] D. Dakternieks, R. Di Giacomo, R. W. Gable, B. Padmanabhan, *J. Am. Soc. Chem.* **1988**, *110*, 6753−6761. − [11b] D. Dakternieks, R. Di Giacomo, R. W. Gable, B. F. Hoskins, *J. Organomet. Chem.* **1988**, *349*, 305−315. − [11c] J. O. Bogason, D. Dakternieks, S. Husebye, K. Maartmann-Moe, H. Zhu, *Phosphorus Sulfur Silicon Relat. Elem.* **1992**, *71*, 13−24. − [11d] V. García-Montalvo, R. A. Toscano, A. Badillo-Delgado, R. Cea-Olivares, *Polyhedron* **2001**, *20*, 203−208.

[12] V. García-Montalvo, A. Marcelo-Polo, R. Montoya, S. Hernández-Ortega, R. A. Toscano, R. Cea-Olivares, *J. Organomet. Chem.* **2001**, *623*, 74−80.

[13] J. E. Drake, L. N. Khasrou, A. G. Mislankar, R. Ratnani, *Inorg. Chem.* **1994**, *33*, 6154−6162.

[14] J. E. Drake, L. N. Khasrou, A. G. Mislankar, R. Ratnani, *Can. J. Chem.* **1994**, *72*, 1328−1337.

[15] [15a] P. C. Srivastava, S. Bajpai, R. J. Butcher, *J. Organomet. Chem.* **1999**, *586*, 119−124. − [15b] N. W. Alcock, W. D. Harrison, C Howes, *J. Chem. Soc., Dalton Trans.* **1984**, 1709−1716. − [15c] N. W. Alcock, J. Culver, S. M. Ross, *J. Chem. Soc., Dalton Trans.* **1992**, 1477−1484.

[16] [16a] A. Silvestru, I. Haiduc, R. A. Toscano, H. J. Breunig, *Polyhedron* **1995**, *14*, 2047−2053. − [16b] J. E. Drake, A. Silvestru, J. Yang, I. Haiduc, *Inorg. Chim. Acta* **1998**, *271*, 75−82. − [16c] J. E. Drake, R. J. Drake, A. Silvestru, J. Yang, *Can. J. Chem.* **1999**, *77*, 356−366. − [16d] D. J. Birdsall, J. Novosad, A. M. Z. Slawin, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **2000**, 435−439.

[17] J. Novosad, K. W. Törnroos, M. Necas, A. M. Z. Slawin, J. D. Woollins, S. Husebye, *Polyhedron* **1999**, *18*, 2861−2867.

[18] I. G. Morgan, F. H. Burstall, *J. Chem. Soc.* **1931**, 180−184.

[19] [19b] J. D. McCullough, C. Knobler, R. F. Ziolo, *Inorg. Chem.* **1985**, 1814−1818. − [19a]. R. F. Ziolo, W. H. H. Günther, *J. Organomet. Chem.* **1979**, *178*, 423−431.

[20] J. D. McCullough, C. Knobler, *Inorg. Chem.* **1976**, *15*, 2728−2731.

[21] [21a] N. L. Allinger, *J. Am. Chem. Soc.* **1959**, *81*, 5727−5732. − [21b] J. B. Hendrickson, *J. Am. Chem. Soc.* **1964**, *86*, 4854−4860.

[22] N. W. Alcock, *Bonding and structure principles in inorganic and organic chemistry*, Ellis Horwood, NY, **1993**, p. 195.

[23] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441−451.

[24] A. Z. Al-Rubaie, H. A. Y. Alshirayda, P. Granger, S. Chapelle, *J. Organomet. Chem.* **1985**, *287*, 321−327.

[25] G. M. Sheldrick, *SHELXS-97, Crystal Structure Solution*, version 97-1, Institut für Anorganische Chemie, Universität, Göttingen, Germany, **1997**.

[26] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **1999**, *32*, 115−119.

[27] G. M. Sheldrick, *SHELXL-97, Crystal Structure Refinement*, version 97.1, Institut für Anorganische Chemie, Universität Göttingen, Germany, **1997**.

[28] H. D. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876−881.

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