Structural Characteristics of Three-Coordinate Arylhalide Tellurium(II) Complexes with Chalcogen Ligands. Synthesis, Spectroscopic Characterization and X-Ray Structural Studies of Bromo[N-methylbenzothiazole-2(3H)-selone]phenyltellurium(II), Bromophenyl[tris(dimethylamino)phosphaneselenide]-tellurium(II) and Tris(dimethylamino)phosphanesulfide

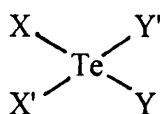Martin D. Rudd, Sergey V. Lindeman and Steinar Husebye*

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Rudd, M. D., Lindeman, S. V. and Husebye, S., 1996. Structural Characteristics of Three-Coordinate Arylhalide Tellurium(II) Complexes with Chalcogen Ligands. Synthesis, Spectroscopic and X-Ray Structural Studies of Bromo-[N-methylbenzothiazole-2(3H)-selone]phenyltellurium(II), Bromophenyl[tris-(dimethylamino)phosphaneselenide]tellurium(II) and Tris(dimethylamino)-phosphanesulfide. – Acta Chem. Scand. 50: 759–774 © Acta Chemica Scandinavica 1996.

The three title compounds have been synthesized and their structures solved by means of conventional X-ray crystallographic methods. The crystals of bromo[N-methylbenzothiazole-2(3H)-selone]phenyltellurium(II) (I) are monoclinic; at 143 K $a=9.728(1)$, $b=19.192(4)$, $c=17.099(3)$ Å, $\beta=105.12(1)°$, $Z=8$, space group $P2_1/c$. The crystals of bromophenyl[tris(dimethylamino)-phosphaneselenide]tellurium(II) (II) are monoclinic; at 293 K $a=9.718(2)$, $b=17.043(3)$, $c=11.983(2)$ Å, $\beta=105.83(3)°$, $Z=4$, space group $P2_1/c$. The crystals of tris(dimethylamino)phosphanesulfide (III) are monoclinic; at 143 K $a=8.347(2)$, $b=11.369(2)$, $c=11.260(2)$ Å, $\beta=92.94(3)°$, $Z=4$, space group $P2_1/n$. Final R values are 0.035, 0.036 and 0.034, respectively. Compounds I and II represent T-shaped complexes of Te^{II} containing an almost linear Br–Te–Se group with Te–Br and Te–Se bond lengths of 2.744–2.836(1) and 2.694–2.744(1) Å, respectively. The Te–C bond lengths lie in the range 2.110–2.123(5) Å. The *trans*-influence of the chalcogen ligands above and related ligands are discussed and suggested to be a function of the ability of the ligands to accept positive charge from the central tellurium(II) atom. Ligands of the type tris(dialkylamino)phosphanechalcogenide possess a unique nitrogen atom whose hybridization changes from sp^3 towards sp^2 upon complexation. This unique N atom is always found to form a M–chalcogen–P–N torsion angle near 0 (or 180°) upon complexation. This is related to the delocalization of positive charge discussed above. A preliminary deformation electron density study of III supports this, and also indicates that the hybridization of phosphorus in these ligands differs from sp^3. NMR and IR spectra of the compounds are discussed.

Dedicated to Professor Eberhard Hoyer on the occasion of his 65th birthday

Divalent tellurium is well known for its ability to take part in 3-centre, 4-electron or secondary bonding. In many cases, it forms square-planar neutral or ionic complexes of common formula:

where two p-orbitals of tellurium become involved in two three-centre, four-electron molecular orbital systems with two mutually orthogonal, linear groups X–Te–Y and X'–Te–Y'.[1,2] It is also possible to present this as a usual σ-bonded covalent compound, X–Te–X', containing two additional, 'secondary' ligands Y and Y' donating their lone electron pairs onto the Te–X and Te–X' σ-antibonding orbitals and inducing the weakening of the corresponding Te–X and Te–X' bonds (or *vice versa*).[3] Thus, the weaker the Te–X (Te–X')

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bond, the stronger is the *trans* situated Y–Te (Y′–Te) bond. The ability of ligands to form strong 'primary' bonds and, therefore, to weaken 'secondary' bonds *trans* to themselves, is known from the literature as the *trans*-influence.[4] The most useful real physical characteristic to estimate the *trans*-influence of ligands is their polarisability (based on the concept of 'soft' and 'hard' ions) in combination with (but of secondary importance to) the electronegativity.

The variety of four-coordinated complexes of bivalent tellurium comprises compounds containing ligands of weak to medium *trans*-influence such as halides, organic and phosphorus chalcogenides *etc.* These ligands sometimes act in a bridging mode and give polymeric structures.[1] On the other hand, pure organotellurium compounds have a negligible ability to form secondary bonds, as the *trans*-influence of alkyl and aryl groups is very large. These Te^{II} compounds appear as classical covalent bicoordinated compounds and represent isolated molecules.

From the point of view of chemical theory and molecular modelling, a particularly interesting intermediate group comprises three-coordinated complexes of Te^{II}, especially asymmetric electroneutral compounds of type X–Te(–R)–Y=L, where R is aryl, X is halogen and Y is a double-bonded chalcogen atom from a large neutral organic or phosphorus ligand (the remainder of the ligand is marked as L). At present all possible combinations of X (Cl, Br, I) and Y (O, S, Se) are known and structurally characterized.

The most widely investigated combination is Br/S, where S belongs to different thiourea-derived ligands: thiourea itself (**tu**),[5] tetramethylthiourea (**tmtu**),[6] ethylene-thiourea (**etu**; two crystalline forms are known)[7] and trimethylenethiourea (**trtu**).[8] The analogous set of complexes is known for the Cl/S combination (with the exception of the **trtu** derivative).[5,6,9] The I/S combination is only known by a single **etu** example.[10]

Examples of compounds with Se-containing ligands are not so numerous: there are only two derivatives of *N,N′*-ethyleneselenourea (**esu**) with Br^9 and I^{10} and one complex of trimethyleneselenourea (**trsu**) with Cl as the halide.[8] However, two complexes with the trimorpholinophosphaneselenide (**trmse**) ligand and X=Cl or Br are known.[6]

Structural characteristics of all these complexes (R is Ph in all) are summarized in a paper by Hauge and Vikane,[8] who investigated the majority of these structures. They suggested that the relative *trans*-influence of the ligands in this group was: **tu ~ trsu ~ etu > trtu > I > tmtu > trmse ~ Br ~ Cl** (the **esu** ligand was not included), by looking at the ratio of Te–X and Te–Y bond lengths. The authors did not give any explanation to account for the nature of the differences in the *trans*-influences for these ligands. We will discuss these differences below.

Another group of compounds, very similar to those mentioned previously, comprises chelate complexes containing a Te-coordinated carbonyl group in an *o*-position on the phenyl ligand: chlorotelluro-2-*N*-methylbenzamide (**ClTemfaPh**),[11] bromo(*o*-formylphenyl)tellurium (**BrTefPh**),[12] bromotelluro-2-benzamide (**BrTefaPh**; dimethyl sulfoxide solvate 1:1)[11] and *o*-(3-iodopropionyl)-phenyliodotellurium (**ITeiprPh**).[13] The *trans*-influence of the carbonyl group should be significantly weaker than that of its S- and Se-analogues, and oxygen-coordinated complexes of this type are isolated only as chelate compounds.

In this paper we have tried to give a more detailed analysis of the nature of the chemical bonding in this group of compounds, supplemented by two of our own examples: bromo[*N*-methylbenzothiazole-2(3*H*)-selone]phenyltellurium(II) (**I**) and bromophenyl[tris-(dimethylamino)phosphaneselenide]tellurium(II) (**II**). Moreover, for a better understanding of the relationship between the electronic structure of chalcogen-containing ligands and their coordinating behaviour, we have taken into consideration some available structural data on non-coordinated chalcogenourea and phosphanechalcogenide ligands, including our results for tris(dimethylamino)-phosphanesulfide (**III**).

Using *N*-methylbenzothiazole-2(3*H*)-selone (**mbts**), we have been trying to diversify the traditional set of ligands used in the coordination chemistry of tellurium. This selone ligand has not been structurally characterized separately, but work by Demartin *et al.* involving iodine complex cations and adducts has resulted in the publication of a number of structures including [I(**mbts**)$_2$][I$_3$],[14] and **mbts·2I**$_2$ and **mbts·2IBr**.[15] A substantial amount of crystallographic and synthetic data is now available on many other selones, and a search of the Cambridge Crystallographic Database reveals a selection of over 15 such ligands ranging from selenourea[16] to biomolecular-type glucofurano selones.[17,18] However, the coordination chemistry of metals with such ligands is still dominated by that of selenourea.

Another ligand, tris(dimethylamino)phosphaneselenide (**tdmse**), is a representative of a less common group of ligands and has been used by us to add to the few experimental data available on the phosphanechalcogenide complexes (in addition, the only reported work on such complexes[6] does not contain any spectroscopic data). In general, reactions with phosphane selenides have mostly been concerned with transition metals, involving the more stable selenides such as Se=PPh$_3$, e.g. AuClSe=PPh$_3$,[19] [HgCl$_2$(Se=PPh$_3$]$_2$.[20] Complexes with main group elements have been isolated as well; AlCl$_3$·Se=PPh$_3$ has been structurally characterized,[21] as has SbI$_3$·Se=PPh$_3$.[22]

Tdmse is a nicely crystalline material at room temperature and its synthesis is straightforward. Its structure was determined by Songstad *et al.*[23] Apart from this structure, only one other paper has appeared reporting structural work on this ligand; an attempt to synthesize a bismuth(III) chloride adduct by Willey *et al.*[24] produced the dication [(Me$_2$N)$_3$PSe–SeP(NMe$_2$)$_3$]$^{2+}$. They

suggested that the selenium ligand was air-oxidized in the presence of bismuth, giving the salt with the $[(BiCl_4)_2]_n^{2n-}$ polyanion.

Experimental

Materials. Diphenylditelluride, **mbts** and bromine were used as supplied commercially (Aldrich). The compounds **tdmse**,[25] **trmse**[26] and **III**[27] were prepared as described in the literature, and BrTePhtrmse (**IV**) was synthesized according to published procedures.[6] Acetonitrile was stored over 4 Å molecular sieves prior to use. Melting points are uncorrected. NMR spectra were recorded on a Bruker DMX600 spectrometer; ^1H 600 MHz, ^{13}C 150.9 MHz and ^{31}P 242.93 MHz. Infrared spectra were recorded on a Nicolet Impact 400 FTIR spectrometer, with samples as Nujol mulls placed between KBr plates.

Synthesis. (**I**). **Mbts** (0.285 g, 1.25 mmol) was dissolved in methanol (10 cm³) and added to a stirred solution of diphenylditelluride (0.256 g, 0.625 mmol) in the same solvent (30 cm³) (Scheme 1). Bromine (0.10 g, 0.625 mmol) in methanol (10 cm³) was added to give a yellow precipitate which was collected by filtration, washed with a little ice-cold methanol and pumped dry. Recrystallization from hot thf followed by slow cooling to $-5\,°C$ produced a batch of deep red–orange block crystals. Yield 0.52 g, 81%. M.p. 160.5–161.5 °C. IR v_{max}/cm^{-1} (Nujol) 1314, 1269, 1173, 1079, 1045, 1000, 954, 750, 738, 720, 686, 605, 554, 493. ^1H NMR (δ ppm): 3.91s, CH_3, 3*H*, 7.57–6.96m, 9H (arom); ^{13}C: 184.2 (C = Se), 134.2, 131.9, 130.5, 130.3, 129.0, 128.0, 127.0, 121.5, 117.0, 116.5, 109.4, 104.6, 28.0.

(**II**). To a solution of diphenylditelluride (0.256 g, 0.625 mmol) in warm methanol (40 cm³) was added **tdmse** (0.303 g, 1.25 mmol) dissolved in methanol (20 cm³) (Scheme 1). The solution was stirred, and then bromine (0.10 g, 0.625 mmol) in methanol (5 cm³) was added to give a clear red–orange solution. After being stirred for 30 min at room temperature, the solution was filtered and the solvent removed *in vacuo*. Recrystallization of the product from hot acetonitrile followed by cooling overnight at $-20\,°C$ produced a crop of yellow–orange crystals. Yield 0.56 g, 85%. M.p. 179–81 °C. IR v_{max}/cm^{-1} (Nujol) 1287, 1155, 1051, 974, 737, 679, 677, 675, 648, 496, 456. ^1H NMR (δ ppm):

PhTeTePh + 2Se=L + Br_2 ⟶ 2BrTePhSe=L

Se=L =

mbts   tdmse
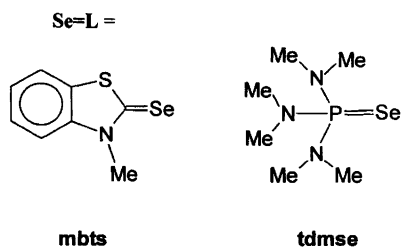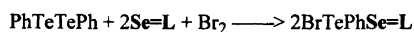
Scheme 1. Synthesis of compounds **I** and **II**.

2.66s, 2.70s ($N(CH_3)_2$),18H, 7.67–7.12m (Ph), 5H ; ^{13}C: 37.89, 37.83 ($N(CH_3)_2$), 123.3, 124,9, 125.6, 128.7, 129.0, 130.9 (Ph); ^{31}P: 81.19 [$^1J(^{77}Se-^{31}P$) 775 Hz].

Both **I** and **II** have good solubility in halogenated hydrocarbons, thf and acetonitrile and are stable to oxygen/air.

III was prepared according to the literature[27] and recrystallized from lukewarm pentane/diethyl ether by cooling the solution slowly at $-20\,°C$. The colourless crystals were filtered off and stored at 0 °C.

Structure determinations. Crystal data are given in Table 1, together with some data collection and refinement details. Data for all crystals were collected with $MoK\alpha$ radiation using an Enraf–Nonius CAD4 diffractometer. We had to operate with crystals of **II** at ambient temperature due to a loss of crystallinity at low temperatures. The unit-cell parameters and orientation matrices were obtained by a least-squares fit of 25 randomly orientated intense reflections in all cases. The diffracted intensities were collected using a variable scan speed. Three standard reflections were measured at regular intervals. All structures were solved using direct methods with the SHELXS86 program.[28] All non-hydrogen atoms were refined with anisotropic thermal parameters. An empirical absorption correction was supplied for the structure **II** using the DIFABS procedure[29] due to the failure of a psi-scan procedure, possibly caused by the rapid decay of the crystal. The psi-scan procedure converged successfully for the crystal of **I**. For the structure **III** an absorption correction was not applied because of the low value of μR. All hydrogen atom positions for the structures **I** and **III** were found from difference Fourier maps and refined isotropically. In **II** the phenyl and methyl group hydrogens were put in idealized calculated positions and processed with a least-squares refinement as a 'riding' model (for Me groups a torsion angle was optimized) with a common thermal parameter refined for each set of H atoms belonging to the same group. Refinement was with SHELXL93[30] on a MicroVax2000 computer.

Positional and displacement parameters of non-hydrogen atoms of the structures **I**–**III** are given in Tables 2–4. Bond distances and angles are listed in Tables 5–7. Molecular structures of the complexes are shown in Figs. 1–3 with 50% level of probability for thermal ellipsoids of atoms. Additional material available from the Cambridge Crystallographic Data Centre comprises anisotropic thermal parameters of non-hydrogen atoms, H-atom coordinates, thermal parameters, remaining bond lengths and angles, and tables of structure factors.

Results and discussion

Structure of the compounds. In the three-coordinate complexes of bivalent tellurium of the type X–Te(–Ar)–Y=L, where X = halogen and Y = chalcogen, two p-orbitals of the Te atom take part in the bonding. One gives a usual

Table 1. Crystal data and structure refinement parameters for compounds I–III.

Compound	I	II	III
Empirical formula	$C_{14}H_{12}NBrSSeTe$	$C_{12}H_{23}N_3PBrSeTe$	$C_6H_{18}N_3PS$
M	512.78	526.77	195.26
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a/Å	9.728(1)	9.718(2)	8.347(2)
b/Å	19.192(4)	17.043(3)	11.369(2)
c/Å	17.099(3)	11.983(2)	11.260(2)
α/°	90	90	90
β/°	105.12(1)	105.83(3)	92.94(3)
γ/°	90	90	90
T/K	143(2)	293(2)	143(2)
V/Å³	3081.7(10)	1909.4(6)	1067.1(4)
Z	8	4	4
D_c/Mg m⁻³	2.210	1.832	1.215
μ/mm⁻¹	7.006	5.633	0.405
F(000)	1920	1008	424
Crystal size (mm)	0.22 × 0.16 × 0.24	0.12 × 0.17 × 0.20	0.20 × 0.25 × 0.30
θ range/°	2.0–30.0	2.0–24.0	2.5–30.0
hkl ranges	0/13, 0/26, −24/22	−10/10, 0/19, 0/13	0/11, 0/16, −15/15
Total no. of reflections	9263	3145	3216
Crystal decay correction	0.915–1.000	0.535–1.000	0.964–1.000
Transmission coeff.	0.016–0.049	0.065–0.102	—
Independent reflections $I>2\sigma(I)$ (R_{int})	5817 (0.099)	1960 (0.083)	2317 (0.035)
Data (all)/parameters	8826/439	2976/180	3024/172
Goodness of fit on F^2 (obs./all data)	1.020/0.932	1.083/0.984	1.073/1.425
Final R indices: R_1 (obs./all data)	0.0345/0.0836	0.0357/0.0615,	0.0342/0.0635
wR_2 (obs./all data)	0.0842/0.1240	0.0843/0.0993	0.0972/0.1493
Largest difference peak and hole/e Å⁻³	1.293, −1.381	0.515, −0.499	0.607, −0.417

Table 2. Non-hydrogen atomic coordinates (× 10⁴) and equivalent isotropic temperature factors (× 10³) for compound I.

	Molecule IA				Molecule IB			
Atom	*x*	*y*	*z*	$U_{iso/eq}$[a]	*x*	*y*	*z*	$U_{iso/eq}$[a]
Te(1)	6686.5(3)	4204.8(1)	984.7(1)	26.6(1)	1816.4(3)	10573.7(1)	763.9(2)	29.5(1)
Br(1)	6094.9(4)	3152.8(2)	1971.1(3)	32.8(1)	1090.5(5)	11736.3(2)	1599.3(3)	37.8(1)
Se(1)	7459.0(5)	5136.7(2)	−15.9(2)	31.9(1)	2679.3(5)	9516.7(2)	−30.1(2)	33.7(1)
S(1)	6117(1)	6051.2(5)	1138.0(6)	28.9(2)	1076(1)	8782.5(5)	1138.8(6)	30.4(2)
C(2)	6907(4)	5977(2)	349(2)	27(1)	1958(4)	8744(2)	389(2)	30(1)
N(3)	7081(3)	6595(2)	29(2)	27(1)	2075(3)	8092(2)	138(2)	30(1)
C(4)	6605(4)	7156(2)	400(2)	28(1)	1451(4)	7590(2)	527(2)	30(1)
C(5)	6698(4)	7853(2)	210(2)	32(1)	1404(5)	6876(2)	394(3)	35(1)
C(6)	6164(5)	8348(2)	653(3)	34(1)	750(5)	6462(2)	851(3)	36(1)
C(7)	5572(5)	8137(2)	1281(3)	35(1)	170(5)	6752(2)	1445(3)	35(1)
C(8)	5509(5)	7442(2)	1471(3)	32(1)	208(5)	7459(2)	1578(3)	33(1)
C(9)	6033(4)	6955(2)	1026(2)	29(1)	855(4)	7880(2)	1110(2)	30(1)
C(10)	7683(5)	6687(2)	−671(3)	32(1)	2715(5)	7908(3)	522(3)	38(1)
C(11)	8746(4)	4300(2)	1791(2)	27(1)	3811(4)	10561(2)	1645(2)	27(1)
C(12)	9111(4)	4907(2)	2251(2)	29(1)	4248(4)	9965(2)	2100(2)	28(1)
C(13)	10457(4)	4973(2)	2772(2)	33(1)	5571(4)	9952(2)	2669(2)	31(1)
C(14)	11433(4)	4439(2)	2844(3)	34(1)	6437(4)	10533(2)	2789(3)	34(1)
C(15)	11083(4)	3836(2)	2391(3)	33(1)	6000(4)	11136(2)	2336(3)	34(1)
C(16)	9732(4)	3764(2)	1863(2)	30(1)	4686(4)	11151(2)	1765(2)	30(1)

[a]$U_{eq}=(1/3)\ \Sigma_i\Sigma_j U_{ij}\ a_i{}^* a_j{}^* a_i a_j.$

σ-bond with the aryl ligand. The Te–C(Ph) bond lengths vary mostly in the range 2.10–2.14(1) Å,[5–13] and the deviations observed are rather an effect of the low precision of the majority of the structures investigated. The other one gives a three-centre, four-electron bond with the ligand atoms X and Y. In conformity with this,

Table 3. Non-hydrogen atomic coordinates (×10⁴) and equivalent isotropic temperature factors (×10³) for compound II.

Atom	x	y	z	$U_{iso/eq}$[a]
Te(1)	322.8(4)	3542.0(2)	2141.8(4)	60.7(2)
Br(1)	−2187.1(8)	3635.5(5)	407.7(7)	98.4(3)
Se(1)	2782.2(6)	3487.6(4)	3962.3(5)	64.7(2)
C(1)	235(5)	2307(3)	2022(4)	48(1)
C(2)	−21(6)	1857(4)	2903(5)	68(2)
C(3)	−22(7)	1051(4)	2819(6)	86(2)
C(4)	209(7)	702(4)	1864(8)	92(2)
C(5)	420(7)	1135(4)	999(6)	79(2)
C(6)	451(6)	1937(5)	1071(5)	61(1)
P(1)	4455(2)	3558.2(8)	3066(1)	52.6(4)
N(1)	3997(6)	4017(3)	1835(4)	72(1)
N(2)	4990(5)	2683(3)	2866(4)	75(1)
N(3)	5774(5)	4066(3)	3882(5)	77(2)
C(11)	3686(9)	3619(5)	730(6)	108(3)
C(12)	3525(10)	4829(4)	1804(7)	127(3)
C(13)	4163(7)	1965(4)	2780(7)	94(2)
C(14)	6423(8)	2573(4)	2673(7)	117(3)
C(15)	6750(8)	4536(5)	3428(8)	117(3)
C(16)	6267(8)	3942(6)	5108(6)	120(3)

[a] See Table 2.

Table 4. Non-hydrogen atomic coordinates (×10⁴) and equivalent isotropic temperature factors (×10⁴) for compound III.

Atom	x	y	z	$U_{iso/eq}$[a]
S(1)	324.7(5)	8587.9(4)	2798.6(4)	287(1)
P(1)	235.5(4)	7597.8(3)	1378.0(3)	160(1)
N(1)	−646(2)	8302(1)	243(1)	218(3)
N(2)	2012(1)	7134(1)	1001(1)	203(2)
N(3)	−750(2)	6327(1)	1511(1)	206(3)
C(1)	−1851(2)	9215(2)	363(2)	338(4)
C(2)	−604(2)	7832(2)	−962(2)	347(4)
C(3)	3364(2)	7942(2)	1037(2)	262(3)
C(4)	2314(2)	6050(2)	348(2)	286(3)
C(5)	−2506(2)	6442(2)	1486(2)	283(3)
C(6)	−150(2)	5554(2)	2472(2)	305(4)

[a] See Table 2.

all the complexes have a T-shaped planar configuration with the linear group X–Te–Y perpendicular to the Te–Ar bond. Deviations of valence angles XTeAr and YTeAr from 90° and valence angle XTeY from 180° are not very large (usually a few degrees) and may be explained by large spatial volume of a lone electron pair of Te and by influence of packing factors. An exception to this is found in the chelate complexes with Y=O,[11–13] where geometrical restrictions caused by the chelate bite angle force additional deviations. Both complexes I and II conform to these principles (Tables 5 and 6).

Despite the large trans-influence of the Ph group, some compounds of this type have in the crystalline state additional weak intermolecular contacts in the direction trans to the aryl ligand. Most often, these contacts are with a halogen atom of a neighbouring molecule [for example, in isomorphous ClTePhetu and BrTePhesu, intermolecular contacts Te⋯Cl and Te⋯Br are 3.740(1)

and 3.849(2) Å, respectively;[9] in isomorphous ClTePhtu and BrTePhtu corresponding contacts are 3.71(2) and 3.77(1) Å[5]], but there are a few examples when some other elecron donors take a part in such weak coordination [e.g. in the structure of BrTefPh[12] molecules are connected in chains by the contacts Te⋯O 3.59(1) Å, but the authors did not consider this as an additional interaction]. Of course, there are many examples where these contacts are really absent. In particular, this is the case for compound II.

In contrast to the above, molecules of I are joined together in the crystals into centrosymmetric dimers in an unusual manner (Fig. 4). For both of the symmetrically independent molecules, the additional coordination occurs as η-coordination from an −S−C(=Se)−NMe− group of a neighbouring molecule. The dimers of molecules IA are closest: the distance between the Te atom and the coordinated planar π-system is 3.656(1) Å, and the Te atom 'hangs' over the central carbon atom of the group [the angle C(Ph)–Te⋯C(2)′ is 178.1(2)°, the angle between the Te⋯C(2)′ vector and the Se′,S′,N′,C(2)′ mean plane is 86.9(2)°, the distances Te⋯C(2)′ = 3.655(1), Te⋯Se′ = 4.138(1), Te⋯S′ = 3.961(1), Te⋯N′ = 3.934(1) Å]. The dimers of IB are significantly looser: the distance between the Te atom and the plane of the π-system is 3.705(1) Å, and the Te atom is 'shifted' a bit away from the central carbon atom [the angle C(Ph)–Te⋯C(2)′ is 157.9(2)°, the angle between the Te⋯C(2)′ vector and the Se′,S′,N′,C(2)′ mean plane is 71.2(2)°, the distances Te⋯C(2)′ = 3.911(1), Te⋯Se′ = 4.227(1), Te⋯S′ = 3.906(1) and Te⋯N′ = 4.502(1) Å].

This type of secondary coordination in tellurium complexes was first noticed by us in the crystal structure of bromobis(dimethyldithiocarbamato-S,S′)(4-methoxyphenyl)tellurium(IV)[31] where a dithiocarbamate group of a neighbouring molecule coordinates to an empty position in the Te^{IV} coordination sphere trans to the aryl ligand in the same way [C–Te⋯C = 170.2(1)°, Te⋯C = 3.751(3) Å]. Moreover, we have found this type of Te^{II} coordination (not mentioned in the paper) by a neighbouring −NH−C(=S)−NH− group in the crystal structure of BrTePhetu (i form)[7] (C–Te⋯C = 175.5°, Te⋯C = 3.688 Å).

The X–Te–Y sequence is the most labile constituent in the coordination environment of the tellurium atom. In terms of resonance forms it is possible to present this as:

$$\begin{array}{ccc} \text{Ar} & & \text{Ar} \\ | & & | \\ \text{X——Te<——Y=L} & \longleftrightarrow & \text{X}^-\text{——>Te——Y—L}^+ \end{array}$$
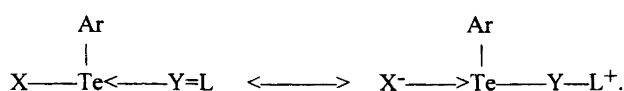
As a result of the three-centre, four-electron bonding, both X–Te and Te–Y bond orders are less than 1. Now, iodine has a larger trans-influence than bromine, which again has a larger trans-influence than chlorine. In the same manner, selenium should have a stronger trans-influence than sulfur and oxygen for the chalcogen series. Table 8 demonstrates this in quantitative form.

Indeed, all X(halogen)–Te distances are larger than

Table 5. Bond lengths (d/Å) and angles (ω/°) in molecule **IA** and **IB**.

Bond	d IA	IB	Bond	d IA	IB
Te(1)-C(11)	2.123(4)	2.123(4)	C(5)-C(6)	1.397(6)	1.380(7)
Te(1)-Se(1)	2.7133(6)	2.6940(6)	C(6)-C(7)	1.403(6)	1.399(7)
Te(1)-Br(1)	2.7854(6)	2.8362(7)	C(7)-C(8)	1.379(6)	1.376(6)
Se(1)-C(2)	1.858(4)	1.861(4)	C(8)-C(9)	1.384(6)	1.397(6)
S(1)-C(2)	1.724(4)	1.721(4)	C(11)-C(12)	1.398(5)	1.385(5)
S(1)-C(9)	1.744(4)	1.744(4)	C(11)-C(16)	1.389(5)	1.400(5)
C(2)-N(3)	1.335(5)	1.337(5)	C(12)-C(13)	1.384(5)	1.397(5)
N(3)-C(4)	1.390(5)	1.397(5)	C(13)-C(14)	1.381(6)	1.381(6)
N(3)-C(10)	1.473(5)	1.467(5)	C(14)-C(15)	1.384(6)	1.395(6)
C(4)-C(5)	1.383(5)	1.387(6)	C(15)-C(16)	1.394(6)	1.392(6)
C(4)-C(9)	1.385(5)	1.393(6)			

Angle	ω IA	IB	Angle	ω IA	IB
Br(1)-Te(1)-Se(1)	174.04(2)	175.92(2)	C(4)-C(5)-C(6)	118.3(4)	118.4(4)
Br(1)-Te(1)-C(11)	88.7(1)	87.3(1)	C(5)-C(6)-C(7)	120.2(4)	121.0(4)
Se(1)-Te(1)-C(11)	89.0(1)	90.1(1)	C(6)-C(7)-C(8)	120.7(4)	120.9(4)
Te(1)-Se(1)-C(2)	102.1(1)	102.0(1)	C(7)-C(8)-C(9)	118.6(4)	118.2(4)
C(2)-S(1)-C(9)	90.8(2)	91.0(2)	S(1)-C(9)-C(4)	110.3(3)	110.3(3)
Se(1)-C(2)-S(1)	124.1(2)	124.4(2)	S(1)-C(9)-C(8)	128.7(3)	128.9(3)
Se(1)-C(2)-N(3)	123.7(3)	123.3(3)	C(4)-C(9)-C(8)	121.1(4)	120.8(4)
S(1)-C(2)-N(3)	112.2(3)	112.3(3)	Te(1)-C(11)-C(12)	119.7(3)	119.9(3)
C(2)-N(3)-C(4)	114.1(3)	114.2(3)	Te(1)-C(11)-C(16)	120.4(3)	120.2(3)
C(2)-N(3)-C(10)	124.0(3)	124.1(4)	C(12)-C(11)-C(16)	119.9(4)	119.9(3)
C(4)-N(3)-C(10)	121.8(3)	121.6(4)	C(11)-C(12)-C(13)	119.8(4)	120.0(4)
N(3)-C(4)-C(5)	126.3(4)	127.1(4)	C(12)-C(13)-C(14)	120.1(4)	120.3(4)
N(3)-C(4)-C(9)	112.6(3)	112.2(4)	C(13)-C(14)-C(15)	120.5(4)	120.1(4)
C(5)-C(4)-C(9)	121.0(4)	120.7(4)	C(14)-C(15)-C(16)	119.8(4)	119.9(4)
			C(11)-C(16)-C(15)	119.8(4)	119.9(4)

the corresponding sum of covalent bond radii[32] and tend to increase going from left to right (from Y = O to Se). In turn, all Te–Y(chalcogen) distances are also lengthened and tend to increase going from top to bottom (from X = Cl to I). Nevertheless, there are many deviations from this rule. Firstly, bonds of this type are very sensitive to the crystalline environment (c.f., e.g., the bond lengths in the two crystalline modifications of BrTePhetu, or in the two symmetrically independent molecules of I). On the other hand, ligands with a different L but with the same Y donor centre have a different coordination ability. In general, phosphine derivatives (outlined in the table) have weaker *trans*-influences than urea derivatives. Hauge and Vikane noted this in their summarizing paper,[8] when they ordered the ligands by their different *trans*-influences, but they did not give any explanation of the possible origins for the differences.

Coming back to the resonance forms mentioned, we can see, that both ligands, X and Y = L, can act both as p-donor ligands (two-electron donation onto an anti-bonding σ-orbital) and σ-ligands (1-electron donation onto a bonding σ-orbital). The formula on the left corresponds to a σ-bonded X ligand and a 'secondary' datively bonded Y = L ligand (donating a lone electron

pair onto a σ*-orbital of the X–Te single bond with a resulting weakening of this); the formula on the right, on the contrary, contains a 'secondary' datively bonded X⁻ ligand and a σ-bonded -Y-L⁺ ligand. In the last case we have an ylide form with the positive charge transferred completely to the -Y-L⁺ ligand. Evidently, the better the ability of the L component of a ligand to adopt this charge, the more stable is this ligand form. In addition, the larger the contribution of this form to the structure, the stronger the bonding effect of the Te–Y interaction. We may also note that the more or less pronounced σ- or dative character of the ligands can perceptibly modify the manifestation of *trans*-influences of the ligands.

Both the urea and phosphoramide derivatives are actually quite good 'depots' for the positive charge of the central Te^{II} ion, as indicated by the following resonance structures:
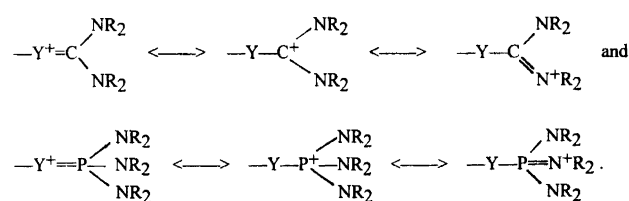
$$-Y^+{=}C\Big\langle{}^{NR_2}_{NR_2} \longleftrightarrow -Y-C^+\Big\langle{}^{NR_2}_{NR_2} \longleftrightarrow -Y-C\Big\langle{}^{NR_2}_{N^+R_2} \quad \text{and}$$

$$-Y^+{=}P\Big\langle{}^{NR_2}_{NR_2}\!\!{}_{NR_2} \longleftrightarrow -Y-P^+\Big\langle{}^{NR_2}_{NR_2}\!\!{}_{NR_2} \longleftrightarrow -Y-P{=}N^+R_2\Big\langle{}^{NR_2}_{NR_2}.$$

Table 6. Bond lengths (d/Å) and angles (ω/°) in molecule II.

Bond	d	Bond	d
Te(1)–Br(1)	2.744(1)	P(1)–N(2)	1.619(5)
Te(1)–Se(1)	2.763(1)	P(1)–N(1)	1.620(5)
Te(1)–C(1)	2.110(5)	P(1)–N(3)	1.632(5)
Se(1)–P(1)	2.183(2)	N(1)–C(11)	1.445(8)
C(1)–C(2)	1.381(7)	N(1)–C(12)	1.456(9)
C(1)–C(6)	1.367(7)	N(2)–C(13)	1.453(8)
C(2)–C(3)	1.378(9)	N(2)–C(14)	1.484(8)
C(3)–C(4)	1.361(9)	N(3)–C(16)	1.432(8)
C(4)–C(5)	1.334(9)	N(3)–C(15)	1.455(8)
C(5)–C(6)	1.370(8)		

Angle	ω	Angle	ω
Br(1)–Te(1)–Se(1)	177.06(2)	Se(1)–P(1)–N(2)	109.6(2)
Br(1)–Te(1)–C(1)	89.7(1)	Se(1)–P(1)–N(3)	107.7(2)
Se(1)–Te(1)–C(1)	91.7(1)	N(1)–P(1)–N(2)	109.2(3)
Te(1)–Se(1)–P(1)	102.10(5)	N(1)–P(1)–N(3)	105.4(3)
Te(1)–C(1)–C(2)	120.9(4)	N(2)–P(1)–N(3)	110.2(3)
Te(1)–C(1)–C(6)	120.3(4)	P(1)–N(1)–C(11)	123.0(5)
C(2)–C(1)–C(6)	118.8(5)	P(1)–N(1)–C(12)	119.2(5)
C(1)–C(2)–C(3)	119.6(5)	C(11)–N(1)–C(12)	115.9(6)
C(2)–C(3)–C(4)	120.0(6)	P(1)–N(2)–C(13)	126.4(4)
C(3)–C(4)–C(5)	120.5(6)	P(1)–N(2)–C(14)	119.5(4)
C(4)–C(5)–C(6)	120.5(6)	C(13)–N(2)–C(14)	114.0(5)
C(1)–C(6)–C(5)	120.5(5)	P(1)–N(3)–C(15)	123.6(5)
Se(1)–P(1)–N(1)	114.7(2)	P(1)–N(3)–C(16)	121.6(5)
		C(15)–N(3)–C(16)	113.3(6)

Table 7. Bond lengths (d/Å) and angles (ω/°) in molecule III..

Bond	d	Bond	d
S(1)–P(1)	1.9542(6)	N(1)–C(2)	1.461(2)
P(1)–N(1)	1.649(1)	N(2)–C(3)	1.454(2)
P(1)–N(2)	1.650(1)	N(2)–C(4)	1.464(2)
P(1)–N(3)	1.673(1)	N(3)–C(6)	1.463(2)
N(1)–C(1)	1.456(2)	N(3)–C(5)	1.471(2)

Angle	ω	Angle	ω
S(1)–P(1)–N(1)	110.56(5)	P(1)–N(1)–C(2)	120.7(1)
S(1)–P(1)–N(2)	113.42(6)	C(1)–N(1)–C(2)	113.4(2)
S(1)–P(1)–N(3)	114.99(5)	P(1)–N(2)–C(3)	119.8(1)
N(1)–P(1)–N(2)	109.11(7)	P(1)–N(2)–C(4)	125.3(1)
N(1)–P(1)–N(3)	106.67(7)	C(3)–N(2)–C(4)	113.1(1)
N(2)–P(1)–N(3)	101.51(7)	P(1)–N(3)–C(5)	114.6(1)
P(1)–N(1)–C(1)	123.9(1)	P(1)–N(3)–C(6)	115.7(1)
		C(5)–N(3)–C(6)	111.7(1)

Of course, the stability of the cationic form of the ligand is dependent not only on the nature of the central *ipso* (C or P) atom, but also on the possibility to delocalize the positive charge. This is dependent, in turn, on sterical and electronic properties of the surrounding atoms and their subtituents. To estimate this, we have to consider the structure of the ligands and the changes that occur during coordination more thoroughly.

The correspondence between the ability of ligands to delocalize the positive charge and their increased coordination ability is clearly displayed by the oxygen-containing chelate complexes. Thus, the Te–O distance
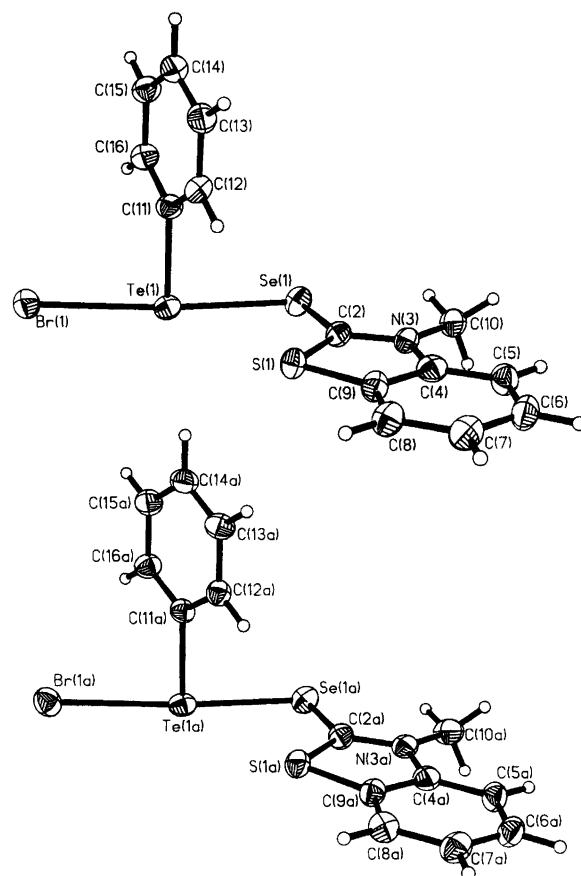

Fig. 1. Perspective projections of the two symmetrycally independent molecules of **I** given in a comparable orientation of the Te coordination plane. Atoms of the molecule **IB** (bottom) are numbered with addition of 'a' symbol.
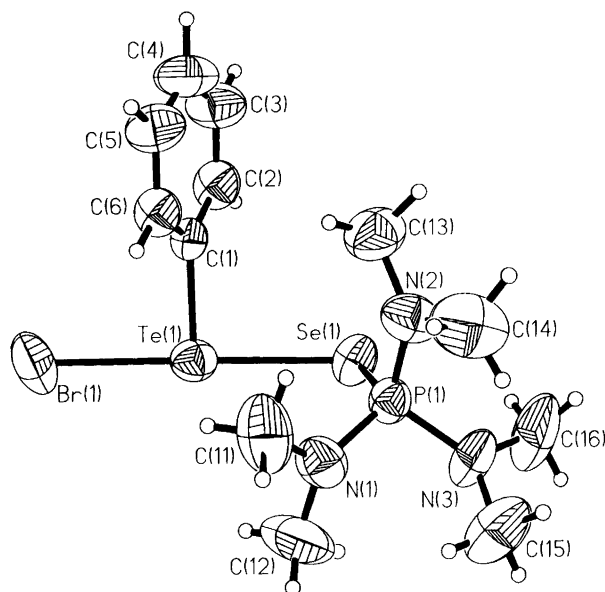

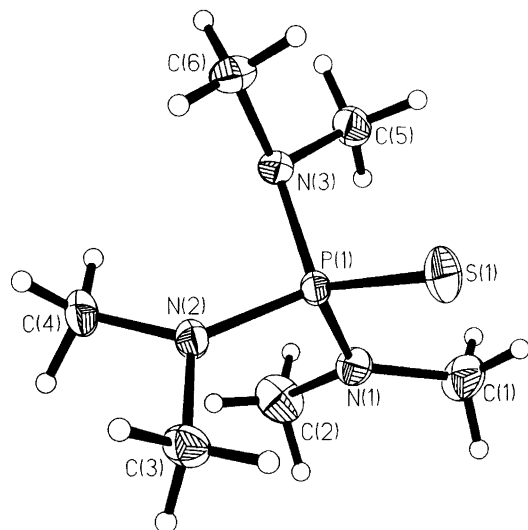*Fig. 2.* Perspective projection of the molecule **II** with numbering of the atoms.

Fig. 3. Perspective projection of the molecule **III** with numbering of the atoms.

to affirm that the S=C bonds in all the complexes are lengthened as compared with those in the corresponding non-coordinated ligands (1.713 and 1.714(1) Å in **tu**,[34] 1.692(1) or 1.694(3) Å in **etu**,[35,36] 1.72 Å in **trtu**;[37] no data are available on non-coordinated **tmtu**). This lengthening is especially pronounced in the complexes of non-alkylated thiourea, which have, in turn, the shortest Te–S distances. The increase of the Te–S distances for complexes of *N*-alkyl-substituted thioureas has usually been explained by sterical repulsion between the bulky substituents and the Te atom (especially in the case of **tmtu** derivatives). If we look at the bond angles Te–S=C we can see that the reverse is true: the smallest are found for **tmtu** derivatives and the largest for **tu** derivatives. A better explanation may be that non-substituted thiourea is better able to delocalize a positive charge accepted upon coordination than its *N,N'*-dialkylated (cyclic) analogues and the *N,N,N',N'*-tetraalkylated (**tmtu**) analogue, and consequently forms a somewhat stronger bond to Te (more σ-character).

Evidence for this may be seen in the size of the bond angle Te–S=C. It has been shown that in non-coordinated **tu** itself there is a non-hybridized valence state of the S atom with two lone electron pairs occupying the s- and a p-orbital (the p_y-orbital lying in the plane of the ligand).[38] We have found for the complex *cis*-Tetu$_2$Cl$_2$ (the paper is currently under preparation for publication) that the electron density distribution in the coordinated **tu** molecule corresponds to an sp^2-hybridized state for S. So, when the coordinated thiourea ligand has a predominantly σ-type rather than a dative type bonding, the Te–S=C angle should be large. It is necessary to note that the angles can never reach ideal values: for thiourea as an 'ideal' p-donor ligand, the angle should usually be slightly larger than 90°, owing
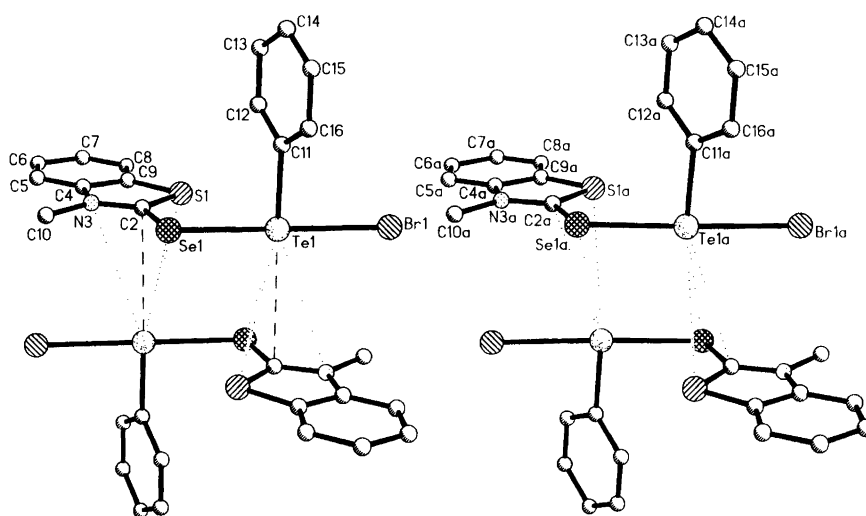
is noticeably shorter [2.237(8) Å] in the amide **BrTefaPh**[11] than in its close formyl analog **BrTefPh** (2.31(2) Å).[12] In all the four structures known, the C=O bond seems to be lengthened [1.28(2) Å in **ClTemfaPh**,[11] 1.28(3) Å in **BrTefPh**, 1.27(1) Å in **BrTefaPh** and 1.24(1) Å in **ITeiprPh**,[13] as compared to the standard value for benzoyl derivatives, 1.22 Å[33]]. However, the precision of these structures is not particularly good, and the Te–O interactions are comparatively weak.

For thiourea derivatives, it is possible to discuss this in more detail (Table 9). From looking at these data (unfortunately, some of them are relatively old and therefore not of a high precision), it is difficult to say unambiguously that a correlation exists between the bond distances Te–S and S=C. However, it is possible

Fig. 4. Perspective projections of the centrosymmetric dimers of molecules **IA** (left; by an inversion centre [[½,½,0]]) and **IB** (right; by an inversion centre [[0,1,0]]) given in a comparable orientation of the Te coordination plane. Numeration of atoms is given as on Fig. 1. Hydrogen atoms are removed for clarity. Close contacts Te···C in the **IA** dimer are shown by dashed lines, other shortened contacts in both dimers by dotted lines (see the text).

Table 8. Bond distances (X–Te\Te–Y) in complexes of the type X–TeAr–Y=L (sums of covalent radii of Te and a corresponding element[32] are given in brackets).

X/Y	O [2.11]	S [2.41]	Se [2.54]
Cl [2.36]	ClTemfaPh[11] 2.516(3)\2.250(7)	ClTePhtu[5] 3.00(2)\2.50(2) ClTePhetu[9] 2.849(1)\2.521(1) ClTePhtmtu[6] 2.668(2)\2.595(2)	ClTePhtrsu[8] 2.979(3)\2.592(1) ClTePhtrmse[6] 2.600(2)\2.783(1)
Br [2.51]	BrTefPh[12] 2.618(3)\2.31(2) BrTefaPh[a,11] 2.646(1)\2.237(8)	BrTePhtu[5] 3.11(1)\2.50(2) BrTePhetu[b,7] 2.969(1)\2.523(1) 2.835(1)\2.556(2) BrTePhtrtu[8] 2.904(1)\2.529(3) BrTePhtmtu[6] 2.833(1)\2.589(2)	BrTePhesu[9] 3.054(2)\2.616(2) (I)[c,d] 2.785(1)\2.713(1) 2.836(1)\2.694(1) (IV)[d] 2.761(1)\2.769(1) (II)[d] 2.744(1)\2.763(1)
I [2.70]	ITeiprPh[13] 2.735(1)\2.368(6)	ITePhetu[10] 3.003(1)\2.614(2)	ITePhesu[10] 3.095(1)\2.679(2)

[a] Dimethyl sulfoxide solvate 1:1. [b] Two crystalline modifications: $P2_1/c$ and $C2/c$. [c] Two symmetrically independent molecules. [d] This work.

to the sterical repulsion between Te and one of the NH_2 groups; for an 'ideal' σ-ligand, the angle should usually be somewhat smaller than 120°, because of the large repulsion effect of the sp^2-hybridized lone electron pair. Moreover, dative coordination should occur, in this case, preferably in the plane of the thiourea ligand. However, σ-bonding does not have such geometrical limitations. Indeed, the experimental data available do not conflict with this suggestion: in chloro-complexes (Cl⁻ has a weak *trans*-influence) the dihedral angle Te–S–C–N deviates somewhat from 0°, in complexes with Br we can see both skewed and periplanar conformations and in the iodo-complex (I⁻ has a strong *trans*-influence) we observe a periplanar conformation only (Table 9).

A clearer notion about the degree of positive charge delocalization might be obtained from the bond length distribution in the moiety $(H,R)_2N–C(=Y)–N(H,R)_2$, but the precision of the data available makes this difficult. Nevertheless, the $C(sp^2)$–N bond lengths in the more strongly coordinated N,N'-dialkylated **etu** and **trtu** are, in general, shorter than these in the more weakly coordinated N,N,N',N'-tetraalkylated **tmtu**. The old data on $C(sp^2)$–N bond lengths in the **tu** complexes are somewhat inaccurate; but the values of 1.303–1.308(3–4) Å found in related complexes of type $Tetu_2X_2$ (X=Cl, Br or I)[39] seem to be more reliable and are in agreement with our suggestions.

Structures of the Te complexes with selenourea derivatives are not so numerous: only two with **esu** and one with **trsu** have been structurally investigated (see Introduction). In the available literature, there are no suitable examples of structures of uncomplexed selenourea (or its derivatives) for comparison. There is only some inaccurate data on selenourea itself[16] and on its disordered clathrate with adamantane.[40] According to these publications, the Se=C bond length ranges from 1.83 to 1.94 Å. We can only note that in the Te complexes, the Se=C bond lengths seem to be slightly elongated in **esu** ligands [1.866(7) Å in ITePhesu[10] and 1.875(8) Å in BrTePhesu[9]] as compared with the **trsu** ligand [1.852(9) Å in ClTePhtrsu[8]]. This is observed despite the stronger *trans*-influence of I⁻ and Br⁻ ions (as compared with Cl⁻) and, consequently, longer Te–Se bond distances in two first compounds. However, one should keep in mind that these bond lengths really are equal within error limits. The Cl- and Br-derivatives have a skewed conformation along the Se–C bond (the Te–Se–C–N dihedral angles are 59.1 and 44.2°) but the I-derivative (isomorphous with **etu**-analog) has a periplanar conformation (3.1°). The bond angle TeSeC is approximately 100±0.5° in all of these compounds, and the C–N bond distances show a large experimental spread (1.29–1.42 Å).

The **mbts** ligand represents a very close analogue of the thiourea derived ligands. With regards to its electronic properties upon coordination, it may function as a depot for positive charge due to a possibility to delocalise the positive charge via conjugation with the lone electron

Table 9. Some geometrical parameters of Te-coordinated thiourea-derived ligands.

Compound	Te–S/Å	S=C/Å	Te–S=C/°	C(sp²)–N/Å	Te–S–C–N/°
ClTePhtu[a,5]	2.50(2)	1.78(6)	110(2)	1.35; 1.32	28
BrTePhtu[a,5]	2.50(2)	1.78(6)	108(2)	1.34; 1.34	28
ClTePhetu[b,9]	2.521(1)	1.728(3)	102.6	1.311;1.313(3)	42.9
BrTePhetu[7] $P2_1/c$[b]	2.523(2)	1.723(5)	102.5(2)	1.31; 1.32(1)	42.3
$C2/c$	2.556(2)	1.712(4)	104.6(2)	1.311; 1.319(6)	1.1
ITePhetu[10]	2.614(2)	1.720(6)	102.6(2)	1.305; 1.340(7)	1.4
BrTePhtrtu[8]	2.529(3)	1.756(9)	107.1(3)	1.32; 1.33(1)	5.2
ClTePhtmtu[c,6]	2.595(2)	1.745(6)	96.6(2)	1.336; 1.340(8)	64.7
BrTePhtmtu[c,6]	2.589(2)	1.765(8)	96.7(3)	1.33; 1.33(1)	64.5

[a] Isomorphous; photo-method. [b] Isomorphous. [c] Isomorphous.

pairs of both nitrogen and sulfur heteroatoms. Moreover, the benzene ring may take part in the delocalization too; the cationic form of the ligand represents a 10-electron π-aromatic system. In the complex investigated I it can be seen that the bond lengths from heteroatoms to the *ipso*-carbon atoms are distinctly shorter than the corresponding bond lengths to sp²-hybridized atoms of the benzene nucleus [1.335 and 1.337(5) Å vs. 1.390 and 1.397(5) Å for C–N bonds and 1.724 and 1.721(4) Å vs. 1.744 and 1.744(4) Å for C–S bonds]. The Se=C bond length is 1.858 and 1.861(4) Å, i.e. lies in the same range as has been found for coordinated esu and trsu ligands.

Unfortunately, at the moment we do not have data on the structure of the non-coordinated mbts ligand for comparison with our results. We can only note that in related complexes [I₃–I–mbts] and [BrIBr–I–mbts],[15] the bond lengths found in the mbts ligand part of the complexes are very similar to those found by us: the Se=C bond is 1.853–1.864(8) and 1.880(8) Å, the N–C(*ipso*) bond is 1.330–1.337(9) and 1.317(10) Å as compared to the N–C(benzene) bond of 1.384–1.407(9) and 1.413(10) Å; the S–C(*ipso*) bond is 1.713–1.730(7) and 1.711(8) Å vs. S–C(benzene) bond of 1.734–1.743(8) and 1.754(8) Å in [I₃–I–mbts] (three independent molecules) and [BrIBr–I–mbts], respectively. It is interesting to note that in the [BrIBr–I–mbts] molecule, the structural effects of the positive charge transfer onto the ligand with its consequent delocalization are quite pronounced as compared with the I₃–I–mbts molecules, in full agreement with the weaker *trans*-influence of bromine as compared to iodine. The increase of the σ-character of the I–mbts bonding contributes to the shortening of the I–Se distance to 2.564(1) Å in [BrIBr–I–mbts] as compared to 2.639–2.720(1) Å in [I₃–I–mbts].

Nevertheless, the mbts ligand does not show such a high σ-coordinating ability as the esu ligand and it is more comparable to the trmse ligand (Table 8). This may possibly be a result of the lower ability of a sulfur atom to take a part in π-electron delocalization as compared to nitrogen.

In all the mbts complexes investigated, the bond angle Te/I–Se=C is closer to 90° than to 120° [102.1 and 102.0(1)° in I, 97.4–102.3(2)° in I₃–I–mbts and 97.8(3)°

in BrBr–I–mbts] and the torsion angle Te/I–Se=C–S is close to 0° [periplanar conformation; 0.2 and 3.3(2)° in I, 4.1–7.3° in I₃–I– mbts and 7.7° in BrBr–I–mbts]. This may be taken as evidence that mbts is more likely to form a dative bond rather than a σ-bond. The relative *cis*-orientation of the central Te/I atom and the S atom of the mbts ligand in all the complexes may be both a result of steric hindrance and of secondary interaction [Te–S distances are 3.609 and 3.607(2) Å in II, and I–S distances are 3.411–3.636(3) Å in [I₃–I–mbts] and 3.400(3) Å in [BrBr–I–mbts]].[15]

To date, not many examples of chalcogen analogues of symmetrically substituted phosphoramides and more especially their complexes, where these act as ligands, have been structurally investigated. Only one structure of a sulfide compound is known, triethylene thiophosphoramide,[41] but no complexes of this ligand have been structurally characterized. Two telluride derivatives: tris (pyrrolidino)phosphanetelluride[42] and tris-(morpholino)phosphanetelluride,[43] have also been structurally investigated. Structural examples of selenide derivatives are more numerous: tris(pyrrolidino)phos-phaneselenide,[42] tdmse,[23] tris(piperidino)phosphane-selenide[23] and trmse.[23] For the last example, two isomorphous complexes with Te[II] are the only instances known[6] (Table 8). It is surprising that no structures of complexes of any other element with the ligands of this type are actually known at present.†

Thus, the complex II represented in this paper is only the second structural example of complexes with a triaminophosphanechalcogenide ligand and the first with tdmse.

† Incidentally, phosphortriamides themselves have not been widely investigated: only a structure of tris(morpholino)phosphineoxide and two complexes of tris(piperidino)phosphineoxide (with Ti and Si) are known. However, for the simplest representative, hexamethylposphoramide, there is a large variety of structures (but no structure of the compound itself): its molecular complexes (more than 10 structures), complexes with ions of alkaline and alkaline-earth metals, lanthanides and actinides (many dozen), coordination compounds with transition (Ti, V, Mo, W, Fe, Co; in total ca. 20 compounds) and post-transition metals (some complexes with Cu, Cd and Hg), compounds of non-transition elements of IIIA (In), VA (three Bi-complexes) groups and, especially, of IVA group (Si, Sn, Pb; totally more than 30 examples).

The structural parameters of **II** are very similar to those found in **IV** investigated earlier. The Te–Br distance in **II** is only ca. 0.02 Å shorter than in **IV**, and Te–Se distances are equal within 0.006(1) Å (Table 8). The Se=P bond length of 2.183(2) Å is in good agreement with the corresponding values 2.182(2) and 2.176(2) Å found in **IV** and ClTePhtrmse.[6] These distances are lengthened by 0.06–0.08 Å as compared with corresponding distances in the non-coordinated ligands [2.114(1) Å in **tdmse** and 2.103(1) Å in **trmse**], but are still shorter than single bonds P–Se [2.227 and 2.234(8) Å] found in the $[(Me_2N)_3PSeSeP(NMe_2)_3]^{2+}$ cation.[24] Unfortunately we can not compare this elongation with what is happening upon coordination in selenourea derivatives, but it is more expressed than that found for coordinated and non-coordinated thiourea derivatives (see above). Nevertheless, the coordinating ability of phosphaneselenide ligands is substantially poorer than that of selenourea derived ligands and than that of thiourea ligands (from looking at *trans*-influences on X–Te distances in corresponding complexes; Table 8). To explain the difference between these two families of ligands, we have to thoroughly consider their structural (and electronic) characteristics.

Songstad *et al.*, who have studied most of the structures of individual triaminophosphanechalcogenides,[23,42,43] paid much attention to a very strange peculiarity of these compounds: their asymmetry. The classical point of view states that the phosphorus atom in such compounds is sp³-hybridized with its lone n-electron pair donated to an empty orbital of a chalcogen, but no compound has C_3-symmetry or anything close to this. In fact, every one of these compounds contains two different sorts of nitrogen atoms: one ('special') nitrogen has a pronounced sp³-hybridized pyramidal configuration with the lone n-electron pair directed in an antiparallel fashion to the P=Y bond (its coordination plane is nearly perpendicular to the P=Y bond), and the other two other nitrogens are essentially sp²-hybridized with their coordination planes only slightly inclined (usually, less than 30°) to the P=Y bond. As a result, the P–N bond lengths and N–P–N and N–P=Y bond angles differ very noticeably (Table 10).‡

We did not include the only previously known sulfur derivative $[(CH_2)_2N]_3P=S^{41}$ in Table 10 because of the very specific electron configuration of the aziridine nitrogens, but have added our own results on $(Me_3N)_3P=S$

‡ This phenomenon seems to be a general one in phosphorus stereochemistry: not only do all compounds of type $(R_2N)_3P=Y$ with Y = O, S, Se, Te have such geometry (both in individual and in complexed state), but also compounds, where Y = CR_2 or NR groups. Moreover, the molecular geometry both of individual triaminophosphines $(R_2N)_3P$ and their complexes with transition metals and silver is of the same type! Nevertheless, in compounds of phosphonium-type $(R_2N)_3P^+$–Y–, if only the phosphorus atom is really positively charged (i.e. it is trivalent and four-coordinated unambiguously), no difference exists between the three amine groups.

III, which are in a good agreement with these on other compounds of this series.

We can see that in all individual ligands represented, the 'special' nitrogen atom, N*, approaches more closely sp³-hybridization than the two others. Its lone pair has a very stable *anti*-orientation relative to the P=Y bond, the P–N* bond is substantially lengthened and the bond angle N*–P=Y is significantly enlarged as compared with the two others. Moreover, the values of the N*–P–N angles are smaller when compared both with the ideal tetrahedral value and with the value of the N–P–N angle. Songstad and co-workers mentioned these interesting geometrical details but commented only on their relation to the difference of P–N bond lengths.[42] Indeed, it is very difficult to explain these distortions (especially in the angles) from both a classical model and a concept involving unfilled 3d-orbitals of the phosphorus atom. We can add to this list of strange distortions unexpectedly small values of C–N–C bond angles, which seem to be tetrahedral rather than trigonal in all these molecules and are practically independent of the degree of hybridization of the nitrogen atoms.

Moreover, a very interesting transformation of these geometrical parameters occurs upon complexation of these ligands. Hauge and Vikane, in their paper on ClTePhtrmse and **IV**, gave only a very formal description of the geometry around the phosphorus atom.[6] First of all, we note that upon coordination of the ligands, the N* atom becomes practically sp²-hybridized, in line with the other two nitrogen atoms, but that it still keeps its 'special' orientation. Also, the P–N* bond becomes much shorter, often more than the two other P–N bonds (these are practically unchanged). And, finally, in all the three complexes the coordinated Te atom lies very close to the plane defined by the N*–P=Y group: the torsion angle N*–P–Se–Te is 2.1 and 2.6° in the isomorphous ClTePhtrmse and **IV** and 27.8(2)° in **II**.‡

At the moment, we can not give a complete explanation of all these interesting features. This will have to be the subject of a future investigation. Here, we have made only a preliminary attempt to estimate the character of the electron density distribution around the phosphorus atom in compound **III** (using a rather restricted experimental diffraction data set). Nevertheless, some results of this quasi-high-angle refinement (Figs. 5–7) are in good agreement with the experimental facts mentioned, although we have to use them with caution until we obtain a better experimental and quantum-chemical confirmation and interpretation.

We find that the deformation electron density distribution around phosphorus and sulfur, although rather incomplete and distorted, seems to be closer to octahedral symmetry than to tetrahedral. We did not find any large electron density along the P=S bond but there are two

‡ We can mention that in most complexes of the related ligands, hexamethylphosphoramide, the coordination occurs preferably in the plane including the 'special' nitrogen too: more often *cis*, less common *trans*.

Table 10. Molecular geometric parameters (angles in °, distances in Å) of individual and coordinated (italics) triaminophosphane–chalcogenide ligands.[a]

Compound	ψN*	ψN	τN*	τ(N)	YPN*	YPN	NPN*	NPN	CN*C	CNC	P–N*	P–N
morph₃P=Te[43]	128.1	139.5	178.5	−60.3	113.8	111.2	101.4	114.6	109.1	110.6	1.684	1.674
		150.7		73.1		112.8	102.2			110.4		1.663
trmse[23]	128.8	152.5	−178.9	−77.5	115.1	112.0	102.4	114.1	108.8	110.4	1.681	1.659
		141.7		65.7		111.4	101.2			110.4		1.668
ClTePhtrmse[b,6]	*149.3*	*152.8*	*176.3*	*69.4*	*118.1*	*109.1*	*102.8*	*116.3*	*112.4*	*108.0*	*1.637*	*1.659*
		146.9		*−70.1*		*107.9*	*102.8*			*111.5*		*1.647*
IV[a,6]	*151.0*	*155.4*	*176.3*	*69.6*	*117.8*	*108.9*	*103.5*	*115.4*	*112.7*	*111.3*	*1.646*	*1.665*
		149.7		*−70.9*		*107.9*	*103.6*			*111.3*		*1.651*
[(CH₂)₅N]₃P=Se[40]	132.9	170.4	−173.3	84.5	115.5	111.4	105.4	110.7	110.7	112.8	1.677	1.651
		156.9		56.1		112.2	101.0			112.0		1.658
[(CH₂)₄N]₃P=Te[42]	139.7	159.9	−177.5	−80.1	116.3	112.0	103.5	111.9	110.2	104.5	1.652	1.643
		166.2		60.2		110.5	102.1			110.5		1.622
[(CH₂)₄N]₃P=Se[c,23]	132.9	173.5	−178.3	85.9	116.7	110.2	104.6	112.4	109.5	110.0	1.654	1.634
		151.7		66.5		111.6	100.9			111.0		1.659
	130.3	164.5	−170.5	81.7	116.9	110.0	107.2	110.4	108.3	110.9	1.652	1.638
		157.6		58.4		112.1	99.7			111.1		1.643
tdmse[23]	132.3	163.8	170.7	−68.0	114.4	110.4	107.3	109.3	112.0	113.2	1.679	1.649
		163.7		−54.3		113.4	101.5			113.4		1.650
II[d]	*163.9*	*176.0*	*156.7*	*−66.1*	*114.7*	*109.6*	*109.2*	*110.2*	*115.9*	*114.0*	*1.620*	*1.619*
		165.2		*−53.8*		*107.7*	*105.4*			*113.3*		*1.632*
III[d]	*132.3*	*162.6*	*−171.3*	*70.4*	*115.0*	*110.6*	*106.7*	*109.1*	*111.7*	*113.4*	*1.673*	*1.649*
		164.0		*54.9*		*113.4*	*101.5*			*113.1*		*1.650*

[a] The 'special' nitrogen atom is labelled as N*; ψ is the difference between two coupled torsion angles Y=P–N–C (which must be 120 and 180° for ideally sp²- and sp³-hybridized nitrogen, respectively); τ is the torsion angle Y=P–N–(lone pair). [b] Isomorphous. [c] Two symmetrically independent molecules. [d] This work.
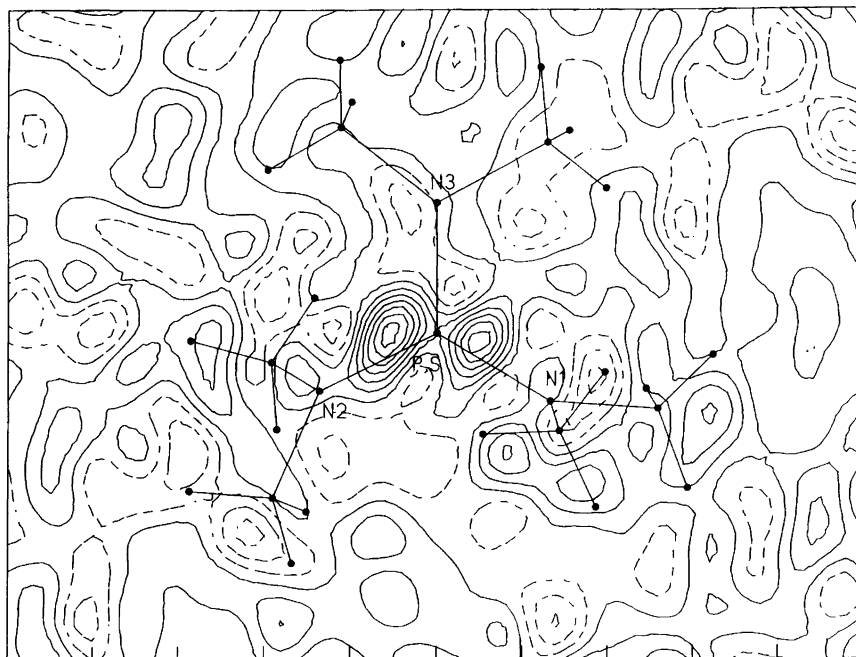
Fig. 5. The cross-section of deformation electron density (resolution 0.8 Å^{-1}) in the structure **III** in the plane perpendicular to the P=S bond through the midpoint of this bond. Negative density contours are dashed. Difference between levels of contours is 0.05 e Å^{-3}.
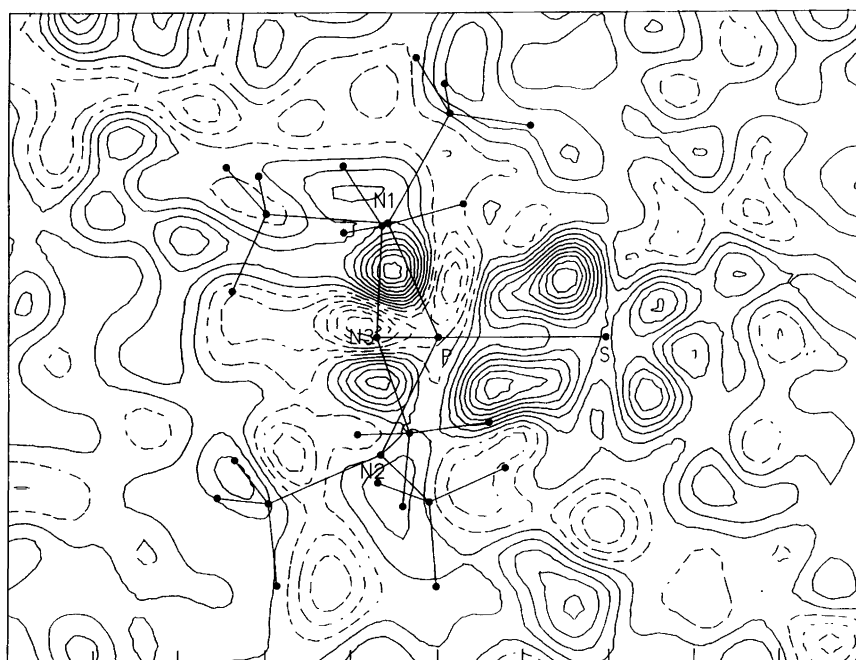

Fig. 6. The cross-section of deformation electron density (resolution 0.8 Å^{-1}) in the structure **III** in the plane perpendicular to the N(3)*-P=S sequence through the atoms P and S. Negative density contours are dashed. Difference between levels of contours is 0.05 e Å^{-3}.

well pronounced and intense peaks of π-character on either side of this, in a plane orthogonal to the plane of the N*–P=S sequence (Fig. 5). In addition, both phosphorus and sulfur have two peaks, each lying opposite to those of the P=S bond and practically in the same plane (Fig. 6). The two peaks at phosphorus are consist-

ent with σ-bonding and are somewhat shifted out of the plane toward the neighbouring 'common' N(1) and N(2) atoms but still lie a little outside the directions of the P–N bonds. A fifth peak located near the phosphorus is directed orthogonal to the plane through the four other peaks toward the neighbouring 'special' N*(3) atom
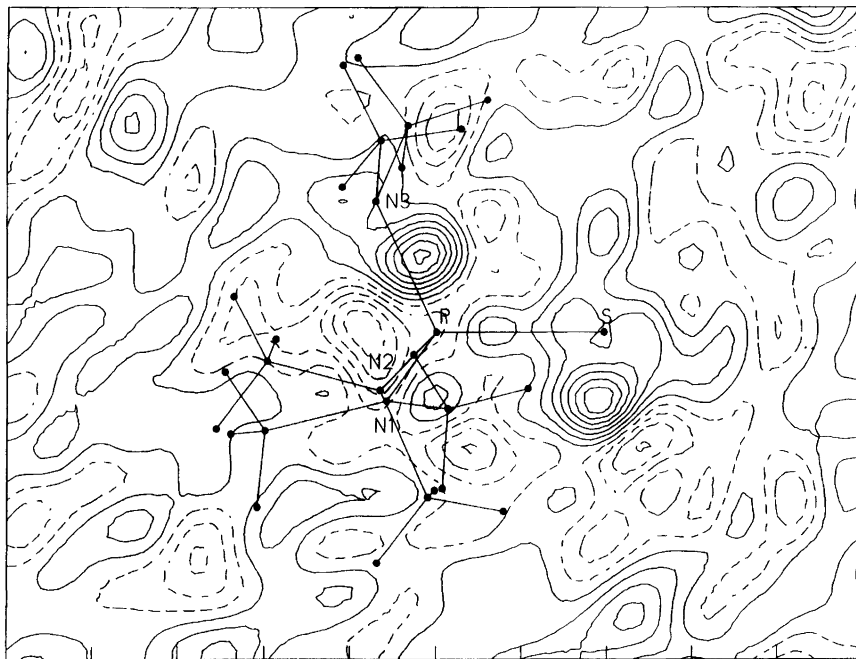
Fig. 7. The cross-section of deformation electron density (resolution $0.8\,\text{Å}^{-1}$) in the structure **III** in the plane of the $N(3)^*-P=S$ sequence. Negative density contours are dashed. Difference between levels of contours is $0.05\,e\,\text{Å}^{-3}$.

(Fig. 7). It also lies outside the direction of the P–N* bond and is shifted towards the sulfur atom. Thus, all σ-bonds along P–N vectors seem to be 'banana'-like. The fifth peak at sulfur (probably a lone p-electron pair) lies in a direction orthogonal to the 'square' of the four other peaks too, *trans* to the special nitrogen atom (and to the peak of its σ-bond) but without a visible opposite peak (Fig. 7).

This picture observed corresponds surprisingly well to the geometrical and coordination peculiarities observed, but it is very difficult for quantum-chemical interpretation. We can say only that it describes the non-equivalence of the nitrogen atoms, some angle distortions, the shortening of P–N bonds and coordination geometry in complexes. It does not correspond to the 'classical' representation of a phosphorus atom in such compounds as being sp^3-hybridized. Possibly we are observing a result of a complicated interaction between non-hybridized phosphorus and sulfur atoms (with 'non-classical' overlapping of their p-orbitals) which corresponds well in some details to a model of Ω bonding proposed for phosphine oxides.[44] Alternatively, the electron configuration of phosphorus may be represented by some form of spd-hybridization.

In any case, we can say that the lone p-electron pair of the chalcogen atom lies in the same plane as the P–N* bond and seems to be interacting (conjugated?) only with that bond. Thus, the abovementioned formal resonance may in fact take place. Besides this, only one of the three amino groups can be involved in conjugation. This situation is quite different from urea derivatives, which have a more extended conjugated system. This may be a reason for the poorer coordinating ability of trisamino-

phosphanechalcogenide ligands in comparison with urea analogues.

Infrared spectra. The IR spectra show band patterns in the $1200-600\,\text{cm}^{-1}$ range characteristic of the corresponding selenium ligands. For **II** the very strong ligand $v(P=Se)$ band at $528\,\text{cm}^{-1}$ is shifted $32\,\text{cm}^{-1}$ to lower energy following selenium coordination to the metal. This shift is of the right order of magnitude for such coordination; upon coordination, the $v(P=Se)$ vibration generally shifts $10-40\,\text{cm}^{-1}$ to lower energy versus the free ligand.[45] No infrared data are reported in Ref. 6 for the related compounds, so the complex **IV** was prepared and its infrared spectrum recorded for comparison. In the free ligand, **trmse**, the $v(P=Se)$ band appears at $526\,\text{cm}^{-1}$ and is shifted to lower energy following coordination through selenium to the phenyl tellurium fragment by $20\,\text{cm}^{-1}$.

NMR spectra. The ^1H NMR spectra of **I** and **II** were uninformative in terms of the bonding of the ligands to the metal; the ^{31}P NMR for **II** revealed a single resonance at $81.19\,\text{ppm}$ $[^1J(^{31}P-^{77}Se)\ 775\,\text{Hz}]$ located ca. $1.8\,\text{ppm}$ downfield from the parent ligand. Similar decreases in the selenium–phosphorus coupling constants have been reported previously but these complexes were not stucturally characterized at the time of the present study.[46] In the mercury(II) complexes $HgX_2(^nBu_3P=Se)_2$ ($X=Cl$, Br, I) the $^{31}P-^{77}Se$ coupling constant was reduced from $693\,\text{Hz}$ (free ligand) to 551, 560 and $587\,\text{Hz}$ (Cl, Br, I, respectively). The results were confirmed in a paper by Colton *et al.*[47] Complexes of the type $Zr(SePR_3)_n^{2+}$ ($R=Ph$, $o\text{-}C_6H_4Me$, Cy; $n=2$, 3, 4) were prepared and

Table 11. NMR data for compounds **I** and **mbts, II** and **tdmse, IV** and **trmse.**

Compound	^1H	$^{13}C\{^1H\}$	$^{31}P\{^1H\}$	$^1J\,(^{31}P-^{77}Se)$
I	7.57–6.96m, 9H; 3.91s 3H	184.2, 134.2, 131.9, 130.5, 130.3, 129.0, 128.0, 127.0, 121.5, 117.0, 116.5, 109.4, 104.6, 28.0	–	–
mbts	7.56–7.30m, 4H; 3.96s 3H	185.0, 142.9, 130.3, 127.2, 125.2, 121.1, 112.9, 35.6	–	–
II	7.67–7.12m, 5H (Ph), 2.66s, 2.70s [N(CH₃)₂]	123.3, 124.9, 125.6, 128.7, 130.9 (Ph), 37.89, 37.83	81.19	775
tdmse	2.61s, 2.59s	37.60, 37.56	83.08	805
IV	7.64–7.32m 5H; 3.75d 12H, 3.26 12H	133.7, 130.6, 129.6, 129.0, 128.3, 127.5, 65.71, 65.66 (J=7.2 Hz) 45.26	76.97	814
trmse	3.68–3.64 12H 3.21–3.16 12H	66.82, 66.70, $^3J(^{31}P-N-C-^{13}C)$ 7.4 Hz, 46.26	77.96	791

studied by ^{31}P NMR spectroscopy and again showed a decrease of ca. 100 Hz upon coordination as compared to the free ligand.[48]

A study was also undertaken on **IV** to see how large the decrease in the coupling constant of the ligands was upon coordination in this complex; a single ^{31}P resonance appeared at 76.97 ppm [$^1J(^{31}P-^{77}Se)$=791 Hz]. The free **trmse** ligand shows a single resonance at 77.96 ppm. The NMR data are summarized in Table 11.

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