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Complexes of Bidentate Phosphane Selenide Ligands with Mesitylenetellurenyl Iodide and with Tellurium Diiodide[‡]

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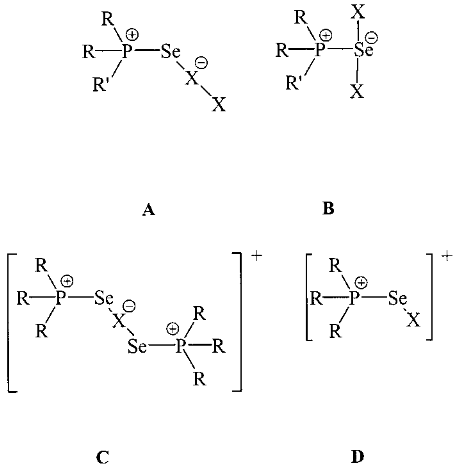
Bis(diphenylphosphanyl)methane diselenide (dppmSe$_2$, **1**) and bis(diphenylphosphanyl)ethane diselenide (dppeSe$_2$, **2**) reacted with 2 equiv. Br$_2$ or I$_2$ to form the insoluble solid products, dppm(SeX$_2$)$_2$ (X = Br, **3**; X = I, **4**) and dppe(SeX$_2$)$_2$ (X = Br, **5**; X = I, **6**). However, using the iodine-like electrophile mesitylenetellurenyl iodide (MesTeI, **7**), fairly soluble complexes, dppmSe$_2$[Te(I)Mes]$_2$ (**8**) and dppeSe$_2$[Te(I)Mes]$_2$ (**9**), were obtained. Complexes **8** and **9** contain two T-shaped (10-Te-3) Se–Te(Mes)–I moieties bridged by dppm or dppe; solid **9** exhibits intermolecular *soft–soft* interactions between approximately linear Se–Te–I units. In a side reaction accompanying the crystallisation of complex **8**, or by the reaction of **1** with Te and I$_2$, a chelate complex dppmSe$_2$TeI$_2$ (**10**) was formed. Fortuitously, a crystal of the related compound dppeSe$_2$TeI$_2$ (**11**) was also obtained. In **10**, a square planar *cis*-Se$_2$TeI$_2$ group is part of a six-membered ring, and **11** is a coordination polymer with *trans*-Se$_2$TeI$_2$ moieties bridged by dppe. Averaged ^{31}P- and ^{77}Se NMR signals including ^{77}Se–^{31}P couplings, together with broad ^{125}Te NMR singlets indicate phosphane selenide ligand exchange in solution, that is, the kinetically labile behaviour of complexes **8** and **9**.

Introduction

Phosphane chalcogenides R$_2$R′P=Y (Y = S, Se) are known to act as donors towards dihalogen molecules.[2–5] Using phosphane selenides, which are stronger donors than the sulfides, a considerable number of 1:1 adducts R$_2$R′PSeX$_2$ have been isolated.[6–9] Iodine adducts exhibit type **A** (10-I-2) *molecular* structures R$_2$R′PSeI$_2$ (R, R′ = C$_6$H$_5$, NMe$_2$, NEt$_2$[7] and R = *t*Bu, R′ = I)[8] or type **C** (10-I-2) *ionic* structures (R$_3$PSe)$_2$I$^+$I$_3^-$,[6,10,11a] whereas bromination products exhibit type **B** (10-Se-3) T-shaped PSeBr$_2$ moieties in their structures (R, R′ = NMe$_2$, C$_6$H$_{11}$, *i*C$_3$H$_7$).[9,11a] With excess iodine, polyiodide salts featuring R$_3$PSeI$^+$ countercations (type **D**),[4,10,12] could be formed (Scheme 1). Many of these compounds are aggregated by further *soft–soft* contacts that lead to ion pairs, chains and extended networks.[3,4,6,8,9,11b,12] In particular, type **D**-like (iodoseleno)phosphonium cations behave as soft electrophiles by the iodine atom in the β position to the formally charged phosphorus atom (β-heteroatom Lewis acidity).[3,10,12]



Scheme 1. Various Lewis-type structures of halogen adducts of phosphane selenides. These structures must be intended purely as a formal illustration of the various compounds with no implication as to the real distribution of charges. The same considerations apply to Scheme 2 and Scheme 3.

To stimulate the formation of supramolecular networks using the earlier mentioned types of soft–soft interactions, we are introducing *bifunctional* donor-acceptor systems into our studies. In a previous paper we described the self-assembly of iodophosphane selenides RR′P(=Se)I as bifunctional donor-acceptor molecules (selenium donor, iodine acceptor).[8] The bifunctional selenocarbonyl ligand 1,2-bis(3-methyl-4-imidazolin-2-selone)ethane was recently

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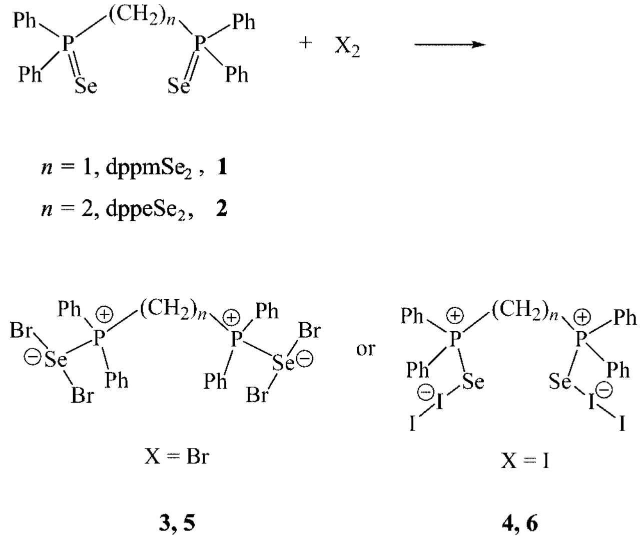
shown to undergo Br_2[13] and IBr[14] oxidative addition at the Se atom of the >C=Se group, exhibiting a subtle interplay of soft–soft and hydrogen-bonding interactions in the solid.

In our present work we evaluate the use of bifunctional phosphane selenides, bis(diphenylphosphanyl)methane diselenide ($dppmSe_2$, **1**) and bis(diphenylphosphanyl)ethane diselenide ($dppeSe_2$, **2**), towards halogens (Br_2, I_2) and towards the halogen-like electrophile mesitylenetellurenyl iodide [MesTeI, **7**; Mes = 2,4,6-$(CH_3)_3C_6H_2$][15] with the intention of creating supramolecular soft–soft networks. Arenetellurenyl chlorides and bromides are known to give stable 1:1 complexes with triphenylphosphane selenide,[16a] tri(morpholine)phosphane selenide[16a,16b] and tris(dimethylamino)phosphane selenide.[17]

Results and Discussion

Formation of 1:2 Adducts of $dppmSe_2$ (1) and $dppeSe_2$ (2) with Br_2 and I_2

Addition of 2 equiv. Br_2 or I_2 to solutions of bidentate phosphane selenides ($dppmSe_2$, **1**, and $dppeSe_2$, **2**) led to precipitation of solids of the composition $dppm(SeX_2)_2$ (X = Br, **3**; X = I, **4**) and $dppe(SeX_2)_2$ (X = Br, **5**; X = I, **6**) (Scheme 2).



Scheme 2. 1:2 Reactions of $dppmSe_2$ and $dppeSe_2$ with Br_2 and I_2. For an alternative structure of **4**, see vibrational spectra.

Since these materials are insoluble in aprotic-dipolar solvents and thus cannot be recrystallised, compounds **3**–**6** were not obtained as single crystals. In the absence of crystal data, only Raman spectra could be of help in investigating the structural features of the expected $PSeX_2$ functions of the compounds (see later). Reaction of dppe-diselenide **2** with only 1 equiv. I_2 also led to precipitation of the 1:2 product **6**; however, from CH_2Cl_2 solutions containing 1:1 mixtures of dppm-diselenide **1** with iodine, precipitation did not occur. The ^{31}P NMR spectrum of this solution shows only one resonance with a $^{77}Se,^{31}P$ satellite coupling that is smaller than that of the starting material. The ^{31}P NMR singlet may be due to a symmetric bonding mode of **1** with iodine, or, alternatively, to a rapid equilibration of coordinated and noncoordinated PSe functions (that is, signal averaging). In the ^{77}Se NMR spectra, titration-like addition of I_2 led to stepwise deshielding [**1**: $\delta^{77}Se$ = –240 ppm, **1**/I_2 (1:1 complex): $\delta^{77}Se$ = –68 ppm] and line broadening. This observation implies signal averaging at all stages of the iodine addition. Crystals of the 1:1 product were not obtained; precipitation by addition of pentane led to the solid 1:2 product **4**. Similarly, attempts to prepare 1:1 adducts of **1** and **2** with bromine led to formation of insoluble **5** and **6**.

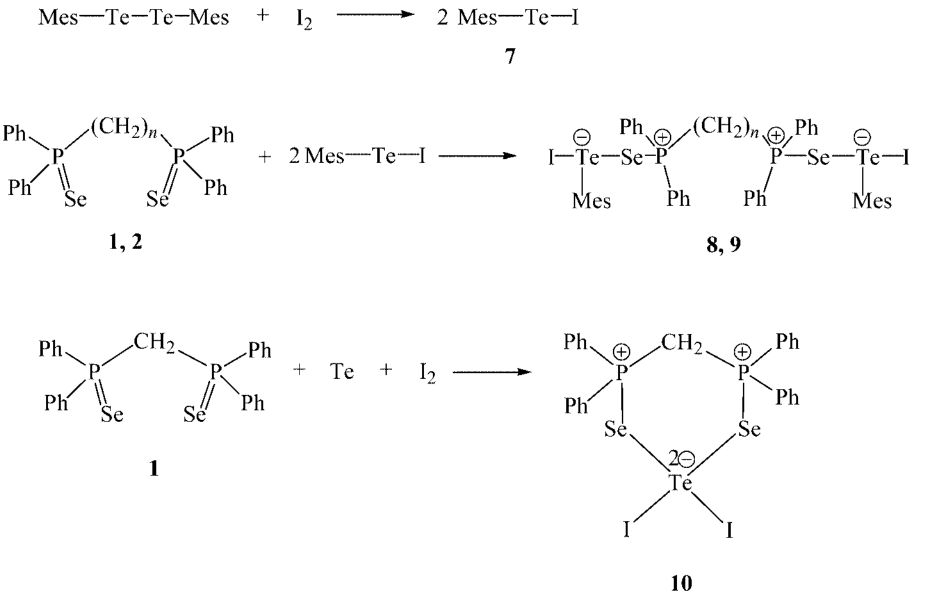
Reactions of $dppmSe_2$ (1) and $dppeSe_2$ (2) with MesTeI (7)

With the intention of exerting control over solubility properties and of introducing the NMR-active ^{125}Te nucleus as an additional probe for solution studies, we decided to include tellurenyl iodides in our study. Arenetellurenyl halides are known to exhibit electrophilic properties towards soft ligands; typically bromide, iodide and S-donor ligands lead to T-shaped complexes. A few phosphane selenide–tellurenyl bromide and chloride complexes have been crystallographically studied,[16,17] but neither a systematic structural study nor any heteronuclear NMR spectroscopic data has yet appeared in the literature. To favour aryl packing in the solid, we chose the in situ generated mesitylenetellurenyl iodide [MesTeI, **7**; Mes = 2,4,6-$(CH_3)_3C_6H_2$][15] as the iodine-related electrophile for coordination with **1** and **2**.

Addition of **1** or **2** to 2 equiv. **7**, prepared from Mes_2Te_2 with I_2, led to compounds **8** and **9**, which were isolated in moderate yields by crystallisation (Scheme 3). Complexes **8** and **9** were characterised by multinuclear NMR spectroscopy in solution, and a single crystal of the $dppeSe_2$ complex **9** was studied by X-ray crystallography.

Attempts to grow single crystals from crude solutions of **8** led to a few single crystals of an unexpected tellurium diiodide chelate complex **10**. Compound **10** was also isolated in small yield from reaction mixtures that were intended to produce a 1:1 complex of **1** with **7**. The ^{31}P NMR spectra of the 1:1 complexes of **1** and **2** with MesTeI show $^{1}J_{^{77}Se,^{31}P}$ coupling constants between those of **1**,**2** and **8**,**9** (Table 1). Compound **10** was also accessible by addition of elemental tellurium and iodine to dissolved **1** (Scheme 3). Fortuitously, upon crystallisation of compound **9**, a single crystal of the related tellurium diiodide complex **11** of ligand **2** was also isolated and studied by X-ray crystallography.

Formation of the TeI_2 complexes **10** and **11** from **7** involves breaking the Te–C bond, but the fate of the "lost" mesityl group remains unclear. Te–C bond cleavage with mesityl group transfer has previously been observed after a bromination/bromide abstraction sequence started with Mes_2Te and led to Mes_3Te^+ SbF_6^- and $Mes_5Te_2^+$ SbF_6^-.[1]



Scheme 3. Reactions of $dppmSe_2$ and $dppeSe_2$ with MesTeI.

Table 1. ^{31}P-, ^{77}Se- and ^{125}Te NMR spectroscopic data of ligands **1**,**2**, acceptor **7** and complexes **8**,**9**,**10** (solvent: CD_2Cl_2, *$CDCl_3$).

	$\delta = {}^{31}P$ [ppm]	$^1J_{P,Se}$ [Hz]	$^nJ_{P,Se}$ [Hz]	$\delta = {}^{77}Se$ [ppm]	$\delta = {}^{125}Te$ [ppm]	$^nJ_{P,P}$ [Hz]
$dppmSe_2$ (**1**)[19,20]	25.8	744.5	2.5	–240.4	–	17.6
$dppmSe_2[Te(I)Mes]_2$ (**8**)	24.1	717.7	–	–161	796	12.4
$dppmSe_2TeI_2$ (**10**)	21.8	682.3	–	–93*	–	8.9
$dppeSe_2$ (**2**)[19]	36.6	730.0	0.7	–353.4	–	64.8
$dppeSe_2[Te(I)Mes]_2$ (**9**)	35.8	711.6	12.2	–281	798	63.7
MesTeI (**7**)	–	–	–	–	867	–
1:1 complex (**1**:**7**)*	24.2	727.5	–	–170	727	–
1:1 complex (**2**:**7**)*	35.6	720.8	–	–	614	–

Thermal decomposition of arenetellurenyl halides can also involve Te–C bond cleavage (loss of tellurium).[15]

NMR Spectroscopic Investigation of Binuclear Complexes 8 and 9

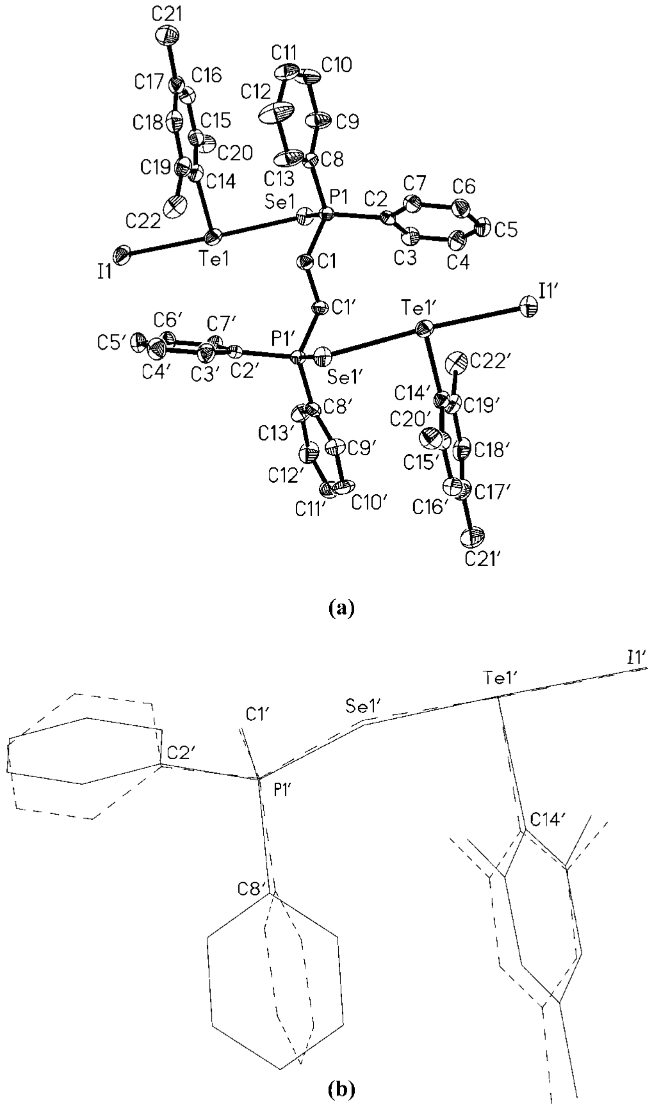
The coordination of phosphane selenides with iodine or the oxidative addition of bromine to phosphane selenides is accompanied by a decrease in the NMR coupling constant $^1J_{^{31}P,^{77}Se}$.[7–10] The same observation is made when the bidentate phosphane selenide **1** reacts with 1 equiv. iodine, and when **1** or **2** coordinate with 2 equiv. mesitylenetellurenyl iodide **7**. Solutions containing **1** or **2** with fewer than 2 equiv. **7** do not give separate ^{31}P NMR signals for the different species in solution, instead averaged signals appear, which also show averaged ^{77}Se satellites. The averaged magnitudes of $^1J_{^{31}P,^{77}Se}$ decrease with increasing amounts of the electrophile **7**. The changes in the ^{77}Se NMR resonances of **1** and **2**[18,19] upon coordination with **7** (deshielding coordination shifts) are much larger than those of the ^{31}P NMR signals (Table 1). The ^{77}Se NMR resonances of **8** and **9** appear as (pseudo) doublets [X-parts of AA′X systems][18–20] due to $J_{^{77}Se,^{31}P}$, but they do not exhibit satellites from coupling with ^{125}Te. Similarly, the broad ^{125}Te NMR signals do not allow the resolution of couplings with ^{31}P: the kinetic lability (fast ligand exchange) of complexes **8** and **9** involves Se–Te bond breaking, whereas P–Se bonds stay intact. In relation to the signals of noncoordinated monomeric alkane- and arenetellurenyl halides [$(Me_3Si)_3CTeI$: $\delta^{125}Te$ = 1185 ppm,[21] 2,4,6-$iPr_3C_6H_2TeI$: $\delta^{125}Te$ = 842 ppm,[15] 2,4,6-$tBu_3C_6H_2TeI$: $\delta^{125}Te$ = 1162 ppm,[15] 2,4,6-$Me_3C_6H_2TeI$: $\delta^{125}Te$ = 867 ppm], the ^{125}Te NMR signals of complexes **8** and **9** are deshielded by about 44–390 ppm. In the case of **8** and **9** and their mixtures with **1** and **2**, the exchange is apparently very fast on the NMR time scale.

X-ray Crystallographic Studies

In solid $dppeSe_2[Te(I)Mes]_2$ (**9**), $dppeSe_2$ acts as a bridging bidentate ligand between two Te(I)Mes acceptor moieties (Figure 1a). The heavy-atom positions correspond to local inversion symmetry (rmsd = 6.6 pm; Figure 1b).

The molecules are packed in a way that allows side-on intermolecular soft–soft interactions between approximately linear Se–Te–I units, thus linking the molecules in chains parallel to the *x* axis (Figure 2).

The Te–I contacts are in the range of the sum of the relevant van der Waals radii. The "T"-type Se–Te(–C)–I



(a)

(b)

Figure 1. (**a**) Structure of dppeSe$_2$[Te(I)Mes]$_2$ (**9**); ellipsoid probability level 50%; all hydrogen atoms omitted for clarity; primes indicate atoms related by pseudosymmetry. (**b**) Least-squares fit of the two halves of molecule **9** (only heavy atoms and *ipso*-C fitted).

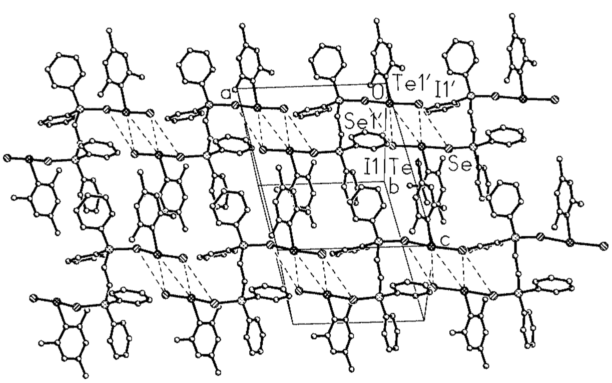


Figure 2. Intermolecular interactions in the packing diagram of **9**; selected contact distances [pm]: Se(1)–I(1′) 404.32(5), I(1′)–Te(1) 398.87(4), Te(1)–Te(1′) 415.83(3), I(1)–Te(1′) 400.35(4), Se(1′)–I(1) 414.30(5).

units deviate slightly from planarity (angles C–Te–Se 90°, C–Te–I 89°, Se–Te–I 173°; for standard deviations see Table 2); Se–Te and Te–I distances are in agreement with typical 3c-4e bonding (10-Te-3,[11] both bond orders are close to 0.5).[15,22,23]

Table 2. Bond lengths, interatomic contact distances [pm] and angles [°] of dppeSe$_2$[Te(I)Mes]$_2$ (**9**).[a]

Te(1)–C(14)	213.2(4)	C(1)–C(1′)	151.8(4)
Te(1)–Se(1)	287.75(4)	Te(1′)–C(14′)	213.8(3)
Te(1)–I(1)	289.61(4)	Te(1′)–I(1′)	288.69(3)
Te(1)–Te(1′)#1	415.83(3)	Te(1′)–Se(1′)	288.74(4)
I(1)–Te(1′)#1	400.35(4)	I(1′)–Te(1)#2	398.87(4)
Se(1)–P(1)	215.13(9)	Se(1′)–P(1′)	215.08(9)
Se(1)–I(1′)#1	404.32(5)	Se(1′)–I(1)#2	414.30(5)
C(14)–Te(1)–Se(1)	91.5(1)	C(1)–P(1)–Se(1)	113.4(1)
C(14)–Te(1)–I(1)	89.85(9)	C(14′)–Te(1′)–I(1′)	88.95(9)
Se(1)–Te(1)–I(1)	172.96(1)	C(14′)–Te(1′)–Se(1′)	89.96(9)
C(14)–Te(1)–Te(1′)#1	155.37(9)	I(1′)–Te(1′)–Se(1′)	172.55(1)
Se(1)–Te(1)–Te(1′)#1	111.30(1)	Te(1′)–I(1′)–Te(1)#2	72.430(8)
I(1)–Te(1)–Te(1′)#1	66.379(8)	P(1′)–Se(1′)–Te(1′)	107.05(3)
Te(1)–I(1)–Te(1′)#1	72.110(8)	P(1′)–Se(1′)–I(1)#2	119.70(3)
P(1)–Se(1)–Te(1)	106.32(3)	Te(1′)–Se(1′)–I(1)#2	66.673(9)
P(1)–Se(1)–I(1′)#1	119.20(2)	C(8′)–P(1′)–Se(1′)	113.4(1)
Te(1)–Se(1)–I(1′)#1	67.996(9)	C(2′)–P(1′)–Se(1′)	110.0(1)
C(2)–P(1)–Se(1)	110.2(1)	C(1′)–P(1′)–Se(1′)	111.7(1)
C(8)–P(1)–Se(1)	112.7(1)		

[a] Symmetry transformations used to generate equivalent atoms: #1: $x - 1, y, z$; #2: $x + 1, y, z$.

The Se–Te bonds in complex **9** are longer (Table 3) than those in chloro- and bromo-phenyl(trimorpholinophosphane selenide)tellurium(II)[16a,16b] and bromophenyl[tris(dimethylamino)phosphane selenide]tellurium(II),[17] and this correlates well with the weaker donor properties of alkyl-/arylphosphane selenides compared with aminophosphane selenides.[16a,16b,17,23] As expected, Se→Te donation is accompanied by P–Se bond expansion (ligand **2**: 209.4 pm,[18b] complex **9**: 215.1 pm).

Table 3. Important bond lengths (P–Se, Se–Te, Te–X) in solid phosphane selenides and phosphane selenidetellurenyl halogenides [pm].

	P–Se	Se–Te	Te–X
dppmSe$_2$ (**1**)[18a]	210.3(1)	–	–
dppeSe$_2$ (**2**)[18b]	209.4(2)	–	–
dppeSe$_2$[Te(I)Mes]$_2$ (**9**)	215.13(9)	287.75(4)	289.61(4)
	215.08(9)	288.74(4)	288.69(3)
dppmSe$_2$TeI$_2$ (**10**)	215.33(8)	284.10(5)	290.67(4)
	214.47(8)	283.00(4)	291.42(4)
dppeSe$_2$TeI$_2$ (**11**)	215.80(4)	280.37(2)	294.28(2)
Mor$_3$PSeTe(Ph)Br[16b]	218.2(2)	276.89(9)	276.1(1)
Mor$_3$PSeTe(Ph)Cl[16b]	217.6(2)	278.27(9)	260.0(2)
[(CH$_3$)$_2$N]$_3$PSeTe(Ph)Br[17]	218.3(2)	276.3(1)	274.4(1)

The chelate complex dppmSe$_2$TeI$_2$ (**10**) contains a distorted square planar *cis*-Se$_2$TeI$_2$ group (12-Te-4) as part of a puckered six-membered heterocycle with two different P–Se–Te angles (95.4 and 102.9°) (Figure 3, Table 4).

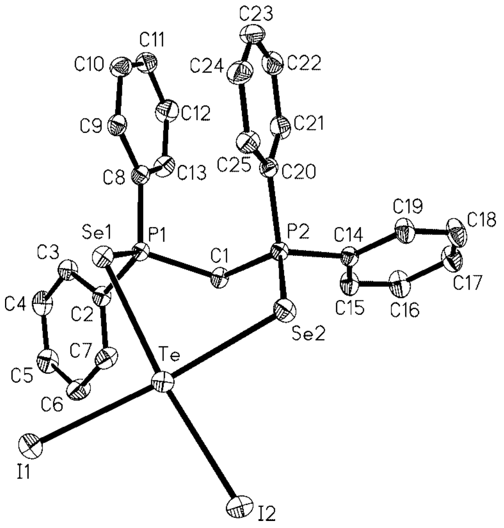


Figure 3. Structure of dppmSe_2TeI_2 (**10**); ellipsoid probability level 50%; all hydrogen atoms omitted for clarity.

Table 4. Bond lengths, interatomic contact distances [pm] and angles [°] of dppmSe_2TeI_2 (**10**).[a]

Te–Se(2)	283.00(4)	Se(2)–I(2)#2	414.98(6)
Te–Se(1)	284.10(5)	P(1)–C(8)	179.7(3)
Te–I(1)	290.67(4)	P(1)–C(2)	179.9(3)
Te–I(2)	291.42(4)	P(1)–C(1)	182.7(3)
Se(1)–P(1)	215.33(8)	P(2)–C(20)	179.7(3)
Se(1)–Se(1)#1	345.42(7)	P(2)–C(14)	179.9(3)
Se(2)–P(2)	214.47(8)	P(2)–C(1)	182.1(3)
Se(2)–Te–Se(1)	86.53(1)	P(2)–Se(2)–I(2)#2	90.09(2)
Se(2)–Te–I(1)	171.38(1)	Te–Se(2)–I(2)#2	147.28(1)
Se(1)–Te–I(1)	90.19(1)	C(8)–P(1)–Se(1)	110.9(1)
Se(2)–Te–I(2)	88.18(1)	C(2)–P(1)–Se(1)	115.4(1)
Se(1)–Te–I(2)	172.01(1)	C(1)–P(1)–Se(1)	112.77(9)
I(1)–Te–I(2)	95.86(1)	C(20)–P(2)–Se(2)	112.6(1)
P(1)–Se(1)–Te	95.34(2)	C(14)–P(2)–Se(2)	111.68(9)
P(1)–Se(1)–Se(1)#1	140.58(2)	C(1)–P(2)–Se(2)	111.93(9)
Te–Se(1)–Se(1)#1	121.91(1)	P(2)–C(1)–P(1)	118.6(2)
P(2)–Se(2)–Te	102.86(2)		

[a] Symmetry transformations used to generate equivalent atoms: #1: –*x* + 1, –*y* +1, –*z*; #2: –*x* + , *y* – ½, –*z* + ½.

A similar kind of distortion is documented in the chelate complexes dppmS_2TeCl_4,[24] dppmSe_2HgI_2,[25] dppmSe_2HgBr_2[25] and dppmSe_2ZnBr_2.[26] The distortion of the tellurium coordination spheres can be explained by the tendency of the ligands dppmE_2 (E = O, S, Se)[18a,27,28] to avoid intramolecular repulsion of the P(=E)Ph_2 groups (**1**: E = Se). In **10** the torsion angle Se(1)P(1)···P(2)Se(2) is 32°. The small bite angle Se(1)–Te–Se(2) (86.5°) is associated with a widening of the opposite angle I(1)–Te–I(2) (95.9°). Se–Te bond lengths in **10** are shorter than those of **9** because of the better acceptor properties of TeI_2 compared with MesTeI. Te–I distances [Te–I(1) 290.6 pm, Te–I(2) 291.4 pm] are slightly longer than those in **9** but shorter than those in the square planar TeI_4^{2-} anion [298.5(2) pm].[29] In the case of bis[(μ_2-iodo)bis(ethyleneselenourea-Se)tellurium] diiodide[30] [Te–Se 261.8(1) pm] and *cis*-diiodobis(thiourea-S)tellurium,[31] Te–I distances

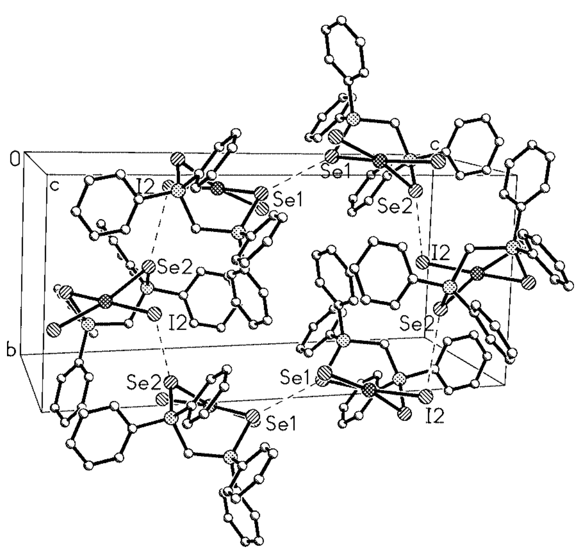
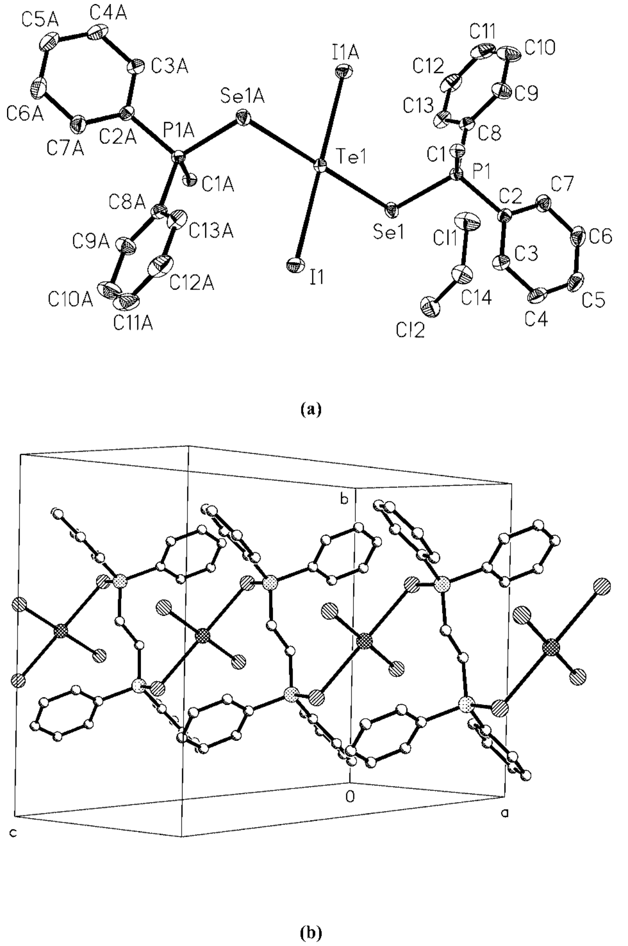


Figure 4. Intermolecular interactions in the packing diagram of **10**; selected contact distances [pm]: Se(1)–Se(1) 345.42(7), Se(2)–I(2) 414.98(6).



(a)

(b)

Figure 5. (**a**) Structure of dppeSe_2TeI_2 (**11**); asymmetric unit; ellipsoid probability level 50%; all hydrogen atoms omitted for clarity. (**b**) Polymeric structure of dppeSe_2TeI_2 (**11**). The chain direction is parallel to the *x* axis.

are very long [325.1(1) and 316.2(1) pm, respectively]. Complex **10** also exhibits intermolecular soft–soft interactions (Figure 4).

The Se(1)–Se(1′) interaction is shorter than the sum of the van der Waals radii and the Se(2)–I(1′) interaction is at the limit of the van der Waals radii. The selenium and iodine atoms exhibit borderline H···Se(I) intermolecular contacts (H···Se 316–334 pm, H···I 296–330 pm).

Complex **11** is a helical coordination polymer with centrosymmetric *trans*-Se_2TeI_2 moieties (12-Te-4) bridged by centrosymmetric dppe units (Figure 5, Table 5).

Table 5. Bond lengths [pm] and angles [°] of dppeSe_2TeI_2 (**11**).[a]

Te(1)–Se(1)	280.37(2)	P(1)–C(2)	180.4(2)
Te(1)–I(1)	294.28(2)	P(1)–C(1)	182.4(2)
Se(1)–P(1)	215.80(4)	C(1)–C(1)#2	153.0(3)
P(1)–C(8)	179.9(2)		
Se(1)–Te(1)–Se(1)#1	180.0	I(1)–Te(1)–I(1)#1	180.0
Se(1)–Te(1)–I(1)	86.834(5)	P(1)–Se(1)–Te(1)	102.74(1)
Se(1)#1–Te(1)–I(1)	93.167(5)	C(8)–P(1)–Se(1)	113.29(5)
Se(1)–Te(1)–I(1)#1	93.165(5)	C(2)–P(1)–Se(1)	106.89(5)
Se(1)#1–Te(1)–I(1)#1	86.833(6)	C(1)–P(1)–Se(1)	112.49(5)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, -y, -z$; #2: $-x, -y, -z$.

The tellurium atom lies on the inversion centre ½, 0, 0 and the midpoint of the C1–C1′ bond lies on 0, 0, 0. Compared with the distorted chelate complex **10**, the coordination polymer **11** exhibits Se–Te bonds shorter by 3–4 pm and Te–I bonds longer by 3–4 pm. The coordination environment of Te in **11** deviates from square by expansion of the angle Se(1)–Te–I(1)#1 (93.2°) and compression of the angle Se(1)–Te–I(1) (86.8°). Among the three compounds **9**, **10** and **11**, the latter exhibits the shortest coordinative Se–Te bond (280.3 pm). The Te–I bond lengths are close to those in *trans*-diiodobis(tetramethylselenourea-Se)tellurium (*trans*-Se_2TeI_2 moieties) [295.4(1) pm][31] [Te–Se 282.1(1) pm], and are also similar to Te–I bonds in related *trans*-S_2TeI_2 moieties (293.3–298.2 pm).[32]

Vibrational Spectra

FT-Raman spectroscopy is the main method of investigating the nature of the products obtained by the reactions of dihalogens/interhalogens with donor molecules containing 15- and 16-group elements in the absence of X-ray structural data.[33–38]

Among the compounds reported here, **3**–**6** are molecular adducts of dppm and dppe with Br_2 and I_2, while **8**–**11** are obtained by reacting the same ligands with MesTeI. No crystallographic data are available for **3**–**6**, but structural information can be obtained by comparing their FT-Raman spectra with those of several structurally characterised I_2 and Br_2 adducts with Se-donor molecules.[33–38] In contrast, no FT-Raman data are available from the literature for compounds similar to **8**–**11**, but the knowledge of the crystal structures of **9**–**11** allows a first tentative correlation between structural and FT-Raman data for these compounds.

Compounds **3** and **5** have similar FT-Raman spectra with two peaks at 144 and 195 cm^{-1} for **3**, and at 157 and 191 cm^{-1} for **5**, which agree with the presence of asymmetric Br–Se–Br groups in both compounds.[13,38,39]

The FT-Raman spectra of the corresponding adducts with I_2, **4** and **6**, differ from each other; compound **4** has a strong peak at 116 cm^{-1} accompanied by a weaker peak at 145 cm^{-1}, whereas **6** has two well-defined peaks at 145 and 152 cm^{-1} (see Figure 6).

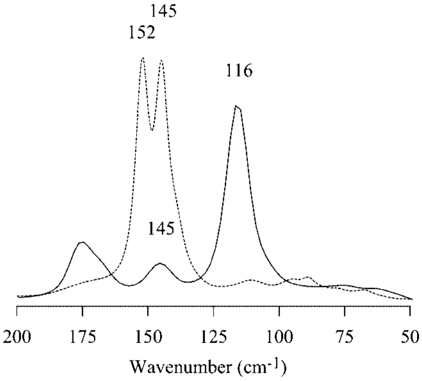


Figure 6. FT-Raman spectra of **4** (solid line) and **6** (dotted line).

The spectrum of **4** indicates the presence of asymmetric linear I–Se–I moieties,[35] whereas the spectrum of **6** is more consistent with a charge-transfer nature, characterised by the presence of linear Se–I–I groups. Strong I_2-charge-transfer adducts with selenium-donor molecules generally feature two bands in their FT-Raman spectra near 150 and 130 cm^{-1} which are assigned to the antisymmetric and symmetric stretching modes, respectively, of the Se–I–I system.[34,35,37]

Complexes **8** and **9** have similar FT-Raman spectra with a strong peak at 126 cm^{-1} accompanied by a weaker shoulder at 142 cm^{-1} for **8**, and, correspondingly, at 129 and 146 cm^{-1} for **9** (see Figure 7 for the FT-Raman spectrum of **8**).

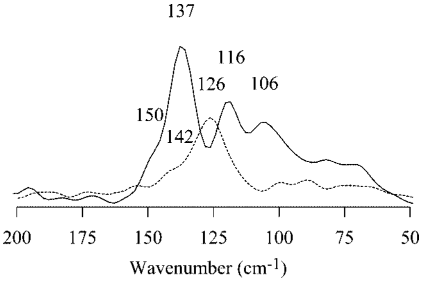


Figure 7. FT-Raman spectra of **8** (dotted line) and **10** (solid line).

On the basis of this similarity, it is possible to infer that the structural features of **8** are analogous to those of **9**; therefore, for both compounds the two FT-Raman peaks should be tentatively assigned to the symmetric and antisymmetric stretching vibrations of the Se–Te–I system. As already mentioned, these assignments cannot be supported by any data from the literature.[40] Significantly, the FT-Raman peaks observed for **8** and **9** occur at frequencies close to those normally observed for the peaks typical of strong charge-transfer adducts featuring linear Se–I–I groups. Therefore, the two systems Se–Te–I and Se–I–I appear to have a similar vibrational behaviour.

The spectrum of **10** shows four peaks at 150 (shoulder), 137, 116 and 106 cm^{-1} in good agreement with its structural features (see Figure 7). In fact, by approximating the local symmetry around the Te atom to the C_{2v} point group, four Raman-active stretching vibration modes are to be expected. Therefore, on the basis of the different atomic weight of Se and I, the peaks at 106 and 116 cm^{-1} should have a predominant contribution from the symmetric and antisymmetric stretching modes of the TeI_2 group, respectively, while the peaks at 137 and 150 cm^{-1} should have a predominant contribution from the analogous vibrations of the $TeSe_2$ group.

The local symmetry around the Te atom in **11** can be approximated instead to the D_{2h} point group, and only the A_g vibrations for the linear I–Te–I and Se–Te–Se groups should be Raman-active. Indeed, the FT-Raman spectrum of **11** shows a very strong peak at 110 cm^{-1} and a much weaker peak at around 150 cm^{-1}. Also in this case, the peak at lower frequency should have a predominant contribution from the symmetric stretching vibration of the I–Te–I moiety, whereas that at higher frequency should have a predominant contribution from the symmetric stretching vibration of the Se–Te–Se moiety. This assignment can be considered as reasonable since the symmetric I–Te–I and Se–Te–Se groups are structurally comparable to the symmetric I_3^- and IBr_2^-, respectively. Indeed, I_3^- and IBr_2^-, when symmetric, are characterised by only one Raman peak at around 110 and 160 cm^{-1}, respectively.[37,38,41]

Unfortunately, the quality of the FTIR spectra for all the compounds considered prevents any further discussion.

Experimental Section

NMR spectra were recorded using Bruker spectrometers AC 200, Avance 200, Avance 400 and AMX 300, with 85% H_3PO_4, $(CH_3)_2Se$, $(CH_3)_2Te$ and $SiMe_4$ as external or internal standards.

FT-Raman spectra, in the range 500–50 cm^{-1}, were recorded with a resolution of 2 cm^{-1} with a Bruker RFS100 FT-Raman spectrometer, fitted with an In-Ga-As detector (room temp.) operating with a Nd-YAG laser (excitation wavelength 1064 nm; 50–100 mW), with a 180° scattering geometry. The values in parentheses next to the wavenumber values reported for each compound represent the intensities of the peaks relating to the strongest, taken to be 10.

3: Diselenide **1** (1.08 g, 2.0 mmol) was dissolved in dichloromethane (20 mL) and a solution of bromine (0.63 g, 4.0 mmol) in dichloromethane (20 mL) was added. The reaction mixture was stirred at room temp. for 2 h, after which the raw product **3** was isolated by vacuum evaporation of the solvent, and purified by washing with pentane and drying under vacuum evaporation. An orange dppm$(SeBr_2)_2$ complex was obtained. Yield: 1.53 g, 89%; m.p. 133–134 °C. $C_{25}H_{22}Br_4P_2Se_2$ (861.93): calcd. C 34.84, H 2.57; found C 34.19, H 2.34. FT-Raman: $\tilde{\nu}$ = 195 (10), 144 (10) cm^{-1}.

4: Diselenide **1** (1.08 g, 2.0 mmol) was dissolved in dichloromethane (20 mL) and a solution of iodine (1.01 g, 4.0 mmol) in dichloromethane (20 mL) was added. The reaction mixture was stirred at room temp. for 3 h, after which the raw product **4** was isolated by vacuum evaporation of the solvent, and purified by washing with pentane and drying under vacuum evaporation. A red dppm$(SeI_2)_2$ complex was obtained. Yield: 1.93 g, 92%; m.p. 138–139 °C. $C_{25}H_{22}I_4P_2Se_2$ (1049.23): calcd. C 28.60, H 2.11; found C 28.57, H 2.06. FT-Raman: $\tilde{\nu}$ = 145 (2), 116 (10) cm^{-1}.

5: Diselenide **2** (1.11 g, 2.0 mmol) was dissolved in dichloromethane (20 mL) and a solution of bromine (0.63 g, 4.0 mmol) in dichloromethane (20 mL) was added. The reaction mixture was stirred at room temp. for 2 h, after which the raw product **5** was isolated by vacuum evaporation of the solvent, and purified by washing with pentane and drying under vacuum evaporation. A yellow dppe$(SeBr_2)_2$ complex was obtained. Yield: 1.66 g, 95%; m.p. 148–149 °C. $C_{26}H_{24}Br_4P_2Se_2$ (875.95): calcd. C 35.05, H 2.76; found C 34.98, H 2.98. FT-Raman: $\tilde{\nu}$ = 191 (9.5), 157 (10) cm^{-1}.

6: Diselenide **2** (1.11 g, 2.0 mmol) was dissolved in dichloromethane (20 mL) and a solution of iodine (1.01 g, 4.0 mmol) in dichloromethane (20 mL) was added. The reaction mixture was stirred at room temp. for 2.5 h, after which the raw product **6** was isolated by vacuum evaporation of the solvent, and purified by washing with pentane and drying under vacuum evaporation. A red dppe$(SeI_2)_2$ complex was obtained. Yield: 1.96 g, 92%; m.p. 197–198 °C. $C_{26}H_{24}I_4P_2Se_2$ (1063.95): calcd. C 29.35, H 2.27; found C 29.29, H 2.23. FT-Raman: $\tilde{\nu}$ = 152 (10), 145 (10) cm^{-1}.

8: Dimesityl ditelluride (0.99 g, 2.0 mmol) was dissolved in dichloromethane (20 mL) and a solution of iodine (0.51 g, 2.0 mmol) in dichloromethane (10 mL) was added. The reaction mixture was added to a solution of diselenide **1** (1.08 g, 2 mmol) in dichloromethane and was stirred for 24 h at room temp., after which the raw product **8** was isolated by vacuum evaporation of the solvent, and purified by washing with pentane, drying under vacuum evaporation and recrystallised by gas diffusion from dichloromethane/pentane. Yield: 1.93 g, 75%; m.p. 77–78 °C. $C_{43}H_{44}I_2P_2Se_2Te_2$ (1289.69): calcd. C 40.05, H 3.44; found C 39.80, H 3.44. ^{31}P NMR (CD_2Cl_2): δ = 24.1 (s, $^1J_{P,Se}$ = 717.7 Hz, $^2J_{P,P}$ = 12.4 Hz, 2 P) ppm. ^{77}Se NMR (CD_2Cl_2): δ = –161 (br. d, $^1J_{Se,P}$ = 750 ± 50 Hz) ppm. ^{125}Te NMR (CD_2Cl_2): δ = 796 (br. s) ppm. ^{1}H NMR (CD_2Cl_2): δ = 2.2 (s, 6 H), 2.5 (s, 12 H), 4.3 (t, $J_{H,P}$ = 13.1 Hz, 2 H), 6.9 (s, 4 H), 7.3 (m, 8 H), 7.4 (m, 4 H), 7.6 (m, 8 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.3 (s, 2 C), 31.2 (s, 4 C), 34.2 (s, 1 C), 117.5 (s, 2 C), 127.5 (s, 4 C), 127.8 (s, 4 C), 129.2 (t, $J_{C,P}$ = 6.6 Hz, 8 C), 132.8 (t, $J_{C,P}$ = 5.9 Hz, 8 C), 141.4 (s, 2 C), 147.2 (s, 4 C) ppm. FT-Raman: $\tilde{\nu}$ = 142 (5), 126 (10) cm^{-1}.

9: Dimesityl ditelluride (0.99 g, 2.0 mmol) was dissolved in dichloromethane (20 mL) and a solution of iodine (0.51 g, 2.0 mmol) in dichloromethane (10 mL) was added. The reaction mixture was added to a solution of diselenide **2** (1.11 g, 2 mmol) in dichloromethane and was stirred for 24 h at room temp., after which the raw product **9** was isolated by vacuum evaporation of the solvent, and purified by washing with pentane, drying under vacuum evaporation and recrystallised by gas diffusion from dichloromethane/pentane. Yield: 2.00 g, 77%; m.p. 158–159 °C. $C_{44}H_{46}I_2P_2Se_2Te_2$ (1303.67): calcd. C 40.54, H 3.56; found C 39.00, H 3.57. ^{31}P NMR (CD_2Cl_2): δ = 35.8 (s, $^1J_{P,Se}$ = 711.6 Hz, $^3J_{P,P}$ = 63.7 Hz, $^4J_{P,Se}$ = 12.2 Hz, 2 P) ppm. ^{77}Se NMR (CD_2Cl_2): δ = –281 (br. d, $^1J_{Se,P}$ = 690 ± 50 Hz) ppm. ^{125}Te NMR (CD_2Cl_2): δ = 798 (br. s) ppm. ^{1}H NMR (CD_2Cl_2): δ = 2.4 (s, 6 H), 2.7 (s, 12 H), 2.9 (d, $^2J_{H,P}$ = 2.3 Hz, 4 H), 7.03 (s, 4 H), 7.5 (m, 8 H), 7.6 (m, 4 H), 7.8 (m, 8 H) ppm. ^{13}C NMR (CD_2Cl_2): δ = 21.1 (s, 2 C), 25.3 (s, 2 C), 30.1 (s,

Table 6. Crystallographic data.

Compound	**9**	**10**	**11**
Formula	$C_{44}H_{46}I_2P_2Se_2Te_2$	$C_{25}H_{22}I_2P_2Se_2Te$	$C_{28}H_{28}Cl_4I_2P_2Se_2Te$
M_r	1303.67	923.69	1107.56
Habit	red prism	red prism	red tablet
Crystal size [mm]	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.6 × 0.5 × 0.18
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/n$	$P2_1/n$
Cell constants			
a [pm]	1017.60(6)	1309.0(2)	757.13(4)
b [pm]	1917.2(1)	979.0(1)	1313.67(8)
c [pm]	1190.25(8)	2254.7(3)	1819.0(1)
β [°]	102.9(3)	103.8(3)	101.2(3)
V [nm^3]	2.2635(2)	2.8054(7)	1.7751(2)
Z	2	4	2
D_x [Mg m^{-3}]	1.913	2.187	2.072
μ [mm^{-1}]	4.3	5.9	5.0
$F(000)$	1236	1712	1040
T [°C]	–140	–140	–140
$2\theta_{max}$	60	60	61
Reflections measured	46435	52343	37457
Reflections independent	13698	8559	5410
Transmissions	0.829–0.928	0.555–0.928	0.714–0.928
R_{int}	0.023	0.047	0.019
Parameters	476	289	178
Restraints	1	0	0
wR (F_2, all reflections)	0.063	0.092	0.042
R [F, $>4\sigma(F)$]	0.027	0.034	0.017
S	0.99	1.06	1.07
Max. $\Delta\rho$ [e nm^{-3}]	1774	2464	975

4 C), 116.2 (s, 2 C), 127.4 (s, 4 C), 129.3 (t, $^2J_{C,P}$ = 6.1 Hz, 8 C), 129.4 (s, 4 C), 132.0 (t, $^3J_{C,P}$ = 5.6 Hz, 8 C), 142.1 (s, 2 C), 147.3 (s, 4 C) ppm. FT-Raman: $\tilde{\nu}$ = 146 (7.6), 129 (10) cm^{-1}.

10: Diselenide **1** (0.99 g, 2.0 mmol) was dissolved in dichloromethane (20 mL). Tellurium (0.26 g, 2 mmol) and iodine (0.51 g, 2.0 mmol) were added. The reaction mixture was stirred for 4 d at room temp., after which the raw product **10** was isolated by vacuum evaporation of the solvent, and purified by washing with pentane, drying under vacuum evaporation and recrystallised by gas diffusion from dichloromethane/hexane. Yield: 1.61 g, 85%; m.p. 192–193 °C. $C_{25}H_{22}I_2P_2Se_2Te$ (923.69): calcd. C 32.51, H 2.40; found C 32.07, H 2.40. ^{31}P NMR (CD_2Cl_2): δ = 21.8 (s, $^1J_{P,Se}$ = 682.3 Hz, $^2J_{P,P}$ = 8.9 Hz) ppm. ^{77}Se NMR ($CDCl_3$): δ = –93 (br. d, $^1J_{Se,P}$ = 653 ± 50 Hz) ppm. FT-Raman: $\tilde{\nu}$ = 150 (3, shoulder), 137 (10), 116 (6) and 106 (5) cm^{-1}.

Structure Determinations: Numerical details are presented in Table 6. All X-ray data were collected with monochromated Mo-K_α radiation (λ = 0.71073 Å) on a Bruker SMART 1000 CCD area detector. Absorption corrections were based on multiple scans. The structures were solved by direct methods and refined anisotropically by full-matrix least-squares on F^2 (Program SHELXTL: Prof. G. M. Sheldrick, Univ. of Göttingen). Hydrogen atoms were included using a riding model (except methyl groups which were refined as rigid groups). Structure **9** was refined as a racemic twin. Structure **11** contains one ordered molecule of dichloromethane per asymmetric unit. CCDC-289068 (for **9**), -289069 (for **10**) and -289070 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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