# Bromination and Iodination of Diphosphane Dichalcogenides

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## Supplementary Material

# 1. Packing diagrams of compounds 2, 3, 5, 6, 10, 11, 12, 13, 14

Most of the compound described in the main part of this paper display a number of C—H☐Hal contacts (especially from the central carbons between the phosphorus atoms). Here, however, we mainly concentrate on halogen☐halogen contacts and other types of "soft-soft" interaction.

Compound **2** displays two borderline I☐I contacts, I2☐I4 3.9123(3) and 3.9377(3) Å, via the operators ½–$x$, ½+$y$, ½–$z$ and –½+$x$, 1½–$y$, ½+$z$ respectively.

For compound **3**, the molecules are connected to form chains parallel to [101] by the contact Se1☐Br1(1–$x$, $y$, 1.5–$z$) 3.4548(4) Å (Fig. S1).
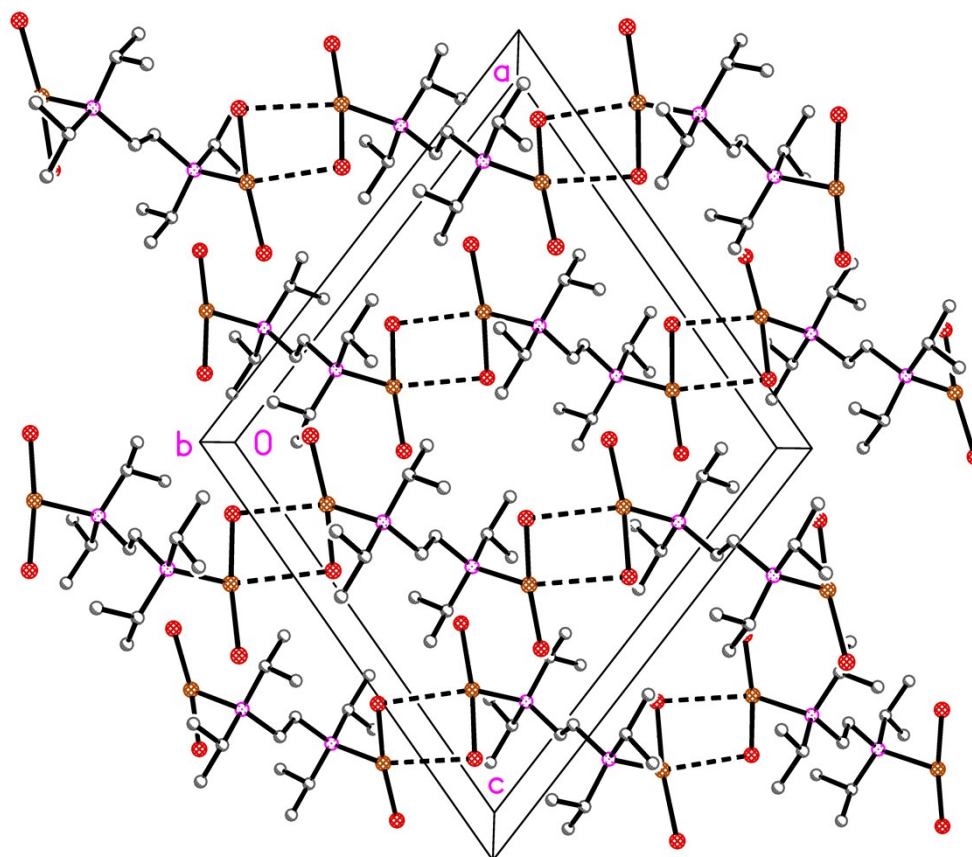


Fig. S1. Packing diagram of compound **3** viewed parallel to the $b$ axis. Short Se☐Br contacts are indicated by dashed lines.

Compound **5** has several Br☐Br contacts apart from those in the asymmetric unit. A complete list is given in Table S1. Fig. S2 shows part of the layer structure, including all contacts up to 3.87 Å (excluding 1,3-type contacts). The very short contact Br8☐Br8 can be recognised at the centre of Br$_4$ rhombuses. The contact Br7☐Br12 connects adjacent layers in the thord dimension.
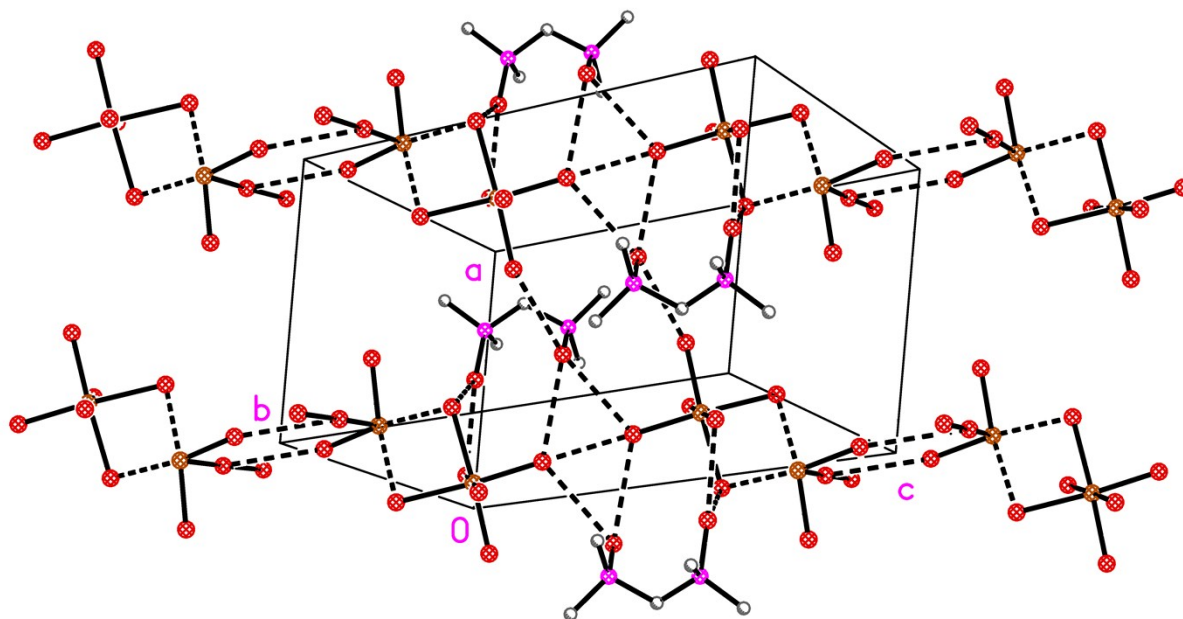
Fig. S2. Packing diagram of compound **5** viewed perpendicular to (011). Short contacts are indicated by dashed lines. Phenyl rings are reduced to the *ipso* carbons for clarity.

Table S1. Br⋯Br contacts for compound **5**.

| Contact | Distance (Å) | Operator |
|---|---|---|
| Br1⋯Br3 | 3.5911(7) | |
| Br1⋯Br7 | 3.3783(8) | |
| Br1⋯Br9 | 3.9542(7) | |
| Br2⋯Br8 | 3.8678(8) | |
| Br2⋯Br6 | 3.5746(8) | $x–1, y, z$ |
| Br2⋯Br8 | 3.7302(8) | $–x+2, –y+1, –z+1$ |
| Br7⋯Br12 | 3.3410(7) | $x, y+1, z$ |
| Br8⋯Br8 | 3.2402(9) | $–x+2, –y+1, –z+1$ |
| Br10⋯Br10 | 3.8969(10) | $–x+2, –y, –z+2$ |
| Br10⋯Br11 | 3.7065(6) | $–x+2, –y, –z+2$ |
| Br10⋯Br12 | 3.9189(7) | $–x+2, –y, –z+2$ |

Compound **6** also displays several Br⋯Br and also Se⋯Br contacts (Table S2). The packing is quite complex, but can be broken down into two sections. The $SeBr_4$ and tribromide residues combine to form ribbons parallel to the *x* axis in the region $z \approx 0$ (Fig. S3). The residues based on the diphosphine and on Se1 assemble in the region $z \approx \frac{1}{2}$ (Fig. S4).
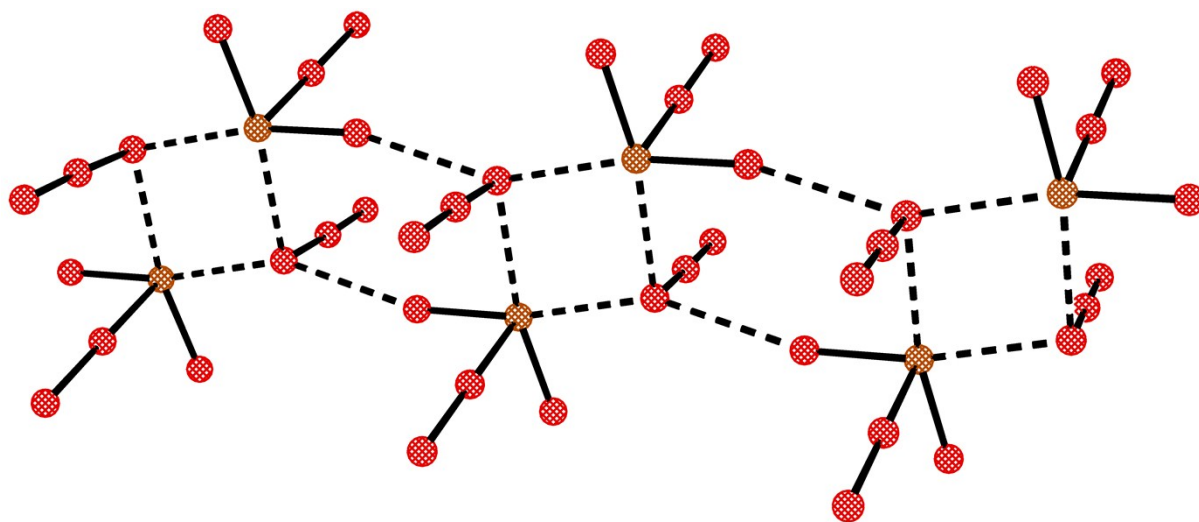
Fig. S3. Packing diagram of compound **6**; ribbon of SeBr$_4$ residues and tribromide ions. Short contacts are indicated by dashed lines.


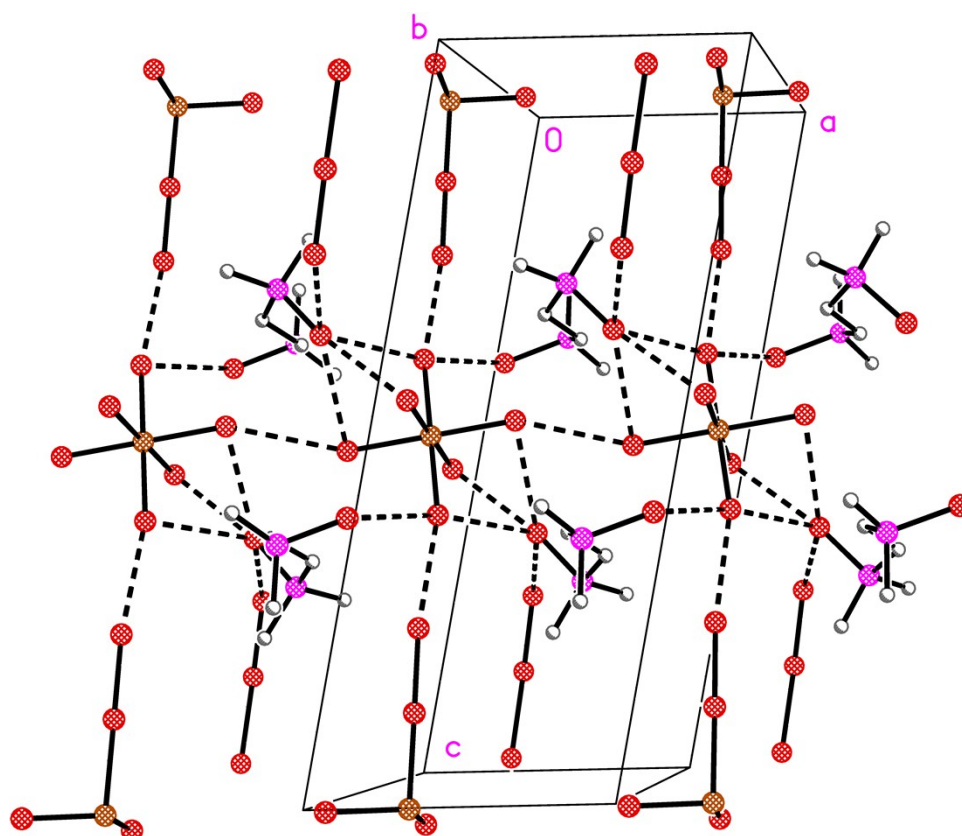
Fig. S4. Packing diagram of compound **6**; ribbon of diphosphine and Se1 residues (parallel to the *a* axis in the region $z \approx \frac{1}{2}$) viewed perpendicular to the *ac* plane. Some SeBr$_4$ and tribromide residues are shown in the regions $z \approx 0$ and 1. Short contacts are indicated by dashed lines.

Table S2. Br☐Br and Se☐Br contacts for compound **6**.

| Contact | Distance (Å) | Operator |
|---------|--------------|----------|
| Br2☐Br3 | 3.3783(7) | |
| Br2☐Br4 | 3.8189(6) | |
| Br2☐Br5 | 3.8085(6) | |
| Br5☐Br12 | 3.4137(7) | |
| Se2☐Br6 | 2.9850(7) | |
| Br1☐Br5 | 3.8611(7) | $x+1, y, z$ |
| Br2☐Br8 | 3.7394(7) | $-x+1, -y+1, -z+2$ |
| Br4☐Br4 | 3.7063(9) | $-x+1, -y+1, -z+1$ |
| Br6☐Br6 | 3.9438(10) | $-x+1, -y+2, -z+2$ |
| Br6☐Br10 | 3.3520(7) | $x+1, y, z$ |
| Br6☐Se2 | 3.1288(8) | $-x+1, -y+2, -z+2$ |
| Br7☐Br11 | 3.9223(7) | $-x+1, -y+2, -z+2$ |
| Br10☐Br10 | 3.9546(10) | $-x, -y+2, -z+2$ |

Compound **10** forms broad ribbons parallel to the *ac* plane (Fig. S5). In the centre of the ribbons, the cations form dimers via Se☐Br interactions; the tribromide ions are attached at the periphery by hydrogen bonds C–H$_{methano}$☐Br.
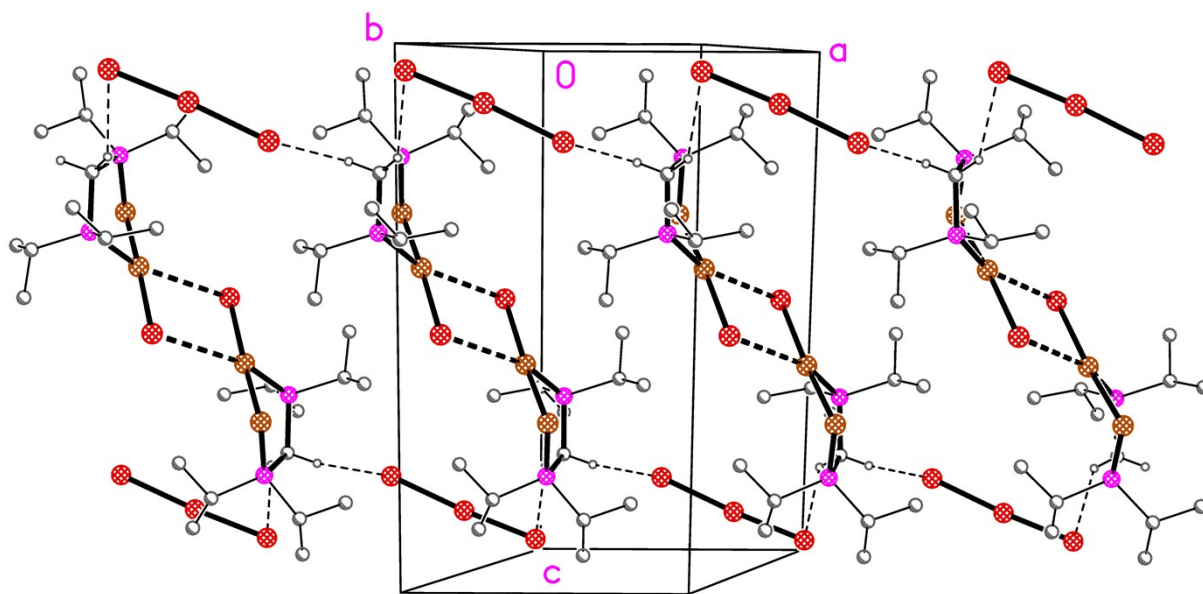


Fig. S5. Packing diagram of compound **10** viewed perpendicular to the *ac* plane. Dashed lines indicate Se☐Br contacts (thick) or hydrogen bonds C−H☐Br (thin).

Compound **11** forms a cation chain structure parallel to [101], via the contacts Se1☐Br2($-x$, $-y$, $-z$) 3.3866(7) and Br1☐Br3($-x$, $-y$, $1-z$) 3.6910(9) Å (Fig. S6). The bromide anions Br4 are not involved in such contacts. The further, borderline, contacts Br1☐Br1($-x$, $-y$, $-z$) 3.9607(13), Br2☐Br3($x$, $y$, $-1+z$) 3.9024(8) and Br2☐Br2($-x$, $-y$, $-z$) 3.9758(10) Å (the latter across the Se$_2$Br$_2$ rhombuses) are not included in the Figure.
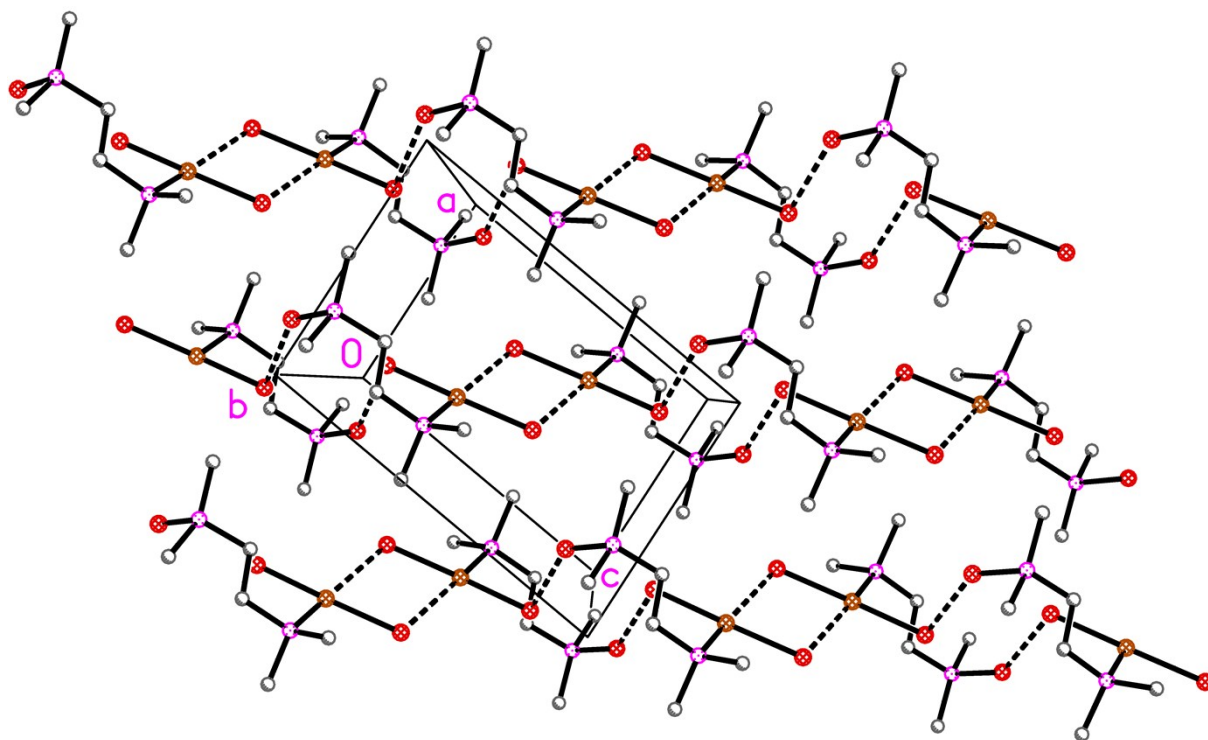
Fig. S6. Packing diagram of compound **11** viewed perpendicular to the *ac* plane. Short Br⬚Br and Se⬚Br contacts are indicated by dashed lines. Methyl carbons are omitted for clarity.

Compound **12** forms a layer structure parallel to the *ab* plane, whereby the contacts Br1⬚Br3 3.8630(4), Br1⬚Br3(–*x*, –*y*, 1–*z*) 3.8565(5) and Br3⬚Br3(–*x*, –*y*, 1–*z*) 3.7360(6) Å combine to form Br$_4$ rhombuses (Fig. S7).

Compound **13** is a dichloromethane solvate; the dichloromethane is well-ordered and forms chains of molecules parallel to the *a* axis with Cl98⬚Cl98 (1–*x*, 1–*y*, 2–*z*) 3.492(2) and Cl99⬚Cl99 (–*x*, 1–*y*, 2–*z*) 3.457(2) Å (Fig. S8).

For compound **14**, an S1⬚S1 contact of 3.686(2) Å via the twofold axis (–*x*, *y*, ½–*z*) connects the cations in pairs. For compound **15**, apart from the two Br⬚Br contracts within the asymmetric unit, a short S1⬚Br1 contact of 3.4215(6) Å links the cations via **b** translation (Fig. S9).
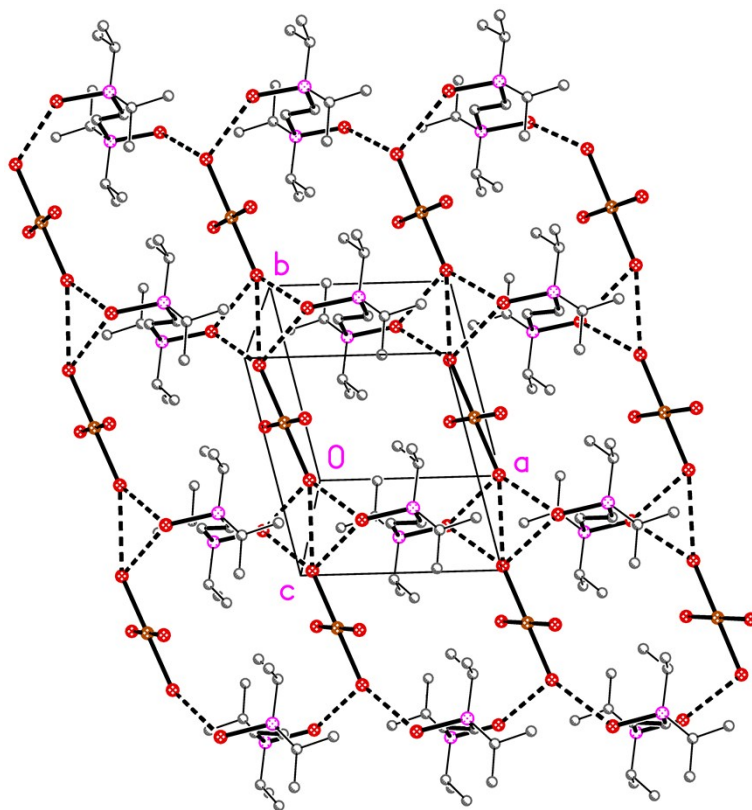
Fig. S7. Packing diagram of compound **12** viewed perpendicular to the *ab* plane. Short Br☐Br contacts are indicated by dashed lines.
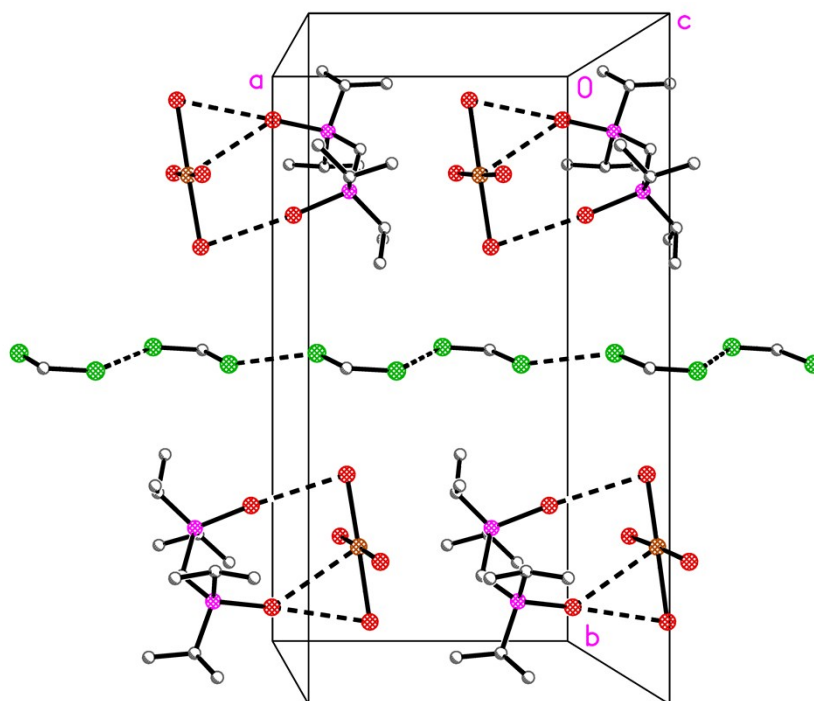


Fig. S8. Packing diagram of compound **13** viewed perpendicular to the *ab* plane at $z \approx 0$. Short contacts are indicated by dashed lines.
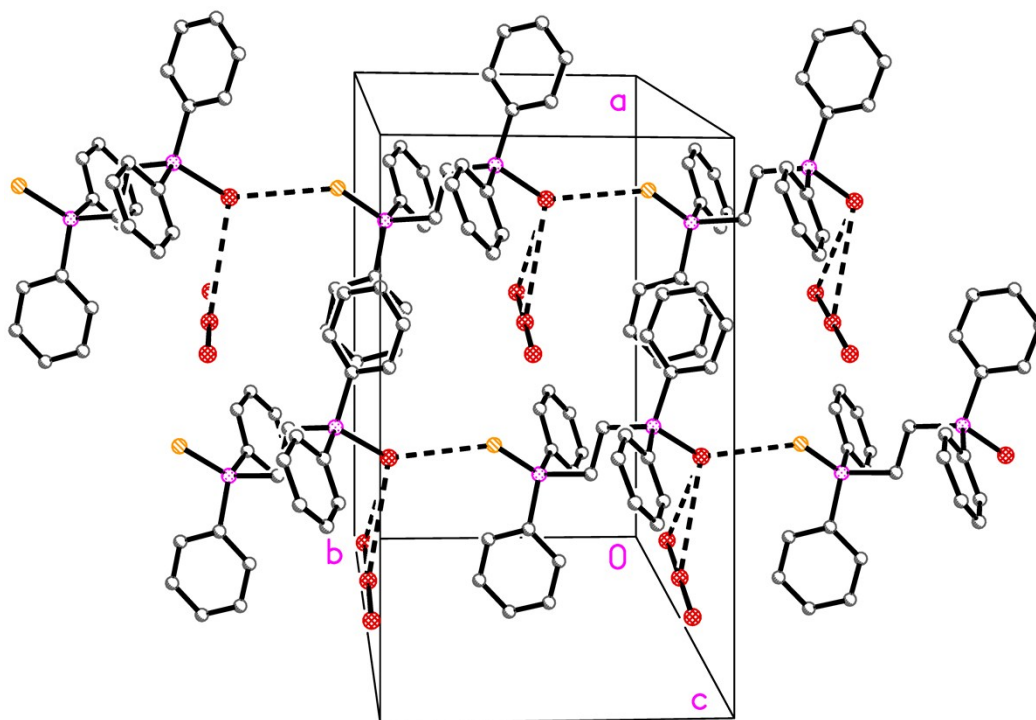
Fig. S9. Packing diagram of compound **15** viewed (approximately) perpendicular to the *ab* plane. Short Br⋯Br contacts are indicated by dashed lines.

# 2. X-Ray structure determinations of the oxygen-containing by-products 16–19.

Halogen derivatives of phosphine chalcogenides are (in)famous for their sensitivity to moisture and the related tendency to form hydrolysis products containing P=O and P—OH groups.[1-4]

The structures were determined as described in the main paper; data for compound **19** were measured using Cu $K\alpha$ radiation.

CCDC 1496346-1496349 contain the supplementary crystallographic data for compounds **16-19** (in the same order). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/.

**Structure of compound 16, [d$^i$prpm(O)(OH)$^+$]$_2$ [Se$_2$Br$_6$]$^{2-}$**

Crystal data for **16**: $C_{26}H_{62}Br_6O_4P_4Se_2$, $M = 1200.02$, triclinic, $a = 10.2092(4)$, $b = 13.8414(5)$, $c = 16.6253(6)$ Å, $\alpha = 81.773(4)$, $\beta = 73.151(4)$, $\gamma = 73.308(4)°$, $V = 2149.10$ Å$^3$, space group $P\bar{1}$, $Z = 2$, 163196 reflections measured, 12992 independent ($R_{int} = 0.052$). Final $R(F)$ 0.0270 ($I > 2\sigma(I)$); final $wR(F^2)$ 0.0518 (all data). See Fig. S10.
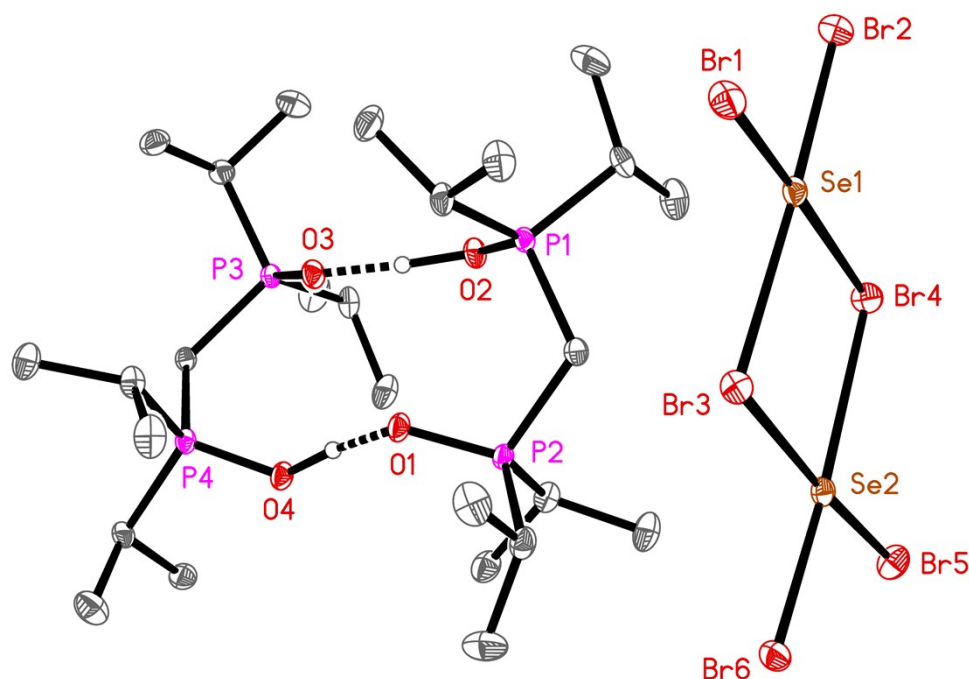


Fig. S10. Structure of compound **16** in the crystal; ellipsoids correspond to 50% probability levels. Dashed lines indicate hydrogen bonds. Only one position of the disordered isopropyl group is shown. Hydrogen atoms (except OH) are omitted. Selected bond lengths (Å): Br1-Se1 2.4275(3), Br2-Se1 2.4590(3), Br3-Se1 2.7719(3), Br3-Se2 2.8497(3), Br4-Se1 2.8221(3), Br4-Se2 2.8549(3), Br5-Se2 2.4169(3), Br6-Se2 2.4087(3). Contact distances (Å): O2⋯O3 2.422(2), O4⋯O1 2.418(2).

One isopropyl group is disordered over two positions. The OH hydrogens have slightly high $U$ values and somewhat long OH bond lengths and might be slightly disordered. It is often difficult to distinguish between ordered unsymmetrical POH☐O=P and symmetrical PO☐H☐OP hydrogen bond systems (or a disordered mixture of both) using X-ray methods.

## Structure of compound 17, [d$^i$prpm(O)(OH)$^+$]$_2$ [Se$_2$Br$_4$]$^{2-}$

Crystal data for **17**: C$_{26}$H$_{62}$Br$_4$O$_4$P$_4$Se$_2$, $M$ = 1040.20, monoclinic, $a$ = 29.346(2), $b$ = 13.8633(5), $c$ = 20.2475(8) Å, $\beta$ = 99.575(4)°, $V$ = 8122.5 Å$^3$, space group $C2/c$, $Z$ = 8, 104958 reflections measured, 11785 independent ($R_{int}$ = 0.068). Final $R(F)$ 0.0353 ($I > 2\sigma(I)$), final $wR(F^2)$ 0.0698 (all data). See Fig. S11.

Two isopropyl groups are disordered over two positions. As for **16**, there is some uncertainty as to the exact positions of the OH hydrogens, but the short contacts O2☐O3 2.411(3), O1☐O1 2.418(3) (over a twofold axis) and O4☐O4 2.423(3) Å (over an inversion centre) clearly indicate strong classical hydrogen bonding. The cationic part of the structure is an undulating hydrogen-bonded chain polymer with overall direction parallel to [101] (Fig. S12), in contrast to the isolated cation pairs in **16**.

Perhaps the most interesting feature are the [Se$_2$Br$_4$]$^{2-}$ anions, formally involving Se$^I$; these had not been previously observed by X-ray diffraction, although there is one structure containing the corresponding [Se$_2$Cl$_4$]$^{2-}$ anion.[5] There is a marked disparity between the bond lengths Se1-Br2, Se2-Br3 (ca. 2.5 Å) and Se1-Br1, Se2-Br4 (ca. 2.75 Å). The two SeBr$_2$ groups subtend an interplanar angle of 88.59(3)°, although the planes are poorly defined for almost linear moieties.
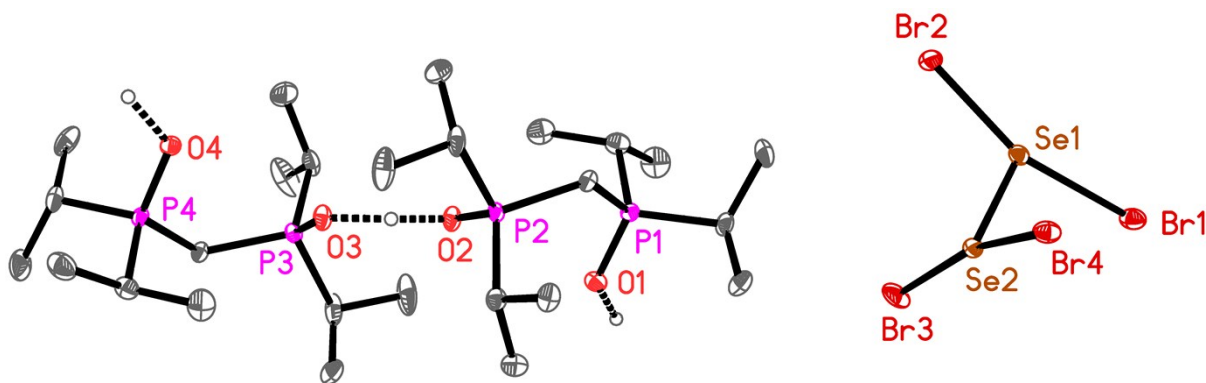


Fig. S11. Structure of the asymmetric unit of compound **17** in the crystal; ellipsoids correspond to 50% probability levels. Dashed lines indicate hydrogen bonds. Only one position of the disordered isopropyl groups is shown. Hydrogen atoms (except OH) are omitted. Selected bond lengths (Å) and angles (°): Se1-Se2 2.2793(4), Br1-Se1 2.7726(4), Br2-Se1 2.5029(4), Br3-Se2 2.5276(4), Br4-Se2 2.7447(4); Br1-Se1-Br2 159.406(14), Br3-Se2-Br4 161.319(14).
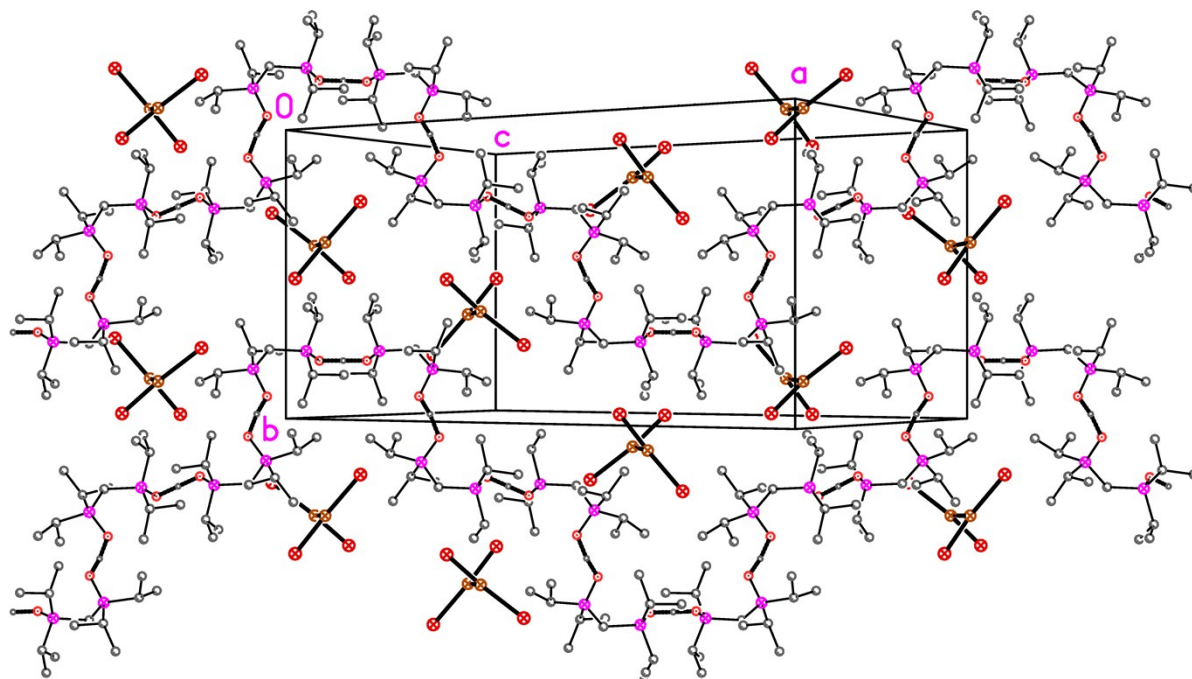
Fig. S12. Packing diagram of compound **17**. Only one position of the disordered isopropyl groups is shown. Hydrogen atoms (except OH) are omitted. The view direction is perpendicular to $(10\bar{1})$. Note the undulating chains of hydrogen-bonded cations.

## Structure of compound 18, [dppm(O)(OH)$^+$]$_2$ [Se$_3$Br$_8$]$^{2-}$

Crystal data for **18**: C$_{50}$H$_{46}$Br$_8$O$_4$P$_4$Se$_3$, $M$ = 1710.91, triclinic, $a$ = 10.4803(5), $b$ = 11.8359(8), $c$ = 12.1607(6) Å, $\alpha$ = 68.775(6), $\beta$ = 85.723(4), $\gamma$ = 86.800(5)°, $V$ = 1401.54 Å$^3$, space group $P\bar{1}$, $Z$ = 1, 68560 reflections measured, 6684 independent ($R_{int}$ = 0.082). Final $R(F)$ 0.0420 ($I > 2\sigma(I)$), final $wR(F^2)$ 0.0907 (all data). See Fig. S13.
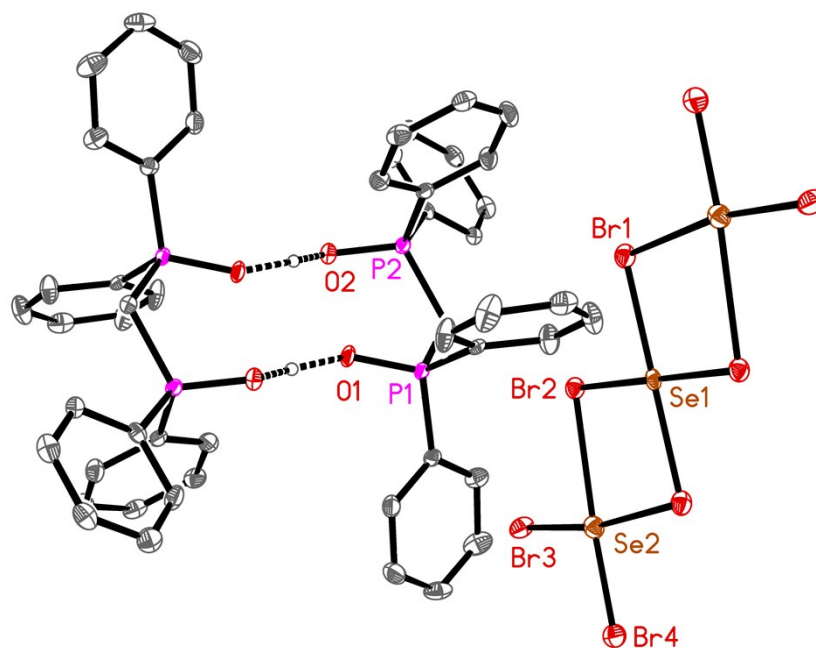


Fig. S13. Structure of compound **18** in the crystal; ellipsoids correspond to 50% probability levels. Dashed lines indicate hydrogen bonds. Selected bond lengths (Å): Se1-Br2 2.5968(5), Se1-Br1 2.5996(5), Br2-Se2 3.0323(7), Se2-Br4 2.3588(7), Se2-Br3 2.3841(7), Se2-Br1#1 2.9090(7). Symmetry operator #1: 1–$x$, 1–$y$, 1–$z$.

Again, there is some uncertainty as to the exact position of the OH hydrogen, but the short contact O1$\Box$O1 2.438(4) Å (over an inversion centre) corresponds to a strong classical hydrogen bond. The $[Se_3Br_8]^{2-}$ anion possesses crystallographic inversion symmetry; the bonds from Se2 to the bridging bromines are very long, and the ion might almost be considered as $[SeBr_4]^{2-}$ with loose contacts to two $SeBr_2$ molecules. The corresponding angle at Se2 is very acute at 77.975(18)°. The $SeBr_4$ planes at Se1 and Se2 subtend an angle of 4.96(2)°. In the other known structure of this anion,[6] the interplanar angle is much larger at 20.7°.

**Structure of compound 19, [dppm(O)(OH)⁺]₂ [Se₂Br₆]²⁻**

Crystal data for **19**: $C_{50}H_{46}Br_6O_4P_4Se_2$, $M$ = 1472.13, monoclinic, $a$ = 13.0635(3), $b$ = 9.5315(2), $c$ = 20.8476(5) Å, $\beta$ = 90.676(2)°, $V$ = 2595.65 Å³, space group $P2_1/n$, $Z$ = 2, 51628 reflections measured, 5421 independent ($R_{int}$ = 0.068). Final $R(F)$ 0.0263 ($I > 2\sigma(I)$), final $wR(F^2)$ 0.0617 (all data). See Fig. S14.

Again the position of the OH hydrogen is ambiguous, and there is a peak of 2 e Å⁻³ near the $CH_2$ group that may correspond to an unidentified disorder or twinning component. The O1$\Box$O2 hydrogen bonding distance is 2.409(3) Å across an inversion centre.
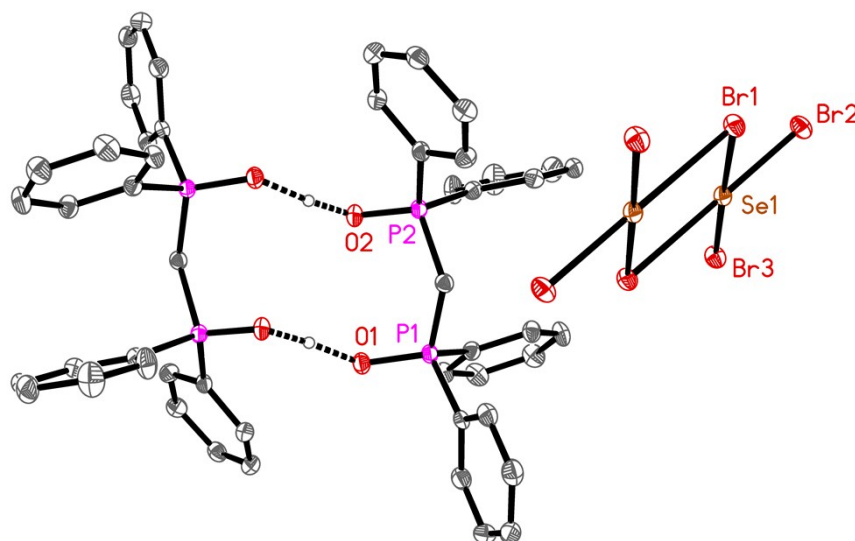


Fig. S14. Structure of compound **19** in the crystal; ellipsoids correspond to 50% probability levels. Dashed lines indicate hydrogen bonds. Selected bond lengths (Å): Se1-Br2 2.4099(4), Se1-Br3 2.4612(4), Se1-Br1 2.7600(4), Br1-Se1#1 2.9176(4). Symmetry operator #1: 1–*x*, 1–*y*, 1–*z*.

# 3. Four X-ray structures of diphosphane diselenides 20–23.

Bis(diphenylphosphano)ethane diselenide has already been the subject of three X-ray structure determinations. The solvent-free compound crystallizes in $P\bar{1}$ with $Z = 2$ (two independent molecules, each displaying crystallographic inversion symmetry) [7] or in $C2/c$ with $Z = 4$ (one molecule with crystallographic twofold symmetry).[8] The p-xylene ⅓-solvate crystallizes in $P\bar{1}$ with $Z = 3$ (one dppeSe$_2$ on a general position and one with inversion symmetry).[9] By chance we have discovered two further forms during studies of metal complexes of dppeSe$_2$; one solvent-free in $P2_1/n$ (**20**) and the dichloromethane solvate (also $P2_1/n$, **21**), which we briefly present here. We also present the structures of bis(diisopropylphosphano)methane diselenide (**22**) and bis(diisopropylphosphano)ethane diselenide (**23**).

The structures were determined as in the main paper. CCDC 1579323-1579326 contain the supplementary crystallographic data for compounds **20-23** (in the same order). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/.

<u>Synthesis of d$^i$prpmSe$_2$</u>

To a solution of d$^i$prpm (0.874 g, 3.5 mmol) in toluene (20 mL) an excess of elemental selenium was added and the suspension was refluxed for 3 h. The remaining selenium was filtered off and the toluene removed in vacuum. The remaining solid was dried in vacuum (1.342 g, 94%). Diffusion of n-pentane into a dichloromethane solution gave colourless single crystals of **22**. $^{31}$**P-NMR** (200 MHz, CDCl$_3$): δ 57.51 (s, J$_{P-Se}$ = 713.2 Hz). **Elemental analysis**: Found: C 38.09, H 7.27. Required for C$_{13}$H$_{30}$I$_4$P$_2$Se$_2$: C 38.44, H 7.44 %.

<u>Synthesis of d$^i$prpeSe$_2$</u>

To a solution of d$^i$prpe (0.731 g, 2.8 mmol) in toluene (20 mL) an excess of elemental selenium was added and the suspension was refluxed for 3 h. The remaining selenium was filtered off and the toluene removed in vacuum. The remaining solid was dried in vacuum (1.023 g, 87%). Diffusion of n-pentane into a dichloromethane solution gave colourless single crystals of **23**. $^{31}$**P-NMR** (200 MHz, CDCl$_3$): δ 65.87 (s, J$_{P-Se}$ = 702.4 Hz). **Elemental analysis**: Found: C 39.79, H 7.53. Required for C$_{13}$H$_{30}$I$_4$P$_2$Se$_2$: C 40.01, H 7.67 %.

**Structure of a third polymorph of dppeSe$_2$ (20)**

Crystal data for **20**: C$_{26}$H$_{24}$P$_2$Se$_2$, $M$ = 556.31, monoclinic, $a$ = 9.5936(2), $b$ = 16.1956(3), $c$ = 15.7995(3) Å, $\beta$ = 103.381(2)°, $V$ = 2388.21 Å$^3$, space group $P2_1/n$, $Z$ = 4, 151754 reflections measured, 6977 independent ($R_{int}$ = 0.050). Final $R(F)$ 0.0264 ($I > 2\sigma(I)$), final $wR(F^2)$ 0.0580 (all data). See Fig. S15.
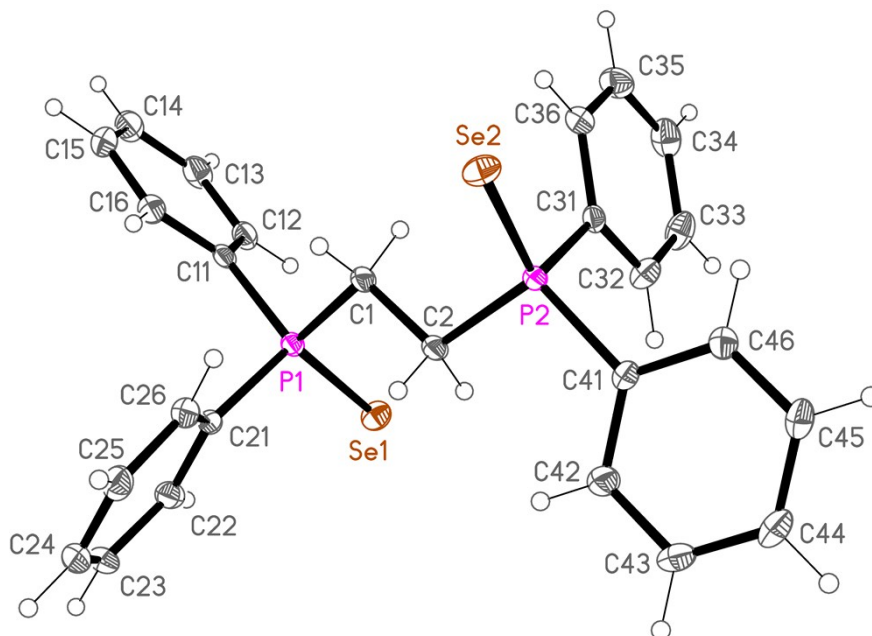


Fig. S15. Structure of compound **20** in the crystal; ellipsoids correspond to 50% probability levels. Selected bond lengths (Å): P1-Se1 2.1047(4), P2-Se2 2.1082(4).

The conformation of the backbone is described by the torsion angles Se1–P1–C1–C2 –54.54(12), P1–C1–C2–P2 165.52(8), Se2–P2–C2–C1 59.54(12)°.

**Structure of dppeSe$_2$ dichloromethane solvate (21)**

Crystal data for **21**: C$_{26}$H$_{24}$P$_2$Se$_2$·CH$_2$Cl$_2$, $M$ = 641.24, monoclinic, $a$ = 12.1314(4), $b$ = 16.1003(3), $c$ = 14.9640(5) Å, $\beta$ = 111.591(4)°, $V$ = 2717.67 Å$^3$, space group $P2_1/n$, $Z$ = 4, 105404 reflections measured, 7312 independent ($R_{int}$ = 0.050). Final $R(F)$ 0.0332 ($I > 2\sigma(I)$), final $wR(F^2)$ 0.0800 (all data). See Fig. S16.

Both dppeSe$_2$ molecules lie across inversion centres. The torsion angles P-C-C-P are therefore 180° by symmetry. The conformations are further described by the torsion angles Se1–P1–C1–C1' –54.8(2), Se2–P2–C2–C2' –59.1(2)°.
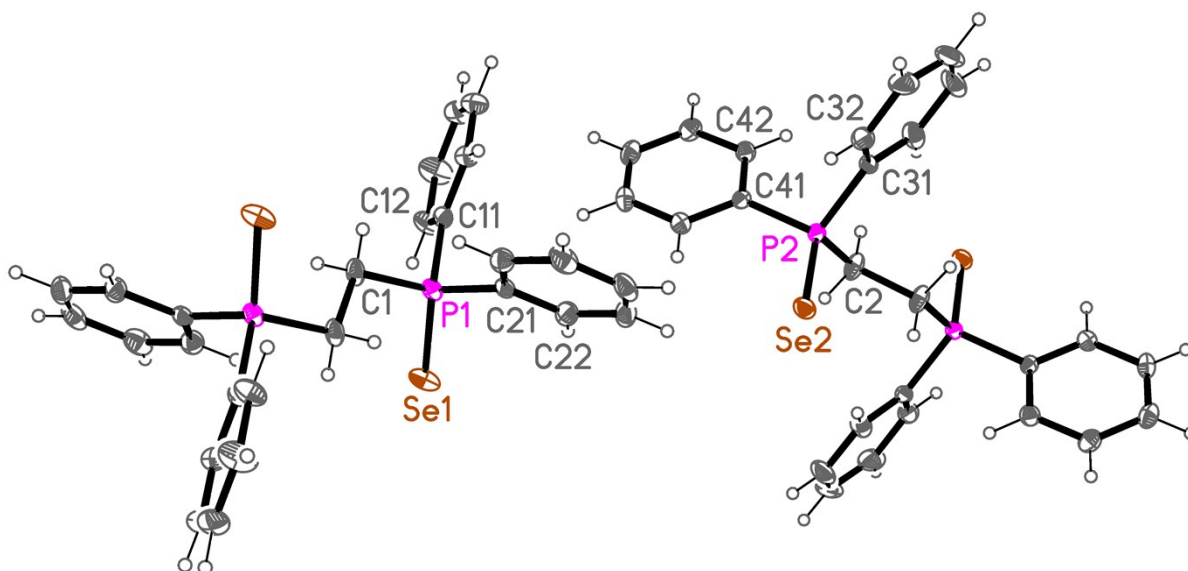
Fig. S16. Structure of compound **21** in the crystal; ellipsoids correspond to 50% probability levels. Only the asymmetric unit is numbered. Selected bond lengths (Å): P1-Se1 2.1185(6), P2-Se2 2.1106(6).

**Structure of d$^i$prpmSe$_2$ (22)**

Crystal data for **22**: $C_{13}H_{30}P_2Se_2$, $M$ = 406.23, monoclinic, $a$ = 13.7347(4), $b$ = 10.4735(3), $c$ = 12.6411(4) Å, $\beta$ = 100.759(3)°, $V$ = 1786.46 Å$^3$, space group $P2_1/c$, $Z$ = 4, 119830 reflections measured, 5210 independent ($R_{int}$ = 0.052). Final $R(F)$ 0.0250 ($I > 2\sigma(I)$), final $wR(F^2)$ 0.0534 (all data). See Fig. S17.
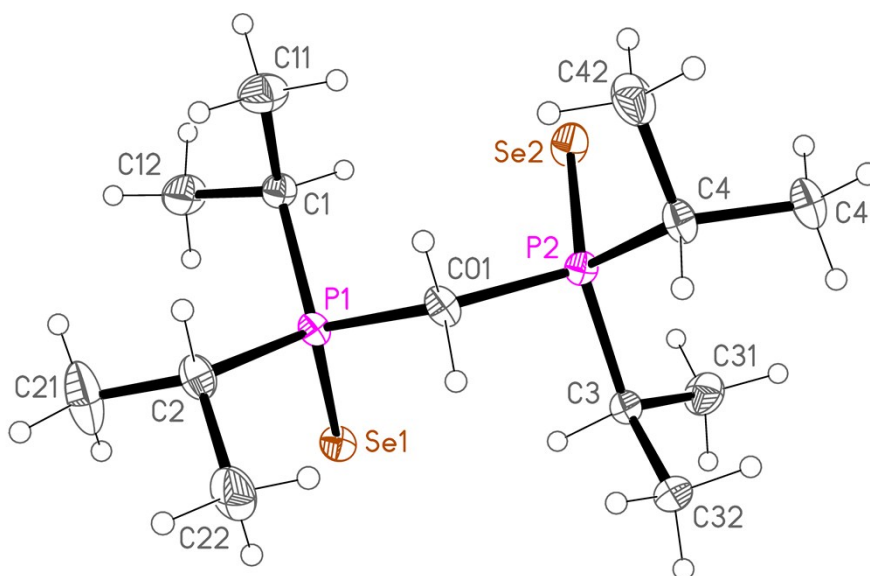


Fig. S17. Structure of compound **22** in the crystal; ellipsoids correspond to 50% probability levels. Only the major position (87%) of the disordered *i*-propyl group (C3, C31, C32) is shown. Selected bond lengths (Å): P1-Se1 2.1111(4), P2-Se2 2.1099(4).

The molecule lies on a general position. The conformation is described by the torsion angles Se1–P1–C01–P2 54.73(12) and Se2–P2–C01–P1 47.04(13)°. The short intramolecular

contacts H1☐Se2 and H3☐Se1 (both 2.79 Å) may be a factor in determining the conformation. The P–C–P angle is unusually wide (for an $sp^3$ carbon) at 122.48(9)°.

**Structure of d$^i$prpeSe$_2$ (23)**

Crystal data for **23**: $C_{14}H_{32}P_2Se_2$, $M$ = 420.26, monoclinic, $a$ = 9.3133(5), $b$ = 10.4104(4), $c$ = 10.1508(4) Å, $\beta$ = 104.577(4)°, $V$ = 952.49 Å$^3$, space group $P2_1/n$, $Z$ = 2, 24692 reflections measured, 2767 independent ($R_{int}$ = 0.042). Final $R(F)$ 0.0309 ($I > 2\sigma(I)$), final $wR(F^2)$ 0.0643 (all data). See Fig. S18.
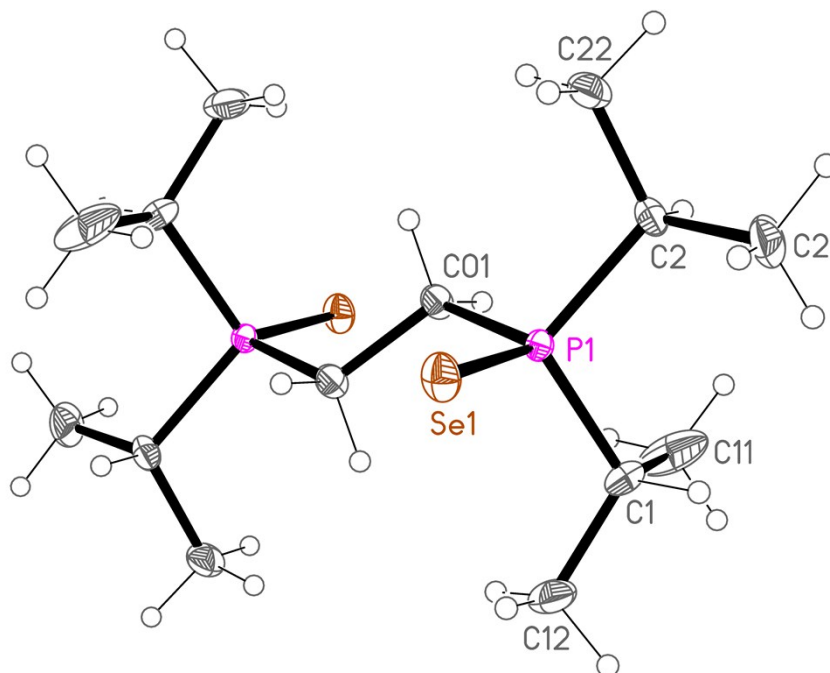


Fig. S18. Structure of compound **23** in the crystal; ellipsoids correspond to 30% probability levels. Only the asymmetric unit is numbered. Selected bond length (Å): P1-Se1 2.1150(5).

The molecule lies across an inversion centre. The torsion angle P–C–C–P is therefore 180° by symmetry. The conformation is further described by the torsion angle Se1–P1–C01–C01' −50.7(2)°.

## References

[1] see e.g. C. Taouss, P. G. Jones, *Z. Naturforsch*., **2016**, *71b*, 249–265.

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