

Crystal structures of fourteen halochalcogenylphosphonium tetrahalogenidoaurates(III)

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Phosphane chalcogenides and their metal complexes, Part 8. For Part 7, see Upmann *et al.* (2024).**Keywords:** crystal structure; gold; halochalcogenylphosphonium; secondary interactions.**CCDC references:** 2156871; 2345294; 2345295; 2156781; 2156391; 2345296; 2345297; 2156880; 2156882; 2156884; 2156886; 2156881; 2156883; 2156885**Supporting information:** this article has supporting information at journals.iucr.org/e

The structures of fourteen halochalcogenylphosphonium tetrahalogenidoaurates(III), phosphane chalcogenide derivatives with general formula $[R_{3-n}^1R_n^2PEX][AuX_4]$ ($R^1 = t$ -butyl; $R^2 =$ isopropyl; $n = 0$ to 3; $E = S$ or Se; $X = Cl$ or Br) are presented. The eight possible chlorido derivatives are: **17a**, $n = 3$, $E = S$; **18a**, $n = 2$, $E = S$; **19a**, $n = 1$, $E = S$; **20a**, $n = 0$, $E = S$; **21a**, $n = 3$, $E = Se$; **22a**, $n = 2$, $E = Se$; **23a**, $n = 1$, $E = Se$; and **24a**, $n = 0$, $E = Se$, and the corresponding bromido derivatives are **17b–24b** in the same order. Structures were obtained for all compounds except for the tri-*t*-butyl derivatives **24a** and **24b**. Isotypy is observed for **18a/18b/22a/22b**, **19a/23a**, **17b/21b** and **19b/23b**. In eleven of the compounds, $X \cdots X$ contacts (mostly very short) are observed between the cation and anion, whereby the $E-X \cdots X$ groups are approximately linear and the $X \cdots X-Au$ angles approximately 90° . The exceptions are **17a**, **19a** and **23a**, which instead display short $E \cdots X$ contacts. Bond lengths in the cations correspond to single bonds $P-E$ and $E-X$. For each group with constant E and X , the $P-E-X$ bond-angle values increase monotonically with the steric bulk of the alkyl groups. The packing is analysed in terms of $E \cdots X$, $X \cdots X$ (some between anions alone), $H \cdots X$ and $H \cdots Au$ contacts. Even for isotopic compounds, some significant differences can be discerned.

1. Chemical context

Some years ago, in Part 3 of this series (Taouss *et al.*, 2015), we investigated the oxidation of the phosphane chalcogenide gold(I) complexes Ph_3PEAuX ($E = S$ or Se, $X = Cl$ or Br) with iodobenzene dichloride $PhICl_2$ (as a more controllable substitute for elemental chlorine) or elemental bromine. We were expecting to obtain the corresponding Ph_3PEAuX_3 complexes, and these were indeed formed, but excess halogen led to the unexpected doubly oxidized ionic products $[Ph_3PEX][AuX_4]$ (for $E = S$, $X = Cl$ and Br and $E = Se$, $X = Br$), involving halochalcogenylphosphonium cations, previously unknown for $X = Cl$ or Br (but known for $X = I$; du Mont *et al.* (2008) and references therein). The combination $E = Se$, $X = Cl$ led instead to $[Ph_3PSeCl]_2[Au_4Se_2Cl_{10}]$. We also obtained one structure of a similar compound with [2.2]-paracyclophanyldiisopropylphosphane and $E = Se$, $X = Cl$ (Upmann *et al.*, 2019).

We then extended our studies to phosphane chalcogenides involving alkyl groups. In Part 6 of this series (Upmann *et al.*, 2024a) we presented the structures of sixteen halogenido-gold(I) complexes of various trialkylphosphane chalcogenides, and in Part 7 (Upmann *et al.*, 2024b) the structures of ten corresponding trihalogenido-gold(III) complexes. Further background material, including a more extensive summary of our previous results, can be found in Part 6 and is not repeated here.

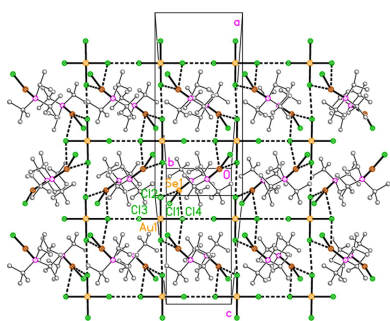
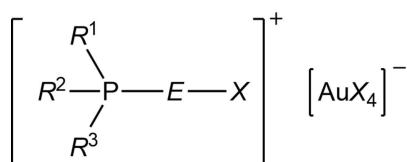


Table 1

Compositions of the $[R^1R^2R^3PEX][AuX_4]$ structures presented in this paper (see Scheme).

| Compound | R^1 | R^2 | R^3 | E | X |
|------------|-----------------|-----------------|-----------------|-----|-----|
| 17a | ⁱ Pr | ⁱ Pr | ⁱ Pr | S | Cl |
| 18a | ⁱ Pr | ⁱ Pr | ^t Bu | S | Cl |
| 19a | ⁱ Pr | ^t Bu | ^t Bu | S | Cl |
| 20a | ^t Bu | ^t Bu | ^t Bu | S | Cl |
| 21a | ⁱ Pr | ⁱ Pr | ⁱ Pr | Se | Cl |
| 22a | ⁱ Pr | ⁱ Pr | ^t Bu | Se | Cl |
| 23a | ⁱ Pr | ^t Bu | ^t Bu | Se | Cl |
| 17b | ⁱ Pr | ⁱ Pr | ⁱ Pr | S | Br |
| 18b | ⁱ Pr | ⁱ Pr | ^t Bu | S | Br |
| 19b | ⁱ Pr | ^t Bu | ^t Bu | S | Br |
| 20b | ^t Bu | ^t Bu | ^t Bu | S | Br |
| 21b | ⁱ Pr | ⁱ Pr | ⁱ Pr | Se | Br |
| 22b | ⁱ Pr | ⁱ Pr | ^t Bu | Se | Br |
| 23b | ⁱ Pr | ^t Bu | ^t Bu | Se | Br |



In this paper, we report the structures of fourteen (halochalcogenyl)trialkylphosphonium tetrahalogenidoaurates(III) of general formula $[^iBu_{3-n}^iPr_nPEX][AuX_4]$. In total there are sixteen possible permutations of n (0–3), the chalcogenide E (S or Se) and the halogen X (Cl or Br), but the two compounds with $n = 0$ and $E = Se$ were not obtained. The chlorine derivatives are numbered **17a–23a** and the bromine derivatives **17b–23b**, following on from the gold(I) complexes **1–8** and the gold(III) complexes **9–16** in the previous papers (Upmann *et al.*, 2024a,b). Details of the composition of each compound studied are given in Table 1. The structures of **18a**, **19a**, **22a** and **23a** were briefly presented in a preliminary

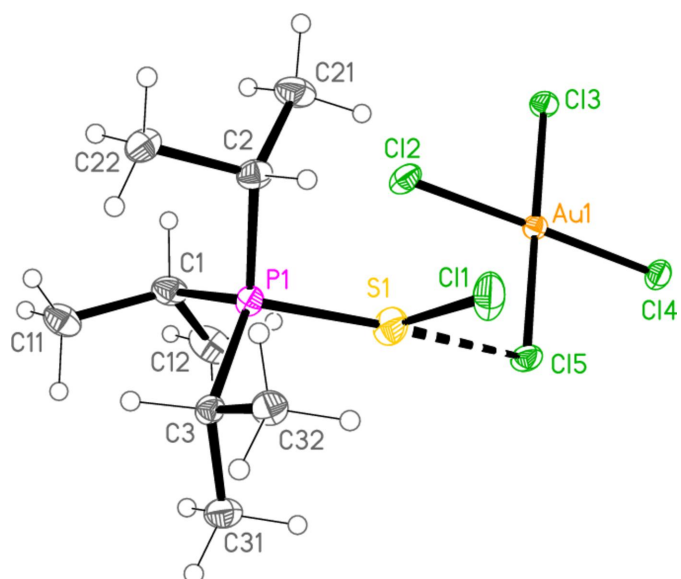


Figure 1
The structure of compound **17a** in the crystal. Ellipsoids represent 30% probability levels.

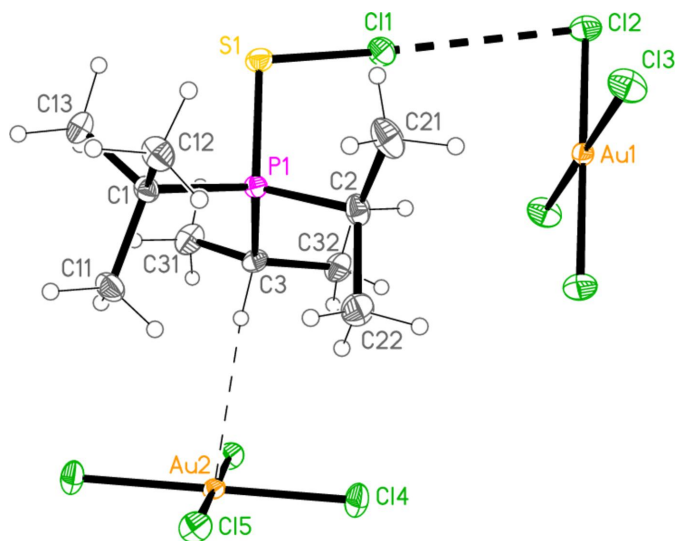


Figure 2
The structure of compound **18a** in the crystal. Ellipsoids represent 50% probability levels.

communication (Upmann & Jones, 2013), but have been re-refined using a much more recent version of *SHELXL* (2019 rather than 1997; Sheldrick, 2015) and are discussed in more detail here. We abstain from giving the systematic names for all these compounds; compound **21a**, for instance, is (chloroselanyl)triisopropylphosphonium tetrachloridoaurate(III), **18b** is (bromosulfanyl)(*tert*-butyl)diisopropylphosphonium tetrachloridoaurate(III), and the others may be named analogously.

2. Structural commentary

General comments: All compounds crystallized solvent-free and with $Z' = 1$ (although all structures except **17a** contain two

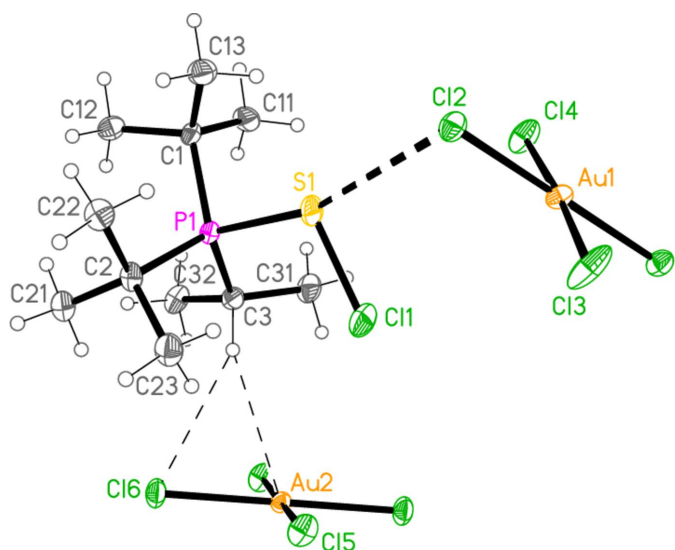


Figure 3
The structure of compound **19a** in the crystal. Ellipsoids represent 50% probability levels. Only one position of the disordered atoms Cl3 and Cl4 is shown.

Table 2
Selected geometric parameters (Å, °) for **17a**.

| | | | |
|---------------|-------------|---------|-------------|
| P1—S1 | 2.091 (2) | Au1—Cl3 | 2.2789 (16) |
| S1—Cl1 | 2.023 (3) | Au1—Cl5 | 2.2797 (16) |
| Au1—Cl2 | 2.2745 (17) | Au1—Cl4 | 2.2884 (17) |
| Cl1—S1—P1 | 99.25 (11) | | |
| Cl1—P1—S1—Cl1 | 164.4 (2) | | |

Table 3
Selected geometric parameters (Å, °) for **18a**.

| | | | |
|---------------|------------|---------|------------|
| P1—S1 | 2.0970 (7) | Au1—Cl2 | 2.2847 (5) |
| S1—Cl1 | 2.0316 (7) | Au2—Cl4 | 2.2753 (5) |
| Au1—Cl3 | 2.2744 (5) | Au2—Cl5 | 2.2801 (5) |
| Cl1—S1—P1 | 101.57 (3) | | |
| Cl1—P1—S1—Cl1 | 164.48 (7) | | |

Table 4
Selected geometric parameters (Å, °) for **19a**.

| | | | |
|---------------|--------------|---------|-------------|
| P1—S1 | 2.1035 (16) | Au1—Cl3 | 2.274 (2) |
| S1—Cl1 | 2.0310 (19) | Au2—Cl6 | 2.2738 (11) |
| Au1—Cl4 | 2.269 (2) | Au2—Cl5 | 2.2796 (12) |
| Cl1—S1—P1 | 103.06 (7) | | |
| Cl1—P1—S1—Cl1 | −160.17 (16) | | |

Table 5
Selected geometric parameters (Å, °) for **20a**.

| | | | |
|---------------|-------------|---------|-------------|
| P1—S1 | 2.0983 (13) | Au1—Cl2 | 2.2850 (10) |
| S1—Cl1 | 2.0307 (13) | Au2—Cl5 | 2.2821 (11) |
| Au1—Cl3 | 2.2818 (10) | Au2—Cl4 | 2.2860 (11) |
| Cl1—S1—P1 | 104.74 (5) | | |
| Cl1—P1—S1—Cl1 | 163.38 (16) | | |

Table 6
Selected geometric parameters (Å, °) for **21a**.

| | | | |
|----------------|-------------|---------|------------|
| P1—Se1 | 2.2488 (5) | Au1—Cl3 | 2.2838 (5) |
| Se1—Cl1 | 2.1736 (5) | Au2—Cl4 | 2.2795 (5) |
| Au1—Cl2 | 2.2778 (5) | Au2—Cl5 | 2.2836 (5) |
| Cl1—Se1—P1 | 98.381 (19) | | |
| Cl1—P1—Se1—Cl1 | 161.60 (7) | | |

Table 7
Selected geometric parameters (Å, °) for **22a**.

| | | | |
|----------------|------------|---------|------------|
| P1—Se1 | 2.2467 (7) | Au1—Cl2 | 2.2842 (7) |
| Se1—Cl1 | 2.1654 (7) | Au2—Cl4 | 2.2781 (7) |
| Au1—Cl3 | 2.2736 (7) | Au2—Cl5 | 2.2823 (6) |
| Cl1—Se1—P1 | 98.35 (3) | | |
| Cl1—P1—Se1—Cl1 | 163.52 (9) | | |

Table 8
Selected geometric parameters (Å, °) for **23a**.

| | | | |
|----------------|-------------|---------|------------|
| P1—Se1 | 2.2557 (6) | Au1—Cl2 | 2.2833 (6) |
| Se1—Cl1 | 2.1645 (7) | Au2—Cl6 | 2.2735 (6) |
| Au1—Cl4 | 2.2681 (13) | Au2—Cl5 | 2.2784 (6) |
| Au1—Cl3 | 2.2765 (12) | | |
| Cl1—Se1—P1 | 100.40 (3) | | |
| Cl1—P1—Se1—Cl1 | −159.50 (8) | | |

Table 9
Selected geometric parameters (Å, °) for **17b**.

| | | | |
|---------------|-------------|---------|------------|
| P1—S1 | 2.0852 (10) | Au1—Br3 | 2.4308 (3) |
| S1—Br1 | 2.1977 (8) | Au2—Br4 | 2.4259 (3) |
| Au1—Br2 | 2.4201 (3) | Au2—Br5 | 2.4265 (3) |
| P1—S1—Br1 | 99.46 (4) | | |
| Cl1—P1—S1—Br1 | 174.93 (9) | | |

Table 10
Selected geometric parameters (Å, °) for **18b**.

| | | | |
|---------------|-------------|---------|------------|
| P1—S1 | 2.0902 (12) | Au1—Br2 | 2.4287 (4) |
| S1—Br1 | 2.2028 (10) | Au2—Br4 | 2.4154 (4) |
| Au1—Br3 | 2.4180 (4) | Au2—Br5 | 2.4199 (4) |
| P1—S1—Br1 | 102.51 (5) | | |
| Cl1—P1—S1—Br1 | 162.05 (13) | | |

Table 11
Selected geometric parameters (Å, °) for **19b**.

| | | | |
|---------------|--------------|---------|------------|
| P1—S1 | 2.0992 (16) | Au1—Br2 | 2.4247 (5) |
| S1—Br1 | 2.2077 (12) | Au2—Br5 | 2.4207 (4) |
| Au1—Br3 | 2.4179 (5) | Au2—Br4 | 2.4228 (4) |
| P1—S1—Br1 | 104.48 (6) | | |
| Cl1—P1—S1—Br1 | −160.33 (16) | | |

Table 12
Selected geometric parameters (Å, °) for **20b**.

| | | | |
|---------------|-------------|---------|------------|
| S1—P1 | 2.0973 (16) | Au1—Br3 | 2.4257 (5) |
| Br1—S1 | 2.1934 (13) | Au2—Br4 | 2.4171 (5) |
| Au1—Br2 | 2.4178 (5) | Au2—Br5 | 2.4234 (5) |
| P1—S1—Br1 | 105.70 (6) | | |
| Br1—S1—P1—Cl1 | 161.63 (16) | | |

Table 13
Selected geometric parameters (Å, °) for **21b**.

| | | | |
|----------------|-------------|---------|------------|
| P1—Se1 | 2.2364 (9) | Au1—Br3 | 2.4264 (4) |
| Se1—Br1 | 2.3179 (5) | Au2—Br4 | 2.4230 (4) |
| Au1—Br2 | 2.4162 (4) | Au2—Br5 | 2.4258 (3) |
| P1—Se1—Br1 | 96.32 (3) | | |
| Cl1—P1—Se1—Br1 | 174.59 (11) | | |

independent $[\text{AuX}_4]^-$ anions, each with crystallographic symmetry). The molecular structures are shown in Figs. 1–14, with selected bond lengths and angles in Tables 2–15.

Isotypy: The four structures **18a**, **22a**, **18b** and **22b** form an isotypic set; the pairs **19a/23a**, **17b/21b**, and **19b/23b** are also

Table 14
Selected geometric parameters (Å, °) for **22b**.

| | | | |
|---------------|-------------|---------|------------|
| P1—Se1 | 2.2453 (10) | Au1—Br2 | 2.4287 (4) |
| Se1—Br1 | 2.3237 (5) | Au2—Br4 | 2.4178 (4) |
| Au1—Br3 | 2.4162 (4) | Au2—Br5 | 2.4202 (4) |
| P1—Se1—Br1 | 99.52 (3) | | |
| C1—P1—Se1—Br1 | 161.21 (13) | | |

isotypic. Within each set of isotypic structures, the n value is the same.

Bond lengths and angles (1). $[AuX_4]^-$ anions: For **17a**, the anion lies on a general position. For **19a** and **23a**, Au1 lies on a twofold axis and Au2 on an inversion centre, and the chlorine atoms at Au1 are disordered (with the atoms Cl3 and Cl4 being slightly displaced from the ideal positions on the twofold axis). All other anions lie with the gold atoms on inversion centres. The local symmetry approximates closely to the ideal $4/mmm$, and there are no clear trends in the influence of the

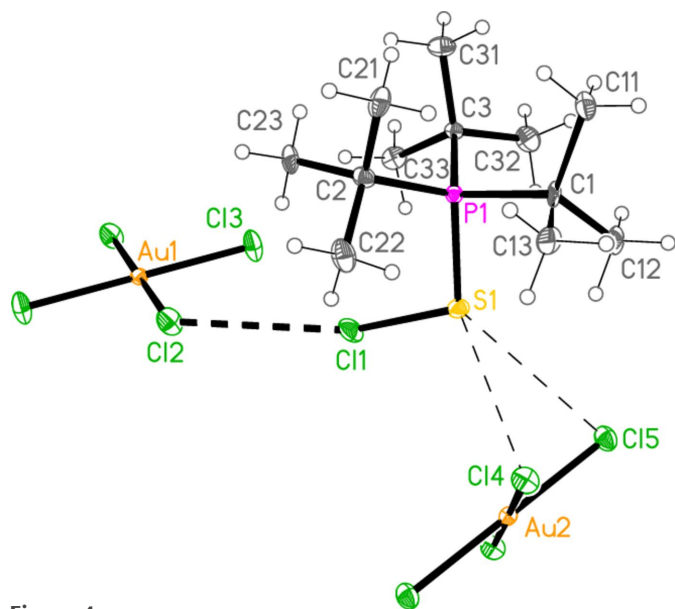


Figure 4
The structure of compound **20a** in the crystal. Ellipsoids represent 50% probability levels.

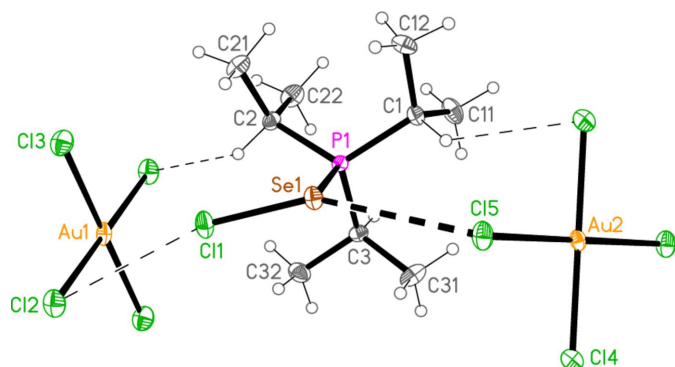


Figure 5
The structure of compound **21a** in the crystal. Ellipsoids represent 50% probability levels.

Table 15
Selected geometric parameters (Å, °) for **23b**.

| | | | |
|---------------|-------------|---------|------------|
| P1—Se1 | 2.2534 (19) | Au1—Br2 | 2.4249 (8) |
| Se1—Br1 | 2.3255 (10) | Au2—Br5 | 2.4201 (7) |
| Au1—Br3 | 2.4142 (8) | Au2—Br4 | 2.4221 (7) |
| P1—Se1—Br1 | 101.91 (6) | | |
| C1—P1—Se1—Br1 | −160.4 (2) | | |

short $X \cdots X$ contacts on the Au—X bond lengths (see *Supramolecular features*).

Bond lengths and angles (2). (Halochalcogenyl)trialkylphosphonium cations: The P—S bond lengths lie in the range

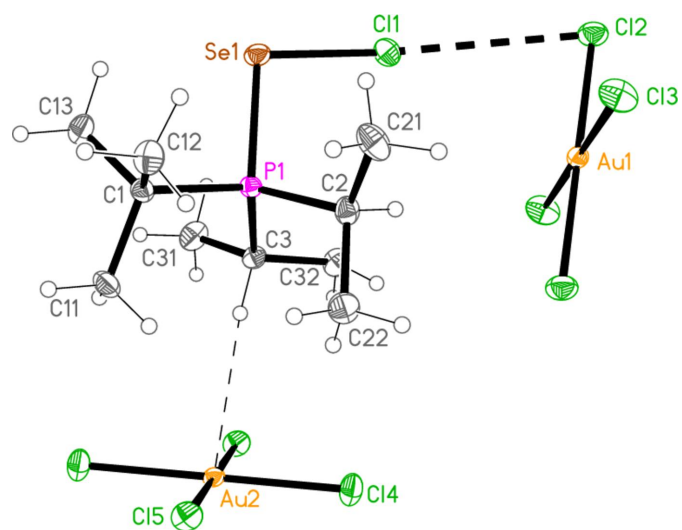


Figure 6
The structure of compound **22a** in the crystal. Ellipsoids represent 50% probability levels.

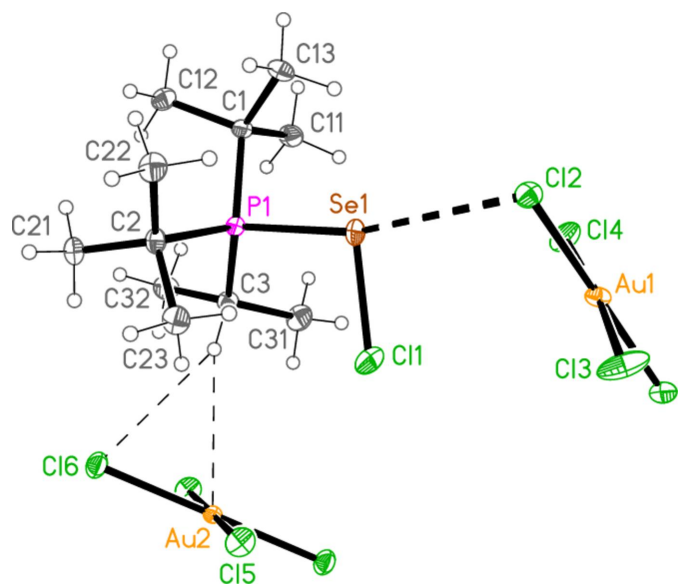


Figure 7
The structure of compound **23a** in the crystal. Ellipsoids represent 50% probability levels. Only one position of the disordered atoms Cl3 and Cl4 is shown.

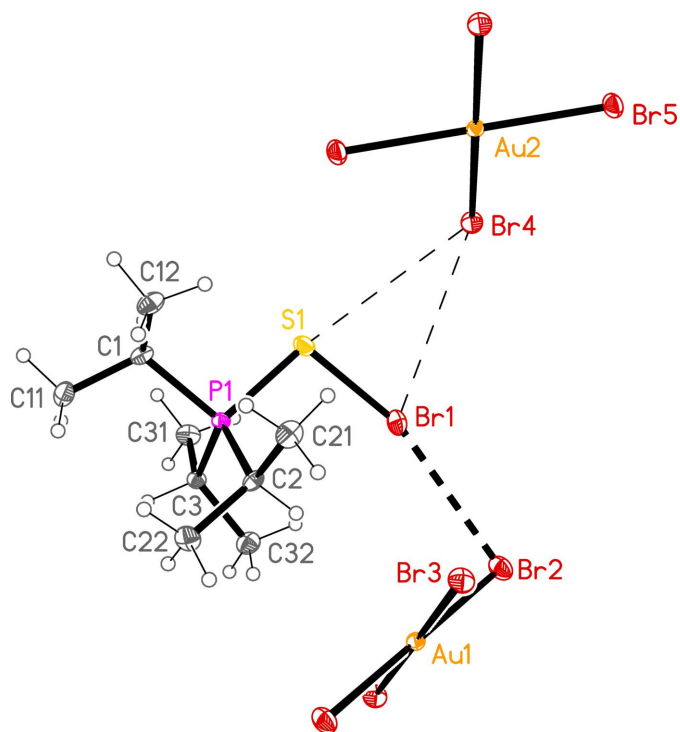


Figure 8
The structure of compound **17b** in the crystal. Ellipsoids represent 50% probability levels.

2.0852–2.1035 Å, av. 2.0952 Å; the P–Se bond lengths are 2.2364–2.2557 Å, av. 2.2477 Å. These averages are slightly larger than in the trihalogenido-gold(III) complexes (2.0602 and 2.2183 Å), and may reasonably be regarded as corresponding to essentially single P–E bonds (for the mild controversy about the P–E bond order in phosphane chalcogenides, see *e.g.* Schmøkel *et al.*, 2012). The E–X bond lengths are: S–Cl = 2.023–2.0316 Å, av. 2.0291 Å; Se–Cl =

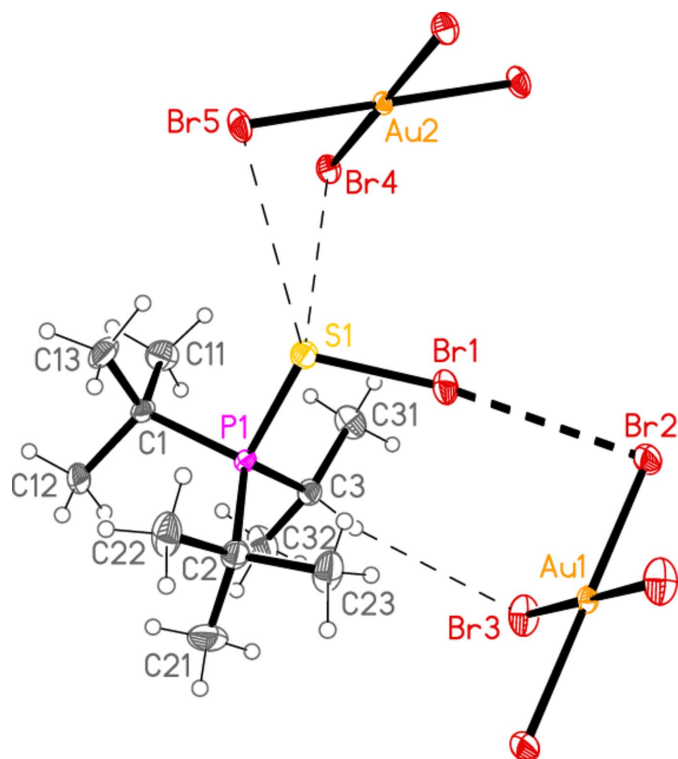


Figure 10
The structure of compound **19b** in the crystal. Ellipsoids represent 50% probability levels.

2.1645–2.1736 Å, av. 2.1678 Å; S–Br = 2.1934–2.2077 Å, av. 2.2004 Å; Se–Br = 2.3179–2.3255 Å, av. 2.3224 Å. For CCDC results on related bond lengths, see the *Database survey* below.

For each group of P–E–X bond angles, the values increase monotonically (with one extremely slight exception) with the steric bulk of the alkyl groups (P–S–Cl = 99.25–104.74°, P–Se–Cl = 98.38–100.40°, P–S–Br = 99.46–105.70°,

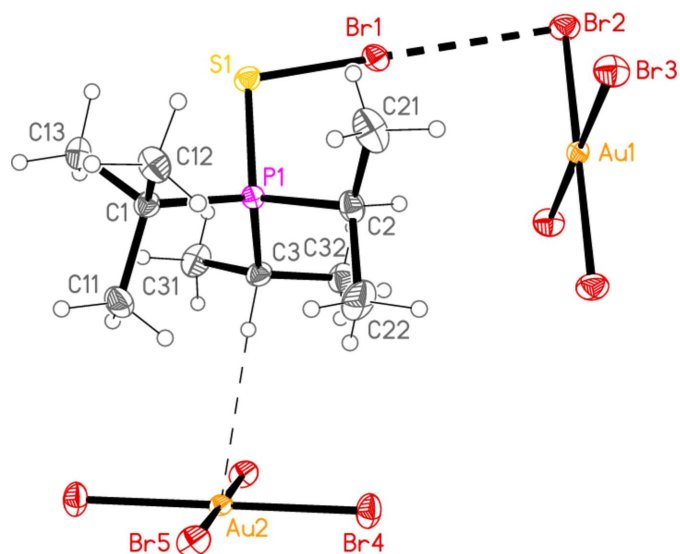


Figure 9
The structure of compound **18b** in the crystal. Ellipsoids represent 50% probability levels.

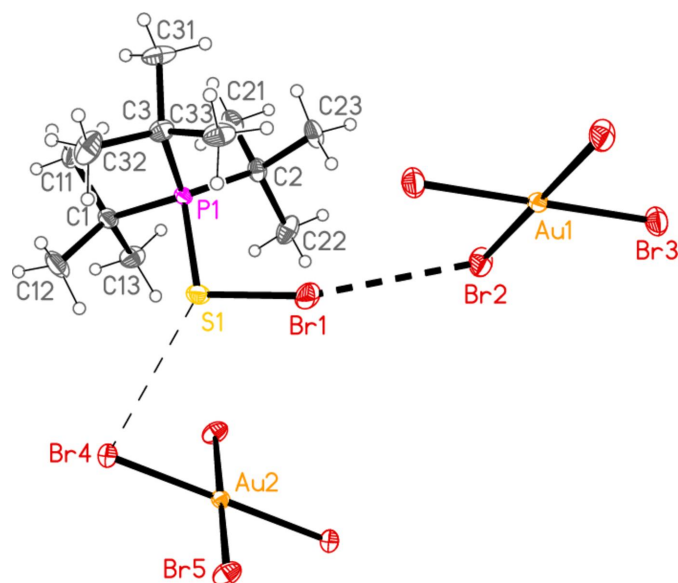


Figure 11
The structure of compound **20b** in the crystal. Ellipsoids represent 50% probability levels.

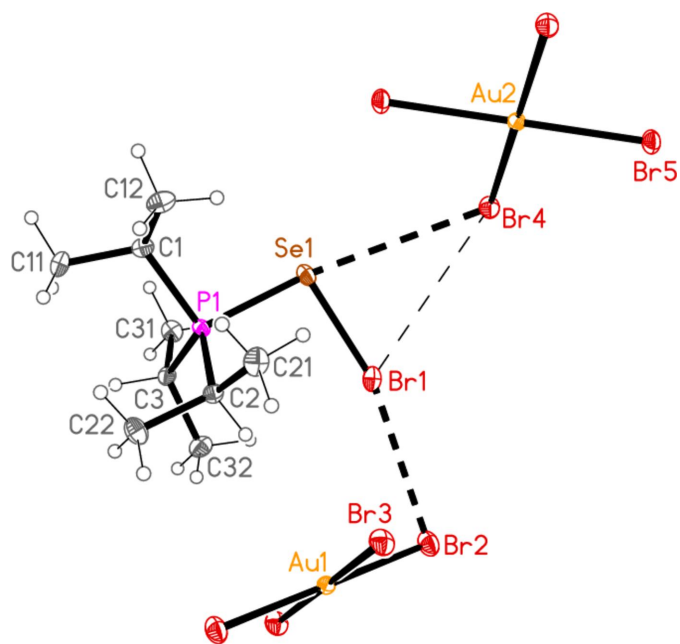


Figure 12
The structure of compound **21b** in the crystal. Ellipsoids represent 50% probability levels.

P–Se–Br = 96.32–101.91°). For analogous S/Se pairs, the angles at Se are consistently smaller than those at S. For each cation, one of the alkyl groups (always a *t*-butyl group, if present) lies approximately antiperiplanar (*trans*) to *X* in the atom sequence C–P–E–*X*; the central carbon atom of this group is consistently labelled C1. This behaviour, for which we see no clear explanation, contrasts with that of the gold(I) derivatives in Part 6, where the isopropyl group (where present, with two exceptions) occupied the *trans* position, and also with that of the gold(III) derivatives in Part 7, where the tendency of the isopropyl group to lie *trans* to *X* was over-

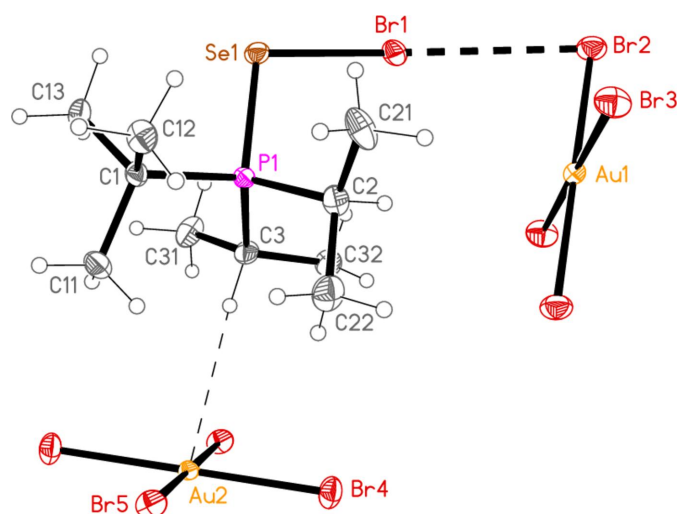


Figure 13
The structure of compound **22b** in the crystal. Ellipsoids represent 50% probability levels.

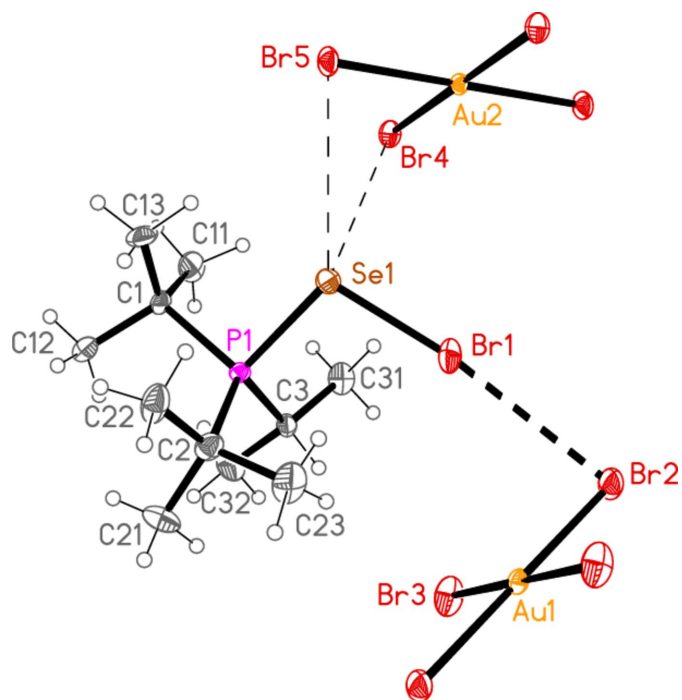


Figure 14
The structure of compound **23c** in the crystal. Ellipsoids represent 50% probability levels.

ridden in all the Bu_2^iPrPE derivatives; we interpreted this in terms of a greater importance of intramolecular hydrogen bonds C–H_{methine}⋯*X*. Selected dimensions of previously published halochalcogenylphosphonium cations are shown in Table 16. There are some differences, *e.g.* the somewhat shorter Se–Cl bonds in this paper compared to the previous values, for which we also see no obvious explanation.

Contacts between the anion and cation of the asymmetric unit, as shown in Figs. 1–14, are discussed in the next section.

3. Supramolecular features

For general aspects of packing and types of secondary interaction, as applied to these compounds, a series of general articles are cited in our previous paper (Upmann *et al.*, 2024a). Details of contacts are given in Tables 16–18, while hydrogen bonds are given in Tables 19–32; these include intramolecular contacts (see above) and several borderline cases, and not all of them will be discussed. The corresponding symmetry operators, not given explicitly in the following discussion, may also be found in those Tables. In all packing diagrams presented here, hydrogen atoms not involved in hydrogen bonding are omitted for clarity, and the atom labels indicate the asymmetric unit. It is worth repeating the caveat that X-ray methods reveal short intermolecular contacts, but not the corresponding energies, so that descriptions of molecular packing in terms of particular secondary contacts must to some extent be subjective. Furthermore, there is no clear objective judgement, on the basis of contact lengths and angles, as to which contacts should be regarded as more

Table 16
Selected dimensions (Å, °) of published structures of halochalcogenylphosphonium cations.

| Compound | P–E | E–X | P–E–X | Reference |
|--|-------------|-------------|------------|-----------------------------|
| [Ph ₃ PSCl][AuCl ₄] | 2.0912 (12) | 2.2278 (13) | 99.87 (5) | Taouss <i>et al.</i> (2015) |
| [Ph ₃ PSBr][AuBr ₄] | 2.0854 (16) | 2.2023 (14) | 101.31 (6) | Taouss <i>et al.</i> (2015) |
| [Ph ₃ PSeBr][AuBr ₄] | 2.2250 (7) | 2.3121 (4) | 97.10 (2) | Taouss <i>et al.</i> (2015) |
| [Ph ₃ PSeCl] ₂ [Au ₄ Se ₂ Cl ₁₀] | 2.216 (2) | 2.222 (3) | 96.83 (9) | Taouss <i>et al.</i> (2015) |
| [(PCP) ⁺ Pr ₂ PSeCl][AuCl ₄] ^a | 2.257 (2) | 2.207 (2) | 94.69 (9) | Upmann <i>et al.</i> (2019) |

Note: (a) PCP = [2.2]paracyclophanyl.

Table 17
Dimensions (Å, °) of halogen···halogen contacts between cations and anions.

The halogen atoms are numbered such that the contact is always X1···X2. For references, see Table 16.

| Compound | X···X | E–X···X | X···X–Au | X···X–Au–X _{cis} ^b |
|---|-------------|-------------|------------|--|
| 18a (X = Cl) | 3.3964 (8) | 171.74 (3) | 75.21 (2) | 86.61 (2) |
| 20a (X = Cl) | 3.2652 (14) | 159.83 (6) | 115.19 (4) | 8.88 (5) |
| 21a (X = Cl) | 3.6071 (5) | 164.28 (2) | 72.72 (2) | 74.65 (2) |
| 22a (X = Cl) | 3.4465 (10) | 171.45 (3) | 73.52 (2) | 85.07 (3) |
| 17b (X = Br) | 3.3206 (5) | 165.22 (2) | 86.52 (1) | 69.07 (1) |
| 18b (X = Br) | 3.2874 (6) | 174.89 (3) | 78.06 (1) | 89.71 (1) |
| 19b (X = Br) | 3.2696 (7) | 173.07 (4) | 84.19 (2) | 76.31 (2) |
| 20b (X = Br) | 3.3465 (7) | 157.33 (3) | 112.62 (2) | 9.80 (2) |
| 21b (X = Br) | 3.3445 (6) | 166.59 (2) | 85.49 (1) | 69.34 (1) |
| 22b (X = Br) | 3.3687 (6) | 175.31 (2) | 75.54 (1) | 88.46 (1) |
| 23b (X = Br) | 3.3416 (11) | 172.85 (4) | 82.51 (3) | 77.96 (3) |
| [Ph ₃ PSCl][AuCl ₄] | 3.2489 (13) | 169.81 (5) | 105.99 (4) | 79.74 (4) |
| [(PCP) ⁺ Pr ₂ PSeCl][AuCl ₄] ^a | 3.696 (3) | 162.71 (11) | 72.40 (4) | 87.76 (9) |
| [Ph ₃ PSBr][AuBr ₄] | 3.1509 (7) | 174.79 (4) | 99.41 (2) | 80.04 (2) |
| [Ph ₃ PSeBr][AuBr ₄] | 3.4009 (5) | 160.89 (1) | 98.79 (1) | 48.32 (1) |

Notes: (a) PCP = [2.2]paracyclophanyl; (b) the smaller absolute torsion angle (of two) is shown; the value to the other X_{cis} is the complementary angle (exactly or approximately, depending on the symmetry) with the opposite sign.

Table 18
Dimensions (Å, °) of chalcogen···chlorine contacts between cations and anions.

| Compound | E···Cl | P–E···Cl | E···Cl–Au | E···Cl–Au–Cl _{cis} ^b |
|---|----------------------|-------------|------------|--|
| 17a (E = S) | S1···Cl5 3.553 (3) | 152.59 (11) | 109.61 (7) | 26.54 (8) |
| 19a (E = S) ^a | S1···Cl2 3.3240 (17) | 162.69 (7) | 95.10 (4) | 61.7 (2) |
| 23a (E = Se) ^a | Se1···Cl2 3.3052 (6) | 164.50 (2) | 95.40 (6) | 59.37 (2) |
| [Ph ₃ PSeCl] ₂ [Au ₄ Se ₂ Cl ₁₀] ^c | Se1···Cl6 3.308 (3) | 158.99 (9) | 116.86 (9) | 55.06 (10) |

Notes: (a) Compounds **19a** and **23a** are isotypic. In both structures, the *cis* chlorines are disordered. (b) The smaller absolute torsion angle (of two) is shown; the value to the other Cl_{cis} is the complementary angle (exactly or approximately, depending on the symmetry) with the opposite sign. (c) Upmann *et al.* (2019).

important or less important for the packing. Finally, the exposed nature of the one-coordinate halogen atoms, taken together with the large number of hydrogen atoms, means that some short H···X contacts are inevitable. Nevertheless, it is possible to provide informative packing diagrams.

The most striking secondary interactions are the short halogen···halogen contacts between cation and anion; these are shown explicitly in Figs. 1–14 (except for compounds **17a**, **19a** and **23a**, for which instead chalcogen···halogen contacts are observed; see below). From our previous experiences, we expected this type of interaction to be ubiquitous for these compounds, but this proved to be an erroneous assumption; only eleven of the fourteen structures display such X···X contacts, and we discuss these first. Selected contact dimensions are given in Table 17. The common features (exceptions are discussed below) are: (1) The X···X distance is generally shorter than the double van der Waals radius and in some cases extremely short, e.g. the Br···Br distance of 3.1509 (7) Å in [Ph₃PSBr][AuBr₄]. Being ‘softer’ than chlorine, bromine would be expected to form stronger (and thus shorter

compared to the van der Waals distance) contacts. (2) The E–X···X grouping is approximately linear. (3) The X···X–Au angle is approximately 90°. (4) The relative orientation of the anion and cation is described by the torsion angle X···X–Au–X_{cis}; this too is approximately 90° (positive for one X_{cis} and negative for the other).

The combination of linear E–X···X and right-angled X···X–Au parallels the model for short contacts C–X···X–C in organic compounds, and both may be regarded as a form of ‘halogen bonding’ (see e.g. Metrangolo *et al.*, 2008). The strongest C–X···X–C interactions are termed ‘type II’ according to the classification of Pedireddi *et al.* (1994) and are characterized by C–X···X angles of approximately 180 and 90°. The simple model is that (as shown by calculation) there is a small region of positive charge δ+ in the direction extending one C–X vector, while the overall δ- charge of the other X atom (because of its higher electronegativity compared to carbon) is distributed perpendicular to the C–X bond (Legon, 2010). We are, however, not aware of similar calculations for atoms other than carbon.

Table 19
Hydrogen-bond geometry (Å, °) for **17a**.

| <i>D</i> — <i>H</i> ··· <i>A</i> | <i>D</i> — <i>H</i> | <i>H</i> ··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> — <i>H</i> ··· <i>A</i> |
|----------------------------------|---------------------|-----------------------|-----------------------|----------------------------------|
| C2—H2···Cl1 | 1.00 | 2.86 | 3.343 (7) | 110 |
| C32—H32C···Cl1 | 0.98 | 2.83 | 3.527 (7) | 129 |
| C12—H12B···S1 | 0.98 | 2.57 | 3.069 (9) | 111 |
| C21—H21B···S1 | 0.98 | 2.88 | 3.415 (8) | 115 |
| C22—H22C···Cl3 ⁱ | 0.98 | 2.89 | 3.843 (7) | 164 |
| C1—H1···Cl4 ⁱ | 1.00 | 2.83 | 3.721 (7) | 149 |
| C32—H32A···Cl4 ⁱⁱ | 0.98 | 2.88 | 3.731 (7) | 145 |
| C3—H3···Cl5 ⁱⁱ | 1.00 | 2.72 | 3.701 (7) | 167 |

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 20
Hydrogen-bond geometry (Å, °) for **18a**.

| <i>D</i> — <i>H</i> ··· <i>A</i> | <i>D</i> — <i>H</i> | <i>H</i> ··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> — <i>H</i> ··· <i>A</i> |
|----------------------------------|---------------------|-----------------------|-----------------------|----------------------------------|
| C13—H13B···S1 | 0.98 | 2.63 | 3.073 (2) | 107 |
| C2—H2···Cl1 | 1.00 | 2.95 | 3.383 (2) | 107 |
| C32—H32C···Cl1 | 0.98 | 2.90 | 3.635 (2) | 133 |
| C21—H21C···Cl3 | 0.98 | 2.93 | 3.705 (2) | 137 |
| C11—H11A···Cl5 | 0.98 | 2.97 | 3.742 (2) | 136 |
| C3—H3···Au2 | 1.00 | 2.75 | 3.693 (2) | 158 |
| C2—H2···Cl2 ⁱ | 1.00 | 2.93 | 3.688 (2) | 133 |
| C22—H22A···Cl3 ⁱⁱ | 0.98 | 2.82 | 3.642 (2) | 142 |
| C12—H12B···Cl3 ⁱⁱⁱ | 0.98 | 2.91 | 3.754 (2) | 145 |
| C13—H13B···Cl3 ⁱⁱⁱ | 0.98 | 2.98 | 3.876 (2) | 153 |
| C12—H12A···Cl4 ^{iv} | 0.98 | 2.78 | 3.699 (2) | 157 |
| C13—H13A···Cl4 ^v | 0.98 | 2.93 | 3.760 (2) | 143 |

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y, -z + 1$; (iv) $x + 1, y - 1, z$; (v) $x, y - 1, z$.

Table 21
Hydrogen-bond geometry (Å, °) for **19a**.

| <i>D</i> — <i>H</i> ··· <i>A</i> | <i>D</i> — <i>H</i> | <i>H</i> ··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> — <i>H</i> ··· <i>A</i> |
|----------------------------------|---------------------|-----------------------|-----------------------|----------------------------------|
| C3—H3···Au2 | 1.00 | 2.93 | 3.786 (5) | 144 |
| C3—H3···Cl6 | 1.00 | 2.90 | 3.751 (5) | 143 |
| C13—H13A···S1 | 0.98 | 2.46 | 3.049 (5) | 118 |
| C23—H23B···Cl1 | 0.98 | 2.74 | 3.305 (5) | 117 |
| C31—H31B···Cl1 | 0.98 | 2.66 | 3.393 (5) | 132 |
| C23—H23A···Cl6 ⁱ | 0.98 | 2.74 | 3.713 (5) | 173 |
| C21—H21C···Cl6 ⁱⁱ | 0.98 | 2.90 | 3.672 (5) | 137 |
| C13—H13B···Cl3 ⁱⁱⁱ | 0.98 | 2.81 | 3.536 (8) | 131 |
| C22—H22B···Cl2 ^{iv} | 0.98 | 2.87 | 3.783 (5) | 156 |
| C13—H13C···Cl4 ^v | 0.98 | 2.89 | 3.677 (19) | 138 |

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, -y + 2, z - \frac{1}{2}$; (iv) $-x + 1, -y + 2, -z + 1$; (v) $-x + 1, -y + 1, -z + 1$.

Table 22
Hydrogen-bond geometry (Å, °) for **20a**.

| <i>D</i> — <i>H</i> ··· <i>A</i> | <i>D</i> — <i>H</i> | <i>H</i> ··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> — <i>H</i> ··· <i>A</i> |
|----------------------------------|---------------------|-----------------------|-----------------------|----------------------------------|
| C23—H23B···Cl1 | 0.98 | 2.71 | 3.522 (4) | 141 |
| C22—H22B···Cl1 | 0.98 | 2.68 | 3.497 (4) | 141 |
| C33—H33B···Cl1 | 0.98 | 2.82 | 3.401 (4) | 118 |
| C13—H13A···Cl5 ⁱ | 0.98 | 2.88 | 3.796 (4) | 156 |
| C12—H12C···Cl5 | 0.98 | 2.92 | 3.810 (4) | 151 |
| C31—H31C···Cl5 ⁱⁱ | 0.98 | 2.84 | 3.763 (4) | 158 |
| C12—H12C···S1 | 0.98 | 2.44 | 3.027 (4) | 118 |
| C22—H22B···S1 | 0.98 | 2.92 | 3.370 (4) | 109 |
| C33—H33B···S1 | 0.98 | 2.92 | 3.424 (4) | 113 |
| C21—H21A···Cl4 ⁱⁱⁱ | 0.98 | 2.77 | 3.708 (4) | 161 |

Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

The main exceptions to the above generalities involve the tri-*t*-butyl derivatives **20a** and **20b**, which show the narrowest *E*—*X*···*X* angles [159.83 (6) and 157.33 (4)°], the widest *X*···*X*—Au angles [115.19 (4) and 112.62 (2)°] and completely

Table 23
Hydrogen-bond geometry (Å, °) for **21a**.

| <i>D</i> — <i>H</i> ··· <i>A</i> | <i>D</i> — <i>H</i> | <i>H</i> ··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> — <i>H</i> ··· <i>A</i> |
|----------------------------------|---------------------|-----------------------|-----------------------|----------------------------------|
| C21—H21B···Cl1 | 0.98 | 2.84 | 3.545 (2) | 129 |
| C32—H32C···Cl1 | 0.98 | 2.95 | 3.712 (2) | 135 |
| C1—H1···Cl5 | 1.00 | 2.93 | 3.8615 (19) | 156 |
| C2—H2···Cl2 ⁱ | 1.00 | 2.82 | 3.6147 (19) | 137 |
| C3—H3···Cl2 ⁱⁱ | 1.00 | 2.94 | 3.5249 (19) | 118 |
| C31—H31C···Cl2 ⁱⁱ | 0.98 | 2.98 | 3.626 (2) | 125 |
| C21—H21C···Cl2 ⁱⁱⁱ | 0.98 | 2.98 | 3.868 (2) | 151 |
| C11—H11C···Cl4 ⁱⁱⁱ | 0.98 | 2.87 | 3.828 (2) | 166 |
| C1—H1···Cl4 ^{iv} | 1.00 | 2.78 | 3.5341 (19) | 133 |

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $x, y + 1, z$; (iii) $x - 1, y, z$; (iv) $-x + 2, -y + 2, -z + 1$.

Table 24
Hydrogen-bond geometry (Å, °) for **22a**.

| <i>D</i> — <i>H</i> ··· <i>A</i> | <i>D</i> — <i>H</i> | <i>H</i> ··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> — <i>H</i> ··· <i>A</i> |
|----------------------------------|---------------------|-----------------------|-----------------------|----------------------------------|
| C13—H13B···Se1 | 0.98 | 2.65 | 3.142 (3) | 111 |
| C2—H2···Cl1 | 1.00 | 2.99 | 3.454 (3) | 110 |
| C3—H3···Au2 | 1.00 | 2.75 | 3.690 (3) | 157 |
| C32—H32C···Cl1 | 0.98 | 2.92 | 3.682 (3) | 135 |
| C21—H21C···Cl3 | 0.98 | 2.99 | 3.774 (3) | 138 |
| C11—H11A···Cl5 | 0.98 | 2.97 | 3.741 (3) | 137 |
| C2—H2···Cl2 ⁱ | 1.00 | 2.87 | 3.629 (3) | 133 |
| C22—H22A···Cl3 ⁱⁱ | 0.98 | 2.79 | 3.629 (3) | 144 |
| C12—H12B···Cl3 ⁱⁱⁱ | 0.98 | 2.95 | 3.783 (3) | 143 |
| C13—H13B···Cl3 ⁱⁱⁱ | 0.98 | 3.01 | 3.902 (3) | 152 |
| C12—H12A···Cl4 ^{iv} | 0.98 | 2.80 | 3.721 (3) | 156 |
| C13—H13A···Cl4 ^v | 0.98 | 2.94 | 3.751 (3) | 141 |

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y, -z + 1$; (iv) $x + 1, y - 1, z$; (v) $x, y - 1, z$.

Table 25
Hydrogen-bond geometry (Å, °) for **23a**.

| <i>D</i> — <i>H</i> ··· <i>A</i> | <i>D</i> — <i>H</i> | <i>H</i> ··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> — <i>H</i> ··· <i>A</i> |
|----------------------------------|---------------------|-----------------------|-----------------------|----------------------------------|
| C3—H3···Au2 | 1.00 | 2.95 | 3.805 (2) | 144 |
| C3—H3···Cl6 | 1.00 | 2.88 | 3.730 (2) | 143 |
| C13—H13A···Se1 | 0.98 | 2.52 | 3.110 (3) | 119 |
| C23—H23B···Cl1 | 0.98 | 2.81 | 3.385 (3) | 118 |
| C31—H31B···Cl1 | 0.98 | 2.66 | 3.451 (3) | 138 |
| C23—H23A···Cl6 ⁱ | 0.98 | 2.76 | 3.736 (2) | 173 |
| C21—H21C···Cl6 ⁱⁱ | 0.98 | 2.90 | 3.674 (2) | 137 |
| C13—H13B···Cl3 ⁱⁱⁱ | 0.98 | 2.80 | 3.498 (4) | 129 |
| C22—H22B···Cl2 ^{iv} | 0.98 | 2.86 | 3.787 (3) | 157 |
| C13—H13C···Cl4 ^v | 0.98 | 2.85 | 3.685 (15) | 143 |

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iii) $x, -y + 2, z - \frac{1}{2}$; (iv) $-x + 1, -y + 2, -z + 1$; (v) $-x + 1, -y + 1, -z + 1$.

Table 26
Hydrogen-bond geometry (Å, °) for **17b**.

| <i>D</i> — <i>H</i> ··· <i>A</i> | <i>D</i> — <i>H</i> | <i>H</i> ··· <i>A</i> | <i>D</i> ··· <i>A</i> | <i>D</i> — <i>H</i> ··· <i>A</i> |
|----------------------------------|---------------------|-----------------------|-----------------------|----------------------------------|
| C21—H21B···Br1 | 0.98 | 3.28 | 3.864 (3) | 120 |
| C3—H3···Br2 ⁱ | 1.00 | 3.29 | 3.792 (3) | 113 |
| C31—H31C···Br2 ⁱ | 0.98 | 3.00 | 3.787 (3) | 138 |
| C32—H32A···Br2 ⁱ | 0.98 | 2.98 | 3.763 (3) | 137 |
| C1—H1···Br4 ⁱ | 1.00 | 3.15 | 3.997 (3) | 144 |
| C21—H21C···Br4 ⁱⁱ | 0.98 | 3.06 | 3.943 (3) | 151 |
| C31—H31B···Br4 ⁱ | 0.98 | 3.04 | 3.983 (3) | 162 |
| C1—H1···Br5 ⁱ | 1.00 | 2.98 | 3.802 (3) | 140 |
| C22—H22C···Br5 ⁱⁱⁱ | 0.98 | 3.11 | 3.911 (3) | 140 |

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

different absolute torsion angles *X*···*X*—Au—*X*_{cis} of 8.88 (5) and 9.80 (2)° [paired with 171.12 (2) and 170.20 (2)° for the other *X*_{cis} atom], so that these four atoms form a synperiplanar grouping. The compound [Ph₃PSeBr][AuBr₄] is also an

Table 27
Hydrogen-bond geometry (Å, °) for **18b**.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| C13—H13B...S1 | 0.98 | 2.66 | 3.095 (4) | 107 |
| C2—H2...Br1 | 1.00 | 2.99 | 3.459 (4) | 110 |
| C3—H3...Au2 | 1.00 | 2.89 | 3.828 (4) | 156 |
| C32—H32C...Br1 | 0.98 | 3.01 | 3.739 (4) | 132 |
| C21—H21C...Br3 | 0.98 | 2.98 | 3.814 (4) | 143 |
| C11—H11A...Br5 | 0.98 | 3.07 | 3.778 (4) | 130 |
| C2—H2...Br2 ⁱ | 1.00 | 3.28 | 4.017 (4) | 132 |
| C22—H22A...Br3 ⁱⁱ | 0.98 | 2.95 | 3.771 (4) | 142 |
| C12—H12B...Br3 ⁱⁱⁱ | 0.98 | 2.93 | 3.832 (4) | 154 |
| C13—H13B...Br3 ⁱⁱⁱ | 0.98 | 3.18 | 4.075 (4) | 152 |
| C12—H12A...Br4 ^{iv} | 0.98 | 2.80 | 3.747 (4) | 163 |
| C13—H13A...Br4 ^v | 0.98 | 3.07 | 3.776 (4) | 130 |

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y, -z + 1$; (iv) $x + 1, y - 1, z$; (v) $x, y - 1, z$.

Table 28
Hydrogen-bond geometry (Å, °) for **19b**.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| C13—H13A...S1 | 0.98 | 2.59 | 3.089 (5) | 112 |
| C31—H31B...Br1 | 0.98 | 2.72 | 3.487 (5) | 135 |
| C23—H23B...Br1 | 0.98 | 2.91 | 3.407 (6) | 112 |
| C3—H3...Br3 | 1.00 | 3.04 | 4.007 (5) | 164 |
| C23—H23C...Br3 | 0.98 | 3.09 | 4.040 (5) | 165 |
| C11—H11C...Br4 | 0.98 | 3.11 | 4.084 (5) | 171 |
| C31—H31C...Br2 ⁱ | 0.98 | 3.06 | 3.781 (5) | 132 |
| C23—H23A...Br4 ⁱⁱ | 0.98 | 2.90 | 3.824 (5) | 157 |
| C13—H13C...Br4 ⁱⁱⁱ | 0.98 | 3.08 | 4.024 (5) | 162 |
| C32—H32C...Br4 ⁱ | 0.98 | 3.03 | 3.814 (5) | 138 |
| C11—H11A...Br5 ⁱⁱⁱ | 0.98 | 3.06 | 3.846 (5) | 138 |
| C32—H32C...Br5 ^{iv} | 0.98 | 3.00 | 3.864 (5) | 148 |

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + 1, -y, -z$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

Table 29
Hydrogen-bond geometry (Å, °) for **20b**.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| C12—H12C...S1 | 0.98 | 2.53 | 3.036 (5) | 112 |
| C22—H22B...Br1 | 0.98 | 2.74 | 3.569 (5) | 143 |
| C23—H23A...Br1 | 0.98 | 2.80 | 3.617 (5) | 142 |
| C22—H22A...Br2 ⁱ | 0.98 | 2.97 | 3.739 (5) | 137 |
| C13—H13C...Br4 ⁱⁱ | 0.98 | 2.95 | 3.859 (5) | 154 |
| C21—H21A...Br4 ⁱⁱⁱ | 0.98 | 2.85 | 3.785 (5) | 160 |

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

outlier, with $X \cdots X - Au - X_{cis}$ values of 48.32 (1) and -131.68 (1)°.

The other three structures (**17a**, **19a** and **23a**) involve $E \cdots Cl$ contacts between the cation and the anion, as we had previously observed for $[Ph_3PSeCl]_2[Au_4Se_2Cl_{10}]$ (Upmann *et al.*, 2019), rather than halogen...halogen contacts. Details are given in Table 18. The $P - E \cdots Cl$ angles are approximately linear and the $E \cdots Cl - Au$ angles are somewhat larger than right angles, but there are no clear trends for the torsion angles $E \cdots Cl - Au - Cl_{cis}$. Since the E atoms presumably carry a partial positive charge, and the Cl atoms a partial negative charge, these $E \cdots Cl$ contacts may be termed as ‘chalcogen bonds’, a class of secondary contact named in analogy to ‘halogen bonds’. Other criteria also fulfil the requirements given by Aakeroy *et al.* (2019). The topic of chalcogen bonds has been reviewed by Vogel *et al.* (2019).

Table 30
Hydrogen-bond geometry (Å, °) for **21b**.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| C21—H21B...Br1 | 0.98 | 3.34 | 3.927 (4) | 120 |
| C3—H3...Br2 ⁱ | 1.00 | 3.27 | 3.788 (3) | 114 |
| C31—H31C...Br2 ⁱ | 0.98 | 3.08 | 3.836 (3) | 135 |
| C32—H32A...Br2 ⁱ | 0.98 | 2.96 | 3.740 (3) | 137 |
| C1—H1...Br4 ⁱ | 1.00 | 3.18 | 4.045 (3) | 145 |
| C21—H21C...Br4 ⁱⁱ | 0.98 | 3.08 | 3.953 (3) | 149 |
| C31—H31B...Br4 ⁱ | 0.98 | 3.03 | 3.972 (4) | 162 |
| C1—H1...Br5 ⁱ | 1.00 | 2.93 | 3.756 (4) | 140 |
| C22—H22C...Br5 ⁱⁱⁱ | 0.98 | 3.15 | 3.893 (4) | 134 |

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

Table 31
Hydrogen-bond geometry (Å, °) for **22b**.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| C13—H13B...Se1 | 0.98 | 2.70 | 3.167 (4) | 109 |
| C2—H2...Br1 | 1.00 | 3.05 | 3.540 (4) | 112 |
| C3—H3...Au2 | 1.00 | 2.85 | 3.783 (4) | 155 |
| C32—H32C...Br1 | 0.98 | 3.05 | 3.788 (4) | 134 |
| C21—H21C...Br3 | 0.98 | 3.03 | 3.848 (4) | 142 |
| C11—H11A...Br5 | 0.98 | 3.05 | 3.787 (4) | 133 |
| C2—H2...Br2 ⁱ | 1.00 | 3.17 | 3.901 (4) | 131 |
| C22—H22A...Br3 ⁱⁱ | 0.98 | 2.92 | 3.764 (4) | 144 |
| C12—H12B...Br3 ⁱⁱⁱ | 0.98 | 2.96 | 3.826 (4) | 148 |
| C13—H13B...Br3 ⁱⁱⁱ | 0.98 | 3.15 | 4.051 (4) | 153 |
| C12—H12A...Br4 ^{iv} | 0.98 | 2.82 | 3.761 (4) | 160 |
| C13—H13A...Br4 ^v | 0.98 | 3.05 | 3.771 (5) | 132 |

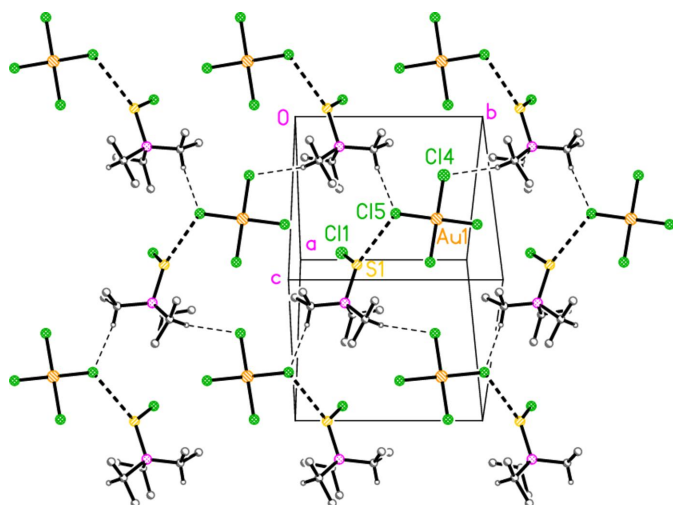
Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z + 1$; (iii) $-x + 1, -y, -z + 1$; (iv) $x + 1, y - 1, z$; (v) $x, y - 1, z$.

Table 32
Hydrogen-bond geometry (Å, °) for **23b**.

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|-------------------------------|-------------|---------------|-----------------------|-------------------------|
| C13—H13A...Se1 | 0.98 | 2.60 | 3.163 (8) | 116 |
| C31—H31B...Br1 | 0.98 | 2.78 | 3.551 (7) | 137 |
| C23—H23B...Br1 | 0.98 | 2.98 | 3.476 (8) | 112 |
| C3—H3...Br3 | 1.00 | 3.13 | 4.108 (7) | 166 |
| C23—H23C...Br3 | 0.98 | 3.05 | 3.994 (9) | 161 |
| C11—H11C...Br4 | 0.98 | 3.23 | 4.182 (7) | 165 |
| C31—H31C...Br2 ⁱ | 0.98 | 3.06 | 3.825 (7) | 136 |
| C23—H23A...Br4 ⁱⁱ | 0.98 | 2.91 | 3.824 (7) | 156 |
| C13—H13C...Br4 ⁱⁱⁱ | 0.98 | 3.06 | 3.998 (8) | 160 |
| C32—H32C...Br4 ⁱ | 0.98 | 3.01 | 3.782 (7) | 136 |
| C11—H11A...Br5 ⁱⁱⁱ | 0.98 | 3.12 | 3.874 (7) | 135 |
| C32—H32C...Br5 ^{iv} | 0.98 | 2.93 | 3.804 (8) | 149 |

Symmetry codes: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $x - \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + 1, -y, -z$; (iv) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

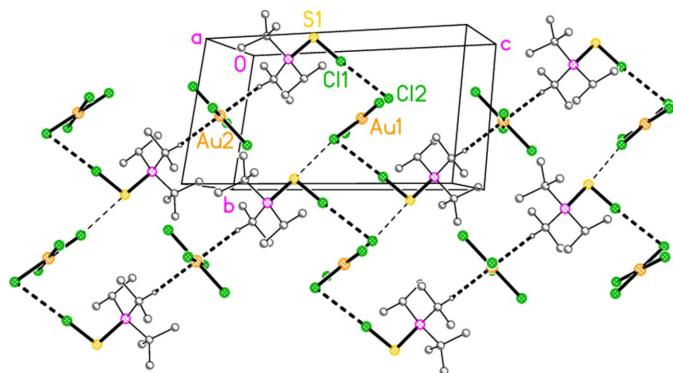
Of course other types of intermolecular contact are also involved in the overall packing, which we now describe. The decision as to which contacts are more or less important is, as remarked above, to some extent subjective; a packing pattern is more assimilable to the human eye if it involves a small number of contacts, and we have tended to choose heavy-atom contacts rather than possible hydrogen bonds. Where the latter are considered, we tend to concentrate on the interactions of the methine rather than the methyl hydrogens; we established in the series of $R^1R^2R^3PEAuX_3$ complexes that the methine hydrogen atoms have a greater tendency than methyl hydrogens to form ‘weak’ hydrogen bonds, thereby influencing the molecular conformation by forming intramolecular $H \cdots X$ hydrogen bonds.


Figure 15

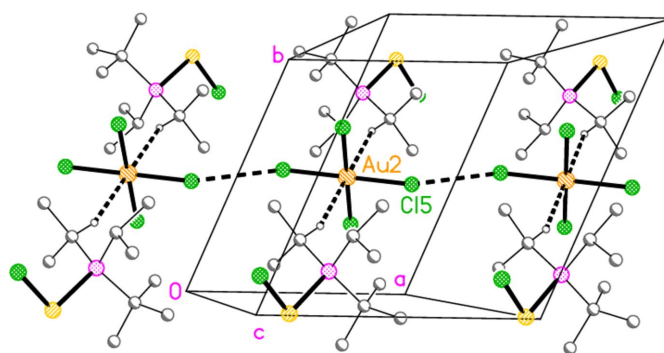
Packing diagram of **17a**. Two H...Cl contacts combine with the S...Cl interactions to form a layer structure parallel to $(\bar{1}01)$; the viewing direction is perpendicular to this plane. The dashed lines indicate S...Cl interactions (thick) or H...Cl contacts (thin). For all packing diagrams, atom labels correspond to the asymmetric unit, and hydrogen atoms not involved in hydrogen bonds are omitted for clarity.

Dance (2003) has pointed out (our paraphrasing) that packing energies are probably determined in many cases by a large number of slightly favourable interactions, such as H...H van der Waals contacts, rather than a small number of very short contacts (of which the shortest may even be unfavourable in energy terms). Despite this, it is probably inevitable that one will (over)emphasize the contacts between heavy atoms in order to make the diagrams more interpretable. Packing diagrams based on the extremely numerous weakly attractive H...H interactions would be neither easily drawn nor easily interpreted.

For compound **17a**, the S...Cl interaction combines with two hydrogen bonds from the methine hydrogens H1 and H3 to form a layer structure parallel to $(\bar{1}01)$ (Fig. 15). The atom H2 makes a short intracationic contact to Cl1, but the angle is necessarily very narrow.


Figure 16

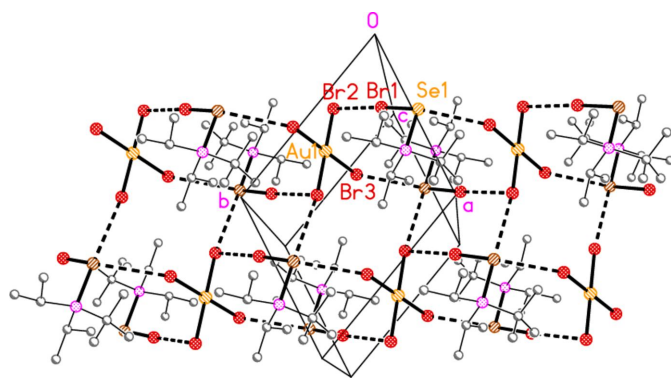
Packing diagram of **18a** viewed perpendicular to (212) , showing two zigzag chains of residues (running horizontally). Dashed lines indicate Cl...Cl and H...Au contacts (thick) or S...Cl contacts (thin).


Figure 17

Packing diagram of **18a** viewed perpendicular to the xy plane in the region $z \approx 0$. Dashed lines indicate Cl...Cl and H...Au contacts.

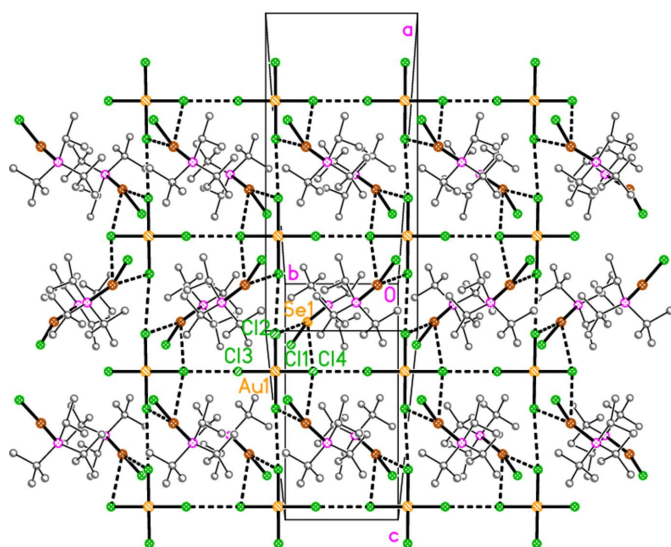
The packing of compound **18a** may be described in terms of three secondary interactions: the short Cl1...Cl2 contact, an unusually short contact C3—H3...Au2 (H...Au = 2.75 Å) that could be classified as a hydrogen bond (Schmidbaur *et al.*, 2014 and Schmidbaur, 2019) and another strikingly short contact, Cl5...Cl5(2 - x, 1 - y, -z) = 3.2632 (10) Å, between anions. The angle Au2—Cl5...Cl5' is 149.86 (3)°. We have drawn attention to such short contacts between $[\text{AuX}_4]^-$ anions elsewhere (Döring & Jones, 2016). The first two contacts lead to the formation of zigzag chains with overall direction parallel to $[10\bar{1}]$ (Fig. 16), further linked by the contact S1...Cl2(-x, -y, 1 - z) = 3.5768 (8) Å; the second and third contacts link cations and Au2 anions parallel to the a axis (Fig. 17). The contact H2...Cl2' between the cation and a symmetry-extended anion is rather long at 2.93 Å; it can be recognized in Fig. 2, but is not drawn explicitly there, and is not included in the packing diagram.

Compounds **18a**, **18b**, **22a** and **22b**, with all possible permutations of $E = \text{S/Se}$ and $X = \text{Cl/Br}$, are isotopic, and so it should not be necessary to provide separate packing diagrams. However, this set of compounds provides a good opportunity to consider the definition of 'isotypic' and the subjectivity of packing diagrams. For **18a**, we considered the S1...Cl2 contact to be significant, but did not include the significantly longer contact S1...Cl3(1 - x, -y, 1 - z), 3.7012 (8) Å, regarding it (arbitrarily) as too long. The corresponding contacts (in Å; same operator as above) for the other compounds are: **18b**, S1...Br2 = 4.0635 (10) and S1...Br3 = 3.6779 (11); **22a**, Se1...Cl2 = 3.4602 (7) and Se1...Cl3 = 3.7004 (8); **22b**, Se1...Br2 = 3.7704 (6) and Se1...Br3 = 3.7484 (6). We draw attention to the considerable variations in the lengths of these contacts; thus S1...Br2 might well be ignored for **18b**, while S1...Br3 is the shorter and thus more significant contact. For **22a**, Se1...Cl2 is the much shorter interaction, whereas for **22b** the lengths are almost equal. For **22b**, one can then draw an alternative packing diagram excluding the anion based on Au2, showing both Se...Br contacts (Fig. 18). The residues are linked by these contacts and by Br1...Br2 to provide cross-linked chains of anions and cations parallel to $[1\bar{1}0]$, forming a layer structure parallel to the ab plane, in which ten-membered rings $\text{Au}_2\text{Se}_2\text{Br}_6$ can be recognized.

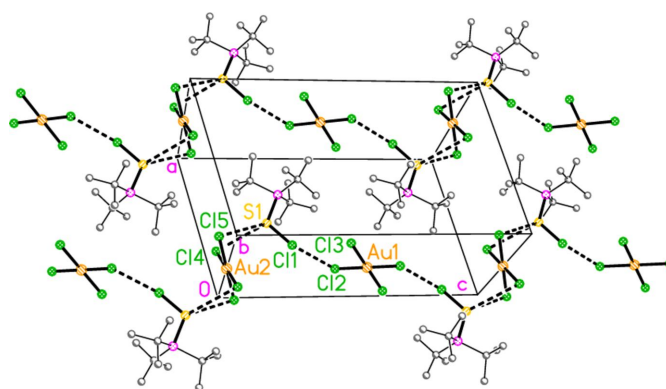

Figure 18

Packing diagram of **22b** viewed perpendicular to the *ab* plane. Hydrogen atoms and the anions based on Au2 are omitted. Residues are linked by Br...Br and Se...Br contacts (thick dashed lines) to form linear arrays (parallel to $[1\bar{1}0]$, horizontal in the diagram), further crosslinked to form a layer.

The potential hydrogen bond H2...Cl2', ignored for **18a** (as discussed above) as being 'too long' at 2.93 Å, also behaves somewhat differently for the other three isotopic structures: for **18b** H2...Cl2' is shorter at 2.87 Å, whereas for the two bromo derivatives **18b** and **22b** the H2...Br2' contacts are very long at 3.28 and 3.17 Å, respectively. This again draws attention to possible significant differences between isotopic structures and to the arbitrary nature of decisions to include or exclude particular contacts in the discussion of the packing. During the preparation of this paper, Bombicz (2024) published a commentary 'What is isostructurality?', in which she raised similar questions, commenting for instance that 'The extent of the difference between corresponding crystal structures referred to as isostructural is not limited', and that


Figure 19

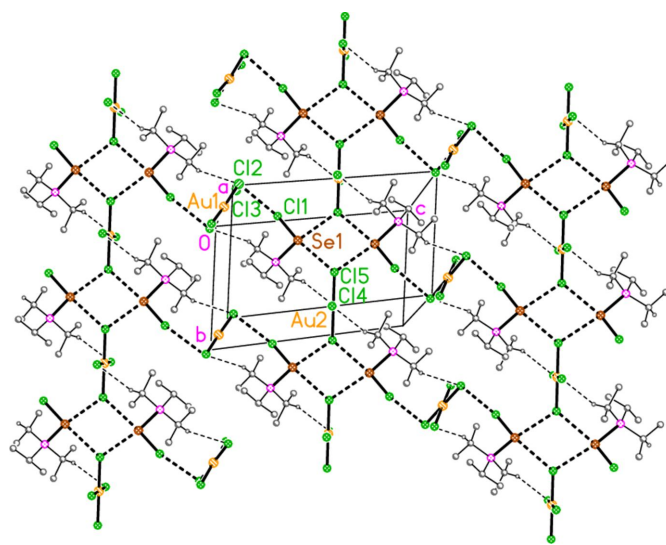
Packing diagram of **23a** viewed perpendicular to the *bc* plane in the region $x \approx 0.5$. Hydrogen atoms and the anion based on Au2 are omitted. For clarity, the positions of the disordered atoms Cl3 and Cl4 are idealized to lie on the twofold axes. Thick dashed lines indicate Cl...Cl or Se...Cl contacts.


Figure 20

Packing diagram of **20a**. The viewing direction has been rotated by *ca* 20° and 10° respectively around the horizontal and vertical directions from the direction parallel to the *b* axis (to avoid overlap of the two S...Cl contacts). Hydrogen atoms are omitted for clarity. Dashed lines indicate Cl...Cl and S...Cl contacts. The unusual orientation of the tetrachloroaurate(III) anion at Au1, with an approximately synperiplanar grouping Cl1...Cl2—Au1—Cl3, can be recognized.

the IUCr definition of 'isostructural/isotypic' (regarded as synonymous terms) is vague on this point.

Compound **19a** and the isotopic **23a** (as discussed above, see Figs. 3 and 7) involve *E*...Cl rather than Cl...Cl interactions between the cation and one anion (based on Au1); the other anion (based on Au2) is close to the methine hydrogen H3, with H3...Au2 and H3...Cl6 distances of 2.93, 2.90 Å for **19a** and 2.95, 2.88 Å for **23a** that might be interpreted as three-centre hydrogen bonds. The main feature of the packing (as shown in Fig. 19 for **23a**) is the formation of almost square networks of $[\text{AuCl}_4]^-$ anions, involving Au1, parallel to the *bc* plane in the regions $x \approx 0, 0.5$, within which the cations are linked *via* *E*...Cl contacts. The contact distances (Å) are $\text{S1}\cdots\text{Cl4}(1-x, y, \frac{3}{2}-z) = 3.80$, $\text{Cl3}\cdots\text{Cl4}(x, 1+y, z) = 3.30$,


Figure 21

Packing diagram of **21a**, viewed perpendicular to $(10\bar{1})$. Dashed lines indicate Cl...Cl and Se...Cl contacts (thick) or H_{methine}...Cl hydrogen bonds (thin). Note that the set of AuCl_4^- anions based on Au2 is seen edge on, whereby the gold atoms are obscured.

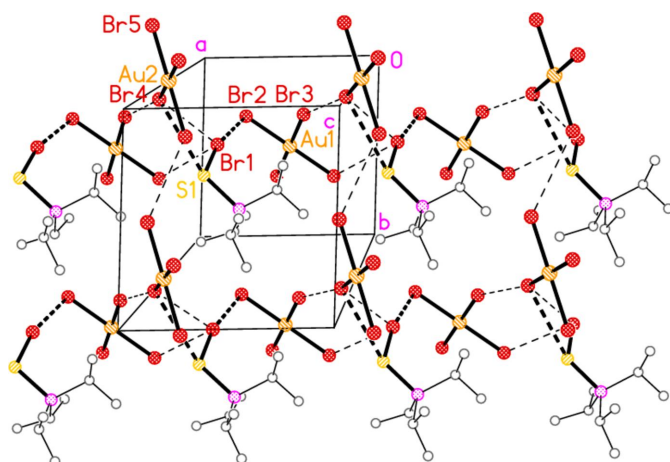


Figure 22
Layer structure of **17b** viewed perpendicular to the *ab* plane in the region $z \approx 0.25$. Dashed lines indicate contacts $S1 \cdots Br4$ and $Br1 \cdots Br2$ (thick) or other appreciably longer $Br \cdots Br$ contacts (thin).

$Cl2 \cdots Cl2(1 - x, 2 - y, 1 - z) = 3.633(2)$ for **19a** and $Se1 \cdots Cl4 = 3.77$, $Cl3 \cdots Cl4 = 3.28$, $Cl2 \cdots Cl2 = 3.6717(12)$ for **23a** (note however that the disorder of $Cl3$ and $Cl4$ make these values uncertain; in Fig. 19, the idealized positions on the twofold axis are used for clarity, and these are the basis for the calculated distances). The $[AuCl_4]^-$ anions involving $Au2$ occupy the regions at $x \approx 0.25, 0.75$.

Compound **20a** forms winding chains parallel to the *c* axis (Fig. 20); residues are linked by the interionic $Cl1 \cdots Cl2$ contact and a double contact from $S1$ to two chlorine atoms of a neighbouring anion [$S1 \cdots Cl4 = 3.6661(14)$, $S1 \cdots Cl5 = 3.5471(14) \text{ \AA}$], whereby the corresponding $S1 \cdots Au2$ distance is necessarily short at $3.7113(9) \text{ \AA}$. Chains are linked by several $H \cdots Cl$ contacts.

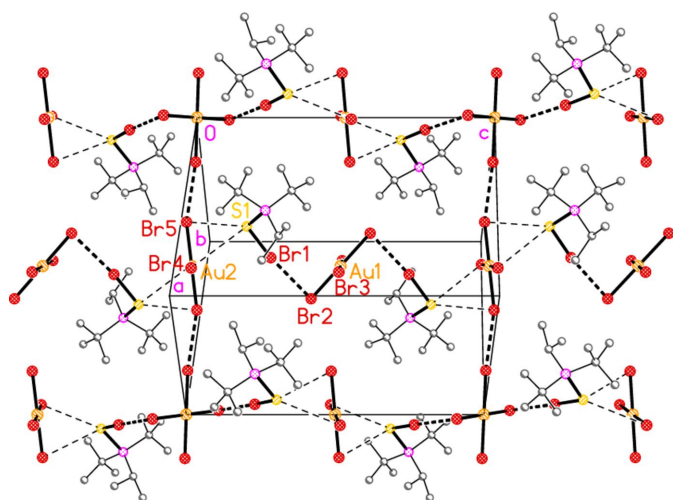


Figure 23
Layer structure of **19b** viewed perpendicular to $(1\bar{0}0)$. Dashed lines indicate short $Br \cdots Br$ contacts (thick) or rather longer $S \cdots Br$ contacts (thin). The anions based on $Au2$ are viewed edge-on, so that the atom $Au2$ is obscured by $Br4$. The corresponding anion at the right-hand edge of the cell is shown more clearly. The probable hydrogen bonds $H3 \cdots Br3$ (see text and Fig. 10) are omitted for clarity.

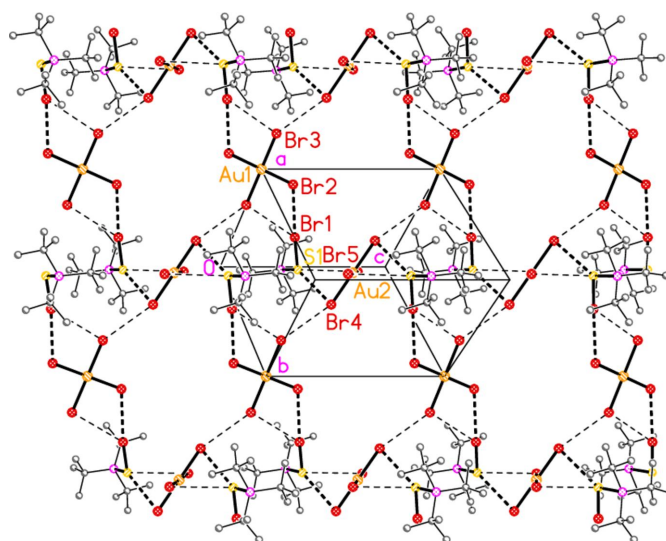


Figure 24
Layer structure of **20b** viewed perpendicular to (110) . Dashed lines indicate short (thick) or long (thin) $Br \cdots Br$ and $S \cdots Br$ contacts. The horizontal direction is $[001]$ and the vertical direction $[1\bar{1}0]$. The anions based on $Au2$ are viewed edge-on, so that the atom $Au2$ is obscured by $Br5$.

In the packing of compound **21a**, two $Se \cdots Cl$ contacts [$Se1 \cdots Cl5 = 3.3504(6)$ and $Se1 \cdots Cl5(2 - x, 1 - y, 1 - z) = 3.3728(5) \text{ \AA}$], which form striking Se_2Cl_2 quadrilaterals, combine with the long $Cl1 \cdots Cl2$ contact, $3.6031(7) \text{ \AA}$, and two $H_{\text{methine}} \cdots Cl$ hydrogen bonds to symmetry-extended anions to form a layer structure parallel to $(10\bar{1})$ (Fig. 21). The quadrilaterals are thereby linked directly by $[AuCl_4]^-$ anions involving $Au2$, parallel to the *b* axis, and indirectly via $[AuCl_4]^-$ anions involving $Au1$, parallel to $[111]$. The methine hydrogen $H1$ makes a short contact to $Cl4'$ (2.78 \AA), but also a longer contact of 2.93 \AA to the neighbouring $Cl5$ atom; this may be regarded as an asymmetric three-centre system, but the longer contact is omitted from the Figures. The third methine hydrogen, $H3$, also makes a longer contact of 2.94 \AA to $Cl2(x, 1 + y, z)$; this contact also lies in the layer but is omitted for clarity.

The packing of **17b** only has one strikingly short contact, $Br1 \cdots Br2 = 3.3206(5) \text{ \AA}$ between anion and cation, but there is also a three-centre grouping with $Br4 \cdots Br1 = 3.8725(5)$ and $Br4 \cdots S1 = 3.7666(8) \text{ \AA}$, also within the asymmetric unit. Additionally, the borderline contacts $Br1 \cdots Br2(2 - x, 1 - y, -z) = 3.8652(5)$, $Br3 \cdots Br4(-1 + x, y, z) = 3.8725(5)$ and $Br5 \cdots Br5(2 - x, -1 - y, 1 - z) = 3.8808(6) \text{ \AA}$ link the residues to form layers parallel to the *ab* plane (Fig. 22). The two possible weak hydrogen bonds $H1 \cdots Br5$ and $H3 \cdots Br3$, quite long but reasonably linear, also lie within these layers, but are omitted from Fig. 22 for clarity. The isotopic structure **21b** has a much shorter corresponding $Se1 \cdots Br4$ contact of $3.6501(5) \text{ \AA}$.

For compound **19b**, there are two very short $Br \cdots Br$ contacts, namely $Br1 \cdots Br2 = 3.2686(7) \text{ \AA}$ between anion and anion and $Br3 \cdots Br5(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z) = 3.3324(6) \text{ \AA}$ between the two anions. These are accompanied by the three-centre association of $S1 \cdots Br4 = 3.7797(13)$ and $S1 \cdots Br5 =$

3.6326 (12) Å and the probable hydrogen bond H3···Br3 (Fig. 10), all within the asymmetric unit, to form a layer structure parallel to (110) (Fig. 23). The corresponding distances for the isotopic **23b** are Br1···Br2 = 3.3416 (11), Br3···Br5 = 3.3205 (10), Se1···Br4 = 3.8310 (11) and Se1···Br5 = 3.5473 (10) Å.

Compound **20b** has three Br···Br contacts: Br1···Br2 = 3.3465 (7) Å, between anion and cation, is very short, whereas the other two, Br1···Br3(2 - x, -y, -z) = 3.7995 (7) and Br3···Br4(1 + x, -1 + y, z) = 3.8361 (7) Å are long. There are also two S···Br contacts, one short and one long, namely S1···Br4 = 3.5208 (13) and S1···Br5(1 - x, 1 - y, 1 - z) = 3.8555 (13) Å. These combine to form a layer structure parallel to (110) (Fig. 24).

4. Database survey

The searches employed the routine ConQuest (Bruno *et al.*, 2002), part of Version 2022.3.0 of the Cambridge Structural Database (Groom *et al.*, 2016).

Except for the structures in our previous work, no hits were registered for the atom sequence P—(S or Se)—(Cl or Br) with coordination numbers restricted to 2 for S/Se and 1 for Cl/Br (but with unrestricted bond orders). To obtain usable values for the E—X single bond lengths, we therefore searched for the sequence C—(S or Se)—(Cl or Br), on the principle that phosphorus and carbon are in many respects similar (see *e.g.* Dillon *et al.*, 1998). We obtained average values of 2.021, 2.224, 2.201 and 2.334 Å for S—Cl (20 values), S—Br (11 values), Se—Cl (12 values) and Se—Br (10 values) bonds, respectively. These are in reasonable agreement with our values given above. Care was, however, necessary in interpreting the search output, because several hits with short intramolecular contacts (some as short as 2.0 Å for Se···O, but not marked as bonds in the Database) involved three-coordinate selenium and, hence, needed to be removed. Thus the compound chloro(8-(*N,N*-dimethylamino)naphthylselenium(II) (Panda *et al.*, 1999; refcode LIWYIZ), with an intramolecular Se—N distance of 2.174 (5) Å and a long Se—Cl bond *trans* to the N atom, was drawn as a formula without an Se—N bond (and therefore, not unreasonably, coded accordingly in the CCDC). The distance was described as ‘non-bonded’, but the displacement ellipsoid plot included this as a normal bond. There seems to be some confusion in the older literature as to what constitutes a bond in such systems.

Similarly, a search for the atom sequence C₃P—S—C, with coordination numbers restricted to 4 for P and 2 for S, gave 19 hits and 21 P—S bond lengths, averaging to 2.076 Å. The analogous search using selenium gave 24 hits and 35 P—Se bond lengths, with an average of 2.233 Å. These are slightly shorter than our average values given above.

5. Synthesis and crystallization

For several of the compounds, the syntheses can be found in the PhD thesis of D. Upmann (Upmann, 2015). There was

however a general problem of incomplete reactions, despite the use of excess oxidants PhICl₂ or Br₂. The following attempted, but not entirely successful, syntheses do not appear there:

Compound **17a**: 212 mg (0.5 mmol) of ⁱPr₃PSAuCl and 344 mg (1.25 mmol) of PhICl₂ were each dissolved in 10 mL of dichloromethane. The solutions were combined and stirred for 30 min, during which time the solution changed from red to yellow; the solvents were then removed under vacuum. All attempts to isolate the product from this solution proved to be unsuccessful because intractable oils or gums were formed; drying and recrystallization generally led to the separation of unidentified insoluble solids. ³¹P-NMR (81 MHz, CDCl₃, 300 K): δ [ppm] 92.56, ¹J_{P-Se} 416.3 Hz. Despite the failure to prepare the substance in quantity, a few single crystals (coated with an adhesive gum) were obtained by overlaying a solution in dichloromethane with *n*-pentane (or diethyl ether) and storing it in a refrigerator (276 K) over the weekend.

Compound **20a**: Pilot experiments suggested that a large excess of PhICl₂ was necessary for complete reaction. 91.8 mg (0.197 mmol) of ⁱBu₃PSAuCl and 541 mg (1.97 mmol) of PhICl₂ were each dissolved in 3 mL of dichloromethane. The solutions were combined; the mixture was then overlaid with *n*-pentane and stored in a refrigerator (276 K) for 7 d. However, no crystals formed. The solvents were then removed under vacuum. The solid residue was washed with *n*-pentane and recrystallized from dichloromethane/*n*-pentane. Yield 77 mg (0.127 mmol, 64%). However, the elemental analysis was poor and some colourless crystals of PhICl₂ were identified by their cell constants. ³¹P-NMR (81 MHz, CDCl₃, 300 K): δ [ppm] 90.18.

Compound **21a**: 236 mg (0.5 mmol) of ⁱPr₃PSeAuCl and 344 mg (1.25 mmol) of PhICl₂ were dissolved in 10/9 mL of dichloromethane, respectively. The solutions were combined and stirred for 30 min, during which time the solution changed from red to yellow; the solvents were then removed under vacuum. The product proved to be very sensitive to air and moisture, and decomposed rapidly in solution. ³¹P-NMR (81 MHz, CDCl₃, 300 K): δ [ppm] 92.56, ¹J_{P-Se} 416 Hz. Despite the failure to prepare the substance in quantity, single crystals were obtained by overlaying a solution in dichloromethane with *n*-pentane and storing it in a refrigerator (276 K) over the weekend.

Compounds **17b** and **21b**: Treatment of solutions of ⁱPr₃PEAuBr₃ in dichloromethane with excess elemental bromine led to solutions whose ³¹P-NMR spectra showed the presence of both starting material and product (**17b** δ 84.15; **21b** δ 80.47). Removal of the solvent, followed by crystallization attempts, led to some single crystals of the products. For **21b**, the NMR spectrum was of poor quality and no P—Se coupling was detected.

Compounds **20b** and **24b**: Treatment of solutions of [(ⁱBu₃PE)₂Au][AuBr₄] (the syntheses and structures of these are still to be published) in dichloromethane with excess elemental bromine led to solutions whose ³¹P-NMR spectra showed the presence of both starting material and product (**20b** δ 91.16; **24b** δ 88.08). Removal of the solvent, followed by

Table 33
Experimental details.

| | 17a | 18a | 19a | 20a | 21a |
|---|---|---|--|--|---|
| Crystal data | | | | | |
| Chemical formula | (C ₉ H ₂₁ ClPS)[AuCl ₄] | (C ₁₀ H ₂₃ ClPS)[AuCl ₄] | (C ₁₁ H ₂₅ ClPS)[AuCl ₄] | (C ₁₂ H ₂₇ ClPS)[AuCl ₄] | (C ₉ H ₂₁ ClPSe)[AuCl ₄] |
| <i>M_r</i> | 566.50 | 580.53 | 594.55 | 608.58 | 613.40 |
| Crystal system, space group | Monoclinic, <i>P2₁/n</i> | Triclinic, <i>P</i> $\bar{1}$ | Monoclinic, <i>C2/c</i> | Monoclinic, <i>P2₁/n</i> | Triclinic, <i>P</i> $\bar{1}$ |
| Temperature (K) | 100 | 100 | 100 | 100 | 100 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 13.3577 (5), 10.0877 (3), 13.9182 (5) | 7.5619 (4), 8.7408 (4), 15.4558 (6) | 33.653 (3), 7.7933 (3), 16.212 (2) | 9.7661 (3), 12.5787 (3), 16.9776 (5) | 7.4202 (3), 8.5966 (3), 15.3980 (6) |
| α , β , γ (°) | 90, 106.290 (4), 90 | 84.346 (4), 78.306 (4), 66.915 (5) | 90, 113.861 (8), 90 | 90, 103.887 (3), 90 | 97.497 (3), 100.128 (4), 109.324 (4) |
| <i>V</i> (Å ³) | 1800.18 (11) | 920.07 (8) | 3888.5 (6) | 2024.67 (10) | 893.42 (6) |
| <i>Z</i> | 4 | 2 | 8 | 4 | 2 |
| Radiation type | Mo <i>K</i> α | Mo <i>K</i> α | Mo <i>K</i> α | Mo <i>K</i> α | Mo <i>K</i> α |
| μ (mm ⁻¹) | 9.10 | 8.90 | 8.43 | 8.10 | 11.09 |
| Crystal size (mm) | 0.2 × 0.1 × 0.03 | 0.2 × 0.18 × 0.05 | 0.2 × 0.02 × 0.01 | 0.15 × 0.07 × 0.04 | 0.18 × 0.15 × 0.10 |
| Data collection | | | | | |
| Diffractometer | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos |
| Absorption correction | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) |
| <i>T_{min}</i> , <i>T_{max}</i> | 0.359, 1.000 | 0.316, 1.000 | 0.698, 1.000 | 0.756, 1.000 | 0.631, 1.000 |
| No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections | 65964, 4458, 3807 | 50339, 5453, 4838 | 84613, 4815, 3861 | 8891, 8891, 4196 | 106851, 5322, 4900 |
| <i>R_{int}</i> | 0.056 | 0.032 | 0.096 | – | 0.039 |
| θ values (°) | $\theta_{\max} = 28.3$, $\theta_{\min} = 2.5$ | $\theta_{\max} = 30.8$, $\theta_{\min} = 2.5$ | $\theta_{\max} = 28.3$, $\theta_{\min} = 2.5$ | $\theta_{\max} = 31.3$, $\theta_{\min} = 2.2$ | $\theta_{\max} = 30.9$, $\theta_{\min} = 2.6$ |
| ($\sin \theta/\lambda$) _{max} (Å ⁻¹) | 0.667 | 0.721 | 0.667 | 0.731 | 0.722 |
| Refinement | | | | | |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.040, 0.102, 1.08 | 0.017, 0.036, 1.05 | 0.033, 0.064, 1.04 | 0.022, 0.045, 0.77 | 0.016, 0.033, 1.10 |
| No. of reflections | 4458 | 5453 | 4815 | 8891 | 5322 |
| No. of parameters | 160 | 174 | 191 | 194 | 164 |
| No. of restraints | 0 | 0 | 1 | 0 | 0 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³) | 5.27, -1.24 | 1.32, -1.07 | 2.43, -1.87 | 1.12, -0.92 | 0.83, -0.85 |
| Extinction method | None | $F_c^* = kF_c[1 + 0.001 F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ (<i>SHELXL2019/3</i> ; Sheldrick, 2015) | None | None | $F_c^* = kF_c[1 + 0.001 F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ (<i>SHELXL2019/3</i> ; Sheldrick, 2015) |
| Extinction coefficient | – | 0.00167 (11) | – | – | 0.00346 (11) |
| | 22a | 23a | 17b | 18b | 19b |
| Crystal data | | | | | |
| Chemical formula | (C ₁₀ H ₂₃ ClPSe)[AuCl ₄] | (C ₁₁ H ₂₅ ClPSe)[AuCl ₄] | (C ₉ H ₂₁ BrPS)[AuBr ₄] | (C ₁₀ H ₂₃ BrPS)[AuBr ₄] | (C ₁₁ H ₂₅ BrPS)[AuBr ₄] |
| <i>M_r</i> | 627.43 | 641.46 | 788.80 | 802.83 | 816.86 |
| Crystal system, space group | Triclinic, <i>P</i> $\bar{1}$ | Monoclinic, <i>C2/c</i> | Triclinic, <i>P</i> $\bar{1}$ | Triclinic, <i>P</i> $\bar{1}$ | Monoclinic, <i>P2₁/n</i> |
| Temperature (K) | 100 | 100 | 100 | 100 | 100 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 7.5836 (2), 8.7603 (2), 15.4719 (6) | 33.7472 (6), 7.79306 (8), 16.2575 (3) | 7.8543 (4), 8.0592 (4), 15.3505 (7) | 7.8455 (6), 9.1380 (6), 15.5440 (9) | 12.4712 (4), 10.3712 (3), 16.2524 (5) |
| α , β , γ (°) | 84.445 (3), 78.641 (3), 67.128 (3) | 90, 113.582 (3), 90 | 76.717 (4), 83.169 (4), 87.722 (4) | 86.600 (5), 81.097 (6), 64.862 (6) | 90, 92.724 (3), 90 |
| <i>V</i> (Å ³) | 928.28 (5) | 3918.54 (14) | 938.89 (8) | 996.65 (13) | 2099.73 (11) |
| <i>Z</i> | 2 | 8 | 2 | 2 | 4 |
| Radiation type | Mo <i>K</i> α | Mo <i>K</i> α | Mo <i>K</i> α | Mo <i>K</i> α | Mo <i>K</i> α |
| μ (mm ⁻¹) | 10.67 | 10.12 | 18.65 | 17.57 | 16.69 |
| Crystal size (mm) | 0.2 × 0.2 × 0.03 | 0.35 × 0.2 × 0.04 | 0.2 × 0.08 × 0.05 | 0.25 × 0.1 × 0.03 | 0.35 × 0.25 × 0.10 |
| Data collection | | | | | |
| Diffractometer | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos |
| Absorption correction | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2015) |

Table 33 (continued)

| | 22a | 23a | 17b | 18b | 19b |
|--|--|--|--|--|--|
| T_{\min} , T_{\max} | 0.232, 1.000 | 0.308, 1.000 | 0.247, 1.000 | 0.097, 0.621 | 0.068, 0.286 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 102916, 5490, 4978 | 257492, 6028, 5453 | 54229, 5646, 5089 | 26487, 5731, 5030 | 70058, 6335, 5041 |
| R_{int} | 0.042 | 0.058 | 0.043 | 0.045 | 0.065 |
| θ values ($^{\circ}$) | $\theta_{\max} = 30.9$, $\theta_{\min} = 2.5$ | $\theta_{\max} = 30.9$, $\theta_{\min} = 2.5$ | $\theta_{\max} = 30.9$, $\theta_{\min} = 2.6$ | $\theta_{\max} = 30.8$, $\theta_{\min} = 2.5$ | $\theta_{\max} = 30.9$, $\theta_{\min} = 2.3$ |
| $(\sin \theta/\lambda)_{\max}$ (\AA^{-1}) | 0.722 | 0.723 | 0.721 | 0.720 | 0.723 |
| Refinement | | | | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S | 0.021, 0.054, 1.05 | 0.021, 0.043, 1.11 | 0.021, 0.040, 1.08 | 0.027, 0.052, 1.06 | 0.033, 0.061, 1.09 |
| No. of reflections | 5490 | 6028 | 5646 | 5731 | 6335 |
| No. of parameters | 174 | 191 | 164 | 173 | 183 |
| No. of restraints | 0 | 0 | 0 | 0 | 0 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ ($e \text{\AA}^{-3}$) | 1.86, -1.59 | 1.13, -1.20 | 1.42, -1.15 | 2.15, -2.24 | 2.43, -1.44 |
| Extinction method | $F_c^* = kF_c[1 + 0.001 F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ (SHELXL2019/3; Sheldrick, 2015) | None | $F_c^* = kF_c[1 + 0.001 F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ (SHELXL2019/3; Sheldrick, 2015) | None | None |
| Extinction coefficient | 0.00144 (18) | – | 0.00112 (7) | – | – |

| | 20b | 21b | 22b | 23b |
|--|---|--|--|--|
| Crystal data | | | | |
| Chemical formula | (C ₁₂ H ₂₇ BrPS)[AuBr ₄] | (C ₉ H ₂₁ BrPSe)[AuBr ₄] | (C ₁₀ H ₂₃ BrPSe)[AuBr ₄] | (C ₁₁ H ₂₅ BrPSe)[AuBr ₄] |
| M_r | 830.88 | 835.70 | 849.73 | 863.76 |
| Crystal system, space group | Triclinic, $P\bar{1}$ | Triclinic, $P\bar{1}$ | Triclinic, $P\bar{1}$ | Monoclinic, $P2_1/n$ |
| Temperature (K) | 100 | 100 | 100 | 101 |
| a , b , c (\AA) | 10.2218 (5), 10.8085 (6), 11.1163 (5) | 7.9212 (4), 8.0606 (4), 15.2911 (8) | 7.8155 (3), 9.1505 (3), 15.5221 (5) | 12.3529 (4), 10.4233 (4), 16.4635 (5) |
| α , β , γ ($^{\circ}$) | 70.909 (4), 71.516 (5), 75.645 (4) | 76.817 (5), 82.668 (5), 87.728 (4) | 85.965 (2), 80.294 (3), 66.049 (3) | 90, 93.453 (3), 90 |
| V (\AA^3) | 1086.40 (10) | 942.78 (9) | 999.97 (6) | 2115.97 (12) |
| Z | 2 | 2 | 2 | 4 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ | Mo $K\alpha$ |
| μ (mm^{-1}) | 16.13 | 20.39 | 19.23 | 18.18 |
| Crystal size (mm) | 0.1 \times 0.05 \times 0.002 | 0.1 \times 0.1 \times 0.05 | 0.3 \times 0.2 \times 0.03 | 0.2 \times 0.1 \times 0.02 |
| Data collection | | | | |
| Diffractometer | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos | Oxford Diffraction Xcalibur, Eos |
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2015) | Multi-scan (CrysAlis PRO; Rigaku OD, 2015) | Multi-scan (CrysAlis PRO; Rigaku OD, 2015) | Multi-scan (CrysAlis PRO; Rigaku OD, 2015) |
| T_{\min} , T_{\max} | 0.284, 1.000 | 0.434, 1.000 | 0.202, 1.000 | 0.122, 0.713 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 73343, 6283, 5151 | 69642, 5661, 4881 | 52431, 5847, 5198 | 7063, 7063, 4089 |
| R_{int} | 0.078 | 0.057 | 0.050 | – |
| θ values ($^{\circ}$) | $\theta_{\max} = 30.0$, $\theta_{\min} = 2.4$ | $\theta_{\max} = 30.9$, $\theta_{\min} = 2.6$ | $\theta_{\max} = 30.9$, $\theta_{\min} = 2.4$ | $\theta_{\max} = 28.3$, $\theta_{\min} = 2.3$ |
| $(\sin \theta/\lambda)_{\max}$ (\AA^{-1}) | 0.704 | 0.723 | 0.722 | 0.667 |
| Refinement | | | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S | 0.032, 0.066, 1.05 | 0.024, 0.045, 1.06 | 0.025, 0.063, 1.04 | 0.034, 0.061, 0.81 |
| No. of reflections | 6283 | 5661 | 5847 | 7063 |
| No. of parameters | 193 | 164 | 173 | 184 |
| No. of restraints | 0 | 0 | 0 | 66 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained | H-atom parameters constrained |
| | $w = 1/[\sigma^2(F_o^2) + (0.022P)^2 + 3.2663P]$ where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0173P)^2 + 0.8539P]$ where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 3.0506P]$ where $P = (F_o^2 + 2F_c^2)/3$ | $w = 1/[\sigma^2(F_o^2) + (0.0239P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ ($e \text{\AA}^{-3}$) | 1.56, -1.67 | 1.53, -1.01 | 1.71, -1.44 | 1.72, -1.10 |
| Extinction method | None | $F_c^* = kF_c[1 + 0.001 F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$ (SHELXL2019/3; Sheldrick, 2015) | None | None |
| Extinction coefficient | – | 0.00116 (7) | – | – |

Computer programs: CrysAlis PRO (Rigaku OD, 2015), SHELXS97 (Sheldrick, 2008), SHELXL2019/3 (Sheldrick, 2015) and XP (Bruker, 1998).

crystallization attempts, led to some single crystals of **20b** (but not of **24b**). For **24b**, the NMR spectrum was of poor quality and no P–Se coupling was detected.

6. Refinement

Details of the measurements and refinements are given in Table 33. Structures were refined anisotropically on F^2 . Methine hydrogens were included at calculated positions and refined using a riding model with C–H = 1.00 Å and $U(\text{H}) = 1.2 \times U_{\text{eq}}(\text{C})$. Methyl groups were refined, using the command ‘AFIX 137’, as idealized rigid groups allowed to rotate but not to tip, with C–H = 0.98 Å, H–C–H = 109.5° and $U(\text{H}) = 1.5 \times U_{\text{eq}}(\text{C})$. This procedure is less reliable for heavy-atom structures, so that any postulated hydrogen bonds involving methyl hydrogen atoms should be interpreted with caution.

Special features: For **17a**, there is a large difference peak of $ca\ 5.6\ \text{e}\ \text{Å}^{-3}$ near the gold atom Au1. This peak may probably be attributed to residual absorption errors. It can be ‘removed’ by assuming a disorder of the AuCl₄ anion (the minor site then has an occupation of $ca\ 3\%$), but we do not find this strategy satisfactory. [Note added during revision. The referee asked for an explanation of ‘unsatisfactory’: Heavy-atom structures generally show significant residual electron density near the heavy atom, and this can be large if the data are not of high quality. These peaks can always be removed by the *ad hoc* method of refining them as an alternative heavy-atom position with low occupation. However, the lighter atom positions (here chlorines with occupation factor 3%) cannot be clearly identified, but only guessed and then refined with strict restraints. We therefore prefer to assume that the large peak is a result of imperfect data, and that it would not be justifiable to remove it for cosmetic reasons.] The U values of this structure are significantly higher than those of the other structures, and the corresponding figure shows 30% rather than 50% ellipsoids. For **19a** (and the isotopic **23a**), the anion centred on Au1 is disordered, with the atoms Cl3 and Cl4 being slightly displaced from the twofold axis. Dimensions of disordered groups should be interpreted with caution. For **20a**, the data were affected by a small twinning component (rotated by 180° about the c axis) that was at first not detected, but which led to poor agreement of data with $l = 4$. Data reduction and refinement (‘HKLf 5’ method; Sheldrick, 2015) as a non-merohedral twin led to a BASF parameter (relative volume of the smaller twin component) of 0.0300 (3). As is often the case with ‘HKLf 5’ refinements, several reflections were severely in error; 20 of these were removed from the dataset. Because equivalent reflections are merged during the generation of the ‘HKLf 5’ intensity dataset, and because both overlapped and non-overlapped reflections are included in the refinement, the number of reflections should be interpreted carefully. The low GOOF value may be associated with the difficulty of estimating s.u.’s for the intensities of the small twin component (and of the weak intensities not corresponding to the pseudo- I centring caused by the presence of two gold atoms on special positions). Similarly, the crystal of **23b** was a two-component non-merohedral twin (by 180° rotation about the a^* axis). The

relative volume of the smaller twin component refined to 0.0807 (6). The U values of the carbon atoms were restrained to be less anisotropic using the command ‘ISOR \$C 0.005’. For several of the non-twinning structures, a few (1–3) poorly fitting reflections ($\Delta/\sigma\ ca\ 7\text{--}11$) were omitted from the refinement.

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supporting information

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Crystal structures of fourteen halochalcogenylphosphonium tetrahalogenidoaurates(III)

Daniel Upmann, Dirk Bockfeld, Peter G. Jones and Eliza Târcoveanu

Computing details

(Chlorosulfanyl)tris(propan-2-yl)phosphonium tetrachloridoaurate(III) (17a)

Crystal data

(C₉H₂₁ClPS)[AuCl₄]
 $M_r = 566.50$
 Monoclinic, $P2_1/n$
 $a = 13.3577$ (5) Å
 $b = 10.0877$ (3) Å
 $c = 13.9182$ (5) Å
 $\beta = 106.290$ (4)°
 $V = 1800.18$ (11) Å³
 $Z = 4$

$F(000) = 1080$
 $D_x = 2.090$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 13392 reflections
 $\theta = 2.5$ – 27.5 °
 $\mu = 9.10$ mm⁻¹
 $T = 100$ K
 Plate, yellow
 $0.2 \times 0.1 \times 0.03$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
 diffractometer
 Radiation source: fine-focus sealed tube
 Detector resolution: 16.1419 pixels mm⁻¹
 ω scan
 Absorption correction: multi-scan
 (CrysAlisPro; Rigaku OD, 2015)
 $T_{\min} = 0.359$, $T_{\max} = 1.000$

65964 measured reflections
 4458 independent reflections
 3807 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.056$
 $\theta_{\max} = 28.3$ °, $\theta_{\min} = 2.5$ °
 $h = -17 \rightarrow 17$
 $k = -13 \rightarrow 13$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.102$
 $S = 1.08$
 4458 reflections
 160 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 16.018P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 5.27$ e Å⁻³
 $\Delta\rho_{\min} = -1.24$ e Å⁻³

Special details

Refinement. The structure can also be refined with a second position of the AuCl₄ anion, occupation ca. 3%, which leads to an improved R factor, but is probably just a way of removing the excess residual electron density at the gold atom, in turn probably caused by residual absorption errors.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{iso} */ <i>U</i> _{eq} |
|------|--------------|--------------|--------------|---|
| P1 | 0.49492 (13) | 0.26458 (15) | 0.71127 (13) | 0.0229 (3) |
| S1 | 0.37078 (15) | 0.3269 (2) | 0.59158 (16) | 0.0411 (5) |
| Cl1 | 0.4167 (2) | 0.24787 (19) | 0.47722 (16) | 0.0518 (6) |
| C1 | 0.4821 (6) | 0.3685 (7) | 0.8153 (6) | 0.0332 (15) |
| H1 | 0.524753 | 0.449958 | 0.815124 | 0.040* |
| C2 | 0.6151 (5) | 0.3045 (7) | 0.6810 (5) | 0.0283 (14) |
| H2 | 0.617064 | 0.249462 | 0.621766 | 0.034* |
| C3 | 0.4873 (5) | 0.0874 (6) | 0.7358 (5) | 0.0244 (12) |
| H3 | 0.538296 | 0.069314 | 0.802265 | 0.029* |
| C11 | 0.5284 (6) | 0.3003 (7) | 0.9151 (6) | 0.0366 (16) |
| H11A | 0.524432 | 0.359834 | 0.969554 | 0.055* |
| H11B | 0.601537 | 0.278020 | 0.922051 | 0.055* |
| H11C | 0.489247 | 0.219045 | 0.918159 | 0.055* |
| C12 | 0.3706 (7) | 0.4145 (8) | 0.8027 (7) | 0.047 (2) |
| H12A | 0.325891 | 0.337373 | 0.802076 | 0.071* |
| H12B | 0.345490 | 0.463001 | 0.739501 | 0.071* |
| H12C | 0.368791 | 0.472870 | 0.858506 | 0.071* |
| C21 | 0.6189 (6) | 0.4495 (7) | 0.6512 (6) | 0.0394 (17) |
| H21A | 0.617945 | 0.506362 | 0.707997 | 0.059* |
| H21B | 0.558271 | 0.469518 | 0.594537 | 0.059* |
| H21C | 0.682984 | 0.465715 | 0.631895 | 0.059* |
| C22 | 0.7085 (5) | 0.2646 (7) | 0.7673 (5) | 0.0319 (15) |
| H22A | 0.772495 | 0.272582 | 0.746412 | 0.048* |
| H22B | 0.700199 | 0.172606 | 0.786402 | 0.048* |
| H22C | 0.713043 | 0.322906 | 0.824699 | 0.048* |
| C31 | 0.3807 (6) | 0.0498 (7) | 0.7447 (6) | 0.0351 (16) |
| H31A | 0.328664 | 0.062437 | 0.679948 | 0.053* |
| H31B | 0.363197 | 0.105981 | 0.795134 | 0.053* |
| H31C | 0.381162 | -0.043333 | 0.764827 | 0.053* |
| C32 | 0.5206 (6) | 0.0026 (6) | 0.6583 (5) | 0.0297 (14) |
| H32A | 0.522900 | -0.090931 | 0.677830 | 0.044* |
| H32B | 0.589870 | 0.030604 | 0.655174 | 0.044* |
| H32C | 0.470257 | 0.014050 | 0.592388 | 0.044* |
| Au1 | 0.19556 (2) | 0.73810 (2) | 0.47234 (2) | 0.02350 (9) |
| Cl2 | 0.34024 (14) | 0.70385 (17) | 0.60253 (15) | 0.0379 (4) |
| Cl3 | 0.24567 (14) | 0.95147 (16) | 0.45821 (13) | 0.0325 (4) |
| Cl4 | 0.04849 (14) | 0.77264 (18) | 0.34302 (14) | 0.0355 (4) |
| Cl5 | 0.14653 (14) | 0.52388 (16) | 0.48526 (14) | 0.0341 (4) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|--------------|
| P1 | 0.0234 (8) | 0.0195 (7) | 0.0242 (8) | 0.0026 (6) | 0.0038 (6) | -0.0009 (6) |
| S1 | 0.0346 (10) | 0.0362 (10) | 0.0437 (11) | 0.0058 (8) | -0.0031 (8) | 0.0093 (8) |
| C11 | 0.0764 (15) | 0.0362 (10) | 0.0309 (10) | -0.0012 (9) | -0.0046 (10) | 0.0011 (7) |
| C1 | 0.043 (4) | 0.022 (3) | 0.038 (4) | -0.006 (3) | 0.017 (3) | -0.004 (3) |
| C2 | 0.028 (3) | 0.025 (3) | 0.033 (4) | -0.004 (3) | 0.012 (3) | -0.007 (3) |
| C3 | 0.025 (3) | 0.020 (3) | 0.025 (3) | -0.001 (2) | 0.002 (2) | 0.000 (2) |
| C11 | 0.048 (4) | 0.027 (3) | 0.040 (4) | 0.000 (3) | 0.021 (3) | 0.001 (3) |
| C12 | 0.051 (5) | 0.041 (4) | 0.063 (6) | 0.017 (4) | 0.037 (4) | 0.011 (4) |
| C21 | 0.049 (4) | 0.027 (4) | 0.047 (4) | -0.011 (3) | 0.021 (4) | -0.002 (3) |
| C22 | 0.026 (3) | 0.040 (4) | 0.031 (4) | -0.005 (3) | 0.011 (3) | -0.010 (3) |
| C31 | 0.037 (4) | 0.031 (4) | 0.040 (4) | -0.009 (3) | 0.014 (3) | -0.004 (3) |
| C32 | 0.039 (4) | 0.018 (3) | 0.031 (3) | -0.001 (3) | 0.010 (3) | -0.004 (2) |
| Au1 | 0.02594 (14) | 0.02090 (13) | 0.02427 (14) | -0.00120 (9) | 0.00804 (9) | -0.00287 (9) |
| Cl2 | 0.0324 (9) | 0.0263 (8) | 0.0454 (10) | -0.0038 (7) | -0.0051 (7) | 0.0020 (7) |
| Cl3 | 0.0371 (9) | 0.0226 (7) | 0.0358 (9) | -0.0045 (6) | 0.0069 (7) | 0.0022 (6) |
| Cl4 | 0.0361 (9) | 0.0334 (8) | 0.0307 (8) | -0.0025 (7) | -0.0008 (7) | -0.0002 (7) |
| Cl5 | 0.0357 (9) | 0.0234 (7) | 0.0398 (9) | -0.0068 (6) | 0.0049 (7) | -0.0012 (6) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|----------|------------|---------------|-------------|
| P1—C2 | 1.815 (7) | C12—H12B | 0.9800 |
| P1—C3 | 1.828 (6) | C12—H12C | 0.9800 |
| P1—C1 | 1.834 (7) | C21—H21A | 0.9800 |
| P1—S1 | 2.091 (2) | C21—H21B | 0.9800 |
| S1—C11 | 2.023 (3) | C21—H21C | 0.9800 |
| S1—Cl5 | 3.553 (3) | C22—H22A | 0.9800 |
| C1—C11 | 1.518 (11) | C22—H22B | 0.9800 |
| C1—C12 | 1.522 (11) | C22—H22C | 0.9800 |
| C1—H1 | 1.0000 | C31—H31A | 0.9800 |
| C2—C22 | 1.525 (10) | C31—H31B | 0.9800 |
| C2—C21 | 1.525 (10) | C31—H31C | 0.9800 |
| C2—H2 | 1.0000 | C32—H32A | 0.9800 |
| C3—C31 | 1.511 (9) | C32—H32B | 0.9800 |
| C3—C32 | 1.537 (9) | C32—H32C | 0.9800 |
| C3—H3 | 1.0000 | Au1—Cl2 | 2.2745 (17) |
| C11—H11A | 0.9800 | Au1—Cl3 | 2.2789 (16) |
| C11—H11B | 0.9800 | Au1—Cl5 | 2.2797 (16) |
| C11—H11C | 0.9800 | Au1—Cl4 | 2.2884 (17) |
| C12—H12A | 0.9800 | | |
| C2—P1—C3 | 111.1 (3) | H12A—C12—H12B | 109.5 |
| C2—P1—C1 | 109.9 (3) | C1—C12—H12C | 109.5 |
| C3—P1—C1 | 112.9 (3) | H12A—C12—H12C | 109.5 |
| C2—P1—S1 | 107.7 (2) | H12B—C12—H12C | 109.5 |
| C3—P1—S1 | 111.7 (2) | C2—C21—H21A | 109.5 |

| | | | |
|---------------|-------------|---------------|------------|
| C1—P1—S1 | 103.2 (3) | C2—C21—H21B | 109.5 |
| C11—S1—P1 | 99.25 (11) | H21A—C21—H21B | 109.5 |
| C11—S1—C15 | 107.39 (10) | C2—C21—H21C | 109.5 |
| P1—S1—C15 | 152.59 (11) | H21A—C21—H21C | 109.5 |
| C11—C1—C12 | 112.2 (6) | H21B—C21—H21C | 109.5 |
| C11—C1—P1 | 111.0 (5) | C2—C22—H22A | 109.5 |
| C12—C1—P1 | 112.9 (6) | C2—C22—H22B | 109.5 |
| C11—C1—H1 | 106.8 | H22A—C22—H22B | 109.5 |
| C12—C1—H1 | 106.8 | C2—C22—H22C | 109.5 |
| P1—C1—H1 | 106.8 | H22A—C22—H22C | 109.5 |
| C22—C2—C21 | 112.6 (6) | H22B—C22—H22C | 109.5 |
| C22—C2—P1 | 109.9 (5) | C3—C31—H31A | 109.5 |
| C21—C2—P1 | 112.0 (5) | C3—C31—H31B | 109.5 |
| C22—C2—H2 | 107.3 | H31A—C31—H31B | 109.5 |
| C21—C2—H2 | 107.3 | C3—C31—H31C | 109.5 |
| P1—C2—H2 | 107.3 | H31A—C31—H31C | 109.5 |
| C31—C3—C32 | 112.5 (5) | H31B—C31—H31C | 109.5 |
| C31—C3—P1 | 111.3 (5) | C3—C32—H32A | 109.5 |
| C32—C3—P1 | 111.8 (4) | C3—C32—H32B | 109.5 |
| C31—C3—H3 | 107.0 | H32A—C32—H32B | 109.5 |
| C32—C3—H3 | 107.0 | C3—C32—H32C | 109.5 |
| P1—C3—H3 | 107.0 | H32A—C32—H32C | 109.5 |
| C1—C11—H11A | 109.5 | H32B—C32—H32C | 109.5 |
| C1—C11—H11B | 109.5 | Cl2—Au1—Cl3 | 90.44 (6) |
| H11A—C11—H11B | 109.5 | Cl2—Au1—Cl5 | 89.54 (6) |
| C1—C11—H11C | 109.5 | Cl3—Au1—Cl5 | 179.34 (7) |
| H11A—C11—H11C | 109.5 | Cl2—Au1—Cl4 | 179.13 (7) |
| H11B—C11—H11C | 109.5 | Cl3—Au1—Cl4 | 89.80 (6) |
| C1—C12—H12A | 109.5 | Cl5—Au1—Cl4 | 90.24 (6) |
| C1—C12—H12B | 109.5 | Au1—Cl5—S1 | 109.61 (7) |
| C2—P1—S1—C11 | 48.2 (3) | C3—P1—C2—C22 | -59.0 (5) |
| C3—P1—S1—C11 | -74.0 (3) | C1—P1—C2—C22 | 66.7 (5) |
| C1—P1—S1—C11 | 164.4 (2) | S1—P1—C2—C22 | 178.4 (4) |
| C2—P1—S1—C15 | -118.1 (3) | C3—P1—C2—C21 | 174.9 (5) |
| C3—P1—S1—C15 | 119.7 (3) | C1—P1—C2—C21 | -59.4 (6) |
| C1—P1—S1—C15 | -1.9 (3) | S1—P1—C2—C21 | 52.4 (5) |
| C2—P1—C1—C11 | -92.0 (6) | C2—P1—C3—C31 | -170.9 (5) |
| C3—P1—C1—C11 | 32.6 (6) | C1—P1—C3—C31 | 65.1 (6) |
| S1—P1—C1—C11 | 153.4 (5) | S1—P1—C3—C31 | -50.7 (5) |
| C2—P1—C1—C12 | 141.0 (5) | C2—P1—C3—C32 | -44.1 (5) |
| C3—P1—C1—C12 | -94.4 (6) | C1—P1—C3—C32 | -168.2 (5) |
| S1—P1—C1—C12 | 26.4 (6) | S1—P1—C3—C32 | 76.1 (5) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------|-------|-------------|-------------|---------------|
| C2—H2 \cdots Cl1 | 1.00 | 2.86 | 3.343 (7) | 110 |

| | | | | |
|--|------|------|-----------|-----|
| C32—H32C [⋯] C11 | 0.98 | 2.83 | 3.527 (7) | 129 |
| C12—H12B [⋯] S1 | 0.98 | 2.57 | 3.069 (9) | 111 |
| C21—H21B [⋯] S1 | 0.98 | 2.88 | 3.415 (8) | 115 |
| C32—H32A [⋯] C11 ⁱ | 0.98 | 2.97 | 3.395 (7) | 108 |
| C22—H22C [⋯] C13 ⁱⁱ | 0.98 | 2.89 | 3.843 (7) | 164 |
| C1—H1 [⋯] C14 ⁱⁱ | 1.00 | 2.83 | 3.721 (7) | 149 |
| C32—H32A [⋯] C14 ⁱⁱⁱ | 0.98 | 2.88 | 3.731 (7) | 145 |
| C3—H3 [⋯] C15 ⁱⁱⁱ | 1.00 | 2.72 | 3.701 (7) | 167 |

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $x+1/2, -y+3/2, z+1/2$; (iii) $x+1/2, -y+1/2, z+1/2$.

(tert-Butyl)(chlorosulfanyl)bis(propan-2-yl)phosphonium tetrachloridoaurate(III) (18a)

Crystal data

(C₁₀H₂₃ClPS)[AuCl₄]

$M_r = 580.53$

Triclinic, $P\bar{1}$

$a = 7.5619$ (4) Å

$b = 8.7408$ (4) Å

$c = 15.4558$ (6) Å

$\alpha = 84.346$ (4)[°]

$\beta = 78.306$ (4)[°]

$\gamma = 66.915$ (5)[°]

$V = 920.07$ (8) Å³

$Z = 2$

$F(000) = 556$

$D_x = 2.095$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 21451 reflections

$\theta = 2.5\text{--}30.7$ [°]

$\mu = 8.90$ mm⁻¹

$T = 100$ K

Plate, yellow

$0.2 \times 0.18 \times 0.05$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω scan

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.316$, $T_{\max} = 1.000$

50339 measured reflections

5453 independent reflections

4838 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 30.8$ [°], $\theta_{\min} = 2.5$ [°]

$h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.017$

$wR(F^2) = 0.036$

$S = 1.05$

5453 reflections

174 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0146P)^2 + 0.7146P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.32$ e Å⁻³

$\Delta\rho_{\min} = -1.07$ e Å⁻³

Extinction correction: *SHELXL2019/3*

(Sheldrick, 2015), $F_c^* = kF_c[1 + 0.001$

$F_c^2\lambda^3/\sin(2\theta)]^{1/4}$

Extinction coefficient: 0.00167 (11)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|-------------|-------------|-------------|----------------------------------|
| P1 | 0.50154 (7) | 0.10754 (6) | 0.25334 (3) | 0.01224 (10) |

| | | | | |
|------|--------------|--------------|--------------|--------------|
| S1 | 0.38459 (8) | -0.05864 (6) | 0.32441 (4) | 0.01794 (10) |
| Cl1 | 0.16037 (8) | 0.09519 (6) | 0.41119 (4) | 0.02207 (11) |
| C1 | 0.7444 (3) | -0.0351 (2) | 0.19677 (13) | 0.0153 (4) |
| C2 | 0.5052 (3) | 0.2531 (3) | 0.32961 (13) | 0.0177 (4) |
| H2 | 0.365008 | 0.322876 | 0.351735 | 0.021* |
| C3 | 0.3485 (3) | 0.2313 (2) | 0.17343 (13) | 0.0150 (4) |
| H3 | 0.425026 | 0.289589 | 0.133508 | 0.018* |
| C11 | 0.8102 (3) | 0.0503 (3) | 0.11176 (14) | 0.0202 (4) |
| H11A | 0.810597 | 0.156811 | 0.126276 | 0.030* |
| H11B | 0.719773 | 0.069885 | 0.070783 | 0.030* |
| H11C | 0.942123 | -0.021278 | 0.084058 | 0.030* |
| C12 | 0.8927 (3) | -0.0766 (3) | 0.25912 (14) | 0.0207 (4) |
| H12A | 1.017861 | -0.159937 | 0.232013 | 0.031* |
| H12B | 0.843556 | -0.120881 | 0.315429 | 0.031* |
| H12C | 0.911108 | 0.024451 | 0.269613 | 0.031* |
| C13 | 0.7340 (3) | -0.1982 (2) | 0.17357 (15) | 0.0206 (4) |
| H13A | 0.628937 | -0.172829 | 0.139798 | 0.031* |
| H13B | 0.707756 | -0.259176 | 0.228090 | 0.031* |
| H13C | 0.858777 | -0.266419 | 0.138057 | 0.031* |
| C21 | 0.5927 (4) | 0.1771 (3) | 0.41227 (15) | 0.0272 (5) |
| H21A | 0.735554 | 0.130546 | 0.396580 | 0.041* |
| H21B | 0.546943 | 0.088628 | 0.436873 | 0.041* |
| H21C | 0.551478 | 0.263411 | 0.456305 | 0.041* |
| C22 | 0.5945 (4) | 0.3744 (3) | 0.27927 (16) | 0.0242 (5) |
| H22A | 0.576412 | 0.462365 | 0.318885 | 0.036* |
| H22B | 0.529594 | 0.424156 | 0.228770 | 0.036* |
| H22C | 0.734407 | 0.314002 | 0.258130 | 0.036* |
| C31 | 0.3042 (3) | 0.1241 (3) | 0.11454 (15) | 0.0229 (5) |
| H31A | 0.231644 | 0.062428 | 0.151359 | 0.034* |
| H31B | 0.427100 | 0.045502 | 0.082497 | 0.034* |
| H31C | 0.225641 | 0.195878 | 0.072150 | 0.034* |
| C32 | 0.1580 (3) | 0.3670 (3) | 0.21726 (15) | 0.0216 (4) |
| H32A | 0.083732 | 0.431051 | 0.171716 | 0.032* |
| H32B | 0.189133 | 0.441441 | 0.249630 | 0.032* |
| H32C | 0.079827 | 0.315144 | 0.258369 | 0.032* |
| Au1 | 0.000000 | 0.500000 | 0.500000 | 0.01355 (3) |
| Cl2 | -0.16568 (8) | 0.34352 (7) | 0.57470 (4) | 0.02303 (11) |
| Cl3 | 0.21372 (8) | 0.41221 (7) | 0.59592 (4) | 0.02613 (12) |
| Au2 | 0.500000 | 0.500000 | 0.000000 | 0.01239 (3) |
| Cl4 | 0.34494 (8) | 0.70229 (6) | 0.10234 (4) | 0.02293 (11) |
| Cl5 | 0.79512 (7) | 0.47158 (6) | 0.02926 (4) | 0.02032 (10) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|---------------|---------------|---------------|
| P1 | 0.0107 (2) | 0.0125 (2) | 0.0131 (2) | -0.00431 (18) | -0.00189 (18) | -0.00008 (18) |
| S1 | 0.0162 (2) | 0.0147 (2) | 0.0212 (3) | -0.00623 (18) | -0.00016 (19) | 0.00216 (19) |
| Cl1 | 0.0175 (2) | 0.0233 (2) | 0.0232 (3) | -0.0088 (2) | 0.00370 (19) | -0.0011 (2) |

| | | | | | | |
|-----|-------------|-------------|-------------|---------------|---------------|--------------|
| C1 | 0.0118 (9) | 0.0165 (9) | 0.0148 (9) | -0.0033 (7) | -0.0010 (7) | 0.0004 (7) |
| C2 | 0.0173 (10) | 0.0222 (10) | 0.0158 (10) | -0.0095 (8) | -0.0012 (8) | -0.0055 (8) |
| C3 | 0.0138 (9) | 0.0129 (9) | 0.0179 (10) | -0.0038 (7) | -0.0055 (8) | 0.0023 (7) |
| C11 | 0.0157 (10) | 0.0233 (10) | 0.0175 (10) | -0.0055 (8) | 0.0013 (8) | 0.0016 (8) |
| C12 | 0.0126 (10) | 0.0265 (11) | 0.0200 (11) | -0.0042 (8) | -0.0034 (8) | 0.0008 (8) |
| C13 | 0.0197 (10) | 0.0143 (9) | 0.0250 (11) | -0.0027 (8) | -0.0040 (9) | -0.0033 (8) |
| C21 | 0.0271 (12) | 0.0406 (14) | 0.0167 (11) | -0.0152 (11) | -0.0036 (9) | -0.0049 (10) |
| C22 | 0.0265 (12) | 0.0249 (11) | 0.0266 (12) | -0.0155 (9) | -0.0027 (9) | -0.0042 (9) |
| C31 | 0.0251 (11) | 0.0194 (10) | 0.0254 (12) | -0.0052 (9) | -0.0138 (9) | -0.0008 (9) |
| C32 | 0.0177 (10) | 0.0165 (10) | 0.0264 (12) | -0.0010 (8) | -0.0065 (9) | -0.0001 (8) |
| Au1 | 0.01509 (6) | 0.01277 (5) | 0.01290 (6) | -0.00503 (4) | -0.00292 (4) | -0.00121 (4) |
| Cl2 | 0.0239 (3) | 0.0218 (2) | 0.0256 (3) | -0.0125 (2) | -0.0035 (2) | 0.0033 (2) |
| Cl3 | 0.0254 (3) | 0.0343 (3) | 0.0223 (3) | -0.0129 (2) | -0.0121 (2) | 0.0057 (2) |
| Au2 | 0.00974 (5) | 0.01046 (5) | 0.01638 (6) | -0.00389 (4) | -0.00134 (4) | 0.00042 (4) |
| Cl4 | 0.0181 (2) | 0.0202 (2) | 0.0277 (3) | -0.00397 (19) | -0.0005 (2) | -0.0092 (2) |
| Cl5 | 0.0134 (2) | 0.0207 (2) | 0.0283 (3) | -0.00719 (18) | -0.00544 (19) | 0.0000 (2) |

Geometric parameters (Å, °)

| | | | |
|----------|-------------|-----------------------|------------|
| P1—C2 | 1.829 (2) | C13—H13B | 0.9800 |
| P1—C3 | 1.836 (2) | C13—H13C | 0.9800 |
| P1—C1 | 1.860 (2) | C21—H21A | 0.9800 |
| P1—S1 | 2.0970 (7) | C21—H21B | 0.9800 |
| S1—C11 | 2.0316 (7) | C21—H21C | 0.9800 |
| C11—C12 | 3.3964 (8) | C22—H22A | 0.9800 |
| C1—C11 | 1.538 (3) | C22—H22B | 0.9800 |
| C1—C13 | 1.538 (3) | C22—H22C | 0.9800 |
| C1—C12 | 1.539 (3) | C31—H31A | 0.9800 |
| C2—C21 | 1.530 (3) | C31—H31B | 0.9800 |
| C2—C22 | 1.540 (3) | C31—H31C | 0.9800 |
| C2—H2 | 1.0000 | C32—H32A | 0.9800 |
| C3—C31 | 1.535 (3) | C32—H32B | 0.9800 |
| C3—C32 | 1.538 (3) | C32—H32C | 0.9800 |
| C3—H3 | 1.0000 | Au1—Cl3 ⁱ | 2.2744 (5) |
| C11—H11A | 0.9800 | Au1—Cl3 | 2.2744 (5) |
| C11—H11B | 0.9800 | Au1—Cl2 | 2.2847 (5) |
| C11—H11C | 0.9800 | Au1—Cl2 ⁱ | 2.2847 (5) |
| C12—H12A | 0.9800 | Au2—Cl4 ⁱⁱ | 2.2753 (5) |
| C12—H12B | 0.9800 | Au2—Cl4 | 2.2753 (5) |
| C12—H12C | 0.9800 | Au2—Cl5 | 2.2801 (5) |
| C13—H13A | 0.9800 | Au2—Cl5 ⁱⁱ | 2.2801 (5) |
| C2—P1—C3 | 107.15 (9) | C1—C13—H13C | 109.5 |
| C2—P1—C1 | 115.86 (10) | H13A—C13—H13C | 109.5 |
| C3—P1—C1 | 111.39 (9) | H13B—C13—H13C | 109.5 |
| C2—P1—S1 | 109.35 (7) | C2—C21—H21A | 109.5 |
| C3—P1—S1 | 110.73 (7) | C2—C21—H21B | 109.5 |
| C1—P1—S1 | 102.30 (7) | H21A—C21—H21B | 109.5 |

| | | | |
|---------------|-------------|--|--------------|
| C11—S1—P1 | 101.57 (3) | C2—C21—H21C | 109.5 |
| S1—C11—C12 | 171.74 (3) | H21A—C21—H21C | 109.5 |
| C11—C1—C13 | 109.53 (17) | H21B—C21—H21C | 109.5 |
| C11—C1—C12 | 109.89 (17) | C2—C22—H22A | 109.5 |
| C13—C1—C12 | 108.50 (17) | C2—C22—H22B | 109.5 |
| C11—C1—P1 | 109.31 (14) | H22A—C22—H22B | 109.5 |
| C13—C1—P1 | 110.59 (14) | C2—C22—H22C | 109.5 |
| C12—C1—P1 | 109.01 (13) | H22A—C22—H22C | 109.5 |
| C21—C2—C22 | 112.40 (19) | H22B—C22—H22C | 109.5 |
| C21—C2—P1 | 116.51 (16) | C3—C31—H31A | 109.5 |
| C22—C2—P1 | 110.40 (14) | C3—C31—H31B | 109.5 |
| C21—C2—H2 | 105.5 | H31A—C31—H31B | 109.5 |
| C22—C2—H2 | 105.5 | C3—C31—H31C | 109.5 |
| P1—C2—H2 | 105.5 | H31A—C31—H31C | 109.5 |
| C31—C3—C32 | 110.39 (17) | H31B—C31—H31C | 109.5 |
| C31—C3—P1 | 112.89 (14) | C3—C32—H32A | 109.5 |
| C32—C3—P1 | 112.80 (14) | C3—C32—H32B | 109.5 |
| C31—C3—H3 | 106.8 | H32A—C32—H32B | 109.5 |
| C32—C3—H3 | 106.8 | C3—C32—H32C | 109.5 |
| P1—C3—H3 | 106.8 | H32A—C32—H32C | 109.5 |
| C1—C11—H11A | 109.5 | H32B—C32—H32C | 109.5 |
| C1—C11—H11B | 109.5 | Cl3 ⁱ —Au1—Cl3 | 180.0 |
| H11A—C11—H11B | 109.5 | Cl3 ⁱ —Au1—Cl2 | 89.57 (2) |
| C1—C11—H11C | 109.5 | Cl3—Au1—Cl2 | 90.43 (2) |
| H11A—C11—H11C | 109.5 | Cl3 ⁱ —Au1—Cl2 ⁱ | 90.43 (2) |
| H11B—C11—H11C | 109.5 | Cl3—Au1—Cl2 ⁱ | 89.57 (2) |
| C1—C12—H12A | 109.5 | Cl2—Au1—Cl2 ⁱ | 180.000 (18) |
| C1—C12—H12B | 109.5 | Au1—Cl2—Cl1 | 75.206 (18) |
| H12A—C12—H12B | 109.5 | Cl4 ⁱⁱ —Au2—Cl4 | 180.0 |
| C1—C12—H12C | 109.5 | Cl4 ⁱⁱ —Au2—Cl5 | 89.65 (2) |
| H12A—C12—H12C | 109.5 | Cl4—Au2—Cl5 | 90.35 (2) |
| H12B—C12—H12C | 109.5 | Cl4 ⁱⁱ —Au2—Cl5 ⁱⁱ | 90.34 (2) |
| C1—C13—H13A | 109.5 | Cl4—Au2—Cl5 ⁱⁱ | 89.66 (2) |
| C1—C13—H13B | 109.5 | Cl5—Au2—Cl5 ⁱⁱ | 180.0 |
| H13A—C13—H13B | 109.5 | | |
| C2—P1—S1—C11 | 41.13 (8) | C3—P1—C2—C21 | 169.11 (16) |
| C3—P1—S1—C11 | -76.73 (7) | C1—P1—C2—C21 | -65.87 (19) |
| C1—P1—S1—C11 | 164.48 (7) | S1—P1—C2—C21 | 49.04 (17) |
| C2—P1—C1—C11 | -87.34 (16) | C3—P1—C2—C22 | -61.10 (17) |
| C3—P1—C1—C11 | 35.47 (17) | C1—P1—C2—C22 | 63.92 (18) |
| S1—P1—C1—C11 | 153.80 (13) | S1—P1—C2—C22 | 178.83 (13) |
| C2—P1—C1—C13 | 152.00 (14) | C2—P1—C3—C31 | -170.50 (15) |
| C3—P1—C1—C13 | -85.19 (16) | C1—P1—C3—C31 | 61.82 (18) |
| S1—P1—C1—C13 | 33.14 (15) | S1—P1—C3—C31 | -51.31 (17) |
| C2—P1—C1—C12 | 32.80 (18) | C2—P1—C3—C32 | -44.51 (17) |

| | | | |
|--------------|-------------|--------------|--------------|
| C3—P1—C1—C12 | 155.61 (14) | C1—P1—C3—C32 | -172.19 (14) |
| S1—P1—C1—C12 | -86.06 (14) | S1—P1—C3—C32 | 74.68 (15) |

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

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-------|-------------|-------------|---------------|
| C13—H13B \cdots S1 | 0.98 | 2.63 | 3.073 (2) | 107 |
| C2—H2 \cdots C11 | 1.00 | 2.95 | 3.383 (2) | 107 |
| C32—H32C \cdots C11 | 0.98 | 2.90 | 3.635 (2) | 133 |
| C21—H21C \cdots C13 | 0.98 | 2.93 | 3.705 (2) | 137 |
| C11—H11A \cdots C15 | 0.98 | 2.97 | 3.742 (2) | 136 |
| C3—H3 \cdots Au2 | 1.00 | 2.75 | 3.693 (2) | 158 |
| C2—H2 \cdots Cl2 ⁱ | 1.00 | 2.93 | 3.688 (2) | 133 |
| C22—H22A \cdots C13 ⁱⁱⁱ | 0.98 | 2.82 | 3.642 (2) | 142 |
| C12—H12B \cdots C13 ^{iv} | 0.98 | 2.91 | 3.754 (2) | 145 |
| C13—H13B \cdots C13 ^{iv} | 0.98 | 2.98 | 3.876 (2) | 153 |
| C12—H12A \cdots C14 ^v | 0.98 | 2.78 | 3.699 (2) | 157 |
| C13—H13A \cdots C14 ^{vi} | 0.98 | 2.93 | 3.760 (2) | 143 |

Symmetry codes: (i) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y, -z+1$; (v) $x+1, y-1, z$; (vi) $x, y-1, z$.

Bis(*tert*-butyl)(chlorosulfanyl)(propan-2-yl)phosphonium tetrachloridoaurate(III) (19a)

Crystal data

(C₁₁H₂₅ClPS)[AuCl₄]

$M_r = 594.55$

Monoclinic, $C2/c$

$a = 33.653$ (3) \AA

$b = 7.7933$ (3) \AA

$c = 16.212$ (2) \AA

$\beta = 113.861$ (8) $^\circ$

$V = 3888.5$ (6) \AA^3

$Z = 8$

$F(000) = 2288$

$D_x = 2.031$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 9326 reflections

$\theta = 2.3\text{--}29.3^\circ$

$\mu = 8.43$ mm⁻¹

$T = 100$ K

Plate, yellow

$0.2 \times 0.02 \times 0.01$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω scan

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.698$, $T_{\max} = 1.000$

84613 measured reflections

4815 independent reflections

3861 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.096$

$\theta_{\max} = 28.3^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -44 \rightarrow 44$

$k = -10 \rightarrow 10$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.064$

$S = 1.04$

4815 reflections

191 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0233P)^2 + 18.2209P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 2.42 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -1.86 \text{ e } \text{\AA}^{-3}$

Special details

Refinement. The anion centred on Au1 is disordered, with the atoms Cl3 and Cl4 being slightly displaced from the twofold axis. Dimensions of disordered groups should be interpreted with caution.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|--------------|--------------|-------------|----------------------------------|-----------|
| P1 | 0.37573 (4) | 0.61321 (15) | 0.40339 (8) | 0.0139 (2) | |
| S1 | 0.42233 (4) | 0.76384 (17) | 0.50388 (8) | 0.0229 (3) | |
| Cl1 | 0.38636 (5) | 0.89460 (17) | 0.55781 (9) | 0.0318 (3) | |
| C1 | 0.41258 (15) | 0.4470 (6) | 0.3892 (3) | 0.0178 (10) | |
| C2 | 0.34680 (15) | 0.7536 (6) | 0.3034 (3) | 0.0168 (9) | |
| C3 | 0.33665 (15) | 0.5286 (6) | 0.4457 (3) | 0.0181 (10) | |
| H3 | 0.315890 | 0.624366 | 0.439720 | 0.022* | |
| C23 | 0.33158 (18) | 0.9160 (6) | 0.3367 (3) | 0.0261 (12) | |
| H23A | 0.315036 | 0.989329 | 0.285100 | 0.039* | |
| H23B | 0.356937 | 0.978978 | 0.378526 | 0.039* | |
| H23C | 0.313093 | 0.882820 | 0.367785 | 0.039* | |
| C21 | 0.30734 (16) | 0.6650 (6) | 0.2324 (3) | 0.0224 (11) | |
| H21A | 0.295630 | 0.736194 | 0.177973 | 0.034* | |
| H21B | 0.285044 | 0.648821 | 0.256126 | 0.034* | |
| H21C | 0.316006 | 0.553128 | 0.217523 | 0.034* | |
| C22 | 0.37784 (16) | 0.8113 (6) | 0.2609 (3) | 0.0225 (11) | |
| H22A | 0.385999 | 0.712175 | 0.233957 | 0.034* | |
| H22B | 0.403976 | 0.861654 | 0.307501 | 0.034* | |
| H22C | 0.363397 | 0.897101 | 0.214100 | 0.034* | |
| C11 | 0.42557 (16) | 0.3207 (6) | 0.4683 (3) | 0.0228 (11) | |
| H11A | 0.446432 | 0.237487 | 0.463790 | 0.034* | |
| H11B | 0.399687 | 0.260225 | 0.466370 | 0.034* | |
| H11C | 0.438904 | 0.383796 | 0.525243 | 0.034* | |
| C12 | 0.38961 (16) | 0.3496 (6) | 0.3002 (3) | 0.0207 (10) | |
| H12A | 0.408965 | 0.260339 | 0.294951 | 0.031* | |
| H12B | 0.382171 | 0.429777 | 0.249589 | 0.031* | |
| H12C | 0.363031 | 0.296526 | 0.299250 | 0.031* | |
| C13 | 0.45356 (16) | 0.5339 (7) | 0.3899 (3) | 0.0247 (11) | |
| H13A | 0.467984 | 0.597214 | 0.446518 | 0.037* | |
| H13B | 0.445536 | 0.613540 | 0.338974 | 0.037* | |
| H13C | 0.473373 | 0.446495 | 0.384784 | 0.037* | |
| C32 | 0.30897 (16) | 0.3797 (6) | 0.3897 (3) | 0.0211 (11) | |
| H32A | 0.326886 | 0.276078 | 0.400758 | 0.032* | |
| H32B | 0.297679 | 0.409135 | 0.325450 | 0.032* | |
| H32C | 0.284660 | 0.358817 | 0.406976 | 0.032* | |
| C31 | 0.35594 (17) | 0.4771 (7) | 0.5463 (3) | 0.0246 (11) | |

| | | | | | |
|------|--------------|--------------|-------------|-------------|-----|
| H31A | 0.332771 | 0.474437 | 0.568312 | 0.037* | |
| H31B | 0.378026 | 0.561094 | 0.581252 | 0.037* | |
| H31C | 0.369270 | 0.363282 | 0.553266 | 0.037* | |
| Au1 | 0.500000 | 0.99691 (3) | 0.750000 | 0.01611 (7) | |
| Cl2 | 0.51000 (4) | 0.99765 (15) | 0.61880 (7) | 0.0205 (2) | |
| Cl3 | 0.49041 (17) | 1.2856 (3) | 0.7334 (3) | 0.0361 (13) | 0.5 |
| Cl4 | 0.5066 (3) | 0.7069 (3) | 0.7565 (13) | 0.0271 (18) | 0.5 |
| Au2 | 0.250000 | 0.750000 | 0.500000 | 0.01468 (7) | |
| Cl5 | 0.27160 (4) | 1.02504 (15) | 0.49346 (8) | 0.0248 (3) | |
| Cl6 | 0.22544 (4) | 0.72530 (15) | 0.34763 (7) | 0.0241 (3) | |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|---------------|
| P1 | 0.0161 (6) | 0.0138 (6) | 0.0118 (5) | −0.0003 (5) | 0.0056 (5) | −0.0005 (4) |
| S1 | 0.0230 (6) | 0.0237 (7) | 0.0186 (6) | −0.0052 (5) | 0.0049 (5) | −0.0082 (5) |
| Cl1 | 0.0389 (8) | 0.0307 (8) | 0.0254 (7) | 0.0011 (6) | 0.0125 (6) | −0.0113 (5) |
| C1 | 0.020 (2) | 0.022 (3) | 0.013 (2) | 0.0033 (19) | 0.0081 (19) | 0.0007 (19) |
| C2 | 0.023 (2) | 0.012 (2) | 0.014 (2) | −0.002 (2) | 0.0067 (19) | 0.0029 (18) |
| C3 | 0.021 (2) | 0.017 (3) | 0.017 (2) | 0.0041 (19) | 0.0087 (19) | 0.0034 (18) |
| C23 | 0.033 (3) | 0.020 (3) | 0.022 (3) | 0.003 (2) | 0.008 (2) | 0.001 (2) |
| C21 | 0.025 (3) | 0.021 (3) | 0.017 (2) | −0.001 (2) | 0.006 (2) | 0.000 (2) |
| C22 | 0.025 (3) | 0.020 (3) | 0.023 (3) | −0.003 (2) | 0.012 (2) | 0.005 (2) |
| C11 | 0.023 (3) | 0.021 (3) | 0.023 (3) | 0.008 (2) | 0.008 (2) | 0.008 (2) |
| C12 | 0.024 (3) | 0.015 (2) | 0.025 (3) | 0.002 (2) | 0.012 (2) | −0.003 (2) |
| C13 | 0.023 (3) | 0.028 (3) | 0.025 (3) | 0.003 (2) | 0.012 (2) | 0.003 (2) |
| C32 | 0.030 (3) | 0.016 (3) | 0.022 (2) | −0.007 (2) | 0.015 (2) | −0.001 (2) |
| C31 | 0.030 (3) | 0.029 (3) | 0.018 (2) | −0.002 (2) | 0.013 (2) | 0.003 (2) |
| Au1 | 0.01937 (13) | 0.01138 (13) | 0.02047 (13) | 0.000 | 0.01105 (10) | 0.000 |
| Cl2 | 0.0246 (6) | 0.0207 (6) | 0.0193 (5) | −0.0025 (5) | 0.0119 (5) | −0.0009 (5) |
| Cl3 | 0.079 (5) | 0.0095 (10) | 0.039 (4) | 0.0076 (13) | 0.044 (3) | 0.0037 (11) |
| Cl4 | 0.047 (6) | 0.0117 (9) | 0.028 (5) | 0.0041 (14) | 0.021 (5) | −0.0002 (16) |
| Au2 | 0.01788 (12) | 0.01255 (13) | 0.01355 (12) | 0.00187 (10) | 0.00630 (9) | −0.00001 (10) |
| Cl5 | 0.0353 (7) | 0.0140 (6) | 0.0274 (6) | −0.0033 (5) | 0.0149 (5) | −0.0009 (5) |
| Cl6 | 0.0342 (7) | 0.0222 (6) | 0.0128 (5) | 0.0050 (5) | 0.0062 (5) | 0.0001 (5) |

Geometric parameters (Å, °)

| | | | |
|--------|-------------|----------------------|-------------|
| P1—C3 | 1.834 (5) | C3—C31 | 1.545 (6) |
| P1—C2 | 1.870 (4) | Au1—Cl4 ⁱ | 2.269 (2) |
| P1—C1 | 1.871 (5) | Au1—Cl4 | 2.269 (2) |
| P1—S1 | 2.1035 (16) | Au1—Cl3 ⁱ | 2.274 (2) |
| S1—Cl1 | 2.0310 (19) | Au1—Cl3 | 2.274 (2) |
| S1—Cl2 | 3.3240 (17) | Au1—Cl2 ⁱ | 2.2839 (11) |
| C1—C13 | 1.532 (7) | Au1—Cl2 | 2.2839 (11) |
| C1—C11 | 1.533 (6) | Cl3—Cl3 ⁱ | 0.653 (8) |
| C1—C12 | 1.534 (6) | Cl4—Cl4 ⁱ | 0.409 (18) |
| C2—C21 | 1.526 (6) | Au2—Cl6 | 2.2738 (11) |

| | | | |
|---------------|--------------|--|-------------|
| C2—C22 | 1.533 (6) | Au2—Cl6 ⁱⁱ | 2.2738 (11) |
| C2—C23 | 1.543 (7) | Au2—Cl5 ⁱⁱ | 2.2796 (12) |
| C3—C32 | 1.534 (6) | Au2—Cl5 | 2.2796 (12) |
| C3—P1—C2 | 109.5 (2) | Cl4 ⁱ —Au1—Cl4 | 10.3 (5) |
| C3—P1—C1 | 114.1 (2) | Cl4 ⁱ —Au1—Cl3 ⁱ | 176.1 (4) |
| C2—P1—C1 | 115.9 (2) | Cl4—Au1—Cl3 ⁱ | 166.8 (3) |
| C3—P1—S1 | 109.51 (16) | Cl4 ⁱ —Au1—Cl3 | 166.8 (3) |
| C2—P1—S1 | 107.97 (16) | Cl4—Au1—Cl3 | 176.1 (4) |
| C1—P1—S1 | 99.09 (16) | Cl3 ⁱ —Au1—Cl3 | 16.50 (19) |
| Cl1—S1—P1 | 103.06 (7) | Cl4 ⁱ —Au1—Cl2 ⁱ | 89.8 (5) |
| Cl1—S1—Cl2 | 91.84 (6) | Cl4—Au1—Cl2 ⁱ | 90.5 (5) |
| P1—S1—Cl2 | 162.69 (7) | Cl3 ⁱ —Au1—Cl2 ⁱ | 87.38 (17) |
| C13—C1—C11 | 109.0 (4) | Cl3—Au1—Cl2 ⁱ | 92.33 (17) |
| C13—C1—C12 | 109.6 (4) | Cl4 ⁱ —Au1—Cl2 | 90.5 (5) |
| C11—C1—C12 | 109.5 (4) | Cl4—Au1—Cl2 | 89.8 (5) |
| C13—C1—P1 | 109.4 (3) | Cl3 ⁱ —Au1—Cl2 | 92.33 (17) |
| C11—C1—P1 | 108.7 (3) | Cl3—Au1—Cl2 | 87.38 (17) |
| C12—C1—P1 | 110.6 (3) | Cl2 ⁱ —Au1—Cl2 | 179.71 (6) |
| C21—C2—C22 | 109.7 (4) | Au1—Cl2—S1 | 95.10 (4) |
| C21—C2—C23 | 108.9 (4) | Cl3 ⁱ —Cl3—Au1 | 81.75 (9) |
| C22—C2—C23 | 107.4 (4) | Cl4 ⁱ —Cl4—Au1 | 84.8 (2) |
| C21—C2—P1 | 112.2 (3) | Cl6—Au2—Cl6 ⁱⁱ | 180.00 (6) |
| C22—C2—P1 | 110.5 (3) | Cl6—Au2—Cl5 ⁱⁱ | 89.33 (4) |
| C23—C2—P1 | 107.8 (3) | Cl6 ⁱⁱ —Au2—Cl5 ⁱⁱ | 90.67 (4) |
| C32—C3—C31 | 108.9 (4) | Cl6—Au2—Cl5 | 90.67 (4) |
| C32—C3—P1 | 114.0 (3) | Cl6 ⁱⁱ —Au2—Cl5 | 89.33 (4) |
| C31—C3—P1 | 115.4 (3) | Cl5 ⁱⁱ —Au2—Cl5 | 180.0 |
| C3—P1—S1—Cl11 | -40.49 (18) | C3—P1—C2—C21 | -51.4 (4) |
| C2—P1—S1—Cl11 | 78.68 (17) | C1—P1—C2—C21 | 79.4 (4) |
| C1—P1—S1—Cl11 | -160.17 (16) | S1—P1—C2—C21 | -170.6 (3) |
| C3—P1—S1—Cl12 | 170.8 (3) | C3—P1—C2—C22 | -174.3 (3) |
| C2—P1—S1—Cl12 | -70.1 (3) | C1—P1—C2—C22 | -43.5 (4) |
| C1—P1—S1—Cl12 | 51.1 (3) | S1—P1—C2—C22 | 66.6 (3) |
| C3—P1—C1—Cl13 | -158.2 (3) | C3—P1—C2—C23 | 68.5 (4) |
| C2—P1—C1—Cl13 | 73.2 (4) | C1—P1—C2—C23 | -160.6 (3) |
| S1—P1—C1—Cl13 | -42.0 (3) | S1—P1—C2—C23 | -50.6 (3) |
| C3—P1—C1—Cl11 | -39.3 (4) | C2—P1—C3—C32 | 77.6 (4) |
| C2—P1—C1—Cl11 | -167.9 (3) | C1—P1—C3—C32 | -54.2 (4) |
| S1—P1—C1—Cl11 | 76.9 (3) | S1—P1—C3—C32 | -164.2 (3) |
| C3—P1—C1—Cl12 | 81.0 (4) | C2—P1—C3—C31 | -155.2 (3) |
| C2—P1—C1—Cl12 | -47.6 (4) | C1—P1—C3—C31 | 73.0 (4) |
| S1—P1—C1—Cl12 | -162.8 (3) | S1—P1—C3—C31 | -37.0 (4) |

Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $-x+1/2, -y+3/2, -z+1$.

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|--|-------------|---------------|-----------------------|-------------------------|
| C3—H3...Au2 | 1.00 | 2.93 | 3.786 (5) | 144 |
| C3—H3...Cl6 | 1.00 | 2.90 | 3.751 (5) | 143 |
| C13—H13 <i>A</i> ...S1 | 0.98 | 2.46 | 3.049 (5) | 118 |
| C23—H23 <i>B</i> ...C11 | 0.98 | 2.74 | 3.305 (5) | 117 |
| C31—H31 <i>B</i> ...C11 | 0.98 | 2.66 | 3.393 (5) | 132 |
| C23—H23 <i>A</i> ...Cl6 ⁱⁱⁱ | 0.98 | 2.74 | 3.713 (5) | 173 |
| C21—H21 <i>C</i> ...Cl6 ^{iv} | 0.98 | 2.90 | 3.672 (5) | 137 |
| C13—H13 <i>B</i> ...Cl3 ^v | 0.98 | 2.81 | 3.536 (8) | 131 |
| C22—H22 <i>B</i> ...Cl2 ^{vi} | 0.98 | 2.87 | 3.783 (5) | 156 |
| C13—H13 <i>C</i> ...Cl4 ^{vii} | 0.98 | 2.89 | 3.677 (19) | 138 |

Symmetry codes: (iii) $-x+1/2, y+1/2, -z+1/2$; (iv) $-x+1/2, y-1/2, -z+1/2$; (v) $x, -y+2, z-1/2$; (vi) $-x+1, -y+2, -z+1$; (vii) $-x+1, -y+1, -z+1$.

Tris(*tert*-butyl)(chlorosulfanyl)phosphonium tetrachloridoaurate(III) (20a)

Crystal data

(C₁₂H₂₇ClPS)[AuCl₄]

M_r = 608.58

Monoclinic, *P*2₁/*n*

a = 9.7661 (3) Å

b = 12.5787 (3) Å

c = 16.9776 (5) Å

β = 103.887 (3)°

V = 2024.67 (10) Å³

Z = 4

F(000) = 1176

D_x = 1.997 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 16785 reflections

θ = 2.1–30.9°

μ = 8.10 mm⁻¹

T = 100 K

Block, yellow

0.15 × 0.07 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω scan

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2015)

T_{min} = 0.756, *T_{max}* = 1.000

8891 measured reflections

8891 independent reflections

4196 reflections with *I* > 2σ(*I*)

R_{int} = 0.0000

θ_{max} = 31.3°, θ_{min} = 2.2°

h = -14→14

k = -17→18

l = -24→24

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.022

wR(*F*²) = 0.045

S = 0.77

8891 reflections

194 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0179*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 1.12 e Å⁻³

Δρ_{min} = -0.92 e Å⁻³

Special details

Refinement. The data were affected by a small twinning component (by 180 degrees about the c axis) that was at first not detected, but which led to poor agreement of data with $l = 4$. Data reduction and refinement ("HKLF 5" method; Sheldrick, 2015) as a non-merohedral twin led to a BASF parameter (relative volume of the smaller twin component) of 0.0300 (3). As is often the case with "HKLF 5" refinements, several reflections were severely in error; 20 of these were removed from the dataset.

Because equivalent reflections are merged during the generation of the "HKLF 5" intensity dataset, and because overlapped and non-overlapped reflections are both included in the refinement, the number of reflections should be interpreted carefully.

The low GOOF value may be due to the difficulty of estimating e.s.d.s for the intensities of the small twin component.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| P1 | 0.49208 (10) | 0.50047 (10) | 0.25997 (5) | 0.00909 (17) |
| S1 | 0.28916 (10) | 0.52505 (7) | 0.18610 (5) | 0.0156 (2) |
| Cl1 | 0.15675 (9) | 0.48996 (10) | 0.25817 (5) | 0.0199 (2) |
| C1 | 0.5898 (3) | 0.4946 (4) | 0.17591 (18) | 0.0136 (7) |
| C2 | 0.5023 (4) | 0.3710 (3) | 0.3180 (2) | 0.0134 (9) |
| C3 | 0.5395 (4) | 0.6193 (3) | 0.3280 (2) | 0.0100 (8) |
| C11 | 0.7488 (4) | 0.5137 (3) | 0.2099 (2) | 0.0175 (9) |
| H11A | 0.785639 | 0.462496 | 0.253266 | 0.026* |
| H11B | 0.763971 | 0.586113 | 0.231554 | 0.026* |
| H11C | 0.798098 | 0.504753 | 0.166349 | 0.026* |
| C12 | 0.5311 (4) | 0.5783 (3) | 0.1101 (2) | 0.0199 (10) |
| H12A | 0.579217 | 0.571551 | 0.065842 | 0.030* |
| H12B | 0.547250 | 0.649637 | 0.133674 | 0.030* |
| H12C | 0.429706 | 0.566905 | 0.088820 | 0.030* |
| C13 | 0.5663 (4) | 0.3869 (3) | 0.1324 (2) | 0.0195 (10) |
| H13A | 0.612098 | 0.387118 | 0.086949 | 0.029* |
| H13B | 0.464954 | 0.374476 | 0.111864 | 0.029* |
| H13C | 0.606958 | 0.330298 | 0.170529 | 0.029* |
| C21 | 0.6553 (4) | 0.3327 (3) | 0.3404 (2) | 0.0183 (9) |
| H21A | 0.661551 | 0.266126 | 0.371053 | 0.027* |
| H21B | 0.714792 | 0.386686 | 0.373639 | 0.027* |
| H21C | 0.687732 | 0.320647 | 0.290764 | 0.027* |
| C22 | 0.4052 (5) | 0.2874 (3) | 0.2668 (2) | 0.0212 (10) |
| H22A | 0.431884 | 0.277283 | 0.215255 | 0.032* |
| H22B | 0.307143 | 0.311762 | 0.256174 | 0.032* |
| H22C | 0.414629 | 0.219859 | 0.296432 | 0.032* |
| C23 | 0.4521 (4) | 0.3838 (3) | 0.3972 (2) | 0.0169 (9) |
| H23A | 0.456451 | 0.314866 | 0.424597 | 0.025* |
| H23B | 0.354722 | 0.409987 | 0.384259 | 0.025* |
| H23C | 0.513195 | 0.434685 | 0.432954 | 0.025* |
| C31 | 0.6780 (4) | 0.6028 (3) | 0.3911 (2) | 0.0167 (9) |
| H31A | 0.753578 | 0.588428 | 0.363620 | 0.025* |
| H31B | 0.668604 | 0.542377 | 0.425844 | 0.025* |
| H31C | 0.700781 | 0.667011 | 0.424346 | 0.025* |
| C32 | 0.5508 (5) | 0.7190 (3) | 0.2774 (2) | 0.0202 (9) |

| | | | | |
|------|--------------|-------------|--------------|-------------|
| H32A | 0.569800 | 0.781178 | 0.313140 | 0.030* |
| H32B | 0.461964 | 0.729475 | 0.236676 | 0.030* |
| H32C | 0.627884 | 0.709811 | 0.250185 | 0.030* |
| C33 | 0.4188 (4) | 0.6433 (3) | 0.3706 (2) | 0.0160 (10) |
| H33A | 0.403029 | 0.580920 | 0.401926 | 0.024* |
| H33B | 0.332170 | 0.659840 | 0.329690 | 0.024* |
| H33C | 0.445164 | 0.704115 | 0.407159 | 0.024* |
| Au1 | 0.000000 | 0.500000 | 0.500000 | 0.01111 (5) |
| Cl2 | 0.03947 (11) | 0.38336 (8) | 0.40465 (6) | 0.0223 (2) |
| Cl3 | 0.10599 (12) | 0.63217 (8) | 0.44413 (6) | 0.0255 (2) |
| Au2 | 0.000000 | 0.500000 | 0.000000 | 0.01066 (5) |
| Cl4 | 0.16838 (12) | 0.37478 (9) | -0.00287 (6) | 0.0176 (2) |
| Cl5 | 0.15525 (12) | 0.63167 (9) | -0.01076 (6) | 0.0180 (2) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|--------------|
| P1 | 0.0088 (4) | 0.0094 (3) | 0.0096 (4) | 0.0006 (6) | 0.0030 (3) | 0.0004 (6) |
| S1 | 0.0098 (4) | 0.0252 (7) | 0.0116 (4) | 0.0007 (4) | 0.0022 (4) | -0.0006 (4) |
| Cl1 | 0.0124 (4) | 0.0251 (6) | 0.0240 (4) | -0.0027 (5) | 0.0078 (4) | -0.0028 (5) |
| C1 | 0.0126 (16) | 0.0211 (19) | 0.0106 (14) | 0.005 (2) | 0.0101 (13) | 0.004 (2) |
| C2 | 0.012 (2) | 0.010 (2) | 0.017 (2) | -0.0012 (17) | 0.0018 (17) | 0.0000 (17) |
| C3 | 0.009 (2) | 0.0081 (19) | 0.0119 (18) | -0.0001 (16) | 0.0012 (16) | -0.0002 (16) |
| C11 | 0.0168 (19) | 0.018 (3) | 0.0202 (17) | 0.0020 (19) | 0.0096 (15) | 0.0055 (18) |
| C12 | 0.017 (2) | 0.031 (3) | 0.015 (2) | 0.004 (2) | 0.0108 (18) | 0.0069 (18) |
| C13 | 0.018 (2) | 0.031 (3) | 0.012 (2) | 0.002 (2) | 0.0091 (18) | -0.0053 (19) |
| C21 | 0.024 (2) | 0.014 (2) | 0.018 (2) | 0.0067 (18) | 0.0077 (18) | 0.0079 (16) |
| C22 | 0.028 (3) | 0.012 (2) | 0.027 (2) | -0.0036 (18) | 0.013 (2) | -0.0003 (17) |
| C23 | 0.021 (2) | 0.011 (2) | 0.021 (2) | -0.0015 (19) | 0.0092 (19) | 0.0065 (18) |
| C31 | 0.016 (2) | 0.014 (2) | 0.0175 (19) | -0.0004 (17) | -0.0005 (17) | -0.0055 (16) |
| C32 | 0.021 (2) | 0.015 (2) | 0.024 (2) | -0.0022 (18) | 0.0067 (18) | -0.0010 (17) |
| C33 | 0.019 (2) | 0.011 (2) | 0.017 (2) | 0.0030 (18) | 0.0028 (18) | -0.0021 (16) |
| Au1 | 0.00871 (10) | 0.01398 (11) | 0.01084 (10) | -0.00008 (14) | 0.00275 (8) | 0.00063 (13) |
| Cl2 | 0.0241 (6) | 0.0240 (6) | 0.0223 (5) | -0.0051 (5) | 0.0126 (5) | -0.0084 (4) |
| Cl3 | 0.0330 (6) | 0.0200 (6) | 0.0291 (6) | -0.0072 (5) | 0.0183 (5) | 0.0010 (5) |
| Au2 | 0.01168 (10) | 0.01105 (10) | 0.00926 (9) | 0.00079 (14) | 0.00256 (8) | 0.00012 (13) |
| Cl4 | 0.0163 (6) | 0.0156 (6) | 0.0217 (5) | 0.0024 (5) | 0.0060 (5) | -0.0026 (5) |
| Cl5 | 0.0161 (6) | 0.0156 (6) | 0.0227 (5) | -0.0002 (5) | 0.0054 (5) | 0.0040 (5) |

Geometric parameters (Å, °)

| | | | |
|---------|-------------|----------|--------|
| P1—C3 | 1.877 (4) | C21—H21B | 0.9800 |
| P1—C2 | 1.894 (4) | C21—H21C | 0.9800 |
| P1—C1 | 1.899 (3) | C22—H22A | 0.9800 |
| P1—S1 | 2.0983 (13) | C22—H22B | 0.9800 |
| S1—Cl1 | 2.0307 (13) | C22—H22C | 0.9800 |
| Cl1—Cl2 | 3.2652 (14) | C23—H23A | 0.9800 |
| Cl1—Cl3 | 1.534 (6) | C23—H23B | 0.9800 |

| | | | |
|---------------|-------------|------------------------|-------------|
| C1—C11 | 1.541 (5) | C23—H23C | 0.9800 |
| C1—C12 | 1.543 (5) | C31—H31A | 0.9800 |
| C2—C21 | 1.529 (5) | C31—H31B | 0.9800 |
| C2—C22 | 1.538 (5) | C31—H31C | 0.9800 |
| C2—C23 | 1.546 (5) | C32—H32A | 0.9800 |
| C3—C31 | 1.525 (5) | C32—H32B | 0.9800 |
| C3—C32 | 1.539 (5) | C32—H32C | 0.9800 |
| C3—C33 | 1.553 (5) | C33—H33A | 0.9800 |
| C11—H11A | 0.9800 | C33—H33B | 0.9800 |
| C11—H11B | 0.9800 | C33—H33C | 0.9800 |
| C11—H11C | 0.9800 | Au1—C13 | 2.2818 (10) |
| C12—H12A | 0.9800 | Au1—C13 ⁱ | 2.2818 (10) |
| C12—H12B | 0.9800 | Au1—C12 ⁱ | 2.2850 (10) |
| C12—H12C | 0.9800 | Au1—C12 | 2.2850 (10) |
| C13—H13A | 0.9800 | Au2—C15 | 2.2821 (11) |
| C13—H13B | 0.9800 | Au2—C15 ⁱⁱ | 2.2822 (11) |
| C13—H13C | 0.9800 | Au2—C14 ⁱⁱⁱ | 2.2859 (11) |
| C21—H21A | 0.9800 | Au2—C14 | 2.2860 (11) |
| | | | |
| C3—P1—C2 | 112.97 (15) | C2—C21—H21C | 109.5 |
| C3—P1—C1 | 113.5 (2) | H21A—C21—H21C | 109.5 |
| C2—P1—C1 | 112.6 (2) | H21B—C21—H21C | 109.5 |
| C3—P1—S1 | 107.96 (13) | C2—C22—H22A | 109.5 |
| C2—P1—S1 | 111.23 (13) | C2—C22—H22B | 109.5 |
| C1—P1—S1 | 97.43 (11) | H22A—C22—H22B | 109.5 |
| C11—S1—P1 | 104.74 (5) | C2—C22—H22C | 109.5 |
| S1—C11—C12 | 159.83 (6) | H22A—C22—H22C | 109.5 |
| C13—C1—C11 | 109.8 (3) | H22B—C22—H22C | 109.5 |
| C13—C1—C12 | 105.5 (3) | C2—C23—H23A | 109.5 |
| C11—C1—C12 | 109.3 (3) | C2—C23—H23B | 109.5 |
| C13—C1—P1 | 110.7 (3) | H23A—C23—H23B | 109.5 |
| C11—C1—P1 | 110.9 (2) | C2—C23—H23C | 109.5 |
| C12—C1—P1 | 110.6 (3) | H23A—C23—H23C | 109.5 |
| C21—C2—C22 | 111.0 (3) | H23B—C23—H23C | 109.5 |
| C21—C2—C23 | 108.2 (3) | C3—C31—H31A | 109.5 |
| C22—C2—C23 | 106.3 (3) | C3—C31—H31B | 109.5 |
| C21—C2—P1 | 109.1 (3) | H31A—C31—H31B | 109.5 |
| C22—C2—P1 | 110.2 (3) | C3—C31—H31C | 109.5 |
| C23—C2—P1 | 112.0 (3) | H31A—C31—H31C | 109.5 |
| C31—C3—C32 | 109.4 (3) | H31B—C31—H31C | 109.5 |
| C31—C3—C33 | 110.1 (3) | C3—C32—H32A | 109.5 |
| C32—C3—C33 | 105.4 (3) | C3—C32—H32B | 109.5 |
| C31—C3—P1 | 111.7 (3) | H32A—C32—H32B | 109.5 |
| C32—C3—P1 | 110.2 (3) | C3—C32—H32C | 109.5 |
| C33—C3—P1 | 109.8 (3) | H32A—C32—H32C | 109.5 |
| C1—C11—H11A | 109.5 | H32B—C32—H32C | 109.5 |
| C1—C11—H11B | 109.5 | C3—C33—H33A | 109.5 |
| H11A—C11—H11B | 109.5 | C3—C33—H33B | 109.5 |

| | | | |
|---------------|-------------|--|------------|
| C1—C11—H11C | 109.5 | H33A—C33—H33B | 109.5 |
| H11A—C11—H11C | 109.5 | C3—C33—H33C | 109.5 |
| H11B—C11—H11C | 109.5 | H33A—C33—H33C | 109.5 |
| C1—C12—H12A | 109.5 | H33B—C33—H33C | 109.5 |
| C1—C12—H12B | 109.5 | Cl3—Au1—Cl3 ⁱ | 180.0 |
| H12A—C12—H12B | 109.5 | Cl3—Au1—Cl2 ⁱ | 89.84 (4) |
| C1—C12—H12C | 109.5 | Cl3 ⁱ —Au1—Cl2 ⁱ | 90.16 (4) |
| H12A—C12—H12C | 109.5 | Cl3—Au1—Cl2 | 90.16 (4) |
| H12B—C12—H12C | 109.5 | Cl3 ⁱ —Au1—Cl2 | 89.84 (4) |
| C1—C13—H13A | 109.5 | Cl2 ⁱ —Au1—Cl2 | 180.0 |
| C1—C13—H13B | 109.5 | Au1—Cl2—Cl1 | 115.19 (4) |
| H13A—C13—H13B | 109.5 | Cl5—Au2—Cl5 ⁱⁱ | 180.0 |
| C1—C13—H13C | 109.5 | Cl5—Au2—Cl4 ⁱⁱ | 89.82 (3) |
| H13A—C13—H13C | 109.5 | Cl5 ⁱⁱ —Au2—Cl4 ⁱⁱ | 90.18 (3) |
| H13B—C13—H13C | 109.5 | Cl5—Au2—Cl4 | 90.18 (3) |
| C2—C21—H21A | 109.5 | Cl5 ⁱⁱ —Au2—Cl4 | 89.82 (3) |
| C2—C21—H21B | 109.5 | Cl4 ⁱⁱ —Au2—Cl4 | 180.0 |
| H21A—C21—H21B | 109.5 | | |
| | | | |
| C3—P1—S1—Cl1 | -78.89 (15) | C3—P1—C2—C22 | 155.2 (3) |
| C2—P1—S1—Cl1 | 45.59 (15) | C1—P1—C2—C22 | -74.5 (3) |
| C1—P1—S1—Cl1 | 163.38 (16) | S1—P1—C2—C22 | 33.6 (3) |
| P1—S1—Cl1—Cl2 | -25.47 (19) | C3—P1—C2—C23 | 37.1 (3) |
| C3—P1—C1—C13 | 170.0 (2) | C1—P1—C2—C23 | 167.3 (3) |
| C2—P1—C1—C13 | 40.0 (3) | S1—P1—C2—C23 | -84.5 (3) |
| S1—P1—C1—C13 | -76.7 (3) | C2—P1—C3—C31 | 49.6 (3) |
| C3—P1—C1—C11 | 47.9 (4) | C1—P1—C3—C31 | -80.1 (3) |
| C2—P1—C1—C11 | -82.0 (3) | S1—P1—C3—C31 | 173.0 (2) |
| S1—P1—C1—C11 | 161.2 (3) | C2—P1—C3—C32 | 171.5 (3) |
| C3—P1—C1—C12 | -73.4 (3) | C1—P1—C3—C32 | 41.7 (3) |
| C2—P1—C1—C12 | 156.6 (3) | S1—P1—C3—C32 | -65.1 (3) |
| S1—P1—C1—C12 | 39.9 (3) | C2—P1—C3—C33 | -72.8 (3) |
| C3—P1—C2—C21 | -82.7 (3) | C1—P1—C3—C33 | 157.5 (2) |
| C1—P1—C2—C21 | 47.6 (3) | S1—P1—C3—C33 | 50.6 (3) |
| S1—P1—C2—C21 | 155.8 (2) | | |

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-------|-------------|-------------|---------------|
| C23—H23B \cdots Cl1 | 0.98 | 2.71 | 3.522 (4) | 141 |
| C22—H22B \cdots Cl1 | 0.98 | 2.68 | 3.497 (4) | 141 |
| C33—H33B \cdots Cl1 | 0.98 | 2.82 | 3.401 (4) | 118 |
| C13—H13A \cdots Cl5 ⁱⁱⁱ | 0.98 | 2.88 | 3.796 (4) | 156 |
| C12—H12C \cdots Cl5 | 0.98 | 2.92 | 3.810 (4) | 151 |
| C31—H31C \cdots Cl5 ^{iv} | 0.98 | 2.84 | 3.763 (4) | 158 |
| C12—H12C \cdots S1 | 0.98 | 2.44 | 3.027 (4) | 118 |

| | | | | |
|-----------------------------|------|------|-----------|-----|
| C22—H22B···S1 | 0.98 | 2.92 | 3.370 (4) | 109 |
| C33—H33B···S1 | 0.98 | 2.92 | 3.424 (4) | 113 |
| C21—H21A···Cl4 ^v | 0.98 | 2.77 | 3.708 (4) | 161 |

Symmetry codes: (iii) $-x+1, -y+1, -z$; (iv) $x+1/2, -y+3/2, z+1/2$; (v) $x+1/2, -y+1/2, z+1/2$.

(Chloroselanyl)tris(propan-2-yl)phosphonium tetrachloridoaurate(III) (21a)

Crystal data

| | |
|--|---|
| (C ₉ H ₂₁ ClPSe)[AuCl ₄] | $Z = 2$ |
| $M_r = 613.40$ | $F(000) = 576$ |
| Triclinic, $P\bar{1}$ | $D_x = 2.280 \text{ Mg m}^{-3}$ |
| $a = 7.4202 (3) \text{ \AA}$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $b = 8.5966 (3) \text{ \AA}$ | Cell parameters from 42603 reflections |
| $c = 15.3980 (6) \text{ \AA}$ | $\theta = 2.6\text{--}30.8^\circ$ |
| $\alpha = 97.497 (3)^\circ$ | $\mu = 11.09 \text{ mm}^{-1}$ |
| $\beta = 100.128 (4)^\circ$ | $T = 100 \text{ K}$ |
| $\gamma = 109.324 (4)^\circ$ | Block, yellow |
| $V = 893.42 (6) \text{ \AA}^3$ | $0.18 \times 0.15 \times 0.10 \text{ mm}$ |

Data collection

| | |
|--|---|
| Oxford Diffraction Xcalibur, Eos diffractometer | 106851 measured reflections |
| Radiation source: Enhance (Mo) X-ray Source | 5322 independent reflections |
| Detector resolution: 16.1419 pixels mm^{-1} | 4900 reflections with $I > 2\sigma(I)$ |
| ω scan | $R_{\text{int}} = 0.039$ |
| Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015) | $\theta_{\text{max}} = 30.9^\circ, \theta_{\text{min}} = 2.6^\circ$ |
| $T_{\text{min}} = 0.631, T_{\text{max}} = 1.000$ | $h = -10 \rightarrow 10$ |
| | $k = -12 \rightarrow 12$ |
| | $l = -22 \rightarrow 22$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.016$ | $w = 1/[\sigma^2(F_o^2) + (0.014P)^2 + 0.5143P]$ |
| $wR(F^2) = 0.033$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.10$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 5322 reflections | $\Delta\rho_{\text{max}} = 0.83 \text{ e \AA}^{-3}$ |
| 164 parameters | $\Delta\rho_{\text{min}} = -0.85 \text{ e \AA}^{-3}$ |
| 0 restraints | Extinction correction: <i>SHELXL2019/3</i> |
| Primary atom site location: structure-invariant direct methods | (Sheldrick, 2015), $F_c^* = kF_c[1 + 0.001 F_c^2 \lambda^3 / \sin(2\theta)]^{1/4}$ |
| Secondary atom site location: difference Fourier map | Extinction coefficient: 0.00346 (11) |

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|--------------|----------------------------------|
| P1 | 0.53786 (6) | 0.48435 (6) | 0.25613 (3) | 0.01070 (9) |
| Se1 | 0.73544 (3) | 0.38369 (2) | 0.34073 (2) | 0.01473 (4) |
| Cl1 | 0.71221 (7) | 0.17157 (6) | 0.23989 (3) | 0.02085 (10) |
| C1 | 0.4802 (3) | 0.6161 (2) | 0.34217 (12) | 0.0148 (4) |
| H1 | 0.605803 | 0.679304 | 0.388314 | 0.018* |
| C2 | 0.3309 (3) | 0.3099 (2) | 0.18196 (12) | 0.0147 (4) |

| | | | | |
|------|-------------|--------------|--------------|--------------|
| H2 | 0.384866 | 0.259066 | 0.135410 | 0.018* |
| C3 | 0.6750 (3) | 0.6170 (2) | 0.18854 (12) | 0.0143 (3) |
| H3 | 0.589658 | 0.673188 | 0.159062 | 0.017* |
| C11 | 0.4107 (3) | 0.7490 (3) | 0.30424 (14) | 0.0233 (4) |
| H11A | 0.287805 | 0.692478 | 0.258152 | 0.035* |
| H11B | 0.511169 | 0.818179 | 0.277363 | 0.035* |
| H11C | 0.388871 | 0.820785 | 0.353057 | 0.035* |
| C12 | 0.3354 (3) | 0.5142 (3) | 0.39157 (14) | 0.0216 (4) |
| H12A | 0.331514 | 0.588542 | 0.444612 | 0.032* |
| H12B | 0.377732 | 0.424896 | 0.410608 | 0.032* |
| H12C | 0.204198 | 0.463957 | 0.351138 | 0.032* |
| C21 | 0.2291 (3) | 0.1679 (3) | 0.22723 (14) | 0.0219 (4) |
| H21A | 0.160227 | 0.208475 | 0.268474 | 0.033* |
| H21B | 0.327474 | 0.131685 | 0.261082 | 0.033* |
| H21C | 0.134425 | 0.072642 | 0.181119 | 0.033* |
| C22 | 0.1837 (3) | 0.3768 (3) | 0.13123 (14) | 0.0221 (4) |
| H22A | 0.082901 | 0.284694 | 0.085424 | 0.033* |
| H22B | 0.252924 | 0.465671 | 0.102071 | 0.033* |
| H22C | 0.121334 | 0.422612 | 0.173898 | 0.033* |
| C31 | 0.8610 (3) | 0.7560 (3) | 0.24968 (14) | 0.0233 (4) |
| H31A | 0.944035 | 0.704355 | 0.282342 | 0.035* |
| H31B | 0.823129 | 0.826372 | 0.292886 | 0.035* |
| H31C | 0.934017 | 0.825763 | 0.212675 | 0.035* |
| C32 | 0.7241 (3) | 0.5134 (3) | 0.11392 (14) | 0.0210 (4) |
| H32A | 0.803099 | 0.589069 | 0.081055 | 0.032* |
| H32B | 0.602206 | 0.435669 | 0.072279 | 0.032* |
| H32C | 0.798569 | 0.449167 | 0.140630 | 0.032* |
| Au1 | 0.500000 | 0.000000 | 0.000000 | 0.01487 (3) |
| Cl3 | 0.30365 (8) | -0.18377 (7) | 0.06920 (3) | 0.02345 (10) |
| Cl2 | 0.75097 (7) | -0.08933 (7) | 0.04630 (3) | 0.02262 (10) |
| Au2 | 1.000000 | 1.000000 | 0.500000 | 0.01214 (3) |
| Cl4 | 1.29351 (7) | 1.06893 (7) | 0.45972 (3) | 0.02286 (10) |
| Cl5 | 0.99249 (7) | 0.73205 (6) | 0.49898 (3) | 0.02014 (10) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|---------------|
| P1 | 0.01038 (19) | 0.0108 (2) | 0.01082 (19) | 0.00406 (17) | 0.00169 (15) | 0.00242 (16) |
| Se1 | 0.01665 (9) | 0.01492 (10) | 0.01344 (8) | 0.00888 (7) | -0.00026 (6) | 0.00238 (7) |
| Cl1 | 0.0250 (2) | 0.0155 (2) | 0.0223 (2) | 0.0110 (2) | 0.00174 (18) | -0.00024 (18) |
| C1 | 0.0159 (8) | 0.0157 (10) | 0.0131 (8) | 0.0072 (7) | 0.0029 (6) | 0.0012 (7) |
| C2 | 0.0126 (8) | 0.0147 (10) | 0.0132 (8) | 0.0024 (7) | 0.0003 (6) | 0.0010 (7) |
| C3 | 0.0130 (8) | 0.0146 (10) | 0.0152 (8) | 0.0042 (7) | 0.0036 (6) | 0.0051 (7) |
| C11 | 0.0325 (11) | 0.0230 (12) | 0.0227 (10) | 0.0198 (10) | 0.0078 (8) | 0.0060 (8) |
| C12 | 0.0218 (10) | 0.0278 (12) | 0.0203 (9) | 0.0114 (9) | 0.0113 (8) | 0.0067 (8) |
| C21 | 0.0178 (9) | 0.0176 (11) | 0.0257 (10) | 0.0014 (8) | 0.0022 (8) | 0.0061 (8) |
| C22 | 0.0158 (9) | 0.0243 (12) | 0.0220 (9) | 0.0055 (8) | -0.0032 (7) | 0.0054 (8) |
| C31 | 0.0178 (9) | 0.0228 (12) | 0.0224 (10) | -0.0009 (8) | 0.0007 (7) | 0.0084 (8) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|---------------|---------------|
| C32 | 0.0244 (10) | 0.0230 (12) | 0.0211 (9) | 0.0109 (9) | 0.0121 (8) | 0.0078 (8) |
| Au1 | 0.02126 (5) | 0.01143 (6) | 0.01034 (5) | 0.00685 (4) | -0.00120 (3) | 0.00097 (3) |
| Cl3 | 0.0289 (2) | 0.0204 (3) | 0.0213 (2) | 0.0083 (2) | 0.00511 (19) | 0.00814 (19) |
| Cl2 | 0.0257 (2) | 0.0215 (3) | 0.0211 (2) | 0.0125 (2) | -0.00138 (18) | 0.00491 (19) |
| Au2 | 0.01478 (5) | 0.01236 (6) | 0.00960 (4) | 0.00728 (4) | 0.00026 (3) | 0.00054 (3) |
| Cl4 | 0.0200 (2) | 0.0224 (3) | 0.0262 (2) | 0.0081 (2) | 0.00875 (18) | -0.00042 (19) |
| Cl5 | 0.0254 (2) | 0.0148 (2) | 0.0214 (2) | 0.01103 (19) | 0.00119 (17) | 0.00335 (17) |

Geometric parameters (Å, °)

| | | | |
|-------------|-------------|-----------------------|------------|
| P1—C2 | 1.8230 (19) | C21—H21A | 0.9800 |
| P1—C3 | 1.8256 (19) | C21—H21B | 0.9800 |
| P1—C1 | 1.8304 (18) | C21—H21C | 0.9800 |
| P1—Se1 | 2.2488 (5) | C22—H22A | 0.9800 |
| Se1—Cl1 | 2.1736 (5) | C22—H22B | 0.9800 |
| Cl1—Cl2 | 3.6031 (7) | C22—H22C | 0.9800 |
| C1—C12 | 1.529 (3) | C31—H31A | 0.9800 |
| C1—C11 | 1.539 (3) | C31—H31B | 0.9800 |
| C1—H1 | 1.0000 | C31—H31C | 0.9800 |
| C2—C21 | 1.531 (3) | C32—H32A | 0.9800 |
| C2—C22 | 1.539 (3) | C32—H32B | 0.9800 |
| C2—H2 | 1.0000 | C32—H32C | 0.9800 |
| C3—C32 | 1.530 (3) | Au1—Cl2 ⁱ | 2.2778 (5) |
| C3—C31 | 1.542 (3) | Au1—Cl2 | 2.2778 (5) |
| C3—H3 | 1.0000 | Au1—Cl3 | 2.2838 (5) |
| C11—H11A | 0.9800 | Au1—Cl3 ⁱ | 2.2839 (5) |
| C11—H11B | 0.9800 | Au2—Cl4 ⁱⁱ | 2.2795 (5) |
| C11—H11C | 0.9800 | Au2—Cl4 | 2.2795 (5) |
| C12—H12A | 0.9800 | Au2—Cl5 ⁱⁱ | 2.2836 (5) |
| C12—H12B | 0.9800 | Au2—Cl5 | 2.2836 (5) |
| C12—H12C | 0.9800 | | |
| C2—P1—C3 | 109.48 (8) | C2—C21—H21A | 109.5 |
| C2—P1—C1 | 116.55 (9) | C2—C21—H21B | 109.5 |
| C3—P1—C1 | 109.25 (9) | H21A—C21—H21B | 109.5 |
| C2—P1—Se1 | 109.69 (6) | C2—C21—H21C | 109.5 |
| C3—P1—Se1 | 109.75 (6) | H21A—C21—H21C | 109.5 |
| C1—P1—Se1 | 101.79 (6) | H21B—C21—H21C | 109.5 |
| Cl1—Se1—P1 | 98.381 (19) | C2—C22—H22A | 109.5 |
| Se1—Cl1—Cl2 | 164.28 (2) | C2—C22—H22B | 109.5 |
| C12—C1—C11 | 111.32 (16) | H22A—C22—H22B | 109.5 |
| C12—C1—P1 | 113.15 (14) | C2—C22—H22C | 109.5 |
| C11—C1—P1 | 112.12 (13) | H22A—C22—H22C | 109.5 |
| C12—C1—H1 | 106.6 | H22B—C22—H22C | 109.5 |
| C11—C1—H1 | 106.6 | C3—C31—H31A | 109.5 |
| P1—C1—H1 | 106.6 | C3—C31—H31B | 109.5 |
| C21—C2—C22 | 111.54 (16) | H31A—C31—H31B | 109.5 |
| C21—C2—P1 | 115.24 (13) | C3—C31—H31C | 109.5 |

| | | | |
|----------------|-------------|--|--------------|
| C22—C2—P1 | 110.02 (14) | H31A—C31—H31C | 109.5 |
| C21—C2—H2 | 106.5 | H31B—C31—H31C | 109.5 |
| C22—C2—H2 | 106.5 | C3—C32—H32A | 109.5 |
| P1—C2—H2 | 106.5 | C3—C32—H32B | 109.5 |
| C32—C3—C31 | 111.75 (16) | H32A—C32—H32B | 109.5 |
| C32—C3—P1 | 111.79 (14) | C3—C32—H32C | 109.5 |
| C31—C3—P1 | 110.18 (13) | H32A—C32—H32C | 109.5 |
| C32—C3—H3 | 107.6 | H32B—C32—H32C | 109.5 |
| C31—C3—H3 | 107.6 | Cl2 ⁱ —Au1—Cl2 | 180.00 (3) |
| P1—C3—H3 | 107.6 | Cl2 ⁱ —Au1—Cl3 | 89.455 (19) |
| C1—C11—H11A | 109.5 | Cl2—Au1—Cl3 | 90.545 (19) |
| C1—C11—H11B | 109.5 | Cl2 ⁱ —Au1—Cl3 ⁱ | 90.544 (19) |
| H11A—C11—H11B | 109.5 | Cl2—Au1—Cl3 ⁱ | 89.456 (19) |
| C1—C11—H11C | 109.5 | Cl3—Au1—Cl3 ⁱ | 180.0 |
| H11A—C11—H11C | 109.5 | Au1—Cl2—Cl1 | 72.720 (15) |
| H11B—C11—H11C | 109.5 | Cl4 ⁱⁱ —Au2—Cl4 | 180.0 |
| C1—C12—H12A | 109.5 | Cl4 ⁱⁱ —Au2—Cl5 ⁱⁱ | 89.900 (19) |
| C1—C12—H12B | 109.5 | Cl4—Au2—Cl5 ⁱⁱ | 90.100 (19) |
| H12A—C12—H12B | 109.5 | Cl4 ⁱⁱ —Au2—Cl5 | 90.100 (19) |
| C1—C12—H12C | 109.5 | Cl4—Au2—Cl5 | 89.900 (19) |
| H12A—C12—H12C | 109.5 | Cl5 ⁱⁱ —Au2—Cl5 | 180.0 |
| H12B—C12—H12C | 109.5 | | |
| | | | |
| C2—P1—Se1—Cl1 | 37.57 (7) | Se1—P1—C2—C21 | 46.80 (15) |
| C3—P1—Se1—Cl1 | -82.75 (7) | C3—P1—C2—C22 | -65.57 (15) |
| C1—P1—Se1—Cl1 | 161.60 (7) | C1—P1—C2—C22 | 59.03 (16) |
| P1—Se1—Cl1—Cl2 | 70.10 (8) | Se1—P1—C2—C22 | 173.95 (11) |
| C2—P1—C1—C12 | 45.26 (16) | C2—P1—C3—C32 | -50.07 (15) |
| C3—P1—C1—C12 | 169.97 (13) | C1—P1—C3—C32 | -178.81 (13) |
| Se1—P1—C1—C12 | -74.02 (13) | Se1—P1—C3—C32 | 70.38 (13) |
| C2—P1—C1—C11 | -81.65 (16) | C2—P1—C3—C31 | -174.96 (13) |
| C3—P1—C1—C11 | 43.06 (16) | C1—P1—C3—C31 | 56.30 (15) |
| Se1—P1—C1—C11 | 159.07 (13) | Se1—P1—C3—C31 | -54.51 (15) |
| C3—P1—C2—C21 | 167.28 (14) | Cl3—Au1—Cl2—Cl1 | -74.650 (17) |
| C1—P1—C2—C21 | -68.12 (17) | Cl3 ⁱ —Au1—Cl2—Cl1 | 105.350 (17) |

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+2, -y+2, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-------|-------------|-------------|---------------|
| C21—H21B \cdots Cl1 | 0.98 | 2.84 | 3.545 (2) | 129 |
| C32—H32C \cdots Cl1 | 0.98 | 2.95 | 3.712 (2) | 135 |
| C1—H1 \cdots Cl5 | 1.00 | 2.93 | 3.8615 (19) | 156 |
| C2—H2 \cdots Cl2 ⁱ | 1.00 | 2.82 | 3.6147 (19) | 137 |
| C3—H3 \cdots Cl2 ⁱⁱⁱ | 1.00 | 2.94 | 3.5249 (19) | 118 |
| C31—H31C \cdots Cl2 ⁱⁱⁱ | 0.98 | 2.98 | 3.626 (2) | 125 |
| C21—H21C \cdots Cl2 ^{iv} | 0.98 | 2.98 | 3.868 (2) | 151 |

| | | | | |
|------------------------------|------|------|-------------|-----|
| C11—H11C···Cl4 ^{iv} | 0.98 | 2.87 | 3.828 (2) | 166 |
| C1—H1···Cl4 ⁱⁱ | 1.00 | 2.78 | 3.5341 (19) | 133 |

Symmetry codes: (i) $-x+1, -y, -z$; (ii) $-x+2, -y+2, -z+1$; (iii) $x, y+1, z$; (iv) $x-1, y, z$.

(*tert*-Butyl)(chloroselanyl)bis(propan-2-yl)phosphonium tetrachloridoaurate(III) (22a)

Crystal data

(C₁₀H₂₃ClPSe)[AuCl₄]

$M_r = 627.43$

Triclinic, $P\bar{1}$

$a = 7.5836$ (2) Å

$b = 8.7603$ (2) Å

$c = 15.4719$ (6) Å

$\alpha = 84.445$ (3)°

$\beta = 78.641$ (3)°

$\gamma = 67.128$ (3)°

$V = 928.28$ (5) Å³

$Z = 2$

$F(000) = 592$

$D_x = 2.245$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 37919 reflections

$\theta = 2.5$ – 30.8 °

$\mu = 10.67$ mm⁻¹

$T = 100$ K

Plate, yellow

$0.2 \times 0.2 \times 0.03$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω scan

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.232$, $T_{\max} = 1.000$

102916 measured reflections

5490 independent reflections

4978 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\max} = 30.9$ °, $\theta_{\min} = 2.5$ °

$h = -10 \rightarrow 10$

$k = -12 \rightarrow 12$

$l = -22 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.021$

$wR(F^2) = 0.054$

$S = 1.05$

5490 reflections

174 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0304P)^2 + 1.3105P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.86$ e Å⁻³

$\Delta\rho_{\min} = -1.59$ e Å⁻³

Extinction correction: *SHELXL2019/3*

(Sheldrick, 2015), $F_c^* = kF_c[1 + 0.001$

$F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.00144 (18)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|--------------|--------------|----------------------------------|
| P1 | 0.50453 (9) | 0.10337 (8) | 0.25119 (4) | 0.01197 (12) |
| Se1 | 0.37816 (4) | -0.07476 (3) | 0.32514 (2) | 0.01739 (6) |
| Cl1 | 0.14673 (9) | 0.09827 (9) | 0.41498 (5) | 0.02223 (14) |
| C1 | 0.7478 (4) | -0.0370 (3) | 0.19534 (17) | 0.0146 (5) |
| C2 | 0.5057 (4) | 0.2483 (4) | 0.32872 (18) | 0.0172 (5) |
| H2 | 0.366050 | 0.317873 | 0.349742 | 0.021* |
| C3 | 0.3524 (4) | 0.2280 (3) | 0.17101 (17) | 0.0148 (5) |

| | | | | |
|------|---------------|--------------|--------------|--------------|
| H3 | 0.427966 | 0.287982 | 0.132381 | 0.018* |
| C11 | 0.8138 (4) | 0.0486 (4) | 0.11101 (18) | 0.0198 (5) |
| H11A | 0.810433 | 0.156260 | 0.125582 | 0.030* |
| H11B | 0.726486 | 0.065134 | 0.068933 | 0.030* |
| H11C | 0.946608 | -0.020860 | 0.084707 | 0.030* |
| C12 | 0.8939 (4) | -0.0783 (4) | 0.25882 (19) | 0.0204 (6) |
| H12A | 1.018092 | -0.162290 | 0.232768 | 0.031* |
| H12B | 0.843022 | -0.120954 | 0.314952 | 0.031* |
| H12C | 0.913544 | 0.022189 | 0.269124 | 0.031* |
| C13 | 0.7372 (4) | -0.2000 (4) | 0.1719 (2) | 0.0203 (5) |
| H13A | 0.634986 | -0.174976 | 0.136537 | 0.030* |
| H13B | 0.707357 | -0.259370 | 0.226264 | 0.030* |
| H13C | 0.862342 | -0.269091 | 0.138141 | 0.030* |
| C21 | 0.5903 (4) | 0.1724 (4) | 0.41189 (19) | 0.0256 (6) |
| H21A | 0.732489 | 0.124501 | 0.397086 | 0.038* |
| H21B | 0.542479 | 0.085370 | 0.436270 | 0.038* |
| H21C | 0.550277 | 0.258607 | 0.455628 | 0.038* |
| C22 | 0.5972 (4) | 0.3690 (4) | 0.2794 (2) | 0.0235 (6) |
| H22A | 0.584058 | 0.453563 | 0.319917 | 0.035* |
| H22B | 0.530347 | 0.422470 | 0.229941 | 0.035* |
| H22C | 0.735163 | 0.307435 | 0.256997 | 0.035* |
| C31 | 0.3105 (4) | 0.1225 (4) | 0.1106 (2) | 0.0231 (6) |
| H31A | 0.232105 | 0.064530 | 0.145738 | 0.035* |
| H31B | 0.433392 | 0.041165 | 0.081395 | 0.035* |
| H31C | 0.239274 | 0.194101 | 0.066081 | 0.035* |
| C32 | 0.1628 (4) | 0.3603 (4) | 0.2149 (2) | 0.0217 (6) |
| H32A | 0.087449 | 0.423452 | 0.169656 | 0.033* |
| H32B | 0.192661 | 0.435385 | 0.247387 | 0.033* |
| H32C | 0.087009 | 0.306743 | 0.255859 | 0.033* |
| Au1 | 0.000000 | 0.500000 | 0.500000 | 0.01294 (5) |
| Cl2 | -0.17349 (10) | 0.35513 (9) | 0.57968 (5) | 0.02250 (14) |
| Cl3 | 0.21088 (11) | 0.41781 (10) | 0.59700 (5) | 0.02634 (15) |
| Au2 | 0.500000 | 0.500000 | 0.000000 | 0.01263 (5) |
| Cl4 | 0.34763 (10) | 0.69883 (9) | 0.10371 (5) | 0.02299 (14) |
| Cl5 | 0.79509 (9) | 0.46997 (9) | 0.02957 (5) | 0.02043 (13) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|--------------|
| P1 | 0.0108 (3) | 0.0126 (3) | 0.0126 (3) | -0.0047 (2) | -0.0017 (2) | -0.0001 (2) |
| Se1 | 0.01475 (12) | 0.01428 (14) | 0.02174 (13) | -0.00624 (10) | 0.00013 (9) | 0.00256 (10) |
| Cl1 | 0.0172 (3) | 0.0237 (4) | 0.0233 (3) | -0.0085 (3) | 0.0041 (2) | -0.0014 (3) |
| C1 | 0.0132 (11) | 0.0149 (13) | 0.0136 (11) | -0.0038 (9) | -0.0012 (9) | 0.0005 (9) |
| C2 | 0.0176 (12) | 0.0188 (14) | 0.0170 (12) | -0.0084 (10) | -0.0020 (9) | -0.0043 (10) |
| C3 | 0.0132 (11) | 0.0136 (13) | 0.0170 (11) | -0.0040 (9) | -0.0044 (9) | 0.0010 (9) |
| C11 | 0.0168 (12) | 0.0227 (15) | 0.0161 (12) | -0.0063 (11) | 0.0023 (9) | 0.0019 (10) |
| C12 | 0.0122 (11) | 0.0222 (15) | 0.0249 (14) | -0.0031 (10) | -0.0057 (10) | -0.0015 (11) |
| C13 | 0.0177 (12) | 0.0153 (14) | 0.0254 (14) | -0.0038 (10) | -0.0025 (10) | -0.0030 (11) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| C21 | 0.0252 (14) | 0.0386 (19) | 0.0162 (13) | -0.0148 (13) | -0.0042 (10) | -0.0023 (12) |
| C22 | 0.0244 (14) | 0.0252 (16) | 0.0259 (14) | -0.0152 (12) | -0.0017 (11) | -0.0042 (12) |
| C31 | 0.0255 (14) | 0.0206 (15) | 0.0252 (14) | -0.0075 (12) | -0.0108 (11) | -0.0012 (11) |
| C32 | 0.0164 (12) | 0.0194 (15) | 0.0254 (14) | -0.0018 (11) | -0.0061 (10) | 0.0009 (11) |
| Au1 | 0.01396 (7) | 0.01208 (8) | 0.01319 (7) | -0.00517 (5) | -0.00260 (5) | -0.00061 (5) |
| Cl2 | 0.0228 (3) | 0.0210 (4) | 0.0253 (3) | -0.0122 (3) | -0.0014 (2) | 0.0031 (3) |
| Cl3 | 0.0248 (3) | 0.0352 (4) | 0.0230 (3) | -0.0134 (3) | -0.0119 (3) | 0.0061 (3) |
| Au2 | 0.01037 (7) | 0.01051 (8) | 0.01674 (7) | -0.00433 (5) | -0.00129 (5) | 0.00044 (5) |
| Cl4 | 0.0187 (3) | 0.0208 (4) | 0.0273 (3) | -0.0049 (3) | -0.0004 (2) | -0.0090 (3) |
| Cl5 | 0.0132 (3) | 0.0206 (3) | 0.0289 (3) | -0.0074 (2) | -0.0051 (2) | -0.0001 (3) |

Geometric parameters (Å, °)

| | | | |
|-------------|-------------|-----------------------|------------|
| P1—C2 | 1.833 (3) | C13—H13B | 0.9800 |
| P1—C3 | 1.839 (3) | C13—H13C | 0.9800 |
| P1—C1 | 1.864 (3) | C21—H21A | 0.9800 |
| P1—Se1 | 2.2467 (7) | C21—H21B | 0.9800 |
| Se1—Cl1 | 2.1654 (7) | C21—H21C | 0.9800 |
| Cl1—Cl2 | 3.4465 (10) | C22—H22A | 0.9800 |
| C1—C11 | 1.536 (4) | C22—H22B | 0.9800 |
| C1—C12 | 1.540 (4) | C22—H22C | 0.9800 |
| C1—C13 | 1.542 (4) | C31—H31A | 0.9800 |
| C2—C21 | 1.529 (4) | C31—H31B | 0.9800 |
| C2—C22 | 1.545 (4) | C31—H31C | 0.9800 |
| C2—H2 | 1.0000 | C32—H32A | 0.9800 |
| C3—C31 | 1.530 (4) | C32—H32B | 0.9800 |
| C3—C32 | 1.531 (4) | C32—H32C | 0.9800 |
| C3—H3 | 1.0000 | Au1—Cl3 | 2.2736 (7) |
| C11—H11A | 0.9800 | Au1—Cl3 ⁱ | 2.2737 (7) |
| C11—H11B | 0.9800 | Au1—Cl2 | 2.2842 (7) |
| C11—H11C | 0.9800 | Au1—Cl2 ⁱ | 2.2842 (7) |
| C12—H12A | 0.9800 | Au2—Cl4 | 2.2781 (7) |
| C12—H12B | 0.9800 | Au2—Cl4 ⁱⁱ | 2.2781 (7) |
| C12—H12C | 0.9800 | Au2—Cl5 ⁱⁱ | 2.2823 (6) |
| C13—H13A | 0.9800 | Au2—Cl5 | 2.2823 (6) |
| C2—P1—C3 | 106.87 (13) | C1—C13—H13C | 109.5 |
| C2—P1—C1 | 115.83 (12) | H13A—C13—H13C | 109.5 |
| C3—P1—C1 | 111.60 (12) | H13B—C13—H13C | 109.5 |
| C2—P1—Se1 | 109.29 (9) | C2—C21—H21A | 109.5 |
| C3—P1—Se1 | 110.42 (9) | C2—C21—H21B | 109.5 |
| C1—P1—Se1 | 102.77 (9) | H21A—C21—H21B | 109.5 |
| Cl1—Se1—P1 | 98.35 (3) | C2—C21—H21C | 109.5 |
| Se1—Cl1—Cl2 | 171.45 (3) | H21A—C21—H21C | 109.5 |
| C11—C1—C12 | 110.2 (2) | H21B—C21—H21C | 109.5 |
| C11—C1—C13 | 109.8 (2) | C2—C22—H22A | 109.5 |
| C12—C1—C13 | 108.4 (2) | C2—C22—H22B | 109.5 |
| C11—C1—P1 | 109.60 (18) | H22A—C22—H22B | 109.5 |

| | | | |
|---------------|-------------|--|--------------|
| C12—C1—P1 | 108.97 (18) | C2—C22—H22C | 109.5 |
| C13—C1—P1 | 109.90 (17) | H22A—C22—H22C | 109.5 |
| C21—C2—C22 | 112.3 (2) | H22B—C22—H22C | 109.5 |
| C21—C2—P1 | 116.6 (2) | C3—C31—H31A | 109.5 |
| C22—C2—P1 | 110.04 (19) | C3—C31—H31B | 109.5 |
| C21—C2—H2 | 105.7 | H31A—C31—H31B | 109.5 |
| C22—C2—H2 | 105.7 | C3—C31—H31C | 109.5 |
| P1—C2—H2 | 105.7 | H31A—C31—H31C | 109.5 |
| C31—C3—C32 | 110.5 (2) | H31B—C31—H31C | 109.5 |
| C31—C3—P1 | 112.97 (19) | C3—C32—H32A | 109.5 |
| C32—C3—P1 | 112.57 (19) | C3—C32—H32B | 109.5 |
| C31—C3—H3 | 106.8 | H32A—C32—H32B | 109.5 |
| C32—C3—H3 | 106.8 | C3—C32—H32C | 109.5 |
| P1—C3—H3 | 106.8 | H32A—C32—H32C | 109.5 |
| C1—C11—H11A | 109.5 | H32B—C32—H32C | 109.5 |
| C1—C11—H11B | 109.5 | Cl3—Au1—Cl3 ⁱ | 180.0 |
| H11A—C11—H11B | 109.5 | Cl3—Au1—Cl2 | 90.35 (3) |
| C1—C11—H11C | 109.5 | Cl3 ⁱ —Au1—Cl2 | 89.65 (3) |
| H11A—C11—H11C | 109.5 | Cl3—Au1—Cl2 ⁱ | 89.65 (3) |
| H11B—C11—H11C | 109.5 | Cl3 ⁱ —Au1—Cl2 ⁱ | 90.35 (3) |
| C1—C12—H12A | 109.5 | Cl2—Au1—Cl2 ⁱ | 180.00 (3) |
| C1—C12—H12B | 109.5 | Au1—Cl2—Cl1 | 73.52 (2) |
| H12A—C12—H12B | 109.5 | Cl4—Au2—Cl4 ⁱⁱ | 180.0 |
| C1—C12—H12C | 109.5 | Cl4—Au2—Cl5 ⁱⁱ | 89.59 (3) |
| H12A—C12—H12C | 109.5 | Cl4 ⁱⁱ —Au2—Cl5 ⁱⁱ | 90.41 (3) |
| H12B—C12—H12C | 109.5 | Cl4—Au2—Cl5 | 90.41 (3) |
| C1—C13—H13A | 109.5 | Cl4 ⁱⁱ —Au2—Cl5 | 89.59 (3) |
| C1—C13—H13B | 109.5 | Cl5 ⁱⁱ —Au2—Cl5 | 180.0 |
| H13A—C13—H13B | 109.5 | | |
| C2—P1—Se1—Cl1 | 39.96 (10) | C1—P1—C2—C21 | -66.3 (2) |
| C3—P1—Se1—Cl1 | -77.33 (10) | Se1—P1—C2—C21 | 49.2 (2) |
| C1—P1—Se1—Cl1 | 163.52 (9) | C3—P1—C2—C22 | -62.0 (2) |
| C2—P1—C1—C11 | -87.7 (2) | C1—P1—C2—C22 | 63.1 (2) |
| C3—P1—C1—C11 | 34.9 (2) | Se1—P1—C2—C22 | 178.52 (17) |
| Se1—P1—C1—C11 | 153.19 (17) | C2—P1—C3—C31 | -170.76 (19) |
| C2—P1—C1—C12 | 32.9 (2) | C1—P1—C3—C31 | 61.7 (2) |
| C3—P1—C1—C12 | 155.51 (18) | Se1—P1—C3—C31 | -52.0 (2) |
| Se1—P1—C1—C12 | -86.16 (19) | C2—P1—C3—C32 | -44.8 (2) |
| C2—P1—C1—C13 | 151.59 (18) | C1—P1—C3—C32 | -172.36 (19) |
| C3—P1—C1—C13 | -85.8 (2) | Se1—P1—C3—C32 | 74.0 (2) |
| Se1—P1—C1—C13 | 32.50 (19) | Cl3—Au1—Cl2—Cl1 | -94.93 (3) |
| C3—P1—C2—C21 | 168.7 (2) | Cl3 ⁱ —Au1—Cl2—Cl1 | 85.07 (3) |

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

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|--------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| C13—H13B \cdots Se1 | 0.98 | 2.65 | 3.142 (3) | 111 |
| C2—H2 \cdots Cl1 | 1.00 | 2.99 | 3.454 (3) | 110 |
| C3—H3 \cdots Au2 | 1.00 | 2.75 | 3.690 (3) | 157 |
| C32—H32C \cdots Cl1 | 0.98 | 2.92 | 3.682 (3) | 135 |
| C21—H21C \cdots Cl3 | 0.98 | 2.99 | 3.774 (3) | 138 |
| C11—H11A \cdots Cl5 | 0.98 | 2.97 | 3.741 (3) | 137 |
| C2—H2 \cdots Cl2 ⁱ | 1.00 | 2.87 | 3.629 (3) | 133 |
| C22—H22A \cdots Cl3 ⁱⁱⁱ | 0.98 | 2.79 | 3.629 (3) | 144 |
| C12—H12B \cdots Cl3 ^{iv} | 0.98 | 2.95 | 3.783 (3) | 143 |
| C13—H13B \cdots Cl3 ^{iv} | 0.98 | 3.01 | 3.902 (3) | 152 |
| C12—H12A \cdots Cl4 ^v | 0.98 | 2.80 | 3.721 (3) | 156 |
| C13—H13A \cdots Cl4 ^{vi} | 0.98 | 2.94 | 3.751 (3) | 141 |

Symmetry codes: (i) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y, -z+1$; (v) $x+1, y-1, z$; (vi) $x, y-1, z$.

Bis(*tert*-butyl)(chloroselanyl)(propan-2-yl)phosphonium tetrachloridoaurate(III) (23a)

Crystal data

(C₁₁H₂₅ClPSe)[AuCl₄]

M_r = 641.46

Monoclinic, *C2/c*

a = 33.7472 (6) Å

b = 7.79306 (8) Å

c = 16.2575 (3) Å

β = 113.582 (3)°

V = 3918.54 (14) Å³

Z = 8

F(000) = 2432

D_x = 2.175 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 55878 reflections

θ = 2.2–30.9°

μ = 10.12 mm⁻¹

T = 100 K

Plate, yellow

0.35 × 0.2 × 0.04 mm

Data collection

Oxford Diffraction Xcalibur, Eos diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω scan

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2015)

T_{min} = 0.308, *T_{max}* = 1.000

257492 measured reflections

6028 independent reflections

5453 reflections with *I* > 2σ(*I*)

R_{int} = 0.058

θ_{\max} = 30.9°, θ_{\min} = 2.5°

h = -48→47

k = -11→11

l = -23→23

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.021

wR (*F*²) = 0.043

S = 1.11

6028 reflections

191 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0165*P*)² + 12.3178*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.002

Δρ_{max} = 1.13 e Å⁻³

Δρ_{min} = -1.20 e Å⁻³

Special details

Refinement. The anion centred on Au1 is disordered, with the atoms Cl3 and Cl4 being slightly displaced from the twofold axis. Dimensions of disordered groups should be interpreted with caution.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|-------------|-------------|--------------|----------------------------------|-----------|
| P1 | 0.37529 (2) | 0.60748 (7) | 0.40097 (4) | 0.01109 (11) | |
| Se1 | 0.42555 (2) | 0.76990 (3) | 0.50633 (2) | 0.01833 (5) | |
| Cl1 | 0.38551 (2) | 0.90386 (9) | 0.56139 (4) | 0.02734 (14) | |
| C2 | 0.34626 (8) | 0.7484 (3) | 0.30151 (15) | 0.0141 (4) | |
| C1 | 0.41121 (8) | 0.4391 (3) | 0.38588 (15) | 0.0138 (4) | |
| C3 | 0.33619 (8) | 0.5250 (3) | 0.44412 (15) | 0.0137 (4) | |
| H3 | 0.315469 | 0.621002 | 0.437455 | 0.016* | |
| C23 | 0.33117 (9) | 0.9092 (3) | 0.33558 (17) | 0.0197 (5) | |
| H23A | 0.314377 | 0.982549 | 0.284553 | 0.030* | |
| H23B | 0.356412 | 0.972528 | 0.376659 | 0.030* | |
| H23C | 0.313092 | 0.874894 | 0.367276 | 0.030* | |
| C21 | 0.30654 (8) | 0.6599 (3) | 0.23160 (16) | 0.0168 (5) | |
| H21A | 0.294574 | 0.731319 | 0.177595 | 0.025* | |
| H21B | 0.284670 | 0.643492 | 0.256332 | 0.025* | |
| H21C | 0.314980 | 0.548066 | 0.216138 | 0.025* | |
| C22 | 0.37709 (9) | 0.8055 (3) | 0.25826 (17) | 0.0202 (5) | |
| H22A | 0.385158 | 0.705974 | 0.231496 | 0.030* | |
| H22B | 0.403128 | 0.856211 | 0.304167 | 0.030* | |
| H22C | 0.362643 | 0.890849 | 0.211536 | 0.030* | |
| C11 | 0.42408 (8) | 0.3114 (3) | 0.46488 (17) | 0.0186 (5) | |
| H11A | 0.445045 | 0.228858 | 0.460457 | 0.028* | |
| H11B | 0.398317 | 0.250180 | 0.462671 | 0.028* | |
| H11C | 0.437065 | 0.374233 | 0.521677 | 0.028* | |
| C12 | 0.38849 (8) | 0.3426 (3) | 0.29689 (17) | 0.0188 (5) | |
| H12A | 0.407547 | 0.251957 | 0.291947 | 0.028* | |
| H12B | 0.381773 | 0.422950 | 0.246727 | 0.028* | |
| H12C | 0.361655 | 0.291381 | 0.295193 | 0.028* | |
| C13 | 0.45260 (8) | 0.5246 (3) | 0.38698 (18) | 0.0204 (5) | |
| H13A | 0.467873 | 0.581618 | 0.444851 | 0.031* | |
| H13B | 0.444862 | 0.609482 | 0.338592 | 0.031* | |
| H13C | 0.471389 | 0.437022 | 0.378194 | 0.031* | |
| C32 | 0.30876 (8) | 0.3748 (3) | 0.38931 (18) | 0.0191 (5) | |
| H32A | 0.326583 | 0.270978 | 0.401435 | 0.029* | |
| H32B | 0.297854 | 0.402248 | 0.325203 | 0.029* | |
| H32C | 0.284348 | 0.355387 | 0.406317 | 0.029* | |
| C31 | 0.35545 (9) | 0.4778 (4) | 0.54445 (17) | 0.0227 (5) | |
| H31A | 0.332039 | 0.463082 | 0.565031 | 0.034* | |
| H31B | 0.374783 | 0.569670 | 0.578924 | 0.034* | |
| H31C | 0.371774 | 0.370435 | 0.553273 | 0.034* | |
| Au1 | 0.500000 | 1.01052 (2) | 0.750000 | 0.01363 (3) | |
| Cl2 | 0.51056 (2) | 1.01088 (7) | 0.61977 (4) | 0.01812 (11) | |

| | | | | | |
|-----|-------------|--------------|--------------|--------------|-----|
| Cl3 | 0.49010 (7) | 1.29947 (15) | 0.73350 (16) | 0.0338 (6) | 0.5 |
| Cl4 | 0.5054 (3) | 0.72026 (14) | 0.7548 (10) | 0.0235 (13) | 0.5 |
| Au2 | 0.250000 | 0.750000 | 0.500000 | 0.01126 (3) | |
| Cl5 | 0.27035 (2) | 1.02584 (7) | 0.49126 (4) | 0.02105 (12) | |
| Cl6 | 0.22611 (2) | 0.72036 (8) | 0.34868 (4) | 0.02033 (12) | |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|-------------|---------------|
| P1 | 0.0116 (3) | 0.0111 (2) | 0.0103 (2) | −0.00052 (19) | 0.0041 (2) | −0.00012 (19) |
| Se1 | 0.01531 (12) | 0.02074 (11) | 0.01544 (11) | −0.00326 (9) | 0.00247 (9) | −0.00587 (9) |
| Cl1 | 0.0316 (4) | 0.0280 (3) | 0.0228 (3) | 0.0020 (3) | 0.0112 (3) | −0.0093 (2) |
| C2 | 0.0157 (11) | 0.0129 (10) | 0.0120 (10) | −0.0007 (8) | 0.0039 (9) | 0.0022 (8) |
| C1 | 0.0122 (11) | 0.0152 (10) | 0.0149 (10) | 0.0020 (8) | 0.0063 (9) | 0.0000 (8) |
| C3 | 0.0143 (11) | 0.0151 (10) | 0.0134 (10) | 0.0001 (8) | 0.0074 (9) | 0.0024 (8) |
| C23 | 0.0239 (13) | 0.0129 (10) | 0.0203 (12) | 0.0030 (9) | 0.0067 (10) | 0.0029 (9) |
| C21 | 0.0161 (12) | 0.0168 (10) | 0.0134 (10) | −0.0013 (9) | 0.0017 (9) | 0.0005 (8) |
| C22 | 0.0229 (13) | 0.0204 (11) | 0.0188 (11) | −0.0034 (10) | 0.0098 (10) | 0.0046 (9) |
| C11 | 0.0187 (12) | 0.0187 (11) | 0.0184 (11) | 0.0067 (9) | 0.0075 (10) | 0.0047 (9) |
| C12 | 0.0213 (13) | 0.0173 (11) | 0.0186 (11) | 0.0016 (9) | 0.0087 (10) | −0.0042 (9) |
| C13 | 0.0130 (11) | 0.0263 (12) | 0.0241 (12) | −0.0007 (9) | 0.0096 (10) | −0.0011 (10) |
| C32 | 0.0183 (12) | 0.0164 (11) | 0.0244 (12) | −0.0036 (9) | 0.0103 (10) | −0.0002 (9) |
| C31 | 0.0266 (14) | 0.0289 (13) | 0.0156 (11) | −0.0006 (11) | 0.0116 (10) | 0.0047 (10) |
| Au1 | 0.01365 (6) | 0.00993 (5) | 0.02032 (6) | 0.000 | 0.00996 (5) | 0.000 |
| Cl2 | 0.0196 (3) | 0.0176 (2) | 0.0199 (3) | −0.0035 (2) | 0.0108 (2) | −0.0004 (2) |
| Cl3 | 0.065 (2) | 0.0113 (4) | 0.0477 (18) | 0.0045 (6) | 0.0463 (14) | 0.0033 (5) |
| Cl4 | 0.040 (4) | 0.0110 (4) | 0.021 (2) | 0.0037 (7) | 0.014 (3) | 0.0006 (9) |
| Au2 | 0.01106 (6) | 0.01076 (5) | 0.01175 (5) | 0.00169 (4) | 0.00433 (4) | 0.00043 (4) |
| Cl5 | 0.0266 (3) | 0.0134 (2) | 0.0244 (3) | −0.0031 (2) | 0.0115 (2) | 0.0005 (2) |
| Cl6 | 0.0252 (3) | 0.0205 (3) | 0.0124 (2) | 0.0039 (2) | 0.0046 (2) | −0.0003 (2) |

Geometric parameters (Å, °)

| | | | |
|---------|------------|----------------------|-------------|
| P1—C3 | 1.840 (2) | C11—H11C | 0.9800 |
| P1—C1 | 1.868 (2) | C12—H12A | 0.9800 |
| P1—C2 | 1.875 (2) | C12—H12B | 0.9800 |
| P1—Se1 | 2.2557 (6) | C12—H12C | 0.9800 |
| Se1—Cl1 | 2.1645 (7) | C13—H13A | 0.9800 |
| Se1—Cl2 | 3.3052 (6) | C13—H13B | 0.9800 |
| C2—C21 | 1.532 (3) | C13—H13C | 0.9800 |
| C2—C22 | 1.536 (4) | C32—H32A | 0.9800 |
| C2—C23 | 1.536 (3) | C32—H32B | 0.9800 |
| C1—C12 | 1.536 (3) | C32—H32C | 0.9800 |
| C1—C13 | 1.541 (3) | C31—H31A | 0.9800 |
| C1—C11 | 1.543 (3) | C31—H31B | 0.9800 |
| C3—C32 | 1.537 (3) | C31—H31C | 0.9800 |
| C3—C31 | 1.540 (3) | Au1—Cl4 ⁱ | 2.2681 (13) |
| C3—H3 | 1.0000 | Au1—Cl4 | 2.2681 (13) |

| | | | |
|---------------|-------------|--|-------------|
| C23—H23A | 0.9800 | Au1—Cl3 ⁱ | 2.2765 (12) |
| C23—H23B | 0.9800 | Au1—Cl3 | 2.2765 (12) |
| C23—H23C | 0.9800 | Au1—Cl2 | 2.2833 (6) |
| C21—H21A | 0.9800 | Au1—Cl2 ⁱ | 2.2833 (6) |
| C21—H21B | 0.9800 | Cl3—Cl3 ⁱ | 0.669 (4) |
| C21—H21C | 0.9800 | Cl4—Cl4 ⁱ | 0.332 (17) |
| C22—H22A | 0.9800 | Au2—Cl6 ⁱⁱ | 2.2734 (6) |
| C22—H22B | 0.9800 | Au2—Cl6 | 2.2735 (6) |
| C22—H22C | 0.9800 | Au2—Cl5 | 2.2784 (6) |
| C11—H11A | 0.9800 | Au2—Cl5 ⁱⁱ | 2.2785 (6) |
| C11—H11B | 0.9800 | | |
| | | | |
| C3—P1—C1 | 113.98 (11) | H11B—C11—H11C | 109.5 |
| C3—P1—C2 | 109.06 (11) | C1—C12—H12A | 109.5 |
| C1—P1—C2 | 116.17 (11) | C1—C12—H12B | 109.5 |
| C3—P1—Se1 | 110.03 (8) | H12A—C12—H12B | 109.5 |
| C1—P1—Se1 | 99.42 (8) | C1—C12—H12C | 109.5 |
| C2—P1—Se1 | 107.51 (7) | H12A—C12—H12C | 109.5 |
| Cl1—Se1—P1 | 100.40 (3) | H12B—C12—H12C | 109.5 |
| Cl1—Se1—Cl2 | 92.37 (2) | C1—C13—H13A | 109.5 |
| P1—Se1—Cl2 | 164.50 (2) | C1—C13—H13B | 109.5 |
| C21—C2—C22 | 110.0 (2) | H13A—C13—H13B | 109.5 |
| C21—C2—C23 | 108.5 (2) | C1—C13—H13C | 109.5 |
| C22—C2—C23 | 108.17 (19) | H13A—C13—H13C | 109.5 |
| C21—C2—P1 | 112.10 (15) | H13B—C13—H13C | 109.5 |
| C22—C2—P1 | 110.40 (17) | C3—C32—H32A | 109.5 |
| C23—C2—P1 | 107.51 (16) | C3—C32—H32B | 109.5 |
| C12—C1—C13 | 109.3 (2) | H32A—C32—H32B | 109.5 |
| C12—C1—C11 | 109.7 (2) | C3—C32—H32C | 109.5 |
| C13—C1—C11 | 108.5 (2) | H32A—C32—H32C | 109.5 |
| C12—C1—P1 | 111.22 (16) | H32B—C32—H32C | 109.5 |
| C13—C1—P1 | 109.11 (16) | C3—C31—H31A | 109.5 |
| C11—C1—P1 | 108.96 (16) | C3—C31—H31B | 109.5 |
| C32—C3—C31 | 109.5 (2) | H31A—C31—H31B | 109.5 |
| C32—C3—P1 | 113.73 (17) | C3—C31—H31C | 109.5 |
| C31—C3—P1 | 115.10 (17) | H31A—C31—H31C | 109.5 |
| C32—C3—H3 | 105.9 | H31B—C31—H31C | 109.5 |
| C31—C3—H3 | 105.9 | Cl4 ⁱ —Au1—Cl4 | 8.4 (4) |
| P1—C3—H3 | 105.9 | Cl4 ⁱ —Au1—Cl3 ⁱ | 175.2 (3) |
| C2—C23—H23A | 109.5 | Cl4—Au1—Cl3 ⁱ | 167.6 (2) |
| C2—C23—H23B | 109.5 | Cl4 ⁱ —Au1—Cl3 | 167.6 (2) |
| H23A—C23—H23B | 109.5 | Cl4—Au1—Cl3 | 175.2 (3) |
| C2—C23—H23C | 109.5 | Cl3 ⁱ —Au1—Cl3 | 16.89 (9) |
| H23A—C23—H23C | 109.5 | Cl4 ⁱ —Au1—Cl2 | 90.5 (4) |
| H23B—C23—H23C | 109.5 | Cl4—Au1—Cl2 | 89.6 (4) |
| C2—C21—H21A | 109.5 | Cl3 ⁱ —Au1—Cl2 | 92.19 (8) |
| C2—C21—H21B | 109.5 | Cl3—Au1—Cl2 | 87.68 (8) |
| H21A—C21—H21B | 109.5 | Cl4 ⁱ —Au1—Cl2 ⁱ | 89.6 (4) |

| | | | |
|---------------|--------------|--|--------------|
| C2—C21—H21C | 109.5 | Cl4—Au1—Cl2 ⁱ | 90.5 (4) |
| H21A—C21—H21C | 109.5 | Cl3 ⁱ —Au1—Cl2 ⁱ | 87.67 (8) |
| H21B—C21—H21C | 109.5 | Cl3—Au1—Cl2 ⁱ | 92.18 (8) |
| C2—C22—H22A | 109.5 | Cl2—Au1—Cl2 ⁱ | 179.86 (3) |
| C2—C22—H22B | 109.5 | Au1—Cl2—Se1 | 95.398 (19) |
| H22A—C22—H22B | 109.5 | Cl3 ⁱ —Cl3—Au1 | 81.55 (5) |
| C2—C22—H22C | 109.5 | Cl4 ⁱ —Cl4—Au1 | 85.8 (2) |
| H22A—C22—H22C | 109.5 | Cl6 ⁱⁱ —Au2—Cl6 | 180.00 (3) |
| H22B—C22—H22C | 109.5 | Cl6 ⁱⁱ —Au2—Cl5 | 89.22 (2) |
| C1—C11—H11A | 109.5 | Cl6—Au2—Cl5 | 90.78 (2) |
| C1—C11—H11B | 109.5 | Cl6 ⁱⁱ —Au2—Cl5 ⁱⁱ | 90.78 (2) |
| H11A—C11—H11B | 109.5 | Cl6—Au2—Cl5 ⁱⁱ | 89.22 (2) |
| C1—C11—H11C | 109.5 | Cl5—Au2—Cl5 ⁱⁱ | 180.0 |
| H11A—C11—H11C | 109.5 | | |
| | | | |
| C3—P1—Se1—Cl1 | -39.56 (8) | Se1—P1—C1—C13 | -40.61 (16) |
| C1—P1—Se1—Cl1 | -159.50 (8) | C3—P1—C1—C11 | -39.33 (19) |
| C2—P1—Se1—Cl1 | 79.09 (9) | C2—P1—C1—C11 | -167.41 (16) |
| C3—P1—Se1—Cl2 | 175.48 (10) | Se1—P1—C1—C11 | 77.67 (16) |
| C1—P1—Se1—Cl2 | 55.54 (11) | C1—P1—C3—C32 | -53.0 (2) |
| C2—P1—Se1—Cl2 | -65.86 (12) | C2—P1—C3—C32 | 78.60 (19) |
| C3—P1—C2—C21 | -51.5 (2) | Se1—P1—C3—C32 | -163.70 (15) |
| C1—P1—C2—C21 | 79.0 (2) | C1—P1—C3—C31 | 74.4 (2) |
| Se1—P1—C2—C21 | -170.76 (15) | C2—P1—C3—C31 | -153.95 (18) |
| C3—P1—C2—C22 | -174.55 (16) | Se1—P1—C3—C31 | -36.25 (19) |
| C1—P1—C2—C22 | -44.1 (2) | Cl4 ⁱ —Au1—Cl2—Se1 | 51.0 (2) |
| Se1—P1—C2—C22 | 66.17 (17) | Cl4—Au1—Cl2—Se1 | 59.4 (2) |
| C3—P1—C2—C23 | 67.66 (18) | Cl3 ⁱ —Au1—Cl2—Se1 | -132.95 (5) |
| C1—P1—C2—C23 | -161.87 (16) | Cl3—Au1—Cl2—Se1 | -116.66 (5) |
| Se1—P1—C2—C23 | -51.61 (18) | Cl4 ⁱ —Au1—Cl3—Cl3 ⁱ | 173 (2) |
| C3—P1—C1—C12 | 81.70 (19) | Cl2—Au1—Cl3—Cl3 ⁱ | -105.4 (5) |
| C2—P1—C1—C12 | -46.4 (2) | Cl2 ⁱ —Au1—Cl3—Cl3 ⁱ | 74.6 (5) |
| Se1—P1—C1—C12 | -161.30 (16) | Cl3 ⁱ —Au1—Cl4—Cl4 ⁱ | 165 (4) |
| C3—P1—C1—C13 | -157.60 (16) | Cl2—Au1—Cl4—Cl4 ⁱ | -96 (6) |
| C2—P1—C1—C13 | 74.31 (19) | Cl2 ⁱ —Au1—Cl4—Cl4 ⁱ | 84 (6) |

Symmetry codes: (i) $-x+1, y, -z+3/2$; (ii) $-x+1/2, -y+3/2, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|--|-------------|---------------------|----------------------------|-------------------------------|
| C3—H3 \cdots Au2 | 1.00 | 2.95 | 3.805 (2) | 144 |
| C3—H3 \cdots Cl6 | 1.00 | 2.88 | 3.730 (2) | 143 |
| C13—H13 <i>A</i> \cdots Se1 | 0.98 | 2.52 | 3.110 (3) | 119 |
| C23—H23 <i>B</i> \cdots C11 | 0.98 | 2.81 | 3.385 (3) | 118 |
| C31—H31 <i>B</i> \cdots C11 | 0.98 | 2.66 | 3.451 (3) | 138 |
| C23—H23 <i>A</i> \cdots Cl6 ⁱⁱⁱ | 0.98 | 2.76 | 3.736 (2) | 173 |
| C21—H21C \cdots Cl6 ^{iv} | 0.98 | 2.90 | 3.674 (2) | 137 |

| | | | | |
|-------------------------------|------|------|------------|-----|
| C13—H13B···Cl3 ^v | 0.98 | 2.80 | 3.498 (4) | 129 |
| C22—H22B···Cl2 ^{vi} | 0.98 | 2.86 | 3.787 (3) | 157 |
| C13—H13C···Cl4 ^{vii} | 0.98 | 2.85 | 3.685 (15) | 143 |

Symmetry codes: (iii) $-x+1/2, y+1/2, -z+1/2$; (iv) $-x+1/2, y-1/2, -z+1/2$; (v) $x, -y+2, z-1/2$; (vi) $-x+1, -y+2, -z+1$; (vii) $-x+1, -y+1, -z+1$.

(Bromosulfanyl)tris(propan-2-yl)phosphonium tetrabromidoaurate(III) (17b)

Crystal data

| | |
|---|---|
| (C ₉ H ₂₁ BrPS)[AuBr ₄] | $Z = 2$ |
| $M_r = 788.80$ | $F(000) = 720$ |
| Triclinic, $P\bar{1}$ | $D_x = 2.790 \text{ Mg m}^{-3}$ |
| $a = 7.8543 (4) \text{ \AA}$ | Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$ |
| $b = 8.0592 (4) \text{ \AA}$ | Cell parameters from 18583 reflections |
| $c = 15.3505 (7) \text{ \AA}$ | $\theta = 2.6\text{--}30.8^\circ$ |
| $\alpha = 76.717 (4)^\circ$ | $\mu = 18.65 \text{ mm}^{-1}$ |
| $\beta = 83.169 (4)^\circ$ | $T = 100 \text{ K}$ |
| $\gamma = 87.722 (4)^\circ$ | Plate, red |
| $V = 938.89 (8) \text{ \AA}^3$ | $0.2 \times 0.08 \times 0.05 \text{ mm}$ |

Data collection

| | |
|--|---|
| Oxford Diffraction Xcalibur, Eos diffractometer | 54229 measured reflections |
| Radiation source: Enhance (Mo) X-ray Source | 5646 independent reflections |
| Detector resolution: 16.1419 pixels mm ⁻¹ | 5089 reflections with $I > 2\sigma(I)$ |
| ω scans | $R_{\text{int}} = 0.043$ |
| Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2015) | $\theta_{\text{max}} = 30.9^\circ, \theta_{\text{min}} = 2.6^\circ$ |
| $T_{\text{min}} = 0.247, T_{\text{max}} = 1.000$ | $h = -11 \rightarrow 11$ |
| | $k = -11 \rightarrow 11$ |
| | $l = -22 \rightarrow 21$ |

Refinement

| | |
|--|--|
| Refinement on F^2 | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H-atom parameters constrained |
| $R[F^2 > 2\sigma(F^2)] = 0.021$ | $w = 1/[\sigma^2(F_o^2) + (0.014P)^2 + 1.1153P]$ |
| $wR(F^2) = 0.040$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.08$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 5646 reflections | $\Delta\rho_{\text{max}} = 1.42 \text{ e \AA}^{-3}$ |
| 164 parameters | $\Delta\rho_{\text{min}} = -1.15 \text{ e \AA}^{-3}$ |
| 0 restraints | Extinction correction: <i>SHELXL2019/3</i> |
| Primary atom site location: structure-invariant direct methods | (Sheldrick, 2015), $F_c^* = kF_c[1 + 0.001 F_c^2 \lambda^3 / \sin(2\theta)]^{1/4}$ |
| Secondary atom site location: difference Fourier map | Extinction coefficient: 0.00112 (7) |

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|--------------|----------------------------------|
| P1 | 0.69771 (9) | 0.74853 (9) | 0.25622 (5) | 0.00958 (13) |
| S1 | 0.88558 (9) | 0.55851 (9) | 0.28013 (5) | 0.01523 (14) |
| Br1 | 0.85534 (4) | 0.43166 (4) | 0.17064 (2) | 0.01714 (6) |
| C1 | 0.7070 (4) | 0.8436 (4) | 0.35348 (18) | 0.0129 (5) |
| H1 | 0.831259 | 0.859646 | 0.357245 | 0.015* |
| C2 | 0.4956 (4) | 0.6524 (3) | 0.24812 (18) | 0.0119 (5) |

| | | | | |
|------|-------------|--------------|--------------|-------------|
| H2 | 0.512417 | 0.609080 | 0.191623 | 0.014* |
| C3 | 0.7561 (4) | 0.9104 (3) | 0.15342 (18) | 0.0113 (5) |
| H3 | 0.681871 | 1.012659 | 0.157636 | 0.014* |
| C11 | 0.6231 (4) | 1.0202 (4) | 0.3420 (2) | 0.0189 (6) |
| H11A | 0.500205 | 1.011195 | 0.338359 | 0.028* |
| H11B | 0.675956 | 1.095104 | 0.286560 | 0.028* |
| H11C | 0.639301 | 1.067813 | 0.393673 | 0.028* |
| C12 | 0.6375 (4) | 0.7254 (4) | 0.44330 (19) | 0.0182 (6) |
| H12A | 0.674091 | 0.766691 | 0.493334 | 0.027* |
| H12B | 0.682260 | 0.609468 | 0.445424 | 0.027* |
| H12C | 0.511981 | 0.724814 | 0.448393 | 0.027* |
| C21 | 0.4448 (4) | 0.4985 (4) | 0.3250 (2) | 0.0186 (6) |
| H21A | 0.409512 | 0.537193 | 0.380510 | 0.028* |
| H21B | 0.542985 | 0.419964 | 0.333736 | 0.028* |
| H21C | 0.349316 | 0.439793 | 0.309798 | 0.028* |
| C22 | 0.3521 (4) | 0.7878 (4) | 0.2357 (2) | 0.0172 (6) |
| H22A | 0.250375 | 0.738280 | 0.220752 | 0.026* |
| H22B | 0.390742 | 0.884531 | 0.186696 | 0.026* |
| H22C | 0.323445 | 0.826977 | 0.291591 | 0.026* |
| C31 | 0.9412 (4) | 0.9658 (4) | 0.14881 (19) | 0.0165 (6) |
| H31A | 1.019276 | 0.872793 | 0.138121 | 0.025* |
| H31B | 0.959506 | 0.993536 | 0.205860 | 0.025* |
| H31C | 0.963641 | 1.066466 | 0.099479 | 0.025* |
| C32 | 0.7224 (4) | 0.8589 (4) | 0.06692 (19) | 0.0178 (6) |
| H32A | 0.746424 | 0.955373 | 0.015331 | 0.027* |
| H32B | 0.602194 | 0.826255 | 0.071665 | 0.027* |
| H32C | 0.797026 | 0.762154 | 0.058485 | 0.027* |
| Au1 | 0.500000 | 0.500000 | 0.000000 | 0.01133 (4) |
| Br2 | 0.76076 (4) | 0.33440 (4) | -0.01670 (2) | 0.01959 (7) |
| Br3 | 0.39092 (4) | 0.28650 (4) | 0.13213 (2) | 0.01803 (7) |
| Au2 | 1.000000 | 0.000000 | 0.500000 | 0.00940 (4) |
| Br4 | 1.11077 (4) | 0.13466 (4) | 0.34673 (2) | 0.01512 (6) |
| Br5 | 1.10194 (4) | -0.27647 (4) | 0.47679 (2) | 0.01735 (6) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|---------------|
| P1 | 0.0090 (3) | 0.0109 (3) | 0.0085 (3) | -0.0001 (2) | -0.0009 (2) | -0.0015 (2) |
| S1 | 0.0135 (4) | 0.0151 (3) | 0.0168 (3) | 0.0036 (3) | -0.0037 (3) | -0.0026 (3) |
| Br1 | 0.01764 (15) | 0.01416 (13) | 0.01919 (14) | 0.00246 (11) | 0.00120 (11) | -0.00502 (11) |
| C1 | 0.0127 (14) | 0.0166 (13) | 0.0100 (12) | -0.0035 (10) | -0.0018 (10) | -0.0032 (10) |
| C2 | 0.0112 (14) | 0.0143 (13) | 0.0112 (12) | -0.0039 (10) | -0.0006 (10) | -0.0045 (10) |
| C3 | 0.0119 (14) | 0.0119 (13) | 0.0092 (12) | -0.0001 (10) | -0.0005 (10) | -0.0010 (9) |
| C11 | 0.0240 (17) | 0.0168 (14) | 0.0178 (14) | 0.0004 (12) | -0.0031 (12) | -0.0075 (11) |
| C12 | 0.0220 (17) | 0.0227 (15) | 0.0099 (13) | -0.0041 (12) | -0.0003 (11) | -0.0037 (11) |
| C21 | 0.0204 (16) | 0.0180 (15) | 0.0161 (14) | -0.0072 (12) | 0.0014 (12) | -0.0017 (11) |
| C22 | 0.0093 (14) | 0.0205 (15) | 0.0218 (15) | -0.0001 (11) | -0.0006 (11) | -0.0050 (12) |
| C31 | 0.0151 (15) | 0.0183 (14) | 0.0139 (13) | -0.0032 (11) | 0.0002 (11) | 0.0006 (11) |

| | | | | | | |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| C32 | 0.0224 (17) | 0.0185 (14) | 0.0115 (13) | -0.0030 (12) | -0.0006 (12) | -0.0017 (11) |
| Au1 | 0.01375 (8) | 0.01132 (7) | 0.00895 (7) | 0.00043 (5) | -0.00182 (5) | -0.00222 (5) |
| Br2 | 0.01882 (16) | 0.01990 (15) | 0.01867 (14) | 0.00610 (11) | -0.00027 (12) | -0.00357 (11) |
| Br3 | 0.02203 (16) | 0.01692 (14) | 0.01267 (13) | -0.00162 (11) | 0.00002 (11) | 0.00091 (10) |
| Au2 | 0.00830 (7) | 0.01071 (7) | 0.00965 (7) | -0.00008 (5) | -0.00162 (5) | -0.00296 (5) |
| Br4 | 0.01749 (15) | 0.01523 (13) | 0.01148 (12) | -0.00092 (10) | 0.00137 (10) | -0.00208 (10) |
| Br5 | 0.02171 (16) | 0.01346 (13) | 0.01655 (13) | 0.00486 (11) | -0.00061 (11) | -0.00435 (10) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|-----------------------|------------|
| P1—C2 | 1.823 (3) | C21—H21A | 0.9800 |
| P1—C3 | 1.825 (3) | C21—H21B | 0.9800 |
| P1—C1 | 1.837 (3) | C21—H21C | 0.9800 |
| P1—S1 | 2.0852 (10) | C22—H22A | 0.9800 |
| S1—Br1 | 2.1977 (8) | C22—H22B | 0.9800 |
| Br1—Br2 | 3.3206 (5) | C22—H22C | 0.9800 |
| C1—C11 | 1.527 (4) | C31—H31A | 0.9800 |
| C1—C12 | 1.538 (4) | C31—H31B | 0.9800 |
| C1—H1 | 1.0000 | C31—H31C | 0.9800 |
| C2—C21 | 1.531 (4) | C32—H32A | 0.9800 |
| C2—C22 | 1.535 (4) | C32—H32B | 0.9800 |
| C2—H2 | 1.0000 | C32—H32C | 0.9800 |
| C3—C31 | 1.526 (4) | Au1—Br2 | 2.4201 (3) |
| C3—C32 | 1.533 (4) | Au1—Br2 ⁱ | 2.4201 (3) |
| C3—H3 | 1.0000 | Au1—Br3 ⁱ | 2.4307 (3) |
| C11—H11A | 0.9800 | Au1—Br3 | 2.4308 (3) |
| C11—H11B | 0.9800 | Au2—Br4 ⁱⁱ | 2.4259 (3) |
| C11—H11C | 0.9800 | Au2—Br4 | 2.4259 (3) |
| C12—H12A | 0.9800 | Au2—Br5 | 2.4265 (3) |
| C12—H12B | 0.9800 | Au2—Br5 ⁱⁱ | 2.4265 (3) |
| C12—H12C | 0.9800 | | |
| | | | |
| C2—P1—C3 | 109.37 (13) | C2—C21—H21A | 109.5 |
| C2—P1—C1 | 116.89 (13) | C2—C21—H21B | 109.5 |
| C3—P1—C1 | 108.56 (13) | H21A—C21—H21B | 109.5 |
| C2—P1—S1 | 109.41 (10) | C2—C21—H21C | 109.5 |
| C3—P1—S1 | 112.29 (10) | H21A—C21—H21C | 109.5 |
| C1—P1—S1 | 100.11 (10) | H21B—C21—H21C | 109.5 |
| P1—S1—Br1 | 99.46 (4) | C2—C22—H22A | 109.5 |
| S1—Br1—Br2 | 165.22 (2) | C2—C22—H22B | 109.5 |
| C11—C1—C12 | 111.3 (2) | H22A—C22—H22B | 109.5 |
| C11—C1—P1 | 113.1 (2) | C2—C22—H22C | 109.5 |
| C12—C1—P1 | 112.9 (2) | H22A—C22—H22C | 109.5 |
| C11—C1—H1 | 106.3 | H22B—C22—H22C | 109.5 |
| C12—C1—H1 | 106.3 | C3—C31—H31A | 109.5 |
| P1—C1—H1 | 106.3 | C3—C31—H31B | 109.5 |
| C21—C2—C22 | 112.2 (2) | H31A—C31—H31B | 109.5 |
| C21—C2—P1 | 114.3 (2) | C3—C31—H31C | 109.5 |

| | | | |
|---------------|-------------|--|--------------|
| C22—C2—P1 | 110.73 (19) | H31A—C31—H31C | 109.5 |
| C21—C2—H2 | 106.3 | H31B—C31—H31C | 109.5 |
| C22—C2—H2 | 106.3 | C3—C32—H32A | 109.5 |
| P1—C2—H2 | 106.3 | C3—C32—H32B | 109.5 |
| C31—C3—C32 | 111.6 (2) | H32A—C32—H32B | 109.5 |
| C31—C3—P1 | 110.68 (19) | C3—C32—H32C | 109.5 |
| C32—C3—P1 | 114.0 (2) | H32A—C32—H32C | 109.5 |
| C31—C3—H3 | 106.7 | H32B—C32—H32C | 109.5 |
| C32—C3—H3 | 106.7 | Br2—Au1—Br2 ⁱ | 180.0 |
| P1—C3—H3 | 106.7 | Br2—Au1—Br3 ⁱ | 89.288 (11) |
| C1—C11—H11A | 109.5 | Br2 ⁱ —Au1—Br3 ⁱ | 90.711 (11) |
| C1—C11—H11B | 109.5 | Br2—Au1—Br3 | 90.712 (11) |
| H11A—C11—H11B | 109.5 | Br2 ⁱ —Au1—Br3 | 89.289 (11) |
| C1—C11—H11C | 109.5 | Br3 ⁱ —Au1—Br3 | 180.0 |
| H11A—C11—H11C | 109.5 | Au1—Br2—Br1 | 86.521 (11) |
| H11B—C11—H11C | 109.5 | Br4 ⁱⁱ —Au2—Br4 | 180.0 |
| C1—C12—H12A | 109.5 | Br4 ⁱⁱ —Au2—Br5 | 89.307 (10) |
| C1—C12—H12B | 109.5 | Br4—Au2—Br5 | 90.692 (10) |
| H12A—C12—H12B | 109.5 | Br4 ⁱⁱ —Au2—Br5 ⁱⁱ | 90.693 (10) |
| C1—C12—H12C | 109.5 | Br4—Au2—Br5 ⁱⁱ | 89.308 (10) |
| H12A—C12—H12C | 109.5 | Br5—Au2—Br5 ⁱⁱ | 180.0 |
| H12B—C12—H12C | 109.5 | | |
| | | | |
| C2—P1—S1—Br1 | 51.56 (10) | C1—P1—C2—C21 | -63.8 (2) |
| C3—P1—S1—Br1 | -70.07 (10) | S1—P1—C2—C21 | 49.0 (2) |
| C1—P1—S1—Br1 | 174.93 (9) | C3—P1—C2—C22 | -59.7 (2) |
| P1—S1—Br1—Br2 | 19.42 (11) | C1—P1—C2—C22 | 64.1 (2) |
| C2—P1—C1—C11 | -79.3 (2) | S1—P1—C2—C22 | 176.91 (17) |
| C3—P1—C1—C11 | 44.9 (2) | C2—P1—C3—C31 | -167.66 (19) |
| S1—P1—C1—C11 | 162.73 (19) | C1—P1—C3—C31 | 63.7 (2) |
| C2—P1—C1—C12 | 48.3 (3) | S1—P1—C3—C31 | -46.0 (2) |
| C3—P1—C1—C12 | 172.5 (2) | C2—P1—C3—C32 | -40.9 (2) |
| S1—P1—C1—C12 | -69.7 (2) | C1—P1—C3—C32 | -169.5 (2) |
| C3—P1—C2—C21 | 172.4 (2) | S1—P1—C3—C32 | 80.8 (2) |

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+2, -y, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-------|-------------|-------------|---------------|
| C21—H21B \cdots Br1 | 0.98 | 3.28 | 3.864 (3) | 120 |
| C3—H3 \cdots Br2 ⁱⁱⁱ | 1.00 | 3.29 | 3.792 (3) | 113 |
| C31—H31C \cdots Br2 ⁱⁱⁱ | 0.98 | 3.00 | 3.787 (3) | 138 |
| C32—H32A \cdots Br2 ⁱⁱⁱ | 0.98 | 2.98 | 3.763 (3) | 137 |
| C1—H1 \cdots Br4 ⁱⁱⁱ | 1.00 | 3.15 | 3.997 (3) | 144 |
| C21—H21C \cdots Br4 ^{iv} | 0.98 | 3.06 | 3.943 (3) | 151 |
| C31—H31B \cdots Br4 ⁱⁱⁱ | 0.98 | 3.04 | 3.983 (3) | 162 |

| | | | | |
|---------------------------|------|------|-----------|-----|
| C1—H1⋯Br5 ⁱⁱⁱ | 1.00 | 2.98 | 3.802 (3) | 140 |
| C22—H22C⋯Br5 ^v | 0.98 | 3.11 | 3.911 (3) | 140 |

Symmetry codes: (iii) $x, y+1, z$; (iv) $x-1, y, z$; (v) $x-1, y+1, z$.

(Bromosulfanyl)(*tert*-butyl)bis(propan-2-yl)phosphonium tetrabromidoaurate(III) (18b)

Crystal data

(C₁₀H₂₃BrPS)[AuBr₄]

$M_r = 802.83$

Triclinic, $P\bar{1}$

$a = 7.8455$ (6) Å

$b = 9.1380$ (6) Å

$c = 15.5440$ (9) Å

$\alpha = 86.600$ (5)°

$\beta = 81.097$ (6)°

$\gamma = 64.862$ (6)°

$V = 996.65$ (13) Å³

$Z = 2$

$F(000) = 736$

$D_x = 2.675$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9831 reflections

$\theta = 2.5$ – 30.8 °

$\mu = 17.57$ mm⁻¹

$T = 100$ K

Plate, orange-red

$0.25 \times 0.1 \times 0.03$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω -scan

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.097$, $T_{\max} = 0.621$

26487 measured reflections

5731 independent reflections

5030 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 30.8$ °, $\theta_{\min} = 2.5$ °

$h = -11 \rightarrow 10$

$k = -12 \rightarrow 13$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.027$

$wR(F^2) = 0.052$

$S = 1.06$

5731 reflections

173 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0167P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 2.15$ e Å⁻³

$\Delta\rho_{\min} = -2.24$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|-------------|----------------------------------|
| P1 | 0.50339 (12) | 0.10905 (11) | 0.24799 (7) | 0.01362 (19) |
| S1 | 0.39290 (12) | -0.05194 (10) | 0.30387 (7) | 0.0183 (2) |
| Br1 | 0.16092 (5) | 0.09936 (4) | 0.40317 (3) | 0.01924 (8) |
| C1 | 0.7420 (5) | -0.0279 (4) | 0.1918 (3) | 0.0167 (8) |
| C2 | 0.5065 (5) | 0.2376 (5) | 0.3328 (3) | 0.0198 (8) |
| H2 | 0.370055 | 0.306364 | 0.355119 | 0.024* |
| C3 | 0.3524 (5) | 0.2400 (4) | 0.1706 (3) | 0.0185 (8) |
| H3 | 0.425737 | 0.295673 | 0.135909 | 0.022* |
| C11 | 0.8009 (5) | 0.0614 (5) | 0.1138 (3) | 0.0250 (9) |

| | | | | |
|------|--------------|-------------|-------------|--------------|
| H11A | 0.797239 | 0.162321 | 0.134229 | 0.038* |
| H11B | 0.712607 | 0.085987 | 0.071261 | 0.038* |
| H11C | 0.930165 | -0.007171 | 0.086514 | 0.038* |
| C12 | 0.8867 (5) | -0.0766 (5) | 0.2555 (3) | 0.0229 (9) |
| H12A | 1.010620 | -0.154105 | 0.227133 | 0.034* |
| H12B | 0.844151 | -0.126343 | 0.306871 | 0.034* |
| H12C | 0.898209 | 0.019605 | 0.273240 | 0.034* |
| C13 | 0.7392 (5) | -0.1820 (4) | 0.1585 (3) | 0.0216 (8) |
| H13A | 0.638084 | -0.152137 | 0.122107 | 0.032* |
| H13B | 0.715560 | -0.245457 | 0.208142 | 0.032* |
| H13C | 0.862209 | -0.246547 | 0.123983 | 0.032* |
| C21 | 0.5961 (6) | 0.1502 (5) | 0.4119 (3) | 0.0299 (10) |
| H21A | 0.734900 | 0.106729 | 0.398138 | 0.045* |
| H21B | 0.558656 | 0.061372 | 0.427490 | 0.045* |
| H21C | 0.552320 | 0.226140 | 0.460940 | 0.045* |
| C22 | 0.5904 (6) | 0.3550 (5) | 0.2935 (3) | 0.0312 (11) |
| H22A | 0.576068 | 0.432071 | 0.338336 | 0.047* |
| H22B | 0.523056 | 0.413800 | 0.245404 | 0.047* |
| H22C | 0.725708 | 0.294173 | 0.271683 | 0.047* |
| C31 | 0.3097 (6) | 0.1447 (5) | 0.1057 (3) | 0.0265 (9) |
| H31A | 0.227586 | 0.096195 | 0.136335 | 0.040* |
| H31B | 0.429052 | 0.059163 | 0.078583 | 0.040* |
| H31C | 0.245011 | 0.217668 | 0.060592 | 0.040* |
| C32 | 0.1676 (5) | 0.3728 (4) | 0.2152 (3) | 0.0231 (9) |
| H32A | 0.096116 | 0.442908 | 0.170905 | 0.035* |
| H32B | 0.197860 | 0.437057 | 0.253499 | 0.035* |
| H32C | 0.090581 | 0.323216 | 0.249639 | 0.035* |
| Au1 | 0.000000 | 0.500000 | 0.500000 | 0.01491 (5) |
| Br2 | -0.15629 (5) | 0.32924 (5) | 0.55955 (3) | 0.02348 (9) |
| Br3 | 0.22769 (6) | 0.38839 (5) | 0.60137 (3) | 0.02456 (9) |
| Au2 | 0.500000 | 0.500000 | 0.000000 | 0.01379 (5) |
| Br4 | 0.35239 (5) | 0.70272 (5) | 0.11380 (3) | 0.02518 (10) |
| Br5 | 0.81073 (5) | 0.45559 (4) | 0.03161 (3) | 0.02119 (9) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|------------|---------------|--------------|--------------|
| P1 | 0.0130 (4) | 0.0145 (4) | 0.0138 (5) | -0.0062 (4) | -0.0016 (4) | -0.0009 (4) |
| S1 | 0.0158 (4) | 0.0154 (4) | 0.0232 (6) | -0.0069 (4) | -0.0008 (4) | 0.0012 (4) |
| Br1 | 0.01646 (17) | 0.02354 (18) | 0.0193 (2) | -0.01088 (15) | 0.00037 (15) | 0.00017 (16) |
| C1 | 0.0159 (17) | 0.0153 (17) | 0.018 (2) | -0.0055 (14) | -0.0022 (15) | 0.0009 (15) |
| C2 | 0.0176 (18) | 0.0248 (19) | 0.019 (2) | -0.0114 (16) | 0.0008 (15) | -0.0054 (16) |
| C3 | 0.0190 (18) | 0.0151 (17) | 0.020 (2) | -0.0055 (15) | -0.0044 (16) | 0.0026 (15) |
| C11 | 0.0207 (19) | 0.027 (2) | 0.022 (2) | -0.0067 (17) | 0.0041 (17) | 0.0010 (18) |
| C12 | 0.0144 (18) | 0.029 (2) | 0.023 (2) | -0.0073 (16) | -0.0027 (16) | -0.0007 (18) |
| C13 | 0.0199 (19) | 0.0196 (19) | 0.022 (2) | -0.0053 (16) | -0.0014 (16) | -0.0038 (17) |
| C21 | 0.023 (2) | 0.049 (3) | 0.023 (3) | -0.019 (2) | -0.0049 (18) | -0.007 (2) |
| C22 | 0.029 (2) | 0.028 (2) | 0.045 (3) | -0.0203 (19) | -0.001 (2) | -0.012 (2) |

| | | | | | | |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| C31 | 0.028 (2) | 0.024 (2) | 0.026 (3) | -0.0051 (17) | -0.0150 (18) | -0.0004 (18) |
| C32 | 0.0213 (19) | 0.0183 (18) | 0.024 (2) | -0.0020 (16) | -0.0059 (17) | 0.0003 (17) |
| Au1 | 0.01684 (10) | 0.01425 (9) | 0.01507 (11) | -0.00780 (8) | -0.00204 (8) | -0.00133 (8) |
| Br2 | 0.0262 (2) | 0.02399 (19) | 0.0257 (2) | -0.01649 (17) | -0.00262 (17) | 0.00259 (17) |
| Br3 | 0.0251 (2) | 0.0284 (2) | 0.0240 (2) | -0.01321 (17) | -0.00993 (17) | 0.00443 (17) |
| Au2 | 0.00922 (9) | 0.01233 (9) | 0.01999 (12) | -0.00528 (7) | -0.00075 (7) | 0.00101 (8) |
| Br4 | 0.01812 (18) | 0.0244 (2) | 0.0315 (3) | -0.00830 (16) | 0.00282 (16) | -0.01051 (18) |
| Br5 | 0.01142 (16) | 0.02067 (18) | 0.0331 (3) | -0.00777 (14) | -0.00541 (15) | 0.00139 (17) |

Geometric parameters (Å, °)

| | | | |
|------------|-------------|-----------------------|------------|
| P1—C2 | 1.827 (4) | C13—H13B | 0.9800 |
| P1—C3 | 1.830 (4) | C13—H13C | 0.9800 |
| P1—C1 | 1.862 (4) | C21—H21A | 0.9800 |
| P1—S1 | 2.0902 (12) | C21—H21B | 0.9800 |
| S1—Br1 | 2.2028 (10) | C21—H21C | 0.9800 |
| Br1—Br2 | 3.2874 (6) | C22—H22A | 0.9800 |
| C1—C12 | 1.527 (5) | C22—H22B | 0.9800 |
| C1—C13 | 1.539 (5) | C22—H22C | 0.9800 |
| C1—C11 | 1.542 (5) | C31—H31A | 0.9800 |
| C2—C21 | 1.522 (6) | C31—H31B | 0.9800 |
| C2—C22 | 1.535 (5) | C31—H31C | 0.9800 |
| C2—H2 | 1.0000 | C32—H32A | 0.9800 |
| C3—C31 | 1.532 (5) | C32—H32B | 0.9800 |
| C3—C32 | 1.533 (5) | C32—H32C | 0.9800 |
| C3—H3 | 1.0000 | Au1—Br3 | 2.4180 (4) |
| C11—H11A | 0.9800 | Au1—Br3 ⁱ | 2.4181 (4) |
| C11—H11B | 0.9800 | Au1—Br2 | 2.4287 (4) |
| C11—H11C | 0.9800 | Au1—Br2 ⁱ | 2.4287 (4) |
| C12—H12A | 0.9800 | Au2—Br4 | 2.4154 (4) |
| C12—H12B | 0.9800 | Au2—Br4 ⁱⁱ | 2.4154 (4) |
| C12—H12C | 0.9800 | Au2—Br5 ⁱⁱ | 2.4199 (4) |
| C13—H13A | 0.9800 | Au2—Br5 | 2.4199 (4) |
| C2—P1—C3 | 107.86 (17) | C1—C13—H13C | 109.5 |
| C2—P1—C1 | 114.96 (17) | H13A—C13—H13C | 109.5 |
| C3—P1—C1 | 111.42 (17) | H13B—C13—H13C | 109.5 |
| C2—P1—S1 | 109.57 (13) | C2—C21—H21A | 109.5 |
| C3—P1—S1 | 110.03 (13) | C2—C21—H21B | 109.5 |
| C1—P1—S1 | 102.89 (12) | H21A—C21—H21B | 109.5 |
| P1—S1—Br1 | 102.51 (5) | C2—C21—H21C | 109.5 |
| S1—Br1—Br2 | 174.89 (3) | H21A—C21—H21C | 109.5 |
| C12—C1—C13 | 108.6 (3) | H21B—C21—H21C | 109.5 |
| C12—C1—C11 | 109.7 (3) | C2—C22—H22A | 109.5 |
| C13—C1—C11 | 109.0 (3) | C2—C22—H22B | 109.5 |
| C12—C1—P1 | 109.4 (3) | H22A—C22—H22B | 109.5 |
| C13—C1—P1 | 111.1 (2) | C2—C22—H22C | 109.5 |
| C11—C1—P1 | 109.1 (2) | H22A—C22—H22C | 109.5 |

| | | | |
|---------------|-------------|--|--------------|
| C21—C2—C22 | 112.2 (3) | H22B—C22—H22C | 109.5 |
| C21—C2—P1 | 115.9 (3) | C3—C31—H31A | 109.5 |
| C22—C2—P1 | 110.5 (3) | C3—C31—H31B | 109.5 |
| C21—C2—H2 | 105.8 | H31A—C31—H31B | 109.5 |
| C22—C2—H2 | 105.8 | C3—C31—H31C | 109.5 |
| P1—C2—H2 | 105.8 | H31A—C31—H31C | 109.5 |
| C31—C3—C32 | 110.6 (3) | H31B—C31—H31C | 109.5 |
| C31—C3—P1 | 112.5 (2) | C3—C32—H32A | 109.5 |
| C32—C3—P1 | 112.9 (3) | C3—C32—H32B | 109.5 |
| C31—C3—H3 | 106.8 | H32A—C32—H32B | 109.5 |
| C32—C3—H3 | 106.8 | C3—C32—H32C | 109.5 |
| P1—C3—H3 | 106.8 | H32A—C32—H32C | 109.5 |
| C1—C11—H11A | 109.5 | H32B—C32—H32C | 109.5 |
| C1—C11—H11B | 109.5 | Br3—Au1—Br3 ⁱ | 180.0 |
| H11A—C11—H11B | 109.5 | Br3—Au1—Br2 | 90.373 (15) |
| C1—C11—H11C | 109.5 | Br3 ⁱ —Au1—Br2 | 89.628 (15) |
| H11A—C11—H11C | 109.5 | Br3—Au1—Br2 ⁱ | 89.627 (15) |
| H11B—C11—H11C | 109.5 | Br3 ⁱ —Au1—Br2 ⁱ | 90.372 (15) |
| C1—C12—H12A | 109.5 | Br2—Au1—Br2 ⁱ | 180.000 (11) |
| C1—C12—H12B | 109.5 | Au1—Br2—Br1 | 78.058 (13) |
| H12A—C12—H12B | 109.5 | Br4—Au2—Br4 ⁱⁱ | 180.0 |
| C1—C12—H12C | 109.5 | Br4—Au2—Br5 ⁱⁱ | 90.027 (15) |
| H12A—C12—H12C | 109.5 | Br4 ⁱⁱ —Au2—Br5 ⁱⁱ | 89.972 (15) |
| H12B—C12—H12C | 109.5 | Br4—Au2—Br5 | 89.972 (15) |
| C1—C13—H13A | 109.5 | Br4 ⁱⁱ —Au2—Br5 | 90.029 (15) |
| C1—C13—H13B | 109.5 | Br5 ⁱⁱ —Au2—Br5 | 180.0 |
| H13A—C13—H13B | 109.5 | | |
| | | | |
| C2—P1—S1—Br1 | 39.31 (14) | C3—P1—C2—C21 | 169.8 (3) |
| C3—P1—S1—Br1 | -79.12 (14) | C1—P1—C2—C21 | -65.3 (3) |
| C1—P1—S1—Br1 | 162.05 (13) | S1—P1—C2—C21 | 50.0 (3) |
| C2—P1—C1—C12 | 31.6 (3) | C3—P1—C2—C22 | -61.2 (3) |
| C3—P1—C1—C12 | 154.7 (2) | C1—P1—C2—C22 | 63.8 (3) |
| S1—P1—C1—C12 | -87.5 (2) | S1—P1—C2—C22 | 179.0 (2) |
| C2—P1—C1—C13 | 151.5 (3) | C2—P1—C3—C31 | -169.6 (3) |
| C3—P1—C1—C13 | -85.4 (3) | C1—P1—C3—C31 | 63.3 (3) |
| S1—P1—C1—C13 | 32.4 (3) | S1—P1—C3—C31 | -50.1 (3) |
| C2—P1—C1—C11 | -88.4 (3) | C2—P1—C3—C32 | -43.6 (3) |
| C3—P1—C1—C11 | 34.7 (3) | C1—P1—C3—C32 | -170.6 (3) |
| S1—P1—C1—C11 | 152.6 (2) | S1—P1—C3—C32 | 75.9 (3) |

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|----------------------|-------|-------------|-------------|---------------|
| C13—H13B \cdots S1 | 0.98 | 2.66 | 3.095 (4) | 107 |
| C2—H2 \cdots Br1 | 1.00 | 2.99 | 3.459 (4) | 110 |

| | | | | |
|-------------------------------|------|------|-----------|-----|
| C3—H3···Au2 | 1.00 | 2.89 | 3.828 (4) | 156 |
| C32—H32C···Br1 | 0.98 | 3.01 | 3.739 (4) | 132 |
| C21—H21C···Br3 | 0.98 | 2.98 | 3.814 (4) | 143 |
| C11—H11A···Br5 | 0.98 | 3.07 | 3.778 (4) | 130 |
| C2—H2···Br2 ⁱ | 1.00 | 3.28 | 4.017 (4) | 132 |
| C22—H22A···Br3 ⁱⁱⁱ | 0.98 | 2.95 | 3.771 (4) | 142 |
| C12—H12B···Br3 ^{iv} | 0.98 | 2.93 | 3.832 (4) | 154 |
| C13—H13B···Br3 ^{iv} | 0.98 | 3.18 | 4.075 (4) | 152 |
| C12—H12A···Br4 ^v | 0.98 | 2.80 | 3.747 (4) | 163 |
| C13—H13A···Br4 ^{vi} | 0.98 | 3.07 | 3.776 (4) | 130 |

Symmetry codes: (i) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y, -z+1$; (v) $x+1, y-1, z$; (vi) $x, y-1, z$.

(Bromosulfanyl)bis(*tert*-butyl)(propan-2-yl)phosphonium tetrabromidoaurate(III) (19b)

Crystal data

(C₁₁H₂₅BrPS)[AuBr₄]

$M_r = 816.86$

Monoclinic, $P2_1/n$

$a = 12.4712$ (4) Å

$b = 10.3712$ (3) Å

$c = 16.2524$ (5) Å

$\beta = 92.724$ (3)°

$V = 2099.73$ (11) Å³

$Z = 4$

$F(000) = 1504$

$D_x = 2.584$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 15934 reflections

$\theta = 2.3$ – 30.9 °

$\mu = 16.68$ mm⁻¹

$T = 100$ K

Plate, orange-red

$0.35 \times 0.25 \times 0.10$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.068$, $T_{\max} = 0.286$

70058 measured reflections

6335 independent reflections

5041 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.065$

$\theta_{\max} = 30.9$ °, $\theta_{\min} = 2.3$ °

$h = -17 \rightarrow 17$

$k = -14 \rightarrow 14$

$l = -23 \rightarrow 23$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.033$

$wR(F^2) = 0.061$

$S = 1.09$

6335 reflections

183 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0128P)^2 + 8.4095P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 2.42$ e Å⁻³

$\Delta\rho_{\min} = -1.44$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|----|-------------|--------------|-------------|----------------------------------|
| P1 | 0.47617 (8) | 0.09340 (11) | 0.25608 (7) | 0.0122 (2) |
| S1 | 0.44209 (9) | 0.26253 (11) | 0.18886 (7) | 0.0194 (2) |

| | | | | |
|------|-------------|-------------|--------------|--------------|
| Br1 | 0.50831 (4) | 0.41904 (4) | 0.26809 (3) | 0.02289 (10) |
| C2 | 0.3752 (4) | 0.0775 (5) | 0.3358 (3) | 0.0227 (10) |
| C1 | 0.4639 (4) | -0.0278 (4) | 0.1711 (3) | 0.0190 (9) |
| C3 | 0.6110 (3) | 0.1033 (4) | 0.3061 (3) | 0.0177 (9) |
| H3 | 0.603870 | 0.156065 | 0.356994 | 0.021* |
| C21 | 0.4031 (5) | -0.0301 (6) | 0.3978 (3) | 0.0363 (14) |
| H21A | 0.346244 | -0.036995 | 0.437141 | 0.054* |
| H21B | 0.471370 | -0.010183 | 0.427380 | 0.054* |
| H21C | 0.409507 | -0.112108 | 0.368404 | 0.054* |
| C22 | 0.2627 (4) | 0.0542 (5) | 0.2959 (3) | 0.0308 (12) |
| H22A | 0.260412 | -0.030698 | 0.269459 | 0.046* |
| H22B | 0.246401 | 0.121028 | 0.254587 | 0.046* |
| H22C | 0.209473 | 0.057430 | 0.338374 | 0.046* |
| C23 | 0.3721 (4) | 0.2056 (5) | 0.3835 (3) | 0.0333 (13) |
| H23A | 0.327063 | 0.195525 | 0.430947 | 0.050* |
| H23B | 0.342049 | 0.273327 | 0.347238 | 0.050* |
| H23C | 0.445015 | 0.229503 | 0.402811 | 0.050* |
| C11 | 0.5660 (4) | -0.0216 (5) | 0.1213 (3) | 0.0284 (11) |
| H11A | 0.558092 | -0.079602 | 0.073841 | 0.043* |
| H11B | 0.628200 | -0.047990 | 0.156406 | 0.043* |
| H11C | 0.576469 | 0.066881 | 0.102076 | 0.043* |
| C12 | 0.4520 (4) | -0.1653 (4) | 0.2062 (3) | 0.0251 (11) |
| H12A | 0.385209 | -0.170931 | 0.235450 | 0.038* |
| H12B | 0.513072 | -0.184233 | 0.244456 | 0.038* |
| H12C | 0.450086 | -0.227835 | 0.160975 | 0.038* |
| C13 | 0.3676 (4) | 0.0033 (5) | 0.1120 (3) | 0.0285 (12) |
| H13A | 0.379906 | 0.085701 | 0.084545 | 0.043* |
| H13B | 0.302400 | 0.009192 | 0.143225 | 0.043* |
| H13C | 0.358977 | -0.065155 | 0.070692 | 0.043* |
| C31 | 0.6958 (3) | 0.1712 (5) | 0.2556 (3) | 0.0249 (11) |
| H31A | 0.757212 | 0.195668 | 0.292127 | 0.037* |
| H31B | 0.664318 | 0.248634 | 0.229716 | 0.037* |
| H31C | 0.719712 | 0.112565 | 0.212930 | 0.037* |
| C32 | 0.6555 (4) | -0.0289 (5) | 0.3348 (4) | 0.0298 (12) |
| H32A | 0.669637 | -0.081990 | 0.286622 | 0.045* |
| H32B | 0.602792 | -0.072220 | 0.368041 | 0.045* |
| H32C | 0.722404 | -0.016356 | 0.367956 | 0.045* |
| Au1 | 0.500000 | 0.500000 | 0.500000 | 0.01294 (5) |
| Br2 | 0.59615 (4) | 0.63077 (5) | 0.40419 (3) | 0.02733 (11) |
| Br3 | 0.64240 (4) | 0.34181 (5) | 0.49969 (3) | 0.02734 (12) |
| Au2 | 0.500000 | 0.500000 | 0.000000 | 0.01160 (5) |
| Br4 | 0.62972 (3) | 0.32712 (4) | 0.01765 (3) | 0.01734 (9) |
| Br5 | 0.35771 (3) | 0.34321 (4) | -0.02188 (3) | 0.01984 (10) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|----|------------|------------|------------|------------|------------|-------------|
| P1 | 0.0133 (5) | 0.0126 (5) | 0.0109 (5) | 0.0000 (4) | 0.0005 (4) | -0.0006 (4) |

| | | | | | | |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| S1 | 0.0249 (6) | 0.0143 (5) | 0.0185 (6) | 0.0028 (4) | -0.0035 (4) | 0.0004 (4) |
| Br1 | 0.0262 (2) | 0.0137 (2) | 0.0285 (3) | 0.00032 (18) | -0.00035 (19) | -0.00333 (19) |
| C2 | 0.023 (2) | 0.028 (3) | 0.018 (2) | -0.009 (2) | 0.0084 (18) | -0.006 (2) |
| C1 | 0.034 (3) | 0.011 (2) | 0.012 (2) | 0.0021 (18) | -0.0016 (18) | -0.0018 (17) |
| C3 | 0.017 (2) | 0.018 (2) | 0.018 (2) | -0.0013 (17) | -0.0034 (17) | 0.0002 (18) |
| C21 | 0.041 (3) | 0.047 (4) | 0.022 (3) | -0.012 (3) | 0.009 (2) | 0.006 (3) |
| C22 | 0.019 (2) | 0.035 (3) | 0.039 (3) | -0.009 (2) | 0.006 (2) | -0.013 (3) |
| C23 | 0.030 (3) | 0.038 (3) | 0.034 (3) | -0.014 (2) | 0.018 (2) | -0.018 (3) |
| C11 | 0.039 (3) | 0.023 (3) | 0.024 (3) | 0.005 (2) | 0.009 (2) | -0.003 (2) |
| C12 | 0.038 (3) | 0.013 (2) | 0.024 (3) | -0.005 (2) | -0.004 (2) | -0.0010 (19) |
| C13 | 0.044 (3) | 0.022 (3) | 0.018 (2) | 0.003 (2) | -0.013 (2) | -0.003 (2) |
| C31 | 0.013 (2) | 0.027 (3) | 0.035 (3) | -0.0022 (19) | 0.0040 (19) | 0.002 (2) |
| C32 | 0.025 (3) | 0.021 (2) | 0.042 (3) | 0.001 (2) | -0.012 (2) | 0.009 (2) |
| Au1 | 0.01148 (10) | 0.01165 (11) | 0.01575 (11) | 0.00025 (8) | 0.00140 (8) | -0.00279 (9) |
| Br2 | 0.0386 (3) | 0.0202 (2) | 0.0243 (2) | -0.0096 (2) | 0.0132 (2) | -0.0023 (2) |
| Br3 | 0.0193 (2) | 0.0219 (2) | 0.0403 (3) | 0.00802 (19) | -0.0039 (2) | -0.0060 (2) |
| Au2 | 0.01165 (10) | 0.01152 (10) | 0.01178 (10) | -0.00266 (8) | 0.00220 (8) | -0.00080 (9) |
| Br4 | 0.0155 (2) | 0.0148 (2) | 0.0219 (2) | 0.00024 (16) | 0.00228 (16) | -0.00118 (18) |
| Br5 | 0.0155 (2) | 0.0149 (2) | 0.0287 (3) | -0.00572 (16) | -0.00267 (17) | 0.00139 (18) |

Geometric parameters (Å, °)

| | | | |
|----------|-------------|-----------------------|------------|
| P1—C3 | 1.836 (4) | C11—H11A | 0.9800 |
| P1—C2 | 1.856 (5) | C11—H11B | 0.9800 |
| P1—C1 | 1.868 (4) | C11—H11C | 0.9800 |
| P1—S1 | 2.0992 (16) | C12—H12A | 0.9800 |
| S1—Br1 | 2.2077 (12) | C12—H12B | 0.9800 |
| Br1—Br2 | 3.2686 (7) | C12—H12C | 0.9800 |
| C2—C21 | 1.532 (7) | C13—H13A | 0.9800 |
| C2—C22 | 1.537 (6) | C13—H13B | 0.9800 |
| C2—C23 | 1.540 (7) | C13—H13C | 0.9800 |
| C1—C13 | 1.537 (6) | C31—H31A | 0.9800 |
| C1—C11 | 1.541 (7) | C31—H31B | 0.9800 |
| C1—C12 | 1.545 (6) | C31—H31C | 0.9800 |
| C3—C31 | 1.538 (6) | C32—H32A | 0.9800 |
| C3—C32 | 1.543 (6) | C32—H32B | 0.9800 |
| C3—H3 | 1.0000 | C32—H32C | 0.9800 |
| C21—H21A | 0.9800 | Au1—Br3 ⁱ | 2.4179 (5) |
| C21—H21B | 0.9800 | Au1—Br3 | 2.4179 (5) |
| C21—H21C | 0.9800 | Au1—Br2 ⁱ | 2.4247 (5) |
| C22—H22A | 0.9800 | Au1—Br2 | 2.4247 (5) |
| C22—H22B | 0.9800 | Au2—Br5 ⁱⁱ | 2.4206 (4) |
| C22—H22C | 0.9800 | Au2—Br5 | 2.4207 (4) |
| C23—H23A | 0.9800 | Au2—Br4 | 2.4228 (4) |
| C23—H23B | 0.9800 | Au2—Br4 ⁱⁱ | 2.4229 (4) |
| C23—H23C | 0.9800 | | |
| C3—P1—C2 | 109.5 (2) | C1—C11—H11A | 109.5 |

| | | | |
|---------------|--------------|--|-------------|
| C3—P1—C1 | 113.9 (2) | C1—C11—H11B | 109.5 |
| C2—P1—C1 | 115.0 (2) | H11A—C11—H11B | 109.5 |
| C3—P1—S1 | 110.01 (15) | C1—C11—H11C | 109.5 |
| C2—P1—S1 | 108.07 (17) | H11A—C11—H11C | 109.5 |
| C1—P1—S1 | 99.81 (14) | H11B—C11—H11C | 109.5 |
| P1—S1—Br1 | 104.48 (6) | C1—C12—H12A | 109.5 |
| S1—Br1—Br2 | 173.07 (4) | C1—C12—H12B | 109.5 |
| C21—C2—C22 | 109.7 (4) | H12A—C12—H12B | 109.5 |
| C21—C2—C23 | 108.0 (4) | C1—C12—H12C | 109.5 |
| C22—C2—C23 | 107.6 (4) | H12A—C12—H12C | 109.5 |
| C21—C2—P1 | 112.5 (4) | H12B—C12—H12C | 109.5 |
| C22—C2—P1 | 110.8 (3) | C1—C13—H13A | 109.5 |
| C23—C2—P1 | 108.0 (3) | C1—C13—H13B | 109.5 |
| C13—C1—C11 | 107.7 (4) | H13A—C13—H13B | 109.5 |
| C13—C1—C12 | 109.8 (4) | C1—C13—H13C | 109.5 |
| C11—C1—C12 | 109.2 (4) | H13A—C13—H13C | 109.5 |
| C13—C1—P1 | 110.8 (3) | H13B—C13—H13C | 109.5 |
| C11—C1—P1 | 108.6 (3) | C3—C31—H31A | 109.5 |
| C12—C1—P1 | 110.7 (3) | C3—C31—H31B | 109.5 |
| C31—C3—C32 | 108.8 (4) | H31A—C31—H31B | 109.5 |
| C31—C3—P1 | 115.3 (3) | C3—C31—H31C | 109.5 |
| C32—C3—P1 | 113.2 (3) | H31A—C31—H31C | 109.5 |
| C31—C3—H3 | 106.3 | H31B—C31—H31C | 109.5 |
| C32—C3—H3 | 106.3 | C3—C32—H32A | 109.5 |
| P1—C3—H3 | 106.3 | C3—C32—H32B | 109.5 |
| C2—C21—H21A | 109.5 | H32A—C32—H32B | 109.5 |
| C2—C21—H21B | 109.5 | C3—C32—H32C | 109.5 |
| H21A—C21—H21B | 109.5 | H32A—C32—H32C | 109.5 |
| C2—C21—H21C | 109.5 | H32B—C32—H32C | 109.5 |
| H21A—C21—H21C | 109.5 | Br3 ⁱ —Au1—Br3 | 180.0 |
| H21B—C21—H21C | 109.5 | Br3 ⁱ —Au1—Br2 ⁱ | 89.572 (19) |
| C2—C22—H22A | 109.5 | Br3—Au1—Br2 ⁱ | 90.429 (19) |
| C2—C22—H22B | 109.5 | Br3 ⁱ —Au1—Br2 | 90.428 (19) |
| H22A—C22—H22B | 109.5 | Br3—Au1—Br2 | 89.571 (19) |
| C2—C22—H22C | 109.5 | Br2 ⁱ —Au1—Br2 | 180.0 |
| H22A—C22—H22C | 109.5 | Au1—Br2—Br1 | 84.190 (16) |
| H22B—C22—H22C | 109.5 | Br5 ⁱⁱ —Au2—Br5 | 180.0 |
| C2—C23—H23A | 109.5 | Br5 ⁱⁱ —Au2—Br4 | 89.945 (15) |
| C2—C23—H23B | 109.5 | Br5—Au2—Br4 | 90.055 (15) |
| H23A—C23—H23B | 109.5 | Br5 ⁱⁱ —Au2—Br4 ⁱⁱ | 90.055 (15) |
| C2—C23—H23C | 109.5 | Br5—Au2—Br4 ⁱⁱ | 89.944 (15) |
| H23A—C23—H23C | 109.5 | Br4—Au2—Br4 ⁱⁱ | 180.0 |
| H23B—C23—H23C | 109.5 | | |
| C3—P1—S1—Br1 | -40.27 (17) | S1—P1—C1—C13 | -41.1 (4) |
| C2—P1—S1—Br1 | 79.21 (16) | C3—P1—C1—C11 | -40.2 (4) |
| C1—P1—S1—Br1 | -160.33 (16) | C2—P1—C1—C11 | -167.7 (3) |
| C3—P1—C2—C21 | -50.6 (4) | S1—P1—C1—C11 | 76.9 (3) |

| | | | |
|--------------|------------|--------------|------------|
| C1—P1—C2—C21 | 79.1 (4) | C3—P1—C1—C12 | 79.7 (4) |
| S1—P1—C2—C21 | -170.5 (3) | C2—P1—C1—C12 | -47.8 (4) |
| C3—P1—C2—C22 | -173.8 (3) | S1—P1—C1—C12 | -163.1 (3) |
| C1—P1—C2—C22 | -44.1 (4) | C2—P1—C3—C31 | -155.5 (3) |
| S1—P1—C2—C22 | 66.3 (4) | C1—P1—C3—C31 | 74.2 (4) |
| C3—P1—C2—C23 | 68.5 (4) | S1—P1—C3—C31 | -36.9 (4) |
| C1—P1—C2—C23 | -161.8 (3) | C2—P1—C3—C32 | 78.3 (4) |
| S1—P1—C2—C23 | -51.4 (4) | C1—P1—C3—C32 | -51.9 (4) |
| C3—P1—C1—C13 | -158.3 (3) | S1—P1—C3—C32 | -163.0 (3) |
| C2—P1—C1—C13 | 74.2 (4) | | |

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

Hydrogen-bond geometry (\AA , $^\circ$)

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|--|-------------|---------------------|----------------------------|-------------------------------|
| C13—H13 <i>A</i> \cdots S1 | 0.98 | 2.59 | 3.089 (5) | 112 |
| C31—H31 <i>B</i> \cdots Br1 | 0.98 | 2.72 | 3.487 (5) | 135 |
| C23—H23 <i>B</i> \cdots Br1 | 0.98 | 2.91 | 3.407 (6) | 112 |
| C3—H3 \cdots Br3 | 1.00 | 3.04 | 4.007 (5) | 164 |
| C23—H23 <i>C</i> \cdots Br3 | 0.98 | 3.09 | 4.040 (5) | 165 |
| C11—H11 <i>C</i> \cdots Br4 | 0.98 | 3.11 | 4.084 (5) | 171 |
| C31—H31 <i>C</i> \cdots Br2 ⁱⁱⁱ | 0.98 | 3.06 | 3.781 (5) | 132 |
| C23—H23 <i>A</i> \cdots Br4 ^{iv} | 0.98 | 2.90 | 3.824 (5) | 157 |
| C13—H13 <i>C</i> \cdots Br4 ^v | 0.98 | 3.08 | 4.024 (5) | 162 |
| C32—H32 <i>C</i> \cdots Br4 ⁱⁱⁱ | 0.98 | 3.03 | 3.814 (5) | 138 |
| C11—H11 <i>A</i> \cdots Br5 ^v | 0.98 | 3.06 | 3.846 (5) | 138 |
| C32—H32 <i>C</i> \cdots Br5 ^{vi} | 0.98 | 3.00 | 3.864 (5) | 148 |

Symmetry codes: (iii) $-x+3/2, y-1/2, -z+1/2$; (iv) $x-1/2, -y+1/2, z+1/2$; (v) $-x+1, -y, -z$; (vi) $x+1/2, -y+1/2, z+1/2$.

(Bromosulfanyl)tris(*tert*-butyl)phosphonium tetrabromidoaurate(III) (20b)

Crystal data

(C₁₂H₂₇BrPS)[AuBr₄]

$M_r = 830.88$

Triclinic, $P\bar{1}$

$a = 10.2218$ (5) \AA

$b = 10.8085$ (6) \AA

$c = 11.1163$ (5) \AA

$\alpha = 70.909$ (4) $^\circ$

$\beta = 71.516$ (5) $^\circ$

$\gamma = 75.645$ (4) $^\circ$

$V = 1086.40$ (10) \AA^3

$Z = 2$

$F(000) = 768$

$D_x = 2.540$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ \AA

Cell parameters from 12650 reflections

$\theta = 2.5\text{--}29.6^\circ$

$\mu = 16.13$ mm⁻¹

$T = 100$ K

Plate, red

$0.1 \times 0.05 \times 0.002$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω scan

Absorption correction: multi-scan
(CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.284$, $T_{\max} = 1.000$

73343 measured reflections

6283 independent reflections

5151 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.078$
 $\theta_{\text{max}} = 30.0^\circ$, $\theta_{\text{min}} = 2.4^\circ$
 $h = -14 \rightarrow 14$

$k = -15 \rightarrow 15$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.066$
 $S = 1.05$
 6283 reflections
 193 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.022P)^2 + 3.2663P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.56 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.67 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| Br1 | 0.59391 (5) | 0.25831 (5) | 0.21953 (5) | 0.02502 (11) |
| S1 | 0.37937 (12) | 0.36541 (12) | 0.26091 (12) | 0.0198 (2) |
| P1 | 0.25702 (12) | 0.25589 (11) | 0.22831 (11) | 0.0129 (2) |
| C1 | 0.0812 (5) | 0.3286 (5) | 0.3233 (5) | 0.0188 (10) |
| C2 | 0.3046 (5) | 0.0719 (4) | 0.3011 (5) | 0.0179 (9) |
| C3 | 0.2756 (5) | 0.3022 (5) | 0.0457 (5) | 0.0192 (10) |
| C11 | -0.0398 (5) | 0.3020 (5) | 0.2854 (5) | 0.0219 (10) |
| H11A | -0.129199 | 0.337699 | 0.338052 | 0.033* |
| H11B | -0.034135 | 0.206245 | 0.302280 | 0.033* |
| H11C | -0.032962 | 0.345254 | 0.191639 | 0.033* |
| C12 | 0.0707 (6) | 0.4787 (5) | 0.2971 (6) | 0.0309 (13) |
| H12A | -0.023234 | 0.515415 | 0.341352 | 0.046* |
| H12B | 0.088708 | 0.520700 | 0.202069 | 0.046* |
| H12C | 0.139943 | 0.496006 | 0.331148 | 0.046* |
| C13 | 0.0652 (5) | 0.2691 (6) | 0.4720 (5) | 0.0259 (11) |
| H13A | 0.142733 | 0.285298 | 0.495774 | 0.039* |
| H13B | 0.066141 | 0.173361 | 0.494761 | 0.039* |
| H13C | -0.023518 | 0.310690 | 0.520411 | 0.039* |
| C21 | 0.1768 (5) | 0.0050 (5) | 0.3309 (5) | 0.0226 (10) |
| H21A | 0.201012 | -0.090907 | 0.367185 | 0.034* |
| H21B | 0.149103 | 0.022308 | 0.249514 | 0.034* |
| H21C | 0.099153 | 0.040962 | 0.395162 | 0.034* |
| C22 | 0.3481 (5) | 0.0441 (5) | 0.4286 (5) | 0.0264 (11) |
| H22A | 0.271080 | 0.081219 | 0.492458 | 0.040* |
| H22B | 0.430415 | 0.085125 | 0.409510 | 0.040* |
| H22C | 0.370600 | -0.051945 | 0.465301 | 0.040* |
| C23 | 0.4267 (5) | 0.0064 (5) | 0.2063 (5) | 0.0224 (10) |
| H23A | 0.508419 | 0.049850 | 0.182407 | 0.034* |
| H23B | 0.399175 | 0.015713 | 0.126606 | 0.034* |
| H23C | 0.450133 | -0.087930 | 0.249799 | 0.034* |
| C31 | 0.2029 (6) | 0.2133 (6) | 0.0115 (5) | 0.0279 (12) |

| | | | | |
|------|-------------|--------------|-------------|--------------|
| H31A | 0.104491 | 0.219770 | 0.061381 | 0.042* |
| H31B | 0.249217 | 0.121068 | 0.034629 | 0.042* |
| H31C | 0.208807 | 0.242862 | -0.083038 | 0.042* |
| C32 | 0.2122 (6) | 0.4465 (5) | -0.0025 (5) | 0.0303 (12) |
| H32A | 0.251143 | 0.502660 | 0.026493 | 0.045* |
| H32B | 0.110589 | 0.457207 | 0.033881 | 0.045* |
| H32C | 0.233973 | 0.472570 | -0.098945 | 0.045* |
| C33 | 0.4314 (5) | 0.2889 (6) | -0.0280 (5) | 0.0262 (11) |
| H33A | 0.440886 | 0.306298 | -0.122386 | 0.039* |
| H33B | 0.478203 | 0.198913 | 0.005595 | 0.039* |
| H33C | 0.474297 | 0.353147 | -0.014286 | 0.039* |
| Au1 | 1.000000 | 0.000000 | 0.000000 | 0.01454 (6) |
| Br2 | 0.84988 (5) | -0.00379 (5) | 0.21819 (5) | 0.02579 (12) |
| Br3 | 1.16132 (5) | -0.18362 (5) | 0.09502 (5) | 0.02498 (11) |
| Au2 | 0.500000 | 0.500000 | 0.500000 | 0.01325 (6) |
| Br4 | 0.33104 (5) | 0.64083 (5) | 0.38216 (5) | 0.01821 (10) |
| Br5 | 0.66249 (5) | 0.65479 (5) | 0.37637 (5) | 0.02208 (11) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| Br1 | 0.0131 (2) | 0.0355 (3) | 0.0279 (3) | -0.0051 (2) | -0.00249 (19) | -0.0123 (2) |
| S1 | 0.0158 (5) | 0.0232 (6) | 0.0250 (6) | -0.0044 (4) | -0.0029 (5) | -0.0136 (5) |
| P1 | 0.0119 (5) | 0.0133 (5) | 0.0146 (6) | -0.0015 (4) | -0.0029 (4) | -0.0063 (5) |
| C1 | 0.016 (2) | 0.018 (2) | 0.023 (2) | -0.0006 (18) | -0.0034 (19) | -0.0105 (19) |
| C2 | 0.016 (2) | 0.015 (2) | 0.020 (2) | -0.0020 (17) | -0.0024 (18) | -0.0027 (18) |
| C3 | 0.021 (2) | 0.022 (2) | 0.015 (2) | -0.0061 (19) | -0.0047 (18) | -0.0031 (19) |
| C11 | 0.015 (2) | 0.023 (2) | 0.027 (3) | 0.0004 (19) | -0.0067 (19) | -0.007 (2) |
| C12 | 0.023 (3) | 0.023 (3) | 0.050 (4) | 0.002 (2) | -0.004 (2) | -0.023 (3) |
| C13 | 0.018 (2) | 0.043 (3) | 0.021 (2) | -0.003 (2) | -0.0013 (19) | -0.019 (2) |
| C21 | 0.019 (2) | 0.017 (2) | 0.029 (3) | -0.0045 (19) | -0.001 (2) | -0.007 (2) |
| C22 | 0.023 (3) | 0.031 (3) | 0.020 (2) | -0.003 (2) | -0.010 (2) | 0.003 (2) |
| C23 | 0.018 (2) | 0.013 (2) | 0.031 (3) | 0.0003 (18) | -0.002 (2) | -0.006 (2) |
| C31 | 0.029 (3) | 0.042 (3) | 0.022 (3) | -0.017 (2) | -0.006 (2) | -0.013 (2) |
| C32 | 0.031 (3) | 0.028 (3) | 0.026 (3) | -0.009 (2) | -0.013 (2) | 0.009 (2) |
| C33 | 0.028 (3) | 0.040 (3) | 0.014 (2) | -0.012 (2) | -0.001 (2) | -0.010 (2) |
| Au1 | 0.01328 (12) | 0.01668 (12) | 0.01528 (12) | -0.00202 (9) | -0.00327 (9) | -0.00712 (9) |
| Br2 | 0.0187 (2) | 0.0374 (3) | 0.0170 (2) | 0.0015 (2) | -0.00159 (18) | -0.0091 (2) |
| Br3 | 0.0238 (3) | 0.0246 (2) | 0.0239 (2) | 0.00549 (19) | -0.0082 (2) | -0.0081 (2) |
| Au2 | 0.01221 (11) | 0.01496 (12) | 0.01321 (11) | -0.00114 (9) | -0.00191 (9) | -0.00671 (9) |
| Br4 | 0.0150 (2) | 0.0181 (2) | 0.0208 (2) | 0.00057 (17) | -0.00566 (17) | -0.00558 (18) |
| Br5 | 0.0208 (2) | 0.0268 (2) | 0.0195 (2) | -0.01088 (19) | -0.00610 (18) | -0.00133 (19) |

Geometric parameters (Å, °)

| | | | |
|---------|-------------|----------|--------|
| S1—P1 | 2.0973 (16) | C21—H21B | 0.9800 |
| Br1—S1 | 2.1934 (13) | C21—H21C | 0.9800 |
| Br1—Br2 | 3.3465 (7) | C22—H22A | 0.9800 |

| | | | |
|------------|-------------|-----------------------|------------|
| P1—C3 | 1.883 (5) | C22—H22B | 0.9800 |
| P1—C2 | 1.888 (5) | C22—H22C | 0.9800 |
| P1—C1 | 1.898 (5) | C23—H23A | 0.9800 |
| C1—C12 | 1.534 (7) | C23—H23B | 0.9800 |
| C1—C13 | 1.535 (7) | C23—H23C | 0.9800 |
| C1—C11 | 1.542 (7) | C31—H31A | 0.9800 |
| C2—C22 | 1.534 (7) | C31—H31B | 0.9800 |
| C2—C21 | 1.541 (6) | C31—H31C | 0.9800 |
| C2—C23 | 1.544 (6) | C32—H32A | 0.9800 |
| C3—C32 | 1.520 (7) | C32—H32B | 0.9800 |
| C3—C33 | 1.537 (7) | C32—H32C | 0.9800 |
| C3—C31 | 1.546 (7) | C33—H33A | 0.9800 |
| C11—H11A | 0.9800 | C33—H33B | 0.9800 |
| C11—H11B | 0.9800 | C33—H33C | 0.9800 |
| C11—H11C | 0.9800 | Au1—Br2 | 2.4178 (5) |
| C12—H12A | 0.9800 | Au1—Br2 ⁱ | 2.4178 (5) |
| C12—H12B | 0.9800 | Au1—Br3 | 2.4257 (5) |
| C12—H12C | 0.9800 | Au1—Br3 ⁱ | 2.4257 (5) |
| C13—H13A | 0.9800 | Au2—Br4 ⁱⁱ | 2.4171 (5) |
| C13—H13B | 0.9800 | Au2—Br4 | 2.4171 (5) |
| C13—H13C | 0.9800 | Au2—Br5 | 2.4234 (5) |
| C21—H21A | 0.9800 | Au2—Br5 ⁱⁱ | 2.4234 (5) |
| | | | |
| S1—Br1—Br2 | 157.33 (4) | C2—C21—H21C | 109.5 |
| P1—S1—Br1 | 105.70 (6) | H21A—C21—H21C | 109.5 |
| C3—P1—C2 | 113.0 (2) | H21B—C21—H21C | 109.5 |
| C3—P1—C1 | 113.2 (2) | C2—C22—H22A | 109.5 |
| C2—P1—C1 | 112.6 (2) | C2—C22—H22B | 109.5 |
| C3—P1—S1 | 107.74 (16) | H22A—C22—H22B | 109.5 |
| C2—P1—S1 | 111.85 (16) | C2—C22—H22C | 109.5 |
| C1—P1—S1 | 97.27 (15) | H22A—C22—H22C | 109.5 |
| C12—C1—C13 | 106.2 (4) | H22B—C22—H22C | 109.5 |
| C12—C1—C11 | 109.0 (4) | C2—C23—H23A | 109.5 |
| C13—C1—C11 | 109.6 (4) | C2—C23—H23B | 109.5 |
| C12—C1—P1 | 110.8 (3) | H23A—C23—H23B | 109.5 |
| C13—C1—P1 | 110.0 (3) | C2—C23—H23C | 109.5 |
| C11—C1—P1 | 111.2 (3) | H23A—C23—H23C | 109.5 |
| C22—C2—C21 | 109.3 (4) | H23B—C23—H23C | 109.5 |
| C22—C2—C23 | 107.4 (4) | C3—C31—H31A | 109.5 |
| C21—C2—C23 | 107.7 (4) | C3—C31—H31B | 109.5 |
| C22—C2—P1 | 111.0 (3) | H31A—C31—H31B | 109.5 |
| C21—C2—P1 | 108.8 (3) | C3—C31—H31C | 109.5 |
| C23—C2—P1 | 112.6 (3) | H31A—C31—H31C | 109.5 |
| C32—C3—C33 | 106.8 (4) | H31B—C31—H31C | 109.5 |
| C32—C3—C31 | 109.0 (4) | C3—C32—H32A | 109.5 |
| C33—C3—C31 | 109.9 (4) | C3—C32—H32B | 109.5 |
| C32—C3—P1 | 110.4 (4) | H32A—C32—H32B | 109.5 |
| C33—C3—P1 | 109.6 (3) | C3—C32—H32C | 109.5 |

| | | | |
|---------------|-------------|--|-------------|
| C31—C3—P1 | 111.0 (3) | H32A—C32—H32C | 109.5 |
| C1—C11—H11A | 109.5 | H32B—C32—H32C | 109.5 |
| C1—C11—H11B | 109.5 | C3—C33—H33A | 109.5 |
| H11A—C11—H11B | 109.5 | C3—C33—H33B | 109.5 |
| C1—C11—H11C | 109.5 | H33A—C33—H33B | 109.5 |
| H11A—C11—H11C | 109.5 | C3—C33—H33C | 109.5 |
| H11B—C11—H11C | 109.5 | H33A—C33—H33C | 109.5 |
| C1—C12—H12A | 109.5 | H33B—C33—H33C | 109.5 |
| C1—C12—H12B | 109.5 | Br2—Au1—Br2 ⁱ | 180.0 |
| H12A—C12—H12B | 109.5 | Br2—Au1—Br3 | 89.836 (18) |
| C1—C12—H12C | 109.5 | Br2 ⁱ —Au1—Br3 | 90.164 (18) |
| H12A—C12—H12C | 109.5 | Br2—Au1—Br3 ⁱ | 90.164 (18) |
| H12B—C12—H12C | 109.5 | Br2 ⁱ —Au1—Br3 ⁱ | 89.836 (18) |
| C1—C13—H13A | 109.5 | Br3—Au1—Br3 ⁱ | 180.00 (2) |
| C1—C13—H13B | 109.5 | Au1—Br2—Br1 | 112.62 (2) |
| H13A—C13—H13B | 109.5 | Br4 ⁱⁱ —Au2—Br4 | 180.0 |
| C1—C13—H13C | 109.5 | Br4 ⁱⁱ —Au2—Br5 | 90.493 (17) |
| H13A—C13—H13C | 109.5 | Br4—Au2—Br5 | 89.507 (17) |
| H13B—C13—H13C | 109.5 | Br4 ⁱⁱ —Au2—Br5 ⁱⁱ | 89.507 (17) |
| C2—C21—H21A | 109.5 | Br4—Au2—Br5 ⁱⁱ | 90.493 (17) |
| C2—C21—H21B | 109.5 | Br5—Au2—Br5 ⁱⁱ | 180.0 |
| H21A—C21—H21B | 109.5 | | |
| Br2—Br1—S1—P1 | -39.96 (14) | C3—P1—C2—C21 | -83.6 (4) |
| Br1—S1—P1—C3 | -81.14 (17) | C1—P1—C2—C21 | 46.2 (4) |
| Br1—S1—P1—C2 | 43.65 (17) | S1—P1—C2—C21 | 154.5 (3) |
| Br1—S1—P1—C1 | 161.63 (16) | C3—P1—C2—C23 | 35.6 (4) |
| C3—P1—C1—C12 | -71.8 (4) | C1—P1—C2—C23 | 165.5 (3) |
| C2—P1—C1—C12 | 158.5 (4) | S1—P1—C2—C23 | -86.2 (3) |
| S1—P1—C1—C12 | 41.1 (4) | C2—P1—C3—C32 | 170.1 (3) |
| C3—P1—C1—C13 | 171.1 (3) | C1—P1—C3—C32 | 40.5 (4) |
| C2—P1—C1—C13 | 41.3 (4) | S1—P1—C3—C32 | -65.9 (4) |
| S1—P1—C1—C13 | -76.0 (3) | C2—P1—C3—C33 | -72.6 (4) |
| C3—P1—C1—C11 | 49.5 (4) | C1—P1—C3—C33 | 157.9 (3) |
| C2—P1—C1—C11 | -80.2 (4) | S1—P1—C3—C33 | 51.5 (4) |
| S1—P1—C1—C11 | 162.4 (3) | C2—P1—C3—C31 | 49.0 (4) |
| C3—P1—C2—C22 | 156.0 (3) | C1—P1—C3—C31 | -80.5 (4) |
| C1—P1—C2—C22 | -74.2 (4) | S1—P1—C3—C31 | 173.1 (3) |
| S1—P1—C2—C22 | 34.2 (4) | | |

Symmetry codes: (i) $-x+2, -y, -z$; (ii) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------|-------|-------------|-------------|---------------|
| C12—H12C \cdots S1 | 0.98 | 2.53 | 3.036 (5) | 112 |
| C22—H22B \cdots Br1 | 0.98 | 2.74 | 3.569 (5) | 143 |
| C23—H23A \cdots Br1 | 0.98 | 2.80 | 3.617 (5) | 142 |

| | | | | |
|---|------|------|-----------|-----|
| C22—H22A ⁱⁱⁱ ···Br2 ⁱⁱⁱ | 0.98 | 2.97 | 3.739 (5) | 137 |
| C13—H13C ^{iv} ···Br4 ^{iv} | 0.98 | 2.95 | 3.859 (5) | 154 |
| C21—H21A ^v ···Br4 ^v | 0.98 | 2.85 | 3.785 (5) | 160 |

Symmetry codes: (iii) $-x+1, -y, -z+1$; (iv) $-x, -y+1, -z+1$; (v) $x, y-1, z$.

(Bromoselanyl)tris(propan-2-yl)phosphonium tetrabromidoaurate(III) (21b)

Crystal data

(C₉H₂₁BrPSe)[AuBr₄]

$M_r = 835.70$

Triclinic, $P\bar{1}$

$a = 7.9212$ (4) Å

$b = 8.0606$ (4) Å

$c = 15.2911$ (8) Å

$\alpha = 76.817$ (5)°

$\beta = 82.668$ (5)°

$\gamma = 87.728$ (4)°

$V = 942.78$ (9) Å³

$Z = 2$

$F(000) = 756$

$D_x = 2.944$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 16838 reflections

$\theta = 2.6$ – 30.8 °

$\mu = 20.39$ mm⁻¹

$T = 100$ K

Plate, red

$0.1 \times 0.1 \times 0.05$ mm

Data collection

Oxford Diffraction Xcalibur, Eos

diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω scan

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.434$, $T_{\max} = 1.000$

69642 measured reflections

5661 independent reflections

4881 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

$\theta_{\max} = 30.9$ °, $\theta_{\min} = 2.6$ °

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.024$

$wR(F^2) = 0.045$

$S = 1.06$

5661 reflections

164 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0173P)^2 + 0.8539P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.53$ e Å⁻³

$\Delta\rho_{\min} = -1.01$ e Å⁻³

Extinction correction: *SHELXL2019/3*

(Sheldrick, 2015), $F_c^* = kF_c[1 + 0.001$

$F_c^2\lambda^3/\sin(2\theta)]^{1/4}$

Extinction coefficient: 0.00116 (7)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|-------------|----------------------------------|
| P1 | 0.69684 (11) | 0.75293 (10) | 0.25729 (6) | 0.01015 (16) |
| Se1 | 0.89396 (4) | 0.54763 (4) | 0.28517 (2) | 0.01562 (8) |
| Br1 | 0.85395 (5) | 0.42244 (4) | 0.16722 (2) | 0.01794 (8) |
| C1 | 0.7009 (4) | 0.8501 (4) | 0.3543 (2) | 0.0149 (7) |
| H1 | 0.823646 | 0.866198 | 0.358989 | 0.018* |
| C2 | 0.4967 (4) | 0.6579 (4) | 0.2481 (2) | 0.0124 (6) |

| | | | | |
|------|-------------|--------------|--------------|-------------|
| H2 | 0.515433 | 0.614546 | 0.191261 | 0.015* |
| C3 | 0.7589 (4) | 0.9128 (4) | 0.1533 (2) | 0.0124 (6) |
| H3 | 0.684416 | 1.015095 | 0.156099 | 0.015* |
| C11 | 0.6179 (5) | 1.0273 (4) | 0.3422 (3) | 0.0203 (8) |
| H11A | 0.496182 | 1.018268 | 0.338242 | 0.031* |
| H11B | 0.671710 | 1.101572 | 0.286496 | 0.031* |
| H11C | 0.632581 | 1.075411 | 0.394026 | 0.031* |
| C12 | 0.6281 (5) | 0.7327 (5) | 0.4448 (2) | 0.0199 (7) |
| H12A | 0.662665 | 0.774416 | 0.495204 | 0.030* |
| H12B | 0.671987 | 0.616491 | 0.447476 | 0.030* |
| H12C | 0.503620 | 0.732766 | 0.449240 | 0.030* |
| C21 | 0.4418 (5) | 0.5047 (4) | 0.3243 (3) | 0.0187 (7) |
| H21A | 0.404408 | 0.543359 | 0.380078 | 0.028* |
| H21B | 0.538022 | 0.425173 | 0.333956 | 0.028* |
| H21C | 0.347723 | 0.447235 | 0.307976 | 0.028* |
| C22 | 0.3559 (5) | 0.7941 (4) | 0.2344 (3) | 0.0189 (7) |
| H22A | 0.253104 | 0.743321 | 0.222620 | 0.028* |
| H22B | 0.393905 | 0.886888 | 0.182871 | 0.028* |
| H22C | 0.330599 | 0.839065 | 0.289114 | 0.028* |
| C31 | 0.9421 (4) | 0.9693 (4) | 0.1496 (2) | 0.0164 (7) |
| H31A | 1.020134 | 0.873840 | 0.143993 | 0.025* |
| H31B | 0.955442 | 1.005973 | 0.205176 | 0.025* |
| H31C | 0.968212 | 1.064298 | 0.097271 | 0.025* |
| C32 | 0.7299 (5) | 0.8572 (4) | 0.0675 (2) | 0.0181 (7) |
| H32A | 0.754886 | 0.952060 | 0.014995 | 0.027* |
| H32B | 0.611020 | 0.823421 | 0.071968 | 0.027* |
| H32C | 0.805043 | 0.760364 | 0.060500 | 0.027* |
| Au1 | 0.500000 | 0.500000 | 0.000000 | 0.01216 (5) |
| Br2 | 0.75282 (5) | 0.32913 (4) | -0.02174 (2) | 0.02058 (8) |
| Br3 | 0.39035 (5) | 0.28624 (4) | 0.13212 (2) | 0.01930 (8) |
| Au2 | 1.000000 | 0.000000 | 0.500000 | 0.01012 (5) |
| Br4 | 1.11176 (4) | 0.13772 (4) | 0.34673 (2) | 0.01553 (7) |
| Br5 | 1.08990 (5) | -0.27636 (4) | 0.47199 (2) | 0.01712 (8) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|---------------|---------------|
| P1 | 0.0091 (4) | 0.0110 (3) | 0.0099 (4) | 0.0006 (3) | -0.0010 (3) | -0.0017 (3) |
| Se1 | 0.01397 (17) | 0.01460 (15) | 0.01786 (18) | 0.00421 (12) | -0.00391 (14) | -0.00242 (13) |
| Br1 | 0.01892 (18) | 0.01379 (15) | 0.02116 (18) | 0.00242 (12) | -0.00027 (15) | -0.00571 (13) |
| C1 | 0.0148 (17) | 0.0170 (15) | 0.0135 (17) | -0.0009 (13) | -0.0024 (14) | -0.0044 (13) |
| C2 | 0.0105 (16) | 0.0122 (14) | 0.0152 (17) | -0.0020 (12) | -0.0025 (13) | -0.0036 (12) |
| C3 | 0.0156 (17) | 0.0112 (14) | 0.0099 (15) | -0.0001 (12) | 0.0002 (13) | -0.0021 (12) |
| C11 | 0.025 (2) | 0.0156 (16) | 0.023 (2) | 0.0032 (14) | -0.0040 (16) | -0.0100 (14) |
| C12 | 0.0208 (19) | 0.0255 (18) | 0.0142 (18) | -0.0045 (15) | -0.0009 (15) | -0.0063 (14) |
| C21 | 0.0156 (18) | 0.0158 (15) | 0.0231 (19) | -0.0059 (13) | 0.0021 (15) | -0.0027 (14) |
| C22 | 0.0124 (17) | 0.0197 (16) | 0.0226 (19) | 0.0023 (13) | -0.0001 (15) | -0.0020 (14) |
| C31 | 0.0145 (17) | 0.0179 (16) | 0.0148 (17) | -0.0008 (13) | 0.0017 (14) | -0.0013 (13) |

| | | | | | | |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| C32 | 0.026 (2) | 0.0162 (15) | 0.0108 (16) | -0.0042 (14) | -0.0005 (15) | -0.0015 (13) |
| Au1 | 0.01495 (10) | 0.01110 (8) | 0.01053 (9) | 0.00066 (6) | -0.00267 (7) | -0.00217 (6) |
| Br2 | 0.02075 (19) | 0.02002 (16) | 0.01994 (18) | 0.00683 (13) | -0.00135 (15) | -0.00417 (14) |
| Br3 | 0.02334 (19) | 0.01676 (15) | 0.01494 (17) | -0.00107 (13) | -0.00055 (15) | 0.00151 (13) |
| Au2 | 0.00935 (9) | 0.01033 (8) | 0.01101 (9) | 0.00037 (6) | -0.00181 (7) | -0.00286 (6) |
| Br4 | 0.01799 (18) | 0.01418 (14) | 0.01292 (16) | 0.00031 (12) | 0.00141 (14) | -0.00183 (12) |
| Br5 | 0.02189 (18) | 0.01260 (14) | 0.01684 (17) | 0.00474 (12) | -0.00159 (14) | -0.00453 (12) |

Geometric parameters (Å, °)

| | | | |
|-------------|--------------|-----------------------|------------|
| P1—C2 | 1.823 (3) | C21—H21A | 0.9800 |
| P1—C3 | 1.829 (3) | C21—H21B | 0.9800 |
| P1—C1 | 1.832 (3) | C21—H21C | 0.9800 |
| P1—Se1 | 2.2364 (9) | C22—H22A | 0.9800 |
| Se1—Br1 | 2.3179 (5) | C22—H22B | 0.9800 |
| Br1—Br2 | 3.3445 (6) | C22—H22C | 0.9800 |
| C1—C11 | 1.530 (4) | C31—H31A | 0.9800 |
| C1—C12 | 1.545 (5) | C31—H31B | 0.9800 |
| C1—H1 | 1.0000 | C31—H31C | 0.9800 |
| C2—C21 | 1.527 (5) | C32—H32A | 0.9800 |
| C2—C22 | 1.533 (4) | C32—H32B | 0.9800 |
| C2—H2 | 1.0000 | C32—H32C | 0.9800 |
| C3—C32 | 1.526 (5) | Au1—Br2 ⁱ | 2.4162 (4) |
| C3—C31 | 1.529 (5) | Au1—Br2 | 2.4162 (4) |
| C3—H3 | 1.0000 | Au1—Br3 | 2.4264 (4) |
| C11—H11A | 0.9800 | Au1—Br3 ⁱ | 2.4264 (4) |
| C11—H11B | 0.9800 | Au2—Br4 | 2.4230 (4) |
| C11—H11C | 0.9800 | Au2—Br4 ⁱⁱ | 2.4230 (4) |
| C12—H12A | 0.9800 | Au2—Br5 | 2.4258 (3) |
| C12—H12B | 0.9800 | Au2—Br5 ⁱⁱ | 2.4258 (3) |
| C12—H12C | 0.9800 | | |
| C2—P1—C3 | 109.07 (16) | C2—C21—H21A | 109.5 |
| C2—P1—C1 | 116.58 (16) | C2—C21—H21B | 109.5 |
| C3—P1—C1 | 108.74 (15) | H21A—C21—H21B | 109.5 |
| C2—P1—Se1 | 109.29 (10) | C2—C21—H21C | 109.5 |
| C3—P1—Se1 | 112.43 (11) | H21A—C21—H21C | 109.5 |
| C1—P1—Se1 | 100.60 (11) | H21B—C21—H21C | 109.5 |
| P1—Se1—Br1 | 96.32 (3) | C2—C22—H22A | 109.5 |
| Se1—Br1—Br2 | 166.590 (17) | C2—C22—H22B | 109.5 |
| C11—C1—C12 | 111.0 (3) | H22A—C22—H22B | 109.5 |
| C11—C1—P1 | 113.7 (2) | C2—C22—H22C | 109.5 |
| C12—C1—P1 | 112.8 (2) | H22A—C22—H22C | 109.5 |
| C11—C1—H1 | 106.2 | H22B—C22—H22C | 109.5 |
| C12—C1—H1 | 106.2 | C3—C31—H31A | 109.5 |
| P1—C1—H1 | 106.2 | C3—C31—H31B | 109.5 |
| C21—C2—C22 | 112.1 (3) | H31A—C31—H31B | 109.5 |
| C21—C2—P1 | 114.8 (2) | C3—C31—H31C | 109.5 |

| | | | |
|---------------|-------------|--|--------------|
| C22—C2—P1 | 110.6 (2) | H31A—C31—H31C | 109.5 |
| C21—C2—H2 | 106.2 | H31B—C31—H31C | 109.5 |
| C22—C2—H2 | 106.2 | C3—C32—H32A | 109.5 |
| P1—C2—H2 | 106.2 | C3—C32—H32B | 109.5 |
| C32—C3—C31 | 111.8 (3) | H32A—C32—H32B | 109.5 |
| C32—C3—P1 | 113.5 (2) | C3—C32—H32C | 109.5 |
| C31—C3—P1 | 110.8 (2) | H32A—C32—H32C | 109.5 |
| C32—C3—H3 | 106.8 | H32B—C32—H32C | 109.5 |
| C31—C3—H3 | 106.8 | Br2 ⁱ —Au1—Br2 | 180.0 |
| P1—C3—H3 | 106.8 | Br2 ⁱ —Au1—Br3 | 89.238 (13) |
| C1—C11—H11A | 109.5 | Br2—Au1—Br3 | 90.763 (13) |
| C1—C11—H11B | 109.5 | Br2 ⁱ —Au1—Br3 ⁱ | 90.762 (13) |
| H11A—C11—H11B | 109.5 | Br2—Au1—Br3 ⁱ | 89.237 (13) |
| C1—C11—H11C | 109.5 | Br3—Au1—Br3 ⁱ | 180.0 |
| H11A—C11—H11C | 109.5 | Au1—Br2—Br1 | 85.485 (12) |
| H11B—C11—H11C | 109.5 | Br4—Au2—Br4 ⁱⁱ | 180.000 (16) |
| C1—C12—H12A | 109.5 | Br4—Au2—Br5 | 90.629 (12) |
| C1—C12—H12B | 109.5 | Br4 ⁱⁱ —Au2—Br5 | 89.371 (12) |
| H12A—C12—H12B | 109.5 | Br4—Au2—Br5 ⁱⁱ | 89.372 (12) |
| C1—C12—H12C | 109.5 | Br4 ⁱⁱ —Au2—Br5 ⁱⁱ | 90.628 (12) |
| H12A—C12—H12C | 109.5 | Br5—Au2—Br5 ⁱⁱ | 179.999 (17) |
| H12B—C12—H12C | 109.5 | | |
| | | | |
| C2—P1—Se1—Br1 | 51.37 (12) | Se1—P1—C2—C21 | 48.5 (3) |
| C3—P1—Se1—Br1 | -69.89 (12) | C3—P1—C2—C22 | -60.0 (3) |
| C1—P1—Se1—Br1 | 174.59 (11) | C1—P1—C2—C22 | 63.6 (3) |
| C2—P1—C1—C11 | -78.8 (3) | Se1—P1—C2—C22 | 176.7 (2) |
| C3—P1—C1—C11 | 44.9 (3) | C2—P1—C3—C32 | -41.5 (3) |
| Se1—P1—C1—C11 | 163.2 (2) | C1—P1—C3—C32 | -169.6 (2) |
| C2—P1—C1—C12 | 48.8 (3) | Se1—P1—C3—C32 | 79.9 (3) |
| C3—P1—C1—C12 | 172.6 (2) | C2—P1—C3—C31 | -168.3 (2) |
| Se1—P1—C1—C12 | -69.2 (3) | C1—P1—C3—C31 | 63.6 (3) |
| C3—P1—C2—C21 | 171.8 (2) | Se1—P1—C3—C31 | -46.9 (2) |
| C1—P1—C2—C21 | -64.6 (3) | | |

Symmetry codes: (i) $-x+1, -y+1, -z$; (ii) $-x+2, -y, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-------|-------------|-------------|---------------|
| C21—H21B \cdots Br1 | 0.98 | 3.34 | 3.927 (4) | 120 |
| C3—H3 \cdots Br2 ⁱⁱⁱ | 1.00 | 3.27 | 3.788 (3) | 114 |
| C31—H31C \cdots Br2 ⁱⁱⁱ | 0.98 | 3.08 | 3.836 (3) | 135 |
| C32—H32A \cdots Br2 ⁱⁱⁱ | 0.98 | 2.96 | 3.740 (3) | 137 |
| C1—H1 \cdots Br4 ⁱⁱⁱ | 1.00 | 3.18 | 4.045 (3) | 145 |
| C21—H21C \cdots Br4 ^{iv} | 0.98 | 3.08 | 3.953 (3) | 149 |
| C31—H31B \cdots Br4 ⁱⁱⁱ | 0.98 | 3.03 | 3.972 (4) | 162 |

| | | | | |
|---------------------------|------|------|-----------|-----|
| C1—H1⋯Br5 ⁱⁱⁱ | 1.00 | 2.93 | 3.756 (4) | 140 |
| C22—H22C⋯Br5 ^v | 0.98 | 3.15 | 3.893 (4) | 134 |

Symmetry codes: (iii) $x, y+1, z$; (iv) $x-1, y, z$; (v) $x-1, y+1, z$.

(Bromoselanyl)(*tert*-butyl)bis(propan-2-yl)phosphonium tetrabromidoaurate(III) (22b)

Crystal data

(C₁₀H₂₃BrPSe)[AuBr₄]

$M_r = 849.73$

Triclinic, $P\bar{1}$

$a = 7.8155$ (3) Å

$b = 9.1505$ (3) Å

$c = 15.5221$ (5) Å

$\alpha = 85.965$ (2)°

$\beta = 80.294$ (3)°

$\gamma = 66.049$ (3)°

$V = 999.97$ (6) Å³

$Z = 2$

$F(000) = 772$

$D_x = 2.822$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 21572 reflections

$\theta = 2.4$ – 30.8 °

$\mu = 19.23$ mm⁻¹

$T = 100$ K

Plate, red

$0.3 \times 0.2 \times 0.03$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.202$, $T_{\max} = 1.000$

52431 measured reflections

5847 independent reflections

5198 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$

$\theta_{\max} = 30.9$ °, $\theta_{\min} = 2.4$ °

$h = -11 \rightarrow 11$

$k = -13 \rightarrow 13$

$l = -22 \rightarrow 22$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.063$

$S = 1.04$

5847 reflections

173 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0295P)^2 + 3.0506P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.71$ e Å⁻³

$\Delta\rho_{\min} = -1.44$ e Å⁻³

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|--------------|-------------|----------------------------------|
| P1 | 0.50396 (13) | 0.10486 (11) | 0.24702 (6) | 0.01234 (17) |
| Se1 | 0.37707 (5) | -0.06510 (4) | 0.30872 (3) | 0.01717 (8) |
| Br1 | 0.14096 (5) | 0.10400 (5) | 0.41193 (3) | 0.01896 (8) |
| C1 | 0.7420 (5) | -0.0300 (4) | 0.1909 (2) | 0.0154 (7) |
| C2 | 0.5064 (6) | 0.2349 (5) | 0.3307 (3) | 0.0202 (8) |
| H2 | 0.370536 | 0.303427 | 0.351902 | 0.024* |
| C3 | 0.3564 (6) | 0.2349 (4) | 0.1684 (3) | 0.0173 (7) |
| H3 | 0.430348 | 0.292376 | 0.134040 | 0.021* |
| C11 | 0.8062 (6) | 0.0571 (5) | 0.1123 (3) | 0.0229 (9) |

| | | | | |
|------|--------------|-------------|-------------|-------------|
| H11A | 0.803491 | 0.157676 | 0.131775 | 0.034* |
| H11B | 0.720630 | 0.079831 | 0.069005 | 0.034* |
| H11C | 0.935429 | -0.010648 | 0.085845 | 0.034* |
| C12 | 0.8846 (6) | -0.0773 (5) | 0.2559 (3) | 0.0212 (8) |
| H12A | 1.006172 | -0.157871 | 0.229224 | 0.032* |
| H12B | 0.835837 | -0.121394 | 0.309079 | 0.032* |
| H12C | 0.902346 | 0.017404 | 0.270870 | 0.032* |
| C13 | 0.7354 (6) | -0.1838 (5) | 0.1604 (3) | 0.0218 (8) |
| H13A | 0.634662 | -0.155692 | 0.124430 | 0.033* |
| H13B | 0.709770 | -0.245346 | 0.211417 | 0.033* |
| H13C | 0.857404 | -0.248159 | 0.125820 | 0.033* |
| C21 | 0.5911 (6) | 0.1508 (6) | 0.4122 (3) | 0.0271 (10) |
| H21A | 0.729668 | 0.104162 | 0.398448 | 0.041* |
| H21B | 0.546541 | 0.065956 | 0.430672 | 0.041* |
| H21C | 0.551020 | 0.228693 | 0.459541 | 0.041* |
| C22 | 0.5960 (7) | 0.3499 (6) | 0.2896 (3) | 0.0273 (9) |
| H22A | 0.584526 | 0.425951 | 0.333887 | 0.041* |
| H22B | 0.530519 | 0.408286 | 0.241327 | 0.041* |
| H22C | 0.730240 | 0.288839 | 0.267432 | 0.041* |
| C31 | 0.3155 (7) | 0.1397 (5) | 0.1030 (3) | 0.0256 (9) |
| H31A | 0.241760 | 0.082244 | 0.134354 | 0.038* |
| H31B | 0.435336 | 0.062881 | 0.072387 | 0.038* |
| H31C | 0.243202 | 0.213235 | 0.060597 | 0.038* |
| C32 | 0.1709 (6) | 0.3628 (5) | 0.2133 (3) | 0.0226 (9) |
| H32A | 0.100581 | 0.431734 | 0.168905 | 0.034* |
| H32B | 0.199553 | 0.427409 | 0.251845 | 0.034* |
| H32C | 0.094104 | 0.310846 | 0.247835 | 0.034* |
| Au1 | 0.000000 | 0.500000 | 0.500000 | 0.01431 (5) |
| Br2 | -0.17342 (6) | 0.34529 (5) | 0.57133 (3) | 0.02321 (9) |
| Br3 | 0.22409 (6) | 0.39711 (5) | 0.60184 (3) | 0.02503 (9) |
| Au2 | 0.500000 | 0.500000 | 0.000000 | 0.01293 (5) |
| Br4 | 0.34937 (6) | 0.69967 (5) | 0.11370 (3) | 0.02330 (9) |
| Br5 | 0.80787 (5) | 0.45789 (5) | 0.03378 (3) | 0.01988 (8) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|---------------|--------------|--------------|
| P1 | 0.0121 (4) | 0.0126 (4) | 0.0121 (4) | -0.0049 (3) | -0.0017 (3) | 0.0003 (3) |
| Se1 | 0.01440 (17) | 0.01364 (17) | 0.02165 (19) | -0.00536 (14) | 0.00047 (14) | 0.00209 (14) |
| Br1 | 0.01548 (17) | 0.02158 (18) | 0.01890 (18) | -0.00821 (14) | 0.00178 (14) | 0.00010 (14) |
| C1 | 0.0126 (16) | 0.0155 (17) | 0.0146 (17) | -0.0026 (14) | -0.0007 (13) | 0.0004 (13) |
| C2 | 0.0192 (19) | 0.0231 (19) | 0.0190 (19) | -0.0096 (16) | -0.0008 (15) | -0.0032 (15) |
| C3 | 0.0183 (18) | 0.0143 (17) | 0.0166 (18) | -0.0031 (14) | -0.0052 (14) | 0.0024 (14) |
| C11 | 0.021 (2) | 0.023 (2) | 0.020 (2) | -0.0072 (16) | 0.0031 (16) | 0.0031 (16) |
| C12 | 0.0127 (17) | 0.025 (2) | 0.024 (2) | -0.0048 (15) | -0.0039 (15) | 0.0001 (16) |
| C13 | 0.0193 (19) | 0.0181 (18) | 0.022 (2) | -0.0024 (15) | 0.0013 (16) | -0.0047 (15) |
| C21 | 0.024 (2) | 0.047 (3) | 0.0137 (19) | -0.016 (2) | -0.0047 (16) | -0.0043 (18) |
| C22 | 0.027 (2) | 0.029 (2) | 0.031 (2) | -0.0158 (19) | -0.0029 (19) | -0.0076 (19) |

| | | | | | | |
|-----|--------------|--------------|--------------|---------------|---------------|---------------|
| C31 | 0.032 (2) | 0.0193 (19) | 0.022 (2) | -0.0027 (17) | -0.0143 (18) | -0.0022 (16) |
| C32 | 0.0182 (19) | 0.0193 (19) | 0.024 (2) | -0.0013 (15) | -0.0039 (16) | 0.0030 (16) |
| Au1 | 0.01577 (10) | 0.01210 (9) | 0.01502 (10) | -0.00555 (7) | -0.00218 (7) | -0.00049 (7) |
| Br2 | 0.0242 (2) | 0.02110 (19) | 0.0269 (2) | -0.01315 (16) | -0.00151 (16) | 0.00323 (16) |
| Br3 | 0.0259 (2) | 0.0288 (2) | 0.0240 (2) | -0.01270 (17) | -0.01168 (17) | 0.00647 (16) |
| Au2 | 0.00891 (9) | 0.01081 (9) | 0.01807 (10) | -0.00374 (7) | -0.00046 (7) | 0.00113 (7) |
| Br4 | 0.01693 (18) | 0.02185 (19) | 0.0283 (2) | -0.00550 (15) | 0.00196 (16) | -0.00920 (16) |
| Br5 | 0.01169 (16) | 0.01865 (18) | 0.0301 (2) | -0.00635 (14) | -0.00504 (15) | 0.00129 (15) |

Geometric parameters (Å, °)

| | | | |
|-------------|-------------|-----------------------|------------|
| P1—C2 | 1.829 (4) | C13—H13B | 0.9800 |
| P1—C3 | 1.841 (4) | C13—H13C | 0.9800 |
| P1—C1 | 1.866 (4) | C21—H21A | 0.9800 |
| P1—Se1 | 2.2453 (10) | C21—H21B | 0.9800 |
| Se1—Br1 | 2.3237 (5) | C21—H21C | 0.9800 |
| Br1—Br2 | 3.3687 (6) | C22—H22A | 0.9800 |
| C1—C11 | 1.536 (6) | C22—H22B | 0.9800 |
| C1—C13 | 1.539 (6) | C22—H22C | 0.9800 |
| C1—C12 | 1.540 (6) | C31—H31A | 0.9800 |
| C2—C22 | 1.536 (6) | C31—H31B | 0.9800 |
| C2—C21 | 1.538 (6) | C31—H31C | 0.9800 |
| C2—H2 | 1.0000 | C32—H32A | 0.9800 |
| C3—C31 | 1.533 (6) | C32—H32B | 0.9800 |
| C3—C32 | 1.534 (5) | C32—H32C | 0.9800 |
| C3—H3 | 1.0000 | Au1—Br3 | 2.4162 (4) |
| C11—H11A | 0.9800 | Au1—Br3 ⁱ | 2.4162 (4) |
| C11—H11B | 0.9800 | Au1—Br2 | 2.4287 (4) |
| C11—H11C | 0.9800 | Au1—Br2 ⁱ | 2.4287 (4) |
| C12—H12A | 0.9800 | Au2—Br4 | 2.4178 (4) |
| C12—H12B | 0.9800 | Au2—Br4 ⁱⁱ | 2.4179 (4) |
| C12—H12C | 0.9800 | Au2—Br5 ⁱⁱ | 2.4202 (4) |
| C13—H13A | 0.9800 | Au2—Br5 | 2.4202 (4) |
| C2—P1—C3 | 107.07 (19) | C1—C13—H13C | 109.5 |
| C2—P1—C1 | 115.23 (19) | H13A—C13—H13C | 109.5 |
| C3—P1—C1 | 111.45 (17) | H13B—C13—H13C | 109.5 |
| C2—P1—Se1 | 109.82 (14) | C2—C21—H21A | 109.5 |
| C3—P1—Se1 | 109.70 (14) | C2—C21—H21B | 109.5 |
| C1—P1—Se1 | 103.51 (13) | H21A—C21—H21B | 109.5 |
| P1—Se1—Br1 | 99.52 (3) | C2—C21—H21C | 109.5 |
| Se1—Br1—Br2 | 175.31 (2) | H21A—C21—H21C | 109.5 |
| C11—C1—C13 | 109.9 (3) | H21B—C21—H21C | 109.5 |
| C11—C1—C12 | 109.6 (3) | C2—C22—H22A | 109.5 |
| C13—C1—C12 | 108.2 (3) | C2—C22—H22B | 109.5 |
| C11—C1—P1 | 109.6 (3) | H22A—C22—H22B | 109.5 |
| C13—C1—P1 | 110.4 (3) | C2—C22—H22C | 109.5 |
| C12—C1—P1 | 109.0 (3) | H22A—C22—H22C | 109.5 |

| | | | |
|---------------|-------------|--|--------------|
| C22—C2—C21 | 111.9 (4) | H22B—C22—H22C | 109.5 |
| C22—C2—P1 | 110.4 (3) | C3—C31—H31A | 109.5 |
| C21—C2—P1 | 116.2 (3) | C3—C31—H31B | 109.5 |
| C22—C2—H2 | 105.8 | H31A—C31—H31B | 109.5 |
| C21—C2—H2 | 105.8 | C3—C31—H31C | 109.5 |
| P1—C2—H2 | 105.8 | H31A—C31—H31C | 109.5 |
| C31—C3—C32 | 110.4 (4) | H31B—C31—H31C | 109.5 |
| C31—C3—P1 | 112.4 (3) | C3—C32—H32A | 109.5 |
| C32—C3—P1 | 112.6 (3) | C3—C32—H32B | 109.5 |
| C31—C3—H3 | 107.0 | H32A—C32—H32B | 109.5 |
| C32—C3—H3 | 107.0 | C3—C32—H32C | 109.5 |
| P1—C3—H3 | 107.0 | H32A—C32—H32C | 109.5 |
| C1—C11—H11A | 109.5 | H32B—C32—H32C | 109.5 |
| C1—C11—H11B | 109.5 | Br3—Au1—Br3 ⁱ | 180.0 |
| H11A—C11—H11B | 109.5 | Br3—Au1—Br2 | 90.432 (15) |
| C1—C11—H11C | 109.5 | Br3 ⁱ —Au1—Br2 | 89.568 (15) |
| H11A—C11—H11C | 109.5 | Br3—Au1—Br2 ⁱ | 89.568 (15) |
| H11B—C11—H11C | 109.5 | Br3 ⁱ —Au1—Br2 ⁱ | 90.432 (15) |
| C1—C12—H12A | 109.5 | Br2—Au1—Br2 ⁱ | 180.000 (13) |
| C1—C12—H12B | 109.5 | Au1—Br2—Br1 | 75.542 (13) |
| H12A—C12—H12B | 109.5 | Br4—Au2—Br4 ⁱⁱ | 179.999 (15) |
| C1—C12—H12C | 109.5 | Br4—Au2—Br5 ⁱⁱ | 89.894 (14) |
| H12A—C12—H12C | 109.5 | Br4 ⁱⁱ —Au2—Br5 ⁱⁱ | 90.105 (14) |
| H12B—C12—H12C | 109.5 | Br4—Au2—Br5 | 90.106 (14) |
| C1—C13—H13A | 109.5 | Br4 ⁱⁱ —Au2—Br5 | 89.895 (14) |
| C1—C13—H13B | 109.5 | Br5 ⁱⁱ —Au2—Br5 | 180.0 |
| H13A—C13—H13B | 109.5 | | |
| | | | |
| C2—P1—Se1—Br1 | 37.67 (15) | C3—P1—C2—C22 | -61.9 (3) |
| C3—P1—Se1—Br1 | -79.74 (13) | C1—P1—C2—C22 | 62.6 (3) |
| C1—P1—Se1—Br1 | 161.21 (13) | Se1—P1—C2—C22 | 179.0 (3) |
| C2—P1—C1—C11 | -87.6 (3) | C3—P1—C2—C21 | 169.3 (3) |
| C3—P1—C1—C11 | 34.6 (3) | C1—P1—C2—C21 | -66.1 (4) |
| Se1—P1—C1—C11 | 152.5 (3) | Se1—P1—C2—C21 | 50.2 (3) |
| C2—P1—C1—C13 | 151.1 (3) | C2—P1—C3—C31 | -170.6 (3) |
| C3—P1—C1—C13 | -86.7 (3) | C1—P1—C3—C31 | 62.5 (4) |
| Se1—P1—C1—C13 | 31.2 (3) | Se1—P1—C3—C31 | -51.5 (3) |
| C2—P1—C1—C12 | 32.4 (3) | C2—P1—C3—C32 | -45.2 (4) |
| C3—P1—C1—C12 | 154.7 (3) | C1—P1—C3—C32 | -172.0 (3) |
| Se1—P1—C1—C12 | -87.5 (3) | Se1—P1—C3—C32 | 74.0 (3) |

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------|-------|-------------|-------------|---------------|
| C13—H13B \cdots Se1 | 0.98 | 2.70 | 3.167 (4) | 109 |
| C2—H2 \cdots Br1 | 1.00 | 3.05 | 3.540 (4) | 112 |

| | | | | |
|-----------------------------|------|------|-----------|-----|
| C3—H3⋯Au2 | 1.00 | 2.85 | 3.783 (4) | 155 |
| C32—H32C⋯Br1 | 0.98 | 3.05 | 3.788 (4) | 134 |
| C21—H21C⋯Br3 | 0.98 | 3.03 | 3.848 (4) | 142 |
| C11—H11A⋯Br5 | 0.98 | 3.05 | 3.787 (4) | 133 |
| C2—H2⋯Br2 ⁱ | 1.00 | 3.17 | 3.901 (4) | 131 |
| C22—H22A⋯Br3 ⁱⁱⁱ | 0.98 | 2.92 | 3.764 (4) | 144 |
| C12—H12B⋯Br3 ^{iv} | 0.98 | 2.96 | 3.826 (4) | 148 |
| C13—H13B⋯Br3 ^{iv} | 0.98 | 3.15 | 4.051 (4) | 153 |
| C12—H12A⋯Br4 ^v | 0.98 | 2.82 | 3.761 (4) | 160 |
| C13—H13A⋯Br4 ^{vi} | 0.98 | 3.05 | 3.771 (5) | 132 |

Symmetry codes: (i) $-x, -y+1, -z+1$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y, -z+1$; (v) $x+1, y-1, z$; (vi) $x, y-1, z$.

(Bromoselanyl)bis(*tert*-butyl)(propan-2-yl)phosphonium tetrabromidoaurate(III) (23b)

Crystal data

(C₁₁H₂₅BrPSe)[AuBr₄]

$M_r = 863.76$

Monoclinic, $P2_1/n$

$a = 12.3529$ (4) Å

$b = 10.4233$ (4) Å

$c = 16.4635$ (5) Å

$\beta = 93.453$ (3)°

$V = 2115.97$ (12) Å³

$Z = 4$

$F(000) = 1576$

$D_x = 2.711$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 13739 reflections

$\theta = 2.1$ – 30.8 °

$\mu = 18.18$ mm⁻¹

$T = 101$ K

Plate, dichroic red/orange

$0.2 \times 0.1 \times 0.02$ mm

Data collection

Oxford Diffraction Xcalibur, Eos
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Detector resolution: 16.1419 pixels mm⁻¹

ω scan

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2015)

$T_{\min} = 0.122$, $T_{\max} = 0.713$

7063 measured reflections

7063 independent reflections

4089 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.0000$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 2.3$ °

$h = -16 \rightarrow 16$

$k = -13 \rightarrow 13$

$l = -21 \rightarrow 21$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.061$

$S = 0.81$

7063 reflections

184 parameters

66 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.72$ e Å⁻³

$\Delta\rho_{\min} = -1.10$ e Å⁻³

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The crystal was a two-component non-merohedral twin (by 180 degree rotation about the a^* axis). The data reduction generated all non-overlapped reflections from the larger component, together with all overlapped reflections. The number of data used for refinement should therefore be interpreted with caution. All equivalents were merged during the untwining process, and the $R(\text{int})$ value is thus meaningless.

The "HKL F 5" method was used for structure refinement. The relative volume of the smaller twin component refined to 0.0807 (6).

The U values of the carbon atoms were restrained to be less anisotropic using the command "ISOR \$C 0.005".

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| P1 | 0.47957 (15) | 0.09088 (17) | 0.25502 (11) | 0.0126 (5) |
| Se1 | 0.44215 (7) | 0.27120 (7) | 0.18322 (4) | 0.01936 (19) |
| Br1 | 0.51433 (7) | 0.42888 (7) | 0.27054 (5) | 0.0248 (2) |
| C2 | 0.3787 (6) | 0.0765 (7) | 0.3332 (4) | 0.0218 (19) |
| C1 | 0.4675 (6) | -0.0298 (6) | 0.1701 (4) | 0.0176 (18) |
| C3 | 0.6156 (6) | 0.1003 (6) | 0.3049 (4) | 0.0153 (17) |
| H3 | 0.607781 | 0.152437 | 0.355216 | 0.018* |
| C21 | 0.4077 (8) | -0.0295 (8) | 0.3953 (4) | 0.039 (3) |
| H21A | 0.351865 | -0.034008 | 0.434986 | 0.059* |
| H21B | 0.478024 | -0.010441 | 0.423418 | 0.059* |
| H21C | 0.411786 | -0.112003 | 0.367010 | 0.059* |
| C22 | 0.2654 (6) | 0.0530 (7) | 0.2937 (5) | 0.030 (2) |
| H22A | 0.262312 | -0.032758 | 0.269269 | 0.045* |
| H22B | 0.249411 | 0.117542 | 0.251352 | 0.045* |
| H22C | 0.211805 | 0.059172 | 0.335033 | 0.045* |
| C23 | 0.3763 (7) | 0.2033 (7) | 0.3804 (5) | 0.036 (2) |
| H23A | 0.331979 | 0.192879 | 0.427376 | 0.054* |
| H23B | 0.344971 | 0.270664 | 0.344723 | 0.054* |
| H23C | 0.450286 | 0.227282 | 0.399210 | 0.054* |
| C11 | 0.5717 (7) | -0.0224 (7) | 0.1231 (4) | 0.029 (2) |
| H11A | 0.562872 | -0.074840 | 0.073791 | 0.044* |
| H11B | 0.633200 | -0.054452 | 0.157640 | 0.044* |
| H11C | 0.585108 | 0.066971 | 0.108119 | 0.044* |
| C12 | 0.4547 (7) | -0.1648 (6) | 0.2060 (4) | 0.025 (2) |
| H12A | 0.382333 | -0.173352 | 0.226697 | 0.038* |
| H12B | 0.509771 | -0.177957 | 0.250631 | 0.038* |
| H12C | 0.463964 | -0.229158 | 0.163584 | 0.038* |
| C13 | 0.3680 (7) | 0.0002 (7) | 0.1136 (4) | 0.0282 (19) |
| H13A | 0.377566 | 0.083827 | 0.087731 | 0.042* |
| H13B | 0.303290 | 0.002393 | 0.145169 | 0.042* |
| H13C | 0.359449 | -0.066272 | 0.071617 | 0.042* |
| C31 | 0.6995 (6) | 0.1702 (7) | 0.2571 (4) | 0.0236 (19) |
| H31A | 0.760721 | 0.195971 | 0.294156 | 0.035* |
| H31B | 0.666388 | 0.246598 | 0.231329 | 0.035* |
| H31C | 0.725290 | 0.113057 | 0.215166 | 0.035* |
| C32 | 0.6621 (6) | -0.0294 (7) | 0.3344 (4) | 0.028 (2) |
| H32A | 0.679990 | -0.081171 | 0.287364 | 0.041* |

| | | | | |
|------|-------------|-------------|--------------|--------------|
| H32B | 0.608123 | -0.074674 | 0.364954 | 0.041* |
| H32C | 0.727718 | -0.015047 | 0.369636 | 0.041* |
| Au1 | 0.500000 | 0.500000 | 0.500000 | 0.01339 (10) |
| Br2 | 0.60826 (7) | 0.63241 (8) | 0.41494 (5) | 0.0277 (2) |
| Br3 | 0.64014 (7) | 0.33828 (8) | 0.50404 (5) | 0.0293 (2) |
| Au2 | 0.500000 | 0.500000 | 0.000000 | 0.01182 (10) |
| Br4 | 0.63241 (6) | 0.32858 (7) | 0.01148 (5) | 0.01770 (19) |
| Br5 | 0.35622 (6) | 0.34365 (7) | -0.02110 (4) | 0.01917 (19) |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|-------------|--------------|---------------|
| P1 | 0.0157 (13) | 0.0116 (10) | 0.0107 (10) | 0.0009 (8) | 0.0023 (9) | -0.0006 (8) |
| Se1 | 0.0256 (5) | 0.0129 (4) | 0.0191 (4) | 0.0043 (4) | -0.0032 (3) | 0.0009 (3) |
| Br1 | 0.0270 (5) | 0.0136 (4) | 0.0336 (5) | -0.0007 (4) | -0.0005 (4) | -0.0034 (3) |
| C2 | 0.020 (4) | 0.026 (4) | 0.019 (4) | -0.003 (3) | 0.004 (3) | -0.004 (3) |
| C1 | 0.028 (4) | 0.009 (4) | 0.015 (3) | 0.002 (3) | -0.002 (3) | -0.004 (3) |
| C3 | 0.016 (4) | 0.013 (3) | 0.017 (3) | -0.002 (3) | -0.001 (3) | 0.000 (3) |
| C21 | 0.055 (6) | 0.043 (6) | 0.021 (4) | -0.010 (4) | 0.011 (4) | 0.010 (4) |
| C22 | 0.028 (5) | 0.029 (4) | 0.035 (5) | -0.009 (4) | 0.014 (4) | -0.013 (4) |
| C23 | 0.038 (5) | 0.034 (5) | 0.039 (5) | -0.005 (4) | 0.026 (4) | -0.016 (4) |
| C11 | 0.046 (5) | 0.018 (5) | 0.025 (4) | 0.000 (4) | 0.012 (4) | -0.008 (3) |
| C12 | 0.035 (5) | 0.022 (4) | 0.018 (4) | -0.005 (4) | -0.006 (4) | -0.003 (3) |
| C13 | 0.043 (5) | 0.024 (4) | 0.016 (4) | 0.002 (4) | -0.014 (3) | 0.001 (4) |
| C31 | 0.017 (4) | 0.021 (4) | 0.033 (4) | 0.003 (3) | 0.004 (4) | -0.002 (3) |
| C32 | 0.022 (4) | 0.023 (5) | 0.037 (5) | 0.004 (3) | -0.010 (4) | 0.011 (3) |
| Au1 | 0.0126 (2) | 0.0117 (2) | 0.0160 (2) | 0.0003 (2) | 0.00209 (17) | -0.0027 (2) |
| Br2 | 0.0375 (6) | 0.0214 (4) | 0.0256 (4) | -0.0115 (4) | 0.0142 (4) | -0.0048 (4) |
| Br3 | 0.0203 (5) | 0.0212 (5) | 0.0456 (6) | 0.0078 (4) | -0.0036 (4) | -0.0058 (4) |
| Au2 | 0.0129 (2) | 0.0111 (2) | 0.0116 (2) | -0.0027 (2) | 0.00226 (16) | -0.00071 (19) |
| Br4 | 0.0162 (5) | 0.0147 (4) | 0.0224 (4) | 0.0009 (3) | 0.0028 (4) | -0.0025 (3) |
| Br5 | 0.0163 (4) | 0.0153 (4) | 0.0256 (5) | -0.0061 (4) | -0.0020 (3) | 0.0010 (3) |

Geometric parameters (Å, °)

| | | | |
|---------|-------------|----------|--------|
| P1—C3 | 1.828 (7) | C11—H11A | 0.9800 |
| P1—C2 | 1.851 (7) | C11—H11B | 0.9800 |
| P1—C1 | 1.880 (7) | C11—H11C | 0.9800 |
| P1—Se1 | 2.2534 (19) | C12—H12A | 0.9800 |
| Se1—Br1 | 2.3255 (10) | C12—H12B | 0.9800 |
| Br1—Br2 | 3.3416 (11) | C12—H12C | 0.9800 |
| C2—C22 | 1.528 (10) | C13—H13A | 0.9800 |
| C2—C21 | 1.533 (10) | C13—H13B | 0.9800 |
| C2—C23 | 1.533 (9) | C13—H13C | 0.9800 |
| C1—C13 | 1.528 (10) | C31—H31A | 0.9800 |
| C1—C12 | 1.538 (9) | C31—H31B | 0.9800 |
| C1—C11 | 1.543 (10) | C31—H31C | 0.9800 |
| C3—C31 | 1.524 (9) | C32—H32A | 0.9800 |

| | | | |
|---------------|------------|--|------------|
| C3—C32 | 1.536 (9) | C32—H32B | 0.9800 |
| C3—H3 | 1.0000 | C32—H32C | 0.9800 |
| C21—H21A | 0.9800 | Au1—Br3 ⁱ | 2.4142 (8) |
| C21—H21B | 0.9800 | Au1—Br3 | 2.4142 (8) |
| C21—H21C | 0.9800 | Au1—Br2 ⁱ | 2.4249 (8) |
| C22—H22A | 0.9800 | Au1—Br2 | 2.4249 (8) |
| C22—H22B | 0.9800 | Au2—Br5 ⁱⁱ | 2.4201 (7) |
| C22—H22C | 0.9800 | Au2—Br5 | 2.4201 (7) |
| C23—H23A | 0.9800 | Au2—Br4 | 2.4221 (7) |
| C23—H23B | 0.9800 | Au2—Br4 ⁱⁱ | 2.4221 (7) |
| C23—H23C | 0.9800 | | |
| | | | |
| C3—P1—C2 | 109.3 (3) | C1—C11—H11A | 109.5 |
| C3—P1—C1 | 113.6 (3) | C1—C11—H11B | 109.5 |
| C2—P1—C1 | 115.9 (3) | H11A—C11—H11B | 109.5 |
| C3—P1—Se1 | 110.2 (2) | C1—C11—H11C | 109.5 |
| C2—P1—Se1 | 107.9 (3) | H11A—C11—H11C | 109.5 |
| C1—P1—Se1 | 99.4 (2) | H11B—C11—H11C | 109.5 |
| P1—Se1—Br1 | 101.91 (6) | C1—C12—H12A | 109.5 |
| Se1—Br1—Br2 | 172.85 (4) | C1—C12—H12B | 109.5 |
| C22—C2—C21 | 109.8 (6) | H12A—C12—H12B | 109.5 |
| C22—C2—C23 | 108.0 (6) | C1—C12—H12C | 109.5 |
| C21—C2—C23 | 107.2 (6) | H12A—C12—H12C | 109.5 |
| C22—C2—P1 | 110.7 (5) | H12B—C12—H12C | 109.5 |
| C21—C2—P1 | 112.4 (6) | C1—C13—H13A | 109.5 |
| C23—C2—P1 | 108.5 (5) | C1—C13—H13B | 109.5 |
| C13—C1—C12 | 108.9 (6) | H13A—C13—H13B | 109.5 |
| C13—C1—C11 | 110.4 (6) | C1—C13—H13C | 109.5 |
| C12—C1—C11 | 110.3 (6) | H13A—C13—H13C | 109.5 |
| C13—C1—P1 | 109.9 (5) | H13B—C13—H13C | 109.5 |
| C12—C1—P1 | 109.4 (5) | C3—C31—H31A | 109.5 |
| C11—C1—P1 | 107.9 (5) | C3—C31—H31B | 109.5 |
| C31—C3—C32 | 109.3 (6) | H31A—C31—H31B | 109.5 |
| C31—C3—P1 | 115.4 (5) | C3—C31—H31C | 109.5 |
| C32—C3—P1 | 114.3 (5) | H31A—C31—H31C | 109.5 |
| C31—C3—H3 | 105.6 | H31B—C31—H31C | 109.5 |
| C32—C3—H3 | 105.6 | C3—C32—H32A | 109.5 |
| P1—C3—H3 | 105.6 | C3—C32—H32B | 109.5 |
| C2—C21—H21A | 109.5 | H32A—C32—H32B | 109.5 |
| C2—C21—H21B | 109.5 | C3—C32—H32C | 109.5 |
| H21A—C21—H21B | 109.5 | H32A—C32—H32C | 109.5 |
| C2—C21—H21C | 109.5 | H32B—C32—H32C | 109.5 |
| H21A—C21—H21C | 109.5 | Br3 ⁱ —Au1—Br3 | 180.00 (3) |
| H21B—C21—H21C | 109.5 | Br3 ⁱ —Au1—Br2 ⁱ | 89.64 (3) |
| C2—C22—H22A | 109.5 | Br3—Au1—Br2 ⁱ | 90.36 (3) |
| C2—C22—H22B | 109.5 | Br3 ⁱ —Au1—Br2 | 90.36 (3) |
| H22A—C22—H22B | 109.5 | Br3—Au1—Br2 | 89.64 (3) |
| C2—C22—H22C | 109.5 | Br2 ⁱ —Au1—Br2 | 180.0 |

| | | | |
|---------------|------------|--|------------|
| H22A—C22—H22C | 109.5 | Au1—Br2—Br1 | 82.51 (3) |
| H22B—C22—H22C | 109.5 | Br5 ⁱⁱ —Au2—Br5 | 180.0 |
| C2—C23—H23A | 109.5 | Br5 ⁱⁱ —Au2—Br4 | 89.96 (2) |
| C2—C23—H23B | 109.5 | Br5—Au2—Br4 | 90.04 (2) |
| H23A—C23—H23B | 109.5 | Br5 ⁱⁱ —Au2—Br4 ⁱⁱ | 90.04 (2) |
| C2—C23—H23C | 109.5 | Br5—Au2—Br4 ⁱⁱ | 89.96 (2) |
| H23A—C23—H23C | 109.5 | Br4—Au2—Br4 ⁱⁱ | 180.0 |
| H23B—C23—H23C | 109.5 | | |
| | | | |
| C3—P1—Se1—Br1 | -40.8 (2) | Se1—P1—C1—C13 | -43.0 (5) |
| C2—P1—Se1—Br1 | 78.4 (3) | C3—P1—C1—C12 | 80.4 (6) |
| C1—P1—Se1—Br1 | -160.4 (2) | C2—P1—C1—C12 | -47.3 (7) |
| C3—P1—C2—C22 | -173.5 (5) | Se1—P1—C1—C12 | -162.6 (5) |
| C1—P1—C2—C22 | -43.7 (6) | C3—P1—C1—C11 | -39.6 (6) |
| Se1—P1—C2—C22 | 66.7 (5) | C2—P1—C1—C11 | -167.3 (5) |
| C3—P1—C2—C21 | -50.2 (6) | Se1—P1—C1—C11 | 77.4 (5) |
| C1—P1—C2—C21 | 79.6 (6) | C2—P1—C3—C31 | -153.5 (5) |
| Se1—P1—C2—C21 | -170.0 (5) | C1—P1—C3—C31 | 75.4 (6) |
| C3—P1—C2—C23 | 68.2 (6) | Se1—P1—C3—C31 | -35.2 (5) |
| C1—P1—C2—C23 | -162.0 (5) | C2—P1—C3—C32 | 78.5 (6) |
| Se1—P1—C2—C23 | -51.6 (6) | C1—P1—C3—C32 | -52.6 (6) |
| C3—P1—C1—C13 | -160.0 (5) | Se1—P1—C3—C32 | -163.2 (4) |
| C2—P1—C1—C13 | 72.2 (6) | | |

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|--------------------------------------|-------|-------------|-------------|---------------|
| C13—H13A \cdots Se1 | 0.98 | 2.60 | 3.163 (8) | 116 |
| C31—H31B \cdots Br1 | 0.98 | 2.78 | 3.551 (7) | 137 |
| C23—H23B \cdots Br1 | 0.98 | 2.98 | 3.476 (8) | 112 |
| C3—H3 \cdots Br3 | 1.00 | 3.13 | 4.108 (7) | 166 |
| C23—H23C \cdots Br3 | 0.98 | 3.05 | 3.994 (9) | 161 |
| C11—H11C \cdots Br4 | 0.98 | 3.23 | 4.182 (7) | 165 |
| C31—H31C \cdots Br2 ⁱⁱⁱ | 0.98 | 3.06 | 3.825 (7) | 136 |
| C23—H23A \cdots Br4 ^{iv} | 0.98 | 2.91 | 3.824 (7) | 156 |
| C13—H13C \cdots Br4 ^v | 0.98 | 3.06 | 3.998 (8) | 160 |
| C32—H32C \cdots Br4 ⁱⁱⁱ | 0.98 | 3.01 | 3.782 (7) | 136 |
| C11—H11A \cdots Br5 ^v | 0.98 | 3.12 | 3.874 (7) | 135 |
| C32—H32C \cdots Br5 ^{vi} | 0.98 | 2.93 | 3.804 (8) | 149 |

Symmetry codes: (iii) $-x+3/2, y-1/2, -z+1/2$; (iv) $x-1/2, -y+1/2, z+1/2$; (v) $-x+1, -y, -z$; (vi) $x+1/2, -y+1/2, z+1/2$.