

Coordination and oxidation of phosphine selenides with iodine: from cation pairs $[(R_3PSe)_2I^+]_2$ to (iodoseleno)phosphonium ions $[R_3PSeI]^+$ existing as guests in polyiodide matrices

Emma Seppälä, Frank Ruthe, Jörg Jeske, Wolf-W. du Mont* and Peter G. Jones

Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany. E-mail: w.du-mont@tu-bs.de

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An X-ray crystallographic study of adducts of trialkylphosphine selenides with > 1 equivalent of diiodine reveals that solid Bu_3PSeI_3 consists of cation pairs $[(Bu_3PSe)_2I^+]_2$ intercalated between I_5^- layers and that solid $R_2R'PSeI_7$ ($R = Bu^t$ or Pr^i , $R' = Pr^i$) contains $[R_2R'P-Se-I]^+$ cations with weak secondary $I \cdots I$ interactions to polyiodide networks.

Phosphine selenides $R_2R'P=Se$ are known to act as donors towards dihalogen molecules, providing 1:1 adducts $R_2R'PSeX_2$.^{1–7} Molecular structures have been determined for $R_2R'PSeI_2$ (type **A**, $R, R' = Ph, NMe_2, NEt_2$, and $R = Bu^t, R' = I^4$) and $R_2R'PSeBr_2$ (type **B**, $R, R' = NMe_2, C_6H_{11}$,⁵ $R = Bu^t, R' = Pr^i$ or Bu^t .^{2,7}). Bromo- and iodo-selenophosphonium ions (type **D**) have been postulated as cations in ionic 1:1 adducts of phosphine selenide and dihalogen.⁶ The first X-ray crystallographically characterised purely ionic solid 1:1 adduct was $(Pr^i_3PSe)_2I^+ I_3^-$ **1a** (type **C**).⁷ NMR spectra, however, suggest that in solutions of such 1:1 adducts equilibrium mixtures of several species are present.^{2,6,7} Solutions prepared from $R_2R'P=Se$ (**2a**: $R, R' = Pr^i$; **2b**: $R = Bu^t, R' = Pr^i$; **2c**: $R, R' = Bu^t$) and various amounts of I_2 always exhibit only one averaged ³¹P NMR line accompanied by satellites arising from $^1J(^{77}Se, ^{31}P)$, which decreases with increasing amounts of iodine. In CD_2Cl_2 solution, couplings $^1J(^{77}Se, ^{31}P)$ are smaller than in C_6D_6 solution. Addition of < 5% of I_2 to $R_3P=Se$ leads to severe broadening and a slight downfield shift of the ⁷⁷Se NMR doublet. With larger amounts of I_2 , as in the pure '1:1 adducts', the ⁷⁷Se resonances become too broad to be detected. This indicates kinetic lability of R_3PSe-I_2 systems and equilibration by exchange reactions that are fast on the ³¹P and ¹H NMR time scales.

Such an equilibrium mixture is 'frozen' in solid Bu_3PSeI_2 **1c** [consisting of molecular $Bu_3PSe-I-I$ and ionic $(Bu_3PSe)_2I^+ I_3^-$].^{2,7}

The transition from the molecular adduct Bu_3PSeI_2 to the cationic species $(Bu_3PSe)_2I^+$ is completed by adding slightly more iodine to solutions of **1c**. This leads to the solid compound $(Bu_3PSe)_2I^+ I_5^-$ **3**. Cations with linear Se-I-Se arrangements that are well separated from each other and from the counter anions, are known from Se_6IASF_6 and from related Se-coordinated $[L_2I]^+$ [$L = N$ -methylbenzothiazole-2(3*H*)-selenone].⁸ Compound **3**, however, consists of pairs of cations $[(Bu_3PSe)_2I^+]_2$ [Fig. 1(a), (b)] intercalated into channels emerging from the corrugated structure of the polymeric I_5^- counter anion. The polymeric I_5^- ion creates channels between adjacent layers that offer suitable space for pairs of cations. Within these pairs, Se \cdots Se contacts are shorter than the van der

Waals radii; these cation pairs are well separated from the anionic network.

Use of an excess of iodine on $[I(py)_2]^+ [I_3]^-$ is known to provide solid $[I(py)_2]^+ [I_7]^-$.⁹ Pr^i_3PSe **2a** and Bu_2Pr^iPSe **2b** on reaction with excess iodine, however, do not form higher polyiodides of $(R_3PSe)_2I^+$ cations, but instead provide compounds of the composition $R_2R'PSeI_7$ **4a**, **4b** that represent the first examples of $[R_3PSeI]^+$ cations (type **D**). ³¹P NMR spectra of these compounds exhibit, in comparison with **1a**, **1b**,⁷ further decreased coupling constants $^1J(^{77}Se, ^{31}P)$, which are now similar to that of the type **B** molecular adduct $Pr^i_3PSeBr_2$, which contains a P-Se single bond.⁷ The higher iodine content of $R_2R'PSeI_7$, compared with $(Me_2N)_3PSeI_4$ and $(Morph)_3PSeI_5$,¹⁰ leads to improved separation of the $[R_2R'PSeI]^+$ cations of **4a** and **4b** from the surrounding weakly donating polyiodide networks.

Rather long cation-anion $I \cdots I$ distances in **4a** and **4b** (between 324.8 and 330 pm) correlate well with the shortest yet observed (P)-Se-I bonds (256.3–257.8 pm) in their $[R_2R'P-Se-I]^+$ cations.

The slight steric differences between the alkyl groups of the cations of **4a** and **4b** lead to quite different long-range order of their polyiodide anion structures. In solid **4b** (Fig. 2), one iodide anion $[I(3)]$ bridges two of the $R_2R'PSeI^+$ cations and is in further contact with three I_2 molecules [$d(I-I)$ 274–275 pm within the I_2 units], one of which $[I(4)-I(5)]$ contacts the other I^- anion $[I(6)]$. $I(6)$ is in contact with five I_2 molecules; of these, $I(11)-I(12)$ is the only terminal I_2 molecule (Fig. 2). In solid **4a** (Fig. 3), one I^- $[I(9)]$ is surrounded by two cations $[Pr^i_3P(1)-Se(1)-I(1)]$ and $[Pr^i_3P(2)-Se(2)-I(4)]$ and four I_2 molecules (when one $I \cdots I_2$ distance of 368 pm is included), two (five-coordinated) I^- are in contact with one cation $[I(7)]$ with $Pr^i_3P(3)-Se(3)-I(22)$, $I(11)$ with $Pr^i_3P(4)-Se(4)-I(5)$ and four I_2 molecules, and the fourth I^- $[I(20)]$ is surrounded by five I_2 molecules (Fig. 3).

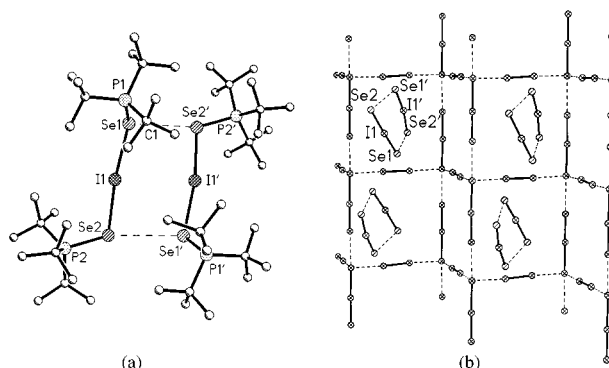
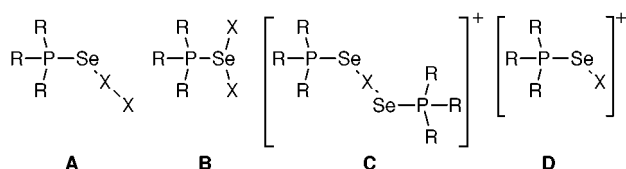


Fig. 1 (a) Cation pairs of **3**, selected bond lengths (pm) and angles ($^\circ$): $I1-Se2$ 273.7(1), $I1-Se1$ 276.7(11), $P1-Se1$ 218.6(2), $P2-Se2$ 219.0(2), $Se1 \cdots Se2'$ 367.9(1), $Se2-I1-Se1$ 170.3(3), $P1-Se1-I1$ 112.6(7), $P2-Se2-I1$ 111.5(7) (symmetry operator for generating equivalent atoms: $-x, 1+y, 0.5-z$); (b) Layer structure of **3**: Bu_3P groups omitted.



Scheme 1 Structural alternatives of phosphine selenide halogen adducts.

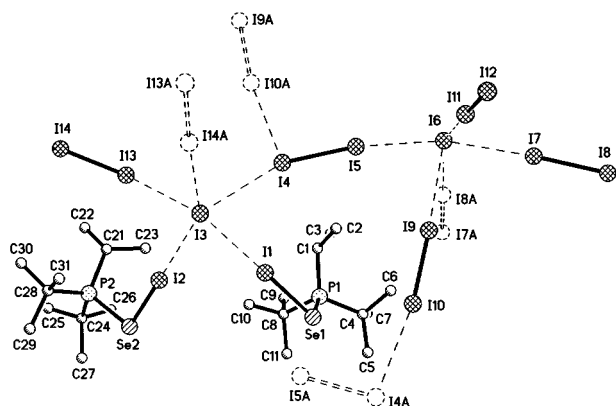


Fig. 2 Structure of **4b**, selected bond lengths (pm) and angles ($^{\circ}$): I1–Se1 256.4(6), P1–Se1 223.5(1), I1...I3 330.2(4), I2–Se2 256.7(6), P2–Se2 223.7(1), I2...I3 324.8(5), P1–Se1–I1 102.1(3), P2–Se2–I2 101.6(4). Broken circles indicate atoms of other asymmetric units.

$[R_2R'P-Se-I]^+$ cations are also related to the rare class of alkane and arene selenenyl iodides $R-Se-I^{11-13}$ and with the (iodoseleno)imidazolium cation R^+-Se-I [$d(Se-I)$ 259.1(5) pm] reported by Kuhn *et al.*¹⁴ Compared with uncharged $R-Se-I$ species,^{11,13} all Se–I distances of the cations in **4a** and **4b** are slightly longer, which can be readily explained by the $n \rightarrow \sigma^*$ nature of their anion-to-cation donor–acceptor interactions involving σ^* orbitals of covalent Se–I bonds. We expect that the use of counter anions of low nucleophilicity will permit syntheses and studies of the electrophilicity of a larger number of stable (halogenoseleno)phosphonium ions of type **D**.

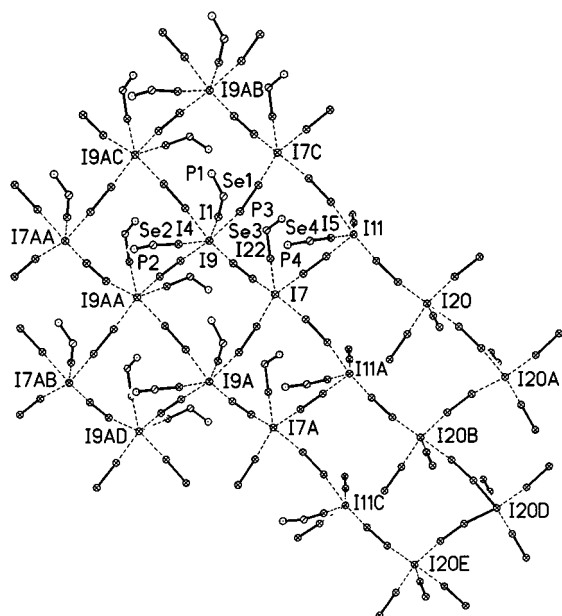


Fig. 3 Topology of I...I interactions within **4a**, selected bond lengths (pm) and angles ($^{\circ}$): I1–Se1 256.3(2), P1–Se1 222.6(4), I1...I9 326.7(2), I4–Se2 256.4(2), P2–Se2 222.8(4), I4...I9 328.6(1), I22–Se3 257.1(2), P3–Se3 220.7(5), I22...I7 330.9(2), I5–Se4 257.8(2), P4–Se4 222.1(4), I5...I11 328.5(2), P1–Se1–I1 99.9(1), P2–Se2–I4 99.9(1), P3–Se3–I22 100.3(3), P4–Se4–I5 99.2(1); Prⁱ groups omitted.

Notes and references

† *Crystal data*: **3**: $C_{27.5}H_{58}P_2Se_2I_6$; $M = 1370.00$, monoclinic, space group $C2/c$, $a = 31.687(5)$, $b = 13.955(2)$, $c = 19.383(2)$ Å, $\beta = 95.193(2)^{\circ}$, $U = 8536.1(2)$ Å³, $Z = 8$, $D_c = 2.132$ Mg m⁻³, $\mu = 6.164$ mm⁻¹, $F(000) = 5112$, 7530 independent reflections to 2θ max. 50° , $T = 143$ K, $S = 1.155$, $R[F, >4\sigma(F)] = 0.0519$, $wR(F^2) = 0.1541$, 207 restraints and 358 parameters, highest peak 1.205 and deepest hole -2.128 e Å⁻³.

4a: $C_{18}H_{42}P_2Se_2I_{14}$; $M = 2254.98$, orthorhombic, space group $Pna2_1$, $a = 50.655(3)$, $b = 15.5224(11)$, $c = 12.5356(8)$ Å, $U = 9856.7(1)$ Å³, $Z = 8$, $D_c = 3.039$ Mg m⁻³, $\mu = 10.348$ mm⁻¹, $F(000) = 7920$, 23779 independent reflections to 2θ max. 56° , $T = 143$ K, $S = 0.952$, $R[F, >4\sigma(F)] = 0.0585$, $wR(F^2) = 0.1180$, absolute structure factor $x = 0.48(2)$, 397 restraints and 651 parameters, highest peak 3.177 and deepest hole -2.624 e Å⁻³.

4b: $C_{11}H_{25}PSeI_7$; $M = 1155.54$, orthorhombic, space group $P2_12_12_1$, $a = 12.6693(10)$, $b = 16.4329(12)$, $c = 25.2272(18)$ Å, $U = 5252.1(7)$ Å³, $Z = 8$, $D_c = 2.923$ Mg m⁻³, $\mu = 9.714$ mm⁻¹, $F(000) = 4088$, 15312 independent reflections to 2θ max. 60° , $T = 143$ K, $S = 0.890$, $R[F, >4\sigma(F)] = 0.0249$, $wR(F^2) = 0.0380$, absolute structure factor $x = 0.011(9)$, 126 restraints and 378 parameters, highest peak 1.743 and deepest hole -1.343 e Å⁻³.

All X-ray datasets were collected with monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) on a Stoe STADI-4 four-circle diffractometer (**3**) or a Bruker SMART 1000 CCD area detector (**4a**, **4b**). Absorption corrections were based on ψ -scans (**3**) or multiple scans (**4a**, **4b**). The structures were solved by direct methods and refined anisotropically by full-matrix least squares on F^2 . H atoms were included using a riding model (except methyl groups in **4b**: refined as rigid groups). Structure **4a** was refined as a racemic twin; structure **3** contains half a molecule of toluene (disordered over an inversion centre) per formula unit. CCDC 182/1317. See: <http://www.rsc.org/suppdata/cc/1999/1471/> for crystallographic files in .cif format.

‡ ³¹P NMR data: **1a** (300 K, CH₂Cl₂-C₆D₆): δ 65.3, $^1J(^{77}Se, ^{31}P) \pm 556$ Hz; **1b** (300 K, C₆D₆): δ 76.2, $^1J(^{77}Se, ^{31}P) \pm 597$ Hz, (300 K, CD₂Cl₂): δ 76.8, $^1J(^{77}Se, ^{31}P) \pm 547$ Hz; **1c** (300 K, CH₂Cl₂-C₆D₆): δ 83.0, $^1J(^{77}Se, ^{31}P) \pm 593$ Hz; **2b** (300 K, C₆D₆): δ 83.6, $^1J(^{77}Se, ^{31}P) \pm 704.8$ Hz, (300 K, CD₂Cl₂): δ 83.8, $^1J(^{77}Se, ^{31}P) \pm 692.0$ Hz; **3** (300 K, CD₂Cl₂): δ 83.0, $^1J(^{77}Se, ^{31}P) \pm 526$ Hz; **4a** (300 K, CH₂Cl₂-C₆D₆): δ 66.5, $^1J(^{77}Se, ^{31}P) \pm 518$ Hz; **4b** (300 K, CD₂Cl₂): δ 76.5, $^1J(^{77}Se, ^{31}P) \pm 528$ Hz.

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